MEDEA Users Guide

I. Installation

A. Overview

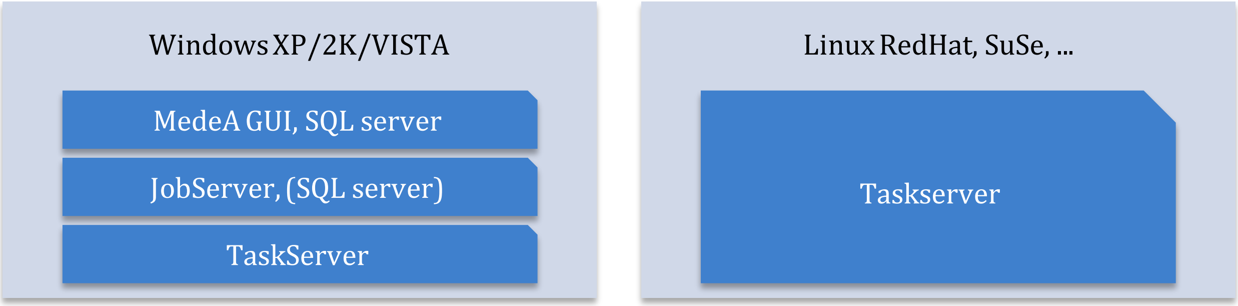
MedeA's tiered architecture consists of the MedeA graphical user interface (main tier), the JobServer (middle tier) and the TaskServer (end tier).

The middle tier or JobServer is the central hub for computational job control, job preprocessing and job postprocessing. The JobServer maintains a SQL database of job related data and by default it is on the JobServer machine, where computational results stored.

There is no communication between MedeA and the TaskServers, instead all data flows through the JobServer.

MedeA and the JobServer are Windows applications, the TaskServer including computationally intensive codes like VASP and GIBBS can be installed under both Windows and Linux operating systems.

MedeA uses a Microsoft SQL database to manage experimental databases, code specific data and data generated by the user. Technically the SQL server can reside on any networked Windows machine; typically it is installed on the machine running MedeA and/or the JobServer.



B. Hardware and Software requirements

While there are no hard limits in terms of hardware resources for any of the MEDEA components, MEDEA's graphical visualization and atomistic modeling require high-end hardware to deliver satisfying performance. As a rule of thumb a recent upper-end dual/quad core Windows PC will be sufficient to run all three components: the graphical interface, the JobServer and the TaskServer with all computational codes for small to medium sized systems.

For larger systems or more demanding tasks a cluster configuration is recommended, typically a Windows or Linux blade server will do a fine job on running the TaskServer and computational codes.

Detailed hardware/software requirements and component specific demands are as follows:

Component	Requirement
Operating system	Windows 2000/XP/Server2003/Vista Linux, supported by TaskServer (GIBBS, VASP)
Architecture/Processor	64 bit: Opteron^{AMD}, Itanium^{Intel}, Dual/Quad Core^{AMD,Intel} 32 bit: Athlon^{AMD}, Pentium IV, XEON^{Intel}
CPU speed	Strong floating point performance required No lower/upper hard limit on clock speed, the more the better
Memory requirements	At least 1 GByte RAM per CPU, the more the better
Hard Drive space	5 GB minimum for a full MEDEA installation 60-180 GB for storing user generated data
Video Card	At least 128 MBytes memory, the more the better
Network	Fast ethernet, 100 MBit or faster
Display	17" or larger for graphics editing

Key requirements by component:

MEDEA	JOBSERVER	TASKSERVER (Gibbs, VASP)
• Graphics memory and speed • Display • main memory	• RAID or automated backup • Disk space	• CPU: floating point performance • main memory

a. Note on running VASP on Windows versions dating from before 2005

Some versions of Windows dating from earlier than 2005 and not subject to regular operating system updates may require a Microsoft Visual C++ runtime library to be installed. This library can be downloaded from Microsoft's website [1] for both 32bit and 64bit architectures:

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[1] Visual C++ runtime library: *http.://www.microsoft.com/downloads/details.aspx?familyid=32bc1bee-a3f9-4c13-9c99-220b62a191ee*

C. Installation scenarios

MEDEA's tiered architecture lets you combine components in a number of ways thus adapting to the needs of your specific compute environment. Here are a few scenarios how to install the software:

a. Single node

In a stand-alone configuration, MEDEA runs on a single Windows machine having one or multiple CPUs. All components, that is the graphical user interface, the SQL server, the JobServer and the TaskServer are installed on this machine and computations are run locally.

b. Small cluster

- One or more Windows PCs, each running the MEDEA GUI
- A **single, central JobServer** running on one of the above machines or on a separate Windows machine
- **TaskServers** on some/each of the above machines, additional TaskServers on other networked resources (Windows/Linux)

In addition to a single central JobServer, individual JobServers may be installed on machines that need to function in stand-alone (like laptops). Note that running different JobServers increases the maintenance effort as computational results reside in different locations, thus making backup and retrieval a challenging task.

c. Larger clusters and external queuing systems

When several compute intensive applications share the same resources, it is recommended to make use of queuing systems like e.g. PBS, LSF or SUN GridEngine. MEDEA supports external queuing systems under Linux/Unix by providing templates for queue submission scripts.

Note that MEDEA does not provide management tools for external queuing systems. You will need to adapt the scripts provided along with the TaskServer to fit your local installation. The current implementation requires one TaskServer client per queue to be installed on the gateway machine. Configurable scripts for the *PBS*, *LSF* and `GridEngine` queuing systems are provided in C:\MD\2.0\TaskServer\Tools\vasp4.6.31\.

D. MEDEA's databases and the SQL server

MEDEA uses an SQL server to host a variety of databases. Some are structure databases such as ICSD and Pauling, others contain user generated results and internal data like potentials and parameters used in VASP calculations.

MEDEA uses Microsoft's Sequel Server Query Language (MSSQL) within the standard Microsoft SQL Server Express, which is redistributed and installed along with the MEDEA DVD/CD.

The default version is SQL Server 2005 Express. The installer also detects already installed versions of the SQL server and tries to use them by attaching the databases. [2]

If you start with a new installation, the following screen is likely to appear:

Welcome to the Materials Design Installer, which will install MedeA along with its associated software and databases.
When you click on the 'Next' button, I will ask you for information about what you want to install and where to install it. Nothing will be actually installed until you ask, so you can review and change the information as you wish.

The security mode used by SQL Server is 'unknown'

SQL Server Express is not installed on this machine. Please install it first, then rerun the MedeA installer. If possible, please download SQL Server Express from the Microsoft web site http://www.microsoft.com/sql/editions/express/default.mspx -- this way you will have the latest version with all updates. If it is not possible or convenient to download SQL Server, copies are provided on the CD/DVD in \Extras\SQLExpress\Windows-x86 or \Extras\SQLExpress\Windows-x86_64

Please be careful to download and use the correct 32- or 64-bit version of SQL Server Express as is appropriate for your machine.

Exit

The following section will cover how to install SQL Server 2005 Express and run the installer. If there are any questions, please don't hesitate to contact support@materialsdesign.com or in Japan medea@rsi.co.jp.

Warning: As of August 2008, Microsoft is starting to roll out SQL Express 2008 Server, but the SQL Server Tools are not available yet. There are unresolved issues on with Vista™ on 64bit machines, so please contact support@materialsdesign.com before considering installing SQL Server Express 2008.

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[2] if you wish to overwrite the defaults you can do so by setting the following environment variables prior to running the SQL server:

MD_USE_MSDE2000	force the use of MSDE2000
MD_MSDE2000	install MSDE2000 if the normal installation fails.

E. Installing SQL Server 2005 Express

Installation of MEDEA is simple, once the SQL Server 2005 is in place and properly configured. Please use the one on the installation DVD in `<DVD>\Extras\SQLExpress\Windows-x86\SQLEXPR32.EXE` for 32bit machines and `<DVD>\Extras\SQLExpress\Windows-x86_64 \SQLEXPR.EXE` for 64bit machines.

Start the appropriate installer program, accept the license agreement and continue

Installing Prerequisites:

✓ *Install Micosoft SQL Native Client*

✓ *Install Microsoft SQL Server 2005 Setup Support Files.*

Continue the Installation Process with **Next>** to the System Configuration Check and

Registration Information

Name: ☐

Company: ☐

☐ *Hide advanced configuration options*

Fill out the Name and Company fields and be sure to uncheck the **Hide advanced configuration options** before continuing with default values till

Instance Name

● *Named instance:* ***MaterialsDesign***

The MEDEA installer expects an instance called *MaterialsDesign*.

Service Account

● *Use the built-in System account:* ***Network service***

The databases are expected to run in the background.

Authentication Mode

● *Windows Authentication Mode*
○ *Mixed Mode (Windows Authentication and SQL Server Authentication)*

To ensure compatibility for importing your old Jobs database use the following setting:

Collation Settings

● *SQL collations (used for compatibility with previous version of SQL Server)*
Dictionary order, case-insensitive, for use with 1252 Character Set.

The final step is to allow SQL Server to import the databases from an earlier installation.

Configuration Options

☑ *Enable User Instances*
☑ *Add user to the SQL Server Administrator role*

Continue with the installation.

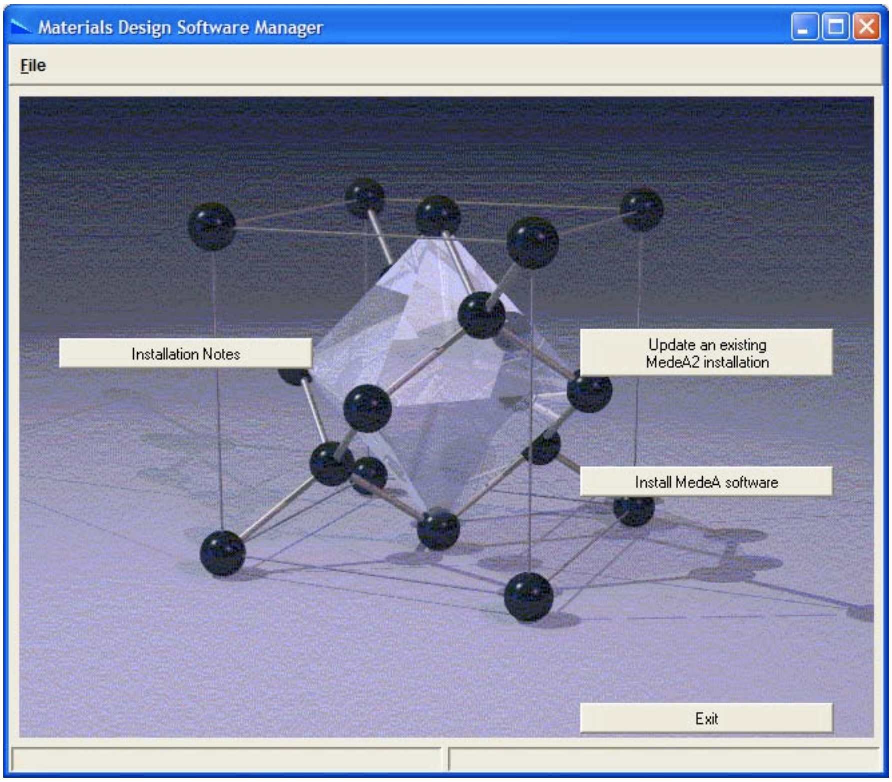
F. Installing MEDEA

The MEDEA installer will guide you through the installation displaying messages and providing feedback on the installation progress. At any time you can scroll back and forth within the installer message window in order to inspect the individual steps of the installation.

For installation of the TaskServer component under Linux please refer to:
I.I Installing the MEDEA TaskServer under Linux.

1. Starting the Installer

1) Insert the MEDEA2.4 DVD to auto start the MEDEA Software manager. In case the Software manager does not start automatically, click on the **Start**/**Run** button in the Windows Start menu and use **Browse** to locate `Setup.bat` on the DVD root directory. Double click **Setup.bat** to start the Materials Design Software Manager



2. Installing

2) If you are updating from a previous version of MEDEA2.x click **Update an existing MEDEA2 installation** and continue in section I.F Using the Materials Design Software Manager

3) In the Materials Design Software Manager Window, click the **Install MEDEA software** button to proceed to the Materials Design Installer window

On startup, the installer checks for a working Microsoft SQL server on your machine:

> *Welcome to the Materials Design Installer, which will install MEDEA along with its associated software and databases.*
>
> *When you click on the 'Next' button, I will ask you for information about what you want to install and where to install it. Nothing will be actually installed until you ask, so you can review and change the information as you wish.*
>
> *The security mode used by SQL Server is 'unknown'.*
>
> *SQL Server 2005 Express is not installed on this machine. Please install it first, then rerun the MedeA installer. If possible, please download SQL Server 2005 Express from the Microsoft web site http://www.microsoft.com/sql/editions/express/default.mspx -- this way you have the latest version with all updates. If it is not possible or convenient to download SQL Server, copies are provided on the CD/DVD in \Extras\SQLExpress\Windows-x86 or \Extras\SQLExpress\Windows-x86_64*
>
> *Please be careful to download and use the correct 32- or 64-bit version of SQL Server Express as is appropriate for your machine*
>
> ***Exit***

In this case follow the instructions in section 0 Installing SQL Server 2005 Express

With SQL Server Express installed the following message will greet you:

> *Welcome to the Materials Design Installer, which will install MEDEA along with its associated software and databases.*
> *When you click on the 'Next' button, I will ask you for information about what you want to install and where to install it. Nothing will be actually installed until you ask, so you can review and change the information as you wish.*
>
> *The security mode used by SQL Server is 'Windows'*
> *MSDE v9.0.3042.00 is installed on this machine. Checking if it is running…it is.*

4) Click **Next** to continue and select the installation mode, **standard installation** or **custom installation**

> ***Installation Parameters***
>
> *Please choose if you want a*
>
> ☑ *Standard installation, which will install everything*
>
> ○ *Custom installation, where you choose what and where to install*
>
> *The following packages will be installed:*

JobServer	*1.72*	*MB*
TaskServer	*156.59*	*MB*
Celeste	*2.94*	*MB*
MEDEA	*72.56*	*MB*
Databases	*1.89*	*GB*
Total	*2.12*	*GB*

> *at C: /MD*
> *Disk C: is 15.99 GB of which 14.39 GB are available.*
>
> *Please make sure all the information above is correct and then click on the 'Install' button to start the installation.*
>
> ***Install***

3. Standard Installation

The standard installation provides default paths and installs all components on the present DVD. Note that **Standard Installation** will most likely select your "last" hard disk partition, e.g. if you have C and D partitions, it will select D. The hardware partition you install MEDEA to, should have at least 20GBytes available for storing results of calculations performed with MEDEA.

5) Continue reading below at 5 Installation Progress

4. Custom Installation

If you would like to change the MEDEA installation or select specific modules for installation, select **Custom Installation**. Keep in mind that for maintenance it is best to have the whole MEDEA program tree, database files and Job data on a single hard disk partition.

Installation Parameters

Please choose if you want a

` ○ *Standard installation, which will install everything*

` ☑ *Custom installation, where you choose what and where to install*

Choose the packages to install:

☑ *JobServer*	*1.72*	*MB*
☑ *TaskServer*	*156.59*	*MB*
☑ *Celeste*	*2.94*	*MB*
☑ *MEDEA*	*72.56*	*MB*
Total	*233.80*	*MB*

at C: /MD ...

Choose the databases to install:

☑ *Pearson*	*622.25*	*MB*
☑ *Pauling*	*110.13*	*MB*
☑ *MedeA*	*210.56*	*MB*
☑ *MaterialsDesign*	*4.88*	*MB*
☑ *NCD_Inorganic*	*101.24*	*MB*
☑ *NCD_Organic*	*206.06.*	*MB*
☑ *ICSD*	*678.50*	*MB*
Total	*1.89*	*GB*

at C: /MD ...

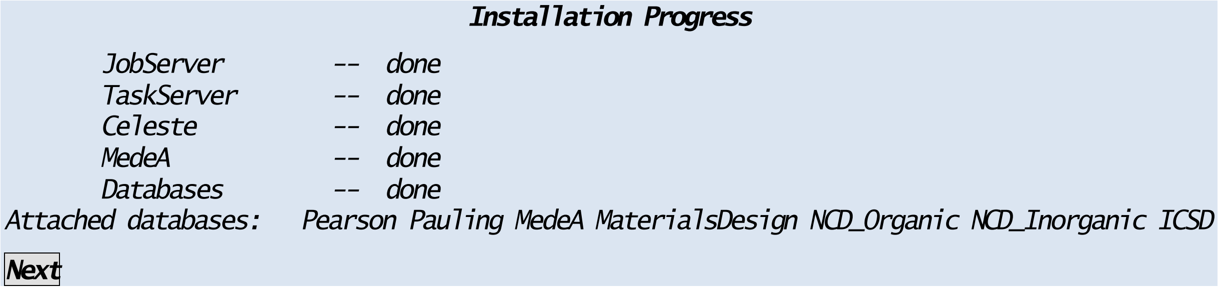
Please make sure all the information above is correct and then click on the 'Install' button to start the installation.

Install

5. Installation Progress

6) Click **Install** to continue

In the next step, the MedeA installer will install all the selected MedeA components:



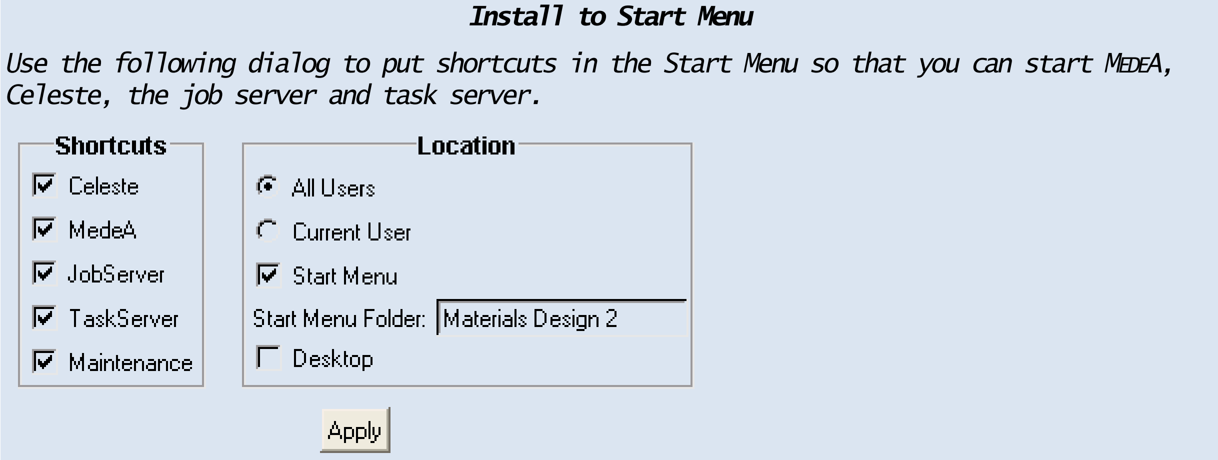
Installation Progress

```
        JobServer        --  done
        TaskServer       --  done
        Celeste          --  done
        MedeA            --  done
        Databases        --  done
Attached databases:   Pearson Pauling MedeA MaterialsDesign NCD_Organic NCD_Inorganic ICSD
```

Make sure you scroll down to the bottom of the installer window to see the latest messages. If you activate other windows while installing, the installer window may turn blank for some time before displaying an updated status. Once all components are selected, the `Installation Progress` in the installer window displays the current status, followed by `done` for successful installation of each component. If databases are installed, you should see a message `Attached databases`:, followed by a list of databases including at least `MedeA` and `MaterialsDesign`.

6. Creating links and shortcuts

7) Click **Next** to continue configuring the MedeA start menu links and job control



Install to Start Menu

Use the following dialog to put shortcuts in the Start Menu so that you can start MedeA, Celeste, the job server and task server.

Shortcuts

☑ Celeste
☑ MedeA
☑ JobServer
☑ TaskServer
☑ Maintenance

Location

● All Users
○ Current User
☑ Start Menu
Start Menu Folder: Materials Design 2
☐ Desktop

In this step the installer will create shortcuts and Start menu entries for MedeA. Please make sure to create the start menu entries (default), as this will later configuration and updates.

8) Click **Apply** to create the default links in the Windows start menu, then **Next**

7. Setting up JobServer and TaskServer services

In the next installation step you will be asked if you would like to configure the JobServer and TaskServer as services. Installing JobServer and TaskServer as services will let Windows start these processes automatically during the boot phase.

Setup the Job and Task Servers as Services

The job and task servers can be run manually, or can be set up as Windows services if you have administrator privileges.

Use the following buttons to set up the services

Both Job and Task Server

Job Server

Task Server

Note that in order to run calculations or look at results from calculation in your browser, you need to start these processes either as a service or through the **Start menu** » **Programs** » **Materials Design 2** » **JobServer / TaskServer** entries.

We recommend that you install and run these processes as services.

Setting up the JobServer as service 'mdJobServer'Completed. The stauts of the Job Server is 'running'
Setting up the TaskServer as service 'mdTaskServer'Completed. The stauts of the Task Server is 'running'

9) Click on **Next** a last time to see

Installation and Setup is Completed

Congratulations! The installation and setup is complete. If you have any other installation CDs you will need to install them in the same way. Otherwise you are finshed.

Press EXIT to leave the installer.

10) Click on **Exit** to leave the installer.

a. Installing TaskServers on multiple machines

For configurations with multiple TaskServers you have to repeat the TaskServer installation on each machine:

- For Linux/Unix machines please refer to I.H Installing the MEDEA TaskServer under Linux
- For Windows machines repeat a **Custom Installation** and select only the TaskServer component

G. Updating an existing MEDEA installation

You can update your version of MEDEA using an install medium (DVD) or via the internet. Updating MEDEA will not affect any of your saved settings, results and other user data.

1. Update from DVD

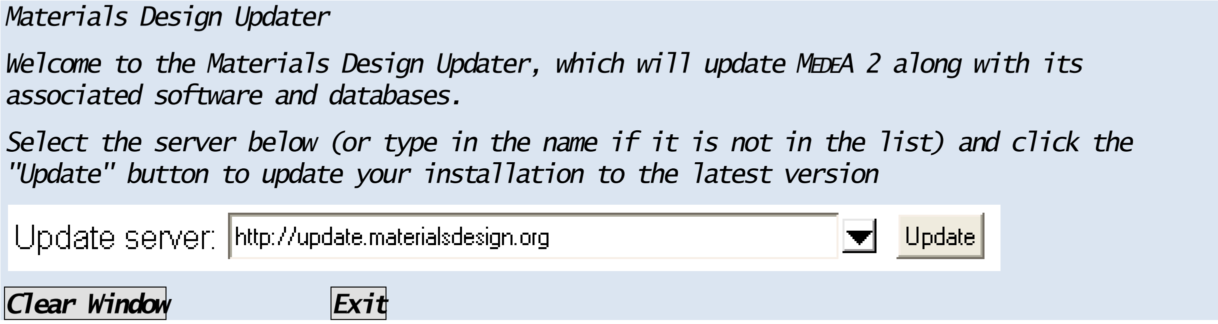
To update from DVD, insert the DVD to bring up the Software Manager and click the **Update existing MEDEA2** button. The instructions that follow are very similar to what is described below for the internet update.

2. Update from the internet

To update via the internet you will need password access to the Materials Design Update web site. If you haven't received a password yet, send us mail to support@materialsdesign.com to receive your personal password.

1) Bring up the MEDEA Software Manager by clicking on **Start** » **Programs** » **Materials Design 2** » **Maintenance**

2) In the MEDEA Software manager click **Update from the web**



Materials Design Updater

Welcome to the Materials Design Updater, which will update MEDEA 2 along with its associated software and databases.

Select the server below (or type in the name if it is not in the list) and click the "Update" button to update your installation to the latest version

Update server: http://update.materialsdesign.org

3) Click on **Update** to continue

In the pop up dialogue type your user-ID and password and click **OK.**

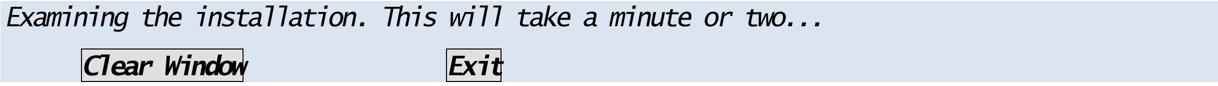
If you haven't received a password yet, send us mail to support@materialsdesign.com to receive your personal password.

Please enter your username and password for the realm 'MD Update'

User:

Password:

The Updater will compare your current installation with the disk image on disk. This process may take a couple of minutes.



Examining the installation. This will take a minute or two...

If there is a more recent version of the updater, the following window appears:

There is a new version of the installer. Do you wish to update it first (recommended)?

```
Click continue to actually update the installer.
      Continue          Exit
Getting the following files:
       ./Windows-x86/Setup.exe -- 211 changes applied.
Transfer statistics:
….
Updating the packing list...done.
Checking maintenance shortcuts...
The maintenance program was updated. You should run it again to make sure that all updates
were installed properly.
The update is complete.
              Finish
```

You need to close and reopen the maintenance program if the updater itself was updated.

Repeat steps 1-3 above to continue the update.

The updater displays the latest version number (here 2.4) followed by the release notes and a listing of changed files, new files and extra files. Click each button to display or hide the corresponding listing. Note that the number and type of files displayed depends on your current version of MEDEA and may therefore differ from the listing displayed below.

Click **Continue** to proceed with the update

```
The newest version is 2.4.2.
                                    Release Notes
MEDEA 2.4.1
1. Minor cleanup of a few typos
…
MEDEA 2.3
1. Initial version of 2.3 ... no significant changes from 2.2.1.20
There are 1 changed files, 18 new files and 0 extra files.
      Show changed files
      Show new files
      Show extra files
Click continue to actually update your installation. Don't worry! I will not delete any
files without your permission.
```

```
      Continue            Exit

Getting the following files:
       ./2.0/Manual.pdf…
…
Transfer statistics:
…
Updating the packing list...done.
Checking maintenance shortcuts...
The update is complete.
                Finish
```

Follow the progress of your update in the installer Window. If the Installer announces the download of patches e.g. for the databases, follow the instructions to install the patches. In most cases the installer will simply update a number of files

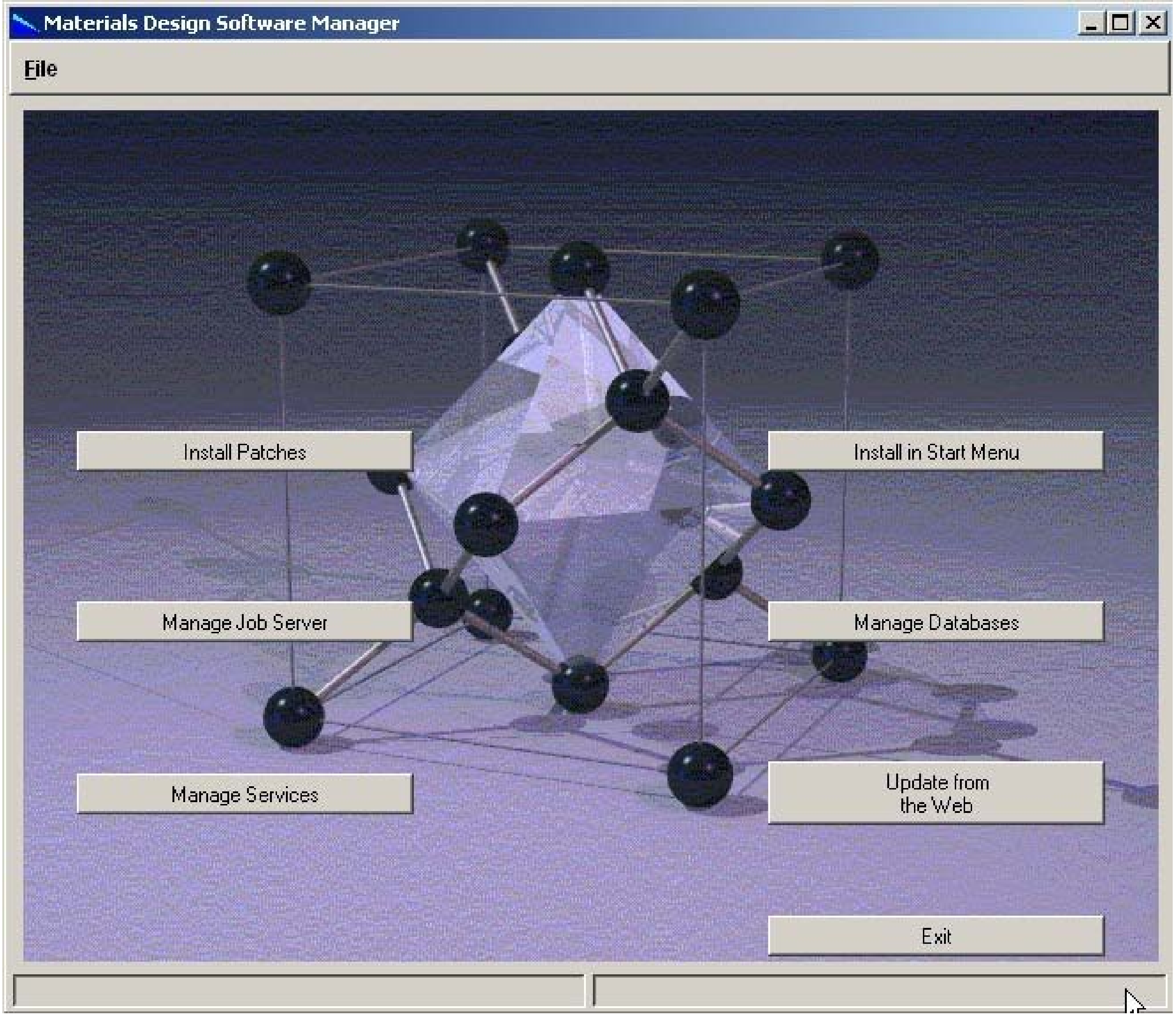
Click **Exit** to terminate the Updater once the update is complete

H. Using the Materials Design Software Manager

The Materials Design Software Manager lets you manage databases and services, program updates and job directories.

1. Starting the Software Manager

To start the Materials Design Software manager, select **Programs** ≫ **Materials Design 2** ≫ **Maintenance** from the Windows Start menu. The Software Manager is depicted below.



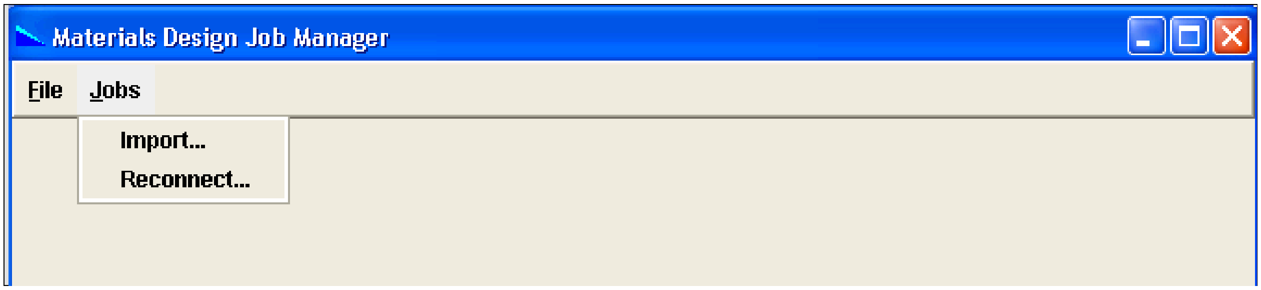
2. Software manager functionality

a. Installing patches

- **Install Patches** – Lets you select patches to the databases or the MEDEA software. Patches are normally downloaded automatically by **Update from the Web**.

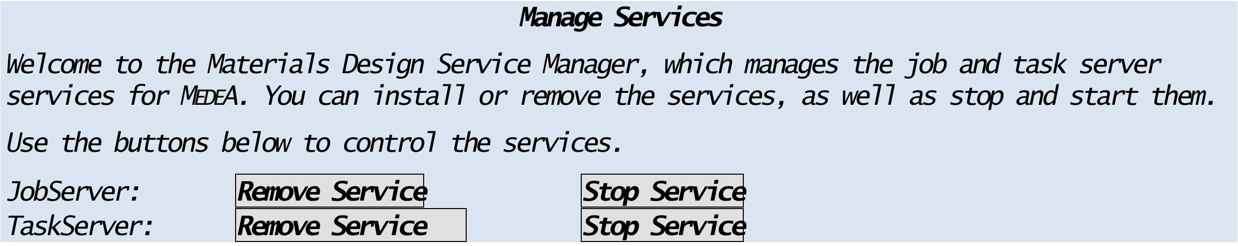
b. Import VASP job directories

- **Manage Job server** – provides an interface to import job directories from disk. Use this feature to import jobs from a different JobServer or to import VASP jobs run outside MedeA. Note that VASP jobs run outside MedeA will lack the MedeA postprocessing, e.g. no Job.out or band structure information is created upon import.



c. Start/stop JobServer and TaskServer

- **Manage Services** – Lets you create/delete JobServer and TaskServer services. You can also use this option to start/stop a JobServer/TaskServer service


Manage Services

Welcome to the Materials Design Service Manager, which manages the job and task server services for MedeA. You can install or remove the services, as well as stop and start them.

Use the buttons below to control the services.

d. Create links and shortcuts

- **Install in Start menu** – creates MedeA program shortcuts in the Start menu and/or on the desktop

e. Attach/detach databases from/to SQL server

- **Manage Databases** – Lets you check which databases are connected to the SQL server. You can attach/detach databases from the sql server if they are not currently used by a program. If the SQL server is not running this functionality is unavailable

f. Update MedeA using a web service

- **Update from the Web** – Lets you update the MedeA software through a Materials Design webserver. Note that your local firewall may block this feature.
-
- **Exit** – exits the software manager.

I. Installing the MEDEA TaskServer under Linux

For the installation under Linux you need **system administrator rights for some steps** which are marked in red in the following section.

It is recommended to create a separate user account for installation of the TaskServer under Linux (for example `medea`). Install the TaskServer as user `medea` and then install the daemon/service `mdtaskserver` as `root`. This way the taskserver daemon will run as user "`medea`".

For security reasons, **do not run the daemon `mdtaskserver` as root.**

You can install the MEDEA TaskServer using a graphical installer interface, much like under Windows. However, on some Linux distributions, the graphical installer is known to report missing graphics libraries. If this occurs on your machine, simply use the alternative installation procedure, namely installing using shell commands. Both methods are described below:

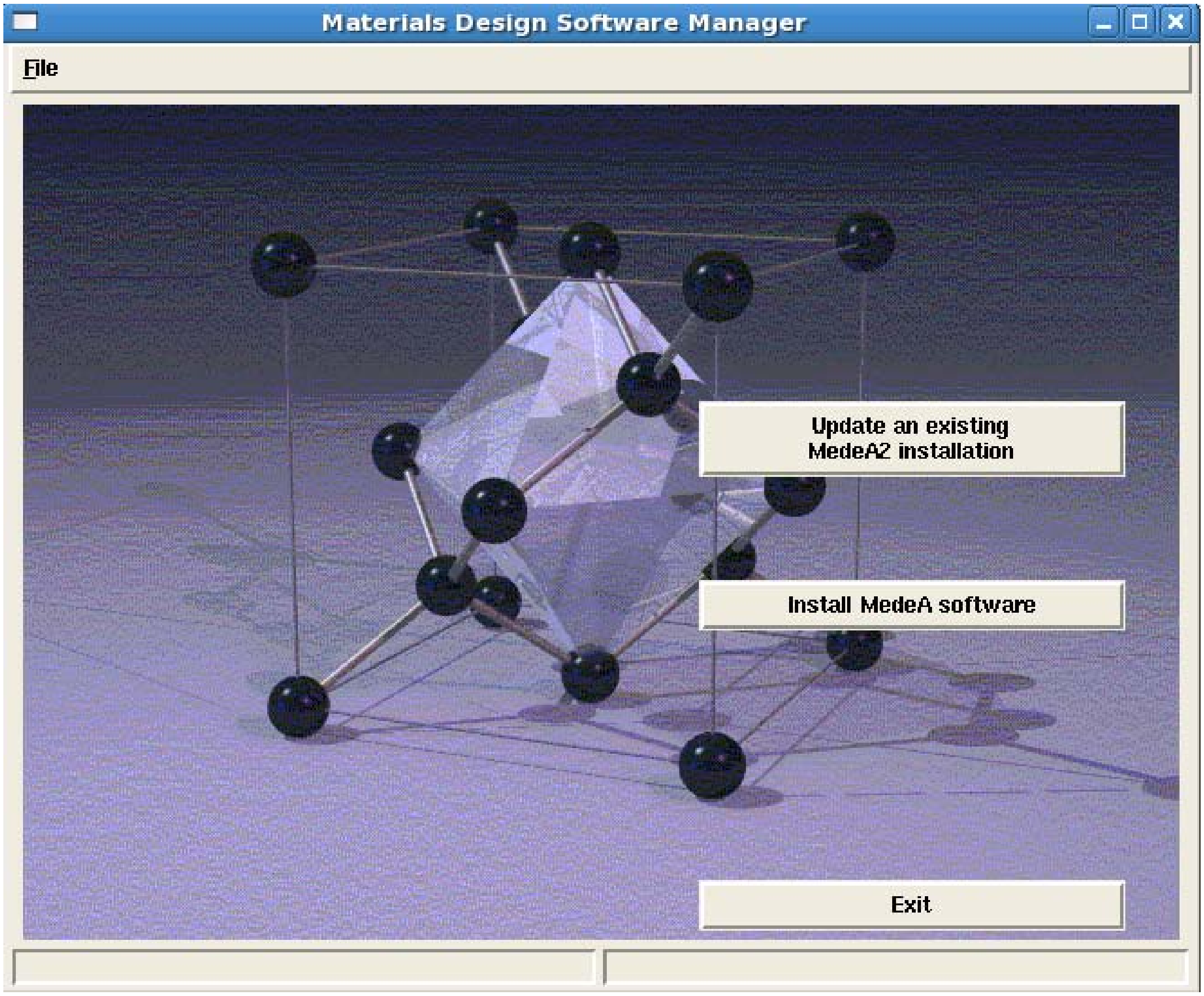
1. Using the graphical installer interface

The MEDEA installation DVD/CD works under both Windows and Linux.

1. **Create a user medea with standard rights (non-root)** and log in to this new account.
2. Mount the install medium, CD or DVD, if necessary set your DISPLAY variable and execute the script '`install.sh`' located in the install medium's top level directory:

```
cd /mnt/dvd/
./install.sh
```

3. Follow the instructions in the graphical user interface



The installer will print progress messages similar to what you experienced under Windows. Follow the instructions to completion.

```
Welcome to the Materials Design Installer, which will install MEDEA along with its
associated software and databases.

When you click on the 'Next' button, I will ask you for information about what you want to
install and where to install it. Nothing will be actually installed until you ask, so you
can review and change the information as you wish.

                              Installation Parameters

Please choose if you want a

default

custom

The following packages will be installed:

TaskServer              18.19    MB

Total                   18.19    MB

at /home/medea/MD
```

```
Disk /dev/shm is 0.00 B of which 0.00 B are available.

Please make sure all the information above is correct and then click on the 'Install'
button to start the installation.

                          Installation Progress

       TaskServer       --  done

Setup the Job Server

                 Setup the Job and Task Servers as Services

The job and task servers can be run manually, or can be set up as daemons if you have root
privileges. I cannot tell if you are root, so you may be able to set up the daemons. If
not, you'll either have to run manually, or log back in as root to set up the daemons.

Use the following buttons to set up the daemons

[Task Serbver]

                     Installation and Setup is Complete

Congratulations! The installation and setup is complete. If you have any other
installation CD's you will need to install them in the same way. Otherwise you are
finished.

Press EXIT to leave the installer.
```

If you decided not to install the TaskServer as a daemon/service at this point, or if you do not have root privileges to do so, you can postpone the installation of the service to a later time. To install the service by hand at a later point, simply follow steps 5-6) in the paragraph below (I.I.2 Installing manually).

You can run the TaskServer out of a normal shell without being root. This is recommended for testing only as the process will stop as soon as you log out. To do so follow the steps outlined in the section below, I.I.3 Troubleshooting.

Your Linux TaskServer should be up and running! You can check by browsing to its homepage http://localhost:23000.

2. Installing manually

Alternatively you can install the Linux TaskServer manually:

1. **Create a user** *medea* **with standard rights (non-root)** and log in to this new account
2. In the home (i.e. ~*medea*) directory make a directory 'MD'

```
mkdir MD
```

3. Transfer the content of the 2.0 directory on CD to the directory MD

```
cp -R /mnt/cdrom/2.0 ~/MD
```

4. **Change the permission for the 2.0 file tree.** You will need the root password at this point

```
cd ~medea/MD/
```

```
sudo chmod -R u+w 2.0
```

5. To install the Linux TaskServer as a daemon/service change directory to *~/medea/MD/2.0/TaskServer*

```
cd ~/medea/MD/2.0/TaskServer
```

6. **Execute the script 'InstallAsService' as root**. If you selected a different installation directory for the TaskServer, you will need to locate the script '*InstallAsService*' relative to this directory

```
sudo./InstallAsService
```

If you do not have root privileges, you can still run the TaskServer out of a normal shell. To do so follow the steps outlined in the section below, I.I.3 Troubleshooting.

Your Linux TaskServer should be up and running! You can check by browsing to its homepage http://localhost:23000.

3. Troubleshooting

On some Linux distributions the *InstallAsService* script produces an error *Cannot start service*, although the service was started successfully. If you receive this message, please check if the process started by looking for a process *mdTaskServer* in the process list or by typing in a command shell:

```
ps -ef | grep  mdtask
```

Running the TaskServer out of a non-root shell:

To run the TaskServer as a normal shell command, execute the script InstallAsService as user *medea* in order to create the script *TaskServer*

```
cd ~medea/MD/2.0/TaskServer
./InstallAsService
```

The script will exit telling you that it needs root privileges for installation of the service and it will leave a script TaskServer behind.

Next, run *TaskServer* to start the process *mdtaskserver* as a background process in a separate shell:

```
./TaskServer
```

Mind, the TaskServer script does not return any messages when executed. To see the output of the script, edit it and remove the *>>/dev/NULL* section in the last line.

Note that the TaskServer process started this way will only last until you shut down or reboot your machine. To have it come up automatically after a reboot, you need to install it as a daemon.

To check if the TaskServer is running, you can access it's control home page using any web browser under http: //localhost: 23000. You may need to replace "localhost"by the machines network name.

For more configuration options of the TaskServer, please refer to the section II.D Job management,.

4. Running the TaskServer using your own VASP binaries

If you decided to use your own VASP binaries with MEDEA and the TaskServer, you will need to rename the executables and place the corresponding TaskServer directories. The following VASP binaries are recognized by the TaskServer:

Windows	**Linux**		
vasp.exe	*vasp_parallel.exe*	*vasp*	*vasp_parallel*
vasp_gamma.exe	*vasp_gamma_parallel.exe*	*vasp_gamma*	*vasp_gamma_parallel*
vasp_so.exe	*vasp_so_parallel.exe*	*vasp_so*	*vasp_so_parallel*
vasp_so_gamma.exe	*vasp_so_gamma_parallel.exe*	*vasp_so_gamma*	*vasp_so_gamma_parallel*

The TaskServer looks for VASP binaries depending on the operating system and platform in the following directories:

- Windows (x86): <MEDEA>\TaskServer\Tools\vasp4.6.31\Windows-x86\
- Windows (x86_64): <MEDEA>\TaskServer\Tools\vasp4.6.31\Windows-x86_64\
- Linux (x86): <MEDEA>/TaskServer/Tools/vasp4.6.31/Linux-x86/
- Linux (x86_64): <MEDEA>/TaskServer/Tools/vasp4.6.31/Linux-x86_64/
- Linux (ia64): <MEDEA>/TaskServer/Tools/vasp4.6.31/Linux-ia64/

Example: You are installing a TaskServer on an AMD Opteron 64bit machine running a Linux OS. You have created a user *medea* and you have installed the TaskServer in the directory ~/*medea*. Your TaskServer install directory therefore is:

~medea/MD/2.0/TaskServer

You should copy your VASP binaries to the following directory:

~medea/MD/2.0/TaskServer/Tools/vasp4.6.31/Linux-x86_64/

Depending on how you compiled VASP, it may need a number of dynamic link libraries. You can tell the TaskServer about their location by editing the LD_LIBRARY_PATH variable in

~medea\MD\2.0\TaskServer\Tools\vasp4.6.31\VaspSetup.tcl

We recommend keeping a backup copy of the original file *VaspSetup.tcl*. Also, add comments when changing the original settings to keep track of modifications.

5. Checklist

- The user `medea` is set up and owns the TaskServer directory tree and all files therein
- The process mdTaskServer is installed as daemon/service. It belongs to user `medea` and it is definitely not running as `root.`
- All Vasp executables are in the right position, executable with correct ownership and rights

II. Functionality and Use

A. MEDEA overview

THE MEDEA environment is designed to give quick access to materials property data both by mining experimental data and by computing properties where experimental data is scarce or only partly available. MEDEA includes graphical user interfaces to accomplish search and retrieval of experimental data, structure building, setup of computations and data visualization and analysis.

Given the increasing complexity of materials and decreasing scale of systems used in industrial devices, decisive experiments are often time consuming and expensive. Computations can help to prepare, design and interpret experiments.

However, just like performing a complex experiment, setting up computations requires scientific and technical rigor, precision and careful analysis. MEDEA helps you to achieves these qualities by

- providing experimental data as starting points for computations
- giving access to industrially qualified routines for structure analysis and structure building
- using high-end computational codes with a complete set of defaults and convergence tests
- automating complex multi-step calculations
- enabling you to run thousands of calculations using a powerful job management and data processing paradigm

In the following, we provide a short overview of key properties and related modules:

1. MedeA capabilities by properties

The individual **MedeA modules** are in **red**.

a. Structure and elastic properties, defects

Experimental structure, powder pattern, neutron diffraction data

- Search & Retrieve lattice parameters atomic positions and related data from structure databases like **ICSD**, **Pauling**, **Pearsons** and **NIST** using **InfomaticA**

Structural analysis and structure building, geometry analysis and symmetry analysis

- Build crystal structures, surfaces and molecules using MedeA's **Builders**
- Analyze structures for symmetry, bonds and angles, visualize empty space, plot nearest neighbors and powder pattern using **Geometry Analysis** and **Empty Space Finder**

Structure prediction, elastic constant, elastic modulus

- Compute energies of formation using **VASP**, compute the temperature dependence of formation energies **PHONON** in combination with **VASP**
- Run a fully autmated strain-stress analysis to derive elastic constants using **MT** in combination with **VASP**

Substitutional and interstitial defects, defect insertion energies

- Study substitutional defects using **Substitutional Search**
- Find empty space and determine coordination of interstitial sites using **Empty Space Finder**

b. Vibrational spectroscopy, thermodynamics, diffusion

Raman/Infrared data

- Use **PHONON** to get the positions of RAMAN/IR peaks from the full PHONON spectrum
- In **PHONON**, graphically visualize, characterize and animate lattice vibrational modes and PHONON density of states

Thermodynamic functions, phase stability

- Compute the Free energy, vibrational entropy and specific heat as a function of Temperature using **PHONON**

Segregation, diffusion barriers

- Compute bulk/surface and bulk/interface segregation energies using **VASP**
- Find transition states and diffusion barriers using **Transition State Search**
- Get temperature dependence using **PHONON**

c. Fluid phases, statistical properties, adsorption in solids

Fluids: single phase properties

- Compute the volume, pressure, density, composition and enthalpy of a single liquide or gas pase using **Gibbs**

Phase equilibria

- Compute liquid/liquid, liquid/gas and gas/gas phase equilibria using **Gibbs**
  - Critical points
  - T,P, composition

Adsorption in solids, surface adsorption

- Compute adsorption isotherm using **Gibbs**
  - Porous solids: MOF's, zeolites
- Determine adsorption geometries, binding energies and bond frequencies of molecules on surfaces using **PHONON** and **VASP**

2. Overview by modules

a. MEDEA capabilities sorted by MEDEA modules

Phonon

- Vibrational properties
- Termodynamic functions
- IR/Raman data

MT

- Elastic constants and moduli
- Heat expansion and Thermodynamic functions (Debye Grüneisen theory)

Fermi

- Brillouin zone visualization and electronic isoenergy surfaces
- Fermi surfaces
- Effective masses

Point Defect analysis

- Defect energies
- Automated convergence
- Supercell creation

VASP

- DFT solver
- Energy of formation
- Electronic structure, stress tensor and forces

Interface builder

- Search for matching interfaces
- Grain boundaries
- Heterogeneous interfaces

Predibond

- Bond energies
- Prediction of catalytic activity: correlation with experimental data

Molecular builder
Surface builder

- Build molecules and surfaces
- Combine to form adsorbate systems

Gibbs

- Single phase and phase equilibria
- Mixed phase systems
- Adsorption isotherms

Substitutional Search

- Explores configurational space for subst. defects
- Structure visualization
- Interface to Combi

Empty space finder

- Determines open space
- Visualization by sphere size and local coordination

Automated convergence

- Converges VASP parameters for energy and stress tensor: k-point mesh, plane wave cutoff, smearing

Combi

- Spreadsheet with combinatorial builder
- Structure visualization
- Interface to VASP and Job submission

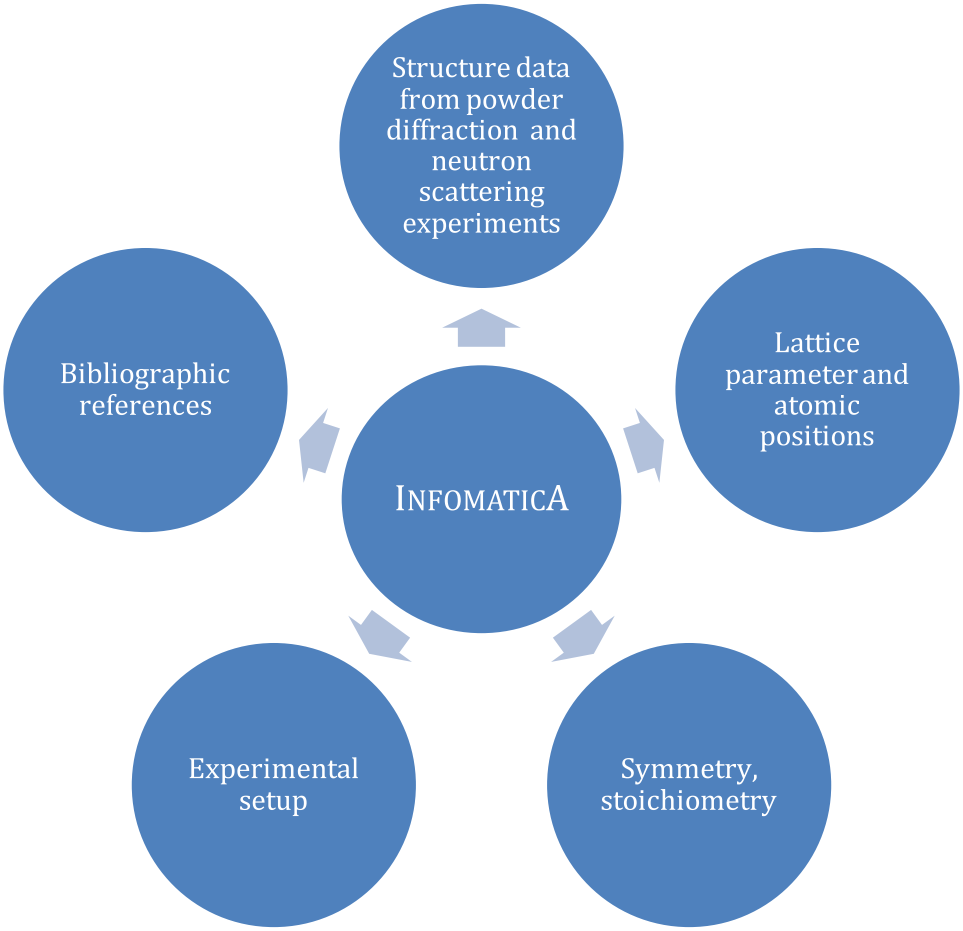
Job Control

- Cross platform tier architecture for computational job control
- Html interface

B. INFOMATICA

Overview

MEDEA INFOMATICA provides a graphical user interface to the experimental databases ICSD, NCD, Pauling and Pearsons. Together these databases contain over half a million structure entries, thus representing one of the largest integrated sources of solid state structure data accessible today.



INFOMATICA provides an easy-to-use keyword search language allowing to formulate complex requests on the full set of experimental and computed data available.

MEDEA offers a simple interface to store computed structure data in INFOMATICA. You can build up your own database of computed structures along with comments and references and search this database in combination with the experimental ones.

1. INFOMATICA's Structure Databases

a. ICSD (Inorganic Crystal Structure Database)

ICSD contains crystal structure information for non-organic compounds mainly including ceramics and minerals and since recently also metallic systems. ICSD entries go back to 1915; currently the database has around 103,000 structure entries. ICSD is maintained by the Fachinformationszentrum Karlsruhe (FIZ), Germany.

b. NIST Crystal Data (NCD)

NCD contains chemical, physical, and crystallographic information on more than 237,671 inorganic and organic crystalline materials. NCD includes reliable data across the entire range of solid state materials including minerals, intermetallic phases, metals, alloys, drugs, antibiotics, and pesticides. Data included in NIST comprise standard cell parameters, cell volume, space group number and symbol, calculated density, chemical formula, chemical name, and classification by chemical type. NCD is maintained by the National Institute of Standards and Technology (NIST), USA.

c. The Pauling file (binary edition)

The Pauling file provides structural data and physical properties for approximately 28,000 binary intermetallic and oxide systems. For a smaller subset of structures, phase diagram information is available (as of MEDEA version 2.4, the visualization of phase diagrams in MEDEA is still in development). The Editor-in-chief of the Pauling file is Prof. Pierre Villars, Switzerland.

d. Pearsons File

The Pearson's data file is a crystallographic database published by ASM International. It contains crystal structures of the full range of inorganic compounds. The present MEDEA release contains close to 150,000 structural data sets (including atom coordinates and displacement parameters, when determined) for more than 95,000 different phases.

e. Computed data

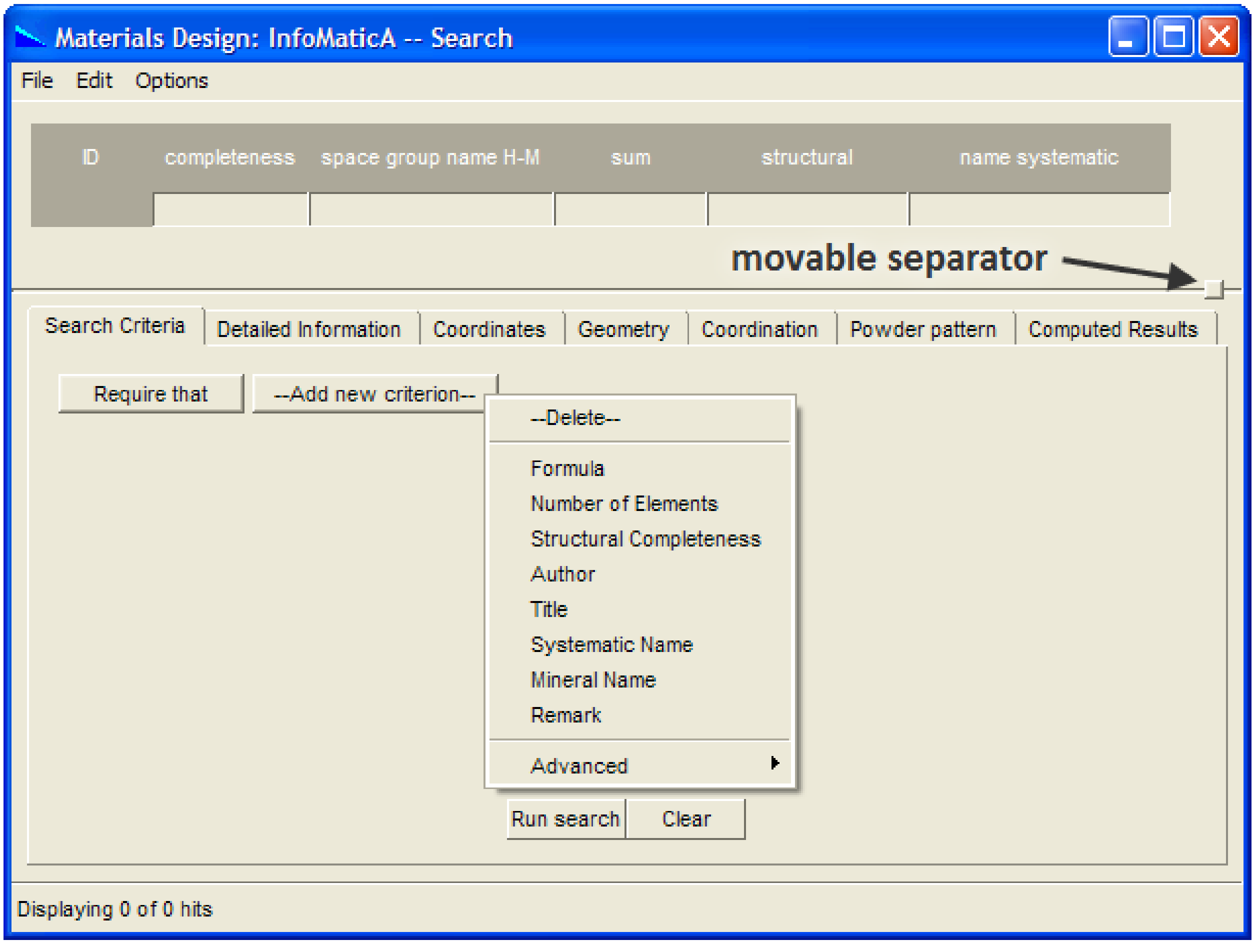
Computed structures can be saved to the "computational database". To save a structure, bring up the structure window in MEDEA (e.g. by loading a minimized structure from a previous calculation) and select **Save** from the MEDEA **File** menu. When saving a structure, you should provide a name and comments to save along with the structure. Structures saved this way can be retrieved through a standard search request along with experimental database entries.

2. Starting INFOMATICA

To bring up the INFOMATICA entry in the MEDEA menu, select **INFOMATICA** from the MEDEA **Tools** menu. Next click **INFOMATICA** ≫ **Search** to bring up the INFOMATICA Search window.

The main elements of the INFOMATICA interface are the following (top to bottom):

- A menu bar containing entries **Files**, **Edit** and **Options**
- A configurable table for displaying search results in the upper region
- A adjustable separator
- A number of panels in the lower region to formulate search phrases and to visualize structure specific results



3. Searching and Retrieving Data

Start your search in the panel labeled **Search Criteria** by formulating a search phrase. To do so, click on **--Add new criterion** and select a search option. The following criteria are available:

- **—Delete—**: Delete present search criterion
- **Formula**: Provide a chemical formula or parts of it
- **Number of Elements**: Allow a certain number or range of elements
- **Structural Completeness**: Display only structures with complete atomic positions
- **Author**: Search by author name
- **Title**: Search by publication title
- **Systematic name**: Search by the systematic name of the structure
- **Mineral name**: Search by mineral name
- **Remark**: Search by content of Remark section
- **Advanced**: Defines additional search criteria (database specific)

Note that, as you select a key word from the list, additional "sub options" may appear next to it. Click these options in order to build a complete search phrase.

For example, the **Formula** criterion has the following sub-options:

- **is**: Exact chemical formula, e.g. Fe2O3, Be, TiC, etc
- **contains exactly**: Number and type of atoms, e.g. **contains exactly** 3 **atoms of** Fe
- **contains any number of**: Atoms type, e.g. **contains any number** **of atoms from group III**
- **contains less than**: Atom type and upper boundary for number
- **contains more than**: Range of number and atom type
- **does not contain**: Excludes atom types
- **has a ratio of**: Exact ratio of two atom types

Some criteria like Author, Remarks, and Title let you search text sections of the datafiles. These options have sub-options

- **Is**: Search for an exact text string
- **Is Not**: As above but "exclusive"
- **Is like**: Search for approximately a text string. Use wildcards "?" (one replacement) and "%" (multiple replacements) to
- **Is Not Like** As above but "exclusive"
- **Contains** : Search for a substring

Furthermore, a given search statement or row can be made active, non active or conditional by clicking on **Require that** on the left hand side of each search phrase and selecting either of the options given below:

- **Require that**: Require that the search criterion in present line is fulfilled
- **If present**: Require criterion in present line to be fulfilled if present or possible
- **Ignore**: Criterion is ignored

Once you have built a search phrase, click **Run search** to actually perform the search and display results. If needed, add additional criteria using a second line and so forth, until you are satisfied with the results.

4. Displaying Detailed Information

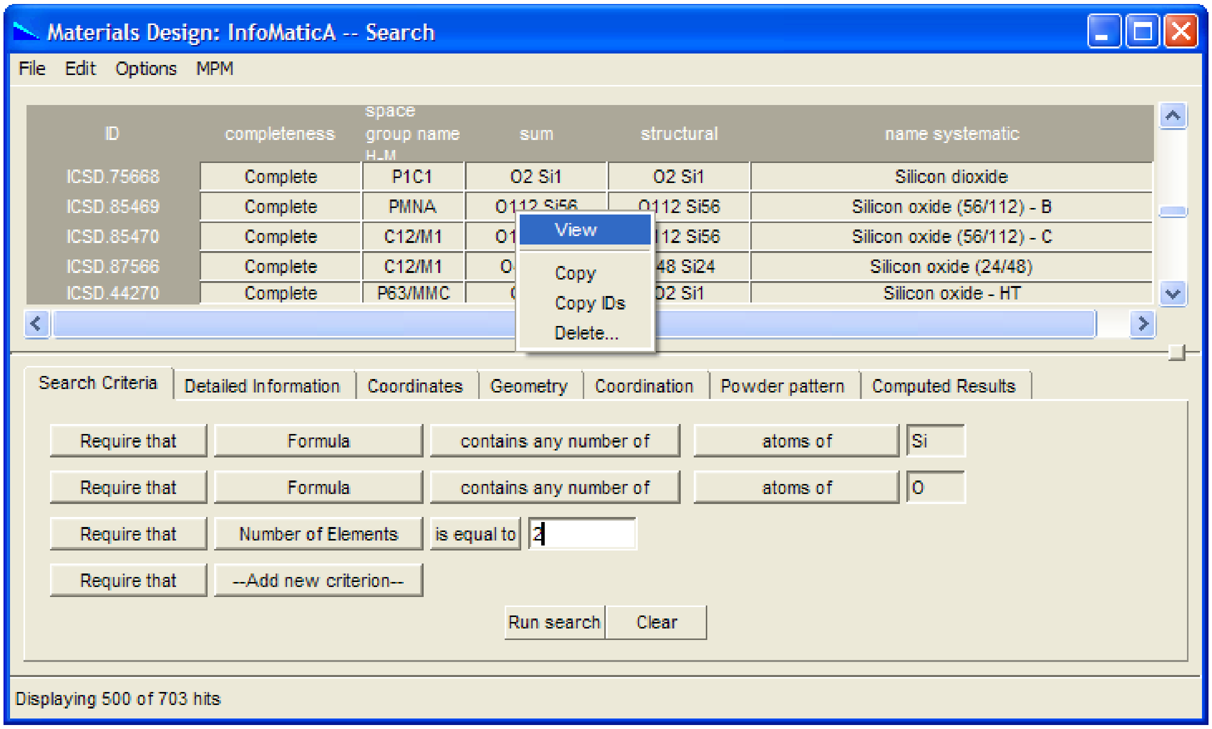
To get more information on a structure entry, select it left-by clicking on the corresponding row in the table of results. Next click the **Detailed Information** panel or any other of the following:

- **Search criteria** Formulate search phrase and run searches on all databases
- **Detailed information** Display main structural data, symmetry data and bibliographic references

Coordinates	Display atomic coordinates, Wyckoff positions and site occupancies
Geometry	Display bond length and angles; Define a cutoff to change range
Coordination	Select a lattice site and display a nearest neighbor diagram
Powder pattern	Select parameters to calculate and display powder pattern
Computed Results	Display results from computations! - Currently empty

5. Viewing and Editing Structures

Structures indicated by MEDEA to be **complete** have all information on unit cell and atomic positions needed to display them in a 3D structure model. To view such a structure, left click on the corresponding row in the table of results to select it, then right-click select **View** from the pop-up menu (see below).



ID	completeness	space group name H_M	sum	structural	name systematic
ICSD.75668	Complete	P1C1	O2 Si1	O2 Si1	Silicon dioxide
ICSD.85469	Complete	PMNA	O112 Si56	O112 Si56	Silicon oxide (56/112) - B
ICSD.85470	Complete	C12/M1	O1	12 Si56	Silicon oxide (56/112) - C
ICSD.87566	Complete	C12/M1	O	48 Si24	Silicon oxide (24/48)
ICSD.44270	Complete	P63/MMC		O2 Si1	Silicon oxide - HT

Require that | Formula | contains any number of | atoms of | Si
Require that | Formula | contains any number of | atoms of | O
Require that | Number of Elements | is equal to | 2
Require that | --Add new criterion--

Displaying 500 of 703 hits

Alternatively to viewing the structure directly, you can use the **Copy** menu entry to copy structure information to MEDEA's internal clipboard for later use, for example with COMBI or with PREDIBOND.

The **Delete** option can be used to delete structure entries from the user database but cannot be applied to the experimental databases.

6. Configuration Options

Use the **Option** menu in INFOMATICA'S top menu bar to change INFOMATICA'S default settings:

- **Options**: Set the number of maximum hits to display in the results table
- **Properties**: Add/Remove properties to be displayed in the results table
- **Databases**: Select the databases to include in a search

C. Building and Structure Editing

1. Building Crystal Structures

In MEDEA, you can either build structures from scratch or you can use experimental structures as templates or building blocks.

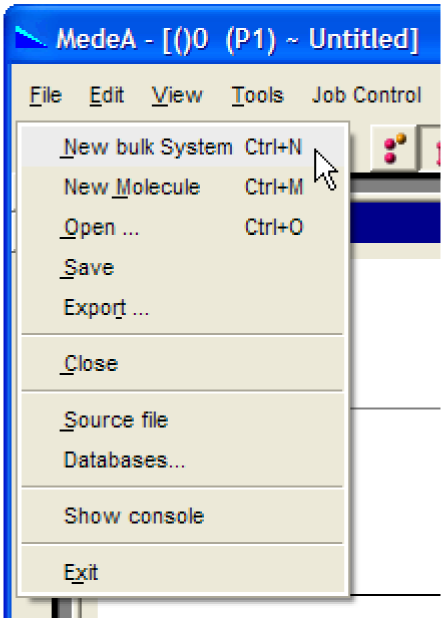
a. Starting from bulk structures in INFOMATICA

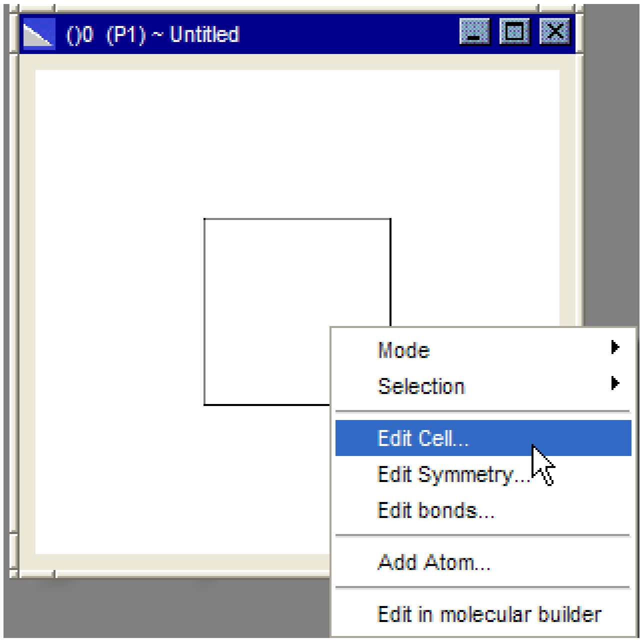
Most likely, you will find your system of interest or a closely related one in one of the experimental data files. From a computational point of view, a crystal structure under ambient pressure and room temperature is close to the low temperature structure determined by a DFT calculation. Starting DFT/GIBBS computations from experimental structure data usually is a very good option. If the system you have in mind is not available in INFOMATICA, try finding a closely related system and modify it by editing/moving atoms and changing lattice parameters.

b. Build it by hand:

To build a crystal structure “by hand” you need to know its crystal symmetry, lattice parameters and atomic positions. If you know the space group of the system, MEDEA will help you setting up the remaining parameters using symmetry.

- To build a crystal structure from scratch, select **New bulk system** from the **File** menu in MEDEA's main window (below left) or press Ctrl-N to bring up the builder window.

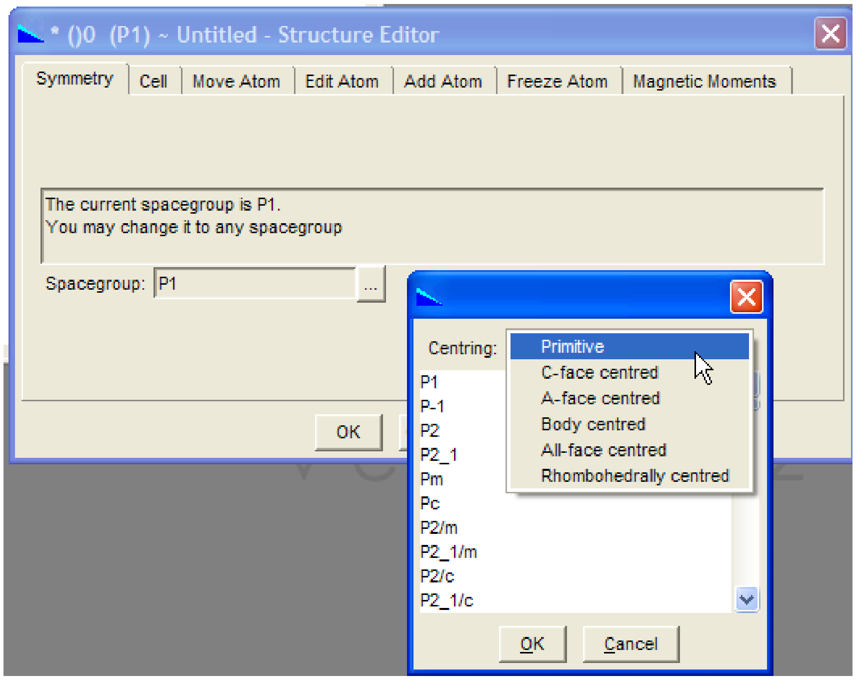




You could start adding atoms right now, but it is more efficient to choose the desired symmetry before adding atoms. This way, symmetrically equivalent atoms will be recognized as such and positioned at the corresponding lattice sites.

- Right-click into the structure window and select **Edit cell** from the context menu (above right). Select the desired space group in the **Symmetry** menu and click **Apply**.

For example, to build an *Immm* structure, you can either type *Immm* in the Spacegroup text field or select **...** next to the Spacegroup field and then select **Body centred** from the **Centring** menu and finally ***Immm*** confirming with **Apply**.



The current spacegroup is P1.
You may change it to any spacegroup

Spacegroup: P1

Note that from the moment you apply the symmetry, MEDEA displays the spacegroup as the current spacegroup of the system.

The current spacegroup is Immm.
You may change it to any spacegroup

All further operations like **Add atom**, **Move atom**, **Edit Cell** will be subject to preserving the new symmetry, unless you explicitly lower it back to P1!

- Next, click on the **Cell** tab to change lattice parameter and angels

In our *Immm* example, the **Cell** panel shows all lattice parameters as grayed out except for the cell length parameters *a*, *b*, *c*. This is consistent with a body centered crystal structure always having cells of 90 degrees angles.

- Click the **Add Atoms** panel and enter atomic coordinates. Note that MEDEA will automatically add atoms at symmetry equivalent positions.

2. Editing Crystal Structures

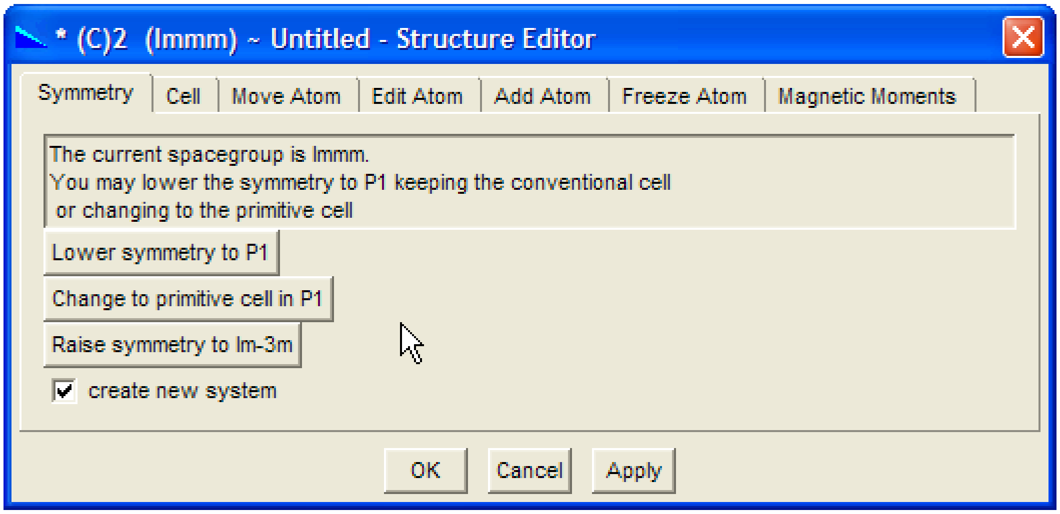
The **Edit** menu lets you change a structure's cell parameters and atomic positions, add or replace atoms and create a magnetic structures by setting magnetic moments for specific atoms.

- Right-click into the structure window and select **Edit Cell** from the context menu or select **Edit** ≫ **Edit Structure** in MedeA's main menu

The following panels make up the **Edit cell** menu:

a. Symmetry panel

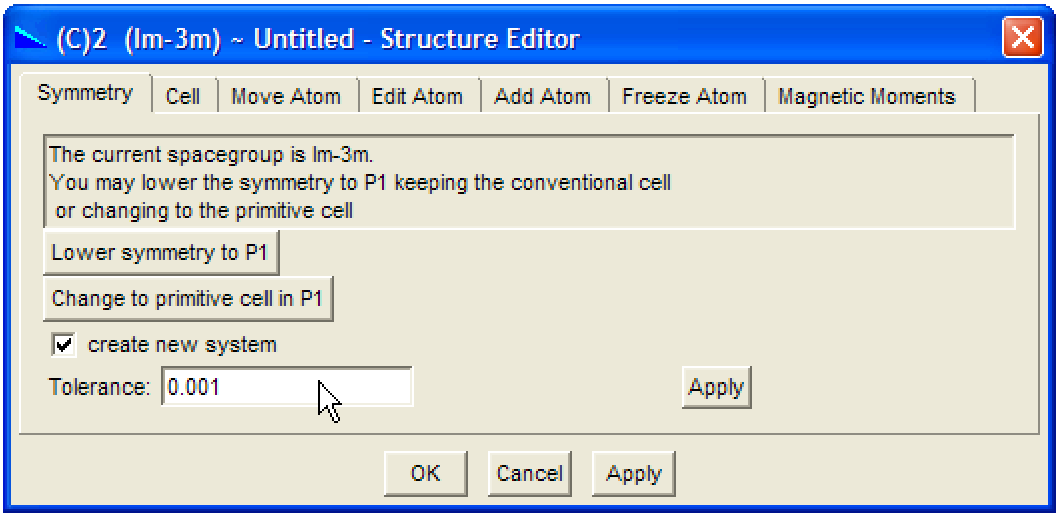
This panel shows the symmetry of the currently active structure window. It allows you to lower the symmetry to *P*1 or raise the symmetry if MedeA finds a higher symmetry group. In addition, if a primitive cell exists for the crystal system edited, MedeA will show an option to create a primitive cell.



The current spacegroup is Immm.
You may lower the symmetry to P1 keeping the conventional cell
or changing to the primitive cell

☑ create new system

- Select **create new system** to create a new structure window when applying any of the actions



The current spacegroup is Im-3m.
You may lower the symmetry to P1 keeping the conventional cell
or changing to the primitive cell

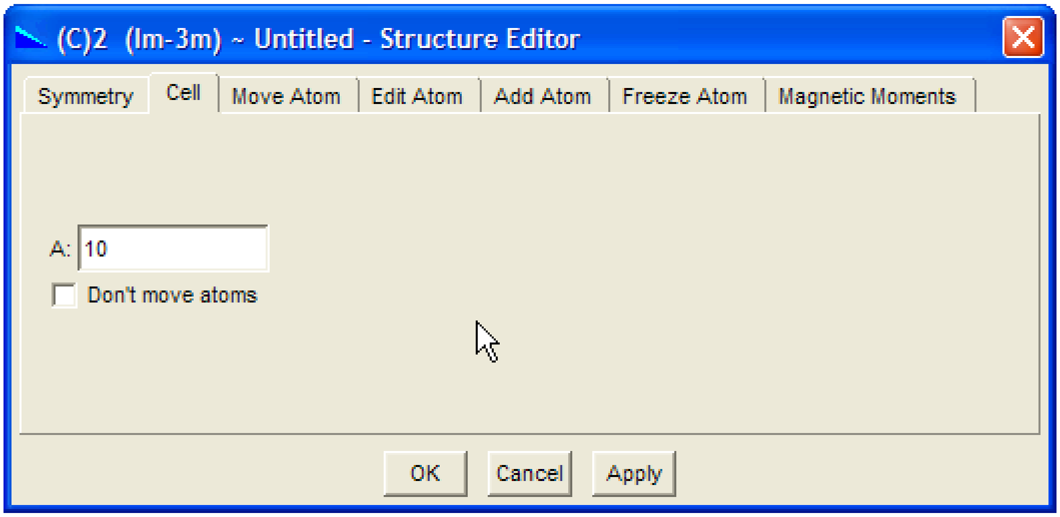
☑ create new system

Tolerance: 0.001

- Set a **Tolerance** parameter to change the precision parameter, MEDEA uses in the symmetry finder: MEDEA allows for a relative error when checking lattice sites for symmetry. Increase the tolerance to e.g. 0.01 to find identical positions. Click **Apply** to use the modified tolerance settings.

b. Cell panel

Lets you change the cell parameter of the currently active structure while respecting the current symmetry. Lower the symmetry to *P*1 before trying to change cell parameters in such a way that breaks the current symmetry.



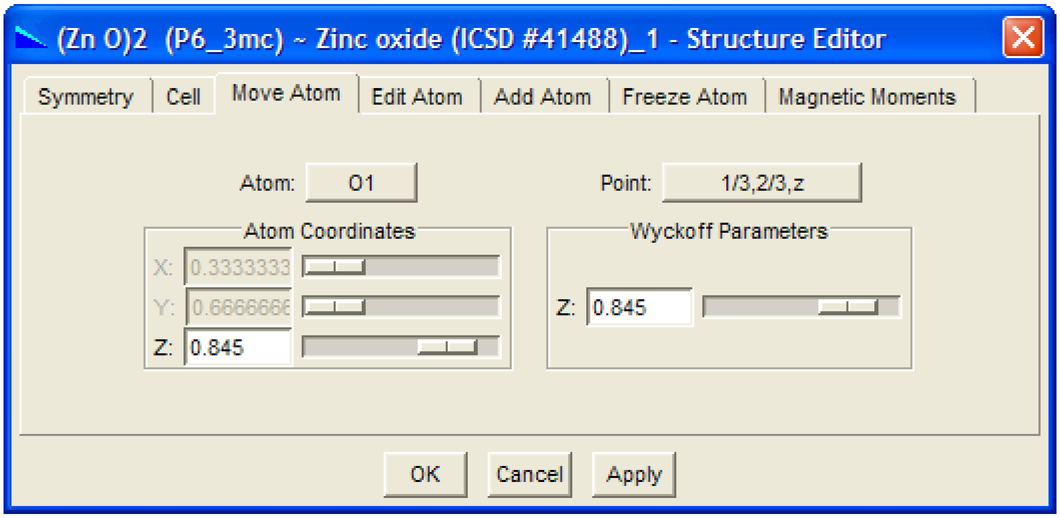
A: 10

☐ Don't move atoms

Check the **Don't move atoms** box to change the lattice parameters without moving atoms. This can be useful for creating gaps or slab structures.

c. Move Atom panel

Shows the internal degrees of freedom for the current symmetry and lets you move atoms in accordance with that symmetry.



Atom: O1

Point: 1/3,2/3,z

X: 0.3333333

Y: 0.6666666

Z: 0.845

Z: 0.845

- Make your changes and then click **Apply** to make a change permanent, click **Cancel** to discard changes.

If you would like to make changes that break the current symmetry do the following:

- Lower the symmetry to P1 in the **Symmetry** panel
- Click the **Cell panel** and make changes (all degrees of freedom will be available)
- Click on **Symmetry** to find the new symmetry
- If a new symmetry was found, you may raise the symmetry by clicking **Raise symmetry**

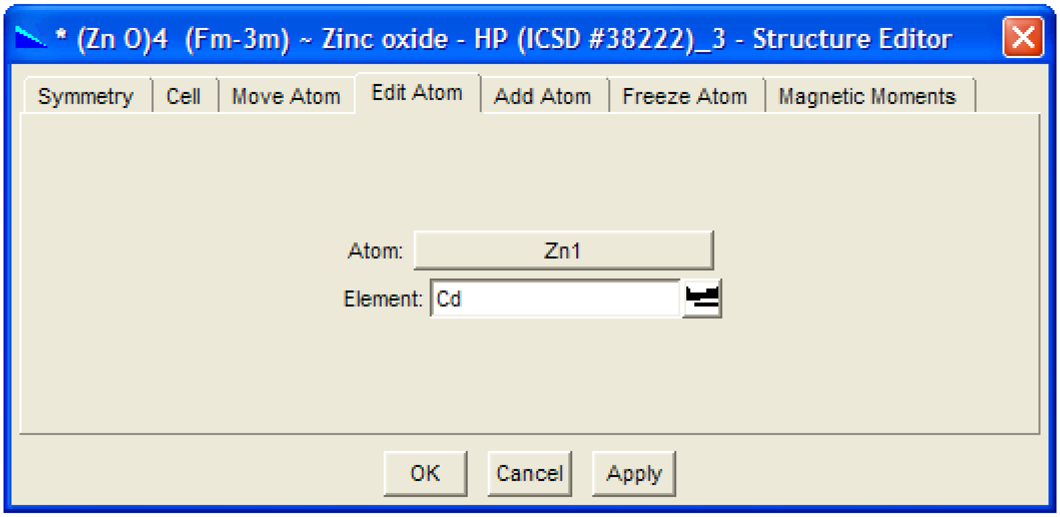
Note: Positions for each atom are given in relative cell coordinates (left) and in Wyckoff symmetry notation (right).

In our first example, namely cubic ZnO, neither the Zn atom nor the O atom can be moved without breaking the symmetry. In hexagonal ZnO, on the other hand, both O and Zn have an internal degree of freedom in z-direction; hence these coordinates are not grayed out.

d. Edit Atom panel

The Edit Atom menu allows selecting an atom from the Atom list and replacing it by a different element. Note that atoms on symmetry equivalent positions are replaced as well. Selected atom types are highlighted in pink in the MEDEA structure window.

To select an atom type to replace the present atom, you can either type in chemical symbol or click on the periodic-table icon to open a small periodic table and select an element from. Confirm every change with **Apply.**


* (Zn O)4 (Fm-3m) ~ Zinc oxide - HP (ICSD #38222)_3 - Structure Editor

Atom: Zn1

Element: Cd

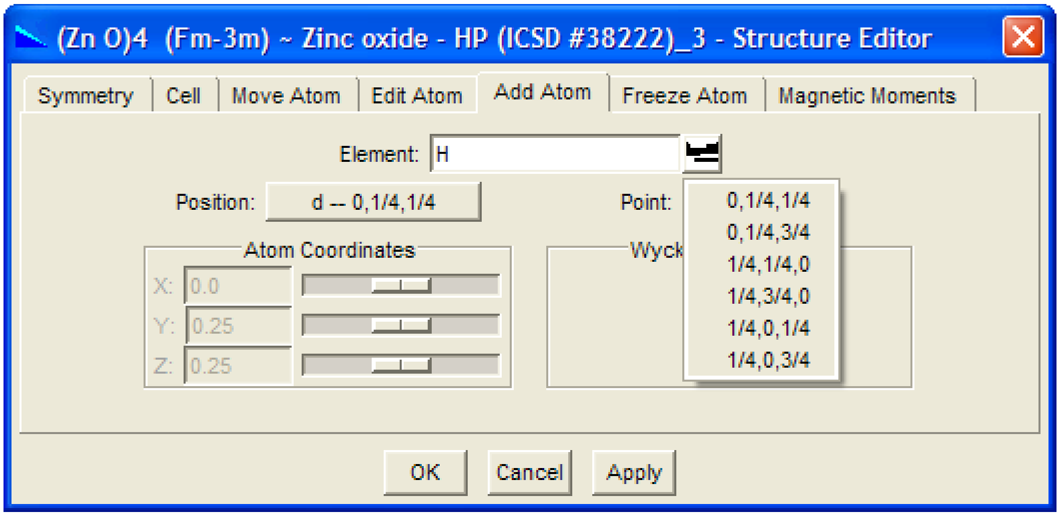
*Note: Alternatively to using the **Edit Atom** dialogue you can use the **Molecular Spreadsheet** to edit atom types.*

e. Add Atom panel

To add atoms to the structure, do the following:

- Type the chemical symbol to add an atom for or select from the periodic table
- Select atomic symmetry positions from the Position menu (left-hand side)
- Use sliders to define position or type in atom coordinates directly: all coordinates are in relative unit cell coordinates

As all other operations affecting symmetry, **Add Atom** respects the symmetry of the current system, so multiple atoms will be added automatically if required by symmetry. Their positions are shown in Wyckhoff parameters on the right hand side.



Element: H

Position: d -- 0,1/4,1/4

Point: 0,1/4,1/4 / 0,1/4,3/4 / 1/4,1/4,0 / 1/4,3/4,0 / 1/4,0,1/4 / 1/4,0,3/4

X: 0.0

Y: 0.25

Z: 0.25

To ignore symmetry constraints, first lower the symmetry of the system to *P*1.

f. Freeze Atom panel

Both VASP and PHONON can handle “frozen atomic positions”. In a VASP Structure relaxation, frozen atoms remain at their initial positions. In a PHONON calculation you can select the option not to displace “frozen atoms”, which implies that their contribution to the lattice vibration spectrum will not be calculated (e.g. you want just the frequency of a stretch bond of a molecule bound to a surface, but not the full PHONON spectrum of the molecule-surface system).

- Select an atom from the list of atoms and click the **x**/**y**/**z** coordinates depending on which directions of motion you would like to freeze.
- Click **Freeze all** to freeze all x, y, and z directions of motion for a given atom.

Atom: Zn1

- Confirm with **Apply** after each change, especially before selecting another atom from the list.

Note that using the MEDEA interface you can freeze atoms in various ways:

- Use the Freeze Atom panel above
- In a structure window, click on an atom or a selection of atoms and choose **Freeze** from the pop-up menu

- Use the **Molecular Spreadsheet** to select which coordinates to freeze

g. Magnetic Moments panel

Set **Magnetic Moments** for specific atoms through this menu. MEDEA will consider magnetic moments set by the user when running a VASP calculation (version 4.6 and higher). This action imposes just an initial magnetic structure; the actual value of the magnetic moment is calculated self consistently by VASP.

- Select an atom from the list and set the magnetic moment (units are μB). Confirm by clicking **Apply** after each change

In order to break the initial symmetry by imposing a magnetic moment, you need to lower the symmetry first, and then set magnetic moments.

Note : The magnetic symmetry is not taken into account in the symmetry panel!

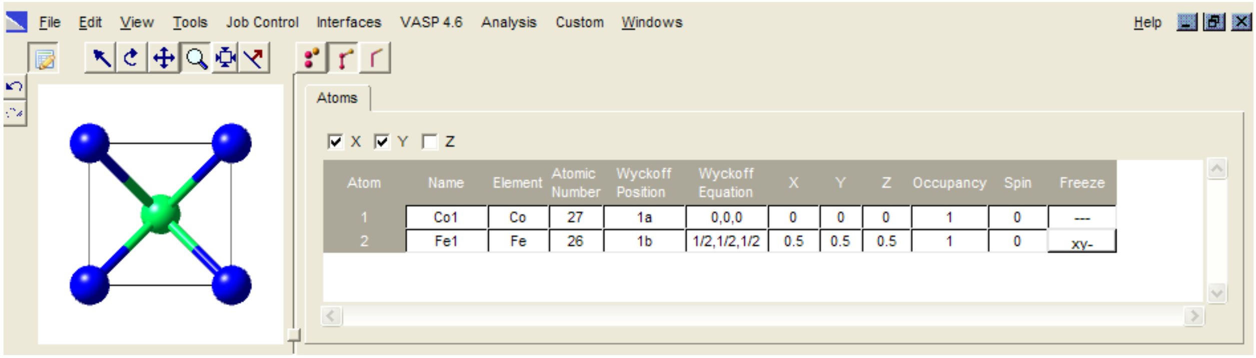
h. Molecular Spreadsheet

Using the molecular spreadsheet you can visualize and change a number of atomic properties. Use the molecular spreadsheet to:

- Quickly visualize atomic properties in complex structures
- Change the following atomic properties:
    - Name
    - Element / Atomic number
    - Spin
    - Freeze state

In addition to the above properties you can use the spreadsheet to change the atomic mass and also to assign a force field to a given atom.

To toggle the spreadsheet view on/off, click on the spreadsheet icon in the MEDEA icon bar. The currently active structure window splits into two panels, left the structure and right the spreadsheet.



☑ X ☑ Y ☐ Z

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation	X	Y	Z	Occupancy	Spin	Freeze
1	Co1	Co	27	1a	0,0,0	0	0	0	1	0	---
2	Fe1	Fe	26	1b	1/2,1/2,1/2	0.5	0.5	0.5	1	0	xy-

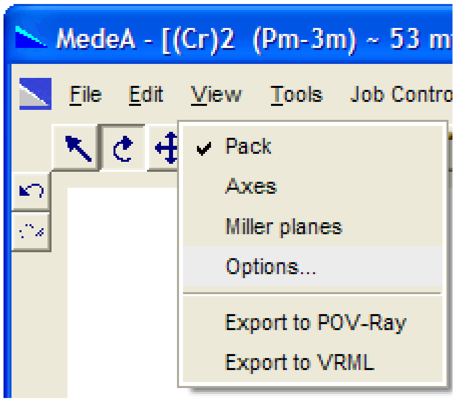
The usual table operations like sorting and filtering also work here.

- To select an atom, in the structure window, change to selection mode (hold s-key down) and left click the atom. Or simply click on a row in the spreadsheet. Note that table rows and atoms in the graphics are linked, i.e. selecting one will automatically highlight the other. Left-click and drag your mouse over a range of rows to select more than one atom at a time

Note that the spreadsheet can be used to visualize constraints, atom types, spin states etc. Simply sort the table on the right according to the criterion you would like to visualize and then select the block of atoms within the range you are interested in.

3. View Options

A range of options can be set to change the way structures are displayed in MEDEA. Use the **View** menu entry to visualize **Miller planes** and **Axes** or select **Options** from the View menu to change the range of atoms displayed on screen, to change the display style to closed packed spheres or to cylinders only, to change an elements color and related operations.



Selecting Options from the View menu

- **Pack** : Displays atoms that are (slightly) off cell boundaries
- **Axes**: Display Cartesian axes in colors, x (red), y (green), z (blue)
- **Miller planes** : Displays Miller planes within the unit cell

To display more than one plane, reselect this option from the **View** menu.

Miller indices: Values for h, k and l that define a Miller plane.

Example:1/h gives the cut of the plane with the x-axis. A Miller plane (120) will cut the axis at (x=1, y=0.5) and will be parallel to z

- **Options**: Change the appearance of the unit cell. Separate tabs for **General**,**View**, **CPK**, **Ball &Stick**, **Cylinder**, **Quality**

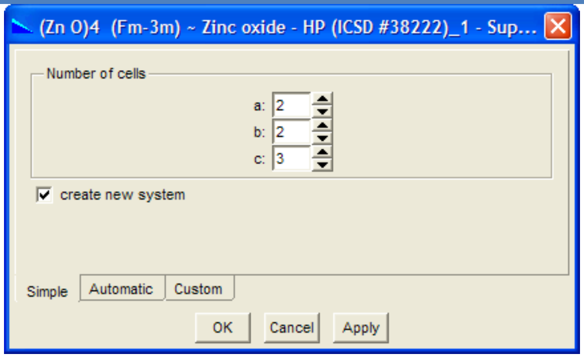
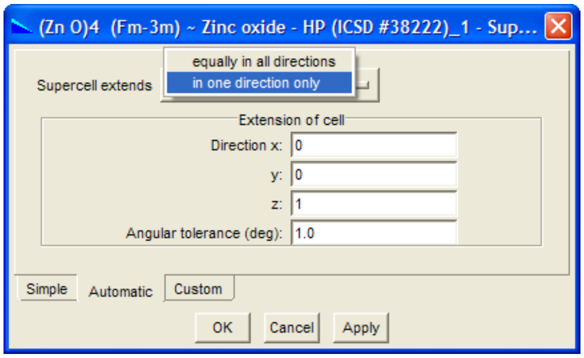
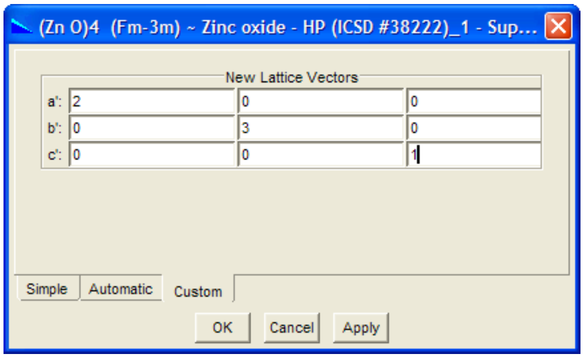
- **Export to Povray** : Exports current view to a Povray[3] file.
- **Export to VRML** : Exports current view to Virtual Reality Markup Language[4]

4. Building Supercells

The supercell builder lets you create a large cell starting from your initial structure.

- Invoke the supercell builder from the MEDEA **Edit** menu.

The following settings are available:

Mode	Description	
Simple	Increases lattice parameters in a,b, and c direction	 (Zn O)4 (Fm-3m) ~ Zinc oxide - HP (ICSD #38222)_1 - Sup... Number of cells a: 2 b: 2 c: 3 ☑ create new system
Automatic	Uses range parameter to build a supercell: • Extension equally in all directions • Extension in one direction	 (Zn O)4 (Fm-3m) ~ Zinc oxide - HP (ICSD #38222)_1 - Sup... Supercell extends: equally in all directions / in one direction only Extension of cell Direction x: 0 y: 0 z: 1 Angular tolerance (deg): 1.0
Custom	Defines a new set of lattice parameters for supercell	 (Zn O)4 (Fm-3m) ~ Zinc oxide - HP (ICSD #38222)_1 - Sup... New Lattice Vectors a': 2 0 0 b': 0 3 0 c': 0 0 1

---

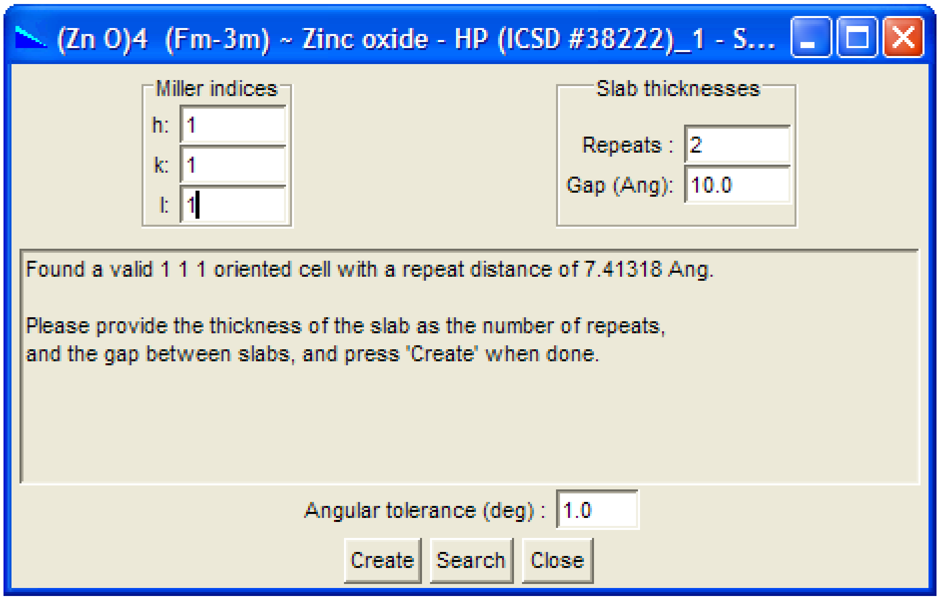
[3] Download Povray (Persistence of Vision) from the official POVRAY website. MedeA will display a link to the Povray download site, if it cannot find a Povray executable.

[4] A free client to visualize VRML can be found at parallelgraphics.com

5. Building Surfaces

The MEDEA surface builder lets you build surfaces from bulk structures by defining a set of Miller indices.

- Start from a bulk structure
- Invoke surface builder through the MEDEA menu entry : **Edit** ≫ **Build Surfaces**
- Select Miller indices (eg. 111) and press **Search**
- Follow the instructions printed by the surface builder to build your surface model



h: 1
k: 1
l: 1
Repeats : 2
Gap (Ang): 10.0

Found a valid 1 1 1 oriented cell with a repeat distance of 7.41318 Ang.

Please provide the thickness of the slab as the number of repeats, and the gap between slabs, and press 'Create' when done.

Angular tolerance (deg) : 1.0

The following options and parameters are available:

a. Orientation and Thickness

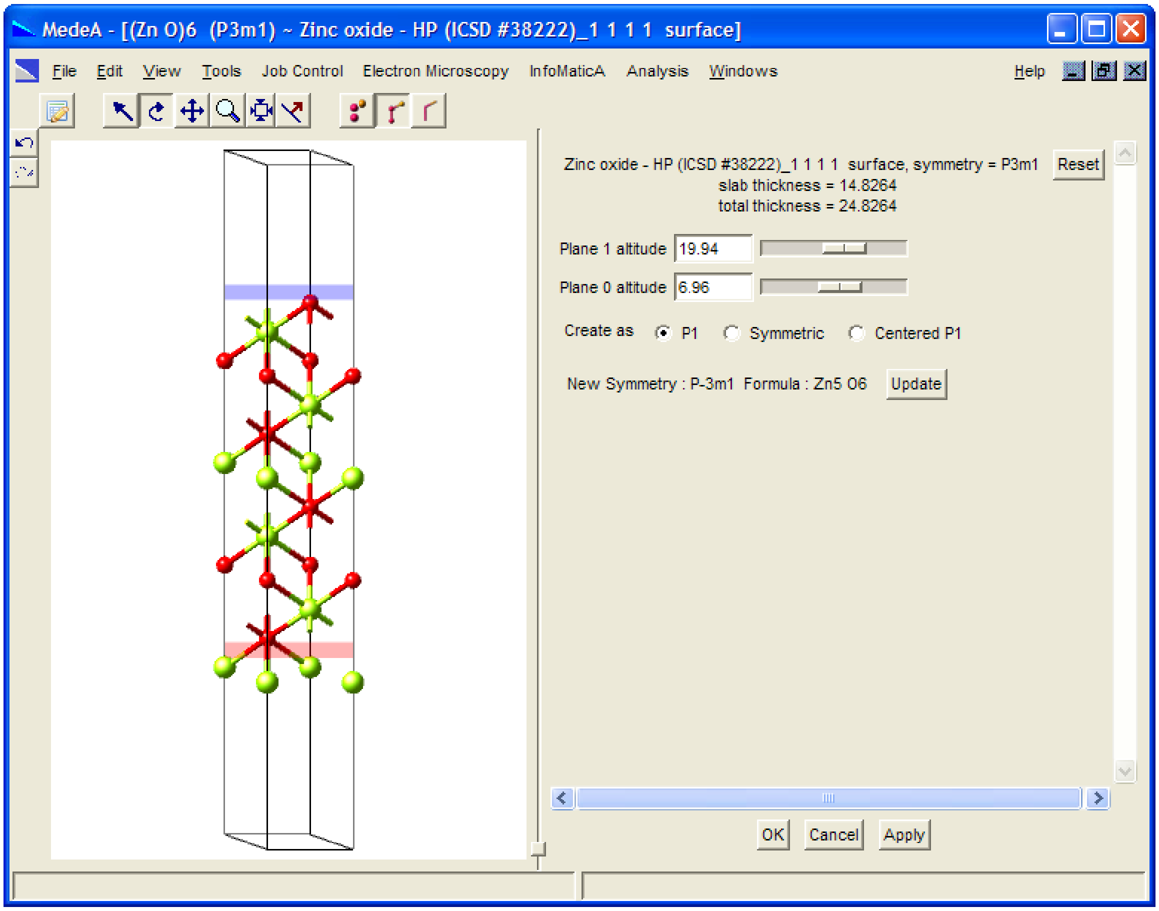
- **Repeats**: Varies the material thickness by changing the number of cells to stack in the direction of the surface plane
- **Gap**: Set the thickness of the vacuum layer. The default of 10 Å is a good value making sure that there's no interaction between surface layers within the periodic boundary model used e.g. by VASP
- **Angular tolerance**: For some bulk structures and surface directions it is not possible to build a coherent cell accommodating the structure with correct stoichometry. An angular tolerance of 1 deg allows for deviation of the surface normal from the desired direction by 1 deg
- **Create**: Build and display a preview of the surface model

MEDEA now displays a preview window allowing you to set further parameters and to check the symmetry of the resulting system before building the final structure.

b. Surface builder preview window

Here, you can verify the model, check its symmetry and possibly move the surface plane in order to cut parts of the structure away.

- Use the sliders *Plane 0* and *Plane 1* to remove surface layers. For example, in hexagonal ZnO above, you may decide to terminate both surfaces by just zinc atoms or by just oxygen
- Click **Update** to display the current symmetry
- Click **Reset** to return to the previous builder screen



Zinc oxide - HP (ICSD #38222)_1 1 1 1 surface, symmetry = P3m1
slab thickness = 14.8264
total thickness = 24.8264

Plane 1 altitude 19.94

Plane 0 altitude 6.96

Create as ● P1 ○ Symmetric ○ Centered P1

New Symmetry : P-3m1 Formula : Zn5 O6

- Click **P1**, **Symmetric** or **Centered P1** to choose in which symmetry to display the final system
- Click **Apply** to create the final surface structure but keep the Preview window open
- Click **OK** to create the final structure and close the Preview window
- Click **Cancel** to abandon the whole operation

Note: Changing the termination of the slab model may change the stoichometry and symmetry of the system. If your goal is to calculate a surface energy you should make sure that both surfaces present in the slab model are identical. Also, in polar systems, you may want to avoid creating a dipole by working with systems that have inversion symmetry.

What symmetry you choose for the final surface depends on your goals: For example, to calculate the surface energy of the above system you would like to use the full symmetry of the system. To add a molecule to the surface, you most likely would use P1, as you are going to further modify the structure.

- **Create as P1** creates a slab model exactly the way you see it on the screen
- **Create as Symmetric** uses the new symmetry to set up the slab model, might change the cell shape
- **Create as Centered P1** creates a slab model as you see it on the screen, but re-centered

6. Finding Empty space

The MEDEA Empty Space Finder (ESF) lets you analyze a given crystal unit cell for empty space. The ESF algorithm divides the unit cell into so-called Voronoi cells around each atom. A Voronoi cell is defined to be the volume enclosing all points that are closer to the center atom than to all other atoms.

The ESF module positions non-overlapping spheres at the vertices of the resulting polyhedral grid and maximizes their radii. In doing so the physical size of different atomic species is taken into account through a set of covalent radii (currently fixed). See the below drawing for a simplified 2-D representation of a Voronoi diagram and spheres at the Voronoi grid vertices. Note that ESF changes the sphere size to make them non-overlapping [1].

a. Void-finder Features

The following features are available for the Void Finder:

- Find and display largest possible void spheres on the vertices of a Voronoi mesh
- Display local coordination and symmetry of voids
- Insert an atom for a void
- Hide/display all/selected voids
- Sort void table by radius, site ID, symmetry, etc.

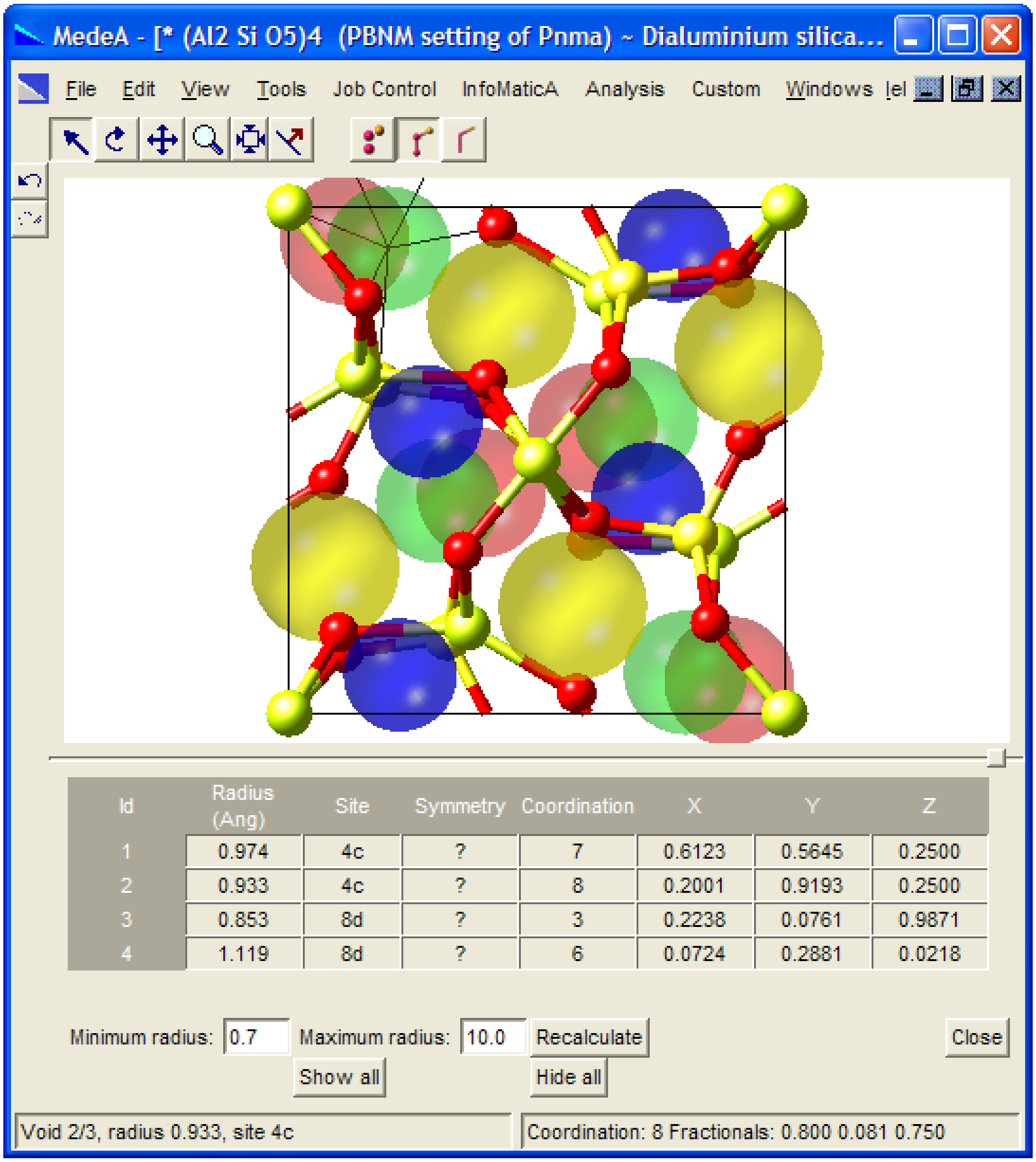
b. Usage

To use the Void finder make sure your window focus is on a MEDEA structure window and invoke **Find empty space** from the Edit menu. After a few moments (depending on the system size and your cpu power) the graphics window will split into two parts, the upper part displaying the initial structure together with translucent spheres where MEDEA has found empty space.

- Click **Recalculate** at the bottom of the page to recalculate void positions and sizes

Adjustable parameters for **Recalculate** are:

- **Minimum radius**: Gives a lower threshold for the void radius. No voids with radii smaller than the minimum radius will be shown
- **Maximum radius**: Upper threshold for the void radius. No voids with radii larger than the maximum radius will be shown



Id	Radius (Ang)	Site	Symmetry	Coordination	X	Y	Z
1	0.974	4c	?	7	0.6123	0.5645	0.2500
2	0.933	4c	?	8	0.2001	0.9193	0.2500
3	0.853	8d	?	3	0.2238	0.0761	0.9871
4	1.119	8d	?	6	0.0724	0.2881	0.0218

Minimum radius: 0.7 Maximum radius: 10.0

Void 2/3, radius 0.933, site 4c

Coordination: 8 Fractionals: 0.800 0.081 0.750

Identical voids are displayed in the same color. Coordinates and coordination are presented in the table.

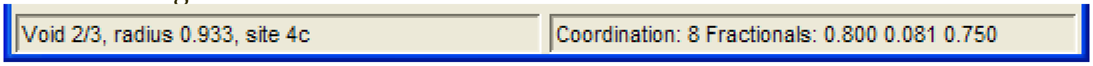
- Move the mouse cursor over a sphere to display the local coordination and symmetry of a void
- Right-click to open a dialogue letting you choose to Hide the void or to **Insert atom** at exactly this position
- Use the buttons **Show all**/**Hide all** at the bottom of window to show / hide all voids
- Right-click on a table entry to open the dialogue to **Hide** or **Insert atom** at this site
- Right-click on the table header, for example on **Radius (Ang)** and select **Sort ascending** or **Sort descending** or select **Units** to change the units

- Click the **Close** button to apply all changes and return to the original structure window

In the above example, 4 different types of voids can be found in the structure. The void in the second line has the following properties:

- "Site 4c" - 4c means that when placing an atom on this position, 4 atoms will be created by symmetry
- "Symmetry?" means that the position is not on a special symmetry position
- "Coordination 8" means that there are 8 nearest neighbors

When moving the cursor over a void status information is shown in the lower left/right:



Void 2/3, radius 0.933, site 4c

Coordination: 8 Fractionals: 0.800 0.081 0.750

Here it is the 3rd occurrence of void 2, with a radius of 0.933 Å on site 4c, the coordination is indicated by black lines, 6 distinct ones are visible in this view, two are hidden due to the projection.

7. Substitutional Search

a. *Features and Algorithm*

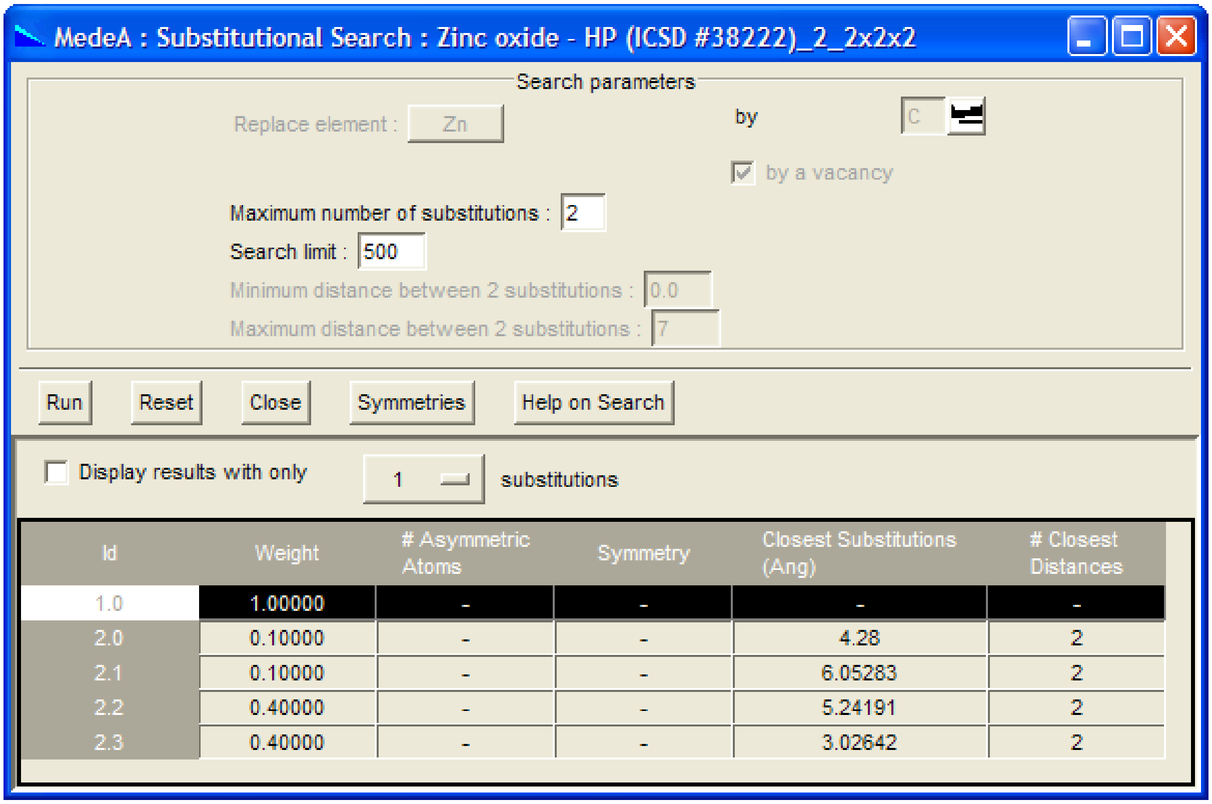
MedeA's Substitutional Search takes the active structure window as an input and searches all symmetrically different systems obtainable by substituting an element A (that has to be part of the system) by an element B at the same site. A vacancy can be chosen as type$B$. The maximum number of allowed substitutions amounts to half the number of atoms of type A already present in the system: Reversing elements A and B yields systems with exactly the inverse stoichiometry.

The search algorithm proceeds as follows: First, a single substitution $A \rightarrow B$ is made for each symmetrically independent site A, hereby generating a set of new structures. The structures resulting from this operation are grouped by their new symmetries. Next, for each element of the new set of structures, a second substitution is performed on each symmetrically independent A site; again the resulting structures are regrouped according to symmetry, and the process is repeated up to the desired number of substitutions.

b. *Usage*

To bring up the Substitutional Search interface, select the structure window you would like to perform the search in and select **Substitutional Search** from the **Edit** menu:

To start with, select which element to replace (here: Zn) and select an element to replace by (here: C)



Replace element : Zn

by C

☑ by a vacancy

Maximum number of substitutions : 2

Search limit : 500

Minimum distance between 2 substitutions : 0.0

Maximum distance between 2 substitutions : 7

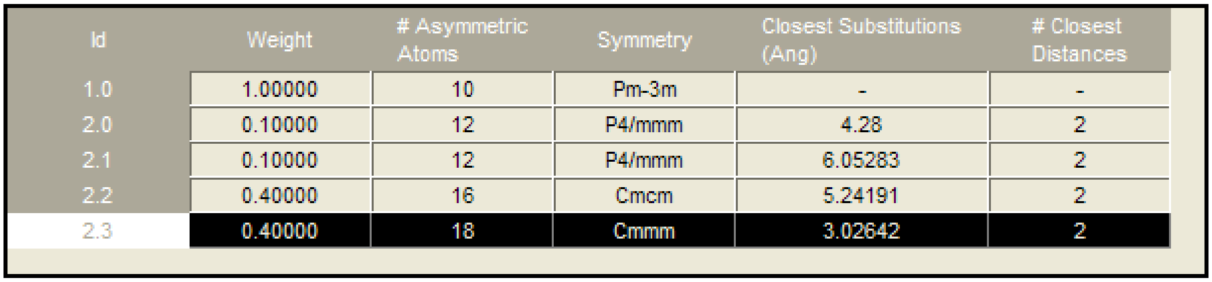
☐ Display results with only 1 substitutions

Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
1.0	1.00000	-	-	-	-
2.0	0.10000	-	-	4.28	2
2.1	0.10000	-	-	6.05283	2
2.2	0.40000	-	-	5.24191	2
2.3	0.40000	-	-	3.02642	2

You can use additional parameters to limit the search, e.g. by defining a minimal or maximal distance between two substitutions.

- **Run**: Starts the Search
- **Reset** : Resets the search without changing the parameter settings
- **Symmetries** : Calculates the symmetries for all structures displayed in the results table
- **Help on Search**: Brings up help text on Substitutional Search

In the previous example of up to two vacancies in ZnO having a maximum distance between two substitutions of 7 Å, clicking **Symmetries** creates information on the number of asymmetric atoms per cell and the cell symmetry:



Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
1.0	1.00000	10	Pm-3m	-	-
2.0	0.10000	12	P4/mmm	4.28	2
2.1	0.10000	12	P4/mmm	6.05283	2
2.2	0.40000	16	Cmcm	5.24191	2
2.3	0.40000	18	Cmmm	3.02642	2

Search results are listed in the results table and classified by an Id number giving the number of substitution in the system followed by an index. For example, Id = 2.1, 2.2, 2.3, 2.4 means that 4 symmetrically different systems with two atoms A replaced by atoms B have been found.

The displayed results can be filtered by the number of substitutions per system.

- To filter, check **Display results with only [n] substitutions** and select a number for substitutions

The table can be sorted by right-clicking on a column header and selecting a sorting criterion

- Right-click on a structure entry to view a structure, compute its symmetry or copy the system to an internal buffer for later pasting to a COMBI Spreadsheet. For this latter option you can select a copy with the symmetry of the system or a P1 copy

Other Search options are:

- **Replace element [ ] by [ ]**: Element to be replaced (A) and element to substitute with (B)
- **Maximum number of substitutions**: to be performed (default=5)
- **Search limit**: The number of systems stored in memory at each level of substitution. Reducing this parameter leads to faster searches, however a smaller search space will be covered (default=500)

- **Minimum distance between 2 substitutions**: Only systems having a distance between substitutions smaller than this parameter are considered (default=0)
- **Maximum distance between 2 substitutions**: Only systems having a distance between substitutions larger than this parameter are considered (default= not set)

An application example on "Indium defects in GaAs" can be found in the “Application notes” section of this guide.

8. Building Interfaces

a. Features and Algorithm

The MEDEA interface builder takes two surfaces slab structures of one and the same or two different materials as an input. It then searches for a relative orientation of these two surfaces such that the lattice mismatch in the resulting system is minimized.

For each of the surfaces, loop over the allowed range of cells, creating new cells that are multiples of the original cell: a' = ma + nb, b'=oa + pb where a and b are the original in-plane lattice vectors and m, n, o and p are integers from -max to +max

4) For each cell find the reduced cell, which gives a standardized list of possible cells
5) Find the matches between the two lists of reduced cells that meet the requested tolerances for the mismatch of the area, lattice parameters and angle
6) Build the surface structures for the reduced cells that match, testing for and removing duplicates. These are saved in in the subdirectory surfaces/
7) Build the trial interfaces from the surface structures
8) Find the reduced cells for the interfaces, looking for translational symmetry
9) Compare the reduced interface with previous ones and remove duplicates

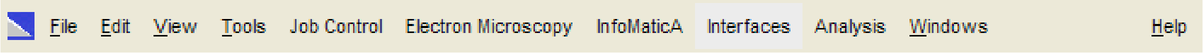
As a result Interface Search produces:

- A spreadsheet of interface structures with geometrical parameters that can be used for visualization, further geometry and symmetry analysis and as an input for computations
- A subdirectory ./interfaces (in the job directory, accessible through Job Control) containing all interfaces using default parameters for gap sizes and γ-surface shifts
- A subdirectory ./surfaces containing all surface structures built from the reduced cells that matched the tolerance criteria

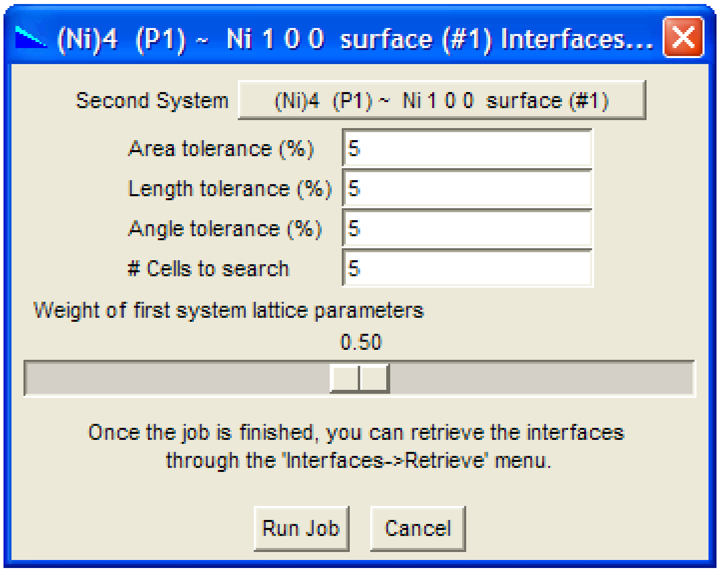
b. Usage

Here are the steps required to create a set of interfaces:

- Prepare two surfaces models using the surface builder. You can also use a single surface model to make a grain boundary
- Select **Interfaces** from the MEDEA **Tools** menu. A new entry **Interfaces** will appear in the MEDEA main menu:



- Make one of the surfaces the active system in MEDEA
- Select **Define and Run** from the Interfaces menu. The interface search dialogue is displayed:



(Ni)4 (P1) ~ Ni 1 0 0 surface (#1) Interfaces...

Second System: (Ni)4 (P1) ~ Ni 1 0 0 surface (#1)
Area tolerance (%): 5
Length tolerance (%): 5
Angle tolerance (%): 5
Cells to search: 5
Weight of first system lattice parameters: 0.50

Once the job is finished, you can retrieve the interfaces through the 'Interfaces->Retrieve' menu.

c. Default search parameters

By default, the algorithm looks for interfaces between the active, selected surface and itself – (shown as default setting for **Second System**. A tolerance of 5% will be allowed for the misfit of the area, length and angle of the two new subsystems respective.
A plane which is in-plane with the selected surfaces area(s) and has the size of 5x5 the original surface cell(s) will be searched for Bravais-type lattice vectors making up the new cell and complying with the mismatch tolerances.
In order to make a coherent cell, the in-plane lattice parameters of the two cells need to be adjusted. By default the interface builder weighs the lattice parameters of each systems with a factor 0.5, meaning both systems will be dilated/constrained by the same amount. In general you may choose a weighting factor depending on your knowledge about the elastic properties of the two materials involved.

d. Description of Search parameters

Second system: Opens a dialogue to select the second system from the list of structures currently open in MEDEA. The second system can be identical to the first one, for example when searching for grain boundaries.

Area tolerance (%): The tolerance for the deviation between the two natural surface areas making up the interface. Here, “natural” means “by construction”, that is before applying any strain to fit the two surfaces together

Length tolerance (%): Tolerance for mismatch of the natural in-plane lattice parameters of the two surface cells

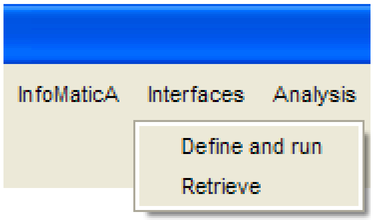
Angle tolerance: Tolerance for the mismatch of the natural in-plane angles of the two surface cells

#cells to search: How many multiples of the original cell to use for constructing new surfaces during step 1 of the search procedure (see algorithm above) .

Weight of first system: Determines how much strain is applied to the first system, when fitting the two surfaces together to form an interface. A weight of (1 - weight of first system) will be applied to the second system.

- Click **Run** to submit the interface search job.

Building the new surface structures, finding the reduced cells and symmetries and constructing and comparing the interfaces may take a considerable amount of CPU time. Depending on input symmetry, search space and system size, time to completion can vary between minutes and hours.



e. Display of results

In order to show the results of a completed interface job, invoke **Retrieve** from the INTERFACES menu entry.

Select the interface job in question from the file selection dialogue and click **Insert** and then **OK**. You will get a spreadsheet-like window showing the data of those systems that fulfill your tolerance criteria. The screenshot below shows an example of Interfaces default output for (100) Ni twist grain boundaries. The following table summarizes the parameters given in the output:

Identical Interfaces: (Yes/No) indicates if the two interfaces present in the cell are identical[5]. Using a structure model having identical interfaces allows for direct calculation of e.g. the interface energy.

ID: Counts the class of the interface, followed by another index, if there are different interfaces in this class. In the example below, the class 1 has two interfaces with different symmetry.

nAtoms: The number of atoms in the interface unit cell

Space group: Symmetry of the resulting interface unit cell

Area (Å): Area of the interface in Å^2

dA: Area mismatch of the two natural surfaces making up the interface

A, B, dA, dB: A and B lattice parameter of the interface, the mismatch of the original (natural) lattice parameters A and B in %.

Theta, dTheta : the angle of the 2-D cell (in-plane angle), the mismatch of the original (natural) in-plane angles

BedÅngle: The twist angle between the two surface layers making up the interface

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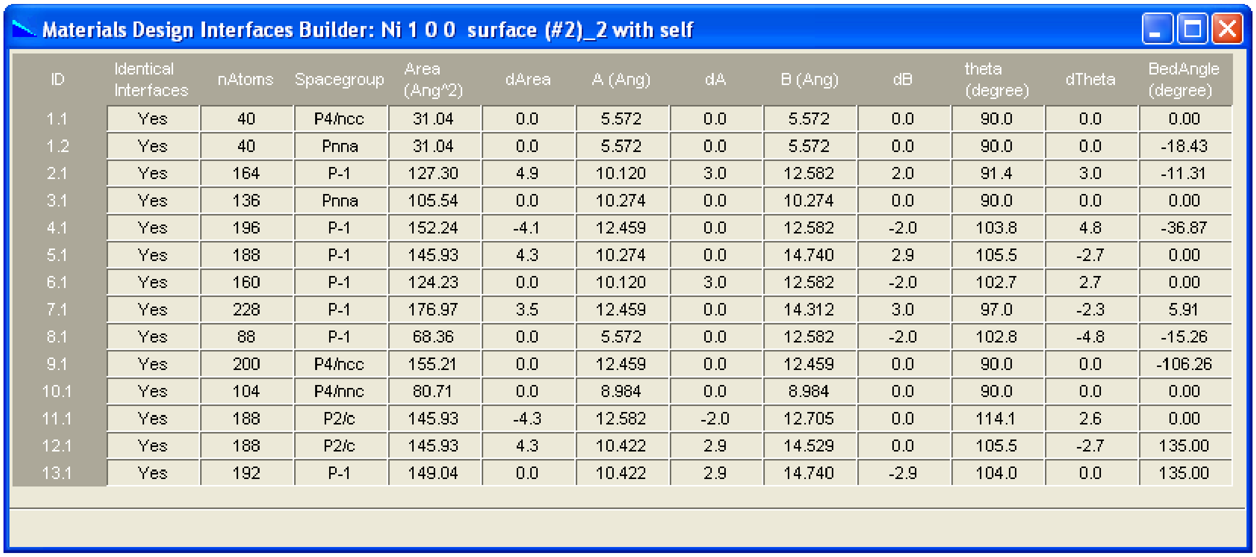
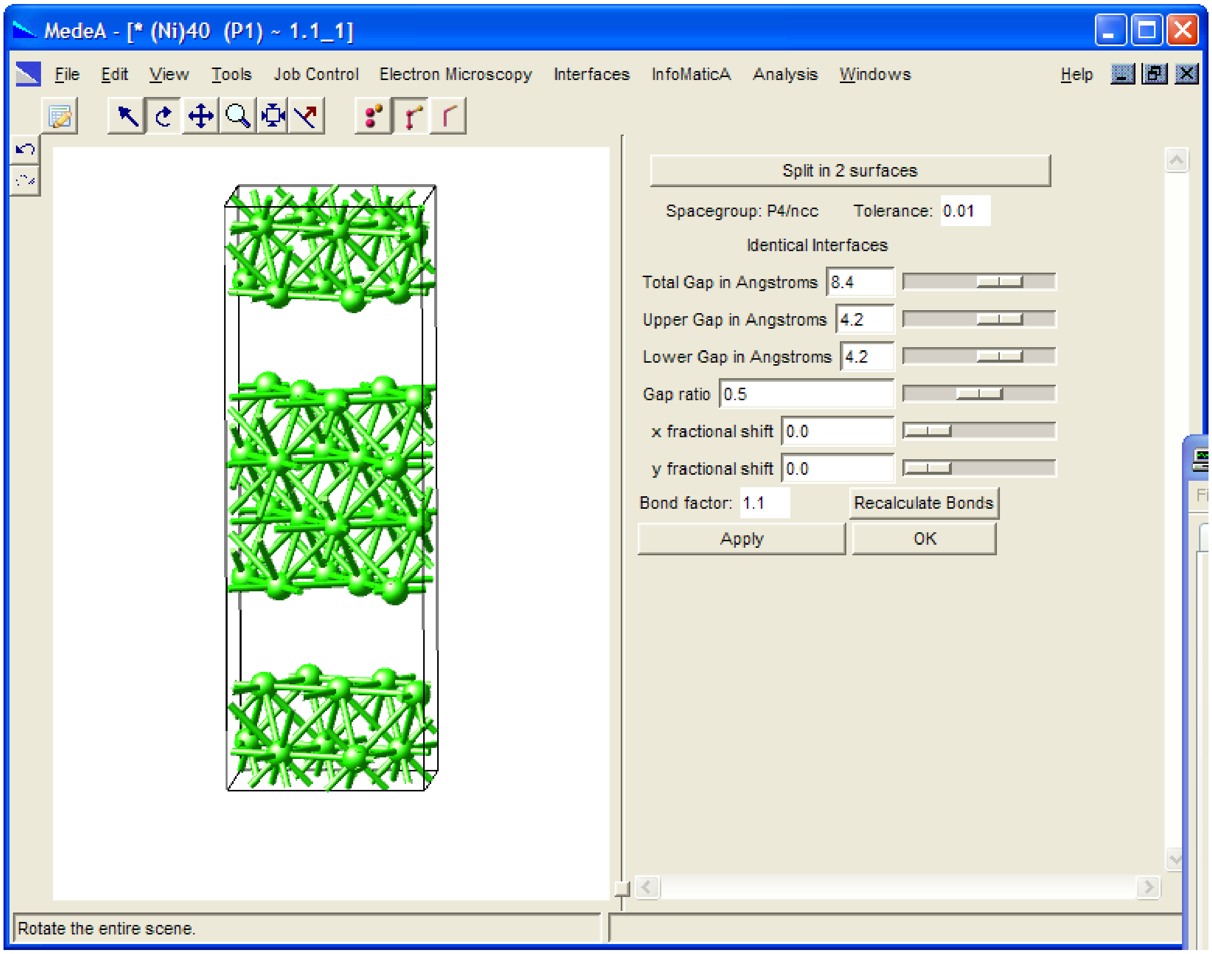
[5] Given that the Interface Search works with 3D period or crystalline structures, a slab model of an interface has to have two actual interfaces in a unit cell.



Materials Design Interfaces Builder: Ni 1 0 0 surface (#2)_2 with self

ID	Identical Interfaces	nAtoms	Spacegroup	Area (Ang^2)	dArea	A (Ang)	dA	B (Ang)	dB	theta (degree)	dTheta	BedAngle (degree)
1.1	Yes	40	P4/ncc	31.04	0.0	5.572	0.0	5.572	0.0	90.0	0.0	0.00
1.2	Yes	40	Pnna	31.04	0.0	5.572	0.0	5.572	0.0	90.0	0.0	-18.43
2.1	Yes	164	P-1	127.30	4.9	10.120	3.0	12.582	2.0	91.4	3.0	-11.31
3.1	Yes	136	Pnna	105.54	0.0	10.274	0.0	10.274	0.0	90.0	0.0	0.00
4.1	Yes	196	P-1	152.24	-4.1	12.459	0.0	12.582	-2.0	103.8	4.8	-36.87
5.1	Yes	188	P-1	145.93	4.3	10.274	0.0	14.740	2.9	105.5	-2.7	0.00
6.1	Yes	160	P-1	124.23	0.0	10.120	3.0	12.582	-2.0	102.7	2.7	0.00
7.1	Yes	228	P-1	176.97	3.5	12.459	0.0	14.312	3.0	97.0	-2.3	5.91
8.1	Yes	88	P-1	68.36	0.0	5.572	0.0	12.582	-2.0	102.8	-4.8	-15.26
9.1	Yes	200	P4/ncc	155.21	0.0	12.459	0.0	12.459	0.0	90.0	0.0	-106.26
10.1	Yes	104	P4/nnc	80.71	0.0	8.984	0.0	8.984	0.0	90.0	0.0	0.00
11.1	Yes	188	P2/c	145.93	-4.3	12.582	-2.0	12.705	0.0	114.1	2.6	0.00
12.1	Yes	188	P2/c	145.93	4.3	10.422	2.9	14.529	0.0	105.5	-2.7	135.00
13.1	Yes	192	P-1	149.04	0.0	10.422	2.9	14.740	-2.9	104.0	0.0	135.00

- To create an interface for one of the listed structure parameters, select a row in the spreadsheet, right-click and select **Create interface** to bring up a preview window with a number of additional options for construction of the final interface structure.



Spacegroup: P4/ncc Tolerance: 0.01

Total Gap in Angstroms 8.4

Upper Gap in Angstroms 4.2

Lower Gap in Angstroms 4.2

Gap ratio 0.5

x fractional shift 0.0

y fractional shift 0.0

Bond factor: 1.1

Rotate the entire scene.

The above preview window provides a number of additional options for building the final interface structure:

Split in two surfaces - Lets you split the interface into the two corresponding subsystems (surfaces). Use this option when calculating e.g. the work of separation for an interface

Spacegroup/Tolerance - Shows the current symmetry and lets you modify the tolerance used to calculate symmetry. Click **Apply** to recalculate symmetry

Identical interfaces - Indicates if the two interfaces present in the cell are identical

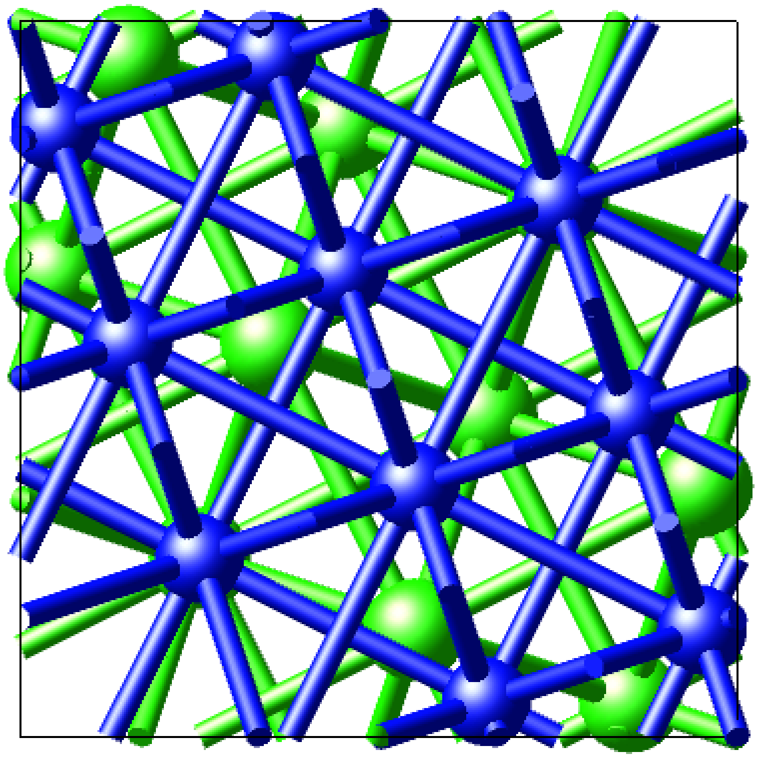
Total/upper/lower gap/Gap ratio - Lets you define two independent gaps for the upper/lower interface

x,y fractional shifts - Lets you move the two substructures making up the interface in a plane parallel to the interface. Use this option to create additional points on the so-called γ -surface

Bond factor/ **Recalculate bonds** - Lets you apply a bond factor and recalculate bonds for the interface

Apply - Applies changes to the interface structure

OK - Applies changes and closes the preview dialogue leaving you with just a structure window



Above, an example of a Ni Σ 5 twist grain boundary: Different colors were used to indicate the two different surface orientations.

9. Molecular Builder

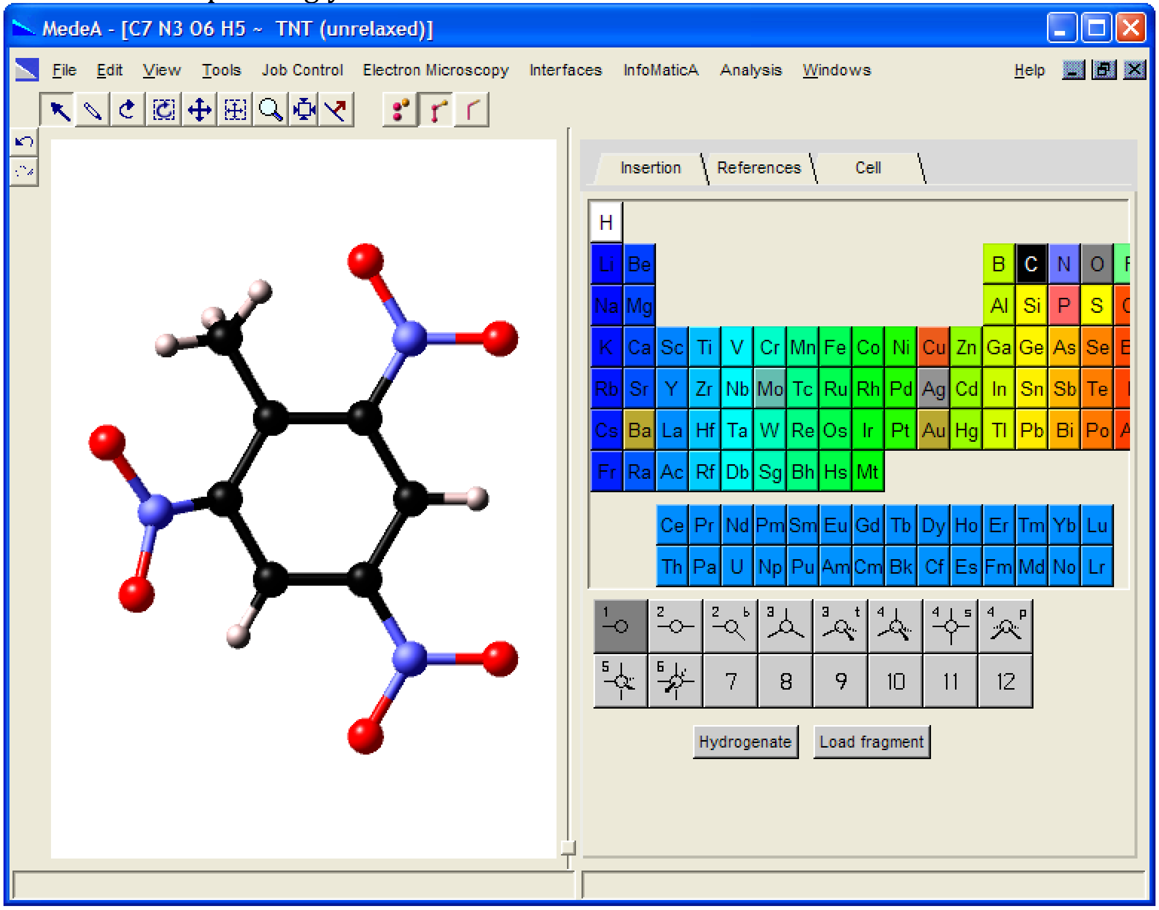
The MEDEA Molecular Builder lets you create molecules from scratch and combine them with bulk/surface systems to build structures ready for use with codes like VASP and GIBBS. In addition, you can build up and store a library of molecular fragments for use as building blocks when constructing more complex systems.

The following application notes illustrate the use of the Molecular Builder:

- Heats of formation of ethyl alcohol and di-methyl ether
- Dehydrogenation energy of Ethanol on Cu

a. Getting started

The Molecular Builder graphical user interface consists of a drawing area (below, left) and three panels **Insertion**, **References** and **Cell** (below, right). To display a specific panel, click the correspondingly labeled tab.



b. Main features in brief

- To invoke the Molecular Builder interface click on **File** ≫ **New molecule** or press **Ctrl-M** or, for an active periodic system, right-click and select **Edit in Molecular Builder**

- To start building a molecule, select an element type and coordination from the Insertion panel. In doing so you “load” your cursor with the selected element
- The cursor being loaded, to deposit an atom in the drawing area, left-click. To connect atoms through their active bonds, move the mouse over one of the bonds of an atom already present in the drawing area to highlicht the bond. Now, left-click to drop an atom thus creating a bond
- To save a molecule as a fragment, the molecule must have exactly **one** active bond. Right-click into the drawing area and select **Save as fragment** from the pop-up menu
- To load the cursor with a fragment, click on **Load fragment** and select a fragment in the fragment list. Click **OK** to load the cursor. Left-click into the drawing area to drop the fragment. To bind the fragment to an active bond, move the mouse over the bond and left-click. Hold down the left mouse key to rotate the fragment around the newly formed bond
- To export a molecule to hard disc, use MEDEA's **Save** and **Export** menu entries
- To convert a molecular (aperiodic) system back to periodic select **Edit** ≫ **Create periodic** from the MEDEA menu

c. The drawing area

As you start building, the drawing area displays the system under construction.

- Right-click into a blank spot of the drawing area invokes the **context sensitive menus**

When adding atoms to build up the molecule, the title bar of the Molecular Builder window displays the current stoichometry of your system. An asterisk (*) indicates that you made changes to the structure but did not save them. You can save a molecule to disk or convert it to a periodic structure and store it in MEDEA's user data base.

- Use the usual MEDEA View options (MEDEA main menu) to add axes or to change the display mode to CPK or Cylinders

Note that some of the options available in the View menu do not apply to molecular systems.

d. Insertion panel

The Insertion panel lets you select atom types and their coordination and consequently add them to the molecule. When selecting an atom type, its default coordination is highlighted in the coordination area.

Example: For Oxygen, the default coordination of (2) is highlighted. You can change the coordination by selecting e.g. (1)

Coordination selectors:

An element with coordination number *n* will be drawn with *n* active bonds. Note that an active bond is a just a visual aid serving to make a connection to other atoms. Using active bonds you can build up realistic molecular structures with a few mouse clicks.

A structure with at least one active bond is considered to be a ***fragment.*** A fragment can be saved to the fragment library for later reuse as a molecular building block.

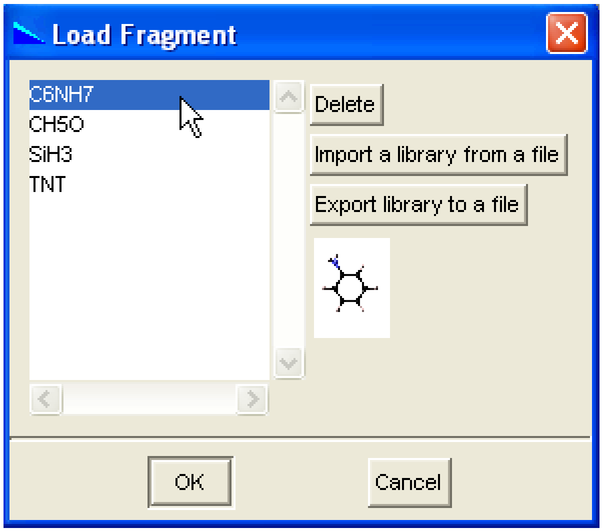
A molecular structure without any active bonds is considered a complete molecule. To save a molecule, export it to disk or convert it into a periodic model and save it to the MEDEA user database.

Further options present in the insertion panel are:

Hydrogenate - Automatically adds hydrogen atoms to all dangling (active) bonds

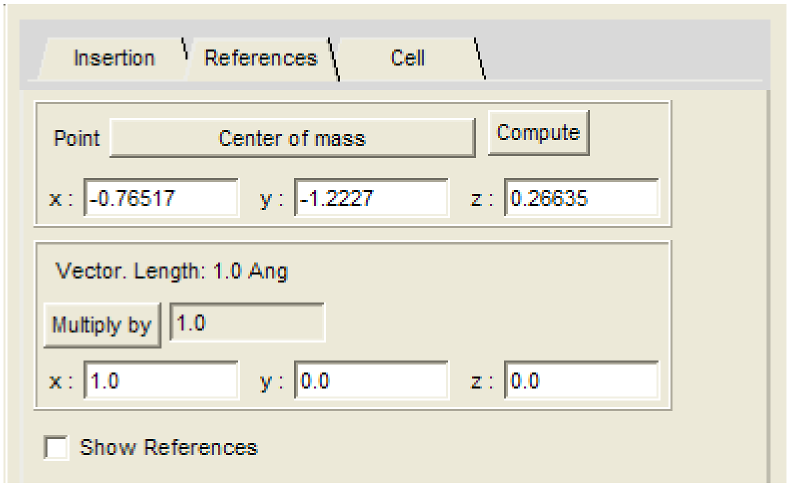
Load fragment - Brings up a dialogue to export your fragment library to file or to import fragments from a file

Example of the Load fragment dialogue



Note that the fragment list is empty by default.

e. References - Point and Vector



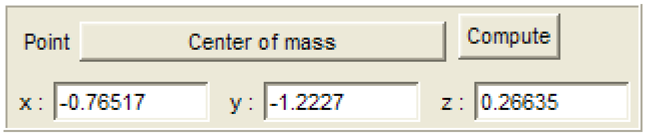
Point: Center of mass
x: -0.76517 y: -1.2227 z: 0.26635
Vector. Length: 1.0 Ang
Multiply by: 1.0
x: 1.0 y: 0.0 z: 0.0
☐ Show References

The References panel lets you define a reference point and a reference vector to perform actions like **Translate**, **Rotate**, **Center** etc...

For example, you can define a reference point to be the center of mass of the molecule or a selection of atoms. You can then translate the molecule so its geometrical center comes to lie on the center of mass. Or you can define a reference point and vector and translate a group of atoms/a molecule around the axis defined by the point and vector.

Below is a list of available options for Point and Vector.

Point - Define a reference point

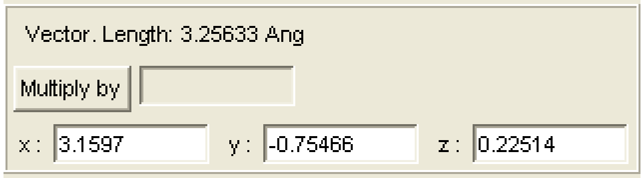


x: -0.76517 y: -1.2227 z: 0.26635

You can type in coordinates of a point (press Return to confirm) or select special points from a list. Below is a list of options to be used with Point. To apply an option, select the corresponding field and click **Compute**. Check the box **Show References** to display the reference point and vector (red bullet and cylinder in drawing area). Note that there may be atoms or axes in front. When applying an option you will note that the coordinates of Point change. The molecule itself will not change until you apply specific actions for example when moving the structure to the reference point.

- **Geometrical center**: geometrical center or average of the current system
- **Center of Mass**: center of mass of the current system
- **Bounding box center**: center of smallest possible box containing all atoms
- **Selection geometrical center**: geometric center of current selection
- **Selection center of mass**: center of mass of the current selection of atoms
- **Selection bounding box center**: smallest box containing all selected atoms

Vector - Define a reference vector



Vector. Length: 3.25633 Ang

x : 3.1597 y : -0.75466 z : 0.22514

To define a vector, simply input its (x,y,z) coordinates. The offset or starting point of the vector will be defined by **Point**. Alternatively you can select two atoms in the drawing area, right-click and select **Selection** ≫ **Set as reference vector**. Also, you can scale the vector by setting **Multiply by** to a value other than 1.0.

Check the box **Show References** to display the reference point and vector (red bullet and cylinder in drawing area). Note that the reference point and vector may be hidden by atoms or bonds

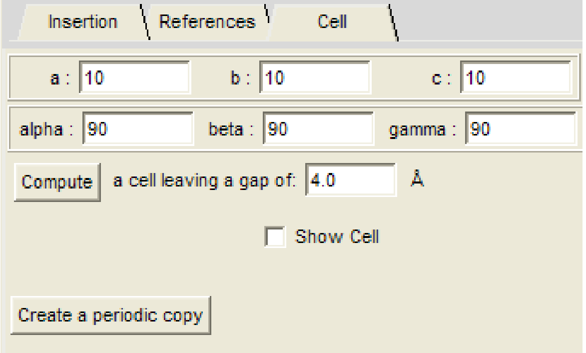
f. Cell

The **Cell** panel lets you define cell parameters for the cell surrounding your molecule. When converted back to a periodic system this cell will be the periodic unit cell representing your slab or molecular model. You can either explicitly define the cell parameters $(a, b, c, \alpha, \beta, \gamma)$ or you can define a void region around the molecule and leave it to the builder to handle cell dimensions.

When editing a periodic structure in the Molecular Builder, the original periodic cell lattice parameters are shown by default.

If you want to convert e.g. a surface structure back to a periodic model (e.g. after having added a molecule) you **MUST** keep the original cell parameters, otherwise the periodic symmetry of the system is lost. In case you accidentally change the original settings the Molecular Builder lets you reset the cell to the initial values (Reset to original cell button).

The cell panel for a molecular system built from scratch



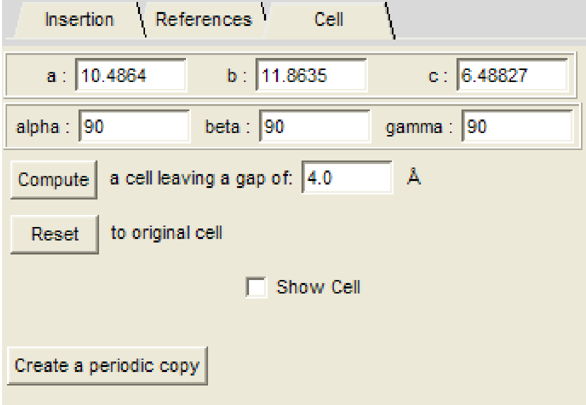
a : 10 b : 10 c : 10

alpha : 90 beta : 90 gamma : 90

a cell leaving a gap of: 4.0 Å

☐ Show Cell

The cell panel for a molecular system converted from a periodic structure



a : 10.4864 b : 11.8635 c : 6.48827

alpha : 90 beta : 90 gamma : 90

a cell leaving a gap of: 4.0 Å

to original cell

☐ Show Cell

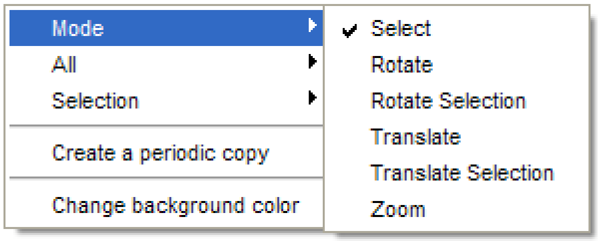
g. Context sensitive menus

Right-clicking into the drawing area of the Molecular Builder interface brings up a context sensitive menu. The following list describes the available options:

The Mode menu

The mode menu lets you select an **action** mode. Current modes are **Select**, **Rotate**, **Rotate Selection**, **Translate**, **Translate Selection** and **Zoom**. Alternatively, the **Insert** mode is invoked by selecting an element from the insert panel or by clicking the **Insert** icon in the MEDEA menu bar.

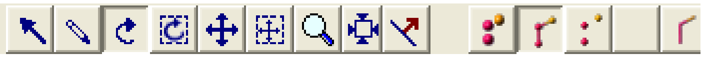
Right-click to use context sensitive menus



All other modes are selected through the context sensitive menu or through menu buttons in the Molecular Builder menu bar. The current viewing mode is indicated by the cursor shape:

- for Insert
- for Select
- for Rotate and for Rotate Selection
- for Translate and for Translate Selection
- for Zoom

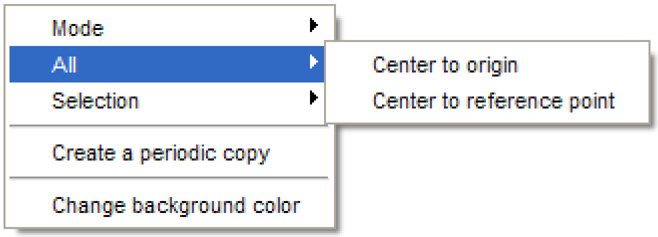
In addition, the MEDEA menu bar displays buttons for selecting modes when a molecular builder window is active:



Move your mouse cursor over these buttons to display a brief description of each mode

The All menu

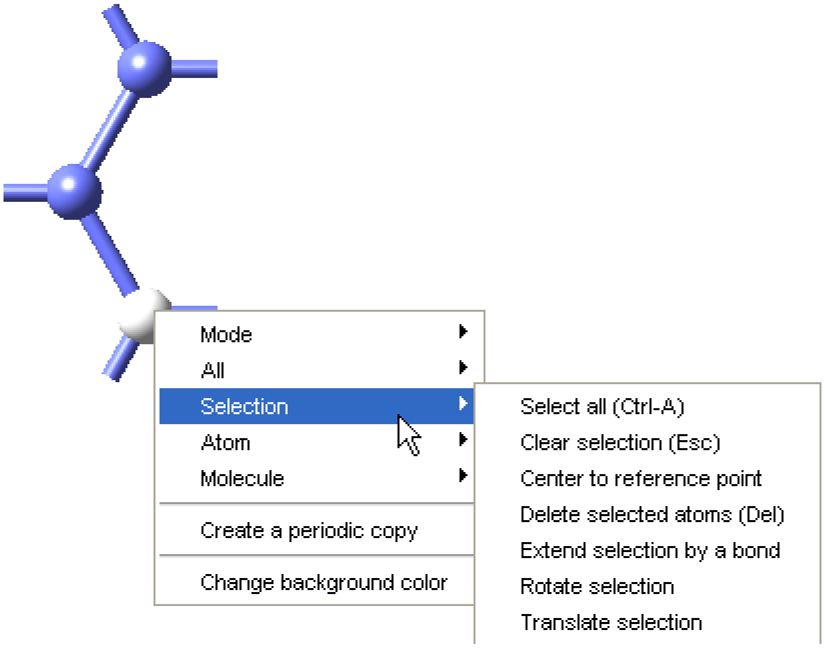
Lets you center all atoms in the drawing area to either the origin or to the origin or a reference point of your choice. Centering means **moving the center of the smallest box which envelopes all atoms (bounding box)** to the reference point/origin.



The selection menu

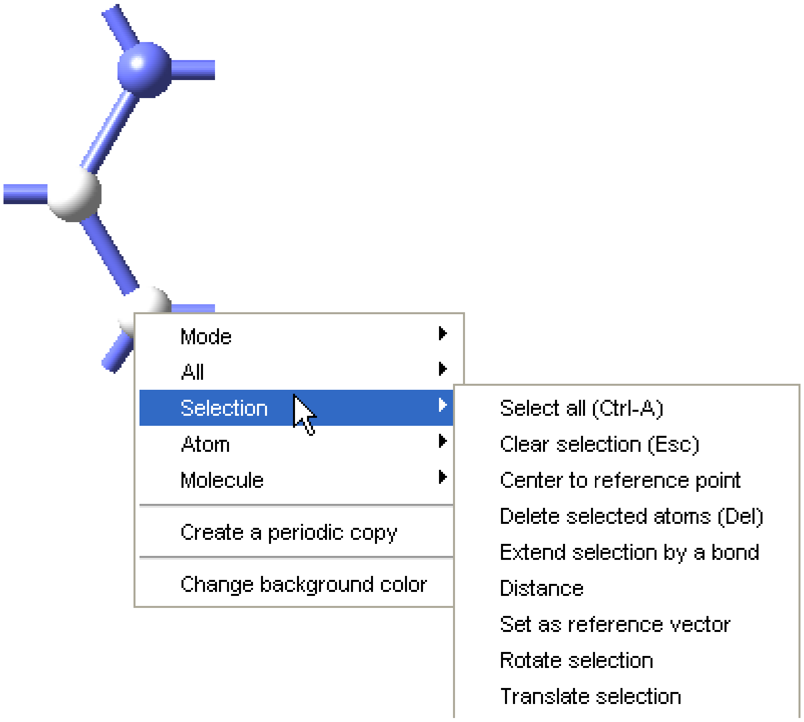
The selection menu lets you perform certain operation on a selection of atoms. What operations are available depends on how many atoms are selected:

a) When one atom is selected



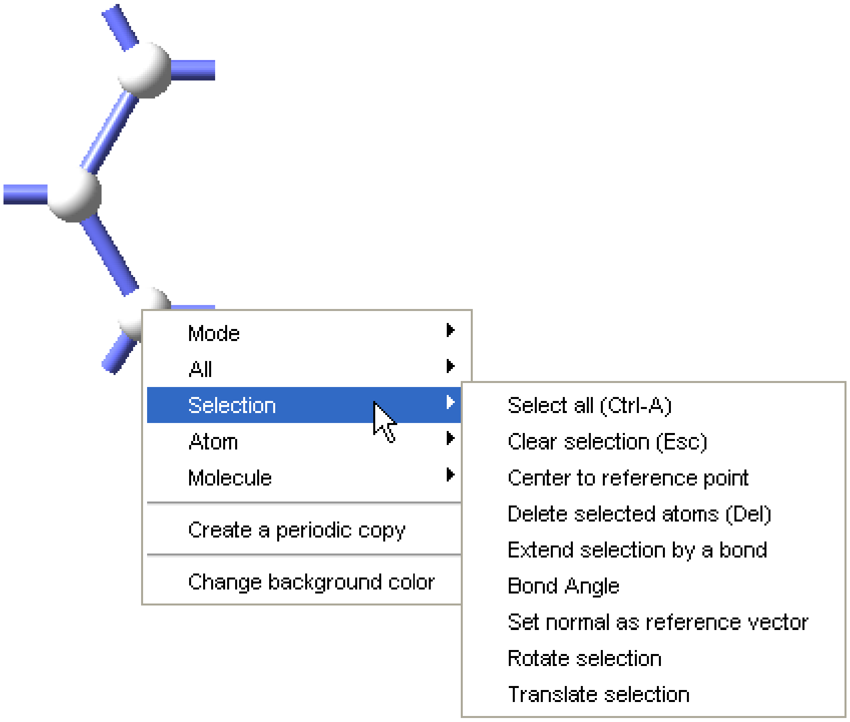
- **Select all** - Selects all atoms in the drawing area (shortcut **Ctrl-Alt**)
- **Clear selection** - Unselects all selected atoms (shortcut **Esc**)
- **Center to reference point** - Moves all atoms present in the drawing area such that their geometric center comes to lie at the reference point. Defining a reference point.
- **Delete selected atoms** - deletes all selected atoms (shortcut **Del**)
- **Extend selection by a bond** - Adds all atoms connected to the selected ones
- **Rotate selection** - Rotates the selected atom around the reference axis. A dialogue will ask for the rotation angle
- **Translate selection** – Translates the selected atom by norm (reference_vector) along the reference vector

b) When two atoms are selected (only options not mentioned earlier are listed)



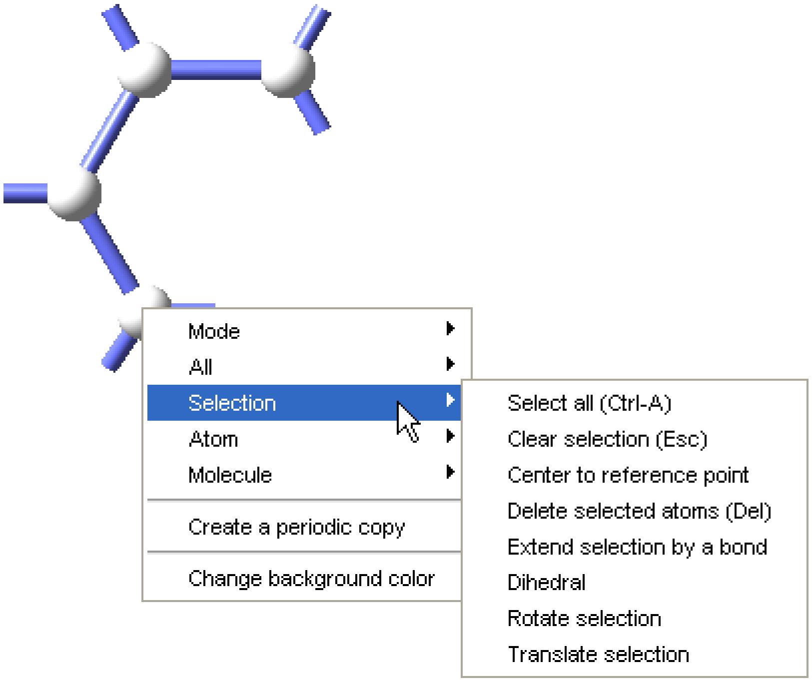
- **Distance** modifies the distance between two atoms, choose which to move
- **Set as a reference vector** - Sets the bond connecting the two selected atoms as a reference vector

c) When three atoms are selected (only options not mentioned earlier are listed)



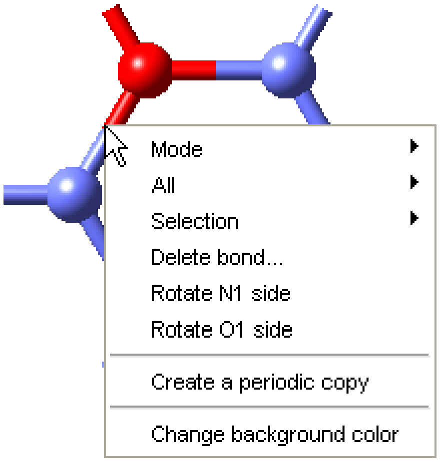
- **Bond angle** - Displays dialogue to view and edit the bond angle including option which atom to displace when changing the angle
- **Set normal as reference vector** selects reference vector normal to plane spanned by three atoms

d) When four atoms are selected



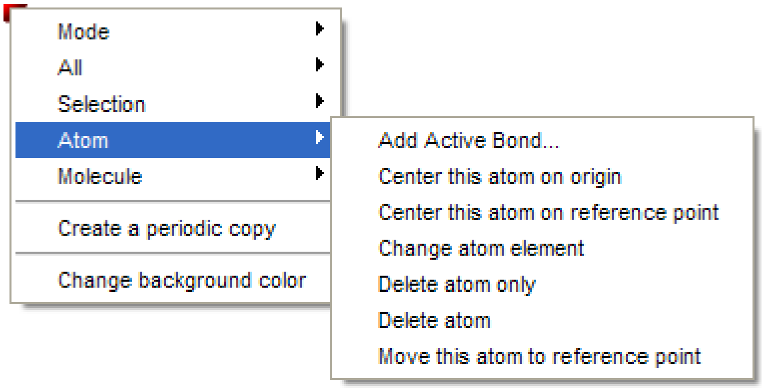
- **Dihedral** - Displays dialogue to view and edit the dihedral angle including choice which of the two atoms at the end of the chain to displace when changing the angle. This option requires 4 linearly bonded atoms

e) Right-click when cursor over a bond dividing the molecule



- **Delete bond... - deletes the bond**
- **Rotate <atom_number> side** - rotates the part of the molecule connected to <atom_number> around the bond (when atoms are selected)

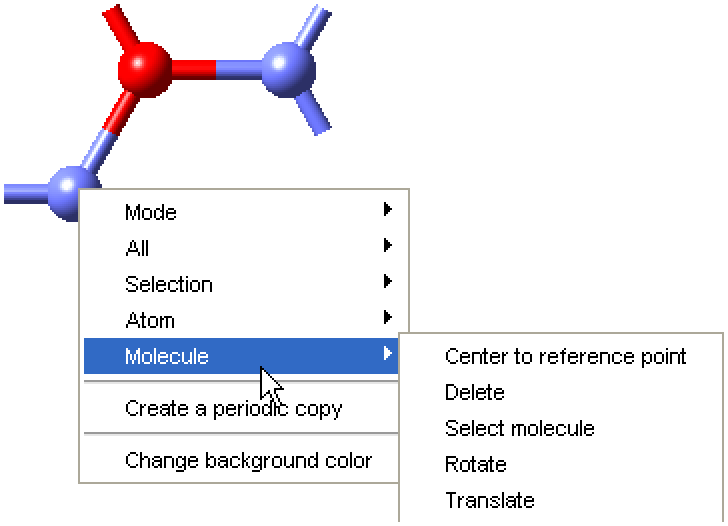
f) When right-Clicking on an atom (only options not described earlier are listed)



- **Add active bond** - creates an active bond perpendicular to the current viewing plane
- **Center this atom on origin** - Moves all atoms such that the atom under the cursor comes to lie at the origin (0,0,0)
- **Center this atom to reference point** - Moves all atoms such that the atom under the cursor comes to lie at the reference point
- **Change atom element** – replace the element under the cursor by the element currently loaded into the cursor
- **Delete atom only** - Deletes the atom leaving the active bonds of the atom(s) bonded to this atom
- **Delete atom** - Deletes the atom and all bonds connecting to this atom
- **Move this atom to reference point** - Moves only the atom under the cursor to the reference point

g) When right-clicking on an atom – Molecule

In the following, "Molecule" refers to all atoms connected to the one under the cursor.



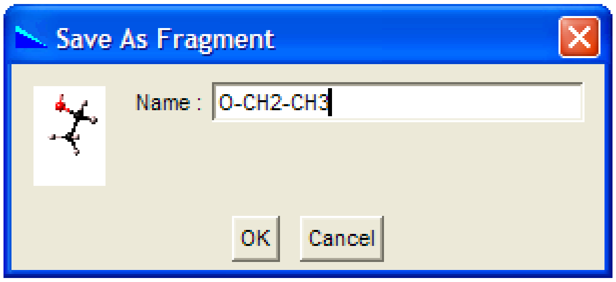
- **Center to reference point** - Centers the molecule to the reference point
- **Delete** - Deletes the molecule
- **Select molecule** – Selects the molecule
- **Rotate** - Rotates the molecule around the axis defined by Point and Vector
- **Translate** - Translates the molecule by the vector defined by Vector

h) Right-click anywhere in the drawing area - Create a periodic copy

- **Create a periodic copy** of the molecular system, which can be used as input for e.g. VASP

i) Save as a fragment

This option is shown only when the structure has exactly one active bond!!



Name : O-CH2-CH3

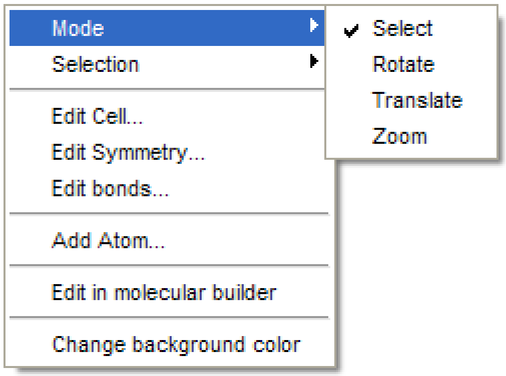
- **Save as a fragment** - Molecules that have exactly one active bond can be saved as fragments for later use as a building block for more complex structures. When saving a fragment make sure to choose a comprehensive name and in the graphics panel zoom in on the fragment beforehand. MEDEA will save a snapshot of the structure along with its name

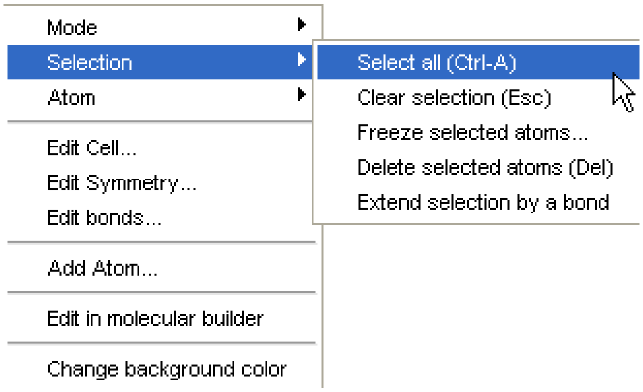
h. Shortcuts

A number of shortcuts are available to simplify operations:

- **Ctrl-M** - invokes the Molecular Builder interface for a new system
- **Ctrl-A** - Selects all atoms in the drawing area
- **Ctrl-Z** - undoes the last action
- **Esc** - Clears the atom selection
- **Del** - deletes all selected atoms
- **R**/**T**/**S**/**Z** – press and hold down one of these keys to temporarily swap between the current mode and Rotate/Translate/Select/Zoom
- **R**/**T**/**S**/**Z** + **←**/**→** - Rotation/Translation/Zoom using small steps
- **R**/**T**/**S**/**Z** + **Shift** +**←**/**→** - Rotation/Translation/Zoom using larger steps
- **S** +**R**/**T** +**←**/**→** / left-mouse-click - Rotates/Translates selected atoms; Rotation around current view axis

10. Context Menu in Structure window





Mode: Change the action mode between select, rotate, translate and zoom

- **Select**: Select atom(s) (left-mouse-click), selected atoms appear white
- **Rotate**: Rotate entire structure
- **Translate**: Move entire structure in window (left-mouse-click-move)
- **Zoom**: Zoom in/out by holding (left-mouse-click-move-cursor)

Selection:

- **Select all** (**Ctrl-A**): Selects all atoms
- **Clear selection** (**ESC**): Removes the selections, but not the selected atoms
- **Freeze selected atoms**: Sets conditions for relaxation in VASP
- **Delete selected atoms** (**DEL**): Removes elected atoms
- **Extend selection by a bond**: Expands selections by atoms connected by a bond

Edit Cell: Opens the **Edit cell** menu, **Cell** panel

Edit Symmetry: Opens the **Edit cell** menu, **Symmetry** panel

Edit bonds: Opens the bond dialogue and lets you recalculate the bonds

Add Atom: Opens the **Edit cell** menu, **Add Atom** panel

Edit in molecular builder: Transfers the structure into the Molecular Builder

Change background colo:: Changes the background color of the window

Atom: Right-clicking with mouse pointer over atom

- **Move atom**: Opens the **Edit cell** menu, **Move atom** panel
- **Edit atom**: Opens a periodic table to pick an element, replacing the present one
- **Freeze atom**: Opens a dialogue allowing you to freeze x,y,z coordinates of atom
- **Magnetic moments**: Opens the **Edit cell** menu, **Magnetic moments** panel
- **Delete atom**: Deletes the atom under the mouse pointer

Bond: Right-clicking with mouse pointer over bond

- **Delete bond:** Deletes the bond under the mouse cursor

D. MEDEA-VASP-4.6

Introduction and capabilities:

VASP [2] is applicable to bulk solids, surfaces, interfaces, molecules on surfaces, and molecules. VASP is a fast and highly reliable electronic structure method based on density functional theory (DFT)[3]. Together with the **all-electron projector augmented wave potentials**[4] VASP has the generality and accuracy of an all-electron method while maintaining the speed and advantages of a plane-wave method.

MEDEA's graphical VASP user interface gives easy access to the relevant VASP parameters in a structured arrangement of topic panels. In addition, the MEDEA interface provides a comprehensive and exhaustive set of defaults for all relevant parameters needed to run standard VASP calculations. For special settings, direct additions to VASP input files through MEDEA are provided.

Besides providing elementary properties as e.g. total energies, trajectories and band structure-DOS plots or charge density data, MEDEA modules use VASP as a DFT solver for the electronic total energy, interatomic forces and the stress tensor to give access to more complex properties derived from "simple" single point runs or structure relaxations. Examples are elastic constants, vibrational frequencies and thermodynamic functions.

VASP Fundamental Capabilities

Single Point

- Total energy for a given fixed arrangement of atoms in a unit cell (atoms, molecules, surfaces, solids)
- Energy of formation, reaction, adsorption, or insertion,
- Relative phase stability at 0K

Structure Optimization

- Structure of bulk solids, surfaces, interfaces, molecules on surfaces by by minimizing forces and energy, relaxing lattice parameters and/or internal degrees of freedom in the process:
- Crystal structure determination, surface, interface relaxation
- Bond lengths, adsorption geometries
- Defects and vacancies

Ab Initio Molecular Dynamics

- Evolution of a system of ions by calculating electronic structure and inter atomic forces from ab-initio and applying Newton mechanics for the ionic movement.
- Temperature effects through kinetic energy term.
- Structure determination for complex systems,
- Simulated annealing

Electronic structure

- Electronic band structures and density of states
- Charge densities, electronic localization function, total potential
- Work function
- Magnetic moments
- Bonding
- (Optics)
- Electronics

History

VASP [2; 5] is short for "**V**ienna **A**b initio **S**imulation **P**ackage". The program has been developed in the group of Prof. Jürgen Hafner, who is heading the Institute for Materials Physics at the University of Vienna, Austria. The key authors of VASP, Georg Kresse and Jürgen Furthmüller, have written The VASP Guide which gives an excellent description of the algorithms underlying VASP.

VASP can be considered as the culmination of many decades of worldwide efforts in electronic structure theory. Through the implementation [4] of the projector augmented wave (PAW) method [6], VASP combines the speed and elegance of plane-wave methods with key features of frozen-core all-electron methods.

The integration of VASP and MEDEA is far beyond a simple graphical user interface: For example the automatic calculation of elastic constants relies on years of experience usually gained during a Ph.D length of time. A sound knowledge of group theory is required to create the specific distortions and combine the results into an elastic matrix. On a technical side the various competing options of potentials, integration methods and cut off energies have to be rigorously tested before using them in industrial R&D projects.

MEDEA's graphical user interface is on top of a set of tested set of parameters, optimized for specific types of computation with very different levels of required accuracy. If needed, this interface gives experts access to the less frequently used features of VASP through viewing and editing capabilities of the standard VASP input files. Non experts find good default values of computational parameters and context sensitive help.

A detailed, technical description of the underlying algorithms is found in The VASP Guide.

Automatic computation of the heat of formation for compounds

MEDEA-VASP4.6 automatically computes the electronic contribution to the heat of formation for a given compound. This is achieved by using a set of internal reference energies calculated for all elements and potentials available within VASP4.6.

The heat of formation of a compound is defined as the difference in Enthalpy at room temperature between the compound and its constituent elements in their standard state. Contributions to this property are:

- The electronic term (difference of VASP total energies) at T=0K
- The temperature dependent electronic term (generally very small)
- The zero point energy term
- The contribution of lattice vibrations at room temperature

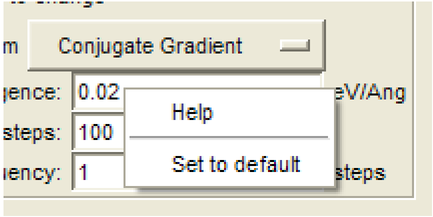
A first (often quite good) approximation is given by the electronic contribution. Details on how to calculate the other contributions can be found in section V.M, Application Note Practical Thermochemistry: Sodium Metal, Chlorine Gas, and Solid Sodium Chloride.

1. The MEDEA VASP4.6 interface

Getting started

From the MEDEA toolbar, select **Tools** ≫ **VASP4.6**. A new menu entry, **VASP4.6** appears in the MEDEA menu bar and remains there for the rest of the current MEDEA session.

Load or select the system, for which you want to perform a VASP calculation. Note that the **File**≫**Open** command allows the import of structural information from *POSCAR/CONTCAR* files as long as a corresponding *POTCAR* file exists in the same directory[6] This is useful to import earlier VASP calculations (e.g. those run outside MEDEA or from those interrupted tasks). In addition a number of other external file formats can be read: `.cif, .car, .xyz, .mol`

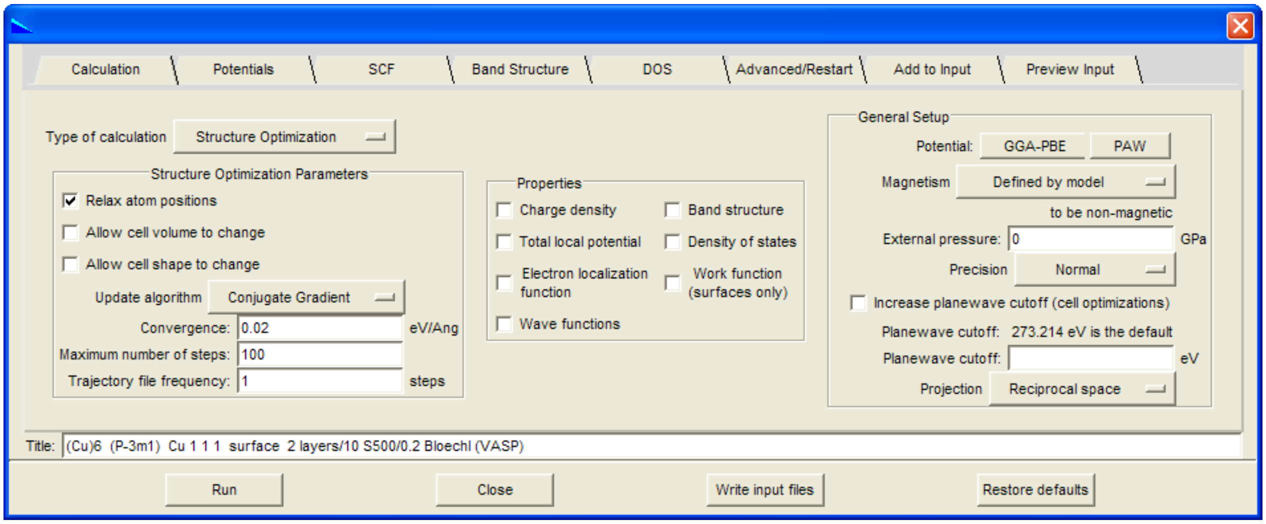


Select **VASP4.6**≫**Run** from the MEDEA tool bar to bring up the VASP graphical user interface. In the VASP user interface, right-click on a text field to get context-sensitive help or to reset a parameter to its default value.

Interface panel overview

The MEDEA VASP graphical user interface consists of a stack of panels or cards grouping together the main parameters relevant for the setup of VASP runs.

For all input parameters, MEDEA provides defaults that were chosen to yield acceptable precision while limiting the computational effort. It is strongly recommended to study convergence for each specific case before concluding any scientific results. However in many cases the defaults provided give an excellent starting point for the structure and heat of formation of a given system.



Type of calculation: Structure Optimization

Structure Optimization Parameters
☑ Relax atom positions
☐ Allow cell volume to change
☐ Allow cell shape to change
Update algorithm: Conjugate Gradient
Convergence: 0.02 eV/Ang
Maximum number of steps: 100
Trajectory file frequency: 1 steps

Properties
☐ Charge density
☐ Band structure
☐ Total local potential
☐ Density of states
☐ Electron localization function
☐ Work function (surfaces only)
☐ Wave functions

General Setup
Potential: GGA-PBE PAW
Magnetism: Defined by model
to be non-magnetic
External pressure: 0 GPa
Precision: Normal
☐ Increase planewave cutoff (cell optimizations)
Planewave cutoff: 273.214 eV is the default
Planewave cutoff: eV
Projection: Reciprocal space

Title: (Cu)6 (P-3m1) Cu 1 1 1 surface 2 layers/10 S500/0.2 Bloechl (VASP)

---

[6] The structure information for VASP is spread over two files: atomic coordinates in POSCAR/CONTCAR and element information in POTCAR.

2. VASP output files:

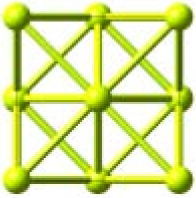
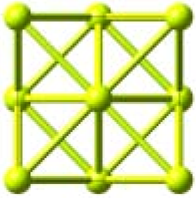
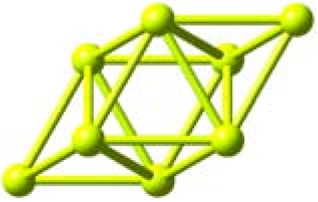
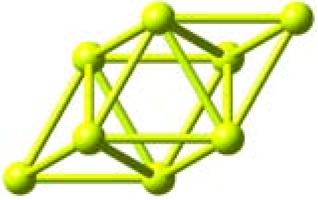
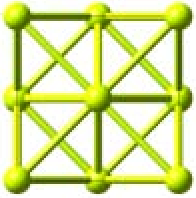
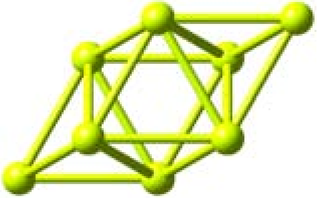
During VASP runs, data is written to the task directory on a TaskServer machine. Upon successful completion of a computational job, all VASP tasks associated with the job are transferred back to the JobServer. You can access output files on the JobServer by browsing to the job directory where all data from completed runs are stored (in the MEDEA menu click **Job Control**≫**View and Control Jobs**).

The most relevant output files are

- *`Job.out`*: Summarizes the computational job including input parameters and main results
- *`Vasp.out`*: or *`OSZICAR.out`*: Summarize convergence information for geometry steps and electronic iterations of a given VASP task
- *`OUTCAR.out`*: Detailed output from a given VASP tasks. A lot of technical information here, not easy to read for the non-expert!

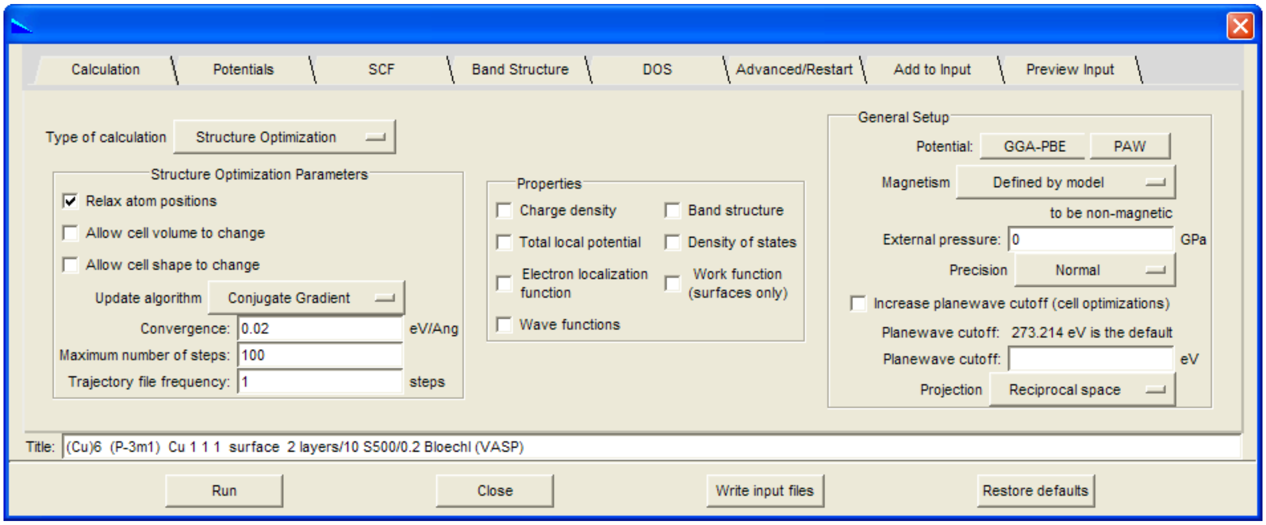
For any given crystal symmetry, Vasp performs the calculations on the primitive cell. If you are in doubt if the actual cell shape used by Vasp corresponds to the one displayed by MEDEA, check if a primitive cell exists (Symmetry panel) or simply choose to reduce symmetry to P1 in MEDEA.

Example:

	Fm-3m	**P1**	**P1 primitive**
Cell displayed by MEDEA			
Cell used by VASP			

Interface description

Click on the tabulators **Calculation**, **Potentials**, **SCF**, etc in order to go to the respective panel, which are described in detail in the following.



Type of calculation: Structure Optimization

Structure Optimization Parameters

☑ Relax atom positions

☐ Allow cell volume to change

☐ Allow cell shape to change

Update algorithm: Conjugate Gradient

Convergence: 0.02 eV/Ang

Maximum number of steps: 100

Trajectory file frequency: 1 steps

Properties

☐ Charge density

☐ Band structure

☐ Total local potential

☐ Density of states

☐ Electron localization function

☐ Work function (surfaces only)

☐ Wave functions

General Setup

Potential: GGA-PBE PAW

Magnetism: Defined by model

to be non-magnetic

External pressure: 0 GPa

Precision: Normal

☐ Increase planewave cutoff (cell optimizations)

Planewave cutoff: 273.214 eV is the default

Planewave cutoff: eV

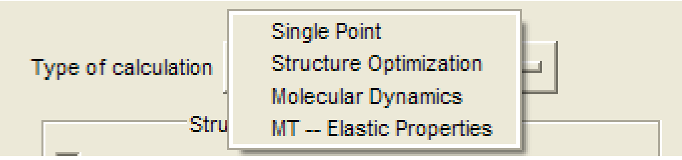
Projection: Reciprocal space

Title: (Cu)6 (P-3m1) Cu 1 1 1 surface 2 layers/10 S500/0.2 Bloechl (VASP)

3. The Calculation panel

Here you set the type of calculation to perform using VASP. The panel has a number of submenus/fields:

a. Type of calculation



The MEDEA VASP interface distinguishes 4 major types of calculations, namely **Single point**, **Structure Optimization**, **Molecular Dymanics**, and **MT —Elastic Properties**. The MT entry is visible only with a valid MT license.

Single Point: Performs an electronic structure calculation for the input geometry without relaxing any structural parameter.

Structure Optimization: Relaxes the atomic position and/or the cell parameters with or without constraints. Perform a full structure optimization to determine the bulk equilibrium structure at T=0K

Molecular Dynamics: Performs ab-initio molecular dynamics for dynamic properties or equilibrium states

MT — Elastic Properties : Computes elastic constants and other mechanical and thermal (based on Debye model)

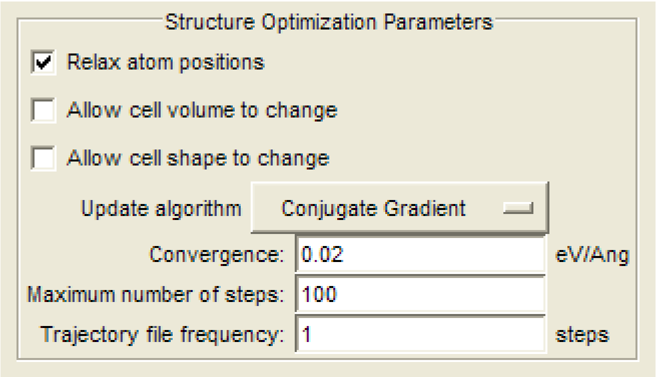
1) Single Point

No further parameters required in this context field. However you may want to check additional settings, in particular, you should know about setting the k-mesh and the plane wave cutoff.

2) Structure Optimization

Selecting **Structure Optimization** activates the field for Structure Optimization parameters.

Available options are listed below, followed by recommended settings for standard tasks.



Structure Optimization Parameters

☑ Relax atom positions

☐ Allow cell volume to change

☐ Allow cell shape to change

Update algorithm: Conjugate Gradient

Convergence: 0.02 eV/Ang

Maximum number of steps: 100

Trajectory file frequency: 1 steps

Relax atom positions: Atoms are moved until forces are smaller than value in **Convergence in eV/Ang**

Allow cell volume to change: Vary volume keeping a constant ratios of a:b:c with unchanged cell angles

Allow cell shape to change: Varies the ratio a:b:c and changes in the cell angles

Update algorithm:

Conjugate Gradient (CG): Default for standard structure relaxations

RMM-DIIS: A Newton-Raphson based algorithm that converges faster than CG, if (**and only if)** you are close to an **extremum** of the total energy surface. This means, that RMM-DIIS will e.g. converge to a saddle point if the starting configuration is close enough. When searching for local minima use with great care!

Convergence: Set an upper limit for the largest allowed residual force between any of the atoms in the unit cell. A value of 0.02 eV/Å is reasonable for most calculations.

- High precision calculations may require 0.01 eV/Å or even smaller residual forces.
- When reducing the criterion for the force convergence, you must use a lower value for the SCF convergence, too: Try 1.0e-06 or 1.0e-07.

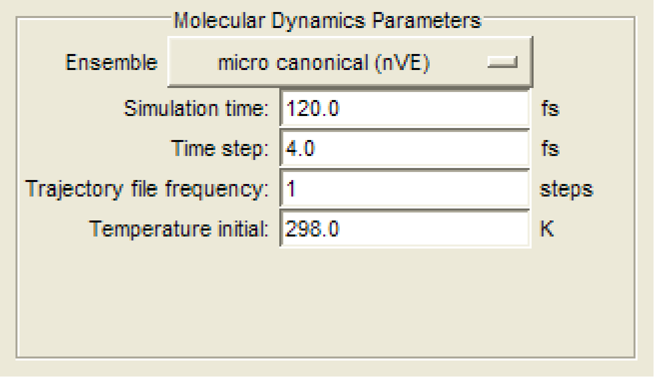
Maximum number of steps: Sets the maximum number of geometry steps to be executed before stopping. Roughly, the number of geometry steps can be of the same order of magnitude as the number of degrees of freedom (DoF) present in the system. If the number of DoF is very large, one may consider using molecular dynamics and simulated annealing to find the minimum structures.

Trajectory file frequency: sets the number of animation frames to be written to disk during a geometry optimization. Default is 1 frame/geometry step.

Goal	Recommended Structure Optimization settings
Determine a bulk equilibrium crystal structure	☑ Relax atom positons ☑ Allow cell volume to change ☑ Allow cell shape to change
Relax a surface (no in-plane relaxation) **Find the equilibrium geometry of a molecule** **Adsorb a molecule on a surface** **Locally relax a structure around a vacancy/defect**	☑ Relax atom positons ☐ Allow cell volume to change ☐ Allow cell shape to change
Optimize a system under pressure **Allow in-plane adjustment during a surface calculation**	☑ Relax atom positons ☐ Allow cell volume to change ☑ Allow cell shape to change

Note: *At present, the combination of only* ***✓Relax atom positions*** *and* ***✓Allow cell volume to change*** *checked are not handled by VASP.*

3) Molecular Dynamics



Molecular Dynamics Parameters

Ensemble	micro canonical (nVE)	
Simulation time:	120.0	fs
Time step:	4.0	fs
Trajectory file frequency:	1	steps
Temperature initial:	298.0	K

In a molecular dynamics run the forces calculated in a given geometry step are used to update the atomic positions. The system dynamics, i.e. the ionic movements are subject to Newton mechanics while the forces acting on the ions are calculated from ab-initio using a self consistent electronic density (Hellmann-Feynman forces).

Note that the natural time step of an ab-initio molecular dynamics run is rather short compared to the time span required for a chemical reaction: For ab-initio dynamics, the typical time range is in the picosecond range! Thus results from a picosecond range ab-initio dynamics run need to be interpreted with care: If you observe a specific event in the analysis of an ab-initio molecular dynamics run, the event is most likely to have physical significance. However, the absence of events, for example the absence of a diffusion jump from a molecular dynamics run cannot immediately be interpreted as a factual result. It may simply mean that the statistical sampling was too short.

Three types of molecular dynamics run are currently handled by the interface. Their purpose and related settings are explained below:

Micro canonical (nVE): Molecular dynamics at constant number of particles, **n**, constant volume, **V**, and constant energy, **E**

> **Time step**: Default is 4 femto seconds (fs), set time step to 1 fs if hydrogen is present

Temperature scaling (nVE): Simulated annealing to find energy minima for a complex structure with many degrees of freedom.

Start with a **crude calculation** to get a first overview of the dynamics of a system and its possible stable or meta-stable states. Later **refine parameters** to ensure quality of structural data. Such a run could look like this: Use a high starting temperature, low precision and soft potentials (_*s*), a single k-point (gamma), **Real space** integration and limit **Scf-convergence** to 1.0E-3 or 1.0E-4

Canonical (nVT): Requires a Nosé thermostat[7] as well as a specification of the initial and final temperature. The choice of the Nosé mass depends on the system, default setting is 2.

---

[7] A description of the theoretical background is given by Nose [109] and references therein.

4) MT-Elastic Properties

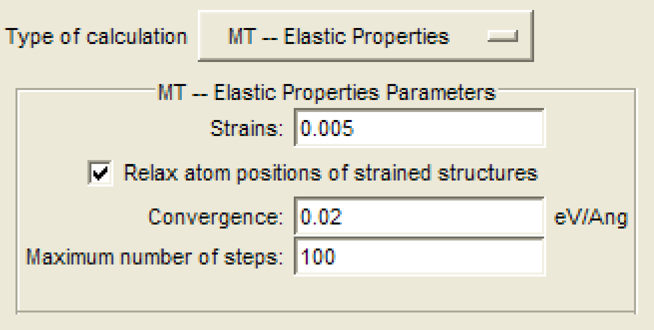
The optional MT- Elastic Properties module is tightly integrated into the VASP interface.

The actual determination occurs in three steps:

- MT analyzes the cell symmetry and determines the required directions of strain to derive elastic constants.
- The JobServer performs a VASP calculation for each of the strained cells.
- MT analyzes the results and computes the elastic constants (elastic constants and compliances matrices together with their Eigenvalues and Eigenvectors). In addition, elastic moduli and sound velocity, as well as derived thermodynamic properties (within the framework of the Debye model) are reported.

For accurate results, optimize the initial cell first to minimize residual forces.
You can enforce a tighter **Convergence** than the standard 0.02 eV/Å.

The most important parameter is the amount of strain: The resulting forces should be as large as possible (to get a better signal to noise ratio) without leaving the confines of the elastic regime.



Type of calculation: MT -- Elastic Properties

MT -- Elastic Properties Parameters

Strains: 0.005

☑ Relax atom positions of strained structures

Convergence: 0.02 eV/Ang

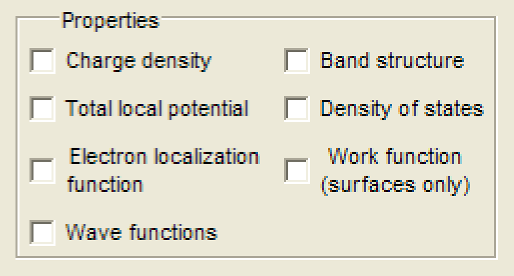
Maximum number of steps: 100

Strains: a list of strains infractions of the unit cell. The value 0.005 refers to 0.5% strain. You can add more than one strain amount to get better results, when the material is anisotropic, e.g. **0.005, 0.01**.

☑ Relax atom positions of strained structures: Straining the structure can break the symmetry of the cell and leaves one or more degrees of freedom for atoms to relax. Check this option if you want to include to optimize these cells.

For more information on results see section V.X MEDEA-MT in Depth: Forsterite Mg_2SiO_4.

b. Properties



Properties

☐ Charge density

☐ Band structure

☐ Total local potential

☐ Density of states

☐ Electron localization function

☐ Work function (surfaces only)

☐ Wave functions

Check items in the **Properties** frame to calculate and write out the related properties following a VASP run.

The above options are available for all types of calculations. However, depending on your target it might be more efficient to run **two independent steps** to get specific properties.

Example: You are running a structure optimization and you would like to determine the total energy, the band structure and the DOS for the resulting system.
During your structure optimization the shape and volume of your starting unit cell change

significantly (>3%). In this case, results for total energies and related properties will improve if you run the optimization first, reload the optimized system and then start a new VASP job to get the desired properties. The reason is that some VASP parameters implicitly depend on the input geometry, i.e. the cell shape and size. For consistency, MEDEA does not change these parameters in the course of a set of tasks within a given job.

Charge density: The electronic charge density (data written to *CHGCAR*)

Total local potential: the Coulomb potential, excluding the exchange-correlation potential (data written to *LOCPOT*)

Electron localization function: The ELF is a particular way to analyze the wave functions in order to understand chemical bonding (data written to *ELFCAR*)

Wave functions: The electronic wave functions. Saving the wave functions requires a lot of hard-disk space, but is very useful when planning to later restart a calculation (data written to *WAVECAR*)

Band structure: Dispersion relation E(**k**), i.e. the electronic energy as a function of momentum (data written to *BANDCAR*, `BandStructure.data`)

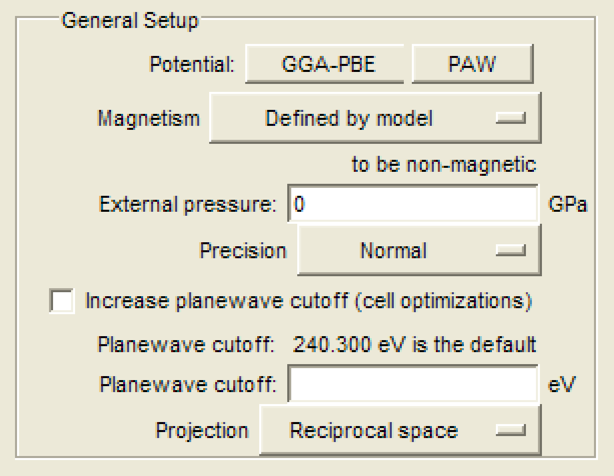
Electronic density of states (DOS): The distribution of electronic states per energy interval. (data written to *DOSCAR*, `DensityOfStates.data`)

Work function: Use for surface models only. Energy required moving an electron from the top of the valence band to infinity. The work functions is reported in Job.out

The following graphical visualization options are available in MEDEA (see also section II.E.2 Computed Properties):

- Band Structure
- Density of States
- Difference Charge Density
- Magnetization Density
- Valence Charge Density
- Electron Localization Function
- Total Local Potential

c. General Setup



General Setup

Potential: GGA-PBE PAW

Magnetism: Defined by model

to be non-magnetic

External pressure: 0 GPa

Precision: Normal

☐ Increase planewave cutoff (cell optimizations)

Planewave cutoff: 240.300 eV is the default

Planewave cutoff: eV

Projection: Reciprocal space

Parameters in this panel affect all calculation types: The potentials, either projector augmented wave potentials or ultrasoft pseudopotentials, determine the absolute values of calculated energies and forces. Geometry optimization, elastic constants, heats of formation and thermodynamic properties rely on the consistent and transparent use of these potentials.

The default settings are carefully chosen and tested to provide reliable results for most systems without being computationally too demanding.

Potential: Approximation to the density functional:

Different approximations to the density functional are used in today's DFT codes. GGA has become a standard through the PW91 [7] implementation and later through PBE[8].

PAW [6] potentials represent the state of the art of fast and efficient potentials for use in electronic structure calculations. Our recommendation is to use **PBE-PAW** throughout new projects and to use the *older potentials* only for comparison with earlier computations.

LDA (Local Density Approximation)

GGA-PW (Generalized Gradient Approximation, after Perdew and Wang [7]

GGA-PBE, after Perdew, Burke and Ernzerhofer[8]

Type of **Potential** to use:

Ultra soft (**US**)

Projector Augmented Wave (**PAW**)

Magnetism: Magnetism plays an important role for the structure of some metals and many molecules, oxides and oxide surfaces. Options for magnetic moments of atoms are

defined by model - MEDEA allows you to set magnetic moments for each atom in the structure window or in the Molecular Spreadsheet (see section II.C.2.h Molecular Spreadsheet). If present, these moments will be used to set up the VASP run as spin-polarized.

non magnetic - No magnetism will be considered

spin polarized - Magnetic calculation (ferromagnetic or antiferromagnetic)

non-collinear magnetic - Accounts for non-collinear spin-quantization axes

spin-orbit magnetic - Accounts for fully relativistic magnetism (Dirac)

Spin-orbit coupling and non-collinear magnetic calculations can be fairly time consuming compared to spin polarized and non-magnetic calculations.

External pressure: Hydrostatic pressure can be specified in units of GPa .

Precision: Influences a number of internal parameters such as plane-wave cutoff (basis set), FFT (Fast Fourier Transform) mesh (normal mesh and fine mesh), fine grid Fourier mesh, and Integration mesh for real space projectors

normal - For standard calculations and "first guesses"

low - For crude molecular dynamics runs

accurate - For precise energies and forces where lattice parameters remain unchanged

standard 500 - Overall high precision cutoff, used for MEDEA's reference heat of formation energies

Increase plane wave cutoff - When doing cell shape optimization. This option increases the cutoff by 30 %

Consider using **extra fine augmentation** grid (**Advanced** panel) for cases where extremely accurate forces are needed (difficult MT, PHONON calculations)

Plane wave cutoff: Defines the precision (=size) of the plane wave basis set. The value determined from the precision flag is shown in the interface. Overwrite to use specific cutoff, e.g. to compare with another calculation

Projection: defines how the projection operators are to be evaluated

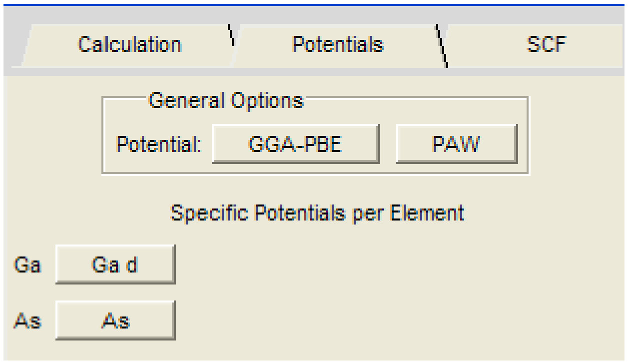
Real space (faster for larger systems)

Reciprocal space (more precise, slower)

For larger systems (all unit cell dim > 8 Å) a considerable amount of time can be saved by using **Projection**: **Real space**.

4. The Potentials panel

Select the **Potentials** panel in order to edit the type of potentials to use. In **General Options** you can select the DFT level of theory to use for calculating the electronic density (e.g. LDA for the local density approximation, GGA for the so-called semi local Generalized Gradient Approximation). On the right you can choose the type of potential to use, i.e. ultra soft pseudo potentials or projector augmented waves. See below for a list giving the element- and potential specific options.



General Options

Potential: GGA-PBE PAW

Specific Potentials per Element

Ga: Ga d

As: As

In the present example (GaAs), three potentials are offered for Ga, a standard one (**Ga**), a hard potential (**Ga_h**) having a very high cut-off and a potential incorporating the Ga semi core d-states into the set of valence states (**Ga_d**).

The following one-electron functionals can be used to describe the electronic density:

> **GGA_PBE**: Generalized Gradient Approximation (GGA) after Perdew, Burke and Ernzerhofer [8]
>
> **GGA_PW91**: Generalized Gradient Approximation (GGA) after Perdew, Wang 1991[7]
>
> **LDA**: Local density approximation

The following **Potentials** can be used:

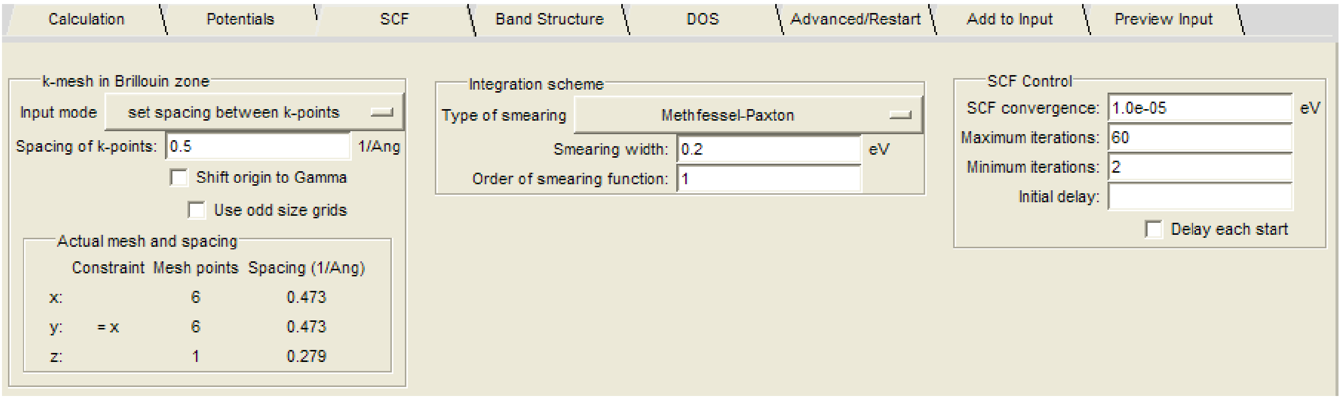
> **US**: Ultrasoft pseudo potential, pseudo-wavefunction and pseudo-potential near nucleus
>
> **PAW**: Projector Augmented Waves, correct nodal structure of electronic density near nucleus

Element specific types of potentials:

> **X_h** - hard potential:_h: potentials are very precise but calculations are time consuming. Use for very small bonds or extremely high compression
>
> **X_s** - soft potential: soft potentials are very fast but less precise. Use for less critical calculations
>
> **X** - standard potential
>
> **X_d**- treats semi core d-states as valence states
>
> **X_sv**- treats semi core s-states as valence states
>
> **X_pv**- treats the semi core p-states as valence states: recommended default for some elements

5. The SCF panel

Constructing the electronic density for a given arrangement of atoms involves a self-consistent-field (SCF) calculation solving the Kohn-Sham equations. The settings needed for this step are controlled by the SCF panel.



Input mode: set spacing between k-points
Spacing of k-points: 0.5 1/Ang
☐ Shift origin to Gamma
☐ Use odd size grids

Actual mesh and spacing

	Constraint	Mesh points	Spacing (1/Ang)
x:		6	0.473
y:	= x	6	0.473
z:		1	0.279

Type of smearing: Methfessel-Paxton
Smearing width: 0.2 eV
Order of smearing function: 1

SCF convergence: 1.0e-05 eV
Maximum iterations: 60
Minimum iterations: 2
Initial delay:
☐ Delay each start

a. K-mesh in Brillouin zone

Input mode

set spacing between k-points - Uses an equidistant mesh of k-points in reciprocal space, defined by the spacing of k-points in 1/Å

set mesh parameters explicitly - Defines explicit values for the k-mesh in x, y and z direction of k-space

The k-mesh is one of the most critical parameters for an electronic structure calculation. Test your models for convergence with respect to the k-mesh.

For example the convergence behavior of the total energy can vary between odd and even sized grids. Carefully check or use either odd or even meshes exclusively. Use a fixed k-spacing to compare calculations for models with different shapes/volumes.

Use odd sized grids: Always have an uneven number of grid points

Shift origin to Gamma: Shifts the origin of the k-mesh to Gamma

The k-mesh should be centered symmetrically around the Gamma point. To this end, a k-mesh containing an even number of mesh points is moved off the origin by default.

Actual mesh and k-spacing: Shows number of k-points and k-point density calculated from the provided input. This field also indicates constraints on the k-mesh due to symmetry, for a cubic cell x=y=z

For surface calculations, ensure to have only 1 k-point in the reciprocal direction of the surface normal.

For molecular systems use a single k-point. (Gamma only)

b. Integration Scheme

The choice of the integration scheme determines how the electronic density of states is integrated. In the limit of an infinitely fine integration mesh, all integration methods should yield identical results. In reality, relatively coarse meshes are used to speed up computations. The most sensitive area in k-space is the area that divides occupied from unoccupied states. For semiconductors and insulators this area falls into a gap between electronic bands while for metals a Fermi energy or Fermi surface exists, in other words occupied and unoccupied states are direct neighbors in energy or k-space. Therefore, great care is required when integrating the density of states for metals. A number of different schemes to achieve this are implemented in VASP:

- **Methfessel-Paxton**, **Fermi**, **Gaussian**: Use smearing of the electronic occupation around the Fermi energy
- **Tetrahedron**, **Tetrahedron with Blöchl correction**: Use tetrahedra to integrate the electronic density

Recommendations:

Metals: Use **Methfessel-Paxton** for structure optimization. If default smearing produces a large entropy term (>1meV) test with varying smearing. For precise total energy calculations use a fine k-mesh (0.2 1/Ang or better) and **Tetrahedron with Blöchl correction**.

Semiconductors/Insulators: Use **Tetrahedron method** or if the number of k-points is too small to allow for the tetrahedron method to be used, use **Gaussian**. If in doubt use the automated convergence tool to test.

Smearing width: numerical parameter used to define the width of the smearing function applied to the electronic density

Smearing out the electronic density around the Fermi surface region is important for metals as the determination of the precise location of the Fermi energy is numerically difficult.

Convergence is improved by using a smearing method for the integration of the electronic density. The reason is that density fluctuations between iterations during the SCF cycle are minimized.

Order of smearing function: The order of the smearing functions to be used: linear, quadratic …

c. SCF Control

SCF convergence: Determines the convergence of the self-consistent-field run. Convergence is reached if between iterations, both the total energy and the electronic eigenvalues (band structure energies) change less than the value given in the input field in eV

The default of 1E-5 eV is sufficient for most structure relaxations. Set the SCF convergence to 1E-6 or 1E-7 if the structure optimization is required to yield more precise forces/geometries (e.g. a PHONON atomic minimization of the “undisplaced” structure)

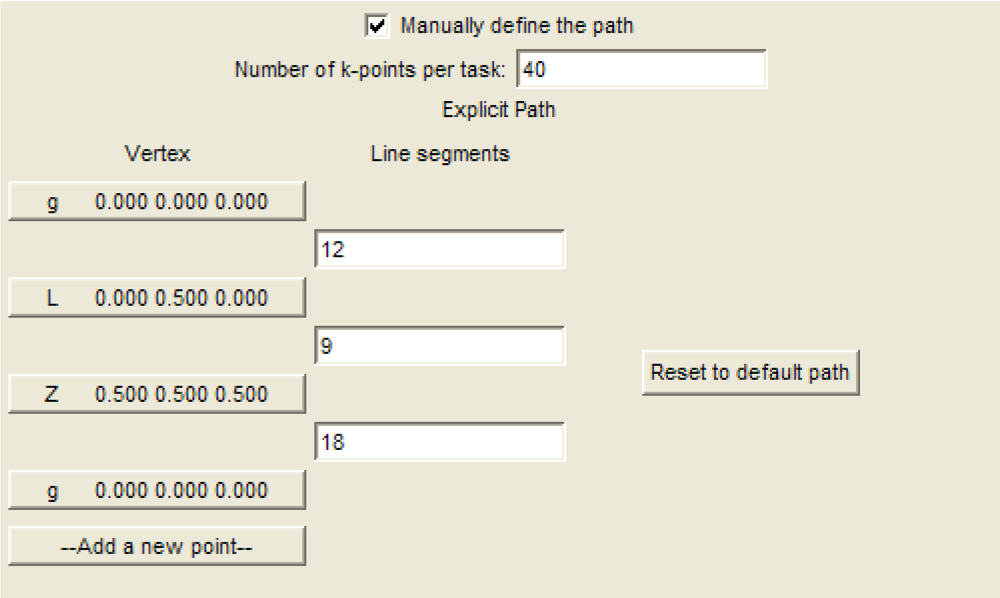
Maximum iterations: The maximum number of iterations before stopping the SCF cycle

Minimum iteration: The minimum number of iterations to do in a SCF cycle

Initial delay: number of initial steps to do without updating the wave functions (non-self consistent)

In most cases the SCF cycle converges within less than 60 steps. When starting a structure optimization from a very unrealistic input structure, the SCF may not converge during the first few geometry steps. An initial delay of 8-12 may be required for difficult surface calculations

6. The Band Structure panel



☑ Manually define the path

Number of k-points per task: 40

Explicit Path

Vertex	Line segments
g 0.000 0.000 0.000	
	12
L 0.000 0.500 0.000	
	9
Z 0.500 0.500 0.500	
	18
g 0.000 0.000 0.000	

A band structure is a plot of the electronic energies as a function of the electronic momentum **k.** It is also referred to as the electronic dispersion relation. In principle the band structure is a 3 dimensional scalar field $e_i(\mathbf{k})$, where the vector **k** takes on all values within the first Brillouin zone of the crystal and i labels the bands. In practice the symmetry of a crystal reduces the number of non equivalent k-vectors (or k-points) considerably. Therefore, one usually plots the band energies along a path connecting points of high symmetry within the Brillouin zone of the crystal.

MEDEA provides these standard paths for all lattice types. In addition, MEDEA offers a set of k-vectors for each lattice type, so a user-defined path for displaying the band structure can be set up.

- Click on a vertex point to change its coordinates

- Click on Add point to add an additional k-point

In the following the available options for the band structure interface are summarized:

Manually define path: Lets you show and edit the list of k-points available for the given system. By default MEDEA makes the choice which Brillouin zone path to display. Alternatively you can display and edit the list of k-point vertices and change the number of line segment points to be calculated and displayed

Number k-points per task: Use this option to limit the number of k-points per VASP task. Main memory requirement and compute time depend on the number of k-points used in a SCF calculation. MEDEA splits a band structure job into separate tasks with **Number of k-points per task** k-points in each task.

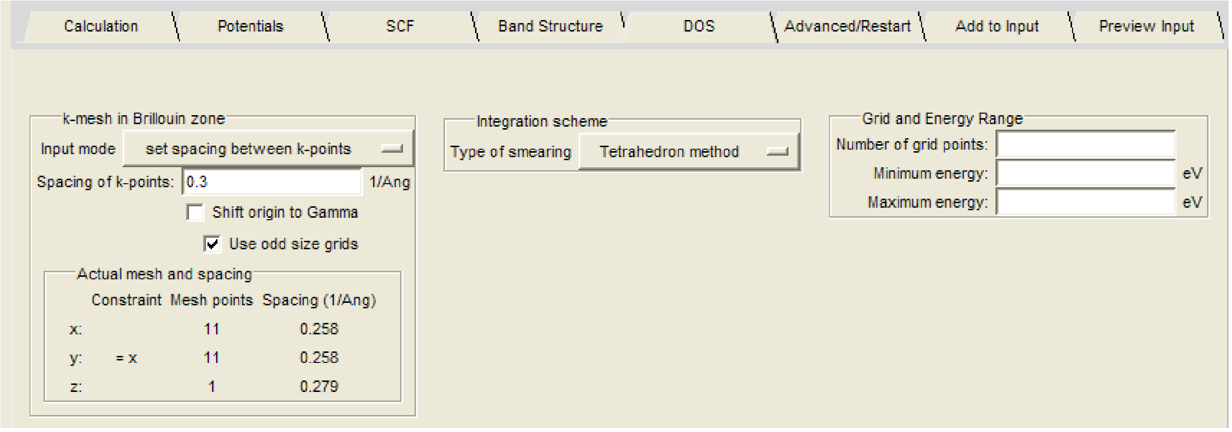
Vertex: A high symmetry point inside the Brillouin zone of the given crystal. The band structure displays the electronic energy as a function of the electronic momentum **k** on a sequence of lines connecting points (vertices) of high symmetry in the Brillouin zone. Each line segment represents a different direction in k-space.

> Axis definitions can vary between publications, resulting in varying coordinates for symmetry points. If in doubt, check out MEDEA's chapter on the Brillouin zone definition.

Line segments: The number of points to calculate and display on a line between two vertexes

7. The DOS panel

The DOS panel controls the precision of the k-point sampling for the calculations of the electronic density of states (DOS). Calculating the DOS requires a fairly dense mesh of k-points in the Brillouin zone (k-space sampling).



k-mesh in Brillouin zone

Input mode: set spacing between k-points

Spacing of k-points: 0.3 1/Ang

☐ Shift origin to Gamma

☑ Use odd size grids

Actual mesh and spacing

	Constraint	Mesh points	Spacing (1/Ang)
x:		11	0.258
y:	= x	11	0.258
z:		1	0.279

Integration scheme

Type of smearing: Tetrahedron method

Grid and Energy Range

Number of grid points:

Minimum energy: eV

Maximum energy: eV

A MEDEA DOS calculation consists of two steps:

1. A self-consistent calculation to generate a converged charge density satisfying the criteria selected in the SCF panel
2. A restart using the converged charge density from the first and a different (usually finer) k-point sampling to calculate the density of states.

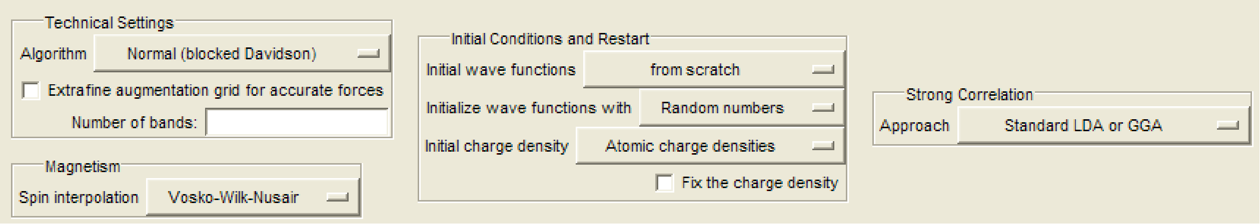
The DOS panel offers the same options as the SCF panel, but with different defaults and additional entries to achieve higher precision:

- By default, the tetrahedron method is used as integration scheme.
- The spacing of k-points is somewhat decreased leading to a denser k-mesh
- An odd k-mesh is used

Grid and Energy Range: This option lets you set the number of grid points for the DOS calculation and the minimum and maximum energy (in eV) relative to the Fermi level (the energy "window").

8. The Advanced/Restart panel

The Advanced/Restart panel summarizes technical control settings, restart settings and options for including strong correlations in the crystal Hamiltonian. For standard calculations it is recommended to keep these defaults. A detailed description of the available settings is given below:



Technical Settings
Algorithm: Normal (blocked Davidson)
☐ Extrafine augmentation grid for accurate forces
Number of bands:

Magnetism
Spin interpolation: Vosko-Wilk-Nusair

Initial Conditions and Restart
Initial wave functions: from scratch
Initialize wave functions with: Random numbers
Initial charge density: Atomic charge densities
☐ Fix the charge density

Strong Correlation
Approach: Standard LDA or GGA

a. Technical settings

1) Algorithm

Normal (blocked Davidson) - Recommended default

Fast- Starts with blocked Davidson and switches to RMM-DIIS after a number of steps

Very fast: The RMM-DIIS algorithm reduces the number of normalization steps considerably and is therefore much faster than the Davidson algorithm for large systems and on workstations with a small memory band width.

> RMM-DIIS stands for Residual Minimization Method with Direct Inversion of the Iterative Subspace.
>
> It does not have as large a radius of convergence as the Davidson method, so it may have convergence problems for some systems, particularly if starting from guessed wave functions.
>
> We recommend testing the 'Fast' or 'Very Fast' RMM-DIIS algorithms together with real space projection for large systems.

2) Extra fine augmentation grid:

Check this option to use an extra fine augmentation grid to yield very accurate forces. This option is recommended for eliminating numerical noise in complex PHONON calculations. Higher accuracy is achieved by defining an additional super fine Fourier grid doubling the sampling of the fine grid used to evaluate the augmentation charges

Number of bands: The number of bands to include in the calculations. At least one empty band should be present. VASP issues a warning in if this is not the case

- The default value is: $\frac{\#electrons}{2} + \frac{\#atoms}{2}$
- In some cases, for large systems, the number can be decreased to $\frac{\#\text{electrons}}{2} + \frac{\#atoms}{4}$.

- Transition metals may require a much larger number up to $\frac{\#\,electrons}{2} + 2 * \#atoms$

To check this parameter, perform several calculations for a fixed potential (ICHARG=12 in **Add to Input**) with an increasing number of bands, e.g. starting from $\frac{\#\text{electrons}}{2} + \frac{\#\text{ atoms}}{2}$. An agreement of the total energies respective of 1e^{-6} should be obtained in 10-15 iterations

Mind that the RMM-DIIS scheme is more sensitive to the number of bands than the default CG algorithm.

The actual value is defined by the keyword *NBANDS* and can be found in *OUTCAR.out.*

b. Magnetism

Spin interpolation

Vosko-Wilk-Nusair - consistent with both LDA and GGA calculations

Barth-Hedin - consistent with LDA calculations

The earlier Bart-Hedin algorithm was used to set up the exchange correlation potential in LDA. With the arrival of the GGA formalism, the Vosko-Wilk-Nusair implementation has become a standard

c. Initial Conditions and Restart

1) Initial wavefunctions

From scratch - reinitializes the wavefunctions at the beginning of a SCF run:

Random number - uses random numbers. Fills the plane waves with lowest kinetic energy for a constant potential

Read in from previous run - use wavefunctions from a previous calculation.

Note that for a fixed energy cutoff the number of planewaves at a given k-point depends implicitly on the cell parameters. When restarting with wavefunctions from a previous calculation either the basis set (=the number of plane waves) or the energy cutoff can be kept constant

It is recommended to use a constant basis set, if your cell parameters changed from the previous calculation.

2) Initial charge density

From initial wavefunctions: If the initial wavefunctions are initialized from scratch, it is recommended to use a superposition of atomic charge densities

Read in from previous run : If suitable wavefunctions and/or charge densities are available, using them to initialize the SCF run will speed up convergence considerably

Atomic charge densities The initial charge density is constructed as a superposition of atomic charge densities

Fix the charge density fixes charge density to its initial value for the whole of the SCF calculation Fixing the charge density can be useful for calculating the band structure, DOS, or for running a Harris-Foulkes functional calculation (using the atomic densities)

3) Strong correlation

Standard LDA or GGA - Standard density functional approach without L(S)DA+U

Simplified LSDA+U - The approach suggested by Dudarev et al. [9] Only one parameter U-J is required to define the on-site Coulomb interaction

Rotationally invariant LSDA+U The approach suggested by Liechtenstein et al. [10]. Both parameters U and J need to be specified

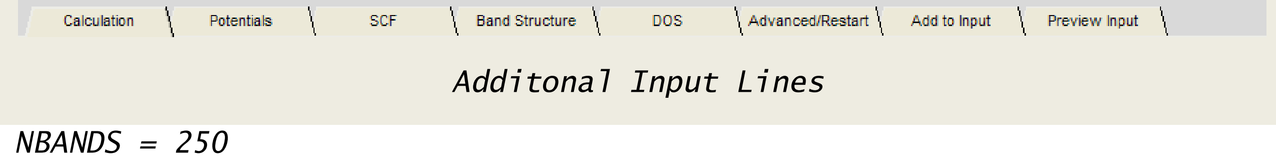
Rotationally invariant LDA+U - Like the LSDA+U variant above, however, with a different definition of the so-called double counting energy

The unscreened electron-electron interaction can be written in terms of Slater integrals. Application of Slater integrals as calculated from atomic wavefunctions results in large overestimation of the true interaction, since the Coulomb interaction in condensed systems is screened. Therefore, in practice these integrals are evaluated in terms of the Coulomb and exchange parameters U and J.

These parameters are adjusted in order to obtain agreement with experimental data such as equilibrium volume, magnetic moments, band gap or crystal structure. This approach is known as L(S)DA+U method. Despite its name it can equally well be applied within GGA.

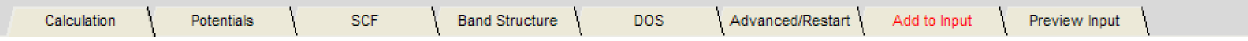
9. The Add to Input panel

The MEDEA-VASP graphical user interface does not expose all possible VASP parameters. In order to give access to all the features of VASP, which are not explicitly part of the interface, VASP keywords and parameters can be entered as additional lines of the INCAR file. This is accomplished by providing the **Add to Input** panel



```
NBANDS = 250
```

As the VASP interface remembers settings for the next calculation, the added input lines might not make sense during the next run. To give you a reminder, the panel is highlighted as Add to Input in red, whenever Additional Input Lines have been specified:



VASP Keywords and parameters are described in the The Vasp Guide. Note that Vasp uses the first instance of a keyword, thus settings defined by the user in **Add to Input** will override settings defined elsewhere in the VASP interface panels.

The modified input files can be inspected in the **Preview** panel.

CAUTION: Settings in the **Add to Input** section remain active until removed, even when you click **Restore Defaults**! As a reminder to you, the color of the panel changes to red: **Add to Input**.

10. The Preview Input panel

File **INCAR**

```
# SCF input for VASP
# Note that VASP uses the FIRST occurrence of a keyword
SYSTEM = (Al)4  (Fm-3m) ~ Al (VASP)

    PREC = Accurate
   ENCUT = 500.000
  IBRION = 2
     NSW = 100
    ISIF = 3
    ALGO = Normal (blocked Davidson)

…
```

File **Copy to clipboard**

This panel lets you preview VASP input files before actually launching a job. Select the type of file you would like to preview from the **Files** menu:

- **POTCAR** - lists the potentials used for each atom in the system
- **script** - job submission script
- **INCAR** - the main VASP input file
- **KPOINTS** - contains k-mesh information
- **POSCAR** - contains atomic positions

This feature is often used to preview and check settings added by hand using the **Add to Input** capability. Note that only the first occurrence of a given keyword will be used and options set elsewhere in the graphical interface are overwritten by **Add to Input**.

E. Analysis of Results

1. Structure Optimization

a. Geometric Analysis

- **General** reports the symmetry information, such as space group, Pearson symbol and Wyckoff positions, as well as elementary physical properties such as cell volume and density

Si_3O_6

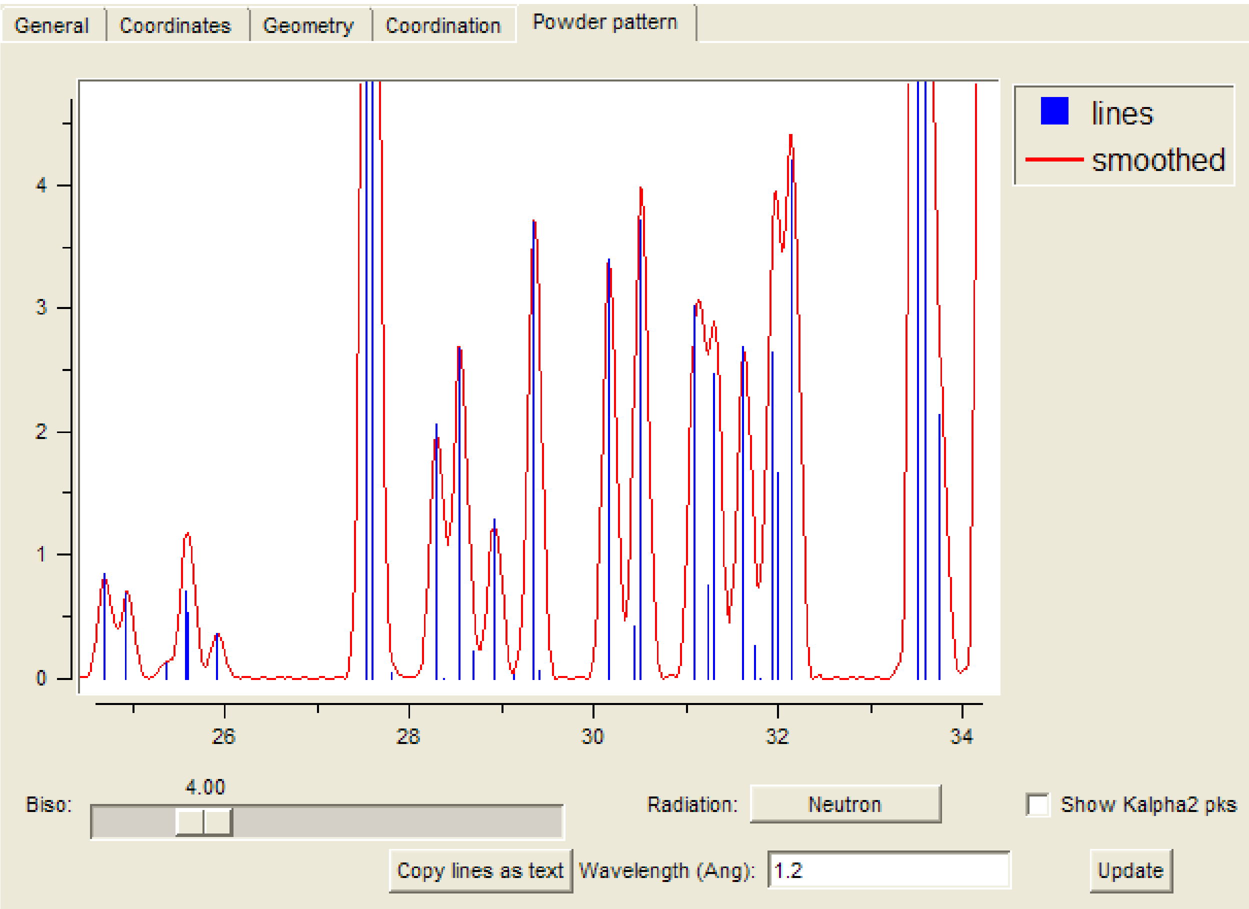
Symmetry			
Spacegroup:	**P3221**	Spacegroup Number	**154 (P3_221)**
Formula:	**SiO_2**	Z:	**3**
Pearson symbol:	**hP9**	Volume	**113.09 Å^3**
Calculated density:	**2.647 Mg/m^3**		

Cell			
a:	**4.91458**	α:	**90.0**
b:	**4.91458**	β:	**90.0**
c:	**5.40649**	γ:	**120.0**

Positions					
6	**c**	**?**	**x,y,z**	**-y,x-y,z+2/3**	**-x+y,-x,z+1/3**
			y,x,-z	**-x,-x+y,-z+2/3**	**x-y,-y,-z+1/3**
3	**b**	**?**	**X,0,1/6**	**0,x,5/6**	**-x,-x,1/2**
3	**a**	**?**	**X,0,2/3**	**0,x,1/3**	**-x,-x,0**

- Details about element positions are displayed in the **Coordinates** panel
- The Geometry panel prints distances and angles with neighboring atoms for a given reference atom

- In the **Coordination** panel, a of the number of nearest neighbors as a function of distance graph is plotted for a given reference atom
- **Powder pattern** shows the calculated powder pattern for different X-ray sources (Co, Mo, Ag, Cr, Fe and synchrotron) and neutron scattering. The isotropic thermal coefficient (Biso) can be varied with the slider, the wavelength for synchrotron radiation and neutrons



Biso: 4.00

Radiation: Neutron

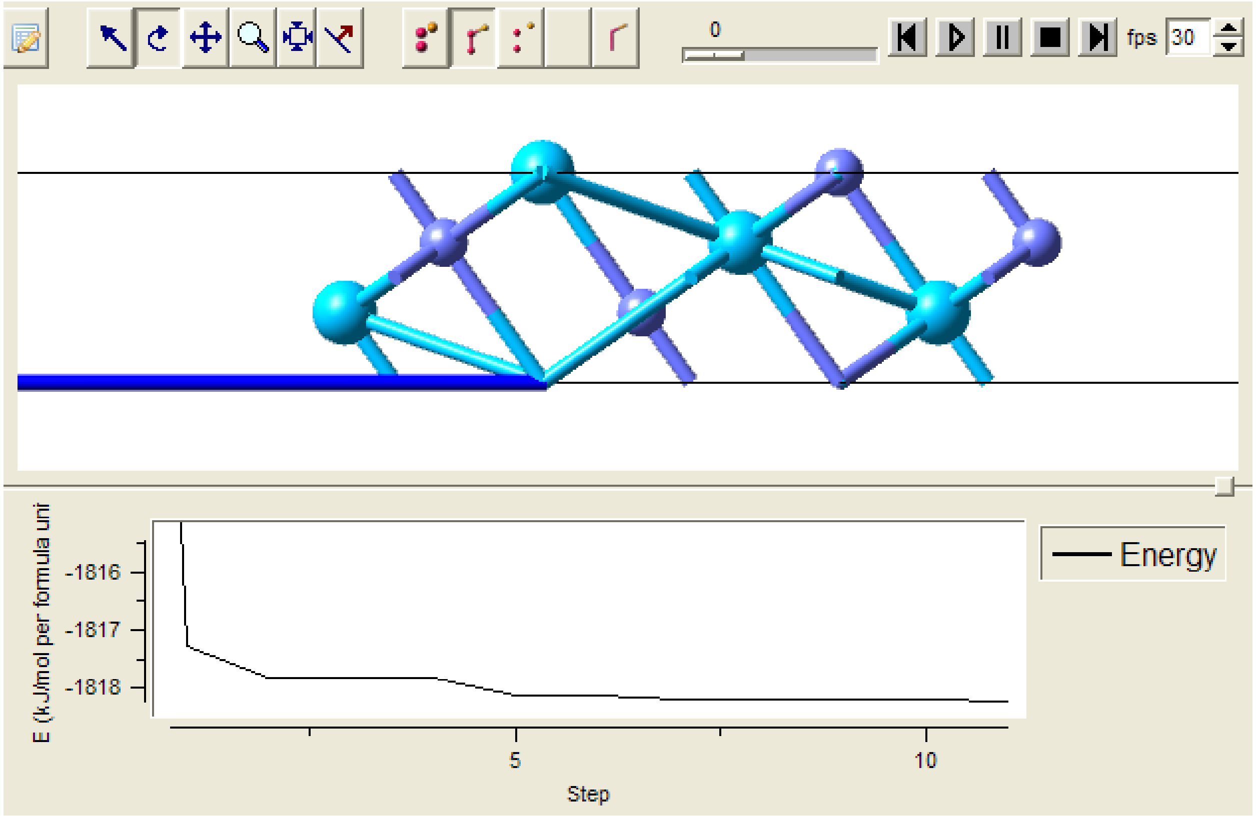
☐ Show Kalpha2 pks

Wavelength (Ang): 1.2

Experts use **Copy lines as text** to transfer the calculated angels and intensities to an external spreadsheet program.

b. Trajectory

Trajectory opens a dialogue with all completed structure optimization runs. Select one or more structures to display a trajectory of their atomic positions and their electronic energy as a function of the geometry step.



- The slider on top allows moving between initial (0) and final structures
- ⏮ and ⏭ skip to the initial and final structure respective
- Start the animation to cycle from the initial struture to the final structure and back with ▷, pause it with ⏸
- Use ■ to stop the animation and get back to the initial structure
- The speed of animation is controlled by the number of frames per second, set via the **fps** button

In the lower part of the window, the energy is plotted for each geometry step.

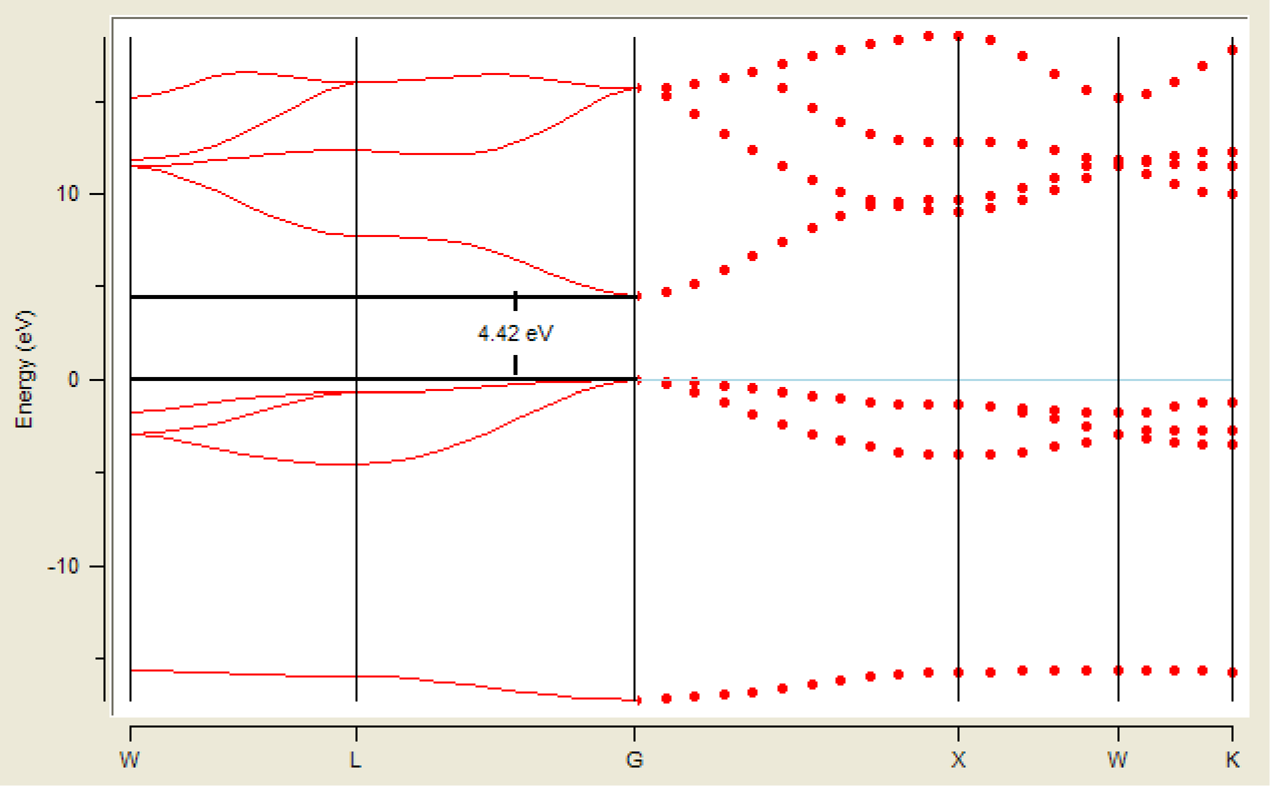
- Zoom-in on an area of interest by left-clicking in the graph and moving the mouse while holding the button
- Right-click to un-zoom or zoom back one level

2. Computed Properties

a. Band Structure

Click on **Analysis** ≫**Band Structures** to open a dialogue for selecting results from completed jobs. Selecting one or more jobs open a graphics window showing the corresponding band structure plots. A **BandStructure** menu entry shows up in the menu bar, given access to further options.

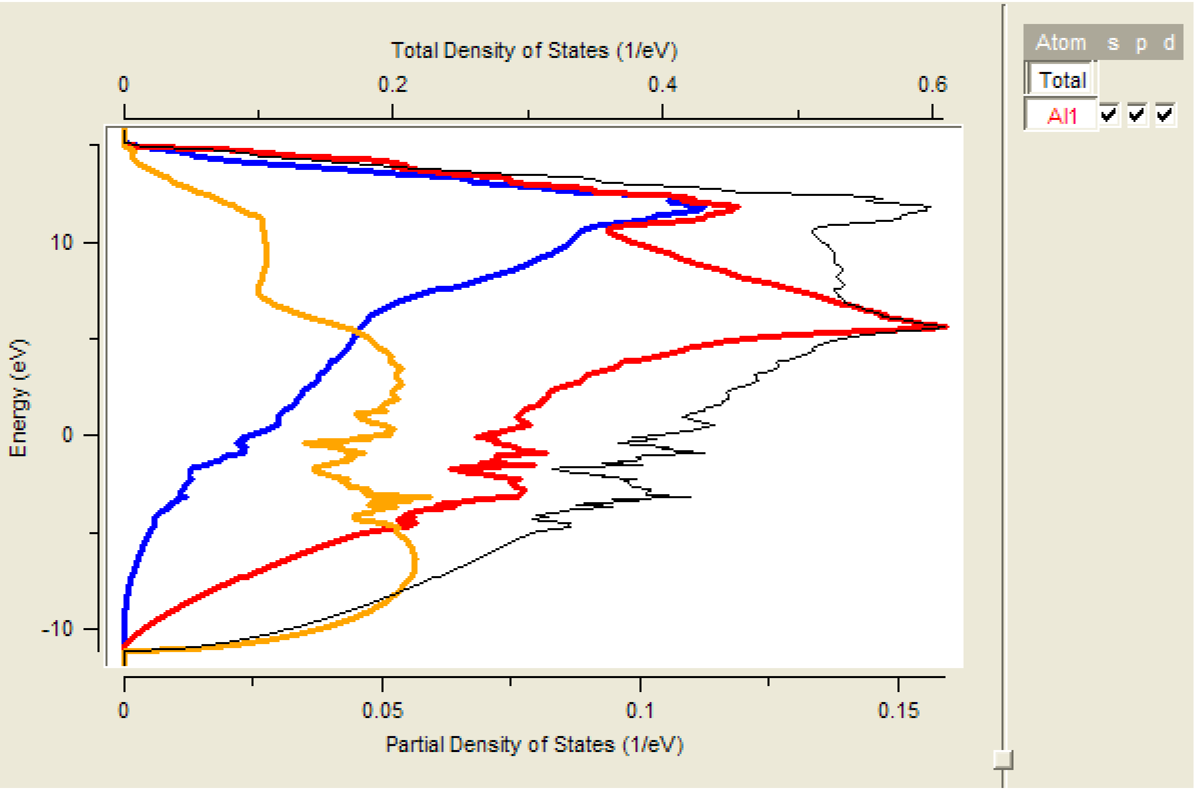
- Uncheck **☐ As Lines** to see each calculated points along the path, as shown on the right side



- Use **☑ Measuring lines** to measure energy differences in the plot
- Left-click and hold to zoom into the plot
- Right-click and select **Save as Postscript** or **Unzoom**

b. Density of States

Click on **Analysis** ≫**Density of States** to open a dialogue for selecting results from completed jobs. Selecting one or more jobs open a new window with the calculated density of states.



The color indicates the orbital or band: orange for s-states, red for p-states, blue for d-states and black for the total DOS.

- On the right hand side, select a field to toggle display of the corresponding partial DOS
- Click on **Total** to toggle on and off the display of the total density of states

Please note the different scales, for the total density of states at the top, for the partial density of states at the bottom.

Core electrons are not included in the density of states. The attribution of electrons to specific atoms in solids is done by projecting the electronic density into Wigner Seitz spheres around the atoms. The Wigner Seitz radii are parameters, therefore the partial atomic density need to be interpreted with care. To change the Wigner Seitz radii, use the **Add to Input** section of the VASP interface (see"The VASP Guide" for more details).

c. Difference Charge Density

MEDEA allows visualizing valence charge densities and charge density differences. Charge density differences are defined as the difference between the initial, atomic charge density distribution as used by VASP to initiate a calculation and the final electronic charge density distribution as it results from a self consistent calculation of the electronic ground state. The later is very useful to actually observe where electrons move during the SCF cycle.

- To compute electronic charge densities and differences using VASP, check ☑ **Valence charge density** in the Properties field of the VASP **Calculation** panel
- To visualize a difference charge density, click on **Analysis** ≫ **Charge Density Difference** to open a dialogue with a list of calculated charge densities. Select one or more structures to visualize their charge densities

The analysis window appears as a split structure window, the left hand side showing the structure, the right hand side showing two panels, **IsoSurface** and **Slice.** By default an isosurface with an average value of the difference charge density is shown

- Specify the **Iso value**, using the slider or by typing in a value
- Choose a Color for the isosurface by clicking **Choose color**
- Type in a value to change the **Transparency** from invisible (0) to opaque (1)
- For quicker rotations and adjusting of the cell, the rendering quality can be modified by lowering the **Precision** from high to medium to very low
- **Viewing Limits** lets you display more than one unit cell of the structure. Click **Update** when making changes

To improve the spatial resolution of the Difference Charge density increase the values of the VASP parameters *NGXF, NGYF, NGZF.* You find these values in the *OUTCAR* file, increase them, preferably to a power of 2. Use **Add to Input** in the Vasp panel to add a line like

NGXF=64; NGYF=64; NGZF=64

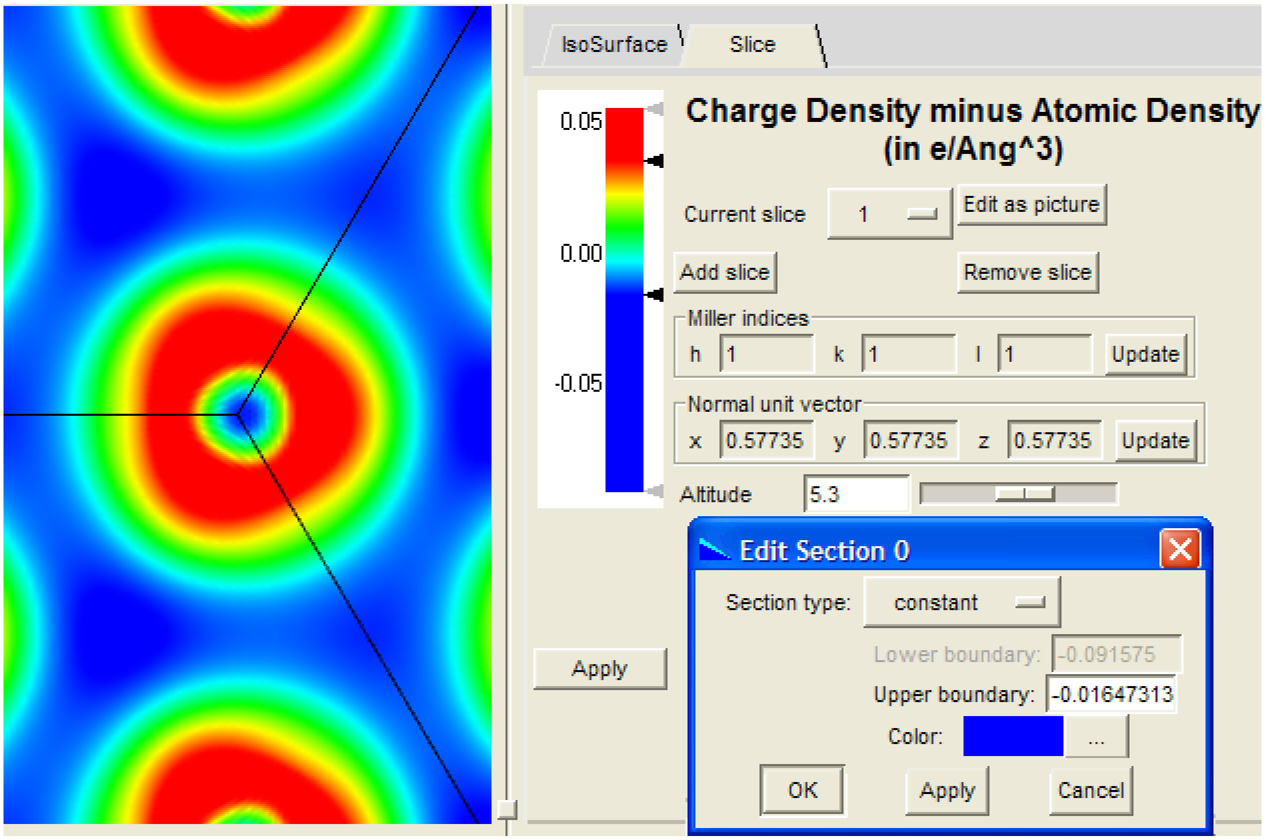
for increasing the computed default values.

In the **Slice** panel you can

- Select planes by giving their **Miller indices** or a **Normal unit vector**
- Change the **Altitude** of a given plane by moving the slider or by typing in a value
- Use the color scale to change the color spectrum
  - Change the range of values covered by the color spectrum using the small black arrows on the right
  - Right-click into the color scheme and select **Edit section** to change the values and colors used as upper/lower boundaries. Click **Apply** to apply after making changes

- Right-click into the color scheme and select **Add section above/below** to add additional section. For each section you can select a continuous spectrum of colors (ramp) or a constant value
- **Edit as picture** to get the current slice (without any superimposed cell boundaries and atoms), set the size to your specifications (either width or height) and save it as Bitmap, PNG or TIFF.

Example of Charge density difference for NaCl:



Charge Density minus Atomic Density (in e/Ang^3)

Current slice: 1

Miller indices: h 1, k 1, l 1

Normal unit vector: x 0.57735, y 0.57735, z 0.57735

Altitude: 5.3

Edit Section 0

Section type: constant

Lower boundary: -0.091575

Upper boundary: -0.01647313

Color:

In the above example, a projection of the difference charge density onto the 111 plane is shown for NaCl. The range of the plot is from -0.09 e/Å^3 to 0.5 e/Å^3. The plot has three sections: The lowest section ranging from -0.09 to -0.016 is colored in blue. The section from -0.016 to 0.035 shows the variation of the electronic density in colors from blue to red, the highest section is all in red. Depending on the altitude of the slice, not the full range of the variation in difference charge density is visible.

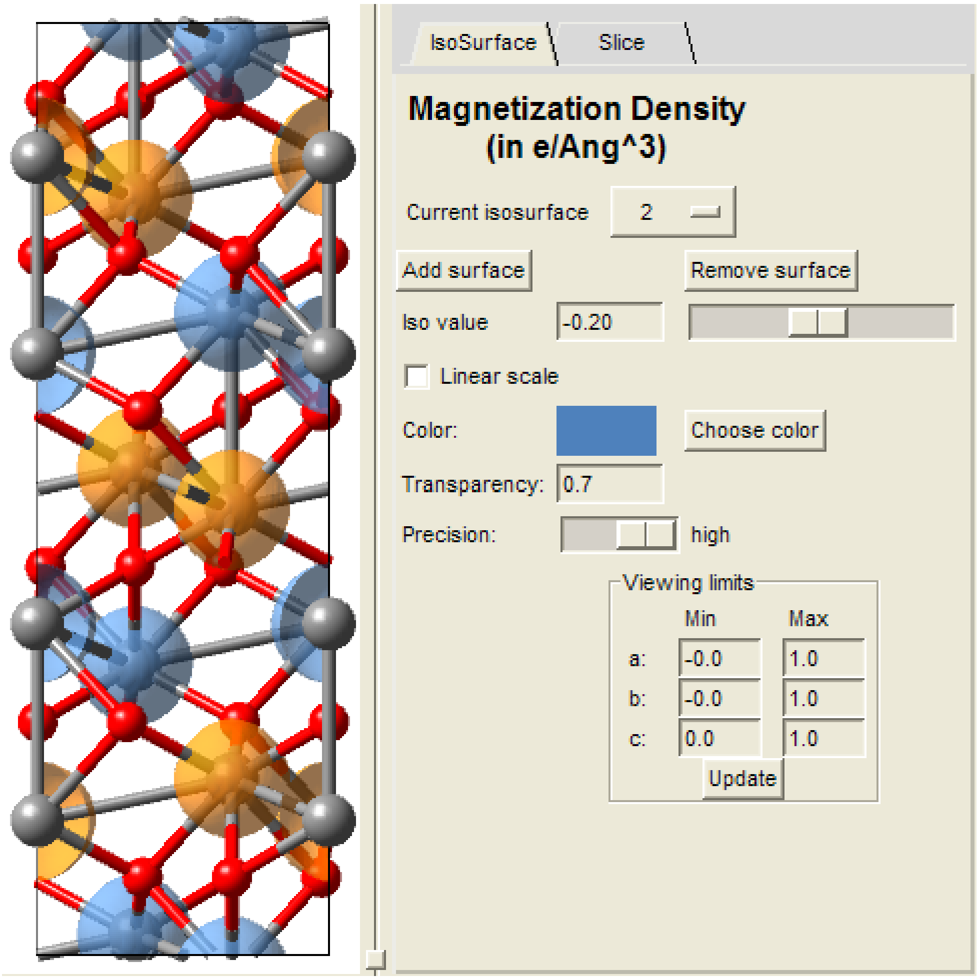
d. Magnetization Density

MEDEA allows visualizing magnetization densities defined as difference between spin-up and spin-down electron density. To compute magnetization densities using VASP, check **☑ Valence charge density** in the Properties field of the VASP **Calculation** panel

- To visualize a difference charge density, click on **Analysis** ≫ **Charge Magnetization Density** to open a dialogue with a list of calculated charge densities. Select one or more structures to visualize their magnetization densities.

The Analysis window has the same options as explained in the previous section.

To improve the spatial resolution of the Magnetization density increase the values of the VASP parameters *NGXF*, *NGYF*, *NGZF*.



Magnetization Density (in e/Ang^3)

Current isosurface 2

Iso value -0.20

☐ Linear scale

Color:

Transparency: 0.7

Precision: high

Viewing limits

	Min	Max
a:	-0.0	1.0
b:	-0.0	1.0
c:	0.0	1.0

In the example above, the antiferromagnetic structure of Hematite (Fe_2O_3) is visualized, two isosurfaces (with +0.2 in orange and -0.2 in blue) surround the Fe atoms and reveal the alternating sequence of Fe_2 layers with either spin up or spin down.

For structures with non-collinear magnetism, the analysis can be refined to x-, y- and z-direction.

e. Valence Charge Density

MEDEA allows visualizing valence charge densities used to construct the charge density differences. This includes all valence electrons not included in the core of the pseudo potential or PAW potential.

- To compute electronic charge densities and differences using VASP, check ☑ **Valence charge density** in the Properties field of the VASP **Calculation** panel
- To visualize a valence charge density, click on **Analysis** ≫ **Valence Charge Density** to open a dialogue with a list of calculated charge densities. Select one or more structures to visualize their charge densities

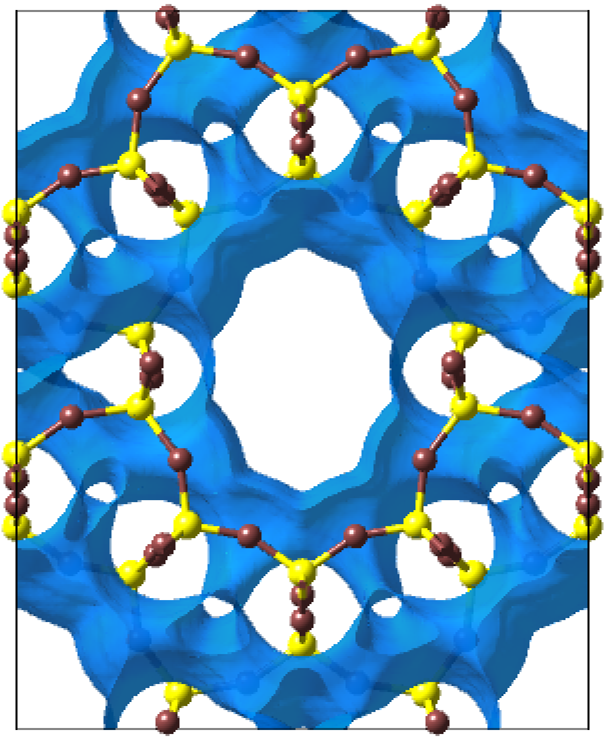
The analysis window appears as a split structure window, the left hand side showing the structure, the right hand side showing two panels, **IsoSurface** and **Slice**. By default an isosurface with an average value of the valence charge density is shown

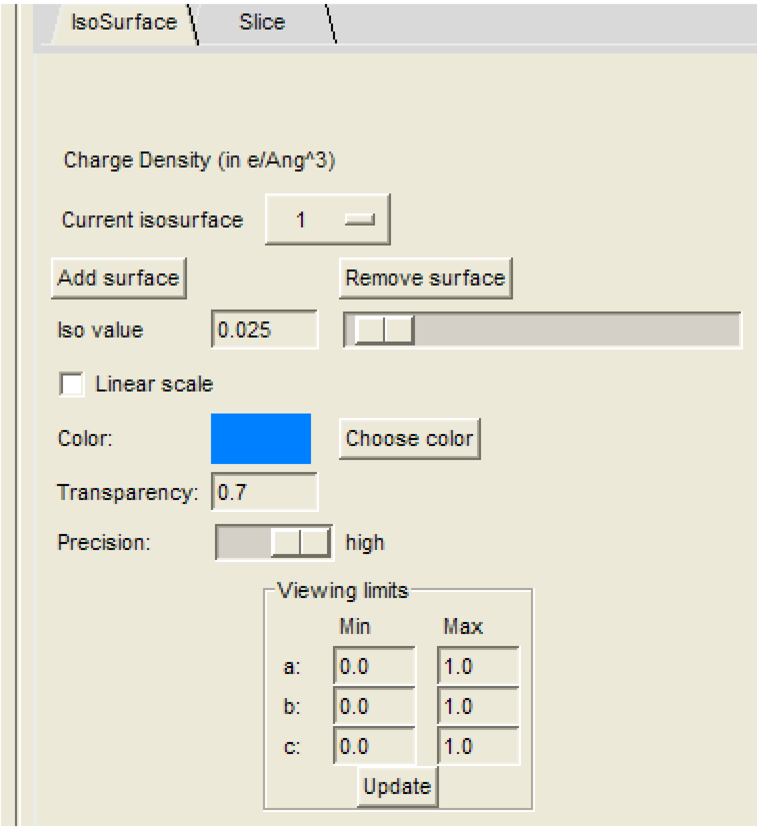
- Specify the **Iso value**, using the slider or by typing in a value
- Choose a Color for the isosurface by clicking **Choose color**
- Type in a value to change the **Transparency** from invisible (0) to opaque (1)
- For quicker rotations and adjusting of the cell, the rendering quality can be modified by lowering the **Precision** from high to medium to very low
- **Viewing Limits** lets you display more than one unit cell of the structure. Click **Update** when making changes

To improve the spatial resolution of the Valence Charge density increase the values of the VASP parameters *NGXF,NGYF,NGZF.* You find these values in the *OUTCAR* file, increase them, preferably to a power of 2. Use **Add to Input** in the Vasp panel to add a line like

NGXF=64; NGYF=64; NGZF=64

for increasing the computed default values.





Charge Density (in e/Ang^3)

Current isosurface: 1

Iso value: 0.025

☐ Linear scale

Color: 🟦

Transparency: 0.7

Precision: high

Viewing limits

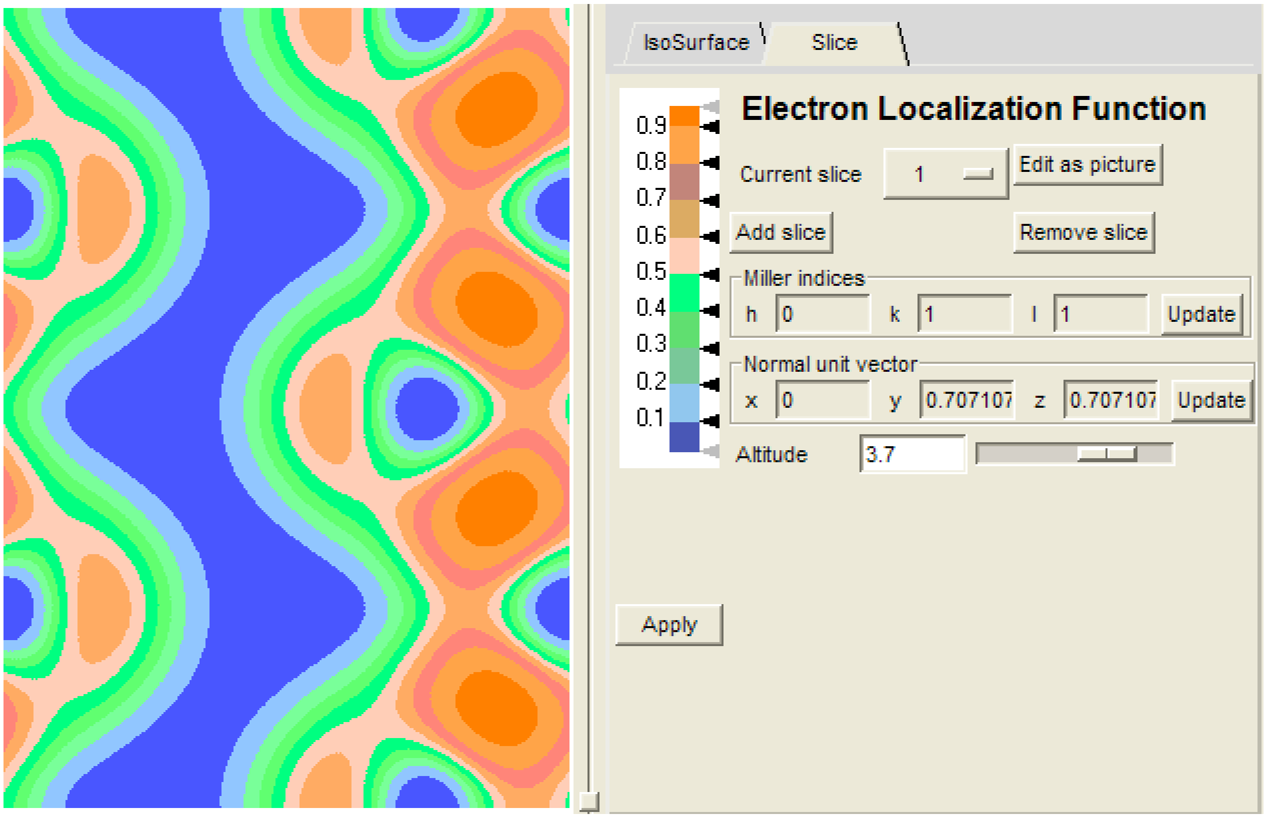
	Min	Max
a:	0.0	1.0
b:	0.0	1.0
c:	0.0	1.0

In the **Slice** panel you can

- Select planes by giving their **Miller indices** or a **Normal unit vector**
- Change the **Altitude** of a given plane by moving the slider or by typing in a value
- Use the color scale to change the color spectrum
  - Change the range of values covered by the color spectrum using the small black arrows on the right
  - Right-click into the color scheme and select **Edit section** to change the values and colors used as upper/lower boundaries. Click **Apply** to apply after making changes
  - Right-click into the color scheme and select **Add section above/below** to add additional section. For each section you can select a continuous spectrum of colors (ramp) or a constant value.
- **Edit as picture** to get the current slice (without any superimposed cell boundaries and atoms), set the size to your specifications (either width or height) and save it as Bitmap, PNG or TIFF.

f. Electron Localization Function

The electron localization function [11] is used to identify binding and lone electron pairs in simple molecular systems The MEDEA interface for this feature is identical to the one for charge densities. The example below shows the (011) plane in diamond.



Electron Localization Function

Current slice 1

Miller indices: h 0, k 1, l 1

Normal unit vector: x 0, y 0.707107, z 0.707107

Altitude 3.7

To improve the spatial resolution of the electron localization function increase the values of the VASP parameters *NGX*, *NGY*, *NGZ*. You find these values in the *OUTCAR* file, increase them, preferably to a power of 2. Use **Add to Input** in the Vasp panel to add a line like

NGX=64; NGY=64; NGZ=64

for increasing the computed default values.

g. Total Local Potential

The MEDEA interface for this feature is identical to the one for charge densities and ELF.

To improve the spatial resolution of the local potential increase the values of the VASP parameters *NGXF*, *NGYF*, *NGZF*. You find these values in the *OUTCAR* file, increase them, preferably to a power of 2. Use **Add to Input** in the Vasp panel to add a line like

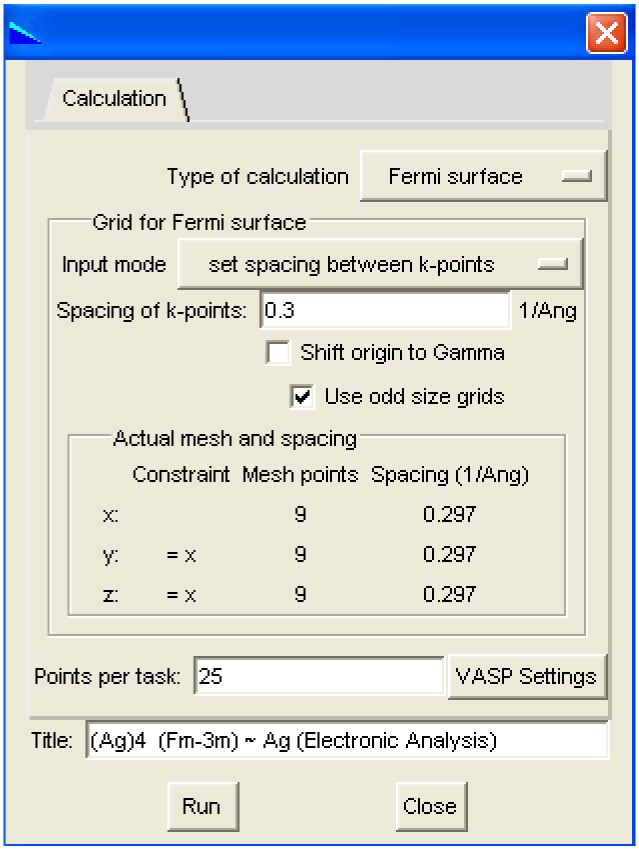
NGXF=64; NGYF=64; NGZF=64

for increasing the computed default values.

3. Electronic Analysis (Fermi)

Electronic Analysis allows you to calculate a 3D mesh of the electronic energy as a function of the k-vector. You can then visualize the resulting 3-dimensional band structure and display isosurfaces and compute effective masses and velocities on a given surface. For metals the Electronic Analysis yields an analysis of the Fermi surface.

To run an Electronic Analysis job, select **Electronic Analysis** from the **Tools** menu, click the new menu entry **Electronic Analysis** in the MedeA main menu and select **Run**.



Type of calculation: Fermi surface

Grid for Fermi surface

Input mode: set spacing between k-points

Spacing of k-points: 0.3 1/Ang

☐ Shift origin to Gamma

☑ Use odd size grids

Actual mesh and spacing

	Constraint	Mesh points	Spacing (1/Ang)
x:		9	0.297
y:	= x	9	0.297
z:	= x	9	0.297

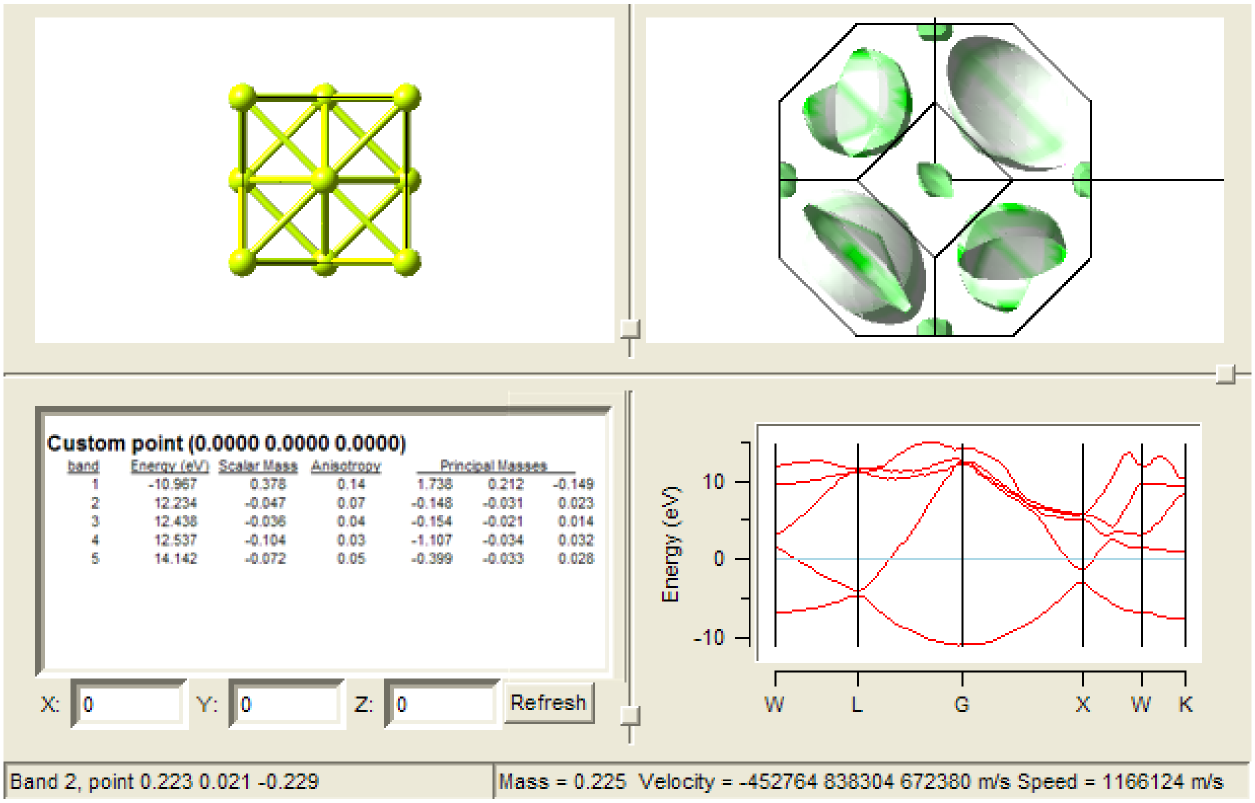
Points per task: 25

Title: (Ag)4 (Fm-3m) ~ Ag (Electronic Analysis)

The Run interface is similar to what you know from the SCF panel of the VASP interface. Select a rather fine mesh (default 0.3/Å), the number of Points to use per VASP task (default = 25), and select further **VASP settings** to set additional VASP parameters. The module will determine a 3D mesh for the Brillouin zone of the current structure and run a number of VASP tasks to yield the 3D mesh.

To visualize an isoelectronic surface, choose **Fermi Surface** from the Electronic Analysis menu and select the completed analysis job.

The window splits in four parts: The top row shows the structure (left) and the reciprocal cell (right). The bottom row displays numerical results per k-point and band (left and a band structure plot (right).



Custom point (0.0000 0.0000 0.0000)

band	Energy (eV)	Scalar Mass	Anisotropy	Principal Masses		
1	-10.967	0.378	0.14	1.738	0.212	-0.149
2	12.234	-0.047	0.07	-0.148	-0.031	0.023
3	12.438	-0.036	0.04	-0.154	-0.021	0.014
4	12.537	-0.104	0.03	-1.107	-0.034	0.032
5	14.142	-0.072	0.05	-0.399	-0.033	0.028

X: 0 Y: 0 Z: 0

Band 2, point 0.223 0.021 -0.229

Mass = 0.225 Velocity = -452764 838304 672380 m/s Speed = 1166124 m/s

For each k-point and band FERMI prints:

- The energy and scalar mass of an electron
- The anisotropy
- The components of the effective mass in x,y, and z direction

The following option are implemented:

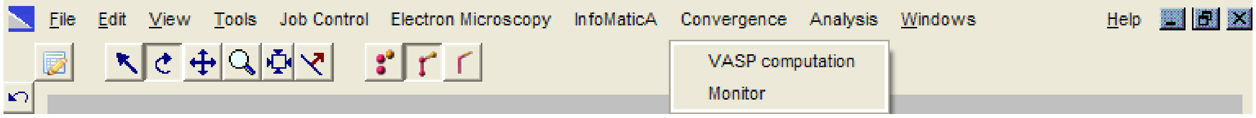
- To specify and (custom) a specific k-point use the three entry fields: X: ☐ Y: ☐ Z: ☐ and confirm with **Refresh.**
- Use **Change the Fermi Surface** to select a different band. To facilitate selecting bands at certain energy, the dialogue reports the highest and lowest energy for each band
- Change the value for which the isosurface is plotted (default is zero, i.e. the Fermi level)
- Moving the mouse over the Fermi surface graph on the right hand side displays information on mass, velocity and speed of the point under the mouse pointer in the status bar at the bottom of the window

F. Automated Convergence

The accuracy of computed materials properties such as equilibrium lattice parameters, binding energies, and elastic moduli depends on a variety of computational parameters, most notably the quality of plane wave basis sets and the density of k-meshes for integrations in reciprocal space.

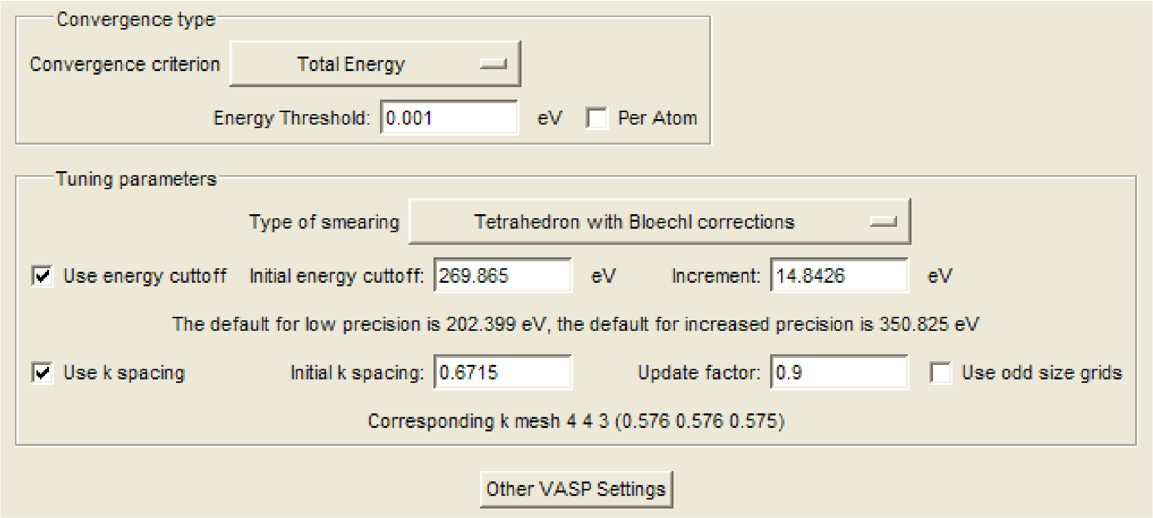
The optimal choice of these parameters depends both on the material under investigation and on the properties of interest. For example, metallic aluminum requires very fine k-meshes to achieve convergence of the total energy while semiconductors are well described by a rather coarse k-mesh. Finding the most appropriate parameter setting is important, but tedious to do by hand. The Convergence Module automates the process of determining optimal parameter settings in VASP for achieving the desired level of accuracy in calculations of materials properties.

Activate the **Convergence** menu entry in MEDEA by clicking **Tools** ≫ **Automated Convergence**. Next select **Convergence** ≫ **VASP computation** to start a Convergence job or **Convergence** ≫ **Monitor** to analyze results.



1. Submitting VASP Convergence Jobs

The Convergence run interface looks like this:



Convergence type

Convergence criterion: Total Energy

Energy Threshold: 0.001 eV ☐ Per Atom

Tuning parameters

Type of smearing: Tetrahedron with Bloechl corrections

☑ Use energy cuttoff Initial energy cutoff: 269.865 eV Increment: 14.8426 eV

The default for low precision is 202.399 eV, the default for increased precision is 350.825 eV

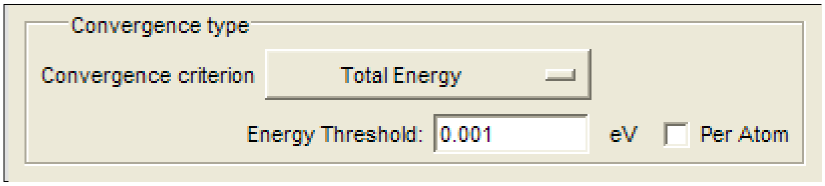
☑ Use k spacing Initial k spacing: 0.6715 Update factor: 0.9 ☐ Use odd size grids

Corresponding k mesh 4 4 3 (0.576 0.576 0.575)

a. Convergence type

You can use the following criteria with Convergence:

Total Energy: Converges the VASP total energy, where you can select a value as convergence threshold, either for the whole system or per atom.


Convergence type

Convergence criterion: Total Energy

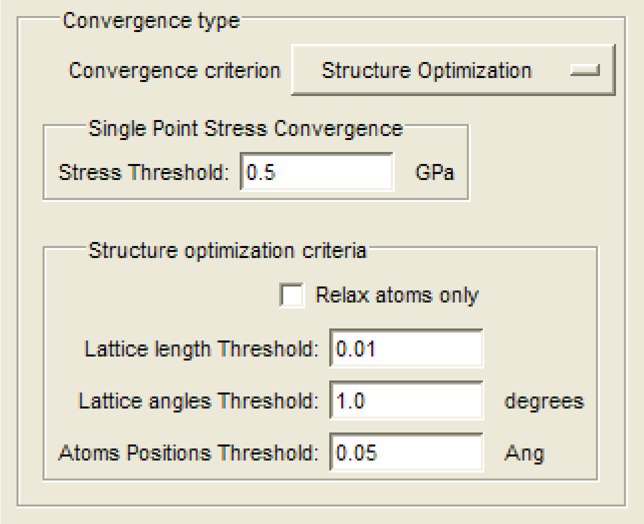
Energy Threshold: 0.001 eV ☐ Per Atom

Structure Optimization: Converges both the single-point stress and the lattice parameters and atomic positions. You can select to **Relax atoms only**.

The convergence will be studied as follows:

Single point stress convergence calculations with the stress tensor (**Stress Threshold** in GPa) as the convergence criterion

Using results from a **Structure optimization** with convergence based on relative change of the cell length, angles and atomic positions. To keep the cell fixed, select **Relax atoms only**


Convergence type

Convergence criterion: Structure Optimization

Single Point Stress Convergence

Stress Threshold: 0.5 GPa

Structure optimization criteria

☐ Relax atoms only

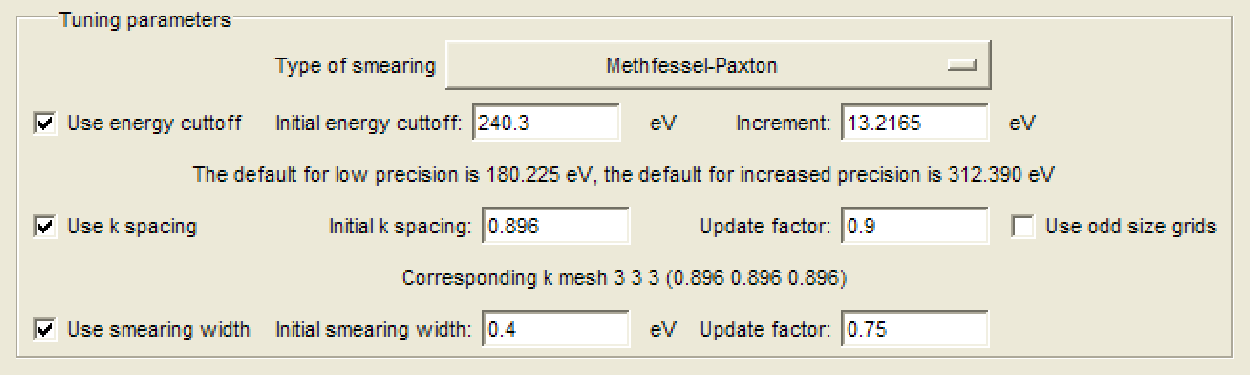
Lattice length Threshold: 0.01

Lattice angles Threshold: 1.0 degrees

Atoms Positions Threshold: 0.05 Ang

b. Tuning parameters

Using the above convergence criteria the module will optimize the following parameters:


Tuning parameters

Type of smearing: Methfessel-Paxton

☑ Use energy cuttoff Initial energy cuttoff: 240.3 eV Increment: 13.2165 eV

The default for low precision is 180.225 eV, the default for increased precision is 312.390 eV

☑ Use k spacing Initial k spacing: 0.896 Update factor: 0.9 ☐ Use odd size grids

Corresponding k mesh 3 3 3 (0.896 0.896 0.896)

☑ Use smearing width Initial smearing width: 0.4 eV Update factor: 0.75

Energy cutoff (Plane wave cutoff, PWC): Starting from the initial energy cutoff the module will increase the cutoff by Increment until convergence is reached. VASP potentials provide a range of cutoff energies for each atom, defined by the limits *EMIN* and *EMAX*. The default value is the average between *EMIN* and *EMAX*. For systems with more than one type of atoms, the average between the highest *EMIN* and the highest *EMAX* is taken. The default increment is 1/10 of the difference between these two values.

K spacing (k-point spacing, KPS): The initial value of the KPS is set by the parameter **k-spacing** in such a way that the resulting k-mesh is at least 3x3x3 in order to allow using the tetrahedron method. In the refinement of the k-mesh, the initial k-spacing is multiplied by the **Update factor** until the actual number in the k-mesh increases.

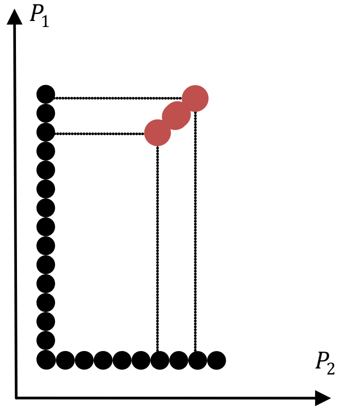
Smearing width: You can optimize this parameter only when **Methfessel-Paxton** k-integration is chosen. The default is to use the tetrahedron method with Blöchl corrections, which has no smearing parameter. The update factor decreases the smearing width during the convergence process.

2. Monitoring VASP Convergence Jobs

a. Choosing a job

The **Monitor** menu queries the selected JobServer for a list of convergence jobs. Select a Job to retrieve and display the results from an ongoing or finished job.

b. Multi-parameter convergence



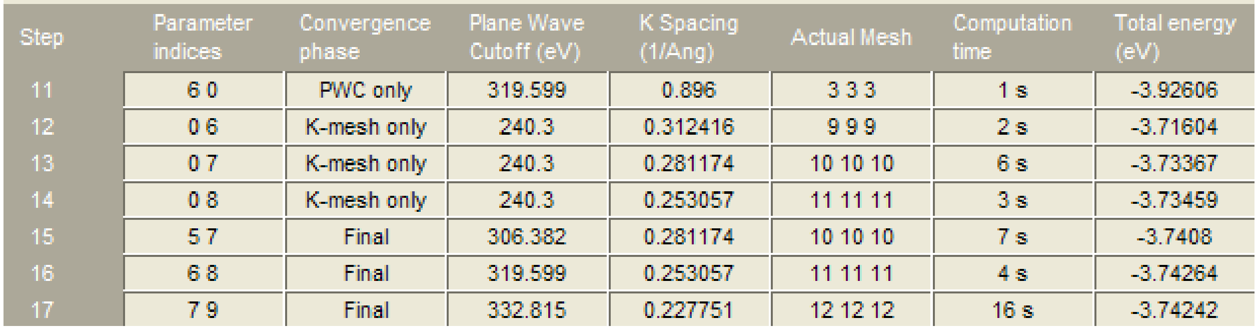
Before detailing the content of the monitor window, let us explain the progress of a convergence Job.

As long as only one parameter is used for tuning, the convergence process simply consists in updating the parameter until convergence is reached. If, however, several parameters are used simultaneously, the parameter space is multi-dimensioned and there might be several paths that lead to different points, where convergence is reached.

The strategy used for our problem is intended to limit the overall cost as follows. For the sake of simplicity, let us consider 2 tuning parameters p_1 and p_2, but this might be extended directly to any number of parameters. Two series of independent tasks are started with the following settings: in the first series, p_2 is set to its initial value and p_1 is tuned until convergence is reached after n_1 steps; in the second series, p_2 is converged in n_2 steps while is p_1 is unchanged. Finally two tasks are launched with the two last values of both parameters: $\left((p_1(n_1-1), p_2(n_2-1)\right)$ and $(p_1(n_1), p_2(n_2))$ and the convergence is tested again with the results of these two tasks. This strategy allows running at least as many tasks in parallel as there are tuning parameters, and even more during in the early stage of the job.

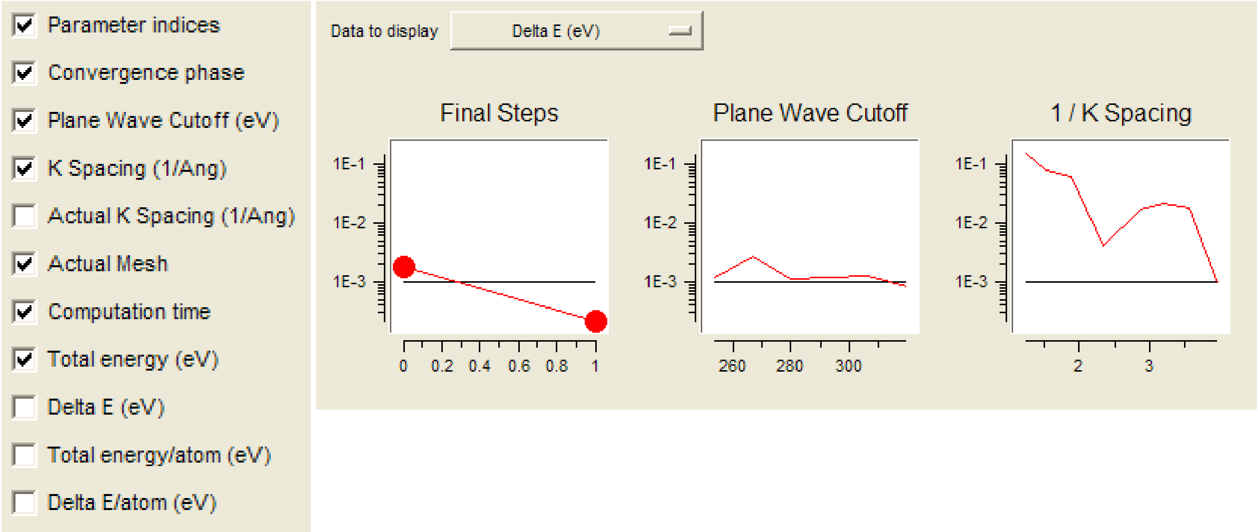
c. Monitor window.

This window presents a report table and a set of graphics. The tables contains a line for each step (VASP task), displaying the parameter values and the computed properties.



Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)
11	6 0	PWC only	319.599	0.896	3 3 3	1 s	-3.92606
12	0 6	K-mesh only	240.3	0.312416	9 9 9	2 s	-3.71604
13	0 7	K-mesh only	240.3	0.281174	10 10 10	6 s	-3.73367
14	0 8	K-mesh only	240.3	0.253057	11 11 11	3 s	-3.73459
15	5 7	Final	306.382	0.281174	10 10 10	7 s	-3.7408
16	6 8	Final	319.599	0.253057	11 11 11	4 s	-3.74264
17	7 9	Final	332.815	0.227751	12 12 12	16 s	-3.74242

The graphics frame contains a graph for each single-parameter convergence axis and one for the final convergence steps (with all parameters):



☑ Parameter indices
☑ Convergence phase
☑ Plane Wave Cutoff (eV)
☑ K Spacing (1/Ang)
☐ Actual K Spacing (1/Ang)
☑ Actual Mesh
☑ Computation time
☑ Total energy (eV)
☐ Delta E (eV)
☐ Total energy/atom (eV)
☐ Delta E/atom (eV)

Data to display: Delta E (eV)

The selection of columns can be adjusted via **Column Display**: **Parameter indices**, **Convergence phase**, **K Spacing**, **Actual K Spacing**, **Actual mesh**, **Computation time**, and **Total energy** and differences per atom and cell.

When the monitored job is running, some of computed values are still missing and are indicated by a - symbol.

An estimate of the minimum completion time is calculated by multiplying the time of the longest completed task by the minimum number of remaining tasks.

Basic features of the **Automatic Convergence** module are also found in **Point Defect Analysis** tool.

G. PHONON

Introduction and Capabilities

PHONON is a computational tool for the calculation of lattice dynamics and vibrational properties. Choosing suitable model structures with periodic boundary conditions, not only solids but also surfaces, interfaces and molecules can be studied. MEDEA-PHONON in conjunction with MEDEA-VASP provides access to vibrational properties of systems containing any elements of the periodic table in a fully automated fashion.

The fundamental capabilities of PHONON are:

- Calculation of phonon dispersion curves along any path through the Brillouin zone
- Animation of phonon modes, i.e. visualization of the collective movements of all atoms in the structural model for any phonon branch throughout the Brillouin zone.
- Calculation of the phonon density of states and its partial contributions of all atoms in each Cartesian direction
- Symmetry analysis, deriving Infrared and Raman activity of all modes at the Gamma point
- Temperature dependent thermodynamic functions, such as internal energy, entropy, free energy, and heat capacity
- Simulation of neutron scattering processes (Debye-Waller factors and mean square displacements, dynamical structure factors of coherent neutron scattering, doubly differential scattering-cross section of incoherent neutron scattering on monocrystals and polycrystalline samples)

PHONON is based on the so-called direct method [12] requiring an underlying method to compute forces on atoms. Together with the ab-initio code VASP as a source for accurate forces, MEDEA-PHONON provides fully automated procedures. PHONON also works with other methods for deriving forces (ab-initio or force fields), however, with reduced levels of automation.

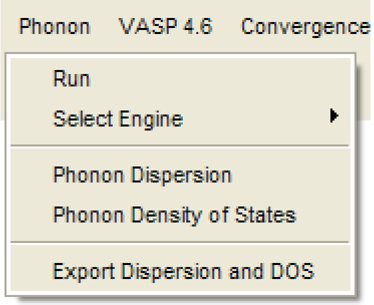
The direct approach to lattice dynamics requires the following procedure; more details are found in section IV.D Vibrations in solids – PHONONS:

- Create a sufficiently large supercell to minimize interactions between equivalent atoms in adjacent supercells and optimize (if required) atom positions of the supercell to ensure that forces on all atoms are vanishingly small. The structure should be at equilibrium
- Generate, based on the cell symmetry, a set of supercells where in each cell one atom is displaced from the optimized supercell and forces are calculate on all other
- Derive force constants from forces and build the dynamical matrix, diagonalize and determine phonon frequencies (eigenvalues) for points in reciprocal space (k vectors), obtain from the corresponding eigenvectors (polarization vectors), intensities (form factors) and movements of atoms (animation of modes).
- Integrate over a sample of k vectors to yield the phonon density of states and calculate thermodynamic functions and neutron scattering data

1. Starting the PHONON interface

From the MEDEA toolbar, select **Tools** ≫ **Phonon** to open a new menu entry **Phonon** which will remain in the tool bar during the MEDEA session. ≫

Clicking PHONON in the MEDEA tool bar provides the following choices:

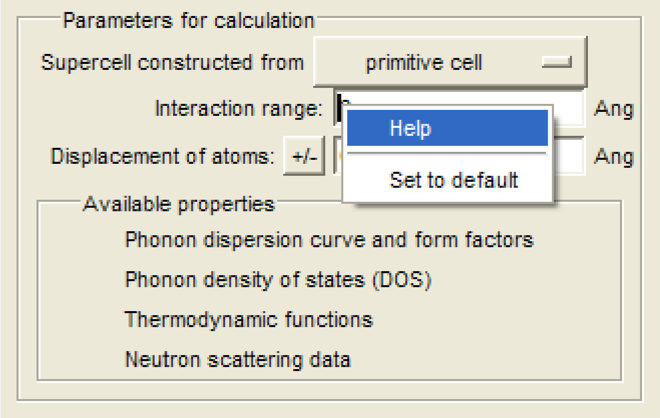


With a structure model window active, select **Run** to set up the computational parameters and run a new PHONON calculation, or to recalculate phonons from a previously finished PHONON job of this system. For a new PHONON calculation it is recommended to start with a geometry optimization, in particular if atomic degrees of freedom are allowed by the crystal symmetry. The residual forces in the initial model have a huge impact on the quality of the results.

Phonon Dispersion: Opens a list of all available phonon dispersion curves from previous PHONON calculations. Selected phonon dispersion curves are displayed, information on form factors (intensities) and exact points is reported and for each point the phonon mode can be animated.

Phonon Density of States: Opens a list of available phonon density of states from previous PHONON calculations. Selected phonon density of states and its partial contributions of atoms in each Cartesian direction are displayed.

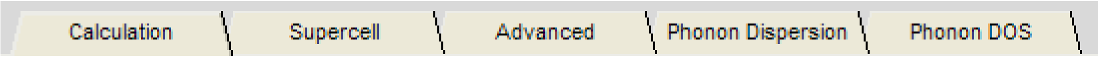
For each variable, context sensitive help and reset capabilities are provided by right-clicking in any input field or check box. A balloon help explains the options and offers a reset to the respective default value.



Context-sensitive help and reset: A click of the right mouse button with the cursor in any of the white entry fields or check-boxes will bring up a help text explaining the options for this particular parameter. This capability also allows resetting the parameter to its default value.

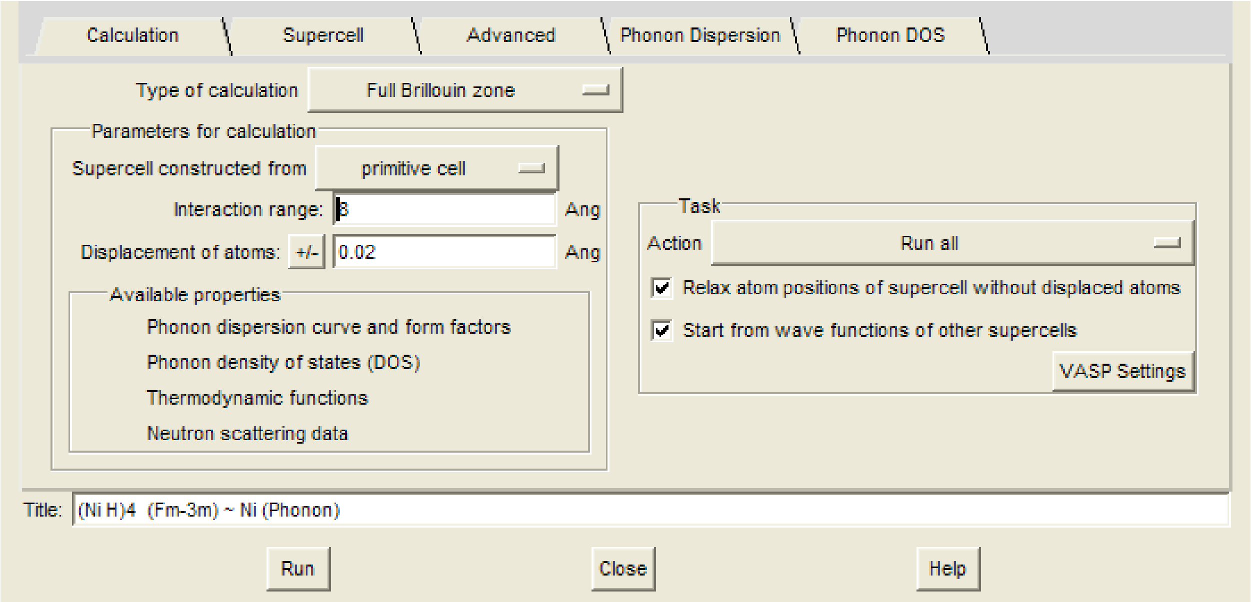
2. Description of the Run PHONON interface

The PHONON graphical user interface consists of a stack of panels which are described in detail below.



a. Type of calculation

The **Calculation** panel controls all major settings of the PHONON calculation and is split in two parts. The left hand section allows to specify the type of calculation and its main parameters, the right hand section controls how much of this task of the PHONON run, which action to execute, has to be done.



Type of calculation: Full Brillouin zone

Supercell constructed from: primitive cell

Interaction range: 8 Ang

Displacement of atoms: +/- 0.02 Ang

Phonon dispersion curve and form factors
Phonon density of states (DOS)
Thermodynamic functions
Neutron scattering data

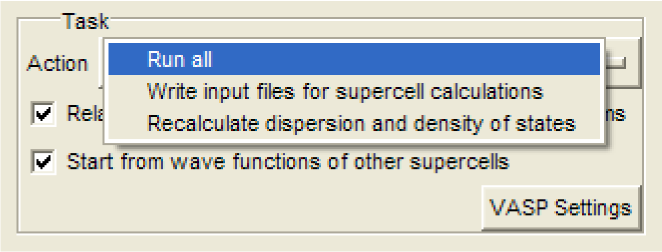
Action: Run all

☑ Relax atom positions of supercell without displaced atoms

☑ Start from wave functions of other supercells

Title: (Ni H)4 (Fm-3m) ~ Ni (Phonon)

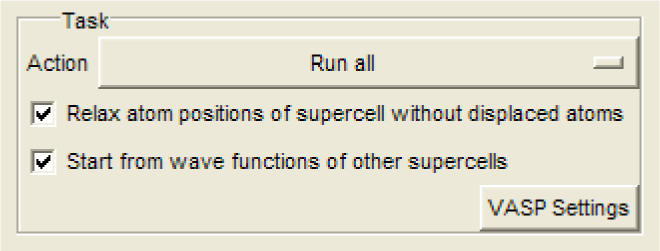
Selecting the **Action**



There are three choices for the required action, which is initiated with **Run**:

Complete PHONON calculation

Run all: all steps of a PHONON calculation are executed in a fully automated fashion: Symmetry analysis, creation of the supercell, optimization of all atom positions by VASP, creation of set of supercells with displaced atoms, single point energy calculations on all supercells with VASP, evaluating force constants and the dynamical matrix, calculation of dispersion curves, phonon density of states, Raman and Infrared activities and thermodynamic functions.



Action: Run all

☑ Relax atom positions of supercell without displaced atoms

☑ Start from wave functions of other supercells

In a computing environment with more than one machine as TaskServer, all of the VASP calculations on supercells can be carried out in a parallel fashion. The geometry optimization of the supercell without displacements is performed first and serves as reference for the displacements. Then, depending on the setup of the JobServer, all of the different supercells with displaced atoms are farmed out to be computed, using the results from the undisplaced cell for in an efficient way with VASP.

Relax atom positions of supercell without displaced atoms:-atom positions of the unperturbed supercell are optimized by VASP, a new minimized cell is created that may differ from the initial structure, and the supercells with displaced atoms are created from this minimized cell. This procedure is recommended whenever atoms of the structure have free parameters according to symmetry. This ensures that the forces are close to zero for the supercell without displaced atoms.

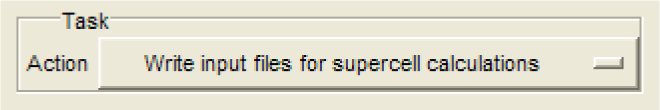
Start from wave functions of other supercells: speeds up VASP calculations with better initial values.

VASP Settings open the MEDEA-VASP interface for the supercell model, allowing customizing all computational parameters but the settings for cell shape and cell volume optimization, which are ignored as they conflict with the purpose of a PHONON calculation.

Run all requires a valid license of the VASP module.

Input files for PHONON calculation

Write input files for supercell calculations: creates all input files for supercell calculations in a job directory when confirmed with **Run**.



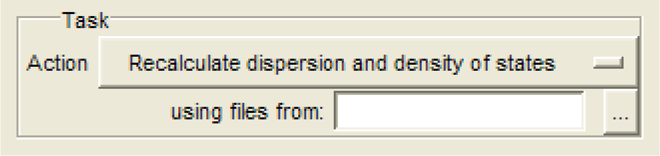
Task

Action Write input files for supercell calculations

This is useful to use with an external code different from VASP to calculate geometry optimization and forces. The PHONON calculation may be resumed later with the **Recalculate** option discussed below. This action might be useful for those interested in analyzing in more detail all of the input structures, or those interested in the symmetry analysis only.

Recalculate PHONON dispersion

Recalculate dispersion and density of state: from a previously finished PHONON calculation with modified computational parameters, without running VASP again.

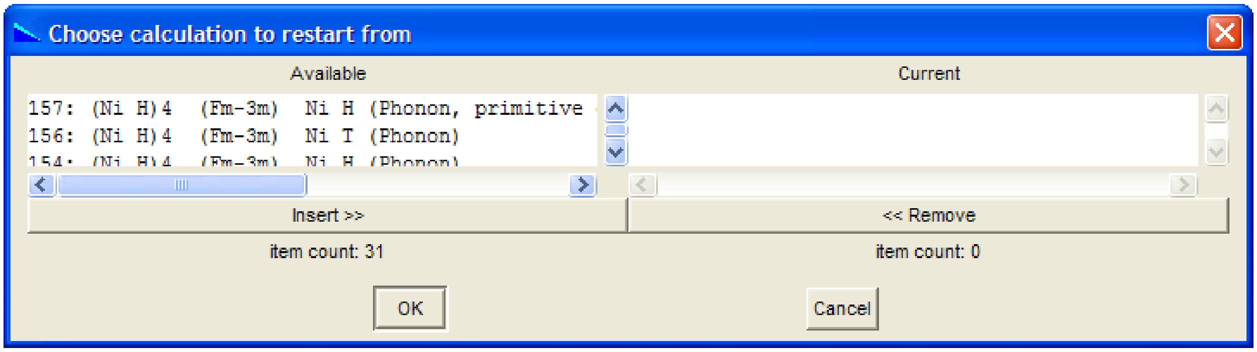


Task

Action Recalculate dispersion and density of states

using files from:

The options defining the supercells provided in the Calculation and Supercell panel cannot be changed without running the VASP calculations again and are inactive and grayed out. All options in **Advanced**, **Phonon Dispersion** and **Phonon DOS** can be modified. For a recalculation, the **Run Phonon** interface must be invoked for the minimized structure of the previous PHONON job (minimized.sci) or - if not available - the initial structure (initial.sci). The previously finished PHONON job can then be selected by clicking on **...** selecting the appropriate directory. The job number is then displayed in the entry field **using files from**. The status of all panels in PHONON is updated with the options as selected in the previous PHONON calculation. Modify the required options, and recalculate PHONON date on the JobServer with **Run**.



Choose calculation to restart from

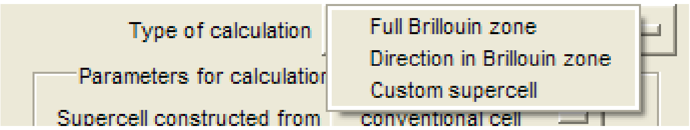
Available

```
157: (Ni H)4  (Fm-3m)  Ni H (Phonon, primitive
156: (Ni H)4  (Fm-3m)  Ni T (Phonon)
154: (Ni H)4  (Fm-3m)  Ni H (Phonon)
```

Current

item count: 31

item count: 0



b. Selecting the Type of Calculation

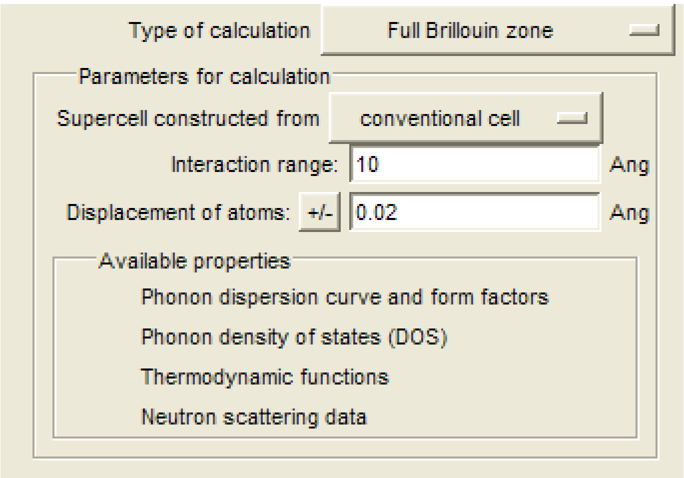
Type of calculation offers three choices as affecting the shape of the supercell and determines which parts of the Brillouin zone or which directions in k space are sampled with high accuracy.

Full Brillouin zone : explore the whole Brillouin zone with a supercell extending equally in all directions.

Direction in Brillouin zone: explore a selected direction in reciprocal space in detail with a supercell extending mainly into one direction and being as short as possible in the other directions. This offers higher accuracy of phonon frequency along this direction, at the expense of rather large errors in most of the other parts of the Brillouin zone.

Custom supercell: can be specified in the Supercell panel.

The size and symmetry of the selected supercell has a tremendous effect on computational demands. It is therefore recommended that you inspect these important issues in the **Supercell** panel. Selecting Supercell automatically creates the supercell and analyses its symmetry and provides the resulting information. The supercell can also be viewed from this panel.



Type of calculation: Full Brillouin zone

Parameters for calculation

Supercell constructed from: conventional cell

Interaction range: 10 Ang

Displacement of atoms: +/- 0.02 Ang

Available properties

- Phonon dispersion curve and form factors
- Phonon density of states (DOS)
- Thermodynamic functions
- Neutron scattering data

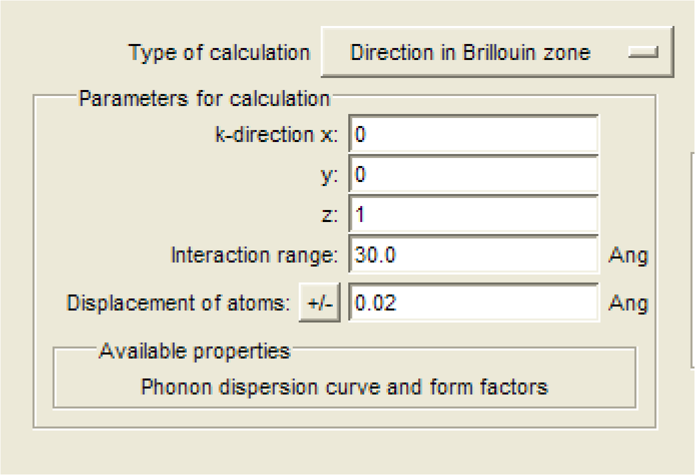
Full Brillouin zone: creates a supercell extending about equally in all directions of space.
The size of the supercell and the magnitude of displacements of atoms are defined in the two entry fields:

Interaction range - defines the approximate size of the supercell in Ångstrom.
A value of 10 Ång provides a supercell with about 10 Ång length of all three lattice parameters.

The size of the supercell cannot be changed continuously by definition. Consequently, a small change of the Interaction range parameter may cause an increase or decreases in the number of atoms in the cell, by up to a factor of eight.

Displacement of atoms defines the displacements of atoms from their equilibrium positions to evaluate resulting force constants. If chosen too small, the forces might be too small and within the computational noise. If chosen too large, one may leave the harmonic regime. The atoms may be displaced into one direction only (**+**) or may in addition be displaced into the opposite direction (**+/-**). The latter option may improve the accuracy in particular for structures of lower symmetry, but doubles computational demands.

Below these entry fields Available properties are shown: Since the whole Brillouin zone is sampled, dispersion curves throughout the whole Brillouin zone, phonon density of states and all derived properties such as thermodynamic functions and neutron scattering data can be obtained by this type of calculation.


Type of calculation: Direction in Brillouin zone

Parameters for calculation

k-direction x: 0

y: 0

z: 1

Interaction range: 30.0 Ang

Displacement of atoms: +/- 0.02 Ang

Available properties

Phonon dispersion curve and form factors

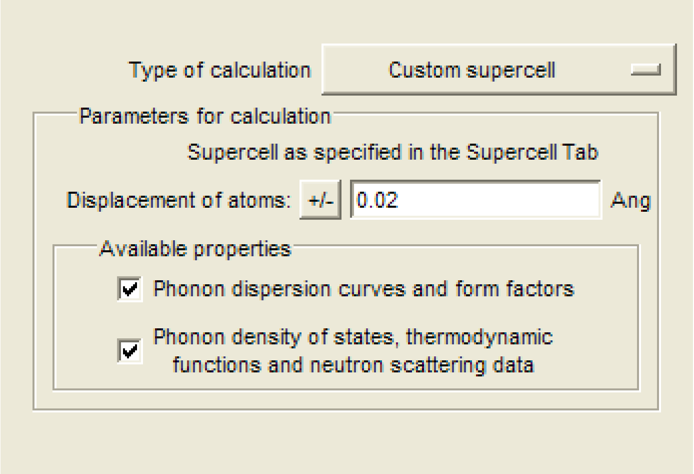
Direction InBrillouin zone: creates a supercell that extends only into one specified direction of space and is as small as possible in the other directions. The lattice vibrations in the selected direction can then be explored with high accuracy. The main parameters define the direction and extension of the supercell, the magnitude of displacements of atoms and the option to calculate displacements in both directions.

k-direction x, **y** and **z**: specify the direction in k-space that is to be explored in detail.

Interaction range - defines the approximate size of the supercell in the direction specified above (in Ångstrom). The extension in other directions is chosen automatically.

Displacement of atoms - defines the displacements of atoms from their equilibrium positions in Ång to evaluate resulting force constants. If chosen too small, the forces might be too small and within the computational noise. If chosen too large, one may leave the harmonic regime. The atoms may be displaced into one direction only (**+**) or may in addition be displaced into the opposite direction (**+/-**). The latter option may improve the accuracy in particular for structures of lower symmetry, but doubles computational demands.

Below these entry fields Available properties are shown. This calculation type provides accurate phonon frequencies in only one direction, for which highly accurate dispersion curves can be plotted. All other data based on the phonon density of states are not accessible here.


Type of calculation: Custom supercell

Parameters for calculation

Supercell as specified in the Supercell Tab

Displacement of atoms: +/- 0.02 Ang

Available properties

☑ Phonon dispersion curves and form factors

☑ Phonon density of states, thermodynamic functions and neutron scattering data

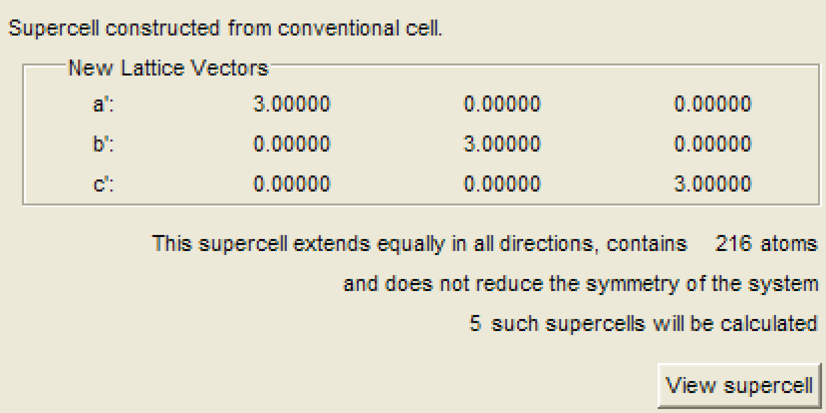
Custom supercell: offers full access to the shape of the supercell in the **Supercell** panel.

Displacement of atoms defines the displacements of atoms from their equilibrium positions in Ång to evaluate resulting force constants. If chosen too small, the forces might be too small and within the computational noise. If chosen too large, one may leave the harmonic regime. The atoms may be displaced into one direction only (**+**) or may in addition be displaced into the opposite direction (**+/-**). The latter option may improve the accuracy in particular for structures of lower symmetry, but doubles computational demands.

Available properties are shown below. Whether these properties can be calculated in a reasonable manner from the selected supercell has to be decided individually. Two properties can be checked: **Phonon dispersion curves and form factor** and **Phonon density of states, thermodynamic functions and neutron scattering data**

c. Size and Symmetry of the supercell

Opening the **Supercell** panel automatically invokes the internal creation and symmetry analysis of the supercell specified by all settings in **Type of calculation**. The generating lattice vectors (in terms of the original lattice vectors) are provided in the frame labeled **New Lattice Vectors**.



Supercell constructed from conventional cell.

New Lattice Vectors

a':	3.00000	0.00000	0.00000
b':	0.00000	3.00000	0.00000
c':	0.00000	0.00000	3.00000

This supercell extends equally in all directions, contains 216 atoms

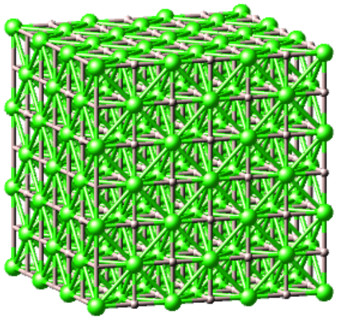
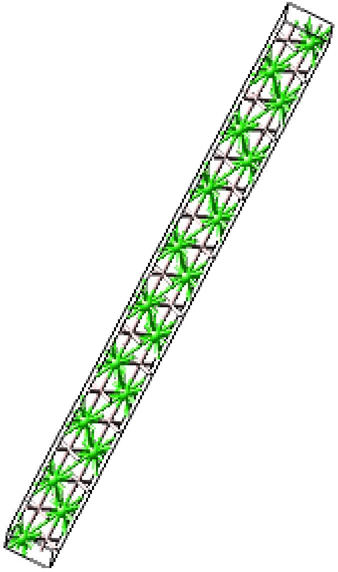
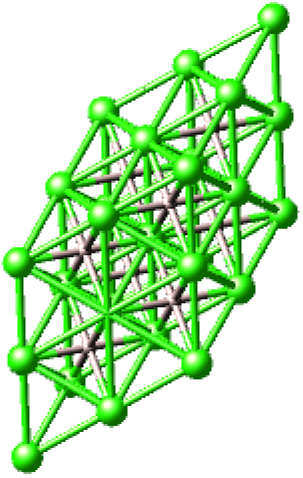
and does not reduce the symmetry of the system

5 such supercells will be calculated

Below this frame you find information on the type of supercell and its number of atoms, and whether the supercell breaks the symmetry of the original cell or not. (The symmetry is broken if some symmetry operations for the original cell are not any more symmetry operations of the supercell, considering lattice vectors as fixed.) Finally, the number of supercells with displaced atoms that need to be calculated is provided.

View supercell creates the supercell in a separate model window. In order to rotate, zoom, analyze the supercell model, it is necessary to close the Run PHONON window and make activate the supercell window. Attention: Before invoking again the Run PHONON graphical user interface, activate the window of the original structure model!

As an example, supercells of the intermetallic compound NiAl and the information provided by the supercell panel are shown below for a default full Brillouin zone calculation and a default calculation for the [001] direction.

	Full Brillouinzone	Direction in Brillouinzone	Custom Supercell
			
$\begin{pmatrix}a'\\b'\\c'\end{pmatrix} =$	$\begin{pmatrix}3&0&0\\0&3&0\\0&0&3\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$	$\begin{pmatrix}1/2&-1/2&0\\1/2&1/2&0\\0&0&9\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$	$\begin{pmatrix}0&1&1\\1&0&1\\1&1&0\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$
Atoms	216	36	16
Cells needed:	5	9	5

Unlike the other types of calculation, where the supercell panel provides only information, with a **Custom supercell** calculation the supercell is specified in the supercell panel.

New Lattice Vectors a', b' and c' provides nine entry fields for specifying the three components of each new lattice vector. This defines the supercell in terms of the lattice vectors of the original cell.

Verify invokes creation and symmetry analysis of the specified supercell. If the new lattice vectors do not specify a valid supercell an error message is issued and the lattice vectors need to be changed.

View creates the supercell in a separate model window. In order to rotate, zoom, analyze the supercell model, it is necessary to close the Run Phonon window and make the supercell the active window.

Before invoking a the **Run Phonon** interface gain, activate the window of the original structure model, otherwise you create a supercell of a supercell

Note: The three types of defining supercells within Phonon are also found in **Edit** ≫ **Build supercell** and the correspondence is the following:

Full Brillouin zone is equal to Automatic with **Supercell extends equally in all directions**

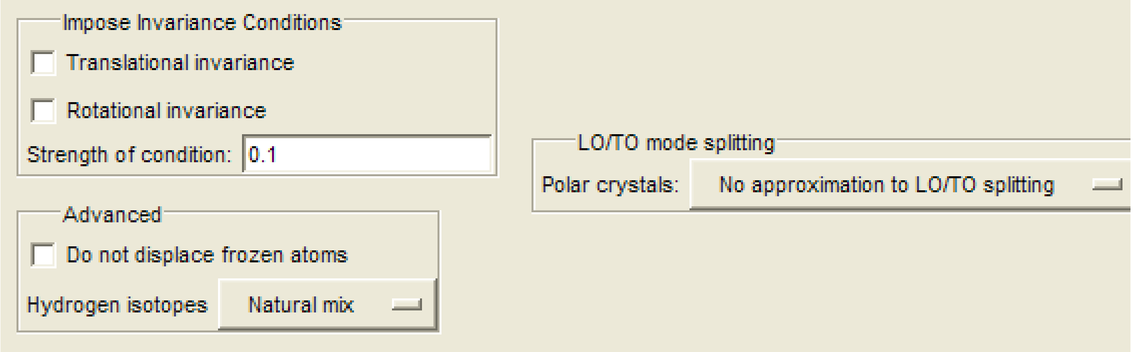
Direction in Brillouin zone is equal to **Automatic** with **Supercell extends in one direction only**.

Custom supercell can also be created with **Custom** in the **Supercell** builder

d. Advanced panel

The **Advanced** panel has two different parts: The left hand section allows one to specify or enforce invariance conditions for the force constants.

The right hand section provides access to an approximate treatment of LO/TO mode splitting.



Impose Invariance Conditions

☐ Translational invariance

☐ Rotational invariance

Strength of condition: 0.1

Advanced

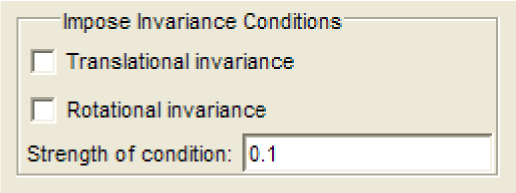
☐ Do not displace frozen atoms

Hydrogen isotopes: Natural mix

LO/TO mode splitting

Polar crystals: No approximation to LO/TO splitting

1) Selecting invariance conditions



Impose Invariance Conditions

☐ Translational invariance

☐ Rotational invariance

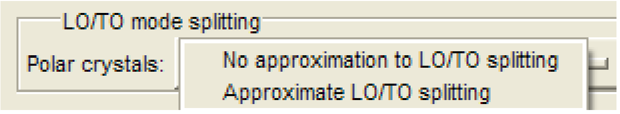
Strength of condition: 0.1

The forces should automatically satisfy translational and rotational invariance conditions. Consequently, the acoustic phonon modes should be zero at the Gamma point. Due to numerical inaccuracies this may not always be the case. As a remedy it is possible to enforce the invariance conditions by checking the boxes for **Translational invariance** and/or **Rotational invariance** and by selecting a non-zero value for the **Strength of condition** parameter. This enforces the invariance conditions affecting all force constant parameters. Choosing the strength parameter too large may result in errors of the force constants. Simple crystals may require higher values than systems containing many atoms.

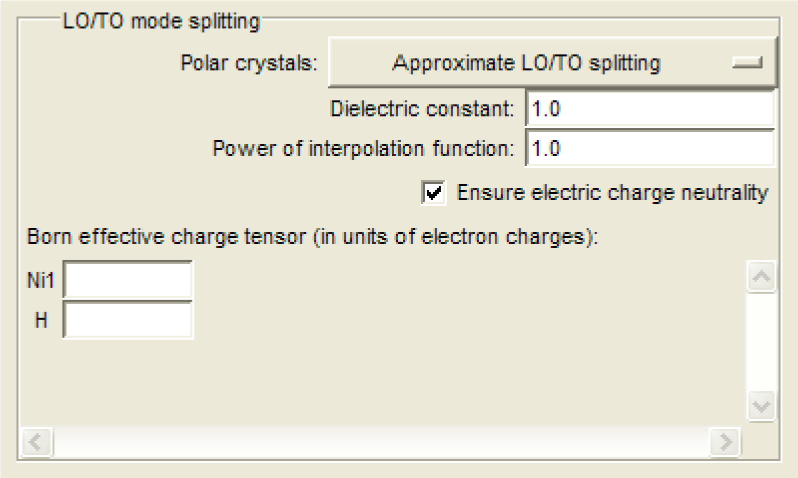
Alternatively, one may again check the invariance boxes but set the **Strength of condition** to zero. In this case, the invariance conditions are used to set the on-site force constants. That might be successful for crystals of lower complexity and higher symmetry. However, it may fail if the number of constraints and the number of on-site force constants are different. The above method affecting all force constants as specified by the strength parameter works in all cases.

2) Approximating LO/TO mode splitting

In polar crystals the macroscopic electric field leads to a non-analytical term of the dynamical matrix at the Gamma point. As a consequence, without any further approximation the LO/TO mode splitting at the Gamma point cannot be treated and only the TO mode is obtained. However, this non-analytic contribution may be taken into account in an approximate form making use of the Born effective charge tensor. More details are in section Theory of Lattice Dynamics Translational-Rotational Invariance



The approximation to **LO/TO mode splitting** is invoked by **Approximate LO/TO mode splitting** for the **Polar crystals** provides access to the following input parameters:



Polar crystals: Approximate LO/TO splitting
Dielectric constant: 1.0
Power of interpolation function: 1.0
☑ Ensure electric charge neutrality
Born effective charge tensor (in units of electron charges):
Ni1
H

Dielectric constant –allows to specify the electronic dielectric constant of the crystal

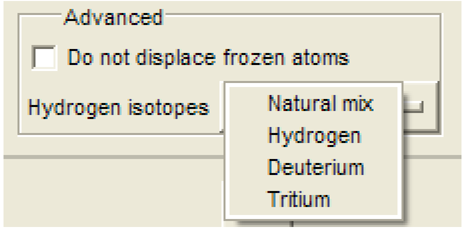
Power of interpolation function - This allows modeling the longitudinal phonon dispersion curve between the Gamma point and the Brillouin zone surface. If chosen larger than 1.0, the longitudinal dispersion curve will tend to be closer to the value at Gamma for most wave vectors, except at the vicinity of the zone surface. If chosen between 0.0 and 1.0, the dispersion curve will reach the longitudinal phonon mode only quite close to the Brillouin zone center.

Ensure electric charge neutrality - This actively ensures electric charge conservation law. Charge neutrality may also be ensured when setting the Born effective charge tensor.

Born effective charge tensor - This is a frame for input of the independent parameters of the Born effective charge tensor for each non-equivalent atom. The number of independent parameters depends on the site symmetry.

3) Hydrogen Isotopes and Restricted Optimization

The following two options apply only to special cases:

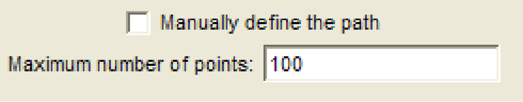


☐ Do not displace frozen atoms
Hydrogen isotopes: Natural mix

Do not displace frozen atoms allows to restrict the calculation to layers of a surface or consider atoms moving in a rigid lattice. Atoms are defined as frozen and excluded from structure optimization if they are defined in the **Edit Structure** menu this box is checked.

The differences in mass between the different **Hydrogen isotopes** is considered in the PHONON calculations, the options are **Natural mix**, **Hydrogen**, **Deuterium**, and **Tritium**

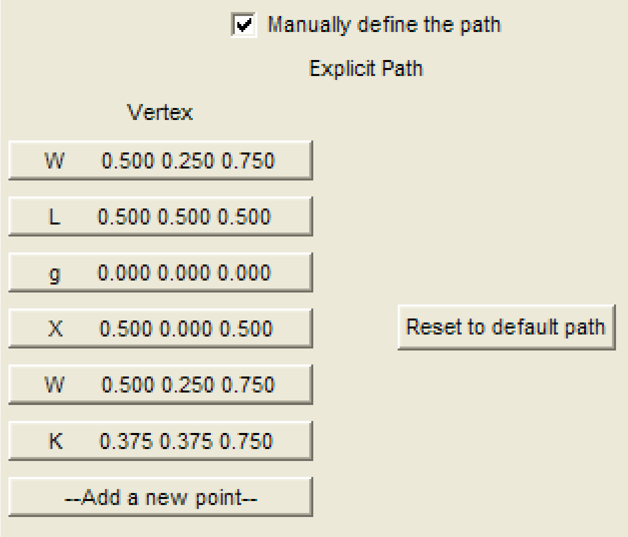
e. Phonon dispersion panel



☐ Manually define the path

Maximum number of points: 100

MEDEA has standard paths for plotting the phonon dispersion curves for all lattice types. The total number of points can be specified in the entry field **Maximum number of points**.



☑ Manually define the path

Explicit Path

Vertex

W 0.500 0.250 0.750

L 0.500 0.500 0.500

g 0.000 0.000 0.000

X 0.500 0.000 0.500

W 0.500 0.250 0.750

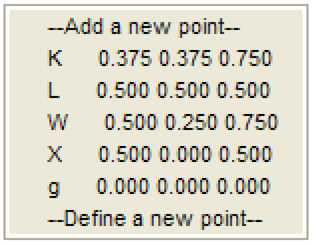
K 0.375 0.375 0.750

--Add a new point--

In addition, MEDEA offers the possibility to select certain segments in the Brillouin zone, which can be accessed by checking the box ☑ **Manually define the path**. The path is defined in k-space by a list of the vertices, and the **vertices** of the default path are displayed if the checkbox is selected. The labels are adapted to the symmetry of the active structure.

Points can be added and deleted by clicking on the menu buttons of the **vertices** or the menu item **Add a new point**. To get back to the default path use **Reset to default path .**

New points and labels can are defined by **Define a new point**.



K 0.375 0.375 0.750

L 0.500 0.500 0.500

W 0.500 0.250 0.750

X 0.500 0.000 0.500

g 0.000 0.000 0.000

In the automatic mode, the number of k-points is still defined by the parameter Maximum number of points. The number of points is not critical for CPU time demands as is the case for ab-initio techniques.

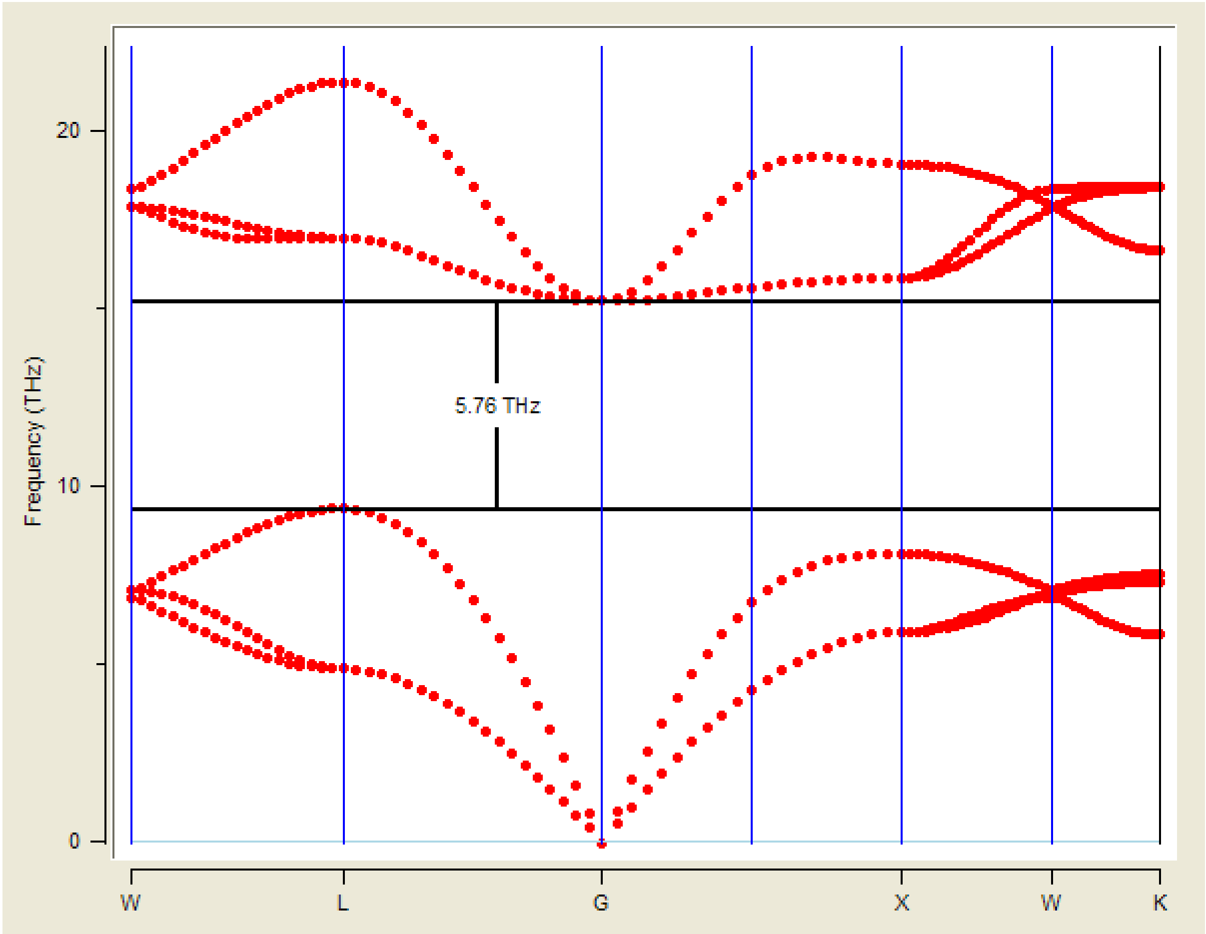
f. Phonon DOS panel

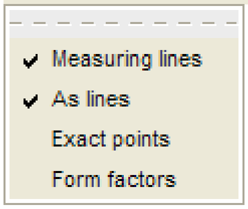
The phonon density of states (Phonon DOS) requires a fairly dense k-space sampling. The mesh density can be specified by **Quality of k-point sampling** and the predefined settings are **Coarse**, **Medium**, **Fine**, **Extrafine**.

In addition, **Custom** opens up an entry field for the **Number of sampling k-points**. The phonon DOS is evaluated with the histogram technique and the width of the frequency mesh is chosen by **Frequency interval** in THz.

3. Phonon Dispersion / Phonon Band Structure

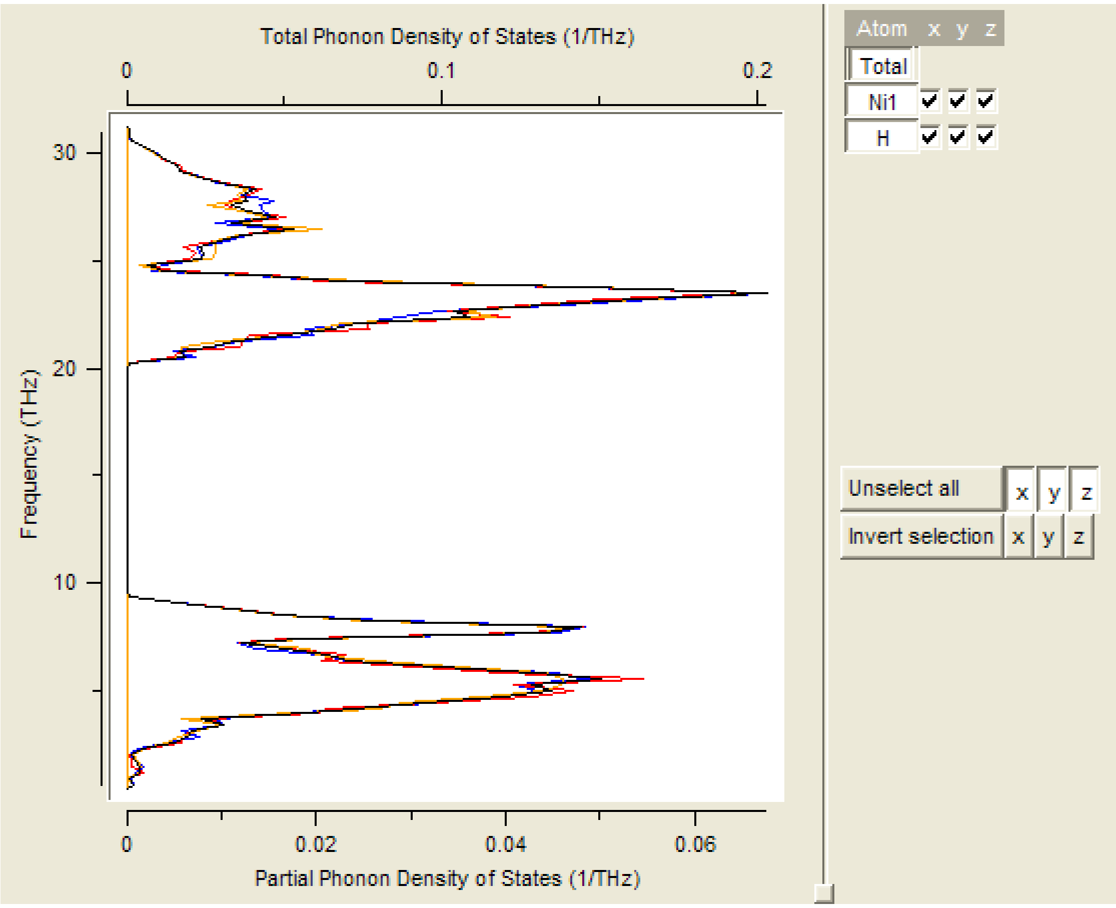
An additional **Phonon dispersion** item appears in the MEDEA Tool bar, when the active window displays Phonon dispersion results: It provides access to display style (lines or points), to measuring facilities, to the display of exact (blue), high precision (green) and low precision (yellow vertical lines) k points along the path, and to coloring dispersion curves according to form factors.





Moving the cursor over points of the dispersion curve provides information on coordinates of the k-point and frequency (THz and 1/cm). The selected phonon mode appears highlighted in green. Right click anywhere in the Phonon Dispersion window provides usual **Unzoom** and **Save as postscript** facilities. If a phonon mode is highlighted an additional item Animate appears in the context menu, which provides access to animation of the selected phonon mode. The supercell underlying the calculation is created in a structure window, and in the MEDEA Toolbar the buttons for starting and stopping an animation appear.

a. Phonon Density of States (DOS)



The plot of the phonon density of states (DOS) provides the total DOS, and the partial DOS for each atom of the original cell, and each Cartesian direction.

b. Infrared and Raman active modes

Symmetry analysis of all modes at the Gamma point provides access to Infrared and Raman activity of these modes. The information is provided in the `Job.out` file.

```
 Symmetry analysis of Gamma point phonon frequencies:
   Crystal  Point  Group: O_h    (m3m)
   Supercell Point Group: D_3d  (-3m)
    Table of irreducible representations of point group:
 ____________________
    IR     1  9  5 13 17 21 25 33 29 37 41 45
 ____________________
 A1g(R)    1  1  1  1  1  1  1  1  1  1  1  1   x^2+y^2, z^2
 A2g       1  1  1 -1 -1 -1  1  1  1 -1 -1 -1
 Eg(R)     2 -1 -1  0  0  0  2 -1 -1  0  0  0   (x^2-y^2,xy), (xz,yz)
 A1u       1  1  1  1  1  1 -1 -1 -1 -1 -1 -1
 A2u(I)    1  1  1 -1 -1 -1 -1 -1 -1  1  1  1   z
 Eu(I)     2 -1 -1  0  0  0 -2  1  1  0  0  0   (x,y)
 ____________________
 Warning: Comments, like x,y,z,xz, etc. might be not oriented towards crystallographic axes[8]
```

---

[8] Because VASP uses the primitive unit cell in many cases

c. Thermodynamic functions

The thermodynamic functions as a function of temperature are listed in the Job.out file. Internal energy, entropy, free energy, heat capacity and zero point energy are available.

```
   T        Cv      E(T)-E(0)     S(T)   -(A(T)-E(0))    E(T)       A(T)
   K     J/K/mol     kJ/mol     J/K/mol     kJ/mol      kJ/mol     kJ/mol
  ---  ---------  ---------  ---------  ---------  ---------  ---------

    0     0.0000     0.0000     0.0000     0.0000    12.9143    12.9143
…
    5     0.0021     0.0000     0.0004     0.0000    12.9143    12.9143
…
  200    23.5541     2.3790    19.6519     1.5513    15.2933    11.3630
  225    25.6192     2.9939    22.5462     2.0790    15.9082    10.8353
  250    27.5915     3.6592    25.3485     2.6779    16.5735    10.2364
  273    29.3062     4.3137    27.8519     3.2898    17.2280     9.6245
  275    29.4503     4.3725    28.0664     3.3457    17.2868     9.5686
  298    31.0452     5.0684    30.4959     4.0193    17.9827     8.8950
  300    31.1784     5.1306    30.7040     4.0805    18.0449     8.8338
…
 3000    49.5523   132.5443   133.2876   267.3160   145.4586  -254.4017
```

Change from version 2.x

Default displacement of atoms is changed from ±0.01 Ång to ±0.02 Ång.

Changes from version 1.8.x

Displacement of atoms default changed from + 0.03 Ång to ± 0.01 Ång. Setting up displacement calculations in both directions proofed to yield more precise forces for a number of systems. Note that the computational time doubles as the number of displacement calculations is doubled.

Supercell constructed from
centered lattices: **conventional cell** or **primitive cell**
rhombohedral lattices: **rhombohedral cell** or **hexagonal cell**
hexagonal lattices: **Supercell has**: **hexagonal shape** or **rhombohedral shape**

Do not displace frozen atoms is by default off, to provide for thermodynamic functions. PHONON exploits the selected dynamics features of VASP, allowing suppressing specific atomic vibrations from the phonon spectrum

Hydrogen isotopes (only for systems containing H) adjusts the mass of Hydrogen. Options are **Natural mix** (=default), **Hydrogen**, **Deuterium**, and **Tritium**. This option does not affect the actual VASP displacement calculations; it merely adjusts atomic masses used to calculate the vibrational frequency spectrum

H. COMBI

COMBI is a structure spreadsheet with combinatorial builder, which allows you to launch calculations for an in principle unlimited number of structures and retrieve results in an automated fashion! COMBI may proof useful when investigating trends through a range of systems where a set of computational parameters needs to be applied to a large number of structures.

In addition COMBI's combinatorial builder lets you build hundreds of systems starting from a structure template. COMBI's link to the MD database ensures that structural results are stored and can be retrieved through INFOMATICA.

1. How COMBI works

The starting point is a single structure or a number of structures from INFOMATICA. These systems are used to generate derived structures by systematically substituting elements. Next a computational target is defined, e.g. structure optimization or a single point calculation to yield the heat of formation. Upon launch of a COMBI job, MEDEA's JobServer processes all COMBI tasks and during execution results are retrieved automatically and added to a spreadsheet in MEDEA. Sorting and copying the structural and energetic properties in the spreadsheet then allows for quickly finding unstable structures and looking for trends.

2. Preparations

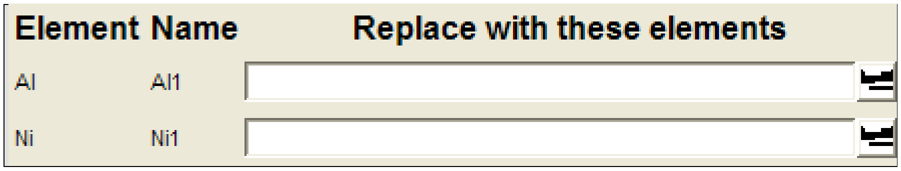
Tools ≫ **Combi** creates a new menu item **Combi** in the toolbar.

New creates an empty spreadsheet, existing spreadsheets can be loaded with **Open from DB** and **Open from file**.

a. Creating structures

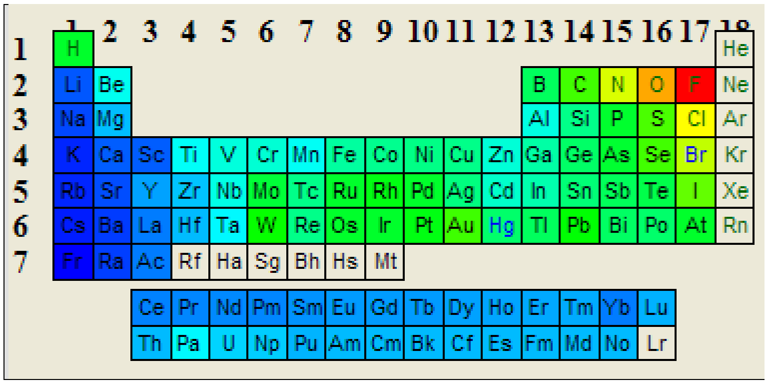
To initiate a COMBI run, copy and paste a structure from INFOMATICA. You can also build your own system and save it to the MD database. Once a structure is saved in the database, you can copy and paste it to COMBI.

In COMBI, select one of the structures and use **Create Combinatorially ...** to substitute elements. A dialogue window will let you define substitutions for each element.



Element Name		Replace with these elements
Al	Al1	
Ni	Ni1	

The button ☰ opens a periodic table to let you pick an element:



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Ha	Sg	Bh	Hs	Mt									
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

The substitution takes place for all equivalent atomic sites, so for example substitution of Si atom in a zeolite replaces just a fraction of Si atoms.

Confirm the substitution process with **OK** and let MEDEA find duplicates, likely to occur when you substitute two or more elements at the same time.

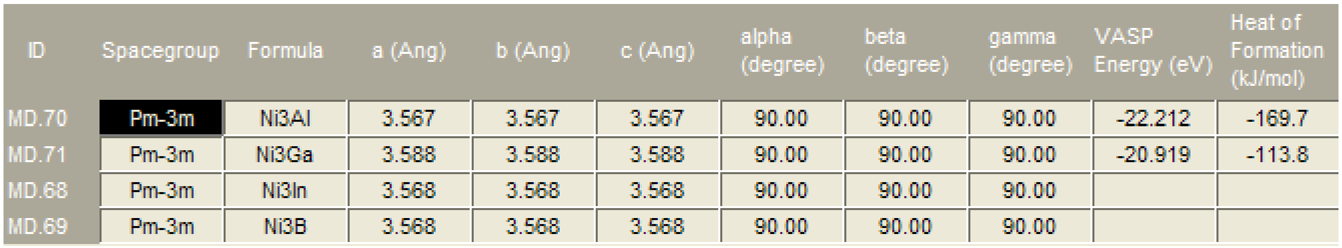
3. Calculation

VASP Options opens the familiar VASP user interface to define the type of **Calculation**: **Single Point** or **Structure Optimization**. The **Potentials** tab shows all elements used in the spreadsheet and the cutoff energy is consistent for the whole spreadsheet, i.e. the cutoff is chosen as a maximum of all individual cutoffs.

Review the Options and use **Run…** to submit all Jobs to the JobServer.

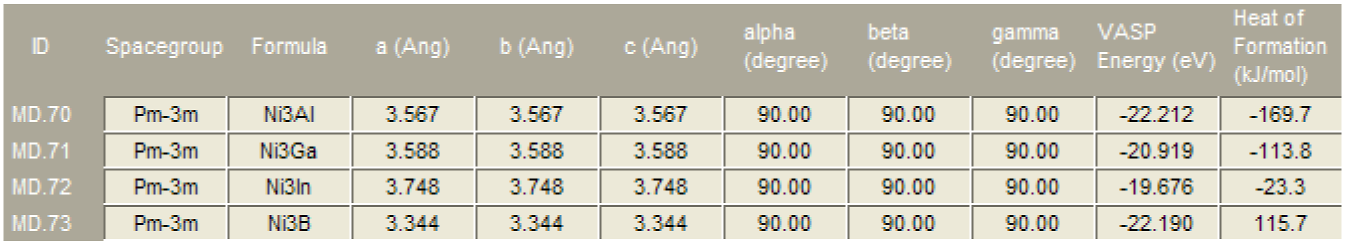
a. Progress

As soon as one of the submitted calculations is finished, the results are shown in the spreadsheet. The lattice constants are updated for structure optimization, the VASP energy and heat of Formation are shown.



ID	Spacegroup	Formula	a (Ang)	b (Ang)	c (Ang)	alpha (degree)	beta (degree)	gamma (degree)	VASP Energy (eV)	Heat of Formation (kJ/mol)
MD.70	Pm-3m	Ni3Al	3.567	3.567	3.567	90.00	90.00	90.00	-22.212	-169.7
MD.71	Pm-3m	Ni3Ga	3.588	3.588	3.588	90.00	90.00	90.00	-20.919	-113.8
MD.68	Pm-3m	Ni3In	3.568	3.568	3.568	90.00	90.00	90.00		
MD.69	Pm-3m	Ni3B	3.568	3.568	3.568	90.00	90.00	90.00		

Right-click on a colum label to open the dialogue to sort data. Sort **Ascending**, **Sort Descending**) or change the display of data (**Format…** and **Units…**). The entire spreadsheet or parts of it can be cut and pasted to an external spreadsheet like Excel or any text editor.



ID	Spacegroup	Formula	a (Ang)	b (Ang)	c (Ang)	alpha (degree)	beta (degree)	gamma (degree)	VASP Energy (eV)	Heat of Formation (kJ/mol)
MD.70	Pm-3m	Ni3Al	3.567	3.567	3.567	90.00	90.00	90.00	-22.212	-169.7
MD.71	Pm-3m	Ni3Ga	3.588	3.588	3.588	90.00	90.00	90.00	-20.919	-113.8
MD.72	Pm-3m	Ni3In	3.748	3.748	3.748	90.00	90.00	90.00	-19.676	-23.3
MD.73	Pm-3m	Ni3B	3.344	3.344	3.344	90.00	90.00	90.00	-22.190	115.7

The changing ID numbers (like 87 to 72 to Ni3In) indicate that there was already a calculated Ni_3In structure in the database, but as lattice parameters are different due to structure optimization, there is now a second entry.

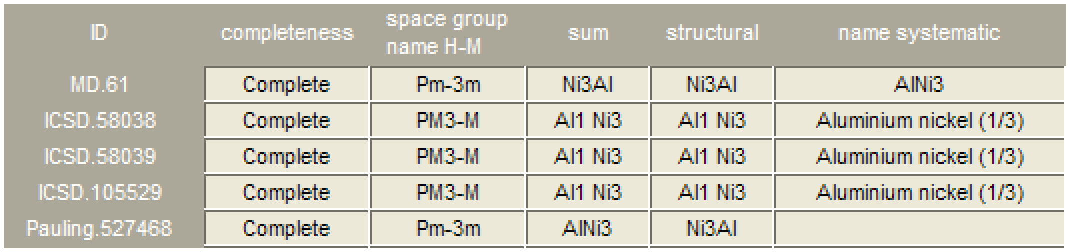
In the above example the calculated structures with a negative heat of formation are very close to the experimental structures, the stable Ni_3B structure has a different unit cell with more than 4 atoms and does not match the unstable cell constructed from Ni_3Al .

4. Saving Results

It can be inconvenient to keep MEDEA running till the last result comes in. COMBI spreadsheets can be stored in the database to avoid any loss of results. Use **Save as ...** to name and **Save** to store the entire spreadsheet in MEDEA's database. **Export** creates a file, suitable for transfer to a different MEDEA installation.

a. Refining:

Structures calculated by COMBI are part of the MD database and show up in INFOMATICA. Their ID is MD and they can be used as a starting point for another spreadsheet, such as a structure optimization after a quick stability assessment.



ID	completeness	space group name H-M	sum	structural	name systematic
MD.61	Complete	Pm-3m	Ni3Al	Ni3Al	AlNi3
ICSD.58038	Complete	PM3-M	Al1 Ni3	Al1 Ni3	Aluminium nickel (1/3)
ICSD.58039	Complete	PM3-M	Al1 Ni3	Al1 Ni3	Aluminium nickel (1/3)
ICSD.105529	Complete	PM3-M	Al1 Ni3	Al1 Ni3	Aluminium nickel (1/3)
Pauling.527468	Complete	Pm-3m	AlNi3	Ni3Al	

I. PREDIBOND

PREDIBOND extends the capabilities of COMBI for screening of catalytic activity. The underlying algorithm [13; 14; 15] was developed and patented by Hervé Toulhoat and relies on comparing crystallographic information with first principles computations to derive bond-specific parameters. More details are in Application Note V.L PREDIBOND™ in Heterogeneous Catalysis: Predicting Activity Patterns.

Please contact support@materialsdesign.com for more information.

J. GIBBS

1. Introduction and Capabilities

The GIBBS code is aimed at computing the equilibrium properties of fluids by molecular simulation, using a force-field based Monte Carlo method. For scientific background on the method, please refer to the section “Statistical Monte Carlo” (currently in development). For practical use there are also a number of application examples available within the MEDEA user’s guide.

a. Properties

The main features of GIBBS are summarized in the following table, where for each computational goal we specify the statistical ensemble (NVT, NPT or μVT) and the properties which can be computed.

Goal	Statistical ensemble	Properties
Properties of single phase	NVT	**Energy, pressure, density, chemical potential, saturated vapor pressure, residual heat capacity, isothermal compressivity, Joule-Thomson coefficient**
	NPT	**Energy, volume, density, chemical potential, isobaric thermal expansivity, residual heat capacity, isothermal compressivity, Joule-Thomson coefficient**

	µVT	
The chemical potential of species in a phase	NPT	**Chemical potentials**
Liquid-Liquid or Liquid-Vapor equilibria (pure component or mixture)	NVT	**Energy, volume, composition of each phase, liquid-vapor coexistence curve, liquid density, vaporization enthalpy, chemical potential**
	NPT	**Energy, volume, composition of each phase, chemical potential, vaporization enthalpy, heat capacity, compressivity, critical point, critical density, critical mole fraction, radial distribution function**
Adsorption in a solid (pure component or mixture)	µVT	**Adsorption isotherms, isosteric heat of adsorption, entropy of adsorption, distribution of species in a solid, average number of molecules, location of molecules inside the microporosity**
	NPT	**Henry constants**
Fluid solubility in polymeric materials	Osmotic ensemble (μ_1,…, μ_{n-1}, N_n, σ, T)	**Solubility of a gas in polymeric materials (gas/heavy alkane)**

b. Type of molecules

Properties of pure fluids as well as multi-component mixtures can be computed with GIBBS. The possible types of molecules are as follows:

- Rigid molecules
- Fully flexible molecules, either linear, branched, cyclic or bicyclic molecules (n-alkanes, iso-alkanes, cyclo-alkane, alkylated derivatives)
- Semi-flexible molecules, with a rigid part and a flexible part (olefins, alkylated derivatives of benzene and naphthalene)

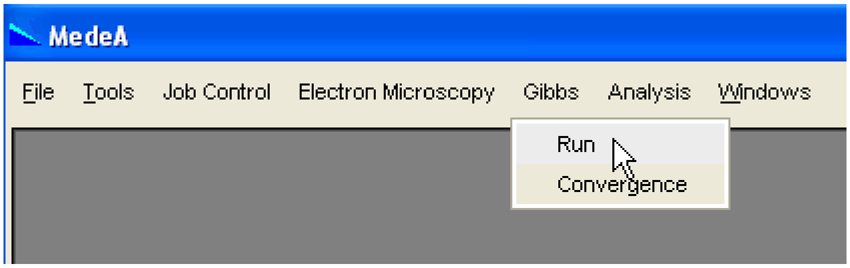
c. Potentials

MEDEA-GIBBS comes with a set of force fields or potential files. These are stored in the file potparam.dat; in particular potparam.dat contains the parameters of the Lennard-Jones centers of force, the interatomic distances, the bending potentials, the torsion potentials, the distances for the centers of force. Once a force field is included in `potparam.dat`, you can assign it to an atomic species through the MedeA graphical interface.

	Molecules	Type of molecules	Molecular model	Centers of force	
Alkane	n-alkanes C_1-C_n	Flexible	AUA (n/iso-alkane)	CH_3-aliph-AUA	[16]
		Flexible		CH_2-aliph-AUA	[17]
	Iso-alkanes mono/di/tri-branched	Flexible	UA (n-alkane)	CH-aliph-AUA	[18]
		Flexible	UA (n-alkane)	CH_4-Moller	[19]
	Cyclo-alkanes (cyc)	Flexible	AUA	CH_3-aliph-UA CH_2-aliph-UA CH_2-cyc-AUA	[20]
Olefin		Semi-flexible	AUA	CH_2-olef-AUA CH-olef-AUA C-olef-AUA	[20]
Aromatic	Xylene	Rigid	AUA	CH-arom-AUA C-arom-AUA	[21]
	o-,m-,p-xylene	Rigid	OPLS	C-arom-OPLS H-arom-OPLS CH_3-arom-OPLS	[22]
Gas	CO_2	Rigid	UA	C-CO2 O-CO2	[23]
	H_2	Rigid	UA	H-in-H_2	[23]
	H_2O	Rigid	UA	H_2O-TIP4P	[23]
	N_2	Rigid	UA	(3.798/71.4)	[24]
Sulfides and thiols	H_2S	Rigid	UA	H_2S-KL	[25]
	S-H	Semi-flexible	AUA	S-SH H-SH	[25]
Aldehyde and ketone	C-O H-C-O	Rigid	UA	C O H	[26]
Graphite	C	Rigid	UA	C-graphite	
Cations in a solid (Faujasite type zeolite)	Na	Rigid	UA	Na-zeolite	[27]
	Na-faujasite K-faujasite Cs-faujasite	Rigid	Jørgensen/Auerbach		[28]

2. Starting Gibbs

To start Gibbs, select **Gibbs** from the MedeA Tools menu. A new entry **Gibbs** appears in the MedeA main menu. Select **Gibbs** ≫ **Run** to bring up the Gibbs interface.



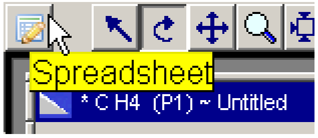
3. Working with Gibbs – the graphical interface

The Gibbs interface differs from other MedeA interfaces to computational codes in as much as you bring up the interface before assigning the structural model you want to run Gibbs for.

In addition, before choosing a structure for Gibbs to run with, the structural model must have been assigned at least one force filed atom type (**FF atom type**).

a. Before invoking Gibbs - Assigning a force field to a structure

- To assign a **FF atom type** to an active structure window, select MedeA's spreadsheet structure editor by clicking the icon in the MedeA icon bar



- Right-click anywhere into the header row and select **New** >> **FF atom type**
- In the row corresponding to the atom you want to add a force field for, click into the column FF atom type and then right-click and select a force field. You need to make sure yourself that the force field selected is indeed appropriate for your structure and the properties you want to calculate!
- Click the icon to close the spreadsheet view for this structure

Now you have assigned a force field to the structure it is ready for use with Gibbs.

The MedeA Gibbs interface is divided in five input/preview panels:

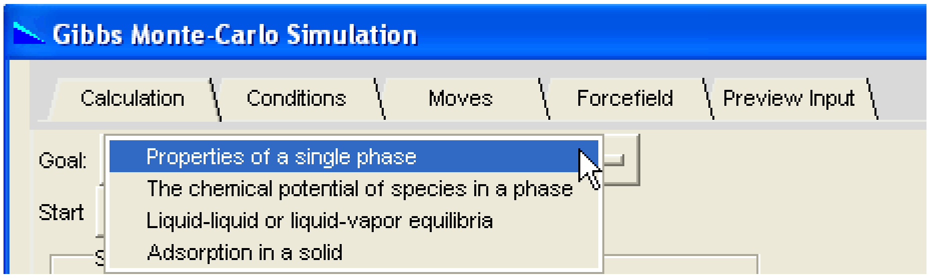
Calculation – where you define what you want to calculate and what your input structures are
Conditions – where you define thermodynamic conditions
Moves – where you define what Monte-Carlo moves are allowed during the simulation
Force field – where you define details for the force fields used in the simulation
Preview input – where you can inspect the input files generated by the interface

b. Calculation

1) Goal

To begin with, you need to define your computational goal and how you would like to start the calculation. For example you could decide to run an adsorption isotherm for a gas in a solid where you want to start from a calculation you ran earlier. Or you would like to calculate the properties of a single phase starting from a structure you built in MEDEA.

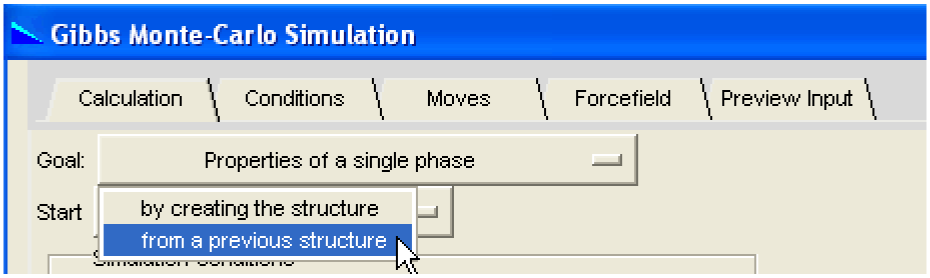
The following options are available:



- **Properties of a single phase** – You want to work with a single phase, liquid or gas. According to Gibbs phase rule you can set the temperature and the pressure/volume and calculate the corresponding volume/pressure and fluctuation properties
- **The chemical potential of species in a phase** – Compute the chemical potential of one or more species in a phase
- **Liquid-Liquid or liquid vapor equilibria** – Compute the equilibrium properties of two phases, e.g. the vapor pressure of a gas-liquid system
- **Adsorption in a solid** – Compute the adsorption of a liquid or gas phase in a solid phase. The solid will be modeled as fixed grid of points interacting with the fluid

2) Start

In this section, you define how you want to start the calculation. Your options are



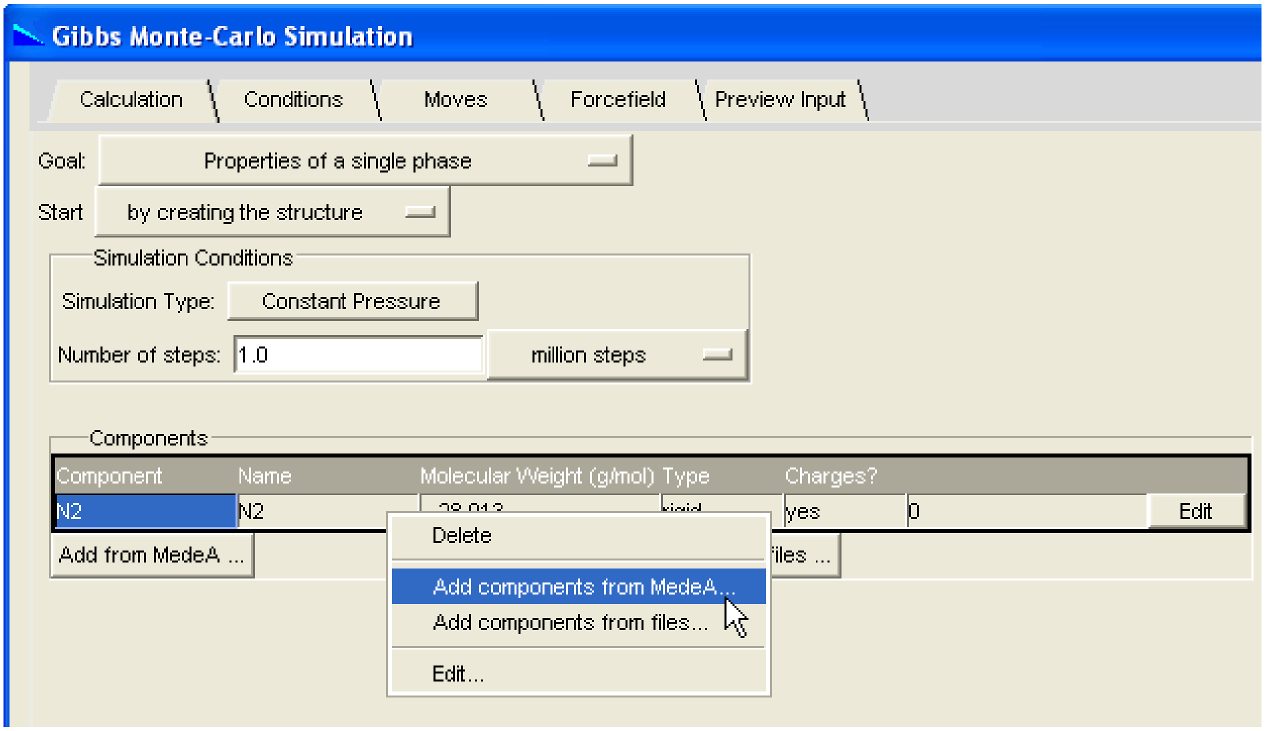
- **By creating the structure** – You will need to load a system from MEDEA or from a file on disk
- **From a previous structure** – You will need to define a job directory containing a system you want to use as input

3) Simulation condition

Here you decide which of the conjugated variables pressure and volume you would like to hold constant during the calculation.

4) Components

Next you need to load one or more components; how many you need depends on the type of calculation you are running! To load components you have built or edited in MedeA click **Add from MedeA**. To load a structure from disk, select **Add from files**. You can also right click into the components table header and select one of the **Add from** options.



Goal: Properties of a single phase

Start: by creating the structure

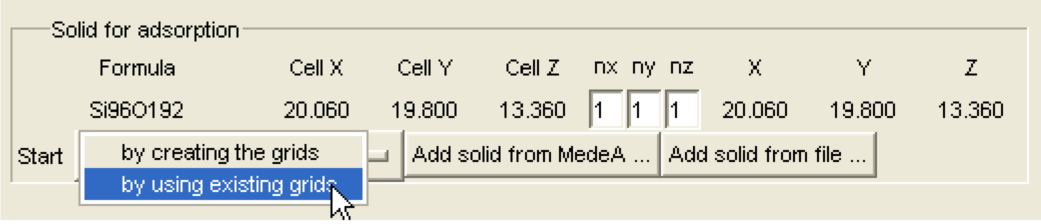
Simulation Type: Constant Pressure

Number of steps: 1.0 million steps

Component	Name	Molecular Weight (g/mol)	Type	Charges?		
N2	N2	28.013	rigid	yes	0	Edit

If your goal is to calculate the adsorption of a fluid phase in a solid, you need to load a solid for adsorption in addition to the component (=fluid to adsorb). MedeA-Gibbs automatically provides the corresponding file selection and input mask if you choose this type of calculation. The solid is imported "as is", i.e. using the number of atoms defined in the chemical unit cell of the structure you are importing. You can then pick **nx**, **ny**, **nz** to define a larger cell for Gibbs to work with.

Gibbs will treat the solid as a fixed potential grid interacting with the fluid components defined above.



Formula	Cell X	Cell Y	Cell Z	nx	ny	nz	X	Y	Z
Si96O192	20.060	19.800	13.360	1	1	1	20.060	19.800	13.360

If you have already calculated an interaction grid for the solid in question you can tell MedeA so by selecting Start **by using existing grid** and providing a job number to load the grid from. Otherwise leave the default **by creating the grids**.

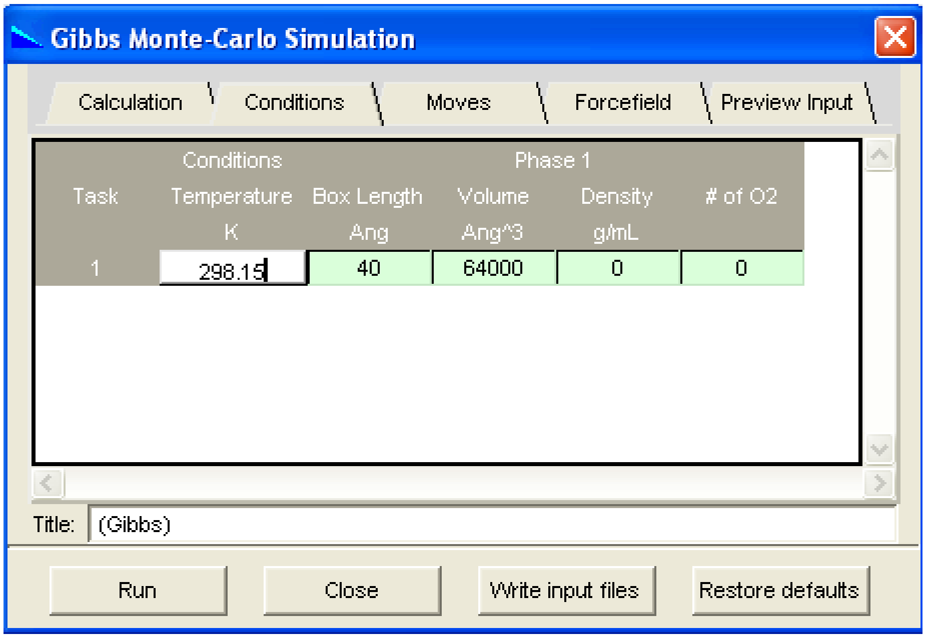
5) Properties

Finally you can select the properties to be calculated, currently options are

Calculate the pressure
Calculated fluctuation properties

c. Conditions

In the **conditions** panel you can set the thermodynamic conditions for GIBBS to run with. The table on this panel behaves like a spreadsheet, you can copy and paste data from external applications like excel and you can create new rows and columns to match your computational goals.



	Conditions		Phase 1		
Task	Temperature K	Box Length Ang	Volume Ang^3	Density g/mL	# of O2
1	298.15	40	64000	0	0

Title: (Gibbs)

How to work with the conditions panel

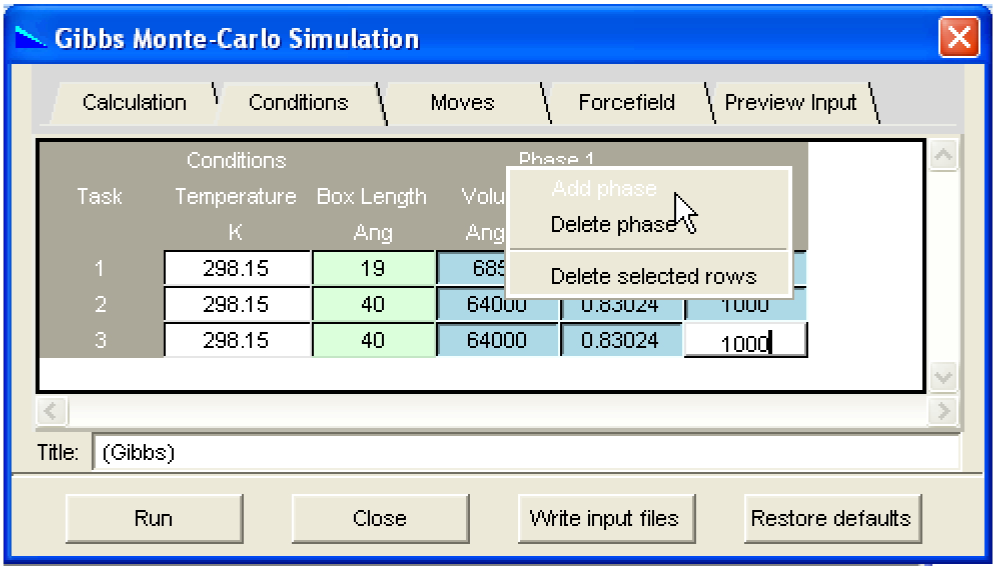
- Each row of the table corresponds to one GIBBS task
- Set the starting conditions for each run by typing data into a row
- Add rows by clicking **Return** in the last row or by pressing the down-arrow key

Setting the parameters for a GIBBS run

- *Task* – displays a counter for the computational tasks
- *Temperature* – displays the temperature for this specific row/task
- *Box length* – gives the box dimensions used for the simulation
- Volume – gives the volume of the box
- *Density* – gives the starting density of the fluid in the box
- *# of <particles>* - gives the number of particles to be used in the simulation

Some of these parameters are interdependent. For example, defining the number of particles sets the initial density based on the box dimensions. With the number of particles set, changing the density in turn changes the size of the box and vice versa.

By default MEDEA displays data for a single phase. To work with more than one phase, right-click into the header area and select Add **phase**.



	Conditions		Phase 1		
Task	Temperature K	Box Length Ang	Volu Ang		
1	298.15	19	685		
2	298.15	40	64000	0.83024	1000
3	298.15	40	64000	0.83024	1000

Title: (Gibbs)

A few more tips on working with the above table:

Use **Ctrl**-**C** and **Ctrl**-**V** to copy and paste between e.g. Excel and the conditions spreadsheet
To add a row, press return in the lowest row or press the Down-Arrow on your keyboard
Right-clicking in the header also provides a pop-up menu with choices displaying a range of options, amongst them:

- **Add phase** – Lets you add a block of input fields for an additional phase
- **Delete phase** – Removes a block of input data for a phase
- **Delete selected rows** - Removes rows from the table and thereby reduces the number of computational tasks

d. The Moves panel

In the **Moves** panels you can set relative probabilities for the various Monte-Carlo moves to be performed by GIBBS.

Types of Monte-Carlo moves

- Rigid molecules
- Molecules with internal degrees of freedom (conformations)
- Moves for configuration-biased Monte-Carlo
- Other moves

e. The Force field panel

The force field panel lets you control setting for the force field defined for your molecules/solids earlier.

☑ AUA model – whether to use the anisotropic united atom model

Mixing rule – Lorentz-Bertholet, Kong, Waldmann-Hagler, and Geometric

☑ Cosine angle term

☑ Power series for torsion

Cutoff: – default 0. (Minimum image convention)

Minimum distance –default 1.

f. The Preview Input panel

Here you can preview the input ASCI files the GIBBS batch program will read. The key files are

- *`Control.dat`* –All calculation specific settings are stored here
- *`<molecule_name>.dat`* – System specific structural and force field data is written
- *`Potparam.dat`* – Contains all force-fields available with GIBBS
- *`Script`* – The tcl script used to launch the GIBBS job

4. Working with GIBBS – The output files

Output from a GIBBS run can be retrieved through MEDEA's jobserver. In MEDEA select **Job Control** and then **View and Control jobs** to open a web browser pointing to the Jobs page. Navigate to the job directory corresponding to your GIBBS run by clicking its job number.

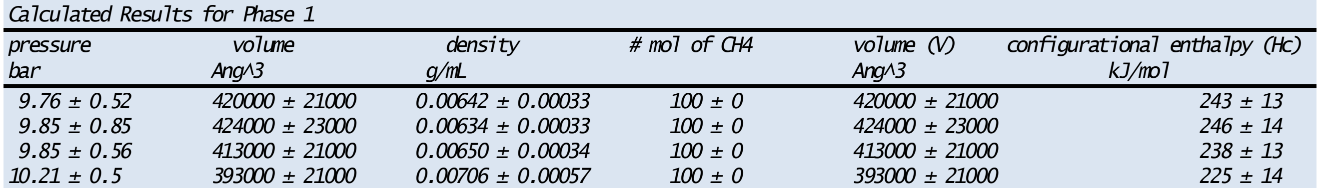
The main output file to study is `Job.out`. Here the main input parameters, results and convergence data are summarized. Job.out is written right at the beginning of a job, so you can review input parameters while the job is running:

```
Job.out output for 506: (Gibbs) 10bar

Status: finished

A Gibbs Monte-Carlo calculation of the properties of a single phase under constant pressure
conditions

Initial Configuration

Components:                                                     component summary
   No.      Component    Type        Electrostatic
  _  ------------- ----------    -------------

     1            CH4      rigid        no

The Monte-Carlo algorithm will run for 100 thousand steps using the following initial move
probabilities:
                   volume =   0.2                               move summary
              translation =  99.8

Gibbs potentials file: C:/MD/2.0/bin/generic/MedeALib.kit/lib/Gibbs/potparam.dat

  Task  Temperature  Pressure  Phase 1: Box Length  Phase 1: Volume  Phase 1: Density  Phase 1: # of CH4
                K       bar                  Ang            Ang^3              g/mL
--------------------------------------------------------------------------------------------------------
     1    298.150    10.000               68.376       319680.000             0.008            100.000
     2    298.150    10.000               64.344       266400.000             0.010            100.000
     3    298.150    10.000               58.461       199800.000             0.013            100.000
     4    298.150    10.000               54.270       159840.000             0.017            100.000
```

A GIBBS run or job can consist of a single or many GIBBS tasks for each of which MEDEA creates a subdirectory in the jobs directory. In the above case we have 4 tasks to run corresponding to 4 rows or conditions created in the conditions panel (the conditions vary just in the starting density/box size for methane).

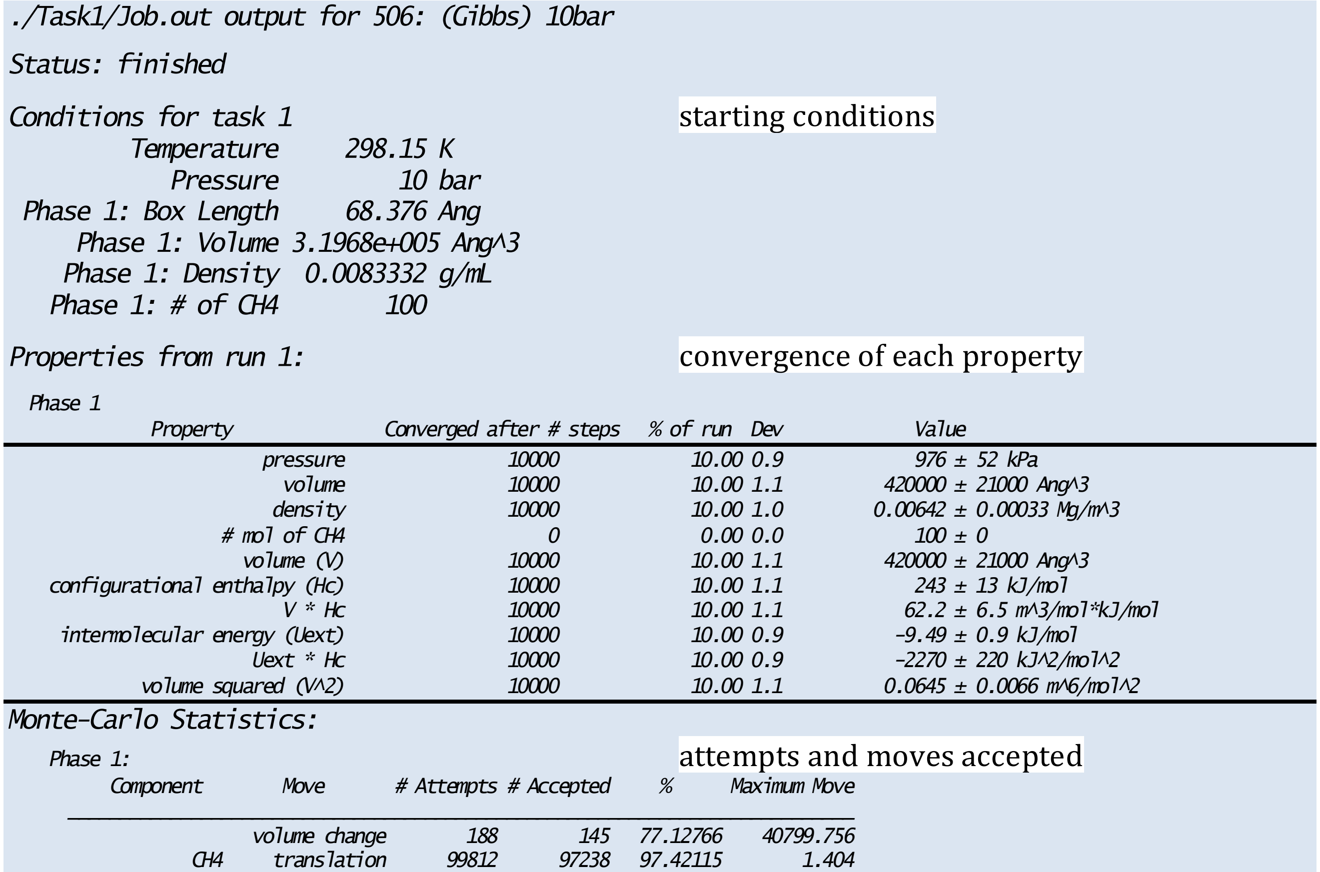
a. Checking for convergence

Once the job is completed, the output of a GIBBS run (Job.out) contains a detailed analysis of each task's convergence. Each task directory contains a task specific Job.out which summarizes detailed statistics about the task convergence and information on the number of accepted and rejected moves for a certain component. For the above job (Methane at 298 K, 10 bar pressure), the main Job.out is shown below: All tasks are converged and the calculated density varies between 0.0064 mol/L and 0.00706 mol/L.



```
Calculated Results for Phase 1
pressure        volume            density             # mol of CH4      volume (V)       configurational enthalpy (Hc)
bar            Ang^3            g/mL                                    Ang^3                     kJ/mol
 9.76 ± 0.52   420000 ± 21000   0.00642 ± 0.00033      100 ± 0          420000 ± 21000                  243 ± 13
 9.85 ± 0.85   424000 ± 23000   0.00634 ± 0.00033      100 ± 0          424000 ± 23000                  246 ± 14
 9.85 ± 0.56   413000 ± 21000   0.00650 ± 0.00034      100 ± 0          413000 ± 21000                  238 ± 13
10.21 ± 0.5    393000 ± 21000   0.00706 ± 0.00057      100 ± 0          393000 ± 21000                  225 ± 14
```

For task 1 the Job.out looks like below:



```
./Task1/Job.out output for 506: (Gibbs) 10bar

Status: finished

Conditions for task 1
         Temperature     298.15 K
            Pressure         10 bar
 Phase 1: Box Length     68.376 Ang
     Phase 1: Volume 3.1968e+005 Ang^3
    Phase 1: Density  0.0083332 g/mL
   Phase 1: # of CH4        100

Properties from run 1:

  Phase 1
                Property             Converged after # steps  % of run  Dev            Value
                         pressure                10000            10.00 0.9        976 ± 52 kPa
                           volume                10000            10.00 1.1     420000 ± 21000 Ang^3
                          density                10000            10.00 1.0   0.00642 ± 0.00033 Mg/m^3
                     # mol of CH4                    0             0.00 0.0        100 ± 0
                       volume (V)                10000            10.00 1.1     420000 ± 21000 Ang^3
   configurational enthalpy (Hc)                10000            10.00 1.1        243 ± 13 kJ/mol
                           V * Hc                10000            10.00 1.1       62.2 ± 6.5 m^3/mol*kJ/mol
       intermolecular energy (Uext)              10000            10.00 0.9      -9.49 ± 0.9 kJ/mol
                        Uext * Hc                10000            10.00 0.9      -2270 ± 220 kJ^2/mol^2
               volume squared (V^2)              10000            10.00 1.1    0.0645 ± 0.0066 m^6/mol^2
Monte-Carlo Statistics:

   Phase 1:
        Component      Move        # Attempts # Accepted     %       Maximum Move
     ________________________________________________________________________
                     volume change       188        145   77.12766     40799.756
              CH4      translation     99812      97238   97.42115         1.404
```

starting conditions

convergence of each property

attempts and moves accepted

Provided you are running enough steps in a GIBBS Ensemble Monte-Carlo simulation, the number of accepted moves for of each type of move should be roughly equal, thus guaranteeing a thorough sampling of configuration space. To improve the sampling of those parts of configuration space lying energetically higher, the probability of the corresponding moves may be increased.

For most applications we recommend to work with MEDEA defaults.

III. Job management

Overview

The MEDEA environment includes a computational job management system allowing the user to launch multiple jobs at a time, control running jobs and quickly find and retrieve data from earlier calculations.

You can think of the MEDEA environment as consisting of three tiers:

1. **MEDEA**, the first tier or front-end program providing a graphical interface to the user
2. The **JobServer** or middle tier, providing job control, data pre/post processing and storage/management of all computational results
3. The **TaskServer** or end tier, managing individual computational tasks performed on either Windows or Linux machines dedicated for numerical high-throughput computations

During MEDEA installation a working configuration of MEDEA, the JobServer and the TaskServer is created on the local machine. While this configuration is fully functional, you will most likely add additional TaskServers and group them into queues.

The installation of the TaskServer is covered in section I.F.4 Custom Installation. Configuration options or described below in section III.G TaskServer administration and configuration.

A. Launching a job in MEDEA

By "job" we refer to a single or a number of non-interactive (batch) computational tasks that are launched from the MEDEA interface by invoking any of the MEDEA modules VASP, ELECTRA, GIBBS, MT, PHONON, TRANSITION STATE SEARCH or INTERFACES. Such a job is controlled by the MEDEA JobServer (Windows process name: *mdjobserver*). All above jobs consist of at least one computational task. The JobServer farms out all tasks to TaskServer machines. An exception is the Interface job that runs directly on the JobServer machine.

To submit a job, click **Run** in the graphical user interface, select a **queue** from the pop-up windows, add optional comments and confirm with **Submit**

Some jobs run directly on the JobServer (like Interface Search). Here, **Run** submits directly to the current JobServer without invoking the Queues dialogue.

Most computational Jobs consist of one or more separate Tasks. A Task is defined as a serial or parallel process (*vasp.exe*, *gibbs.exe*, ...) running on one or more CPUs. A Job can consist of multiple Tasks and may require additional pre/post processing in order to complete.

> **Jobs with multiple tasks**: Displacement calculations to derive a phonon spectrum, GIBBS calculation of an adsorption isotherm, elastic coefficients, band structure calculations, COMBI spreadsheet calculations.
>
> **Jobs with a single task**: A VASP total energy calculation (Single Point), A VASP structure optimization, a GIBBS run with a single thermodynamic condition
>
> **Jobs without tasks**: an Interface Search

When you submit a job to a specific queue, MEDEA figures out how many tasks need to be run to complete the job. MEDEA then submits these tasks to all active TaskServers available in the queue.[9] In more detail, the following happens when launching a job in MEDEA:

1) MEDEA collects information on your structure and the requested job and sends it to the JobServer, including your input on which queue (group of TaskServers) to run the calculations.
2) The JobServer receives and processes this data creating input files for one or several tasks required for the job to complete. For example, this step may involve getting VASP PAW potentials from the SQL database or setting up a number of displacement calculations for PHONON. The status of the job is now "**running**"

---

[9] If TaskServers are not active (maintenance) or not running, the connection to the TaskServers is interrupted (network problem), the job in question has the status *running* (preprocessing and task setup have started) but is unable to submit tasks until you a tleast one TaskServer of the queue is active.

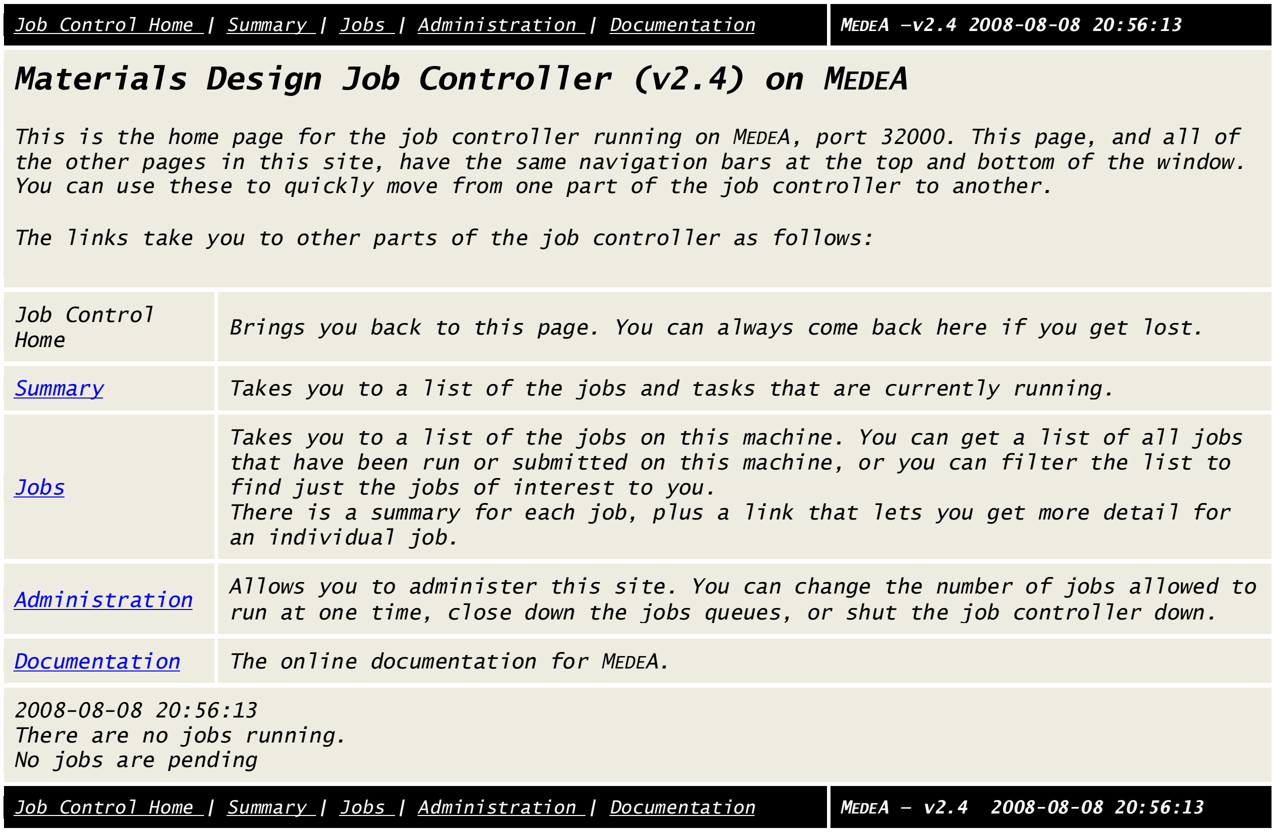
3) Preprocessing finished, the JobServer checks the queue for availability of TaskServers having free CPUs. As soon as TaskServer signals availability, the JOBSERVER TRANSFERS input data and the task is started. If all TaskServers are busy or not available otherwise, the JobServer queues the tasks for later submission
4) Each TaskServer accepts a predefined number of tasks depending on its configuration (e.g. single CPU, multi core etc.). All accepted tasks executed at once
5) When a task has completed the data is sent back from the TaskServer to the JobServer where it is processed and stored
6) Once the JobServer has received and processed all required data to complete the job, the job status changes to "**finished**"

Typically the JobServer is installed as a service, in other words, it runs as a background process and does not require direct interaction from the user in order to do its work. The JobServer resides either on the machine running MEDEA or on a dedicated Windows machine.

MEDEA provides an .html interface to the JobServer to let you view running or completed jobs, to change the way jobs run or to stop or restart jobs.

B. Monitoring a running job

To start the JobServer interface, in the MEDEA main menu, select **Job Control** » **View and Control Jobs**. The following page comes up in your default web browser:



Job Control Home | Summary | Jobs | Administration | Documentation MEDEA -v2.4 2008-08-08 20:56:13

Materials Design Job Controller (v2.4) on MEDEA

This is the home page for the job controller running on MEDEA, port 32000. This page, and all of the other pages in this site, have the same navigation bars at the top and bottom of the window. You can use these to quickly move from one part of the job controller to another.

The links take you to other parts of the job controller as follows:

Job Control Home	*Brings you back to this page. You can always come back here if you get lost.*
Summary	*Takes you to a list of the jobs and tasks that are currently running.*
Jobs	*Takes you to a list of the jobs on this machine. You can get a list of all jobs that have been run or submitted on this machine, or you can filter the list to find just the jobs of interest to you.* *There is a summary for each job, plus a link that lets you get more detail for an individual job.*
Administration	*Allows you to administer this site. You can change the number of jobs allowed to run at one time, close down the jobs queues, or shut the job controller down.*
Documentation	*The online documentation for MEDEA.*

2008-08-08 20:56:13
There are no jobs running.
No jobs are pending

Job Control Home | Summary | Jobs | Administration | Documentation MEDEA – v2.4 2008-08-08 20:56:13

You may want to bookmark the link in order to access directly through your browser's Favorites list in the future. The job control home page navigation bar (black) has a number of links:

Job Control Home: Starting page for job controller on (default) http://localhost:32000 The JobServer listens on port 32000 and can run on a different machine than MEDEA. Multiple JobServers can be configured to work with one instance of MEDEA. Edit the file `servers.dat` in the MEDEA 2.0 directory to change the default settings.

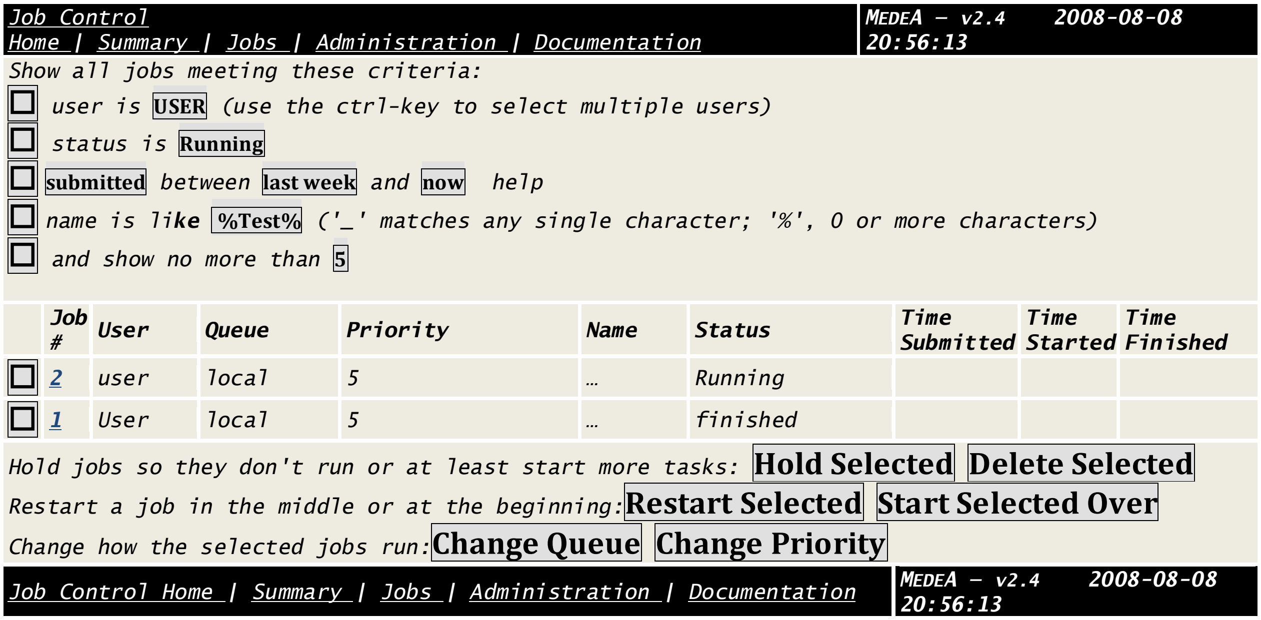
Summary: Job/Task overview page displaying which jobs are currently running and what are their tasks. Use the job and task links on this page to browse to the job/task directory of a given job/task.

Jobs: The Job overview page lists all jobs running or completed on the JobServer. Use filters at the top of this page to narrow down the selection.

Administration: JobServer configuration page with settings like automatic restart, name and port of the JobServer machine. Consistent settings for MEDEA and JobServer(s) are required.

Documentation: MEDEA documentation page with users' guide and application notes.

C. Holding/Deleting a running job/task



Job Control
Home | Summary | Jobs | Administration | Documentation
MEDEA – v2.4 2008-08-08 20:56:13

Show all jobs meeting these criteria:

☐ *user is* USER *(use the ctrl-key to select multiple users)*
☐ *status is* Running
☐ submitted *between* last week *and* now *help*
☐ *name is like* %Test% *('_' matches any single character; '%', 0 or more characters)*
☐ *and show no more than* 5

	Job #	User	Queue	Priority	Name	Status	Time Submitted	Time Started	Time Finished
☐	2	user	local	5	…	Running			
☐	1	User	local	5	…	finished			

Hold jobs so they don't run or at least start more tasks: **Hold Selected** **Delete Selected**
Restart a job in the middle or at the beginning: **Restart Selected** **Start Selected Over**
Change how the selected jobs run: **Change Queue** **Change Priority**

Job Control Home | Summary | Jobs | Administration | Documentation
MEDEA – v2.4 2008-08-08 20:56:13

1. Holding/Deleting a job:

On the jobs page select the job number (Job #) and at the bottom of the page click **Hold Selected**/**Delete Selected**. A job with status held will not submit any more tasks. Select a held job and click **Resume Selected** to continue the computation.

Note that holding or deleting a job does not stop or remove the job's tasks that are currently running. To delete a job and all running tasks associated with it do the following:

Hold the job as described above

Click the job number and then on the Control button next to the task entry of the running task you would like to stop (see below)

2. Stopping a VASP task:

To stop a running VASP task click on the job number in the Jobs page and then on the Control button next to the task you would like to stop. Choose one of the following options:

Stop VASP after this geometry step - VASP will finish the current geometry step and stop. This option provides a valid geometry, e.g. an intermediate step in an ongoing structure relaxation.

Stop VASP after this electronic iteration - VASP will finish the current electronic (scf) step and finish. No valid geometry will be returned. You can however retrieve the previous geometry by loading the CONTCAR file from disk.

Terminate the task right now - This command has differing implementations on Windows and Linux. Moreover you need to be aware that terminating a task does not interact with any external queuing systems:

- Windows TaskServer: Kills the current task if you have `pskill` installed and configured
- Linux TaskServer: Kills the current task using the Unix `kill` command.
- External queuing systems: We recommend not using this command with external queuing systems. Log in to your task server machine instead and use the queuing system specific commands to delete tasks

Stop the task locally - Use this option only when a TaskServer is unreachable due to network problems. This option deletes the task from the JobServer registry. The JobServer will continue to submit remaining tasks and end the job with an error due to the deleted task. You can then restart just the task in question using the restart function.

Start the task over - Use this option only when a TaskServer is unreachable due to network problems. This option deletes the task from the JobServer registry and tells the JobServer to start it all over.

3. Installing the pskill under Windows:

To stop a tasks running on a TaskServer under the Windows operation system you need to install the pstools kit from *Sysinternals*.

Download and save the set of executables to a directory of your choice on the TaskServer machine, e.g. `C:/MD/pstools`.

Browse to your JobServer administration page, click on the blue Task SERVERS link and then on the TaskServer name in the list of TaskServers. This will bring you to the TaskServer home page on the machine in question.

Click on Administration in the green control bar and set the PSTools Directory entry to the appropriate value (C:/MD/pstools in our example)

4. Stopping a parallel VASP task:

To stop a task running in parallel mode use either Stop VASP after this geometry step or Stop VASP after this electronic iteration. If you have to kill a parallel process, please log on to each TaskServer machine and kill the mpi process (e.g. vasp_parallel) using an MPICH commands or the kill command (Linux), pskill (Windows) or the Windows task manager. Note that the current version of MPICH does not have **automatic garbage collection**, so. If you kill a task running in parallel under MPICH, memory will remain allocated until you deal with it through MPICH by restarting the mpi demon.

5. Restarting a held/interrupted job

To restart a job, that has been interrupted by e.g. a network failure or held by a user you have two options:

First option: Select the job in the Jobs page and click **Restart Selected** at the bottom of the page.

The JobServer will retrieve all fully completed tasks

The JobServer will submit all uncompleted tasks to the queue.

Second option: Click on the Job number (Job #) and then on **Restart** at the top of the page. In the following dialogue you can explicitly choose which tasks to rerun and which tasks to attempt to retrieve. This option allows you to rerun specific tasks that may not have finished properly but were registered by the JobServer as completed.

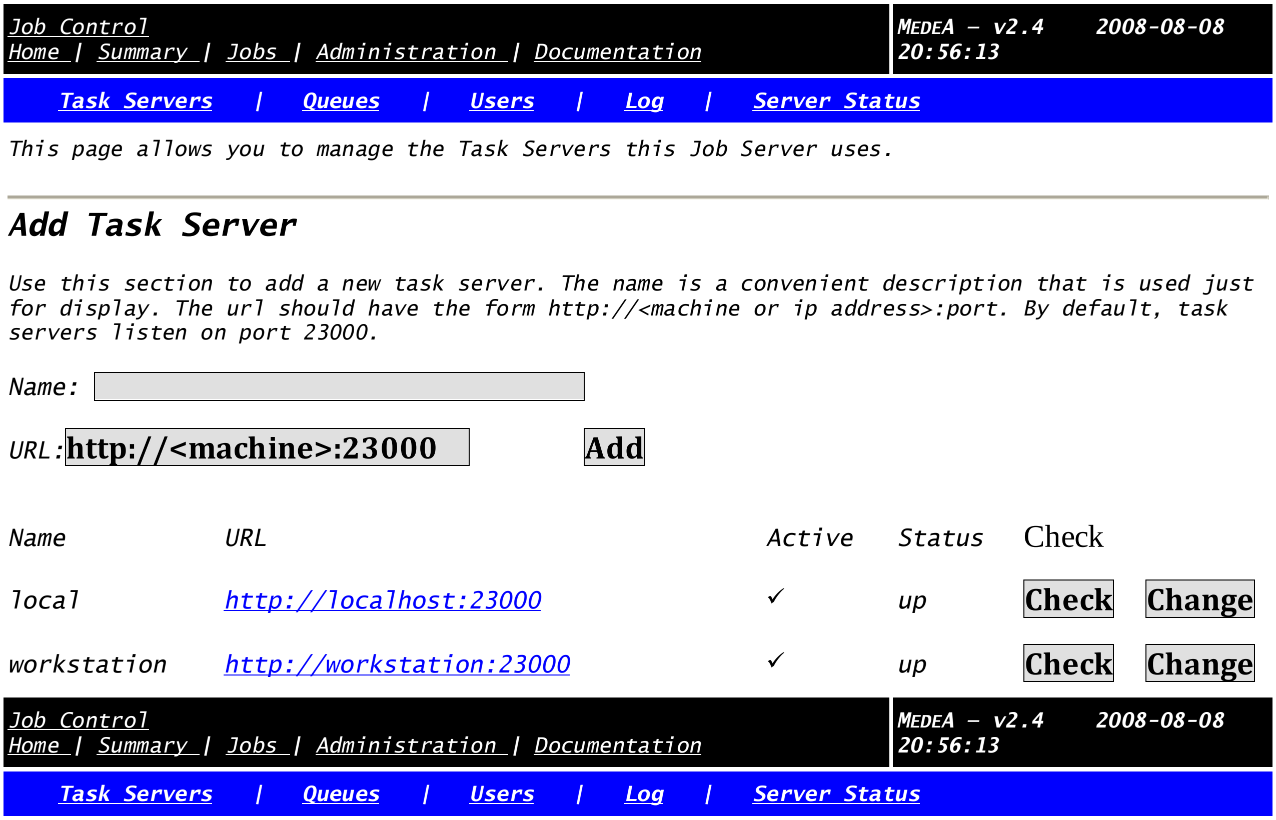
D. Registering additional TaskServers with the JobServer

In order to have the JobServer send computational tasks to TaskServers other than your default machine you need to register these machines with the JobServer. In the following we assume you have successfully installed the TaskServer on a machine, i.e. the page http://<taskserver>:23000 is accessible by a standard web browser.

On the JobServer administration page click the **TaskServer** link in the blue navigation bar. On the following page (see below) type in a name for the TaskServer and the network address of the machine running it: http://<taskserver>:23000

In the below example we have registered two machines, "local" and "workstation".

- Use the **Check** button to check if the TaskServer machine is reachable from the JobServer
- Click **Change** to modify any of the settings for a TaskServer or to make it Active/Inactive



Job Control
Home | Summary | Jobs | Administration | Documentation

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Task Servers | Queues | Users | Log | Server Status

This page allows you to manage the Task Servers this Job Server uses.

Add Task Server

Use this section to add a new task server. The name is a convenient description that is used just for display. The url should have the form http://<machine or ip address>:port. By default, task servers listen on port 23000.

Name:

URL: **http://<machine>:23000** **Add**

Name	URL	Active	Status	Check	
local	http://localhost:23000	✓	up	**Check**	**Change**
workstation	http://workstation:23000	✓	up	**Check**	**Change**

Job Control
Home | Summary | Jobs | Administration | Documentation

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Task Servers | Queues | Users | Log | Server Status

Note that Linux machines may have difficulties recognizing Windows machines in a heterogeneous network. This is a network configuration issue and is not influenced by the way MEDEA handles TaskServers. A simple test to make sure your network is set up correctly is to use the ping command to check if the two machines can "see" each other.

E. Adding additional Queues

When submitting a job through the MEDEA interface you are asked to choose a queue. A queue is simply a group of TaskServers. The JobServer uses queues to let you control where and how to run your jobs.

The JobServer interface lets you define queues and attach TaskServers to it. To define and edit queues click on the **Administration** link in the Job Control home page. Next select **Queues** from the blue navigation bar to bring up the servers queue admin page (see example below).

To define a new queue, fill out the text fields at the bottom and click **Add Queue**

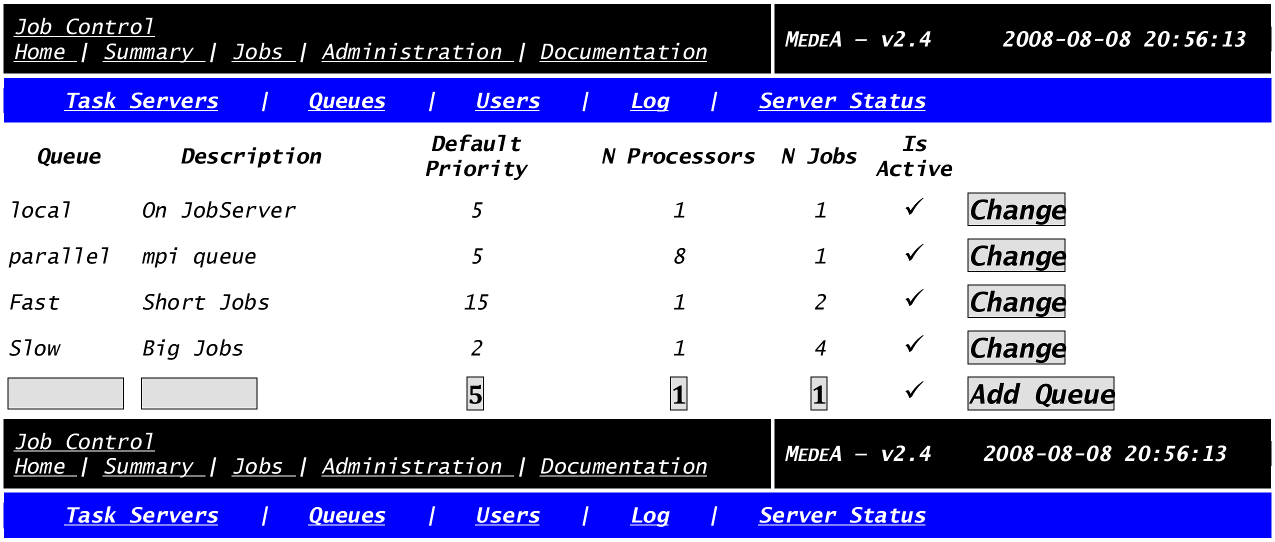
In the below example we have defined 4 queues with varying attributes. Besides the default local queue, we have set up a queue for a parallel system with 8 processors (*parallel*) , a slow queue (*Slow*) and a fast queue (*Fast*). In the following we will attach TaskServers to these queues.

Note that queues are just named groups of TaskServers! To have a queue behave in a certain way, you need to configure a TaskServer correspondingly and attach it to the queue!

Click on the **Change** button on the right of a given queue's row to configure the queue and to attach a TaskServer to the selected queue.

http://localhost:32000/ServerAdmin/queues.tml

The default installation creates a local queue, Jobs are processed in the sequence they are submitted to the JobServer. By creating different queues (such as Fast and Slow), jobs in the Fast queue have a higher priority over jobs in the slow queue.



Queue	Description	Default Priority	N Processors	N Jobs	Is Active	
local	On JobServer	5	1	1	✓	Change
parallel	mpi queue	5	8	1	✓	Change
Fast	Short Jobs	15	1	2	✓	Change
Slow	Big Jobs	2	1	4	✓	Change
		5	1	1	✓	Add Queue

F. Attaching a TaskServer to a Queue

In the following we assume you have installed one or more TaskServers, you have registered them with the JobServer and you have defined one or several Queues. Now all that is left is to tell the JobServer which Queue you want a certain TaskServer to run in.

The installation of the TaskServer is covered in section I.F.7 Setting up JobServer and TaskServer services and I.I Installing the MEDEA TaskServer under Linux.

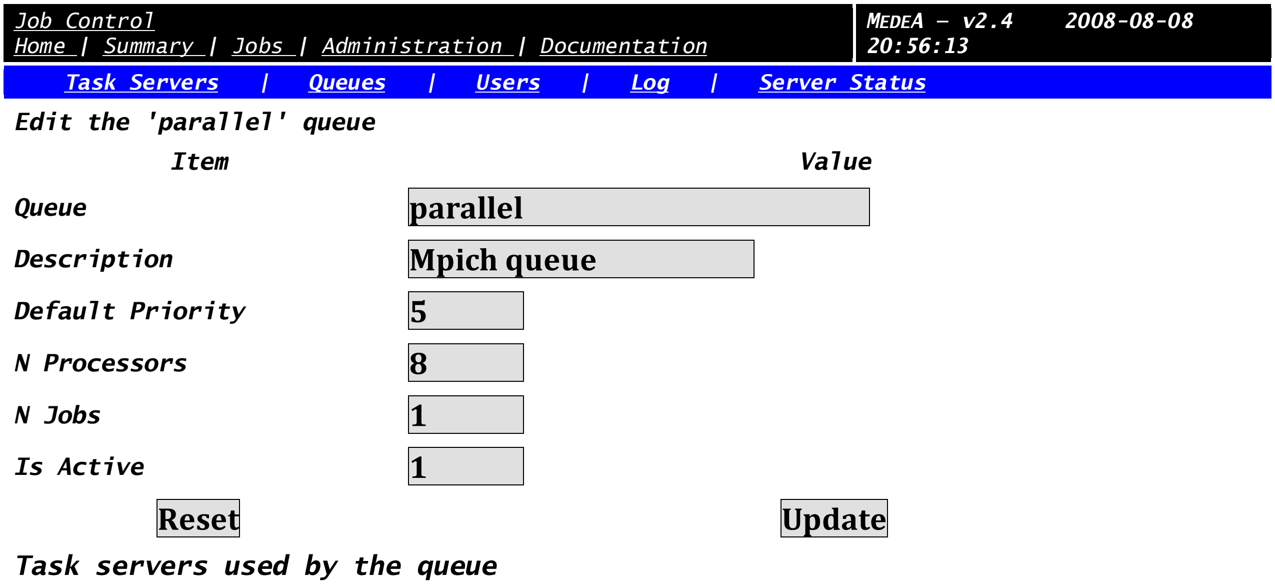
In the present example we have registered a TaskServer machine called `workstation`. Before we can use it though, we need to attach it to a queue.

- To reach the Queue admin page (see above), click **Job Control** » **View and Control Jobs** in MEDEA, then click **Administration** and on the next screen **Queues** (blue navigation bar)
- On the Queue admin page click the **Change** button next to the Queue you would like to edit and you will get to below page

In the upper section of this page you can review and change the attributes of the queue. In the lower half, you need to define which TaskServer to attach to the queue.

- In the table labeled TaskServer (marked in green) select `workstation` and click **Add**. Note that the status of the button changes from **Add** to **Remove** once you have added a TaskServer.

Note that present in the list are only those TaskServers which were previously registered with the JobServer. In other words the JobServer does not know about a TaskServer machine until you register it.

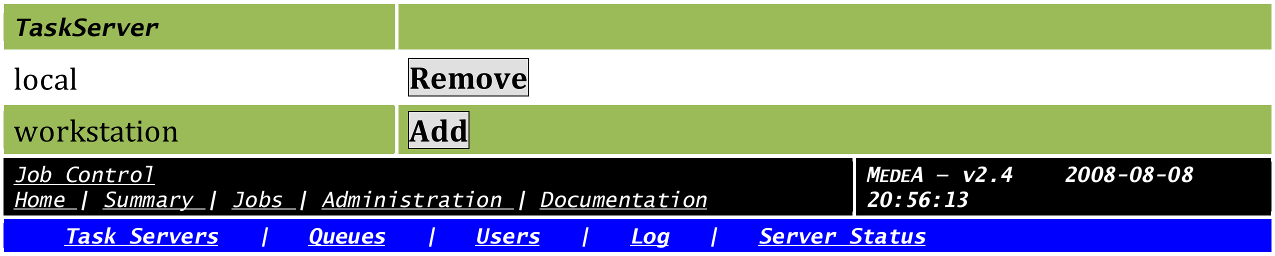


Edit the 'parallel' queue

Item	Value
Queue	parallel
Description	Mpich queue
Default Priority	5
N Processors	8
N Jobs	1
Is Active	1

Task servers used by the queue

The following table shows the task servers connected to this queue. You may remove any task server by pressing the *Remove* button. If there are other task servers available, you can select one or more to add in the last row of the table and then press the *Add* button.



TaskServer	
local	Remove
workstation	Add

Job Control
Home | Summary | Jobs | Administration | Documentation

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Task Servers | Queues | Users | Log | Server Status

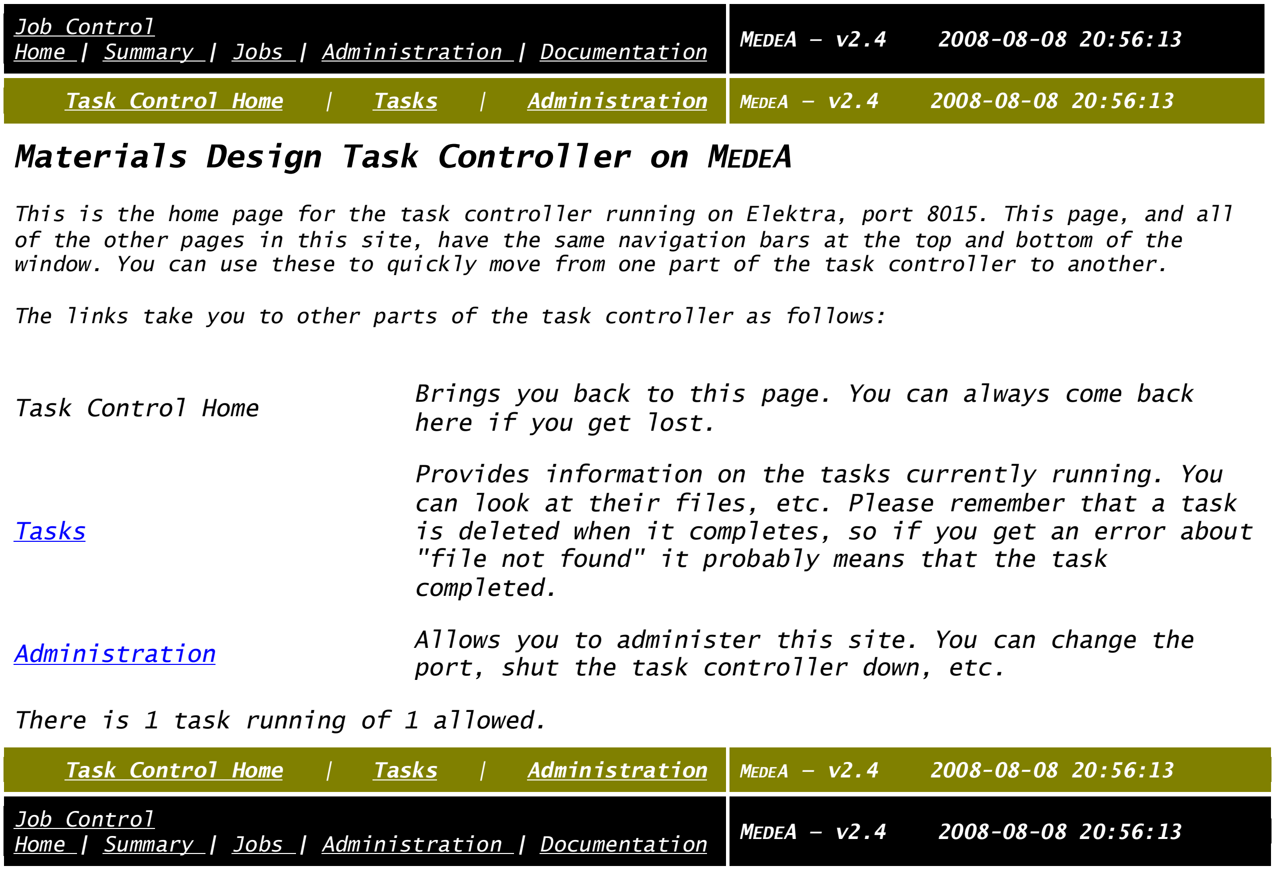
G. TaskServer administration and configuration

The MEDEA TaskServer gives you a number of options how to run your computational tasks, e.g. you can choose to run serial, parallel or through a queuing system or you can limit the number of CPUs used on a specific TaskServer machine. This section describes what options are available to configure how task are run.

1. The TaskServer administration page

In the following we assume that a TaskServer was installed and can be contacted through the links **Job Control home** ≫ **Administration** ≫ **Task Servers** or directly through the link http://<taskserver>:23000 where you need to use the name of your machine instead of <task_server>.

Both links should open the following page:



Materials Design Task Controller on MEDEA

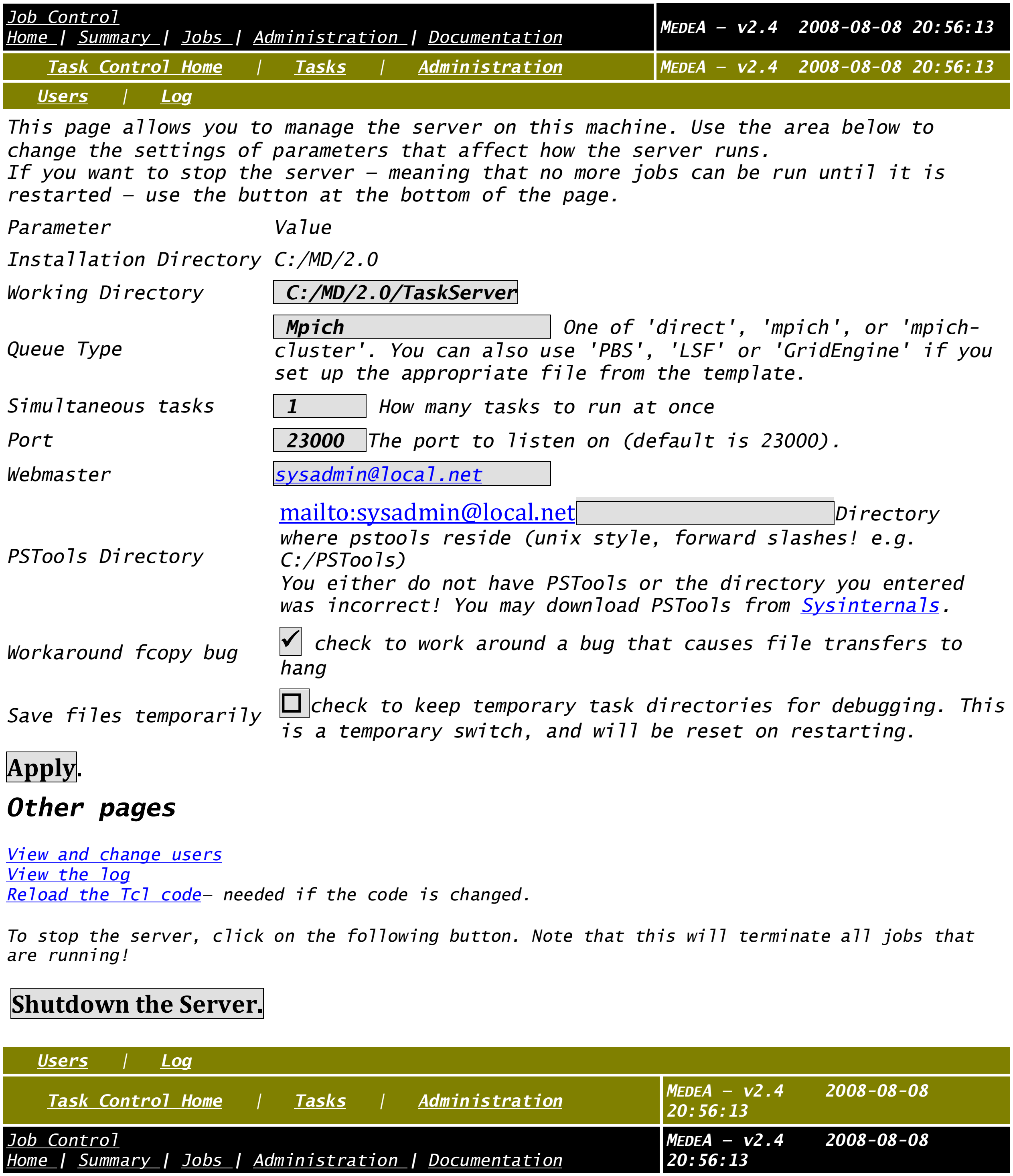
This is the home page for the task controller running on Elektra, port 8015. This page, and all of the other pages in this site, have the same navigation bars at the top and bottom of the window. You can use these to quickly move from one part of the task controller to another.

The links take you to other parts of the task controller as follows:

Task Control Home	*Brings you back to this page. You can always come back here if you get lost.*
Tasks	*Provides information on the tasks currently running. You can look at their files, etc. Please remember that a task is deleted when it completes, so if you get an error about "file not found" it probably means that the task completed.*
Administration	*Allows you to administer this site. You can change the port, shut the task controller down, etc.*

There is 1 task running of 1 allowed.

Click on the **Administration** link in the green navigation bar to proceed to the page with TaskServer configuration options:



This page allows you to manage the server on this machine. Use the area below to change the settings of parameters that affect how the server runs.
If you want to stop the server – meaning that no more jobs can be run until it is restarted – use the button at the bottom of the page.

Parameter	Value
Installation Directory	C:/MD/2.0
Working Directory	**C:/MD/2.0/TaskServer**
Queue Type	**Mpich** One of 'direct', 'mpich', or 'mpich-cluster'. You can also use 'PBS', 'LSF' or 'GridEngine' if you set up the appropriate file from the template.
Simultaneous tasks	**1** How many tasks to run at once
Port	**23000** The port to listen on (default is 23000).
Webmaster	sysadmin@local.net
PSTools Directory	mailto:sysadmin@local.net Directory where pstools reside (unix style, forward slashes! e.g. C:/PSTools) You either do not have PSTools or the directory you entered was incorrect! You may download PSTools from Sysinternals.
Workaround fcopy bug	☑ check to work around a bug that causes file transfers to hang
Save files temporarily	☐ check to keep temporary task directories for debugging. This is a temporary switch, and will be reset on restarting.

Other pages

View and change users
View the log
Reload the Tcl code– needed if the code is changed.

To stop the server, click on the following button. Note that this will terminate all jobs that are running!

The ***Working Directory*** is where the TaskServer writes temporary files. This is just a scratch area as all relevant data are exported back to the JobServer upon completion of tasks.

The ***Queue Type*** determines the way your binary will be run by the TaskServer. The following options exist:

- ***direct*** - uses MEDEA's queuing system and serial binaries
- ***mpich*** - uses the message parsing interface (mpich) included in MEDEA to run parallel jobs. Assumes a single machine running in SMP mode (shared memory).
- ***mpich-cluster*** - uses mpich to run parallel jobs. Assumes a number of independent machines to spread a parallel task over.
- ***PBS, LSF, GridEngine, etc*** - expects a file ***<template>.tcl*** in the directory <md_install_dir>\2.0\TaskServer\Tools\vasp4.6.31. Currently, templates exist for
  - ***PBS*** (Portable queuing system, Linux)
  - ***LSF*** (Unix/Linux)
  - ***GridEngine***

Attention: MEDEA does not include any of the above queuing systems. You need to install and manage external queuing systems like PBS or LSF yourself.

In order to run e.g. with PBS, copy the file `template_PBS.tcl` to `PBS.tcl` and set the queue type to **PBS** in the TaskServer Administration page. The file `PBS.tcl` provides a number of parameters that can be set to adapt the script to your local environment

Choose the number of ***Simultaneous task*** such that there won't be more tasks then processors. If the TaskServer machine is also in interactive use, consider leaving one CPU available for interactivity.

It is not recommended to change the ***Port*** the TaskServer listens on, unless you have a special reason!

PSTools is where you installed the pstools suite. Use forward slashes, e.g. ***C:/PSTools***

Number of Parallel CPU's determines how many parallel CPUs to use to by default, if – and only if – your queue type is mpich. If you are using an external queuing system you may use ***Number of Parallel CPU's*** to set the default number of parallel cpus (see corresponding scripts). ***Number of Parallel CPU's*** is the default and an upper limit and can be modified at run time in the job submission dialogue.

Parallel machines can be set together with `queue type=mpich` or `mpich-cluster`. It defines which machines to use as mpi slaves and how many CPUs to use on each machine. For example set ***Parallel machines*** to "`node1 2 node2 1 node3 2`" to use 2 cpus on node1, 1 cpu on node2 and 2 cpus on node3.

In case of running on one shared memory machine (SMP) leave it empty.

Save files temporarily - Check this option to keep temporary output files in the TaskServer scratch directory. This option is useful for debugging problems like e.g. submission to queuing systems.

2. Configuring a TaskServer to use an external queue

For use with an external queuing system like PBS, LSF or GridEngine under the Linux operating system, the TaskServer takes the role of a queue filter. Computational tasks are submitted to the queuing system which handles the computation in serial or parallel mode. It is up to the user to understand how a specific queuing system works and what settings need to be predefined in the queue submission script. MEDEA provides a few template scripts that can be modified to suit your specific settings. Some flags like e.g. the number of processors to use, the queue type and a project name can be set through the TaskServer administration interface. Other parameters may need to be set directly in the queue specific script by the user. This procedure is feasible for any type of queuing system. Below we give an example for the LSF queue:

Test a queue submission script to be used with the MEDEA TaskServer

The first step is to let the TaskServer automatically create a queue submission script for a given task. To achieve this, do the following:

1) Login to the TaskServer machine and on the TaskServer admin page *http://127.0.0.1:23000/ServerAdmin/manager.tml*

Set the ***Queue Type*** to e.g. LSF and confirm with **Apply**

With these settings, the TaskServer will look for a file **LSF.tcl** in the directory *<Install_dir>/2.0/TaskServer/Tools/vasp4.6.31*, where *<Install_dir>* is the MEDEA install directory (default is *C:/MD* under Windows or */home/<medea_linux_install_dir>/MD* under Linux).

2) Create the queue setup script in <Install_dir>/TaskServer/Tools/vasp4.6.31 by copying the file *LSF_template.tcl* to *LSF.tcl*

If you are working with a queuing system other than LSF, GridEngine or PBS, you need to create a file *<your_queuing_system_name>.tcl* from one of the templates above. You will need to modify this script in order to match the relevant queue submission commands on your machine. Note that the queue type is cases sensitive, so the names in the two previous steps need to match exactly.

3) On the TaskServer admin page, under *http://127.0.0.1:23000/ServerAdmin/manager.tml* check the box **☑ Save files temporarily** in order to keep temporary files on the TaskServer machine during testing. Note that when restarting the TaskServer during testing, this option will be changed back to the default. Click **Apply** or hit **Return**
4) The updated page will show 2 more entries "**LSF Queue**" and "**Project**". You may have to set a LSF queue name and/or a project variable depending on your LSF queue settings
5) Select a value for ***Simultaneous tasks***. The value depends on how many tasks you maximally would like to run in the LSF queue. The LSF queue will handle this parameter depending on resources.

6) ***Number of parallel CPU's*** lets you define a value for the number of CPUs to use if you are running parallel. The MEDEA interface will let you overwrite this value when submitting jobs; however the user defined number has to be smaller or equal to this number.

7) Test the configuration by running a simple job from MEDEA (make sure you submit to the TaskServer you have just modified)

You can look at the output on your TaskServer machine by browsing to http://<TaskServer>:23000/Tasks/ and clicking on the new task directory created by your task (it is not deleted after task completion as we have set the corresponding flag on the TaskServer admin page).

8) Open the text file ***taskxxx.sh*** (where ***xxx*** stands for the task number) and check the commands that have been submitted to the LSF queue. A good way to optimize the testing procedure is to use this file to submit test jobs by hand. If you need to set additional options for the queuing system, you can try them out using this file. Once you are sure what parameters to use you can add them to the section of LSF.tcl where the script is written, so next time you submit a task these values will be set.

Please note that the detailed setup of LSF depends on your site and is not controlled by the MEDEA TaskServer. The TaskServer simply passes on these values to the LSF queue. If your LSF queue is not configured to e.g. run in parallel, these values will have no effect.

Known problems and workarounds:

The machine running the LSF daemon (the scheduler) is running a different flavor of Linux than the actual compute nodes.

Under Linux/Unix the TaskServer determines the architecture and OS version automatically by using the ***uname*** command. When using the TaskServer as a simple queue filter for an external queue, chances are that the actual compute nodes have a different and/or varying architecture. Currently this possibility is not handled by the TaskServer graphical user interface. A simple workaround is the following:

Install the architecture specific binaries in an identical directory path on each machine, e.g. /MD/bin.

Edit the file LSF.tcl and look for a block of commands just below

```
#
# Replace %...% strings in the script
#
```

Look for the line

```
regsub -all {%EXE%} $script $EXE script
```

and change it to

```
regsub -all {%EXE%} $script [file tail $EXE] script
```

This will remove the leading path from the executable string and leave simply the type of VASP binary to run.

Next, also in LSF.tcl, change the line following

```
# The next line should run vasp ... either a full path, or ....
%EXE%
```

To

```
# The next line should run vasp ... either a full path, or ....
/MD/bin/%EXE%
```

(The first line starting with # is only a comment). You can replace `/MD/bin/` by a path of your choice as long as it is where each machine type stores its VASP binaries. Alternatively you can store the machine dependent VASP binaries in a system path and simply make sure you have this path in the environment variables of the user running the TaskServer daemon. In this case you only need to apply the first change to LSF.tcl, i.e. stripping the path info from the EXE variable.

3. Configuring the TaskServer to use MPICH

MEDEA comes with MPICH preinstalled as a part of the distribution. In order to run parallel jobs you need to set up a specific TaskServer machine as an "mpich filter". This way the TaskServer serves as a master node running VASP in parallel either in shared memory mode on e.g. a multi core machine or using additional machines as "MPI slaves".

Before you can enjoy parallel computing with MEDEA VASP you need to make sure a few prerequisites on your TaskServer machines are met:

a. Windows: MPICH prerequisites

On the TaskServer machine, open a command shell (**Start Menu** ≫ **Run** ≫ **cmd**) and in the command shell change directory to `C:\MD\Windows-x86\MPICH2\bin`

```
cd C:\MD\Windows-x86\MPICH2\bin
```

Execute the command

```
smpd -install
```

to install the demon. You may need to allow the executable to pass through the Windows firewall.

Execute

```
mpiexec -register
```

to enter your login password into the registry for MPI. Follow the prompts. You may need to allow the executable for the Windows firewall.

Test the mpi installation by running

```
mpiexec -np 2 cpi
```

Giving it a test of perhaps 1000 iterations. Again, you may need to allow the executable for the Windows firewall.

Go to **Start** > **Control Panels** > **Administrative Tools** and start '***services***' Find the service labeled "MD Task Server 2.0" or similar and double click on it and go to the "Log on" tab. Change it to log on as yourself, putting in the same password that you used to register the mpiexec command (typically your own user name and password).

b. JobServer/TaskServer settings

On the job server web page, go to the **Administration/ Queues** section and set the number of processors to 2 or the appropriate number.

Go to the TaskServer admin page (e.g. http://localhost:23000/ServerAdmin/manager.tml on your local machine) Set the **Queue Type** to **MPICH** (or **MPICH-cluster** for a networked cluster) and click **Apply**

Set **Number of Parallel CPUs** to the default or highest number of cpus you want to use in parallel. For a shared memory processing machine (SMP) you can leave the **Parallel Machines** blank. Otherwise insert a list of machines. If you want to use multiple CPUs on a machine, you can either list the machine several times, or put a number indicating the number of cpus after each machine name. e.g. "`node1 node1 node2 node3 node3`" is equivalent to "`node1 2 node2 1 node3 2`".

If you have Windows Firewall turned on, you will need to open it for the *_parallel* executables in `C:\MD\2.0\TaskServer\Tools\vasp4.6.31\win32-ix86`

c. Linux: MPICH

Under Linux you need to make sure the user running the TaskServer can execute secure shell commands to login to the machines you would like to run in parallel on. If you already have secure shell (`ssh`) in place and configured, you can skip the next section and go back to b JobServer/TaskServer settings above

Configuring ssh

Execute

```
shell> ssh-keygen -t rsa
```

to generate your key. You will be asked a few questions. Use defaults for each questions and do not use a passphrase!

Change directory into the *.ssh* directory by typing

```
shell> cd ~/.ssh
```

Execute

```
shell> cat id_rsa.pub >> authorized_keys
```

Depending on how you home directory is set up on the various machines, you may need to do some more:

If you use *automount* or *nfs* so have a shared home directory, you are done. Otherwise, you either need to make a key on each machine, add it to the authorized keys and move all around. Or -- more simply -- just copy the *.ssh* directory to each home directory.

In doing all this make sure your ssh files and directories have the right permissions:

the directory *$HOME/.ssh* should have **permissions** 700 (rwx------)

file *$HOME/.ssh/authorized_keys* should have **permissions** 600 (rw-------).

You can use the *chmod* command to make sure the permissions are correct, e.g.

```
shell> chmod 700 ~/.ssh
```

and

```
shell> chmod 600 ~/.ssh/authorized_keys
```

If the permissions are not set properly *ssh* will ask for passwords and give you a hard time.

IV. Theoretical Background

A. Density Functional Theory

1. The Kohn-Sham equations

In the mid 1960's, Hohenberg and Kohn[29] and Kohn and Sham [3] formulated a rather remarkable theorem which states that the total energy of a system such as a solid, a surface, and a molecule depends only on the electron density of its *ground state*. In other words, one can express the total energy of an atomistic system as a functional of its electron density

$$E = E[\rho] \tag{1-1}$$

The idea of using the electron density as the fundamental entity of a quantum mechanical theory of matter originates in the early days of quantum mechanics in the 1920's, especially by the work of Thomas [30] and Fermi [31]. However, in the subsequent decades, it was rather the Hartree-Fock approach [32; 33; 34], which was developed and applied to small molecular systems. Calculations on realistic solid state systems were then out of reach. In 1951, Slater [35]used ideas from the electron gas with the intention to simplify Hartree-Fock theory to a point where electronic structure calculations on solids became feasible. Slater's work, which led to the so-called $X\alpha$ method [36] has contributed tremendously to the development of electronic structure calculations. However, the *ad hoc* character of the $X\alpha$ approach, combined with other simplifications in the so-called scattered-wave method have fuelled heated disputes about the "*ab initio*" character of this approach, which was carried over into the comparison of density functional theory *vs.* Hartree-Fock based methods. Today's density functional methods can be considered "*ab initio*". In fact, recent methods such as LDA+U for correlated systems and screened-exchange for excitations in semiconductors synthesize ideas of both theoretical approaches, the wave-function based Hartree-Fock concept and density functional theory.

In solid-state systems, molecules, and atoms, the electron density is a scalar function defined at each point **r** in real space,

$$\rho = \rho(\mathbf{r}) \tag{1-2}$$

The electron density and the total energy depend on the type and arrangements of the atomic nuclei. Therefore, one can write

$$E = E[\rho(\boldsymbol{r}), \{\boldsymbol{R}_\alpha\}] \tag{1-3}$$

The set $\{\boldsymbol{R}_\alpha\}$ denotes the positions of all atoms, α in the system under consideration. Eq. (1-3) is the key to the atomic-scale understanding of electronic, structural, and dynamic properties of matter. If one has a way of evaluating expression (1-3), one can, for example, predict the equilibrium structure of solid, one can predict the reconstruction of surfaces, and the equilibrium geometry of molecules adsorbed on surfaces.

Furthermore, the derivative of the total energy (1-3) with respect to the nuclear position of an atom gives the force acting on that atom. This enables the efficient search for stable structures and, perhaps more importantly, the study of dynamical processes such as diffusion or the reaction of molecules on surfaces. Most of the considerations discussed here are based on the Born-

Oppenheimer approximation in which it is assumed that the motions of the electrons are infinitely faster than those of the nuclei. In practice this means that the electronic structure is calculated for a fixed atomic arrangement and the atoms are then moved according to classical mechanics. This is a fairly good approximation for heavy atoms like W, but may cause errors for light atoms such as H or Li.

In density functional theory, the total energy (1-1) is decomposed into three parts, a kinetic energy, an electrostatic or Coulomb energy, and a so-called exchange-correlation energy,

$$E = \mathrm{T}_0 + \mathrm{U} + \mathrm{E}_{\mathrm{xc}} \tag{1-4}$$

The most straightforward term is the Coulomb energy U. It is purely classical and contains the electrostatic energy arising from the Coulomb attraction between electrons and nuclei, the repulsion between all electronic charges, and the repulsion between nuclei

$$U = U_{en} + U_{ee} + U_{nn} \tag{1-5}$$

With

$$U_{en} = -e^2 \sum_{\alpha} Z_\alpha \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}\_\alpha|}\, d\mathbf{r} \tag{1-6}$$

$$U_{ee} = e^2 \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \tag{1-7}$$

$$U_{nn} = e^2 \sum_{\alpha\alpha'} \frac{Z_\alpha Z'_\alpha}{|\mathrm{R}_\alpha - \mathrm{R}'_\alpha|} \tag{1-8}$$

where e is the elementary charge of a proton and Z_α is the atomic number of atom α. The summations extend over all atoms and the integrations over all space. Once the electron density and the atomic numbers and positions of all atoms are known, expression (1-6)-(1-8) can be evaluated by using the techniques of classical electrostatics.

The kinetic energy term, T_0, is more subtle. In density functional theory, the "real" electrons of a system are replaced by "effective" electrons with the same charge, mass, and density distribution. However, effective electrons move as independent particles in an effective potential, whereas the motion of a "real" electron is correlated with those of all other electrons. T_0 is the sum of the kinetic energies of all effective electrons moving as independent particles. Often, one does not explicitly make this distinction between real and effective electrons.

If each effective electron is described by a single particle wave function, Ψ_i, then the kinetic energy of all effective electrons in the system is given by

$$T_0 = \sum_i n_i \int \Psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \Psi_i(\mathbf{r})\, d\mathbf{r} \tag{1-9}$$

Expression (1-9) is the sum of the expectation values of one-particle kinetic energies; n_i denotes the number of electrons in state i. By construction, dynamical correlations between the electrons are excluded from T_0

The third term of eq.(1-4), called exchange-correlation energy, E_{xc}, includes all remaining complicated electronic contributions to the total energy. The most important of these contributions is the exchange term. Electrons are Fermions and obey the Pauli Exclusion Principle. In real space, the Pauli principle implies that, around each electron with a given spin, all other electrons with the same spin tend to avoid that electron. As a consequence, the average Coulomb repulsion acting on that electron is reduced. This energy gain is called exchange energy. Effectively each electron is surrounded by a positive exchange hole. Slater showed that the total charge integrated over the entire exchange hole equals is $+e$ [36]. By definition, the additional many-body interaction terms between electrons of opposite spin are called correlation energy.

As an illustration, the total energy of a single C atom is approximately -1019 eV, that of a Si atom -7859 eV and that of a W atom -439634 eV. The kinetic energy and the Coulomb energy terms are of similar magnitude but of opposite sign whereas the exchange-correlation term is about 10% of the Coulomb term and attractive for electrons (because the exchange-hole is positive). The correlation energy is smaller than the exchange energy, but plays an important role in determining the details in the length and strength of interatomic bonds. In fact, compared with the total energy, the binding energy of an atom in a solid or on a surface is quite small and lies in the range of about 1 to 8 eV. Energies involved in changes of the position of atoms, such as in the reconstruction of a surface can be even smaller. For example, only about 0.03 eV are required to flip an asymmetric Si-dimer on a reconstructed Si(001) surface from one conformation into another where the role of the upper and lower Si atoms is reversed. It is a tremendous challenge for any theory to cope with such a range of energies. Density functional theory, as it turns out, comes amazingly close to this goal.

The Hohenberg-Kohn-Sham theorem, which is a central part of density functional theory, states that the total energy is at its minimum value for the ground state density and that the total energy is stationary with respect to first-order variations in the density, i.e.

$$\left.\frac{\partial E[\rho]}{\partial \rho}\right|_{\rho=\rho_0} = 0 \qquad (1\text{-}10)$$

In conjunction with the kinetic energy, we have introduced one-particle wave functions $\psi_i(\mathbf{r})$, which generate the electron density

$$\rho(\mathbf{r}) = \sum_i n_i |\Psi_i(\mathbf{r})|^2 \qquad (1\text{-}11)$$

As in the expression (1-9) for the kinetic energy, n_i denotes the occupation number of the eigenstate i, which is represented by the one-particle wave function ψ_i. So far, one has a formally exact theory in the sense that no approximations have been made yet to the many-electron interactions. By construction, $\rho(\mathbf{r})$ in eq. (1-11)is the exact many-electron density.

The goal of the next step is the derivation of equations that can be used for practical density functional calculations. Through equations (1-11) and (1-11) we have introduced one-particle wave functions. A change of these wave functions corresponds to a variation in the electron density. Therefore, the variational condition (1-10) can be used to derive the conditions for the one-particle wave functions that lead to the ground state density. To this end, one substitutes eq.(1-11) in expression (1-10) and varies the total energy with respect to each wave function. This procedure leads to the following equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\Psi_{i(\mathbf{r})} = \epsilon_i \psi_i(\mathbf{r}) \qquad (1\text{-}12)$$

with

$$V_{\text{eff}}(r) = V_c(\mathbf{r}) + \mu_{\text{xc}}[\rho(\mathbf{r})] \qquad (1\text{-}13)$$

Equations (1-12) are called the Kohn-Sham equations. The electron density, which corresponds to these wave functions, is the ground state density which minimizes the total energy. The solutions of the Kohn-Sham equations form an orthonormal set, *i.e.*

$$\int \Psi_i^*(\mathbf{r})\Psi_j(\mathbf{r})\, d\mathbf{r} = \delta_{ij} \qquad (1\text{-}14)$$

This additional constraint is achieved by introducing Lagrange multipliers, ϵ_i, in eq. (1-12). These "Lagrange multipliers" are effective one-electron eigenvalues and their interpretation will be discussed later. These eigenvalues are used to determine the occupation numbers n_i by applying the Aufbau principle. The eigenstates are ordered according to increasing eigenvalues. For non-spin polarized systems each state is occupied by two electrons until all electrons are accommodated. In spin polarized systems, each state is occupied by at most one electron.

As a consequence of the partitioning of the total energy(1-4), the Hamiltonian operator in the Kohn-Sham equations (1-12) contains three terms, one for the kinetic energy, the second for the Coulomb potential, and the third for the exchange-correlation potential.

The kinetic energy term is the standard second-order differential operator of one-particle Schrödinger equations and its construction does not require specific knowledge of a system. In contrast, the Coulomb potential operator, $V_C(\boldsymbol{r})$, and the exchange-correlation potential operator, μ_{xc}, depend on the specific electron distribution in the system under consideration.

The Coulomb or electrostatic potential $V_C(\boldsymbol{r})$at point $\mathbf{r}$ is generated from the electric charges of all nuclei and electrons in the system. It can be evaluated directly in real space,

$$V_{c(\mathbf{r})} = -e^2 \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \qquad (1\text{-}15)$$

In condensed systems it is more convenient to use Poisson's equation

$$\nabla^2 V_c(\mathbf{r}) = -4\pi e^2 q(\mathbf{r}) \qquad (1\text{-}16)$$

to calculate the electrostatic potential. Here, $q(\mathbf{r})$ denotes both the electronic charge distribution $\rho(\mathbf{r})$ and the positive point charges of the nuclei at positions $\boldsymbol{R}_\alpha$.

The exchange-correlation potential is related to the exchange-correlation energy by

$$\mu_{\mathrm{xc}} = \frac{\partial E_{\mathrm{xc}}[\rho]}{\partial \rho} \tag{1-17}$$

Equation (1-17) is formally exact in the sense that it does not contain any approximations to the complete many-body interactions. In practice however, the exchange-correlation energy (and thus the exchange-correlation potential) is not known and one has to make approximations.

As a consequence of the Kohn-Sham theorem, the exchange-correlation energy depends only on the electron density. As a simple and, as it turns out, surprisingly good approximation one can assume that the exchange-correlation energy depends only on the local electron density around each volume element $d\mathbf{r}$. This is called the local density approximation (LDA)

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^{0}[\rho(\mathbf{r})]\, dr \tag{1-18}$$

Figure 1 illustrates the basic idea. In any atomic arrangement such as a crystal, a surface, or a molecule, there is a certain electron density ρ(**r**) at each point **r** in space. The LDA then rests on two basic assumptions:

- the exchange and correlation effects come predominantly from the immediate vicinity of a point **r,** and
- these exchange and correlation effects do not depend strongly on the variations of the electron density in the vicinity of **r**.

If conditions (i) and (ii) are reasonably well fulfilled, then the contribution from volume element d**r** would be the same as if this volume element were surrounded by a constant electron density of the same value as within d**r** (cf. Figure 1). This i an excellent approximation for metallic systems, but represents quite a significant simplification in systems with strongly varying electron densities.

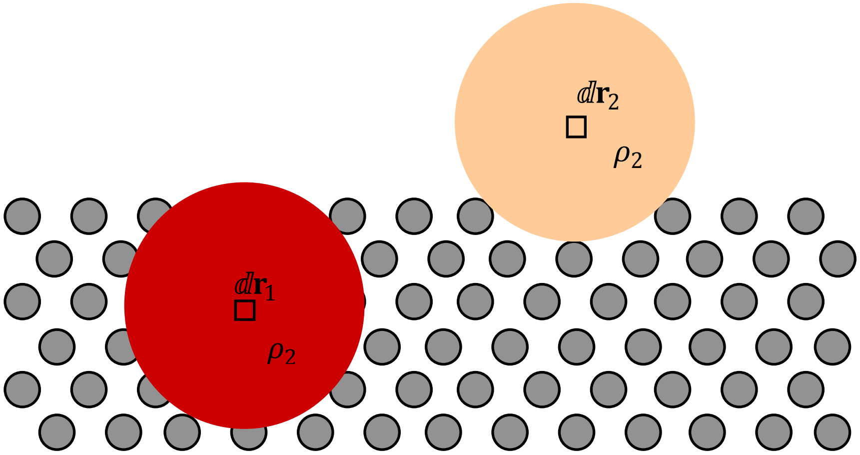


Illustration of the local density approximation:

For the purpose of computing the exchange-correlation energy in a volume element $d\mathbf{r}_\mathbf{i}$, the electron density $\boldsymbol{\rho}_{\boldsymbol{i}}$around point $\mathbf{r}_{\boldsymbol{i}}$ is assumed to be constant in the near surrounding.
Note that the values of $\boldsymbol{\rho}_{\boldsymbol{i}}$ is different in each volume element.

A system of interacting electrons with a constant density is called a homogeneous electron gas. Substantial theoretical efforts have been made to understand and characterize such an idealized system. In particular, the exchange-correlation energy per electron of a homogeneous electron gas, $\epsilon^0_{\mathrm{xc}}[\rho]$ has been calculated by several approaches such as many-body perturbation theory by Hedin and Lundqvist [37][38], quantum Monte-Carlo methods by Cerperley and Alder [39]. As a result, $\epsilon_{\mathrm{xc}}[\rho]$, is quite accurately known for a range of densities. For practical calculations, $\epsilon_{\mathrm{xc}}[\rho]$ is expressed as an analytical function of the electron density. There are various analytical forms with different coefficients in their representation of the exchange-correlation terms. These coefficients are not adjustable parameters, but rather they are determined through first-principles theory. Hence, the LDA is a first-principles approach in the sense that the quantum mechanical problem is solved without any adjustable, arbitrary, or system depended parameters.

Explicit forms for the local density exchange

	Energy	Potential
	$\epsilon_{xc} = \epsilon_x + \epsilon_c$	$\mu = \frac{\partial(\rho\epsilon)}{\partial\rho}$
Exchange	$\epsilon_x = -\frac{3}{2}\left(\frac{3}{\pi}\rho\right)^{\frac{1}{3}}$	$\mu_x = -2\left(\frac{3}{\pi}\rho\right)^{\frac{1}{3}}$
Correlation	$\epsilon_c = -c\left[(1+x^3)\ln\left(1+\frac{1}{x}\right)+\frac{x}{2}-x^3-\frac{1}{3}\right]$	$\mu_c = -c\ln\left(1+\frac{1}{x}\right)$

$$c = 0.0225, \quad x = \frac{r_s}{21}, \quad r_s = \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{3}}$$

Explicit forms for the local density exchange, originally given by Gáspár [40]and Kohn and Sham [3]. Correlation terms are according to Hedin and Lundqvist [38]. Exchange and correlation energies per electron are denoted by ϵ and the corresponding potentials by μ. Both quantities are given in Hartree atomic units (1 Hartree = 2 Rydberg = 27.21165 eV). The units for the electron density are number of electrons/(Bohrradius)^3

Note that there are two types of exchange-correlation terms, one for the energy and one for the potential. The energy, ϵ_{xc}, is needed to evaluate the total energy and the potential term, μ_{xc}, is required for the Kohn-Sham equations. The two terms are, following equations (1-17) and (1-18), related.

$$\mu_{\mathrm{xc}} = \frac{\partial[\rho\,\epsilon_{\mathrm{xc}}(\rho)]}{\partial\rho} \qquad (1\text{-}19)$$

Using the explicit formulas given in the table above, one can evaluate the exchange-correlation potential for any electron density $\rho(\mathbf{r})$. Thus, all terms of the effective one-particle operator in the Kohn-Sham equations are defined and one can proceed with a computational implementation.

2. Interpretation of one-particle energies

The fundamental quantities in density functional theory are the electron density and the corresponding total energy, but not the one-particle eigenvalues. However, the one-electron picture is so useful that one seeks to exploit the Kohn-Sham eigenvalues and one-particle wave functions as much as possible. The one-particle energies of effective electrons have been introduced in the derivation of the Kohn-Sham equations as Lagrange multipliers. The Kohn-Sham equations have the form of an eigenvalue problem in which each wave function has an associated eigenvalues $\epsilon_{▯}$with an occupation number of n_i. Janak's theorem [41] provides a relationship between the total energy and these eigenvalues.

$$\epsilon_i = \frac{\partial E}{\partial n_i} \tag{1-20}$$

The eigenvalue ϵ_i equals the change of the total energy with the change of the occupation number of level i.

However, it is desirable to seek a more direct physical interpretation of these eigenvalues. Already before the formulation of present density functional theory, the one-electron picture has become widely used in solid-state and molecular physics. For example, the distinction between a metal and an insulator is based on the analysis of the energy bands (energy bands are one-electron energies plotted as a function of different directions in reciprocal space); the characteristics of semiconductors and semiconductor/metal junctions are explained in terms of energy band structures; photoemission experiments are conveniently interpreted by a one-electron picture, often with quite reasonable quantitative agreement between theory and experiment. Furthermore, the analysis of the *s*,*p*, and *d* character of partial densities of states has become an extremely useful tool in the understanding of chemical bonding in alloys and compounds. While the direct interpretation of the Kohn-Sham eigenvalues as excitation energies often gives quantitative agreement with experimental photoemission spectra, there are significant differences in quantities such as energy band gaps in semiconductors. In fact, discrepancies of over a factor of two can be found between measured values and the LDA eigenvalues.

Such discrepancies between experimental excitation energies and differences between LDA eigenvalues are not necessarily a failure of the LDA, but rather an inappropriate interpretation of theoretical results. In the derivation of the Kohn-Sham equations given above, the effective one-particle eigenvalues were never required to be excitation energies! Only the total electron density and the corresponding total energy have rigorous meaning. It is possible, though, to use the results of density functional calculations as input into rigorous evaluations of excitation energies, as shown, for example, by Hybertsen and Louie [42].

The highest occupied electronic level in a metallic system is called the Fermi energy or Fermi level, E_F. The nature of the electronic states at E_F play a crucial role in determining materials properties such as electrical conductivity, magnetism, and superconductivity. On surfaces, the energy difference between E_F and the electrostatic potential in the vacm region, V_0, above the surface is the work function, Φ. While in general the Kohn-Sham eigenvalues are not excitation energies, it was shown by Schulte in 1977 [43] that for a metallic system the highest occupied Kohn-Sham eigenvalue can be directly interpreted as the work function. Thus, the agreement between experimental and calculated work functions provides a good test for the quality of actual calculations. With present LDA approaches, the calculated values are typically within 0.1-0.2 eV of the experimental results.

3. Spin-polarization

So far, the discussion of density functional theory was restricted to non-spin-polarized cases. However, many systems such as magnetic transition metals or molecules such as O_2 involve unpaired electrons or molecular radicals and thus require a spin-polarized method. In such systems, the number of electrons with "spin-up" can be different from that with "spin-down". In the early 1970's, von Barth and Hedin [44] and Gunnarson et al. [45] generalized density functional theory to accommodate spin-polarized systems. This resulted in spin density functional theory with the local spin density (LSD) approximation.

Explicit form of local spin density exchange-correlation terms as given by von Barth and Hedin [44]

$$\epsilon_{\mathrm{xc}}(\rho,\zeta) = \epsilon_{\mathrm{xc}}^{p}(\rho) + \left[\epsilon_{\mathrm{xc}}^{f}(\rho) - \epsilon_{\mathrm{xc}}^{p}(\rho)\right] f(\zeta)$$

$$\epsilon_{\mathrm{xc}}^{p} = \epsilon_{\mathrm{x}}^{p} + \epsilon_{\mathrm{c}}^{p} \qquad \epsilon_{\mathrm{x}}^{p} = \frac{3}{2}\left(\frac{3}{\pi}\rho\right)^{1/3} \qquad \epsilon_{\mathrm{c}}^{p} = -0.0225\, F\left(\frac{r_s}{21}\right)$$

$$\epsilon_{\mathrm{xc}}^{f} = \epsilon_{\mathrm{x}}^{f} + \epsilon_{\mathrm{c}}^{f} \qquad \epsilon_{\mathrm{x}}^{f} = 2^{1/3}\epsilon_{\mathrm{x}}^{p} \qquad \epsilon_{\mathrm{c}}^{f} = -0.01125\, F\left(\frac{r_S}{53}\right)$$

$$F(x) = (1+x^3)\ln\left(1+\frac{1}{x}\right) + \frac{x}{2} - x^3 - \frac{1}{3} \qquad f(\zeta) = \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3}} \qquad \zeta = \frac{\rho_\uparrow - \rho_\downarrow}{\rho}$$

Exchange-correlation potential

$$\mu_{\mathrm{xc}}^{\sigma} = A(\rho)\left(\frac{2\rho_\sigma}{\rho}\right)^{1/3} + B(\rho) \text{ with } \sigma = \uparrow or \downarrow$$

$$A(\rho) = \mu_x^p(r_s) + v_c(r_s) \qquad B(\rho) = \mu_c^p(r_s) + v_c(r_s)$$

$$\mu_c^p = -0.0225\ln\left(1+\frac{21}{r_s}\right) \qquad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

$$v_c = -\frac{4}{3}\,\frac{1}{2^{1/3}-1}\left[0.01125\, F\left(\frac{r_s}{53}\right) - 0.0225 F\left(\frac{r_s}{21}\right)\right]$$

Energies and potentials are given in Hartree atomic units; the units for the electron and spin densities are number of electrons/(Bohr radius)^3.

In the local spin density functional (LSDF) theory, the fundamental quantities are both the electron density, $\rho(\boldsymbol{r})$, and the spin density, $\sigma(\boldsymbol{r})$. The spin density is defined as the difference between the density of the spin-up electrons and the density of the spin-down electrons

$$\sigma(\boldsymbol{r}) = \rho_{\uparrow}(\boldsymbol{r}) - \rho_{\downarrow}(\boldsymbol{r}) \tag{1-21}$$

with the total electron density

$$\rho(\boldsymbol{r}) = \rho_{\uparrow}(\boldsymbol{r}) + \rho_{\downarrow}(\boldsymbol{r}) \tag{1-22}$$

In LSDF theory, the exchange-correlation potential for spin-up electrons is in general different from that for spin-down electrons. Consequently, the effective potential (1-13) becomes dependent on the spin. Thus, the Kohn-Sham equations (1-12) in their spin-polarized form are

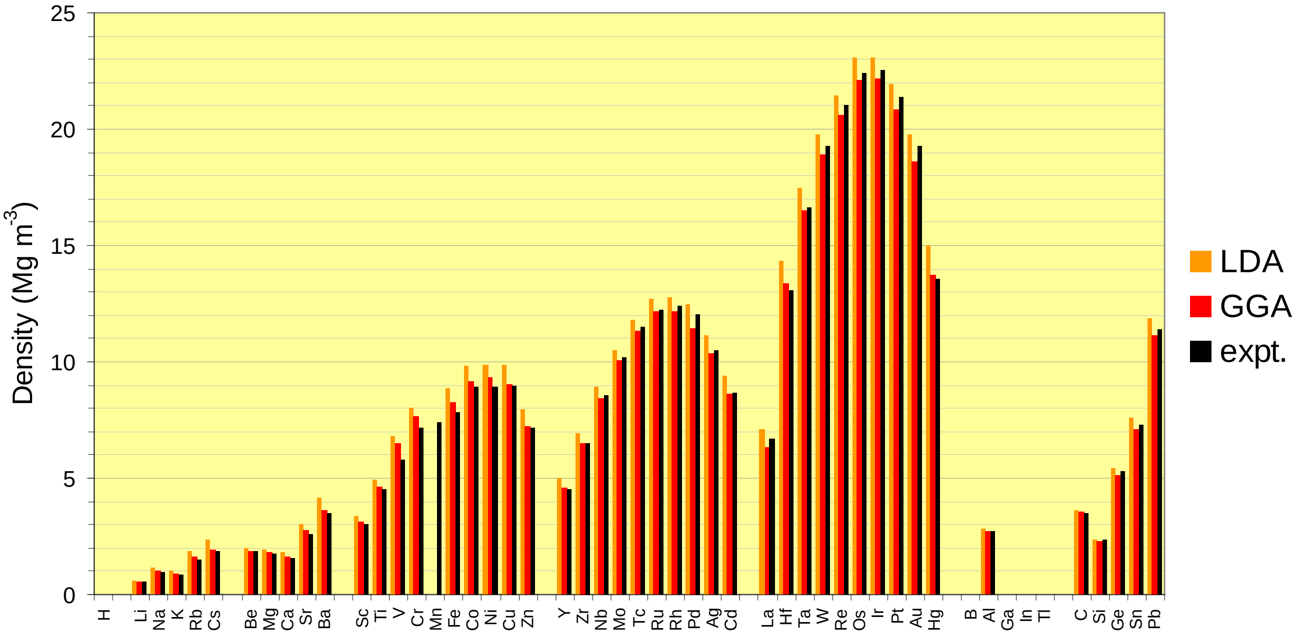
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}^{\sigma}(\epsilon_i^{\sigma})\right]\Psi_i^{\sigma}(\boldsymbol{r}) = \epsilon_i^{\sigma}\Psi_i^{\sigma}(\mathbf{r}), \qquad \sigma = \uparrow \text{ or } \downarrow \tag{1-23}$$

with

$$V_{\text{eff}}^{\sigma}(\mathbf{r}) = V_c + \mu_{\text{xc}}^{\sigma}[\rho(\mathbf{r}), \sigma(\mathbf{r})] \tag{1-24}$$

The exchange-correlation potential in LSDF theory depends on both the electron density and the spin density, as written in equation (1-24). There are two sets of single-particle wave functions, one for spin-up electrons and one for spin-down electrons, each with their corresponding one-electron eigenvalues. For the case of equal spin-up and spin-down densities, the spin density is zero throughout space and LSDF theory becomes identical with the LDF approach. Notice that in spin-polarized calculations, the occupation of single-particle states is 1 or 0, but there is still only one Fermi energy. In magnetic systems, the spin-up and spin-down electrons are often referred to as "majority" and "minority" spin systems. The table in the next section gives an example of the local spin density exchange-correlation formula by von Barth and Hedin [44].

4. Generalized Gradient Approximation



A large number of total energy calculations have shown that the LDA gives interatomic bond lengths within ±0.05 Å of experiment or better for a great variety of solids, surfaces, and molecules. However, the following systematic trends are found:

- most lattice parameters predicted with LDA are too short
- weak bonds are noticeably too short, for example the Ni-C bond in the Ni carbonyl $Ni(CO)_4$, the bond between two magnesium atoms (which are closed shell systems), and the length of hydrogen bonds such as that in the water dimmer $H\text{-}O\text{-}H — OH_2$;
- the binding energies calculated with the LDA are typically too large, sometimes by as much as 50% in strongly bound systems and even more in weakly bound materials.

Gradient-corrected density functionals as suggested by Perdew [46], Becke [47], Perdew and Wang [7], and Perdew, Burke, and Ernzerhof [8]offer a remedy. The basic idea in these schemes is the inclusion of terms in the exchange-correlation expressions that depend on the gradient of the electron density and not only on its value at each point in space. Therefore, these corrections are also sometimes referred to as "non-local" potentials. The table below gives the form suggested by Becke (1988) for the exchange part and Perdew (1986) for the correlation.

While dissociation energies calculated with these corrections rival in accuracy the best post-Hartree-Fock quantum chemistry methods, gradient corrected density functional calculations are computationally much less demanding and more general. Gradient corrected density functionals have been studied extensively for molecular systems, for example by Andzelm and Wimmer [48].The results are very encouraging and this approach could turn out to be of great value in providing quantitative thermochemical data.

The one-particle eigenvalues obtained from gradient-corrected exchange-correlation potentials are not significantly different from the LDA eigenvalues. Therefore, these potentials do not (and are not intended to) remove the discrepancy between calculated and measured energy band gaps.

Gradient-correction to the total energy for exchange by Becke [47]and correlation by Perdew [7]

$$E_{\mathrm{GGA}} = E_{\mathrm{LSD}} + E_{\mathrm{x}}^{G} + E_{\mathrm{C}}^{G}$$

Becke (1988):[47],
gradient-corrected exchange

$$E_{x}^{G} = b\sum\int\frac{\rho_{\sigma}x_{\sigma}^{2}}{1+6bx_{\sigma}\sinh^{-1}x_{\sigma}}\,d\mathbf{r}$$

$$x_{\sigma} = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad \sigma = \uparrow \text{ or } \downarrow$$

Perdew (1986): [46]
gradient-corrected correlation

$$E_{c}^{G} = \int f(\rho_{\uparrow},\rho_{\downarrow})e^{-g(\rho)|\nabla\rho|}|\nabla\rho|^{2}\,d\mathbf{r}$$

Energies are given in Hartree atomic units; the units for the electron and spin densities are number of electrons / (Bohr radius)^3. The constant *b* in Becke's formula is a parameter fitted to the exchange energy of inert gases. The explicit form of the functions *f* and *g* in Perdew's expression for the correlation energy is given in the original paper by Perdew [46].

5. Relativistic Effects

Electrons near an atomic nucleus achieve such high kinetic energies that relativistic effects become noticeable even for light atoms at the beginning of the periodic table. For elements with an atomic number above about 54 (Xe) these relativistic effects become quite important and should be included in electronic structure calculations. The relativistic mass enhancements of electrons near the nuclei lead to a contraction of the electronic charge distribution around the nuclei compared with a non-relativistic treatment. For atoms with about Z>54 non-relativistic calculations therefore can overestimate bond lengths by 0.1 Å and more. Furthermore, relativistic effects change the relative energy of *s*, *p*, *d*, and *f*-states which can have a significant impact on bonding mechanisms and energies.

Relativistic effects lead to a spin-orbit splitting which is, for example, about 0.3 eV for the splitting between the $4f_{5/2}$ and $4f_{7/2}$ in Ce. For core states, the spin orbit splitting can be very large. For example, the $2p_{1/2}$ and the $2p_{3/2}$ core states in W are split by 1351 eV. Important effects on surfaces such as the Kerr rotation in magneto-optical devices or the x-ray dichroism involve spin-orbit splitting. Thus, a relativistic electronic structure theory is necessary. This is accomplished by solving the Dirac equations, as discussed, for example, in the textbooks by Bjorken and Drell [49][50]and Messiah [51]. Within a spherically symmetric potential, the Dirac equations, like the non-relativistic Schrödinger equation, can be decomposed into a radial and angular part. For illustration, we show the radial equations

$$-\frac{dF_{nlj}(\mathbf{r})}{d\mathbf{r}} + \frac{\kappa}{\mathbf{r}}F_{nlj}(\mathbf{r}) = [E - m + V_{\mathrm{eff}}(\mathbf{r})] \tag{1-25}$$

$$\frac{dG_{nlj}(\mathbf{r})}{d\mathbf{r}} + \frac{\kappa}{\mathbf{r}} G_{nlj}(\mathbf{r}) = [E - m + V_{\mathrm{eff}}(\mathbf{r})] \tag{1-26}$$

$$\begin{array}{ccccc} & s & p & d & f \\ l = & 0 & 1 & 2 & 3 \\ j = & \frac{1}{2} & \frac{1}{2}, \frac{3}{2} & \frac{3}{2}, \frac{5}{2} & \frac{5}{2}, \frac{7}{2} \\ \kappa = & -1, & 1, -2 & 2, -3 & 3, -4 \end{array} \tag{1-27}$$

$$\kappa = \begin{cases} -(l+1) \\ l \end{cases} \text{and } j = \begin{cases} l + \frac{1}{2} \\ l - \frac{1}{2} \end{cases} \tag{1-28}$$

F and G are called the large and small component of the radial wave function. The quantum numbers n and l are equivalent to the non-relativistic case; j labels spin-orbit-split states and is used as subscript to label states such as $2p_{1/2}$ $2p_{3/2}$ and the $4f_{5/2}$. The quantum number κ is a convenient quantity used within relativistic computer programs. The radial part of the charge density is constructed from the large and small components by

$$\rho(\mathbf{r}) = \sum_{nlj} \left[\left| F_{nlj}(\mathbf{r}) \right|^2 + \left| \mathrm{G}_{\mathrm{nlj}}(\mathbf{r}) \right|^2 \right] \tag{1-29}$$

The correct treatment of exchange and correlation in a fully relativistic theory is a difficult problem and has not yet been completely resolved. However, reasonable approximations are available.

Koelling and Harmon [52]have proposed a semi-relativistic (or scalar-relativistic) treatment. This approach involves an averaging over the spin-orbit splitting, but retains the kinematic effects. This restores most of the simplicity of a non-relativistic method, but still gives an excellent representation of the core electron distribution and the appropriate (spin-orbit averaged) energies of the valence electrons.

B. Thermodynamics

This section reviews the basic tenets of thermodynamics in application to the phase equilibria. In an open system such as a solid that is absorbing gas, the chemical potential of the gaseous component must be equal in the gas and in the solid. This establishes a critical link between the well-known properties of the gas and the properties (to be computed) of the gaseous component atoms in the solid. The equilibrium constant that relates the composition in the solid to the pressure of the gas is determined by the nature of the standard states that are chosen for two phases. These standard states are discussed at length, as they must be thoroughly understood before one can know how to put thermochemical and computational information together to determine the equilibrium constant.

1. Essential Thermodynamic Equations

It will be beneficial to review thermodynamics so as to provide a single source for the essential equations that are required to analyze the thermodynamics of mixtures. The presentation will be brief, and is not meant to be more than a compilation of reference equations. However, the aim is to provide enough descriptive text so that the equations are understandable. The general approach is taken from the monograph of Kirkwood and Oppenheim [53].

The combined statements of the first and second laws of thermodynamics for an open system that can do no work other than the work of expansion, and which is dominated by bulk phases that have negligible surface area, is given by

$$dE = T\,dS - p\,dV + \sum_i \mu_i\,dn_i \tag{2-1}$$

The symbols have their usual meaning, namely:

T = absolute temperature

S = entropy

p = pressure

V = volume

n_i = number of moles of component *i*

$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,\boldsymbol{n}\backslash n_i}$ is the chemical potential of component i

the notation $\boldsymbol{n}\backslash n_i$ means the set of all n_j , except for n_i.

An intensive variable is independent of the mass of the system. These are , p, and μ_i. Extensive variables are proportional to the mass of the system — E, S, V, and n_i.

Equation can be integrated holding the intensive variables fixed, to get

$$E = TS - pV + \sum_i \mu_i n_i \qquad (2\text{-}2)$$

where the integration constant is seen to be zero because an empty system has no energy, volume, entropy, or mass. Now, eq. (2-12) has been derived for a particular temperature, pressure, and set of chemical potentials. However, we are free to consider arbitrary changes in the state of the system once we have this equation, as nothing special was assumed about the values of the intensive variables, *i.e.*, the equation must hold for all values of those variables. Thus

$$\mathrm{d}E = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i + \sum_i n_i\,\mathrm{d}\mu_i \qquad (2\text{-}3)$$

but eq. (1-1)still holds, and on substituting it for $\mathrm{d}E$ and canceling terms, one gets

$$SdT - Vdp + \sum_i n_i\,\mathrm{d}\mu_i = 0 \qquad (2\text{-}4)$$

which is sometimes known as Gibbs's eq. (97)[53], but is most often called the Gibbs-Duhem equation. This deceptively simple equation is critically important for understanding phase equilibria and mixture thermodynamics.

It is usual to define auxiliary thermodynamic functions for convenience. The enthalpy, H, is $H = E + pV$, the Helmholtz free energy is $A = E - TS$, and the Gibbs free energy G is

$$G = E + pV - TS = H - TS = \sum_i \mu_i n_i \qquad (2\text{-}5)$$

where use is made of eq. (2-2) to provide the -most member.

From the definition $G = E + pV - TS$ one computes the differential

$$dG = dE + pdV + Vdp - TdS - SdT \qquad (2\text{-}6)$$

and substitution from eq.(2-2) for dE gives

$$dG = V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_i \mu_i\,\mathrm{d}n_i \qquad (2\text{-}7)$$

These equations seem to chase their own tails, but they are all slightly different and all true.

Each of these differentials is understood to provide relations between derivatives of the functions on the left by the variables on the right. From eq. (2-7), for example, one sees that $G = G(p, T, n_1, n_2, \ldots) = G(p, T, \boldsymbol{n})$, meaning that the Gibbs free energy is most naturally considered to be a function of the indicated variables. When viewed this way, it follows that

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,\mathbf{n}\backslash n_i} \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,\mathbf{n}} \quad S = -\left(\frac{\partial G}{\partial T}\right)_{p,\mathbf{n}} \tag{2-8}$$

since for any function $F(x, y, \dots)$ the differential is $dF = \left(\frac{\partial F}{\partial x}\right) dx + \left(\frac{\partial F}{\partial y}\right) dy + \cdots$

Furthermore, the second derivatives of a function of several variables are independent of the order of differentiation, which establishes the Euler-Maxwell relations

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\mathbf{n}} = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,\mathbf{n}\backslash n_i} = \bar{V}_i \tag{2-9}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\mathbf{n}} = \left(\frac{\partial S}{\partial n_i}\right)_{p,T,\mathbf{n}\backslash n_i} = -\bar{S}_i \tag{2-10}$$

that are of great use in treating mixtures. The derivatives on the right, those with respect to the number of moles of substance, define the partial molar volume and partial molar entropy, denoted by the over-bar. The chemical potential in eq. (2-8) is seen to be the partial molar Gibbs free energy. For a pure substance, $X = n\bar{X}$, where X is any extensive variable, so that the partial molar $\bar{X}$ for a pure substance is identically the same as the molar X.

2. Thermodynamics of Non-ideal Gases

The equation of state for an ideal gas is

$$V = NkT/p \tag{2-11}$$

in molecular units. For a pure non-ideal gas it is customary to add terms in powers of pressure to the hand side, so that

$$\bar{V} = \frac{RT}{p} + B_2(T)p + B_3(T)p^2 + \dots \tag{2-12}$$

where we've switched to molar units. Eq. (2-7)for constant T and $\mathbf{n}$ is just

$$d\bar{G} = d\mu = \bar{V}\, dp \tag{2-13}$$

per mole of pure gas. Add and subtract $RT\, dp/p$ on the right hand side of eq. (2-13) to get

$$d\mu = \left(\bar{V} - \frac{RT}{p}\right) dp + RT\, d\ln p \tag{2-14}$$

and integrate between two states, the lower labeled by * and the upper arbitrary, to get

$$\mu(p) - \mu(p^*) = \int_{p^*}^{p} \left(\bar{V} - \frac{RT}{p}\right) dp + RT \ln\frac{p}{p^*} \tag{2-15}$$

> *Since p always appears as a ratio under the logarithm, the units are immaterial. However, in the next step the log of the ratio is pulled apart, seemingly creating dimensions. This is only apparent, and one must keep in mind eq. (1-15) with its ratio of pressures.*

We are now positioned to define the standard state for the gas. In asserting eq. (2-12), all gases become ideal when sufficiently dilute. Rearrange the equation and take the limit as p^* goes to zero to first obtain

$$\mu(T,p) = [\mu(T,p^*) - RT\ln p^*] + RT\ln p + \int_{p^*}^{p} \bar{V} - \frac{RT}{p}\,\mathrm{d}p$$

and then

$$\mu(T,p) = \mu^0(T) + RT\ln p + \int_0^p \left(\bar{V} - \frac{RT}{p}\right)\mathrm{d}p \tag{2-16}$$

in the limit, where now

$$\mu^0(T) = \lim_{p^* \to 0}[\,\mu\,(T,p^*) - RT\ln p^*] \tag{2-17}$$

The temperature dependence of the chemical potential, previously omitted from consideration on suppression of the $S\,\mathrm{d}T$ term, is reinstated in the definition of chemical potential as a reminder that this quantity is a function of temperature in general. Note that the standard state chemical potential of the gas is a function of T alone, and is not a real state, but is instead a measure of the intrinsic chemical properties of the gas apart from the equation of state properties. The standard state chemical potential of the gas, $\mu^0(T)$, is precisely what one calculates in the usual isolated molecule (gas phase) quantum statistics calculation of the free energy.

In anticipation of the chapter on chemical equilibrium, it is noted here that chemists like to keep the remaining integral in eq. (2-6) under the logarithm. The fugacity, f, is therefore defined such that

$$\ln f = \ln p + \int_0^p \left(\frac{V}{RT} - \frac{1}{p}\right)\mathrm{d}p \tag{2-18}$$

and

$$\mu(T,p) = \mu^0(T) + RT\ln f \tag{2-19}$$

for all pressures. The fugacity coefficient γ, defined by $f = \gamma p$, is just

$$\gamma = \exp\left[\int_0^p \frac{V}{RT} - \frac{1}{p}\,\mathrm{d}p\right] \tag{2-20}$$

Substitution of the virial equation, eq. (2-12), into eq. (2-20) allows one to write this as a power series in the pressure. However, the virial coefficients, the $B_i(T)$, must be determined by experiment or statistical mechanics; they are not calculable from thermodynamics alone.

It should be apparent that there is a straightforward part of thermodynamics, the $p\,dV$ part and the entwined equation of state, $V(p,T)$, that can be handled explicitly. The other part, the $T\,dS$ term, is more difficult. However, there is a piece of the entropy that we can get at this stage. Eq. (2-9) shows us that $\bar{S} = -\left(\frac{\partial \mu}{\partial T}\right)_p$ for a pure substance. This is messy if we are going to differentiate eqs. (2-19) and (2-20), but for the ideal gas one gets the simple equation

$$\bar{S}^{\text{ideal}}(T,p) = \bar{S}^0(T) - R\ln p \qquad \text{(2-21)}$$

showing that the $\ln p$ term is contributed by the entropy, not the enthalpy.

3. Thermodynamics of Ideal Solutions

A discussion of solutions, including phase equilibria, begins with Gibbs's eq. (97) [our eq.(2-4)]. For a multi-component mixture at constant T and p, one has simply

$$\sum_i n_i \, dn_i = 0 \qquad \text{(2-22)}$$

Divide this equation by the total number of moles of substances that comprise the mixture, $n = \sum_i n_i$ and define the mole fraction of component i as $X_i = n_i/n$, so that $1 = \sum_i \frac{n_i}{n} = \sum_i X_i$, and therefore

$$0 = \sum_i dX_i \qquad \text{(2-23)}$$

Now eq. (2-22) can be written

$$\sum_i X_i \, d\mu_i = 0 \qquad \text{(2-24)}$$

What is the simplest assumption that one can make for the $d\mu_i$ such that this equation is satisfied? The answer is provided by eq.(2-23); simply put $d\mu_i = A\left(\frac{dX_i}{X_i}\right)$, where A is any constant. It follows that the simplest solution to the Gibbs-Duhem equation is provided by chemical potentials of the form

$$\mu_i = \mu_i^{\dagger} + A\ln X_i \qquad \text{(2-25)}$$

This equation must be true for gases as well as for liquids and solids. That is sufficient to establish that $A = RT$.

> *The $\mu_i^{\dagger}$ term is an integration constant, which must be allowed to be a function of any variables not explicitly integrated. For a gas mixture, the pressure is implicit in this term. To expose this dependence one asserts Dalton's law of partial pressure, $p_i = X_i p$, so that eq.(3-3) becomes*

$\mu_i = \mu_i^0 + RT\ ln(X_i p)$. This is perfectly consistent with eq. (2-8) for a pure ideal gas, i.e., $X_i = 1$, and is also consistent with eq (3-3).. This establishes the value of the constant A for gases, and in anticipation of equating chemical potentials for substances at equilibrium in different phases, the constant is RT for all phases.

This simple law is to mixtures what the ideal gas law is to gases, and it defines an "ideal mixture" as one with

$$\mu_i^{\text{ideal}} = \mu_i^0 + RT\ lnX_i \tag{2-26}$$

When this equation is inserted into the right hand side of eq. (2-5) we get, after a little rearrangement,

$$\Delta G_M^{\text{ideal}} = \sum_i n_i\ (\mu_i - \mu_i^0) = RT \sum_i n_i \ln X_i \tag{2-27}$$

which is the change in Gibbs free energy on forming an ideal mixture from the specified number of moles of pure components. Since the right hand side is directly proportional to T, it follows that the free energy change is entirely entropic. There is no heat of mixing for an ideal solution, nor is there a volume change (since the right hand side of eq. (2-27) is independent of pressure). To include these effects, one needs to study non-ideal mixtures.

4. Thermodynamics of Non-ideal Solutions

If a mixture of interest is non-ideal (which can only be decided by experiment or a statistical mechanical calculation), a modification of eq. (2-26) that adheres to the "preservation of logarithmic function" principle asserts that the mole fraction be transformed to "activity," so that

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{2-28}$$

where the activity of component i, a_i, is a function of composition as well as T and p, in general. In applying eq. (2-28) to condensed phases, both liquids and solids, one needs a convention for the standard state. For mixtures that might span the entire range of compositions it is convenient to choose the pure substances as standard states, so that

$$\lim_{X_i \to 1} \frac{a_i}{X_i} = 1 \text{ and } \mu_i^0 = \lim_{X_i \to 1} \mu_i \tag{2-29}$$

On the other hand, if the mixtures are always relatively dilute in at least one component, the k^{th}, the standard state for this component is most conveniently chosen to be the infinitely dilute state, so that

$$\lim_{X_k \to 0} a_k / X_k = 1 \text{ and } \mu_k^0 = \lim_{X_k \to 0} [\mu_k - RT \ln X_k] \tag{2-30}$$

It is unfortunate that the same symbol is used for these two different standard states, as it is a trap for the unwary when consulting tabulated thermochemical data. In any event, eq.

(2-30) is the standard state that one wants to use to describe the solubility of a sparingly soluble gas in a metal, as will be shown in Section Equation of Chemical Equilibrium.

For a non-ideal mixture, one may write the analogue of eq. (2-27) as

$$\Delta G_M = \sum_i n_i \left(\mu_i - \mu_i^0\right) = RT \sum_i n_i \ln a_i. \tag{2-31}$$

This form is preferred if there is only experimental, and no theoretical, knowledge about the system. However, if the departures from the ideality are relatively small, it is common to retain the ideal entropy of mixing and simply add in corrections for the enthalpy of mixing and possibly also an “excess” entropy of mixing. To keep the mathematics simple, restrict attention to a binary mixture. A first approximation to non-ideality may be written

$$\Delta G_M = RT[\, n_1 \ln X_1 + n_2 \ln X_2 + B\, n_1 X_2] \tag{2-32}$$

which supposes that the mixture thermodynamics is symmetric [since $n_1X_2 = n_1n_2/(n_1 + n_2)$]. Here B might be taken to be a (dimensionless) constant; alternatively it may be expressed as a power series in the composition with coefficients that depend on T and p, in the same spirit as the non-ideal gas. Assuming the former behavior to keep this discussion simple, the chemical potential that is derived from eq. (2-32) by differentiation is

$$\mu_1 - \mu_1^0 = \left(\frac{\partial \Delta G_M}{\partial n_1}\right)_{T,p,n_2} = RT[\ln X_1 + BX_2^2] \tag{2-33}$$

[Eq. (2-4) can be used to show that departure from ideality can only enter as the square or higher power of the concentration, *when pure components are the standard states*. The result in eq. (2-33) is thus quite general when the BX_2^2 term is seen as the first term in a power series for the chemical potential. Note that it is a power series in the mole fraction of the other component; it has to be this way so that the added terms go to zero as the mole fraction of the other components vanishes and component 1 becomes pure.]

The behavior of the chemical potential when the dilute limit is chosen for the standard state can be much more complicated. Now one wants to write departures from ideality for the dilute solute, component 2 for this discussion, as

$$\mu_2 = \mu_2^0 + RT \ln X_2 + CX_2^a + \cdots \tag{2-34}$$

where a is any positive power. This choice is made because we want the non-ideal terms to go to zero as the mole fraction of this component goes to zero. For this choice of standard state, it is not difficult to see that eq. (2-4) is almost powerless in constraining the form of the departures from ideality. A case in point is provided by Debye-Hückel theory of electrolytes, for which $a = ½$. The flexibility in the functional form of departures from ideality for this choice of standard state has great consequences for gas solubility, as we will see.

In summary, the choice of standard states has a profound effect on the allowed expressions for the free energy of non-ideal mixtures. For the problem at hand one wants to choose the pure metal, or possibly a pure compound $M_a Y_b$, as the standard state for the solid, and the infinitely dilute absorbed atom (H, O, C, …) as the standard state for the second component.

5. Equation of Chemical Equilibrium

A very brief recapitulation of the equations of chemical equilibrium is in order to clarify some issues of units, where to apply non-ideality corrections, and so on. One begins by associating the components of a mixture with a chemical reaction

$$aA + bB \rightleftarrows cC + dD \tag{2-35}$$

This can be written formally in a manner that is more suitable for thermodynamic analysis as

$$\sum_k \nu_k A_k = 0 \tag{2-36}$$

where the stoichiometric coefficients, ν_k , are positive for products and negative for reactants.

The Gibbs free energy of the mixture, regardless of the reaction, is just

$$G = \sum_k n_k \mu_k \tag{2-37}$$

Suppose now that the system suffers a virtual displacement resulting from the reaction proceeding (virtually, either to the right or to the left). Since $dG_{T,p} = \sum_k \mu_k\, dn_k$ at constant T and p from eq.(2-7), and since the change in the amounts of the substances are related by the chemical eq. (2-36) as expressed by $dn_k = \nu_k\, d\lambda$, one can relate the general change in free energy to the reaction. The *progress variable* λ may have either sign, positive for the reaction to the and negative for the reaction to the . In any case,

$$dG_{T,p} = \sum_k \mu_k\, dn_k = \sum_k \nu_k \mu_k\, d\lambda = \Delta G_{rx}\, d\lambda \tag{2-38}$$

where the free energy change for the reaction, ΔG_{rx} , is defined by the sum of the chemical potentials with given stoichiometric coefficients, positive for products and negative for reactants. Now, if the system is at equilibrium, any virtual displacement away from equilibrium must increase the free energy (as is established by thermodynamic conditions for stability that are not considered in this report, but which may be found in the references[54][53]). That is, at equilibrium the free energy is at a minimum with respect to the progress variable, so that

$$\Delta G_{rx} = 0 \tag{2-39}$$

Now we can proceed rapidly. Use eq.(2-28) for the chemical potential of any component, to write

$$\Delta\, G_{rx} = 0 = \sum\nolimits_{k} \nu_k \mu_k = \sum\nolimits_{k} \nu_k [\mu_k^0 + RT \ln a_k] = \Delta G_{rx}^0 + RT \ln \prod\nolimits_{k} a_k^{\nu_k} \qquad (2\text{-}40)$$

or

$$\prod\nolimits_{k} a_k^{\nu_k} = \exp \frac{\Delta G_{rx}^0}{RT} \qquad (2\text{-}41)$$

with

$$\Delta\, G_{rx}^0 = \sum\nolimits_{k} \nu_k \mu_k^0 = \Delta\, H_{rx}^0 - T\Delta\, S_{rx}^0 \qquad (2\text{-}42)$$

For gaseous components, replace the corresponding activity by fugacity. This is the extremely important *mass action* principle of chemistry. Note that the equation is dimensionless.

> *It is possible to define mass action ratios with dimensions, but compensating standard state terms must appear on the right of eq.(2-41) to make the units balance. Specific examples should be worked through in detail, paying close attention to the definition of standard states, if there is any dimensional ambiguity.*

The thermodynamics is left in this general form at this point, but the equations will be specialized to gas solubility problems later in the report. The equations above apply to any thermodynamic problem that conforms to the restrictions of the second paragraph of Section Essential Thermodynamic Equations, that is the only work is the work of expansion against an isotropic pressure.

The last topic for this section is the use of tabulated data to compute ΔG_{rx}^0. Now that we understand standard states for gases, pure substances, and infinitely dilute solutions, it should be apparent that the data that is tabulated for heats of formation, third law entropies, and free energy functions, can be assembled with use of eq. (2-42) to find the free energy at any temperature that is encompassed by the tabulation. Free energies of formation are normally tabulated, for which the substance in its standard state is produced from the elements in their standard states. But for free energies of formation the temperature is referenced to 25°C, and at this temperature the free energies of formation as well as the heats of formation of the elements in their standard states are zero. However, one will see third law entropies for the elements that are not zero in the standard state, so one must exercise care in combining free energies, enthalpies, and entropies of reactions to be certain that reference states, standard states, and arbitrarily chosen zeros of energy are treated consistently.

C. Theory of Elasticity

1. Definition of Elastic Constants

To determine the elastic constants of a crystal, a deformation of the unit cell is created by changing the Bravais lattice vectors $\mathbf{R} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ of the undisturbed unit cell to $\mathbf{R}' = (\mathbf{a}', \mathbf{b}', \mathbf{c}')$ using a strain matrix ***e***

$$\mathbf{R}' = \mathbf{R}\begin{pmatrix} \mathbf{1 + e_{xx}} & \mathbf{\frac{1}{2} e_{xy}} & \mathbf{\frac{1}{2} e_{xz}} \\ \mathbf{\frac{1}{2} e_{yx}} & \mathbf{1 + e_{yy}} & \mathbf{\frac{1}{2} e_{yz}} \\ \mathbf{\frac{1}{2} e_{zx}} & \mathbf{\frac{1}{2} e_{zy}} & \mathbf{1 + e_{zz}} \end{pmatrix} \qquad (3\text{-}1)$$

The deformation leads to a change of the total energy of the crystal

$$U = \frac{(E_{\text{tot}} - E_0)}{V_0} = \frac{1}{2}\sum_{i=1}^{6}\sum_{j=1}^{6} C_{ij}\, e_i e_j \qquad (3\text{-}2)$$

where E_0 is the total energy of the unstrained lattice, V_0 is the volume of the undistorted cell and the C_{ij} are the elements of the **elastic constant matrix** with a notation that follows standard convention.

Both *i* and *j* run from 1…6 in the sequence {xx, yy, zz, yz, xz, xy}. The tensor of elasticity has 36 elements, the elastic constants, but maximally 21 of these are independent. The symmetry of the unit cell can reduce the number of independent elastic constants for the various symmetry systems as shown in the following table:

Number of independent elastic constants for unit cells of different symmetry

CRYSTAL SYSTEM	ELASTIC CONSTANTS
Triclinic	21
Monoclinic	13
Orthorhombic	9
Tetragonal	6 or 7
Rhombohedral	6 or 7
Hexagonal	5
Cubic	3

2. Calculation of Elastic Constants

The simplest case by far is the cubic system where there are only three independent constants, C_{11}, C_{12},and C_{44}. We use this case to illustrate the manner in which the stiffness matrix elements may be determined from strain fields of the form (3-1).If the applied strain is $e_{xx} = e$ with all other e_i equal to zero, the energy change is $U = C_{11}\frac{e^2}{2}$. This allows a unique determination of C_{11}. If $e_{yz} = e_{zy} = \frac{e}{2}$, with all other strain components zero, then $U = C_{44}\frac{e^2}{2}$ and we have an independent determination of C_{44}. The bulk modulus, B, is the response to a uniform compression so applying the strain field $e_{xx} = e_{yy} = e_{zz} = e$ allows the computation of B via the relation $U = \frac{Be^2}{2}$. Similarly, the shear modulus can be calculated by using the strain field $e_{zz} = e;\ e_{xx} = e_{yy} = -\frac{e}{2}$, whereupon $U = 3C'\frac{e^2}{2}$. Finally, the off-diagonal stiffness matrix element C_{12} can be calculated using one or other of the relations

$$B = 1/3(C_{11} + 2C_{12}) \qquad (3\text{-}3)$$

$$C' = 1/2(C_{11} - C_{12}) \qquad (3\text{-}4)$$

Using both of these relations provides a useful independent check on the accuracy of the computation. A symmetry-general formulation of the calculation of elastic constants from total energy calculations is given by Le Page and Saxe [55].

a. Computational Aspects

The current implementation in MEDEA is based on stress [56]. VASP calculates the stress tensor, *i.e.* the derivatives of the total energy of the cell with respect to changes of the 6 lattice parameters (cell lengths and angles), using analytic expressions. With a single value for the amount of distortion for each of the necessary strains, it is possible to obtain the elastic constants. For simplicity, the amount of distortion is called "strain" in the VASP interface. A good value for the strain is 2%. If this value is too small the changes in the stress may be too small for accurate tracking. If *e* is too large, anharmonicity of the energy may play a role. Several strains can be used to get more points for the fitting procedure involved in the calculation of the elastic constants, thus leading to a higher numerical stability.

The elastic constants can be calculated for the equilibrium structure (at zero pressure) of a crystal, which is the usual case, or for distorted lattices. To ensure that the equilibrium structure does correspond to zero strain, the initial optimization of the theoretical cell parameters must be made with extremely high accuracy. In particular, for metallic systems a fine k-mesh (k-spacing of about 0.2 Å^{-1}) and the tetrahedron integration scheme should be used. The geometry convergence criterion should be 0.01 eV/Å and the SCF convergence criterion needs to be set at 1.0e-06 or 1.0e-07.

Experimental values for the lattice constants, even where these are available, should not be used because the *theoretical* lattice will be in a state of strain for these values. This is because in the first instance, theory and experiment will not agree exactly and in the second, the experimental error is unknown and probably of the same order as the strain field one needs to apply.

3. Polycrystalline Materials: Voigt-Reuß-Hill Method

The stiffness matrix calculated as above refers to the perfect lattice. However, approximate values referring to polycrystalline samples that take into account orientational disorder can be estimated from the single crystal data if one assumes that the elastic behavior is determined by the individual crystallites and not grain boundary effects. A thorough analysis of this issue can be found in a paper by Anderson [57]. The basic method, the Voigt-Reuß-Hill method, devolves from the expression for the shear modulus, G,

$$G_{\text{Hill}} = \frac{1}{2}\left[G_{\text{Voigt}} + G_{\text{Reuß}}\right] \tag{3-5}$$

For cubic lattices, the Voigt and Reuß approximations for the shear modulus, G_{Voigt} and $G_{\text{Reuß}}$, are:

$$G_{\text{Voigt}} = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \tag{3-6}$$

and

$$G_{\text{Reuß}} = \frac{5}{4(S_{11} - S_{12}) + 3S_{44}} \tag{3-7}$$

where $\boldsymbol{S}$ is the compliance matrix (*i.e.* the inverse matrix to $\boldsymbol{C}$). Hill gave arguments that the Voigt and Reuß approximations represent lower and upper bounds to the true value of G and that therefore the arithmetic mean should give a better estimate of G than either approximation. Checks by Anderson showed this to be true. Since the bulk moduli of the perfect crystal and a mono-phase polycrystal are the same, elastic data for the polycrystalline phase amount just to using the shear modulus as given by (3-5), (3-6), (3-7) in place of the value for the perfect crystal.

Once B and G are determined, Poisson's ratio, σ, and Young's modulus, Y, are given by the standard formulae of elasticity

$$\sigma = \frac{1}{2}\frac{B - \frac{2}{3}G}{B + \frac{1}{3}G} \tag{3-8}$$

and

$$Y = \frac{9B}{1 + \frac{3B}{G}} \qquad (3\text{-}9)$$

Correspondingly, the mean values for the transverse and longitudinal sound velocities v_t and v_l are given in terms of the elastic moduli and the mean density, ρ, by

$$v_t = \sqrt{G/\rho} \qquad (3\text{-}10)$$

and

$$v_l = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \qquad (3\text{-}11)$$

Finally, the mean sound velocity, v_m, is

$$v_m = \left(\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right)^{-1/3} \qquad (3\text{-}12)$$

4. Thermal expansion and heat capacity

In the discussion in the previous sections temperature played no role and the computation of the elastic constants referred to zero temperature. For a harmonic lattice, as is well known, the mean lattice parameters and elastic constants are independent of temperature. The observed temperature dependence of these quantities devolves from *anharmonic* behavior of the energy, which is why the computation of the coefficient of thermal expansion is one degree more difficult than the computation of the zero temperature elastic constants. The foundation for the computation of thermal corrections to lattice parameters was laid down by Grüneisen [58], remarkably, before the wide-spread acceptance of quantum mechanics! Of course, Grüneisen could only write down formulae. Even the simplest computation was beyond the capacity of hand calculators. Today, however, it is possible to implement Grüneisen's work, again using DFT as a generator of energies and forces, and the results can be very spectacular.

The full implementation of Grüneisen's theory requires evaluation of the material's phonon spectra and the derivatives of the individual phonon frequencies with respect to the cell parameters. However, there is a lower level of theory, the Grüneisen-Debye approximation, that allows computation of the thermal expansion coefficient with essentially no more effort than the elastic constants. In fact, for a cubic material the only additional information to the elastic constants that is required is an averaged Grüneisen constant, γ_G. As a first step, which is implemented, the Grüneisen constant is set to 2.

The next step, which is planned, is the determination of γ_G from the pressure-volume, or internal energy-volume equation of state. A convenient approximation that incorporates γ_G as a parameter is [59],

$$E(V) = \frac{BV_0}{\frac{5}{6} - \gamma_G} \left(\frac{V}{V_0} \right)^{\frac{5}{6} - \gamma_G} \left(\ln \frac{V}{V_0} - \frac{1}{\frac{5}{6} - \gamma_G} \right) + E_\infty \tag{3-13}$$

where V_0 is the equilibrium volume. Since γ_G is essentially the third derivative of $E(V)$, the computation of this function must be carried out with high accuracy and great care. This can however be done.

Once γ_G is obtained, the only other input required to compute the thermal expansion coefficient is the Debye temperature, which is determined by exploiting its relationship to the sound velocity *i.e.*

$$\theta_D = \frac{\hbar}{k_B} \left(\frac{6\pi^2 q}{V_0} \right)^{1/3} v_m \tag{3-14}$$

where q is the number of atoms in the unit cell, V_0 its volume, and $\hbar$and k_B are the Planck and Boltzmann constants, respectively. The lattice contribution to the specific heat capacity, c_V, as a function of temperature, T, can then be calculated via (see, for example, [59])

$$c_{V(T)} = 9 q k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} \frac{x^4 \exp\, x}{(\exp x - 1)^2} \,ⅆx \tag{3-15}$$

where $x_D = \frac{\theta_D}{T}$, and the linear thermal expansion coefficient, α_L, is given via the standard relation [60]

$$\alpha_L(T) = \frac{1}{3} \gamma_G \frac{c_V(T)}{B\, V_0} \tag{3-16}$$

D. Vibrations in Solids – Phonons

1. Overview

MEDEA-PHONON is a computational tool for deriving vibrational properties of solids from first principles. This section covers the underlying physical theorems and equations, provides a comprehensive overview on methods and numerical techniques.

- Optionally impose translational and rotational invariance on forces to improve accuracy.
- Modelling longitudinal optical branches close to LO/TO splitting with an approximate scheme based on Born effective charges and dielectric constants for polar crystals.
- Analyze irreducible representations of phonon modes at the Γ -point as well as Infrared and Raman activities.
- Debye-Waller factors and incoherent inelastic neutron scattering based on off-diagonal phonon density of states
- Thermodynamic functions decomposed into contributions of individual atoms and polarization directions: internal energy E, free energy F, entropy $S$and heat capacity c_V as a function of temperature.
- Intensity (form factors) of coherent neutron scattering in different Brillouin zones and different geometries.
- Doubly differential incoherent inelastic neutron scattering cross sections of one-phonon processes for monocrystals and of up to five-phonon processes for polycrystals.

2. Background

A detailed knowledge of lattice vibrations is critical for the understanding and quantitative prediction of a wide variety of physical properties of solids. The interpretation of optical, infrared, Raman and synchrotron spectroscopic methods as well as neutron scattering experiments rely on an accurate theoretical approach to lattice dynamics. The fundamental thermodynamic functions of internal and free energy, entropy, heat capacity as well as non-linear properties such as thermal expansion and heat conduction are to a considerable extent determined by the vibrations of the constituent atoms in the lattice. Further phenomena such as electrical resistivity of metals, superconductivity and the temperature dependence of optical spectra are governed by electron-phonon coupling. Fortunately, the quantum theory of lattice dynamics is well developed and has proven to be one of the most successful theories of solid state physics and therewith provides an impressive reassurance of the validity and applicability of the concepts of quantum theory in general.

From a historical point of view, the fundamental theory of lattice dynamics was developed in the 1930's and was reviewed in the book of Born and Huang [61], which is still regarded as a standard textbook in the field. In those early days, the main interest focused on general properties of the dynamical matrix, e.g. its symmetry and analytical properties, but less emphasis was put on its underlying physical origin based on the interactions of the constituent ions and electrons. The first approaches to theoretically determine phonon dispersion relations were based on lattice-dynamical models with adjustable parameters to be fitted to experimentally measured frequencies, e.g. from inelastic neutron scattering experiments, and were mainly used as a mean to interpolate between experimental data points. These model potentials either did not account for electronic polarization at all, like in the force-constant model, Born-von Kármán model, Born-Mayer potentials for alkali halides or Lennard-Jones potentials for noble gas crystals [61], or polarization effects were approximated by electric dipoles generated by relative displacements of the shells of valence electrons relative to the ion cores (shell models [62; 63; 64]). In addition, in order to tackle systems with highly anisotropic electron distributions as found in covalently bonded crystals, alternative models have been developed, relying on angular forces (Keating models [65]) or bond charges (bond charge model[66; 67]). The predictive capabilities of these methods turned out to be quite limited. Although experimental phonon dispersions are accurately reproduced close to the data used for fitting – especially along high symmetry directions – predictions along lower-symmetry directions frequently failed due to the lack of a rigorous description of the interactions among constituent atoms. The first attempts to investigate the connections between the electronic structure and the dynamical properties were made as late as in the early seventies and were based on dielectric matrices or the electron polarizability [68; 69].

With the advent of density functional theory [29; 3] and the progress with numerical methods for solving quantum physical equations together with the emergence of more and more powerful computers made it feasible to accurately describe the interatomic interactions in crystals and molecules based on quantum mechanics. It is thus possible, nowadays, to calculate a large variety of properties of simple materials without relying on input data from experiments. These so-called first-principles or ab-initio methods also revolutionized the practical approaches to lattice dynamics and accurate theoretical phonon dispersion curves can be calculated completely independent of any experimental knowledge.

Three different techniques for *ab initio* evaluation of vibrational properties have been developed, namely

direct methods based on total energy changes or forces calculated for atoms displaced from their equilibrium position,

analytical calculation of force constants based on a perturbative expansion around the equilibrium geometry,

Fourier transform of the atomic velocity autocorrelation function obtained from a molecular dynamics trajectory [70].

The third option usually suffers from difficulties to reach equilibrium within reasonable simulation times, although several technical tricks have been developed to address these problems (e.g. Nosé-Hoover thermostat [71] and multiple signal classification (MUSIC) algorithm [72; 73; 74]).

The second option makes use of the fact that the lattice distortion associated with a phonon is a static perturbation acting on the electrons, causing a linear response of the electron density which determines the energy variation up to third order ($2\nu + 1$ theorem [75]). The linear variation of the electron density is determined in terms of the linear response of the Kohn-Sham orbitals applying first-order density functional perturbation theory [76; 77]. This method is assessed as quite accurate, efficient and elegant, however, requiring highly specialized *ab initio* computer codes and considerable implementation efforts. For a review of the formalism and implementation of density functional perturbation theory and its application see [78].

Direct methods (option (i) above) require the evaluation of total energy and forces for the equilibrium geometry as well as of several distorted geometries from which the force constant matrix can be assembled. Several different techniques are subsumed under the title direct methods: in the early eighties, the first attempts for *ab initio* lattice dynamics simulation were based on frozen phonon total energy calculations to derive accurate phonon frequencies for specific high symmetry points in the Brillouin zone (e.g. [79]). Phonon dispersion curves along specific high symmetry directions in reciprocal space were determined by the method of interplanar force constants [80], where planes perpendicular to these directions are displaced within an elongated supercell. Since these one-dimensional force constants between high-symmetry planes are linear combinations of the three-dimensional interatomic force constants, the phonon dispersion can be derived, in principle, for general directions [81; 82]. The most general direct approach to lattice dynamics is based on the *ab initio* evaluation of forces on all atoms produced by a set of finite displacements of a few atoms within an otherwise perfect crystal. The perfect crystal environment has to be sufficiently large to ensure that interactions of the perturbation with all its translational symmetry equivalent copies are small, which usually requires construction of suitable supercells. The techniques for selecting suitable supercells and atomic displacements, assembling force constant matrices from the calculated forces and calculating phonon dispersion relations via Fourier transform are described in Refs. [83; 84; 12]. Phonon dispersion curves determined from direct approaches are very accurate provided the studied crystal area (supercell) is larger than the interaction range of all constituent atoms. The main advantages of direct methods consist in the fact that no specialized *ab initio* codes are required, as long as forces can be derived, and that anharmonic effects can be treated in a straightforward manner. The necessity to consider supercells in the case of simple crystal structure with small unit cell extensions is one of the main drawbacks with regards to the linear response methods.

The MedeA-Phonon module is based on the general direct approach to lattice dynamics and is designed to work independent of a specific underlying code for deriving forces and total energies. However, together with the Vienna Ab-initio Simulation Package (Vasp) [85; 2; 5; 86] a fully automatic and highly parallel procedure is provided within MedeA.

3. Theory of Lattice Dynamics

In this section the basic theory of lattice dynamics is summarized and the essential analytical and numerical aspects of the direct approach to the calculation of phonon dispersions are discussed in detail. Furthermore, relevant equations for calculating form factors, thermodynamic functions, thermal displacements and neutron scattering cross sections as implemented in the PHONON module are provided. For further details of the theory as well as applications in diverse research fields we refer to several recent review articles [78; 87; 88; 12].

a. Crystal Symmetry

The crystal structure is subject to space group symmetry

$$G = \{h_1|\tau_1\}, \}, \{h_2|\tau_2\}, \dots \{h\_g|\tau_g\} \qquad (4\text{-}1)$$

h_i are the point group symmetry elements and $\tau_{\square}$ are partial translations. The point group of the crystal G contains all point symmetry elements h_i. All atomic positions can be generated from non-equivalent sites applying these symmetry operations. For each non-equivalent atom μ with site point group $P_\mu\{p_i\}$ the space group can be decomposed into left cosets with respect to P_μ

$$G = \left\{h_1^{(\mu)}\middle|\tau_1^{(\mu)}\right\}P_\mu + \left\{h_2^{(\mu)}\middle|\tau_2^{(\mu)}\right\}P_\mu + \cdots + \left\{h_{g/l}^{(\mu)}\middle|\tau_{g/l}^{(\mu)}\right\}P_\mu \qquad (4\text{-}2)$$

Applying the generating symmetry elements $\left\{h_1^{(\mu)}\middle|\tau_1^{(\mu)}\right\}$, all equivalent atom positions are found.

b. Basic Relations and Approximations

The ground state energy E of a crystal as a function of atom positions $R(n,\mu)$ (where n denotes the unit cell and μ the atom index) can be written as a Taylor expansion in terms of atomic displacements around the equilibrium positions

$$E(..R(n,\mu)..R(m,\nu)..) = E_0 + \frac{1}{2}\sum_{n,\mu,m,\nu} \Phi(n,\mu;m,\nu)U(n,\mu)U(m,\nu) + O(U^3) \qquad (4\text{-}3)$$

E_0 is the equilibrium energy. Terms linear in U are absent due to the condition that at equilibrium all forces on the atoms vanish. The elements of the atomic force constant matrix are defined by

$$\Phi_{\mathrm{i},j}\ (n,\mu;m,\nu) = \left[\frac{\partial^2 E}{\partial R_i(n,\mu)\partial R_j(m,\nu)}\right]_0 \qquad (4\text{-}4)$$

with the gradients taken at the minimum energy configuration for which all first order derivatives vanish. The frequently used harmonic approximation consists in retaining in equation (4-3) only terms up to quadratic order in the displacements.

Within the harmonic approximation the classical equations of motion for each atom are

$$M_\mu \ddot{U}(n,\mu) = \sum\nolimits_{n,\mu,m,\nu} \Phi(n,\mu;m,\nu)U(m,\nu) \tag{4-5}$$

where M_μ is the atom mass of atom μ. Solutions are required to exhibit Bloch-wave form because of translational invariance.

$$U(n,\mu) = \frac{1}{M_\mu} e(k) e^{ikR(n,\mu)-i\omega t} \tag{4-6}$$

The k vectors are chosen to fulfill Born-von Kármán periodic boundary conditions:

The equation of motion can thus be cast into the simple form

$$D(k)e(k,j) = \omega^2(k,j)e(k,j) \tag{4-7}$$

where for each mode j the phonon frequencies $\omega^2(k,j)$ are the eigenvalues and the polarization vectors $e(k,j)$ are the eigenvectors of the dynamical matrix $D(k)$, which has been introduced as the discrete Fourier transform

$$D(k;\mu,\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum\nolimits_m \Phi(0,\mu;m,\nu) e^{2\pi i k[R(0,\mu)-R(m,\nu)]} \tag{4-8}$$

The summation m runs over all atoms of the crystal. The forces $F(n,\mu)$ on all atoms generated by the displacement $U(m,\nu)$ of atom ν can be written as

$$F_i(n,\mu) = \sum\nolimits_{m,\nu,j} \Phi_{i,j}(n,\mu;m,\nu)U_j(m,\nu) - \tag{4-9}$$

which relates the generated forces with the force constant matrices and atomic displacements. This is the central relation of the direct method.

The complete quantum mechanical description for a system of ions and electrons requires additional approximations. Since the nuclear mass is much larger than that of an electron, it is reasonable to consider the nuclei in their equilibrium position while dealing with the electronic motion. In mathematical terms this so-called adiabatic (or Born-Oppenheimer) approximation yields a separation of the general Schrödinger equation into one for the motion of nuclei and one for the electrons. The nuclear motion is determined by the potential field generated by the average motion of the electrons and the corresponding nuclear Schrödinger equation yields formally the same results as the classical theory. Above equations remain valid, however, with the exact effective potential. The purely electronic Schrödinger equation can be solved within density functional theory [8], which is discussed in section 1.

c. Symmetry Properties of Force Constants

The atomic force constants exhibit certain symmetry properties related to the crystal symmetry. Because of the translational invariance of the crystal, force constants depend only on the difference $R(n,\mu) - R(m,\nu)$ and satisfy the acoustic sum rule

$$\sum_{n,\mu,m,\nu} \Phi(\,n,\mu;m,\nu) = 0 \qquad (4\text{-}10)$$

which expresses the invariance of the potential energy on uniform translations of the whole crystal.

Therefore, a force constant $\Phi(m,\mu;n,\nu)$ represents a bond between atoms (m,μ) and (n,ν). The bond point group $B\ =\ \{b_1,b_2,\ldots,b_b\}$ leaves this specific bond invariant and its elements b_i span a subgroup of the point group of the crystal. The symmetry of force constants therefore is set by transformations by b_i, which reduces the number of independent parameters. Furthermore, each force constant can be decoupled into a part A determined exclusively by symmetry and a part P which is dependent on potential strength. The potential parameters contained in P are no longer dependent on any other element. This decoupling allows the use of fitting procedures on a minimal set of independent parameters. The crystal space group can be decomposed with respect to the bond point group B

$$G = \left\{h_1^{(b)}\middle|\tau_1^{(b)}\right\}B + \left\{h_2^{(b)}\middle|\tau_2^{(b)}\right\}B + \cdots + \left\{h_{g/l}^{(b)}\middle|\tau_{g/l}^{(b)}\right\}B \qquad (4\text{-}11)$$

Therefore, knowing the symmetry of one force constant, all remaining equivalent ones can be created by applying the generating symmetry elements $\left\{h_i^{(b)}\middle|\tau_i^{(b)}\right\}$

d. Supercell Force Constants for the Direct Method

The *ab initio* calculations for the direct approach are performed for a supercell constructed as a multiplication of the original primitive cell with periodic boundary conditions. There are symmetry implications for the force constants resulting from the supercell geometry. The symmetry elements of the supercell point group $\hat{S}\ =\ \{s_1,s_2,\ldots,s_s\}$ leaves the supercell as parallelepiped (not as crystal) invariant. The point group symmetry of the supercell crystallite $\widehat{H}$consists of the common point symmetry elements of the supercell point group $\hat{S}$ and the point group of the crystal Ĝ, i.e. $\widehat{H}\ =\ \hat{S} \cap \hat{G}$. The supercell crystallite space group H (including translations and partial translations) can be equal to the crystal space group G, or it can be a subgroup of G. In the second case, some equivalent atoms become non-equivalent, and site and bond point groups are reduced to corresponding subgroups. As a consequence, the symmetry of phonon modes derived from these supercell calculations might be reduced and degeneracy of modes may be decreased.

The direct method for calculating vibrational properties starts with an optimization of the atom positions (and lattice parameters) of the unperturbed supercell introduced in the previous paragraph. Any computational method providing atomic forces is suitable for the direct approach, but usually first-principles methods are employed. After the initial total energy minimization process all forces should vanish, and the resulting structure is the reference and starting point for all further steps. In order to obtain complete information on all force constants it is necessary to displace each non-equivalent atom of the supercell along three non-equivalent directions, and to calculate for each of these perturbed supercells the forces on all other atoms generated by this displacement. The non-equivalent atoms and directions are defined with respect to the supercell crystallite space group H. Further reduction of the number of displacements is possible: if the site point group of the atom is cubic, a single displacement along a single fourfold axis is adequate. If the site point group is tetragonal, one displacement along the fourfold symmetry axis and one perpendicular to it are sufficient.

The use of supercells with periodic boundary conditions rather than interaction shells has some consequences on the definition of force constants. The displacement $U(m,\nu)$ of an atom (m,ν) reappears for all atoms $(m+L,\nu)$ in all images L of the supercell due to periodicity. $L = (L_a, L_b, L_c)$ are the lattice constant indices of the supercell. Thus, the displacement of a single atom (m,ν) in the original supercell generates on atom (n,μ) a net force

$$F_i(n,\mu) = -\sum_L \Phi_{i,j}(n,\mu;m+L,\nu)U_j(m,\nu) = -\Phi_{i,j}^{(\Sigma)}(n,\mu;m,\nu)U_j(m,\nu) \qquad (4\text{-}12)$$

where the cumulative force constant is defined as

$$\Phi_{i,j}^{(\Sigma)}(n,\mu;m,\nu) = \sum_{\mathrm{L}} \Phi_{\mathrm{i,j}}(n,\mu;m+L,\nu) \qquad (4\text{-}13)$$

and the summation L runs over all supercell images. In order to make sure that all neighbors of a given interaction shell are taken into account for constructing the dynamical matrix, the atom (n,μ) under consideration is positioned at the center of an extended supercell, which has the same size as the original one but includes all atoms on its surface planes, edges and corners. The extended supercell, in general, contains more atoms than the conventional one. If the displaced atoms $(m+L,\nu)$ for several L are located at the same distance from the considered atom (n,μ), *i.e.* if they are located at the surface of the extended supercell, the corresponding force constant has to be scaled by the factor ${}^{1}\!/_{n_m}$, where n_m is the number of equivalent atoms at the surface. Thus, the supercell force constants are defined as

$$\Phi_{i,j}^{(SC)}(n,\mu;m,\nu) = 1/n_m \sum_L \Phi_{i,j}^{\Sigma}(n,\mu;m+L,\nu) \qquad (4\text{-}14)$$

and the net force can be written as

$$F_i(n,\mu) = -\sum_{(m,\nu)\in SC} \Phi_{i,j}^{(SC)}(n,\mu;m,\nu)U_j(m,\nu) \qquad (4\text{-}15)$$

where the summation is limited to atoms of the extended supercell. The supercell force constants may have higher symmetry than the conventional ones, provided by the symmetry relations among the equivalent surface atoms.

The above equation has to be solved in the direct method, yielding the supercell force constants from the known forces and displacement variables. As stated in section IV.D.3.cSymmetry Properties of Force Constants for force constants in general, also the supercell force constants can be decoupled into a matrix A determined by symmetry and the matrix P of independent potential parameters. The net force is

$$\begin{aligned} F(n,m) & \\ &= -\sum_{m,\nu\in SC} A(n,\mu;m,\nu)P^{(SC)}(n,\mu;m,\nu)U(m,\nu) \\ &= C(n,\mu;m,\nu)P^{(SC)}(n,\mu;m,\nu) \end{aligned} \qquad (4\text{-}16)$$

where the matrix C is defined as

$$C(n,\mu;m,\nu) = -\sum_{(m,\nu)\in SC} A(n,\mu;m,\nu)U(m,\nu) \qquad (4\text{-}17)$$

The main equation of the direct method is cast into the simple global form

$$F = C \cdot P^{(SC)} \Longrightarrow P^{(SC)} = C^{-1} \cdot F \qquad (4\text{-}18)$$

Usually the number of forces is larger than the number of independent parameters, and the system is over-determined. Equation (4-18) is solved by an algorithm for the singular value decomposition of the sparse matrix C [89]. All supercell force constants can be expressed in terms of the potential parameters $P^{(SC)}$.

e. Translational-Rotational Invariance

The forces should satisfy automatically the translational-rotational invariance conditions guaranteeing that all acoustic modes start at zero frequency at the Γ-point. Due to numerical errors of the forces as obtained in actual *ab initio* calculations, this condition is not exactly fulfilled. It is possible, however, to enforce the invariance conditions in the derivation of the force constants.

For the case of supercell force constants with an interaction range confined inside the supercell, the translational-rotational invariance conditions are

$$\sum_{(m,\nu)\backslash inSC} \Phi^{(SC)}_{i,j}(n,\mu;m,\nu) = 0 \qquad (4\text{-}19)$$

$$\sum_{(m,\nu)\in SC} [\varPhi^{(SC)}_{I,j}(n,\mu;m,\nu)R_k(m,\nu) - \varPhi^{(SC)}_{i,j}(n,\mu;m,\nu)R_j(m,\nu)] = 0 \qquad (4\text{-}20)$$

where the summation is limited to the atoms of the extended supercell, $R(m,\nu)$ are position vectors and i, j, k are Cartesian indices. In the simple global form, the invariance conditions can be written as $0 = M \cdot P^{(SC)}$, where M is a $(18n \times p)$ matrix. Here, n is the number of atoms in the primitive unit cell, p is the number of potential parameters and 18 is the sum of 9 translational and 9 rotational equations. This equation may be added to the main equation of the direct method and the resulting equations can be solved by singular value decomposition. The β factor specifies the strength of enforcement of the invariance conditions.

$$\begin{pmatrix} F \\ 0 \end{pmatrix} = \begin{pmatrix} C \\ \beta M \end{pmatrix} \cdot P^{(SC)} \tag{4-21}$$

f. Supercell Dynamical Matrix

The direct method yields supercell force constants from the forces and by discrete Fourier transform the supercell dynamical matrix is obtained:

$$D^{(SC)}(k;\eta,\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum\nolimits_{m\in SC} \Phi^{(SC)}\,(0,\mu;m,\nu)\mathrm{e}^{-2\pi i\; k\cdot[R(0,\mu)-R(m,\nu)]} \tag{4-22}$$

Here, the atom $(0,\mu)$ is located at the center of the extended supercell and summation is limited to all neighbors of this cell. The summation over images of the supercell is already included in the supercell force constant.

The supercell dynamical matrix becomes identical to the conventional dynamical matrix for all k vectors if the supercell is large enough such that the interaction range is confined inside. In this case all phonon frequencies are calculated exactly. If the interaction exceeds the extended supercell size, both dynamical matrices are identical only for special reciprocal vectors k_s fulfilling the condition

$$\exp\{-2\pi i k_s \cdot a_{sc}\} = 1 \quad \exp\{-2\pi i k_s \cdot b_{SC}\} = 1 \quad \exp\{-2\pi i k_s \cdot c_{SC}\} = 1 \tag{4-23}$$

where a_{SC}, b_{SC} and c_{SC} are the basis vectors of the extended supercell. For these special vectors k_s the phonon frequencies are calculated exactly. Furthermore, the accuracy of phonon frequencies mainly depends on the mutual symmetries of the supercell and the wave vector. The precision of phonon frequencies for a discrete wave vector k_s can be assessed by considering the point groups $\hat{G}, \hat{S}$, and $\hat{G}_{ks}$ of the crystal space group G, the supercell and the wave vector k_s, respectively. The accuracy is

Exact if $\hat{S} = \hat{G}$ and $\hat{G}_{k_z} \subseteq \hat{S}$ (4-24)

High precision $\hat{S} \subset \hat{G}$ and $\hat{G}_{k_z} \subseteq \hat{S}$ (4-25)

Low precision $\hat{S} = \hat{G}$ and $\hat{G}_{k_z} \not\subset \hat{S}$ (4-26)

For wave vectors fulfilling the requirements for exact solutions, the phonon frequencies and degeneracy are exactly calculated from the supercell. For wave vectors satisfying the requirement for high precision the supercell approach usually yields highly precise phonon frequencies but the exact mode degeneracy is not guaranteed . As a consequence, modes along equivalent directions with respect to $\hat{G}$ but non-equivalent directions with respect to $\hat{S}$ might have different frequencies and degeneracy. Modes for k_s vectors fulfilling the criterion for low precision suffer from the same deficiencies but in addition may also have poorer frequency values, because the list of neighbors is far from complete. All intermediate phonon branches are interpolated between these special vectors k_s. Supercells providing the maximal number of exact wave vectors are: $n \times n \times n$ for cubic, $n \times n \times m$ for tetragonal, $n \times n \times n$ for hexagonal (rhombohedral), and $n \times m \times l$ for orthorhombic, monoclinic and triclinic symmetry, respectively. The shape of the supercell should be as close as possible to a cube to obtain accurate frequencies for all directions, elongated supercells may be applied to achieve high accuracy in the direction of elongation.

g. Phonon Dispersion and Polarization Vectors

The frequencies $\omega^2(k,j)$ of phonon modes j are calculated by diagonalization of the supercell dynamical matrix for each wave vector k along a specified path through the Brillouin zone, thus creating phonon dispersion curves.

$$D(k) \cdot e(k.j) = \omega^2(k,j)e(k,j) \tag{4-27}$$

The irreducible representations of all phonon modes at the Γ point can be calculated, providing in addition Raman and infrared activities of the modes. The complex polarization vectors satisfy the orthonormality relations

$$\sum_j e_i^*(k,j;\mu) \cdot e_i(k;j;\nu) = \delta_{i,l}\, \delta_{\mu,\nu} \tag{4-28}$$

$$\sum_i \sum_\mu e_i^*(k,j;\mu) \cdot e_i(k,j;\mu) \; = \delta_{i,j} \tag{4-29}$$

The polarization vectors $e(k,j;\mu)$ defined for the wave vector k centered at the origin of reciprocal space differ from the conventional polarization vector $e(k_\tau,j;\mu)$ as defined for the wave vector k_τ pointing from the center of a given Brillouin zone labeled by the reciprocal vector τ. Because of $k = \tau + k_\tau$ the relation between these differently defined polarization vectors is

$$e(k,j;\mu) = e(k_\tau,j;\mu)\exp\left[-2\pi\tau \cdot r_\mu\right] \tag{4-30}$$

Using the polarization vectors, the displacements caused by a particular phonon and its intensity can be calculated. Assuming amplitude Q_k and phase $0 \leq \phi_k \leq 1$ of the displacement wave, the displacements $U(n,\mu)$ of atoms (n,μ) for a given wave vector k and phonon branch j are given by the equation

$$U(n,\mu) = \frac{Q_k}{2\sqrt{M_\mu}} \begin{Bmatrix} \mathrm{Re}\, e(k,j;\mu)\cos[2\pi(k \cdot R(n,\mu) - \phi_k] - \\ -\mathrm{Im}\, e(k,j;\mu)\sin[2\pi(k \cdot R(n,\mu) - \phi_k)] \end{Bmatrix} \tag{4-31}$$

The intensity of phonon modes is obtained from the form factors. The form factor projected on the wave vector is defined as

$$F^{(p)}(k,j) = \frac{1}{k^2}\left|\sum_{\mu k} \frac{k \cdot e(k,j;\mu)}{\sqrt{M_\mu}}\right|^2 \tag{4-32}$$

However, the intensity of a phonon mode is represented by the simple form factors

$$F^{(s)}(k,j) = \frac{1}{k^2}\left|\sum\nolimits_{\mu} \frac{e(k,j;\mu)}{\sqrt{M_\mu}}\right|^2 \tag{4-33}$$

which may be applied to remove unessential phonon branches originating from backfolding, or to estimate relative intensities of all modes in varying Brillouin zones.

h. Phonon Density of States

The phonon density of states $g(\omega)$ provides the frequency distribution of normal modes and is obtained as a histogram plot from

$$g(\omega) = \frac{1}{nd\Delta\,\omega}\sum_{k,j} \delta_{\Delta\omega}\left(\omega - \omega(k,j)\right) \text{ where } \delta_{\Delta\omega}(x) = \begin{cases} 1 & \text{if } -\frac{\Delta\omega}{2} < x \leq \frac{\Delta\omega}{2} \\ 0 & \text{otherwise} \end{cases} \tag{4-34}$$

The summation covers all n wave vectors homogeneously distributed in the first Brillouin zone and all phonon branches. The frequency interval of the histogram is denoted $\Delta\omega$ and d is the dimension of the dynamical matrix (equal to the number of phonon branches and the number of degrees of freedom in the unit cell). The phonon density of states is normalized

$$\int g(\omega)\, d\omega = 1 \tag{4-35}$$

The partial phonon density of states provides the contribution of one specific atom μ vibrating along a particular Cartesian direction

$$g_{i,\mu}(\omega) = \frac{1}{nd\Delta\omega}\sum\nolimits_{k,j} |e_i(k,j;\mu)|^2 \delta_{\Delta\omega}\left(\omega - \omega(k,j)\right) \tag{4-36}$$

satisfying the normalization condition (d being the number of degrees of freedom, again).

$$\int g_{i,\mu}(\omega)\, d\omega = \frac{1}{d} \tag{4-37}$$

The off-diagonal partial phonon density of state is defined as

$$g_{il,\mu}(\omega) = \frac{1}{nd\Delta\omega}\sum\nolimits_{k,j} e_i(k,j;\mu) e_l^*(k,j;\mu) \delta_{\Delta\omega}\left(\omega - \omega(k,j)\right) \tag{4-38}$$

where $e_i(k,j;\mu)$ and $e_l(k,j;\mu)$ are the i-th and l-th Cartesian components of the polarization vectors for particle μ and phonon frequency $\omega(k,j)$. The diagonal elements are the partial phonon density of states.

4. Thermodynamic Functions

The contribution of lattice vibrations to thermodynamic functions such as internal energy, free energy, entropy, heat capacity and thermal displacements are derived from the integrated phonon density of states. For each thermodynamic function the contributions of particular atoms and polarization directions can be separated making use of partial phonon densities of states. This section provides a brief summary of the equations involved. Since thermodynamic functions are sensitive to phonons of low frequencies, it is advised to check for correct low and high temperature limits. These limits are also summarized below.

a. Internal Energy

The internal energy of a crystal of N unit cells is given by $E_{\text{tot}} = NE,$ where E is the internal energy of the unit cell in the harmonic approximation

$$E = \sum_{i,\mu} E_{i,\mu} \qquad (4\text{-}39)$$

$$E_{i,\mu} = \frac{1}{2} d \int_0^\infty g_i,\mu(\omega) \hbar\omega \coth \frac{\hbar\omega}{2\, k_B T} \mathrm{d}\omega \qquad (4\text{-}40)$$

Herein, $E_{i,\mu}$, is the contribution of atom μ and direction i to the internal energy, $g_{i,\omega}(\omega)$ is the corresponding partial phonon density of states, d is the number of degrees of freedom in the unit cell, ħ is the Planck constant, k_B is the Boltzmann constant and T is the temperature. The low and high temperature limits are

$$\lim_{T\to 0} E_{i,\mu} = \frac{1}{2} d \int_0^\infty g_{i,\omega}(\omega) \hbar\omega \, \mathrm{d}\omega \qquad (4\text{-}41)$$

$$\lim_{T\to \infty} E_{i,\mu} = k_B T \qquad (4\text{-}42)$$

b. Free Energy

The Helmholtz free energy of a crystal of N unit cells at a given volume is given by $A_{\text{tot}} = NA,$ where A is the Helmholtz free energy of the unit cell in harmonic approximation

$$A = \sum_{i,\mu} A_{i,\mu} \qquad (4\text{-}43)$$

$$A_{i,\mu} = d k_B T \int_0^\infty g_{i,\mu}(\omega) \ln \left[2 \sinh \frac{\hbar\omega}{2 k_B T} \right] \mathrm{d}\omega \qquad (4\text{-}44)$$

$A_{i,\mu}$ is the contribution of atom μ and direction i to the free energy. The low temperature limit of the free energy is equal to the mean energy of a given degree of freedom.

$$\lim_{T\to 0} A_{i,\mu} = \frac{1}{2} d \int_0^\infty g_{i,\mu}(\omega) \hbar\omega \, \mathrm{d}\omega \qquad (4\text{-}45)$$

c. Entropy

The entropy of the crystal is $S_{\text{tot}} = NS$ and the entropy of the unit cell S is described by

$$S = \sum_{i,\mu} S_{i,\mu} \tag{4-46}$$

$$S_{i,\mu} = dk_B \int_0^{\infty} g_{i,\mu}(\omega) \left\{ \frac{\hbar\omega}{2k_B T} \left[\coth\left(\frac{\hbar\omega}{2k_B T}\right) - 1 \right] - \ln\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right] \right\} \mathbb{d}\omega \tag{4-47}$$

where $S_{i,\mu}$ is the contribution of atom μ and direction i to the entropy. The low temperature limit of the entropy is

$$\lim_{T\to 0} S_{i,\mu} = 0 \tag{4-48}$$

d. Heat Capacity

Within the harmonic approximation the heat capacity at constant volume and at constant pressure are equal. The heat capacity of the crystal is $C_{V,\text{tot}} = C_{p,\text{tot}} = NC$, and the heat capacity of the unit cell C is represented in terms of contributions of atoms and directions $C_{i,\mu}$ by

$$C = \sum_{i,\mu} C_{i,\mu} \tag{4-49}$$

$$C_{i,\mu} = dk_B \int_0^{\infty} g_{i,\mu}(\omega) \left(\frac{\hbar\omega}{2k_B T}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2} \mathbb{d}\omega \tag{4-50}$$

The low and high temperature limits are

$$\lim_{T\to 0} C_{i,\mu} = 0 \tag{4-51}$$

$$\lim_{T\to \infty} C_{i,\mu} = k_B \tag{4-52}$$

e. Thermal Displacements, Debye-Waller Factor

Thermal vibrations have a considerable effect on neutron scattering data. The form factor describing diffraction scattering contains the Debye-Waller factor $exp[W_\mu(k)]$, where the argument $W_\mu(k)$

$$W_\mu(k) = \frac{1}{2}(2\pi k) \cdot B(\mu)(2\pi k) \tag{4-53}$$

is described in term of the 3×3 matrix $B(\mu)$ representing the static correlation function of displacements $U(\mu)$ of atom μ from the equilibrium position

$$B_{ij}(\mu) = \langle U_i(\mu) U_j(\mu) \rangle \qquad \text{(4-54)}$$

The symmetric matrix $B(\mu)$ represents the square mean displacements of an atom μ, and is determined by the off-diagonal partial phonon density of states

$$B_{il}(\mu) = \frac{\hbar d}{2M_\mu} \int_0^\infty g_{il,\mu}(\omega) \frac{1}{\omega} \coth \frac{\hbar\omega}{2k_B T} \, d\omega \qquad \text{(4-55)}$$

Debye-Waller factors are the main ingredient for analyzing cross sections for phonon creation in neutron scattering experiments.

5. Neutron Scattering

There are coherent and incoherent contributions to neutron scattering depending on the properties of the nuclei involved. To obtain sensible results, for each constituent nucleus some neutron scattering input data are required: the coherent scattering length $a_{\text{coh}}(\mu)$, the incoherent scattering cross section $\sigma_{\text{incoh}}(\mu)$, and the total scattering cross section for polycrystals $\sigma_{\text{tot}}(\mu)$. The main equations for obtaining neutron scattering cross sections are summarized below.

a. Coherent Neutron Scattering

The doubly differential coherent scattering cross section for the creation of one phonon is given by the expression

$$\frac{d^2\sigma_{\text{coh}}^{(+)}}{d\Omega \, dE} = \frac{K}{K_0} \sum_j \int F(k,j) \frac{\hbar}{2\omega(k,j)} \Big(n(\omega(k,j)+1) \delta(\kappa - k) \delta\big(\epsilon - \omega(k,j)\big) \Big) \, d\omega \qquad \text{(4-56)}$$

where the coherent form factor, also called dynamical structure factor, is defined as

$$F(k,j) = \left| \sum\nolimits_\mu a_{\text{coh}}(\mu) \exp[-W_{\mu(k)}] \frac{2\pi k \cdot e(k,j;\mu)}{\sqrt{M_\mu}} \right|^2 \qquad \text{(4-57)}$$

and

$$n(\omega(k,j)+1) = \frac{\exp \frac{\hbar\omega}{k_B T}}{\exp \frac{\hbar\omega}{k_B T} - 1} \quad \epsilon = E_0 - E \quad \kappa = K_0 - K \qquad \text{(4-58)}$$

Here, $\exp[-W_\mu(k)]$ denotes the Debye-Waller factor (see section 4.c Entropy and $a_{\text{coh}}(\mu)$ the coherent scattering length. Neutron scattering spectra are sensitive to the direction of incidental and scattered neutron beams and orientation of the monocrystal. This is taken into account in the equation above by the difference ϵ of energy of incident neutrons E_0 and scattered neutrons E, and by the neutron momentum change $\kappa = K_0 - K$, where K_0 indicates the direction of the incident neutron beam and K the direction of scattered neutrons. Both types of neutron scattering experiments, direct geometry (fixed energy of incident neutrons and spectrum given as a function of the energy of scattered neutrons) and inverse geometry (energy of scattered neutrons fixed and spectrum is shown as a function of energy of incident neutrons) may be simulated according to these equations.

b. Incoherent Neutron Scattering on Monocrystals

The one-phonon double differential incoherent neutron scattering cross section is calculated as a sum of contributions from all atoms of the unit cell

$$\frac{\mathbb{d}^2\,\sigma_{\text{incoh}}}{\mathbb{d}\Omega\;\mathbb{d}E} = \sum_{\mu} \frac{\mathbb{d}^2\sigma_{\text{incoh}}}{\mathbb{d}\Omega\;\mathbb{d}E}(\mu) \tag{4-59}$$

The contribution of one atom μ then is

$$\begin{gathered}\frac{\mathbb{d}^2\sigma_{\text{incoh}}}{\mathbb{d}\Omega\;\mathbb{d}E} = \sigma_{\text{incoh}}(\mu)\frac{K}{K_0}\sum_{k,j}\frac{\hbar}{2M_\mu\,\omega(k,j)}\left|\kappa\cdot e(k,j;\mu)\right|^2\cdot \\ \cdot\, n(\omega(k,j)+1)\;\; \mathrm{e}^{-2W_\mu(k)}\,\delta\big(\epsilon-\omega(k,j)\big)\end{gathered} \tag{4-60}$$

$\sigma_{\text{incoh}}(\mu)$ is a materials constant and denotes the incoherent scattering cross section for each atom μ, and all other quantities in this equation are explained in the previous section. In terms of the off-diagonal partial phonon density of states this equation reads

$$\begin{gathered}\frac{\mathbb{d}^2\sigma_{\text{incoh}}}{\mathbb{d}\Omega\;\mathbb{d}E} = \sigma_{\text{incoh}}(\mu)\frac{K}{K_0}\sum_{k,j}\frac{d\hbar}{2M_\mu}\int_0^\infty n(\omega(k,j)+1)\,\cdot \\ \cdot\,\mathrm{e}^{-2W_\mu(\kappa)}\sum_{i,l=1}^{3}\kappa_i\kappa_l\,g_{il,\mu}(\omega)\,\delta(\epsilon-\omega)\,\mathbb{d}\omega\end{gathered} \tag{4-61}$$

c. Incoherent Neutron Scattering on Polycrystalline Materials

For analyzing neutron scattering on polycrystalline materials contributions from both, incoherent and coherent scattering are considered. Since the coherent contribution disregards the wave vector conversation law due to orientational averaging, it is treated as effective incoherent scattering. For polycrystals, the double differential scattering cross section can be expressed for one-phonon as well as for multi-phonon processes.

The n-phonon orientationally averaged double differential neutron scattering cross section is written as a sum of contributions from all atoms in the unit cell

$$\frac{\mathbb{d}^2\sigma_{\text{incoh}}^{(\text{av})}(n)}{\mathbb{d}\Omega\;\mathbb{d}E} = \sum_{\mu}\frac{\mathbb{d}^2\sigma_{\text{incoh}}^{(\text{av})}(n,\mu)}{\mathbb{d}\Omega\;\mathbb{d}E} \tag{4-62}$$

The contribution of atom μ is

$$\frac{\mathrm{d}^2\sigma_{\mathrm{incoh}}^{(\mathrm{av})}(\mathrm{n},\upmu)}{\mathrm{d}\Omega\,\mathrm{d}E} = \sigma_{\mathrm{tot}}(\mu)\frac{K}{K_0}\exp\left[-2W_{\mu}^{(\mathrm{av})}(\kappa)\right]\frac{1}{n!}\left(\frac{\hbar^2\kappa^2}{2M_\mu}\right)^n$$

$$\int_{-\infty}^{\infty} f_\mu(\omega_1)\,\mathrm{d}\omega_1 \int_{-\infty}^{\infty} f_\mu(\omega_2)\,\mathrm{d}\omega_2 \ldots \int_{-\infty}^{\infty} f_\mu(\omega_n)\,\mathrm{d}\omega_n\,\delta(\epsilon-\omega_1-\omega_2-\cdots-\omega_n) \tag{4-63}$$

where

$$W_\mu{}^{(\mathrm{av})}(\kappa) = \frac{1}{6}\kappa^2\,\mathrm{Tr}\big(B(\mu)\big) \tag{4-64}$$

and the orientationally averaged Debye-Waller factor is

$$f_{\mu(\omega)} = \mathrm{d}\exp\frac{\frac{\hbar\omega}{k_BT}}{3\omega\left(\exp\frac{\hbar\omega}{k_BT}-1\right)}\left(g_{x,\mu}(\omega)+g_{y,\mu}(\omega)+g_{z,\mu}(\omega)\right) \tag{4-65}$$

6. LO/TO Splitting

Polar crystals exhibit splitting of infrared active optical modes into longitudinal and transversal modes at the Γ-point (so-called LO/TO split). The frequency of LO modes is raised above those of the TO modes as a consequence of the long-range part of the Coulomb interaction, *i.e.* the macroscopic electric field arising from the displacements of entire ionic sublattices. This field breaks the Born-von Kármán periodic boundary conditions and leads to a non-analytical term of the dynamical matrix at the Γ-point. As a consequence, without any further approximation the LO/TO mode splitting at the Γ-point cannot be treated with the direct method, and only the TO mode only is obtained.

Applying elongated supercells the phonon frequency at Γ will still be degenerate, however, it is possible to recover the $k \to 0$ limit of the LO branch by extrapolating the LO curve along the elongated direction from $k \neq 0$ to $k = 0$.

As an alternative to this procedure, *e.g.* in case the elongation of the cell would raise the system size beyond computational feasibility for the *ab initio* calculations, one may take into account the non-analytical contribution of the dynamical matrix in an approximate form [6]. Introducing phenomenological charges in form of the Born effective charge tensor $Z^*(\mu)$ and the dielectric constant ϵ_∞, this approximate additional term is written as

$$\begin{aligned} D_{\alpha,\beta}^{M}(k;\mu,\nu) &= D_{\alpha,\beta}(k;\mu,\nu) + 4\pi\frac{\mathrm{e}^2}{\mathrm{V}\epsilon_\infty\sqrt{\mathrm{M}_\upmu\mathrm{M}_\nu}}\frac{[k\cdot Z^*(\mu)]_\alpha[k\cdot Z^*(\mu)]}{|k|^2} \\ &\times\exp\{-2\pi i g\cdot[r(\mu)-r(\nu)]\} \\ &\times d(q)\exp\left\{-\pi^2\left[\left(\frac{k_x}{\rho_x}\right)^2+\left(\frac{k_y}{\rho_y}\right)^2+\left(\frac{k_z}{\rho_z}\right)^2\right]\right\} \end{aligned} \tag{4-66}$$

where the damping factor $d(q)$ is

$$d(q) = \begin{cases} \frac{1}{2} + \cos\left[\pi\left(\frac{\sqrt{q_1^2 + q_2^2 + q_3^2}}{\sqrt{b_1^2 + b_2^2 + b_3^2}}\right)^n\right] & \text{if } n \geq 1 \\ \frac{1}{2} + \cos\left[\pi\left(1 - \frac{\sqrt{q_1^2 + q_2^2 + q_3^2}}{\sqrt{b_1^2 + b_2^2 + b_3^2}}\right)^n\right] & \text{if } 0 < n < 1 \end{cases} \tag{4-67}$$

In the non-analytical term the wave vector $k = (k_x, k_y, k_z)$ is counted from the closest Brillouin zone center given by the vector g, $q = (q_1, q_2, q_3)$ is the lattice vector in reciprocal lattice coordinates, and $B = (b_1, b_2, b_3)$ is the lattice vector from the Brillouin zone center to the Brillouin zone surface in the direction specified by q. The volume of the primitive cell is denoted V; M_μ and r_μ are the atomic masses and positions within the primitive cell. The index n is the power of the interpolation function. It allows modeling of the longitudinal phonon dispersion curve between the Brillouin zone center and the Brillouin zone surface. For $n \geq 1$ the longitudinal dispersion curve is closer to the value of at the Brillouin zone center for most wave vectors, except in the close vicinity of the Brillouin zone surface. The opposite behavior is obtained for $0 < n < 1$, where the dispersion curve reaches the longitudinal phonon mode only quite close to the Brillouin zone center. The vector $\rho_i = \rho\kappa_i$ is determined by the scalar quantity ρ and the vector κ_i, the wave vector distance from the Brillouin zone center to the Brillouin zone surface. The macroscopic electric field range factor ρ is is a free parameter that can further suppress the influence of the second term in Eq.(4-66). The fixed default value is 10.0, which eliminates the Gaussian damping factor from suppressing dispersion curves. The electric charge conservation law must be satisfied, and that can be achieved either by setting appropriate parameters of the Born effective charge tensor, or the program may take care of this by manipulating the charge tensor.

E. Ab-Initio Thermodynamics: Calculating the stability of surfaces and interfaces

This is a brief description of a practical scheme often used to study the stability of surfaces and interfaces within the framework of ab initio thermodynamics. In fact, a surface can be seen as a special case of a heterogeneous interface which separates two different phases in equilibrium. For a surface one of these phases would be vapour. In the following, what is said about a surface or interface will in general be applicable to both. For a practical example of how to use this scheme, see the V.T Interface Energy of Metal-Ceramic Interface Co/WC Using ab initio Thermodynamics

1. Interface and surface energy

For an interface-, or surface system in thermodynamical equilibrium, the chemical potential of each component must be identical in every phase (equilibrium condition). A consequence of this is the Gibbs phase rule, stating that for a system with π phases and C components in equilibrium, the number of degrees of freedom F is given by

$$F = C - \pi + 2 \tag{5-1}$$

A degree of freedom is an intensive variable that can be varied while still maintaining equilibrium. Our objective is to study the relative stabilities of various surface structures as a function of these variables. Let's assume there are two phases, with a total of three components (atomic species). This gives three degrees of freedom, which can be e.g. temperature, partial pressure of a gas, or chemical composition of a solid phase.

We can describe the stability in terms of the surface free energy σ. The surface free energy for a surface system with area A, where the number and chemical potential of each atomic species are N_i and μ_i, respectively, is defined as

$$\sigma = \frac{1}{A}\left(G(T,p,N_i) - \sum_i N_i \mu_i(T,p)\right) \tag{5-2}$$

G is the Gibbs free energy. For a given temperature T and pressure p, the thermodynamically most stable system minimizes its surface free energy by adapting the composition of the surface region. This may lead to local surface compositions different from bulk compositions, i.e. the surface system has excesses of one or more components. This deviation from stoichiometry affects the free energy via the chemical potentials. Assuming there is only one excess component, the introduced change in free energy from non-stoichiometry can be expressed in terms of the chemical potential of this component. If the system contained an additional solid phase, an additional reference component would be required. Provided that the chemical potentials of the components are known, σ can be evaluated for a set of candidate surfaces to predict the equilibrium structure.

As an example, consider two-phase systems with a binary compound $X_m Y_n$ in contact with, in one case a gas phase Y_2, and in the other case an elemental bulk phase Z. At equilibrium;

$$X_m Y_n(\text{bulk}) \quad \{X,Y\}(\text{surface}) \quad Y_2(\text{gas}) \tag{5-3}$$

$$X_mY_n(\text{bulk}) \quad \{X,Y,Z\}(\text{interface}) \quad Z(\text{bulk}) \tag{5-4}$$

The surface (interface) region may exchange atoms with the bulk and gas phases, which act as reservoirs. Assuming equilibrium in the calculation of the surface free energy, the dependence of the free energy on the intensive variables enters through the chemical potentials. These are equal to the corresponding chemical potential in the bulk phases and therefore can be obtained from bulk calculations. With a few additional assumptions, their dependence on other intensive variables can be estimated. For example, we use the ideal gas expression (5-14) to get the pressure dependency.

For the free surface, with X_mY_n as substrate, the surface region may contain a number of Y atoms that differs from that required by stoichiometry. The free surface energy becomes

$$\sigma = \frac{1}{A}\left(G(T,p,N_X,N_Y) - N_X\mu_X(T,p) - N_Y\mu_Y(T,p)\right) \tag{5-5}$$

The chemical potentials of the X and Y components at the surface are not independent, but related via the equilibrium condition for exchange of atoms with the reservoirs, in this case;

$$\mu_{X_MY_N,\text{bulk}} = m\mu_X + n\mu_Y \tag{5-6}$$

Which allow us to express the free energy in terms of only the chemical potential of the excess quantity Y and the bulk quantity $\mu_{\text{XmYn, bulk}}$:

$$\sigma = \frac{1}{A}\left(G(T,p,N_X,N_Y) - \frac{N_X}{m}\mu_{X_mY_n,\text{bulk}}(T,p) - \left(N_Y - \frac{n}{m}N_X\right)\mu_Y(T,p)\right) \tag{5-7}$$

For the interface in the example above, the only difference in the expression for the surface free energy is an additional term for the elemental phase Z:

$$\sigma = \frac{1}{A}\left(G(T,p,N_X,N_Y) - \frac{N_X}{m}\mu_{X_mY_n,\text{bulk}}(T,p) - \left(N_Y - \frac{n}{m}N_X\right)\mu_Y(T,p) - N_Z\mu_Z(T,p)\right) \tag{5-8}$$

For μ_Y, a simple approach is to allow it to vary between values for which the phases in the system are stable. That is, it can be regarded as a free parameter in the calculations within a specified range, and we will now discuss how limiting values of this interval can be found.

2. Range of chemical potential

The chemical potentials of components X and Y have to be lower than the Gibbs free energy of respective bulk phases. Otherwise pure bulk phases of X and Y would start precipitate out of the compound, and the X_mY_n phase would not be stable. Thus,

$$\mu_X(T,p) \le g_{X,\text{bulk}}(T,p) \ \text{ and } \ \mu_Y(T,p) \le g_{Y,\text{bulk}}(T,p) \tag{5-9}$$

Furthermore, the chemical potentials are related to Gibbs free energy of the bulk phase X_mY_n ,

$$m\mu_X(T,p) + n\mu_Y(T,p) = g_{X_m Y_N,\mathrm{bulk}}(T,p) \tag{5-10}$$

or, using (5-9)

$$\mu_Y(T,p) = \frac{1}{n} g_{X_m Y_N,\mathrm{bulk}}(T,p) - \frac{m}{n}\mu_X(T,p) \geq \frac{1}{n} g_{X_m Y_N,\mathrm{bulk}}(T,P) - \frac{m}{n} g_{X,\mathrm{bulk}}(T,p) \tag{5-11}$$

So that

$$\begin{aligned}\mu_Y(T,p) - g_{Y,\mathrm{bulk}}(T,p) \geq \frac{1}{n} g_{X_m Y_n,\mathrm{bulk}}(T,p) - \frac{m}{n} g_{X,\mathrm{bulk}}(T,p) - g_{Y,\mathrm{bulk}}(T,p)\\ = \frac{1}{n}\Delta G_f(T,p)\end{aligned} \tag{5-12}$$

$\Delta G_f(T,P)$ is the Gibbs free energy of formation of the $X_m Y_n$ phase.

Equations (5-9) and (5-12) establish natural limiting values of the Y chemical potential.

As for a pure system, the chemical potential is equal to the Gibbs energy per particle, we can write this interval for $\mu_Y(T,p)$ as;

$$\frac{1}{n}\Delta G_f(T,p) \leq \mu_Y(T,p) - \mu_{Y,\mathrm{bulk}}(T,p) \leq 0 \tag{5-13}$$

In reality, it is possible that other stable phases exist within this range. If such phases are known, the interval can be adjusted to the limits given by their stability range.

In cases where the standard state of the component Y is a gas, it is appropriate to use the partial pressure of the gas as an intensive variable. Assuming Y to be a diatomic ideal gas with known chemical potential at standard pressure p^0, we can evaluate the chemical potential at any other pressure using the ideal gas expression

$$\mu_Y\left(T, p_{Y_2}\right) = \mu_Y(T,p^0) + \frac{1}{2} k_B \log\left(\frac{p_{Y_2}}{p^0}\right) \tag{5-14}$$

In principle, the free energy of a gas molecule can be calculated; however, in many cases computations are more precise for solid compounds than for gases. A way to exploit this fact is to consider a thermodynamic cycle corresponding to the formation of a solid compound where Y is involved. One then uses tabulated thermodynamical data to assess the free energy. For example, we can consider the reaction

$$mX(2) + \frac{n}{2} Y_2(g) \rightarrow X_m Y_n(s) \tag{5-15}$$

at standard pressure p^0 and temperature T^0, for which the Gibbs free energy of formation is given as

$$g_{X_m Y_{n,\mathrm{bulk}}}(T^0,p^0) + n\mu_Y(T^0,p^0) + \Delta G_f(T^0,p^0) \tag{5-16}$$

Any cycle can be used as long as the heat of formation $\Delta G_f(T^0, p^0)$ is available from thermodynamical tables.

3. Using density-functional theory as input

So far, the formalism has been based on Gibbs free energies as given by;

$$G = E + pV - TS \tag{5-17}$$

where all quantities have their usual thermodynamic meaning. In general, total energies from DFT correspond to the electronic contribution to Helmholtz free energies at zero temperature, neglecting zero-point vibrations.

For a description of the temperature dependence of the free energy, see section V.M Practical Thermochemistry: Sodium Metal, Chlorine Gas, and Solid Sodium Chloride. Using the energies from DFT as an estimate for the Gibbs free energy, the main approximation we make is to ignore the vibrational modes of the lattice. This approximation should be better for interfaces, where the vibrational contributions to the free energy should be close to the reference bulk systems due to similarity in atomic densities. For solids, the pressure-volume term is normally small, and can be neglected in most cases. [90]

It is recommended to use the heat of formation as given by *`Job.out`* in MEDEA as a measure of the internal energy of the structure rather than the VASP energy. The difference is that using the heat of formation for the internal energy corresponds to expressing the energy with respect to the constituting elements in their standard state, while the VASP energy is based on the non-spin polarized energy of the atomic states. We recommend using MEDEA's heat of formation as this quantity is more physical; in particular it can be compared to experimental values and contains information about the compound's stability.

F. Spectra

1. Main Equations

The imaginary and real part of the **optical conductivity tensor** is given by

$$\sigma_{(\alpha\beta)}(\omega,\vec{q}) = \frac{i\omega}{4\pi}[\delta_{\alpha\beta} - \epsilon_{(\alpha\beta)}(\omega,\vec{q})] \tag{6-1}$$

In the optical range $\vec{q}$ is often very small compared to the electronic momentum. Also for isotropic media and a uniaxial field the conductivity takes a scalar character, hence

$$\sigma(\omega) = \frac{i\omega}{4\pi}[1 - \epsilon(\omega)] \tag{6-2}$$

(6-3)

or using $\sigma = \sigma_1 + i\sigma_2$ and $\epsilon = \epsilon_1 + i\epsilon_2$

$$\sigma_{1(\omega)} = \omega/4\pi[\epsilon_2(\omega)] \tag{6-4}$$

$$\sigma_2(\omega) = \omega/4\pi[1 - \epsilon_1(\omega)] \tag{6-5}$$

ElectrA calculates $\sigma_1(\omega)$ and $\sigma_2(\omega)$ in units of eV. See the table on the main page for conversion to frequencies.

The index of refraction, N, describes how a wave propagating through a material is attenuated with respect to propagation in vacm.

N is a complex function $N = n + ik$, where n is called the real index of refraction and k is the extinction coefficient.

Using plane waves the effect of attenuation through a medium is described by replacing the wave vector k by $N \cdot k$. The refractive index N is related to the dielectric function by

$$N^2 = \epsilon \tag{6-6}$$

ElectrA calculates n and k.

The ratio between incident and reflected light intensities is called the reflectivity. For a normal incident beam the relation with the refractive index is

$$R = \left|\frac{N - 1}{N + 1}\right|^2 \tag{6-7}$$

2. Interpretation of Optical Spectra of Metals

In metals the unfilled nature of the highest occupied bands allows for electronic low-energy intraband transitions. These transitions contribute an important part to the response to an applied electromagnetic field. They are usually described by free electron theory using the Drude formula:

$$\sigma_D(\omega) = \frac{\omega_P^2}{4\pi(\gamma_D - \mathrm{i}\omega)} \tag{6-8}$$

where γ_D is the inverse relaxation time and ω_P^2 the plasma frequency. In principle ω_P^2 can be calculated from a band structure calculation. γ_D depends on the materials impurities and dislocations. Experimental values for the Drude parameters of various materials are tabulated in the literature.

3. Broadening

Among the various physical mechanisms responsible for the smearing of experimental spectra are temperature effects, indirect transitions, finite experimental resolution and – the most important – the finite lifetime of excited states.

ElectrA allows the input of experimental values for lifetime and Drude lifetime broadening.

4. Additional Optical Properties

The absorption coefficient α describes the decline of the light intensity I, way r into the material.

$$\alpha = -\frac{1}{I}\frac{dI}{dr} = \frac{2\omega k}{c} \tag{6-9}$$

The energy loss function L describes the energy loss of a monoenergetic electron beam impinging on a solid.

$$L = -\operatorname{Im}\frac{1}{\epsilon} \tag{6-10}$$

V. Application Notes & Case Studies

A. Structure of Bulk Titanium Carbide

The correct lattice parameters of a crystalline structure are of fundamental importance for any reliable computational predictions of materials properties. This case study shows the calculation of the lattice parameters of titanium carbide, TiC.

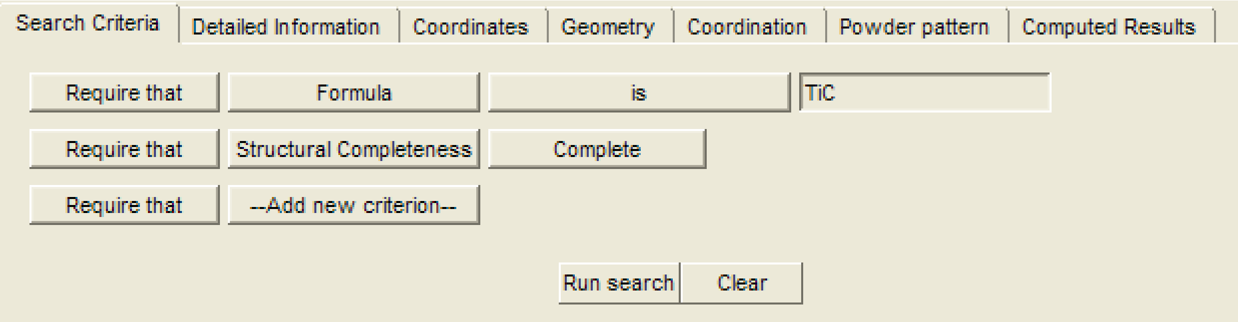
Outline of Approach

The computational procedure involves the following tasks:

- Choose and retrieve crystal structure of TiC
- Compute lattice parameters of TiC
- Analyze results
- Save results

1. Get starting structure

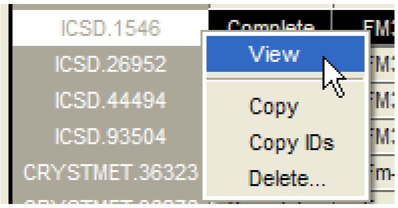
After starting MEDEA, select **INFOMATICA** from **Tools** in the MEDEA tool bar and select **Search…** in the **INFOMATICA** pull-down menu. Choose **Require that Formula is TiC** and **Require that Structural Completeness Complete** and **Run search**.



Require that Formula is TiC
Require that Structural Completeness Complete
Require that --Add new criterion--

The search gives several entries. Move the cursor over the first entry, which is ICSD.1546 and click the left mouse button to select this entry.

ICSD.1546	Complete	FM3-M	C1 Ti1	C1 Ti1	Titanium carbide (1/1)



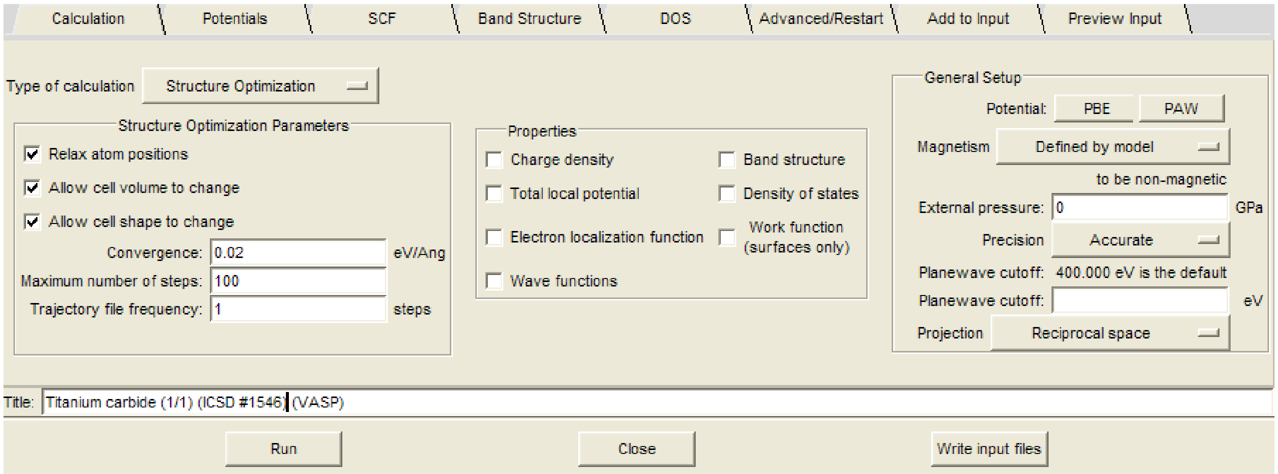
With the cursor in the selected row, right-click to get a small dialog box. Move the cursor to View and left-click to display the structure in MEDEA. The structure comes up in a new sub-window in the main MEDEA window. By default, the structure is oriented such that the positive x-direction points to the right, the positive y-direction points upwards, and the positive z-direction points towards the user.

The structure can be rotated, translated, and one can zoom in and out. The controls to these functions are accessible via the MEDEA menu in the upper left or via a right mouse click.

Note: In most cases, experimental crystal structures are taken at room temperatures whereas ab initio total energy calculations refer to T=0 K unless temperature effects are explicitly taken into account. This introduces an inconsistency in the comparison between calculations and experiment. Quite frequently, this thermal expansion effect is tacitly neglected, since the errors due to the GGA are typically larger than the thermal expansion between T=0 K and room temperature.

2. Choose Vasp parameters and start calculation

With the crystal structure of TiC in the MedeA window as the active window (dark blue top bar), we now compute the lattice parameters using Vasp. From **Tools** in the MedeA menu bar, select **Vasp 4.6** and invoke the Vasp 4.6 graphical user interface by selecting **Vasp 4.6**≫**Run** from the MedeA tool bar.



Type of calculation: Structure Optimization

Structure Optimization Parameters
☑ Relax atom positions
☑ Allow cell volume to change
☑ Allow cell shape to change
Convergence: 0.02 eV/Ang
Maximum number of steps: 100
Trajectory file frequency: 1 steps

Properties
☐ Charge density
☐ Band structure
☐ Total local potential
☐ Density of states
☐ Electron localization function
☐ Work function (surfaces only)
☐ Wave functions

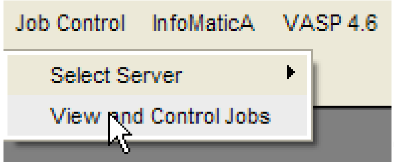
General Setup
Potential: PBE PAW
Magnetism: Defined by model
to be non-magnetic
External pressure: 0 GPa
Precision: Accurate
Planewave cutoff: 400.000 eV is the default
Planewave cutoff: eV
Projection: Reciprocal space

Title: Titanium carbide (1/1) (ICSD #1546) (VASP)

From the first panel (**Calculation**), select **Structure Optimization** from as type of calculation, check **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**. In other words, a full cell optimizations and relaxation of the atom positions is selected. However, the optimization is performed within the constraints of the symmetry of the space group, which in the case of the cubic structure of TiC are quite severe.

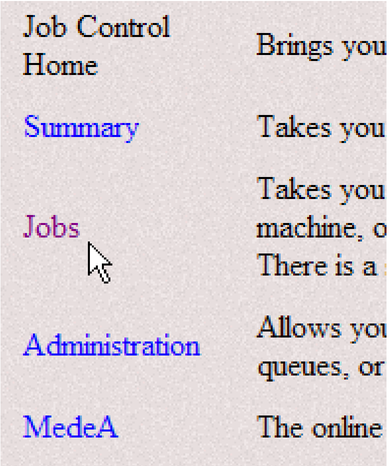
An **Accurate** precision is chosen since volume and cell shape are allowed to change. All other parameters including the k-mesh are left at their defaults. This completes the set-up of the Vasp calculations and you can hit the **Run** button.

3. Monitor progress of calculation



The MedeA interface sends the input parameters to the JobServer, which then dispatches the calculation to the appropriate TaskServers, which are running on the network. (See section III Job management for more details). The actual calculations are done on one (or several) machines under the control of the TaskServer on the particular computer(s).

In order to monitor the progress of the calculation, one has to navigate to the appropriate computer and TaskServer directory. This is accomplished in the following way. In the main MEDEA tool bar, selected **Job Control**≫**View and Contral Jobs**.



Job Control Home	Brings you
Summary	Takes you
Jobs	Takes you machine, o There is a
Administration	Allows you queues, or
MedeA	The online

In the JobServer, view the Jobs. The second column gives the job numbers. Click the job number, which is a hyperlink. This shows the task, which are running with the task number and the identification of the computer. Click on the task number. This hyperlink opens a page of the TaskServer showing the current working files. In particular *OSZICAR*, which shows the total energy for each SCF step, and the *OUTCAR* file, which gives detailed information about the progress of the job.

At the end of each converged SCF step, VASP calculates the stress tensor and the forces on each atom and reports the current values in the *OUTCAR* file. At the successful completion of the task, the relevant files including the *OUTCAR* and *OSZICAR* file are returned from the TaskServer to the JobServer and additional files, namely `Job.out` and the final.sci files are created. After this transfer, the files created by the TaskServer are removed. Therefore, an attempt to view the working files through the TaskServer after successful completion of a job is no longer possible.

Analyze results

a. Inspection of `Job.out` file

From the JobServer on the page "Jobs", one can see the status of the various jobs. After successful completion, the status is **finished**. By clicking on the job number, a page is opened which lists the available output files. Click on `Job.out` to view a summary of the original and optimized cell parameters reported in a table denoted "Cell parameters:"

In the present case, the cell parameters computed with the generalized gradient approximation (GGA) as implemented in VASP give lattice parameters of 4.330 Å, which is 0.1 % larger than the original experimental value of 4.328 Å.

```
Cell parameters:
 Parameter   Original     change      Final       %
---------- ------------ ---------- ------------ -----
         a     4.328000   0.002223     4.330223   0.1
         b     4.328000   0.002223     4.330223   0.1
         c     4.328000   0.002223     4.330223   0.1
     alpha    90.000000   0.000000    90.000000   0.0
      beta    90.000000   0.000000    90.000000   0.0
     gamma    90.000000   0.000000    90.000000   0.0
```

The fraction coordinates, i.e. the position of the atoms expressed in units of the lattice parameters are

```
Fractional Coordinates:
       Atom          Initial Coordinates              Final Coordinates
       -----      -------- -------- --------      -------- -------- --------
       Ti1          0.0000   0.0000   0.0000        0.0000   0.0000   0.0000
       C1           0.5000   0.5000   0.5000        0.5000   0.5000   0.5000
```

In the cubic rock salt structure, there are not free parameters for the positions of the two ions. Therefore the initial and final fractional coordinates are identical.

Remark

The above computation was carried out for the primitive unit cell containing two atoms, as can be seen from an inspection of the *OUTCAR.out* file in the section following the potentials.

Save results

b. Load the optimized structure

From the tool bar of the main MEDEA window, select **File**»**Open**»**Previous Calculations**. In the new window, select the appropriate job by single click and **Insert** or simply by a double-click on the job name. The **OK** button loads the structure into the MEDEA window.

c. Save the structure in the MaterialsDesign database

From the tool bar of the main MEDEA window, select **Save**. The dialog box allows you to enter a name and add remarks.

B. Structure and Bond Lengths in Titanium Dioxide

In addition to the lattice parameters, the rutile structure has an additional degree of freedom, namely the position of the oxygen atom. This case study shows the simultaneous calculation of all these structural degrees of freedom.

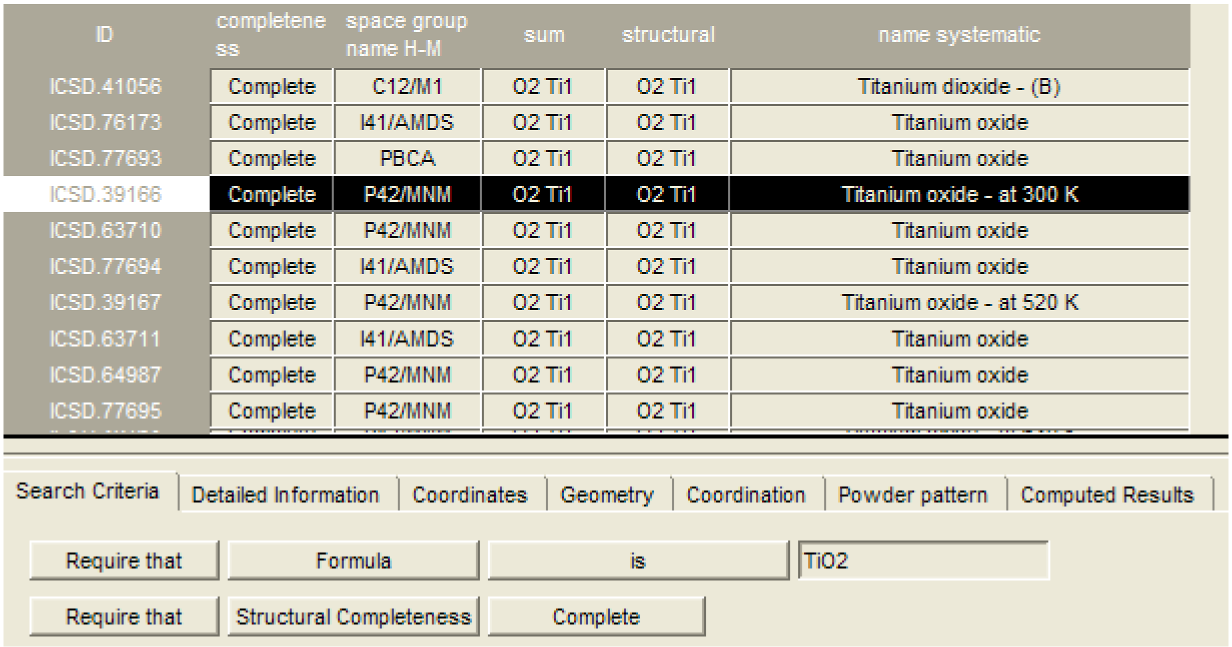
Outline of Approach

The computational procedure involves the following steps

- Choose crystal structure of TiO_2
- Compute lattice parameters of TiC
- Analyze results

1. Choose crystal structure

After starting MedeA, select **InfoMaticA** from **Tools** in the MedeA tool bar and select **Search…** in the **InfoMaticA** pull-down menu. Choose **Require that** **Formula** **is** **TiO2** and **Require that Structural Completeness** **Complete** and run the search.

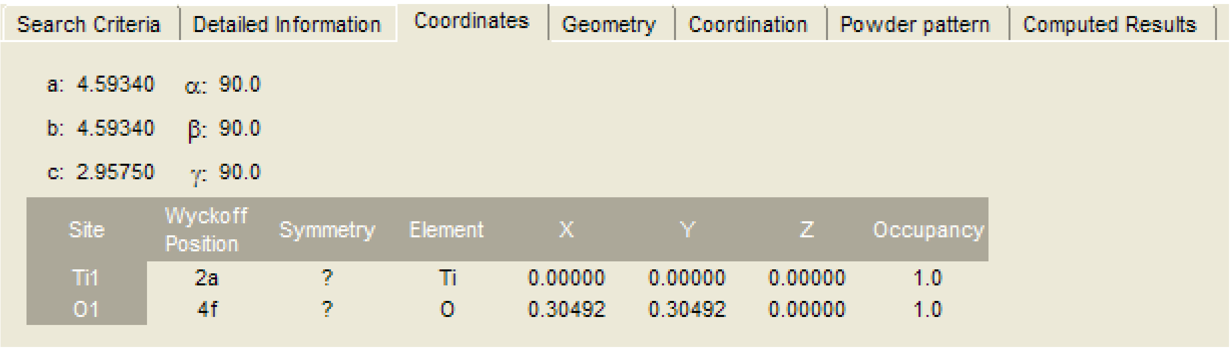


ID	completeness	space group name H-M	sum	structural	name systematic
ICSD.41056	Complete	C12/M1	O2 Ti1	O2 Ti1	Titanium dioxide - (B)
ICSD.76173	Complete	I41/AMDS	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.77693	Complete	PBCA	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.39166	Complete	P42/MNM	O2 Ti1	O2 Ti1	Titanium oxide - at 300 K
ICSD.63710	Complete	P42/MNM	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.77694	Complete	I41/AMDS	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.39167	Complete	P42/MNM	O2 Ti1	O2 Ti1	Titanium oxide - at 520 K
ICSD.63711	Complete	I41/AMDS	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.64987	Complete	P42/MNM	O2 Ti1	O2 Ti1	Titanium oxide
ICSD.77695	Complete	P42/MNM	O2 Ti1	O2 Ti1	Titanium oxide

Require that | Formula | is | TiO2

Require that | Structural Completeness | Complete

Select **ICSD.39166** and click on the tab **Coordinates**.

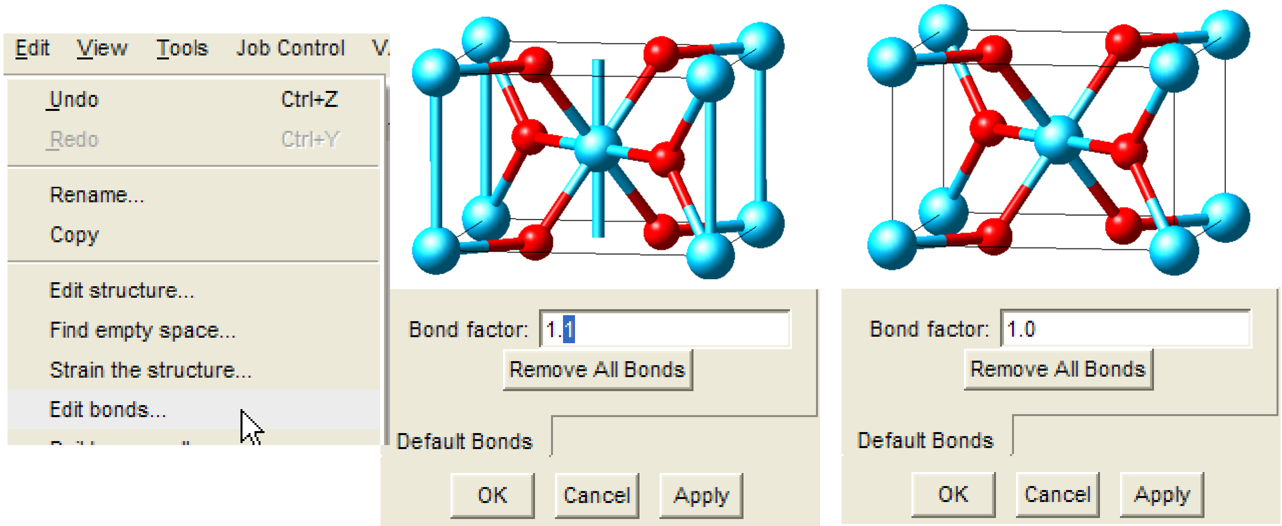


a: 4.59340 α: 90.0
b: 4.59340 β: 90.0
c: 2.95750 γ: 90.0

Site	Wyckoff Position	Symmetry	Element	X	Y	Z	Occupancy
Ti1	2a	?	Ti	0.00000	0.00000	0.00000	1.0
O1	4f	?	O	0.30492	0.30492	0.00000	1.0

The position of the oxygen atom is (*x*,*x*,0). The experimental value of *x* in the case of structure ICSD.39166 is 0.30492. The parameter *x* can be changed without destroying the symmetry of the rutile structure. The following calculation determines this structure by *ab initio* theory.

2. Change displayed bonds



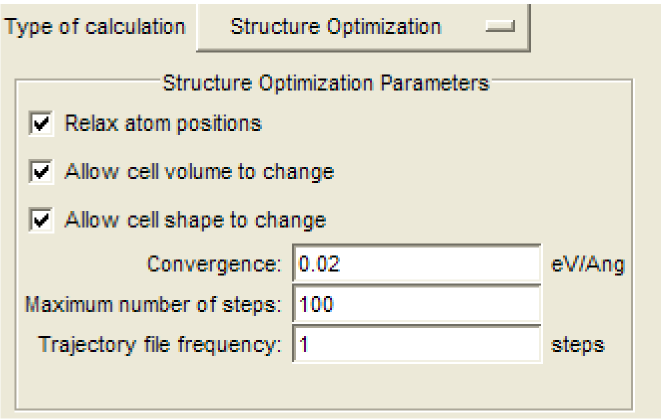
Bond factor: 1.1

Bond factor: 1.0

The display of structure ICSD.39166 with the default criterion for bond lengths gives bonds between neighboring Ti atoms (blue). This can be easily changed. Select **Edit**≫**Edit bonds...** from the MEDEA tool bar. Set the **Bond factor** from 1.1 to 1.0 and **Apply** the change.

3. Compute structure with VASP

With the crystal structure of TiO_2 in the MEDEA window as the active window (dark blue top bar), we now compute the lattice parameters and the internal parameters using VASP. From **Tools** in the MEDEA menu bar, select **VASP 4.6** and invoke the VASP 4.6 graphical user interface by selecting **VASP 4.6**≫**Run** from the MEDEA tool bar. From the first panel (**Calculation**), select **Structure Optimization** as type of calculation, check **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**. This optimizes cell and atom positions without constraints. The calculations are performed with the precision **Accurate**. All other parameters are left at their defaults.



Type of calculation: Structure Optimization

Structure Optimization Parameters

☑ Relax atom positions

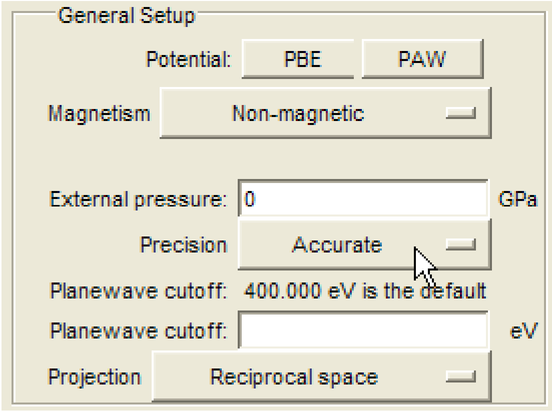
☑ Allow cell volume to change

☑ Allow cell shape to change

Convergence: 0.02 eV/Ang

Maximum number of steps: 100

Trajectory file frequency: 1 steps



General Setup

Potential: PBE PAW

Magnetism: Non-magnetic

External pressure: 0 GPa

Precision: Accurate

Planewave cutoff: 400.000 eV is the default

Planewave cutoff: eV

Projection: Reciprocal space

Analyze results

a. Inspection of `Job.out` file

After successful completion, the status reported by the JobServer is **finished**. By clicking on the job number, a page is opened which lists the available output files. Click on `Job.out` to view the summary, the original and optimized cell parameters are reported in a table denoted "Cell parameters:"

In the present case of TiO_2, the cell parameters computed with the generalized gradient approximation (GGA) and PAW potentials as implemented in VASP give lattice parameters of *a*=4.5959 Å and *c*=2.9558 Å, which are within 0.1 % of the experimental values.

```
Cell parameters:
 Parameter   Original     change      Final       %
---------- ------------ ---------- ------------ -----
         a     4.593400   0.002504     4.595904   0.1
         b     4.593400   0.002504     4.595904   0.1
         c     2.957500  -0.001715     2.955785  -0.1
     alpha    90.000000   0.000000    90.000000   0.0
      beta    90.000000   0.000000    90.000000   0.0
     gamma    90.000000   0.000000    90.000000   0.0
```

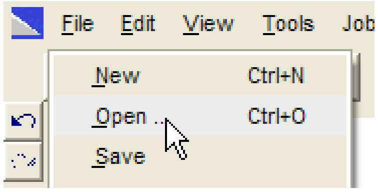
The fractional coordinates, *i.e.* the position of the atoms expressed in units of the lattice parameters are

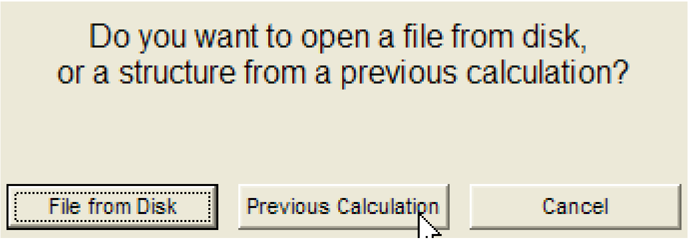
```
Fractional Coordinates:
       Atom         Initial Coordinates            Final Coordinates
       -----      -------- -------- --------     -------- -------- --------
       Ti1          0.0000   0.0000   0.0000       0.0000   0.0000   0.0000
       O1           0.3049   0.3049   0.0000       0.3038   0.3038   0.0000
```

The internal parameter for the oxygen atom changes from 0.3049 to 0.3038.

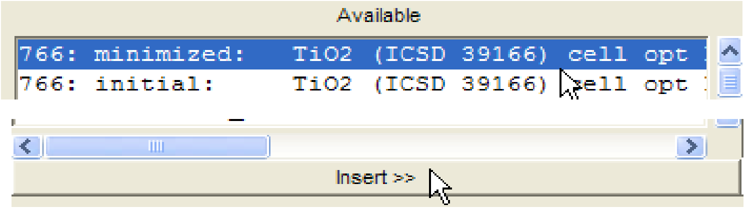
b. Measuring computed bond distances

Choose **File**>>**Open** from the main MEDEA menu bar. Select **Previous Calculation** from the new dialog box. This brings up a list of available structures from previous calculations performed via the JobServer. Select the desired structure, click **Insert > >** and confirm with **OK**. The structure will appear in a new window in MEDEA. Move the cursor over a bond and the bond length is displayed in the lower left of the MEDEA window. In the present case, one of the two computed Ti-O bond lengths is 1.9519 Å, which is very close to the experimental value of 1.9475 Å.



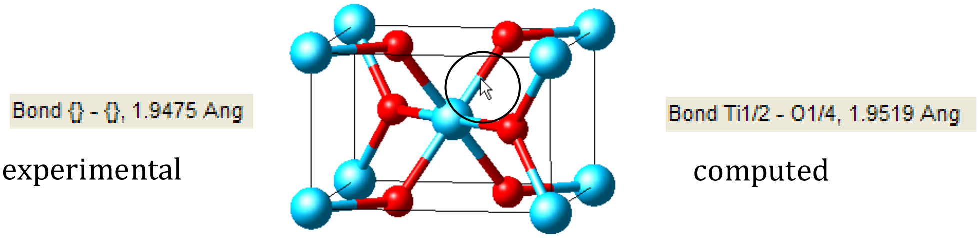


Do you want to open a file from disk,
or a structure from a previous calculation?



Available

766: minimized: TiO2 (ICSD 39166) cell opt
766: initial: TiO2 (ICSD 39166) cell opt



Bond {} - {}, 1.9475 Ang

experimental

Bond Ti1/2 - O1/4, 1.9519 Ang

computed

C. Structure around Oxygen Vacancy in α-Quartz

The introduction of vacancies in a crystalline solid causes a local rearrangement of atoms around the defect. The purpose of this case study is the prediction such changes in α-quartz.

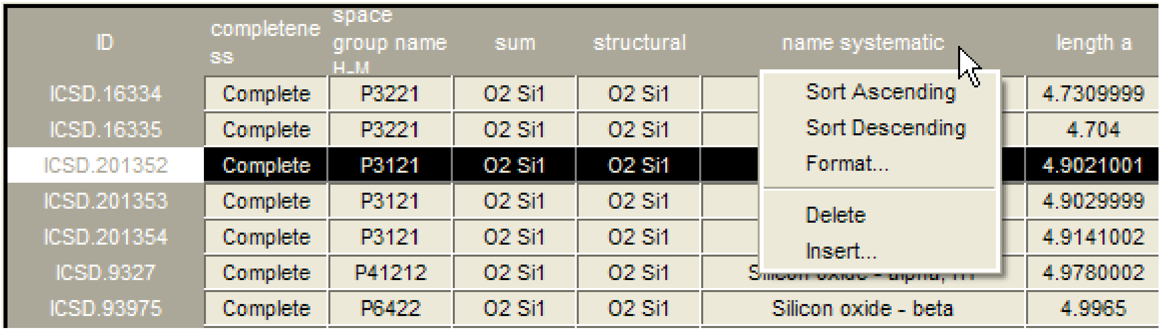
Outline of Procedure

The computational procedure involves the following steps

- Retrieve structure of α-quartz
- Optimize structure of the α-quartz
- Build supercell and delete one O atom
- Relax structure
- Analyze structure

1. Retrieve Structure of α-Quartz

In the InfoMaticA tool, perform a search **Require that** **Formula** **is** **SiO2** and **Require that Structural Completeness** **Complete** and **Run search**. Right-click in the gray area around **name systematic** and **Sort Ascending**. This lists all entries for alpha quartz in a contiguous section. Choose **ICSD.201352**, which is α-quartz measured at low temperature.



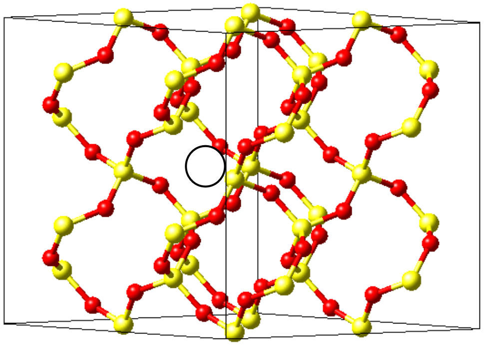
ID	completeness	space group name H_M	sum	structural	name systematic	length a
ICSD.16334	Complete	P3221	O2 Si1	O2 Si1		4.7309999
ICSD.16335	Complete	P3221	O2 Si1	O2 Si1		4.704
ICSD.201352	Complete	P3121	O2 Si1	O2 Si1		4.9021001
ICSD.201353	Complete	P3121	O2 Si1	O2 Si1		4.9029999
ICSD.201354	Complete	P3121	O2 Si1	O2 Si1		4.9141002
ICSD.9327	Complete	P41212	O2 Si1	O2 Si1	[illegible]	4.9780002
ICSD.93975	Complete	P6422	O2 Si1	O2 Si1	Silicon oxide - beta	4.9965

Load the structure in the MedeA window (in the database window, select lines, right-click and **View**).

2. Optimize Structure of α-Quartz

With the crystal structure of α-SiO_2 in the MedeA window as the active window (dark blue top bar), we now compute the lattice parameters and the internal parameters using VASP. From **Tools** in the MedeA menu bar, select **VASP 4.6** and invoke the VASP 4.6 graphical user interface by selecting **VASP 4.6**>>**Run** from the MedeA tool bar. From the first panel ("**Calculation**"), select **Structure Optimization** as type of calculation, check **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**. In other words, a full cell optimizations and relaxation of the atom positions is selected. The calculations are performed with the precision "**Accurate**". All other parameters are left at their defaults.

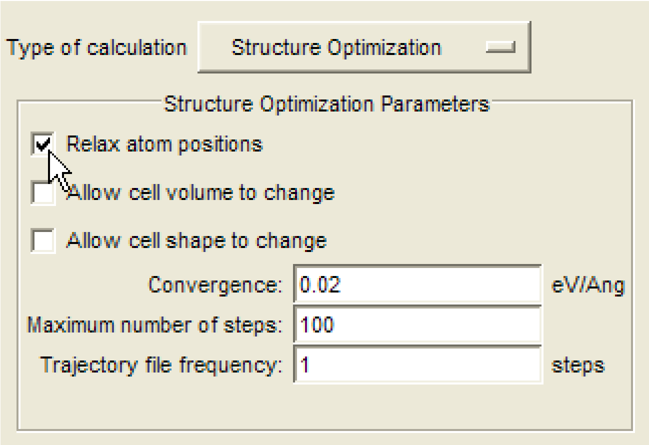
3. Build Supercell



Load the optimized structure of α -SiO$_2$ from **File**≫**Open**≫**Previous Calculation**. Create 2x2x2 supercell using the command **Edit**≫**Build supercells…** The resulting structure has P1 symmetry. Delete one O atom as indicated in the figure on the right. The resulting supercell has the composition Si$_{24}$O$_{47}$.

4. Relax Structure

In the following relaxation with VASP, normal precision is sufficient, since only the atomic positions are changed and not the cell parameters. With the system Si$_{24}$O$_{47}$ in the active window, choose **VASP 4.6**≫**Run** from the Tools. As VASP input parameters, choose **Structure Optimization**≫**Relax atom positions** as shown below.



Type of calculation: Structure Optimization

Structure Optimization Parameters

☑ Relax atom positions

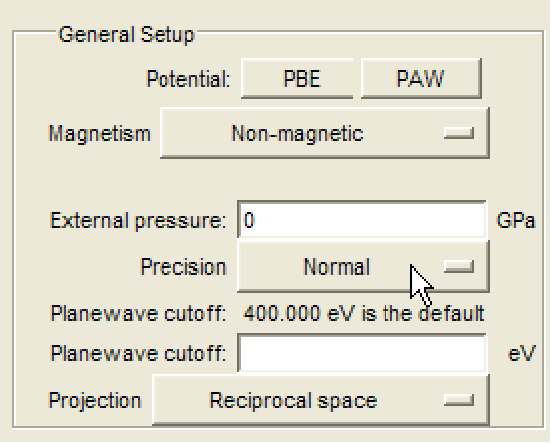
☐ Allow cell volume to change

☐ Allow cell shape to change

Convergence: 0.02 eV/Ang

Maximum number of steps: 100

Trajectory file frequency: 1 steps



General Setup

Potential: PBE PAW

Magnetism: Non-magnetic

External pressure: 0 GPa

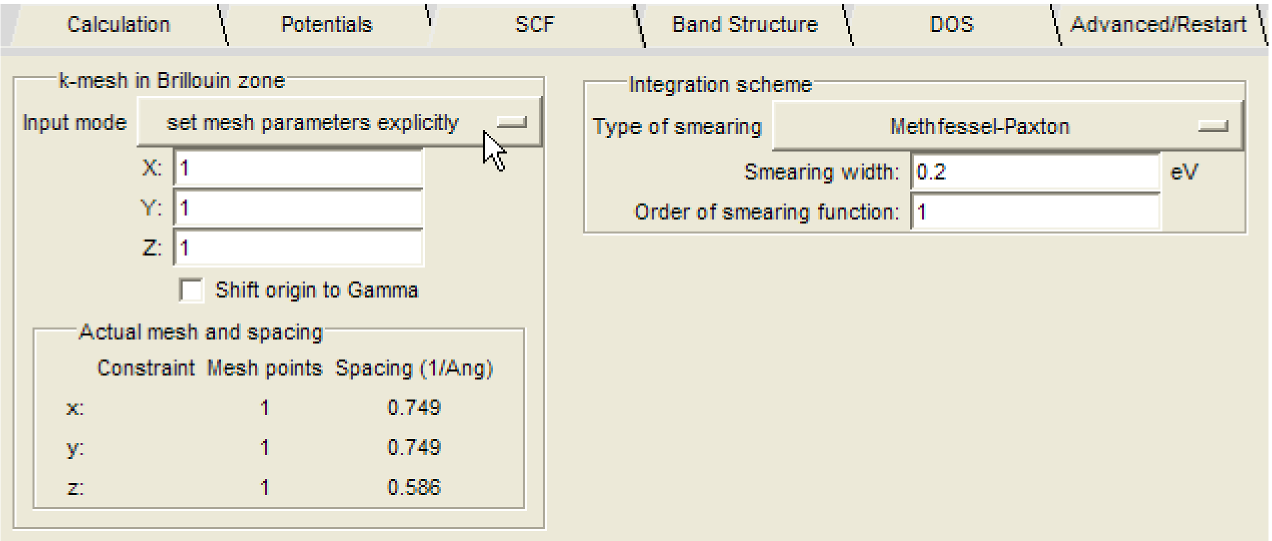
Precision: Normal

Planewave cutoff: 400.000 eV is the default

Planewave cutoff: eV

Projection: Reciprocal space

In the SCF tab, set mesh parameters explicitly as 1, 1, 1. The supercell is fairly large and SiO$_2$ is a wide band gap insulator. Therefore, a geometry optimization with only one k-point, namely , is reasonable.



k-mesh in Brillouin zone

Input mode: set mesh parameters explicitly

X: 1

Y: 1

Z: 1

☐ Shift origin to Gamma

Actual mesh and spacing

	Constraint	Mesh points	Spacing (1/Ang)
x:		1	0.749
y:		1	0.749
z:		1	0.586

Integration scheme

Type of smearing: Methfessel-Paxton

Smearing width: 0.2 eV

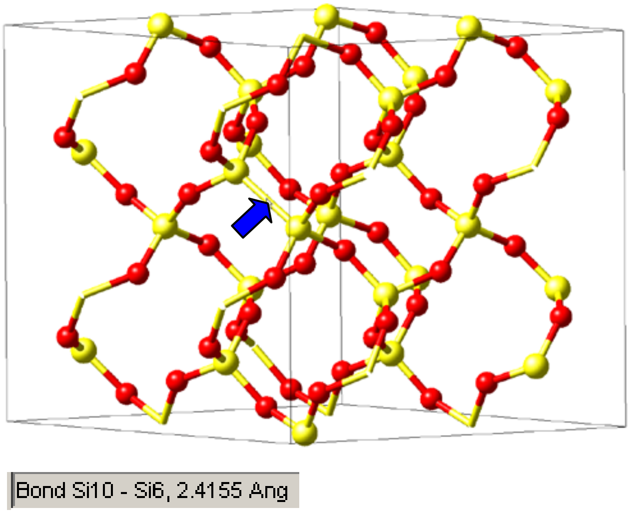
Order of smearing function: 1

All other parameters are left at their default. Execute the job with the **Run** button and the subsequent submission to a particular queue.

The calculation converged after 60 geometry steps to an equilibrium structure, in which the largest force on any atom is less than 0.02 Å/eV. This relaxation took 8 hours and 24 minutes on a single AMD Opteron processor.

Analyze Results

After completion of the job, the structure is retrieved with **File**»**Open**»**Previous Calculation.** Use **Edit**»**Edit Bonds…** to recompute the bonds (they tend to get scrambled during the optimization). An inspection of the optimized structure shows the formation of a Si-Si dimer, which closes the void created by the removal of an oxygen atom. Moving the cursor over this Si-Si bond displays the bond length in the lower left corner of the MedeA window. A value of 2.4155 Å is obtained for this newly formed bond.


Bond Si10 - Si6, 2.4155 Ang

D. Deformation of Silver Lattice by Interstitial Boron and Fluorine Impurities

The insertion of interstitial impurities in a host lattice causes local deformations of the lattice. The purpose of this case study is the comparison of such deformations caused by boron and fluorine impurities in a silver lattice.

Outline of Computational Approach

The computational procedure involves the following steps

- Retrieve and optimize structure of silver
- Build supercell and insert boron and fluorine, respectively
- Relax structures
- Compare the two optimized structures

1. Retrieve Structure of Silver

In the INFOMATICA tool, perform a search **“Require** **that** **Formula is Ag”** and “**Require that Structural Completeness Complete**” and run the search. Select structure ICSD.64996, which is a low temperature measurement with a reported lattice parameter of a_0=4.071Å. Load the structure in the MEDEA window (in the database window, select the line with the entry ICSD.64996, right-click and “**view**”).

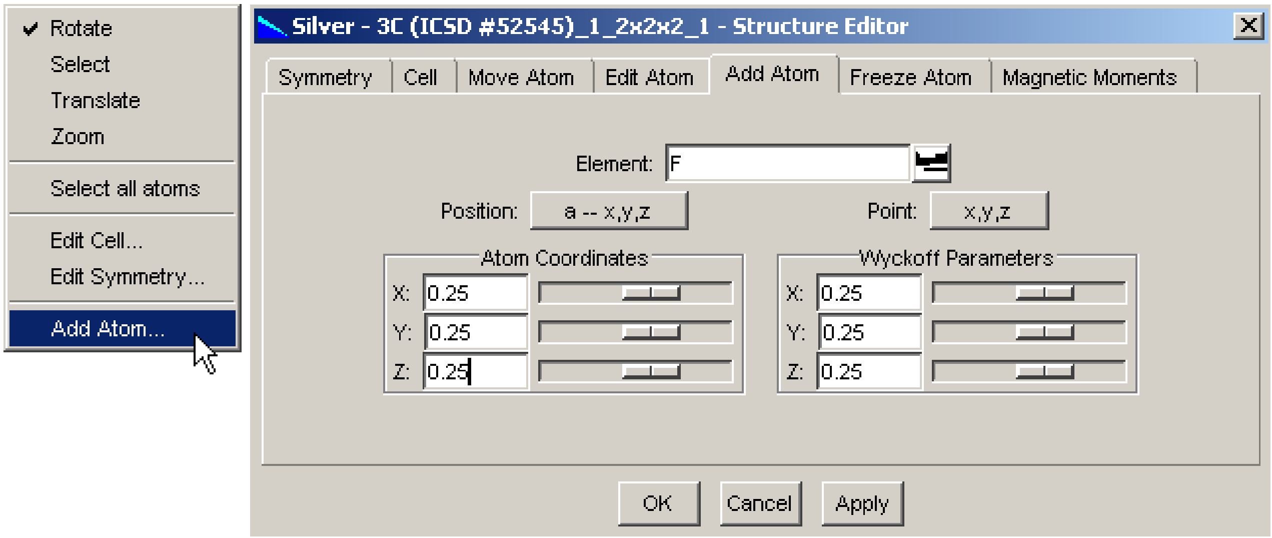
2. Compute Lattice Parameter of Silver

With the crystal structure of Ag in the MEDEA window as the active window (dark blue top bar), we now compute the lattice parameters using VASP. From **Tools** in the MEDEA menu bar, select **VASP 4.6** and invoke the VASP 4.6 graphical user interface by selecting **VASP 4.6**≫**Run** from the MEDEA tool bar. From the first panel (“**Calculation**”), select **Structure Optimization** as type of calculation, check **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**. In other words, a full cell optimizations and relaxation of the atom positions is selected. The calculations are performed with the precision “**Accurate**”. All other parameters are left at their defaults. In the SCF tab, the k-spacing is set to 0.2 $Å^{-1}$, which results in a 14x14x14 k-mesh.

The cell optimization increases the original experimental lattice parameter of 4.071 Å by 0.8 % to 4.1038 Å. The latter value is used in the subsequent calculations.

3. Build Supercell with Impurity

Load the optimized structure of Ag (*a*=4.1038 Å) using **File**≫**Open**≫**Previous Calculation**. Create a 2x2x2 supercell using the command **Edit**≫**Build supercells...** The resulting structure has P1 symmetry. Move the cursor into the white area of the window with the supercell and right-click the mouse button. A dialog comes up. Move the cursor to **Add Atom...** and left-click. A dialog of MEDEA's Structure Editor appears. Insert a fluorine atom at position (0.25,0.25,0.25) as shown below. Then click **Apply** and **OK**.

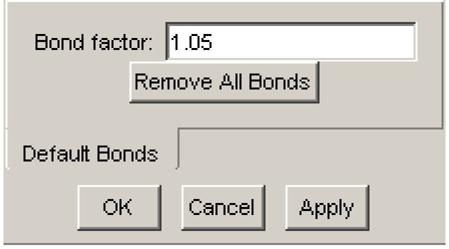


Element: F
Position: a -- x,y,z
Point: x,y,z

Atom Coordinates
X: 0.25
Y: 0.25
Z: 0.25

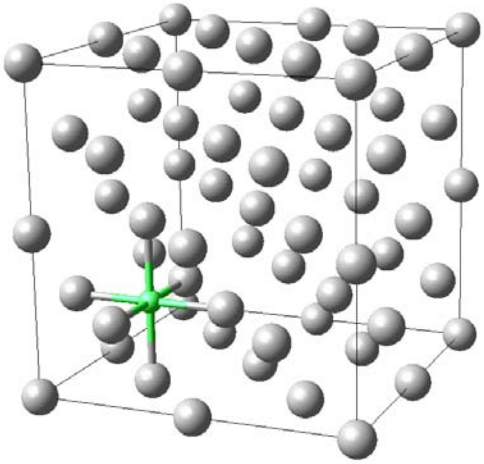
Wyckoff Parameters
X: 0.25
Y: 0.25
Z: 0.25

Rotate the structure to see the inserted atom. Choose **Edit**≫**Edit bonds...** with a bond factor of 1.05. This shows only bonds around the impurity atom.



Bond factor: 1.05

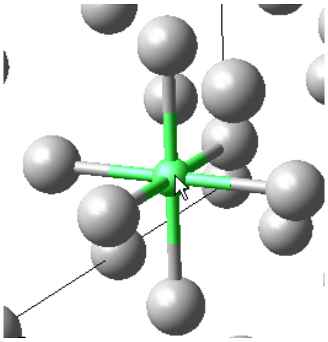
If desired, the color of the Ag atoms can be changed by the commands **View**≫**Options**≫**Change colors...** The resulting structure should look as shown on the right.

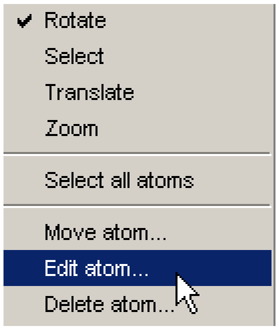


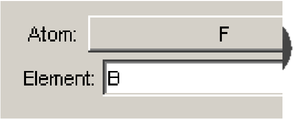
4. Relax Structures

In the following relaxation with VASP, **Normal** precision is sufficient, since only the atomic positions are changed and not the cell parameters. With the system $Ag_{32}F$ in the active window, choose **VASP 4.6**≫**Run** from the Tools. As VASP input parameters, choose **Structure Optimization**≫ **☑ Relax atom positions**. The choice for magnetism is **Non-magnetic**. One can also keep the default "**Defined by model**". In either case, the same non-spin-polarized calculation will be executed. Leave all other parameters at their default values and submit the job.

To perform the same calculation for the boron impurity, activate the supercell structure with the F impurity. Move the cursor over the F atom and right-click the mouse button. A menu should come up with an **Edit atom…** option. (If for some reason a menu without the **Edit atom…** option appears, move the cursor into the white area of the active structure window and just left-click. Then try again.) Replace the Fluor atom by a Boron atom.

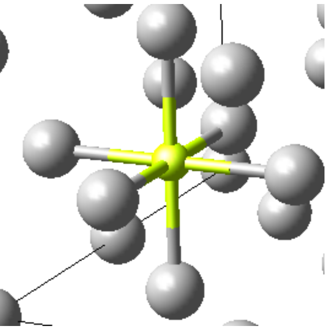






Atom: F

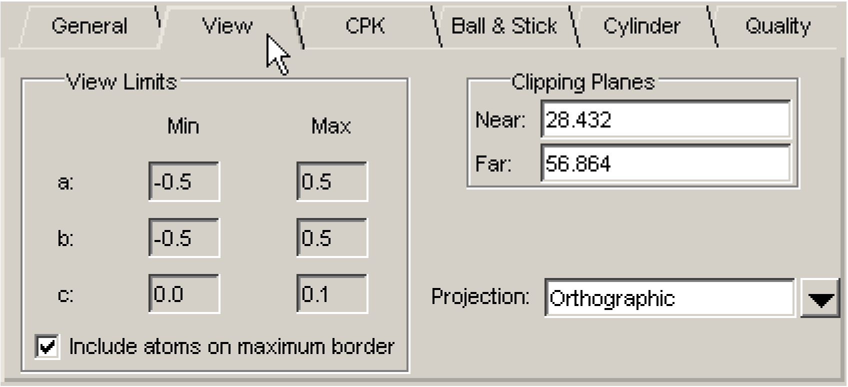
Element: B



Invoke the **VASP 4.6**»**Run** menu. Leave all parameters the same, but you may want to change the title of the calculations. Then submit the job.

Analyze Results

After completion of the job, the structures are retrieved with **File**»**Open**»**Previous Calculation.** Use **Edit**»**Edit Bonds…** to recompute the bonds (they tend to get scrambled during the optimization). For the present purpose, it is convenient to display only a part of the supercell. This is done using the **View**»**Options…** command, which brings up a dialog box as shown to the left. Choose the **Min** and **Max** parameters as indicated.



View Limits

	Min	Max
a:	-0.5	0.5
b:	-0.5	0.5
c:	0.0	0.1

☑ Include atoms on maximum border

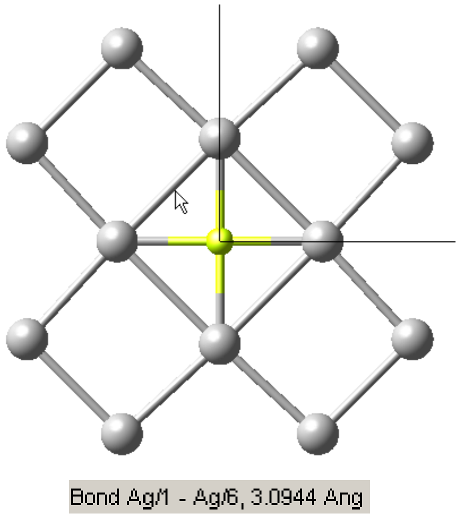
Clipping Planes

Near: 28.432

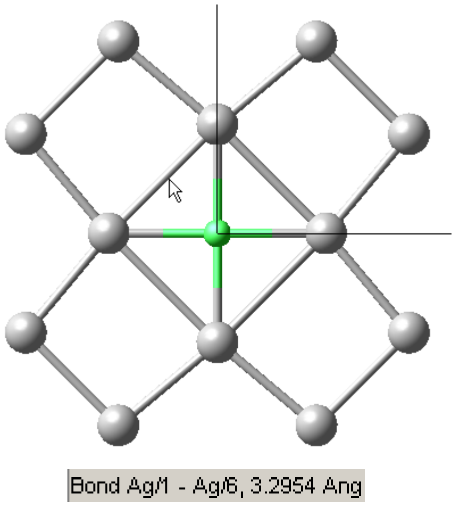
Far: 56.864

Projection: Orthographic

The resulting displays show very clearly that in both cases, the impurity pushes the nearest neighbor Ag atoms away. The distortions are significantly more pronounced for the F impurity than for B, as can be monitored by the distance between two Ag atoms adjacent to the impurity.



Bond Ag/1 - Ag/6, 3.0944 Ang



Bond Ag/1 - Ag/6, 3.2954 Ang

E. Surface Reconstruction of Si(001)

Despite the enormous progress in experimental surface science, notably with spectroscopic methods exploiting synchrotron radiation and scanning tunneling microscopy, computations remain one of the most useful sources for accurate data on surface structures. In fact, quite often it is the combination of experimental and computed results, which gives the most reliable data of surface structures. As an example, let us apply MEDEA to the Si(001) surface. This surface is the typical substrate in the manufacturing of semiconducting devices.

1. Retrieve Bulk Si Structure

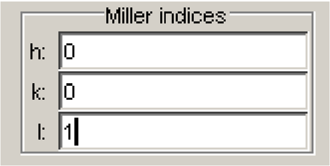
Using INFOMATICA, search for "**Formula is Si**", select **ICSD.76268** and **View structure**.

2. Optimize Lattice Parameters of Bulk Si

Using the Si structure retrieved from INFOMATICA select **VASP 4.6**≫**Run** and perform a **Structure Optimization** (check **☑ Relax atom positions**, **☑ Allow cell shape to change** , and **☑ Allow cell size to change**)with **Accurate** precision. Leave the remaining parameters at their default and launch the calculation. The lattice parameter increases from the initial value of 5.43086 Å by 0.7% to 5.469643 Å.

3. Create Surface

Use **File**≫**Open**≫**Previous Calculation** to load the optimized structure of bulk Si. From the MEDEA menu bar, select **Edit**≫**Build surfaces ...** and define Miller indices 0 0 1 and click on **Search**. The system creates a new unit cell with the (001) plane parallel to the *xy*-plane. You can select the number of cells to stack in the *z*-direction as well as the gap between the slabs. In the present case, leave the values at their defaults as shown on the left side. Use **Create** to open a new window with two panels.



Miller indices

h: 0

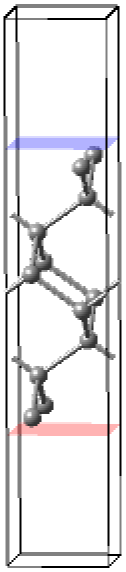
k: 0

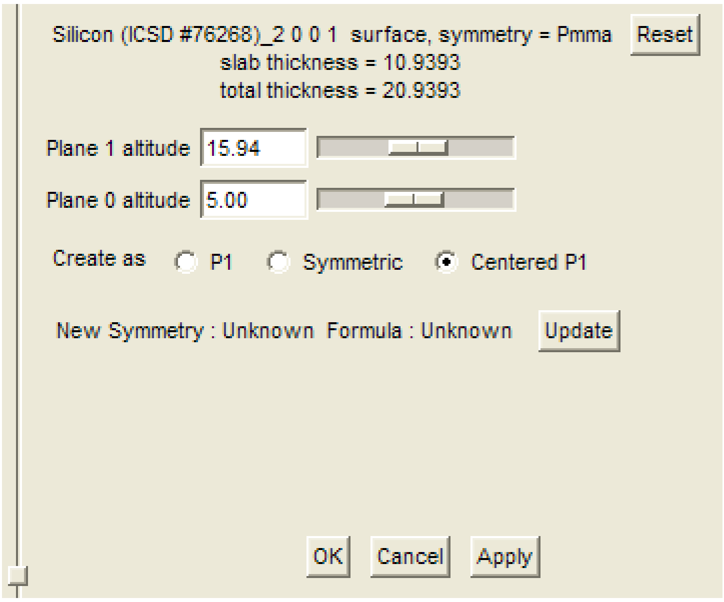
l: 1

Slab thicknesses

Number of cells to stack: 2

Gap thickness (Ang): 10.0





Silicon (ICSD #76268)_2 0 0 1 surface, symmetry = Pmma
slab thickness = 10.9393
total thickness = 20.9393

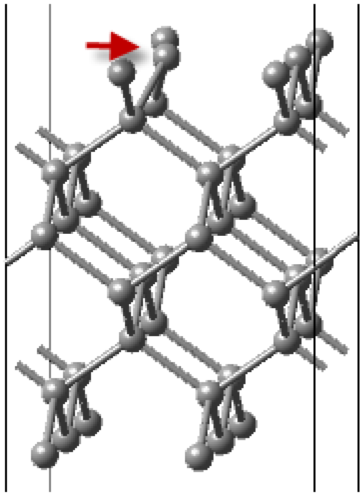
Plane 1 altitude 15.94

Plane 0 altitude 5.00

Create as ○ P1 ○ Symmetric ● Centered P1

New Symmetry : Unknown Formula : Unknown

Rotate the newly created structure in the upper panel to see the supercell, which is a surface model of the Si(001) surface. The sliders in the lower panel allow the trimming of the surface.



Click on **Update** to determine the symmetry of the system. In the present case, this is Pmma. Leave the defaults and select **☑ Create Centered P1** and confirm with **OK**.

This action generates a new structure in a new window. Select this new structure and create a 2x2x1 supercell by using **Edit**≫**Build supercells…**

The resulting structure is shown on the left.

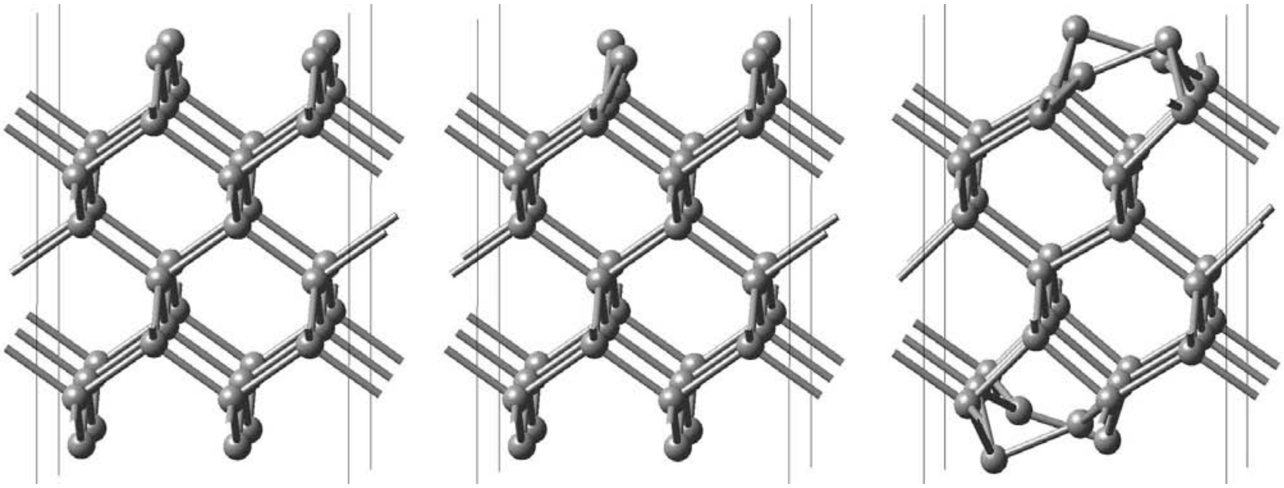
Select the surface atom marked by an arrow and move it from x=0.375 to x=0.45. This breaks the symmetry of the surface and we can now launch an optimization.

4. Set-up and launch VASP Calculation

Make sure that the structural model with the displaced surface atom is selected in the MEDEA window. Choose **VASP 4.6**≫**Run** from the MEDEA tool bar. Choose **Structure Optimization** as the type of calculation. Only the box **☑ Relax atom positions** should be checked. Choose **Normal** accuracy. Leave all other parameters at their default and hit the **Run** button.

Analyze Results

Once the calculation is finished (on an AMD Opteron processor, this takes about 2 hours), retrieve the optimized structure from **File**≫**Open**≫**Previous Calculation**. As shown below, the surface Si atoms form surface dimers with the bond axis tilted with respect to the (001) plane. Within a row, the tilt angles alternates. Note that also the lower surface of the slab model shows this reconstruction, although only one atom at the top surface has been moved initially.



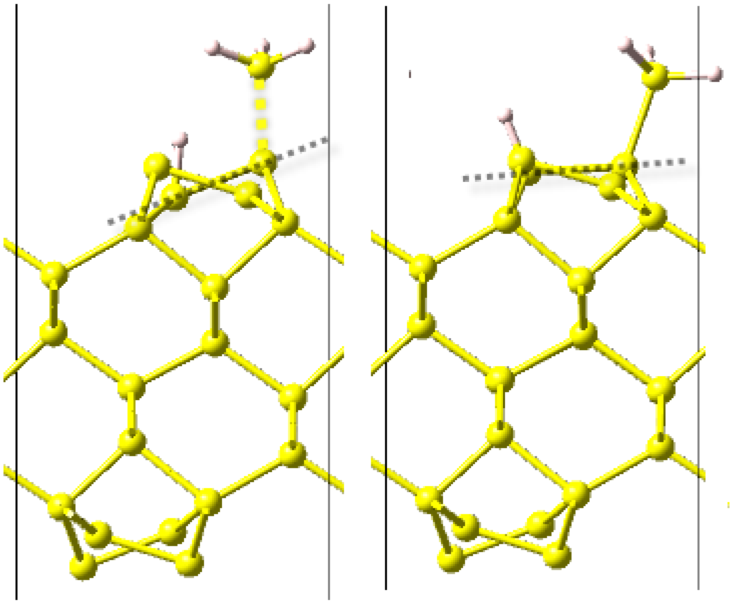
F. Dissociation of SiH_4 on Si(001) Surface

A key process in the semiconductor manufacturing is the reactive adsorption of molecules such as silane (SiH_4) and dichlorosilane ($SiCl_2H_2$) on the surfaces of silicon wafers. This case study demonstrates the calculation of the geometry of a silane molecule on a reconstructed Si(001) surface.

1. Retrieve Structure of Pure Silicon Surface

In a separate case study, the reconstruction of the Si(001) surfaces has been studied. Retrieve the minimized structure from this case using **File**≫**Open**≫**Previous Calculation**.

2. Add Molecule to Surface



Select the structure of the pure reconstructed surface as the active window and right-click the mouse button to get the menu to add atoms. Add one Si atom and four H atoms to the system.

Use the **Move atom…** command to place these atoms approximately in the positions as shown on the left. Or use the Molecular Builder to

3. Relax Structure and Analyze

Select the structure of the silicon surface with the molecular fragments at the starting structure. Choose **VASP 4.6**≫**Run** and select **Structure Optimization** with **☑ Relax atom position**. Leave the other parameters at their default values: **GGA-PBE**-**PAW** potentials, **k-spacing** 0.5 Å^{-1}, **Normal** precision, and **Methfessel-Paxton** smearing width of 0.2 eV. Launch the calculation.

The relaxed structure is shown in the right panel of the figure. The buckling of the Si-surface dimer disappears, when bonds with an –SiH_3 group and an –H atom are formed. The buckling of the neighboring dimer remains unchanged.

G. Magnetic Moment of Iron

Ferromagnetism has its quantum mechanic origin in the difference of spin-up and spin-down electron densities. It is driven by a balance between a gain in exchange energy due to larger spin-polarization and a loss in Coulomb repulsion and kinetic energy of the electron system. Spin-density functional theory is able to predict magnetic moments with astounding accuracy. The present case illustrates this capability for bulk iron.

Outline of Procedure

The computational procedure involves the following steps

- Retrieve structure of bulk iron
- Optimize structure of bulk iron using a spin-polarized Hamiltonian
- Analyze results

1. Retrieve Structure of Bulk Iron

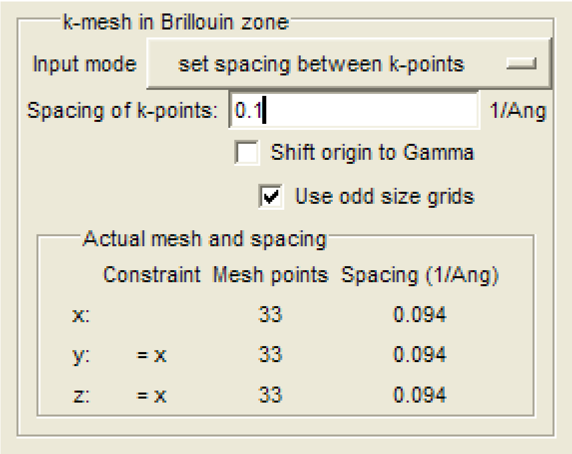
At ambient conditions, the thermodynamically stable form of bulk iron crystallizes in the body-centered cubic structure. A database search with InfoMaticA gives a structure, which was measured at T=79 K with the entry number ICSD.64999. The reported lattice parameter is a=2.8608 Å. Load the structure in the MedeA window (in the database window, select lines, right-click and "**View**").

2. Optimize Lattice Parameters

With the crystal structure of bcc Fe in the MedeA window as the active window (dark blue top bar), we compute the lattice parameters and the internal parameters using VASP. From **Tools** in the MedeA menu bar, select **VASP 4.6** and invoke the VASP 4.6 graphical user interface by selecting **VASP 4.6**»**Run** from the MedeA tool bar.

From the first panel (**Calculation**), select **Structure Optimization** as type of calculation, check **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**.

In other words, a full cell optimizations and relaxation of the atom positions is selected. The calculations are performed with the precision "**Accurate**". In the section **Magnetism** choose **Spin-polarized**. Under the SCF tab, select a **k-spacing** of 0.1 Å^{-1} and check the option **☑ Use odd size grids**. Under the same tab, tighten the **SCF convergence** to 1.0e-06. With these parameters, launch the calculation.



k-mesh in Brillouin zone

Input mode: set spacing between k-points

Spacing of k-points: 0.1 1/Ang

☐ Shift origin to Gamma

☑ Use odd size grids

Actual mesh and spacing

	Constraint	Mesh points	Spacing (1/Ang)
x:		33	0.094
y:	= x	33	0.094
z:	= x	33	0.094

Analyze Results

The computed lattice parameter is 2.8218 Å, which is 1.4 % smaller than the experimental value. Possibly, the reason for this discrepancy is the treatment of correlation in the generalized gradient approximation underlying the present calculations. The GGA may underestimate the Coulomb repulsion of the localized 3*d* electrons of iron.

```
Atomic partial charges (electron charges):
       Atom          s        p        d     total
       -----      -------- -------- -------- --------
       Fe1          0.277    0.275    5.865    6.418
Total magnetic moment: 2.1869 Bohr magnetons
Atomic partial magnetic moments (Bohr magnetons):
       Atom          s        p        d     total
       -----      -------- -------- -------- --------
       Fe1         -0.004   -0.027    2.258    2.227
```

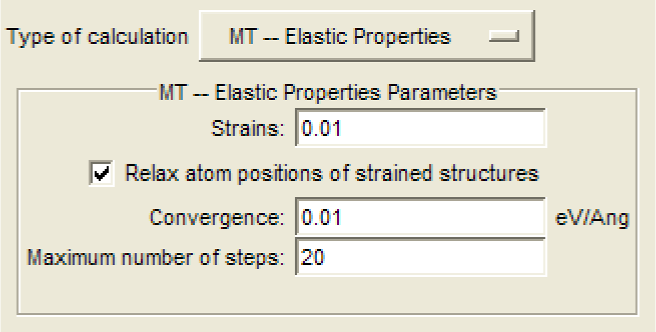
The magnetic moments are reported in the `Job.out` file. The total computed magnetic moment of the primitive cell is 2.1869 μB (Bohr magnetons), which is the difference between the charge density of spin-up and spin-down electrons. This value is close to the experimental result of 2.12 μ B. The deviation between the computed and experimental value is 3.2 %.

VASP computes projected partial charges for each atom. In the case of bcc Fe, the *s*-, *p*-, and *d*-charges are given together with the partial magnetic moments (that is the difference between spin-up and spin-down partial charges). The magnetic moment is dominated by *d*-electrons. The spin-polarization of the *s*- and *p*-electrons is opposite to that of the *d*-electrons, which makes the *d*-moment larger than the total magnetic moment per atom.

H. Elastic Properties of Diamond

1. Determination of the stable structure

The diamond structure ICSD #29068 is retrieved with InfoMaticA and loaded in the MedeA window with the **View** command. The cell parameters are optimized with VASP using the following parameters: **GGA-PBE**-**PAW**, **non-spin-polarized**,**Normal** precision, **k-spacing** 0.5 Å^{-1} (7×7×7 k-mesh), geometry **Convergence** 0.01 eV/Å, **SCF convergence** 1.0e-07, and **Tetrahedron method** for Brillouin-zone integration. The resulting lattice parameter is a=3.563 Å.



Type of calculation: MT -- Elastic Properties

MT -- Elastic Properties Parameters

Strains: 0.01

☑ Relax atom positions of strained structures

Convergence: 0.01 eV/Ang

Maximum number of steps: 20

2. Computation of elastic constants

The structure optimized in step 1 is taken as the starting point for the calculation of elastic constants. Select the model in the MedeA window, invoke **VASP**≫**Run** and choose **MT – Elastic Properties** as type of calculation. Check the box **☑ Relax atom positions** and set the parameters as shown on the left. In this case, only one strain, namely 0.01 (or 1%) is used. **Convergence** refers to the maximum residual force on the atoms after their relaxation for a given deformation of the cell, with a limit on the maximum number of steps, in this case 20. The other computational settings are the same as in step 1, namely GGA, PAW, non-spin-polarized, **Normal** precision, k-spacing 0.5 Å^{-1} (7×7×7 k-mesh), SCF convergence 1.0e-07, and tetrahedron scheme for Brillouin-zone integration.

3. Results

The results are the content of `Job.out` file, here annotated with explanations.

```
Status: finished

Opening the database

Elastic properties calculation using a strain of 0.01

Need to run a total of 4 calculations, 1 for the unstrained system and 3 strained systems
for each of the 1 strain levels.

The atom positions will be relaxed in structures where the atoms are not fixed by symmetry,
i.e. where the number of degrees of freedom (DOF) is greater than zero.

The convergence criterion is 0.01 eV/Ang.
          Strain           Spacegroup      DOF
         -----------    ----------------- ---
         unstrained:    Fd-3m              0  spacegroup will change due to strain
                   plus for each strain
```

```
             +e1:    I4_1/amd         0     expansion of cell
             -e1:    I4_1/amd         0     compression of cell
             +e4:    Imma             1     atoms relax in one direction

VASP parameters
===============

Since no magnetic moments are in the model, this is a non-magnetic calculation using
'normal' precision and a default planewave cutoff energy of 400.000 eV.

The electronic iterations convergence is 1.00E-007 eV using the Normal (blocked Davidson)
algorithm and reciprocal space projection operators.

The requested k-spacing is 0.5 per Angstrom, which leads to a 7x7x7 mesh.

This corresponds to actual k-spacings of 0.436 x 0.436 x 0.436 per Angstrom.

Using the linear-tetrahedron method.

Other non-default parameters:
       Convergence criterion for ionic relaxations is 0.01 eV/Ang
       Number of steps is 20
==========================================
VASP parameters
===============

Since no magnetic moments are in the model, this is a non-magnetic calculation using
'normal' precision
and a default planewave cutoff energy of 400.000 eV.

The electronic iterations convergence is 1.00E-007 eV using the Normal (blocked Davidson)
algorithm and reciprocal space projection operators.
The requested k-spacing is 0.5 per Angstrom, which leads to a 7x7x7 mesh.
This corresponds to actual k-spacings of 0.436 x 0.436 x 0.436 per Angstrom.
Using the linear-tetrahedron method.
Other non-default parameters:
       Convergence criterion for ionic relaxations is 0.01 eV/Ang
       Number of steps is 20
==========================================
-----------------------------------------------------------------------
Using GGA-PBE / PAW potentials:
       C
Results for initial structure
-----------------------------------------------------------------------
There are 20 symmetry-unique k-points
The plane wave cutoff is 400.00 eV
…energy values of Vasp calculation omited
Cell parameters:
 Parameter    Value
---------- -----------
         a     3.562598
         b     3.562598
         c     3.562598
     alpha    90.000000
      beta    90.000000
     gamma    90.000000
        Density:      3.529 Mg/m^3
```

```
       Pressure:   -94.000 MPa
               =  -940.000 bar  quality of optimization: excellent, pressure < 1 kbar
         Stress:    94.000    94.000    94.000     0.000     0.000     0.000 MPa
               =   940.000   940.000   940.000     0.000     0.000     0.000 bar
The pressure and stress include only electronic terms, i.e. the vibrational,
temperature and other terms are not included here.
Fractional Coordinates:
       Atom              Coordinates
       -----      -------- -------- --------
       C1           0.2500   0.2500   0.2500
Atomic partial charges (electron charges):
       Atom            s        p        d     total
       -----      -------- -------- -------- --------
       C1            0.666    1.474    0.038    2.178
-------------------------------------------------------------------------
                               --------- Stress (MPa) ---------
        Strain    Amount       Unstrained  Strained    Change
       ---------- ------       ---------- ---------- ----------
       unstrained
              +e1 1.000%             94      10706      10612  noise from unstrained cell
              -e1 1.000%             94     -10794     -10888  negligible: 50 MPa ≃ 1%
              +e4 1.000%              0       5672       5672
Results for strains 0.01:
Least squares converged in 1 iterations to a residual of 0.69%
Residual strain:
             Residual    Original              Predicted
       Param   Strain      Value       Delta      Value
       ----- ---------- ----------- ----------- -----------
           a  -0.000001    3.562598    0.000002    3.562600
Elastic constants (GPa):
                Least-sq
           ---------------
       C11 1075.00 ± 5.65
       C12  139.30 ± 5.65
       C44  567.20 ± 7.99
The errors are from the least-squares fit and only give the numerical uncertainty.
Elastic constant matrix (GPa):
     |      1          2          3          4          5          6
-----|------------------------------------------------------------------
   1 |   1075.00     139.30     139.30       0.00       0.00       0.00
   2 |    139.30    1075.00     139.30       0.00       0.00       0.00
   3 |    139.30     139.30    1075.00       0.00       0.00       0.00
   4 |      0.00       0.00       0.00     567.20       0.00       0.00
   5 |      0.00       0.00       0.00       0.00     567.20       0.00
   6 |      0.00       0.00       0.00       0.00       0.00     567.20
Elastic compliance matrix (1/GPa) (x 1000):
     |      1          2          3          4          5          6
-----|------------------------------------------------------------------
   1 |    0.9587    -0.1100    -0.1100     0.0000     0.0000     0.0000
   2 |   -0.1100     0.9587    -0.1100     0.0000     0.0000     0.0000
   3 |   -0.1100    -0.1100     0.9587     0.0000     0.0000     0.0000
   4 |    0.0000     0.0000     0.0000     1.7630     0.0000     0.0000
   5 |    0.0000     0.0000     0.0000     0.0000     1.7630     0.0000
```

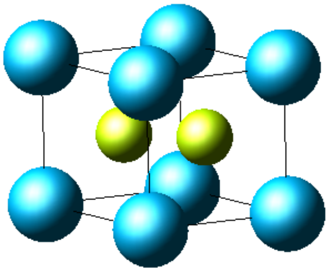
```
   6 |    0.0000    0.0000    0.0000    0.0000    0.0000    1.7630

The following are eigenvalues and corresponding eigenvectors of the elastic constant matrix,
including pressure terms. Negative eigenvalues indicate instability.
See G VSin'ko and N A Smirnov, J. Phys.: Condens. Matter 14 (2002) 6989-7005.
                                    Eigenvector
Eigenvalue          exx      eyy      ezz      eyz      exz      exy
----------        -------- -------- -------- -------- -------- --------
    935.89          0.4082   0.4082  -0.8165   0.0000   0.0000   0.0000
   1353.51          0.5774   0.5774   0.5774   0.0000   0.0000   0.0000
    935.89          0.7071  -0.7071   0.0000   0.0000   0.0000   0.0000
   2269.18          0.0000   0.0000   0.0000   1.0000   0.0000   0.0000
   2269.18          0.0000   0.0000   0.0000   0.0000   1.0000   0.0000
   2269.18          0.0000   0.0000   0.0000   0.0000   0.0000   1.0000
  All Eigenvalues positive, structure is stable
   Modulus     Voigt     Reuss     Hill
------------ --------- --------- ---------
        Bulk    451.20    451.20    451.20 GPa
       Shear    527.46    522.79    525.13
     Young's   1138.67   1131.40   1135.04
Longitudinal                       1151.37
Velocity of sound
       Calculated from Hill moduli:
         transverse waves:    12199 m/s
       longitudinal waves:    18063 m/s
                     mean:    12769 m/s
Debye temperature: 2134.1 K
Thermodynamic Properties and Coefficient of Linear Expansion
   for empirical formula C
The following results are obtained from the Debye model.
Definitions:
      Cv              : vibrational heat capacity at constant volume
E_vib(T)=E(T)-E(0)  : the change in vibrational internal energy from 0 K
                        E(0) is the zero point energy (ZPE)
      S(T)            : the vibrational entropy at temperature T
   -(A(T)-E(0))      : the change in the vibrational Helmholtz free energy from 0 K
      E(T)            : the electronic plus vibrational energy of formation, so this term is
                        E_elec + ZPE + E_vib(T)
      A(T)            : the electronic plus vibrational Helmholtz free energy,
                        E(T) - T.S(T)
     alpha            : the thermal coefficient of linear expansion (x 10^6)
Note that the electronic energy, which is part of the enthalpy and free energies, is
referenced to the elements in their standard state.
Finally, these results are appropriate for the solid, crystalline material below its melting
point. Since the melting point of your compound is unknown (to us), the following table
extends to high temperatures, probably well above the melting point of your compound. The
results near and above the melting point are not physical, but the table extends to those
temperatures for e.g. high-melting point oxides.
Electronic energy of formation =     1.54 kJ/mol (referenced to elements in the standard state)
                       PV term =    -0.32 kJ/mol
             Zero-point energy =    19.96 kJ/mol

    T      Cv      E(T)-E(0)    S(T)  -(A(T)-E(0))   E(T)       A(T)      alpha
    K    J/K/mol    kJ/mol    J/K/mol    kJ/mol     kJ/mol     kJ/mol    x 10^6 **
```

```
 ----- ----------- ----------- ----------- ----------- ----------- ----------- ------------
     1      0.0000      0.0000      0.0000      0.0000     21.5067     21.5067      0.0000
…
     5      0.0000      0.0000      0.0000      0.0000     21.5067     21.5067      0.0000
…
   100      0.2000      0.0050      0.1167      0.0067     21.5117     21.5000      0.0109
…
   298      4.5155      0.3674      2.7574      0.4543     21.8741     21.0524      0.2450
   300      4.5865      0.3765      2.8042      0.4647     21.8832     21.0419      0.2489
…
  1000     20.0724     10.3773     20.2100      9.8326     31.8840     11.6740      1.0891
…
  2000     23.5792     32.7273     34.7401     36.7530     54.2339    -15.2463      1.2794
…
```

I. Elastic Constants of TiB$_2$

This application shows the calculation of the elastic constants of TiB$_2$, a hexagonal structure.

1. Retrieve structure from database



The structure of TiB$_2$ is taken from ICSD #30418.

2. Optimization of unit cell

The unit cell of TiB$_2$ is optimized using the following parameters (taken directly from the `Job.out` file as displayed by the JobServer):

Structure Optimization: **☑ Relax Atom Positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change**,

Convergence of **0.001 eV/Ang**,

☑ Increase Plane wave cutoff with **Normal** **Precision**.

In the **SCF** panel put **set spacing between k-points** to **0.25 /Ång**,

with **☑ Use odd size grids**,

increase the **SCF convergence** to **1.0e-07**

The resulting cell parameters are:

```
Parameter   Original     change      Final        %
---------- ------------ ---------- ------------ -----
         a     3.030000   0.004963     3.034963   0.2
         b     3.030000   0.004963     3.034963   0.2
         c     3.230000  -0.004577     3.225423  -0.1
     alpha    90.000000   0.000000    90.000000   0.0
      beta    90.000000   0.000000    90.000000   0.0
     gamma   120.000000   0.000000   120.000000   0.0
```

3. Calculation of Elastic Constants

Load the optimized structure with **File**≫**Open**≫**Previous Calculation** and keep the computational parameters from the lattice optimization, change the type of calculation to **MT – Elastic Properties** and **Strains** of 1%, with **☐ Relax atoms of strained structures** unchecked.

```
   Strain          Spacegroup      DOF  degrees of  freedom
  -----------    ----------------- ---
  unstrained:     P6/mmm           0
          plus for each strain
        +e1:      Cmmm             1  degree of freedom for relaxation of atoms
        -e1:      Cmmm             1
        +e3:      P6/mmm           0
        -e3:      P6/mmm           0
        +e4:      C2/m             2
```

Checking **☑ Relax atoms of strained structures** includes relaxation of atoms in strained cells, where changes of the space group allow atoms to move, in the example of TiB_2 these are strains +e1, -e1, and +e4.

Experimental and computed elastic constants of TiB_2	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Gilman and Roberts [91]	690	410	320	440	250
Spoor et al[92]	660	48	93	432	260
relaxed atoms of strained structures	649	72	102	457	258
This calculation	651	70	102	457	258

Note: The large value of C_{12} given by Gilman and Roberts appears not to be a simple typographical error.

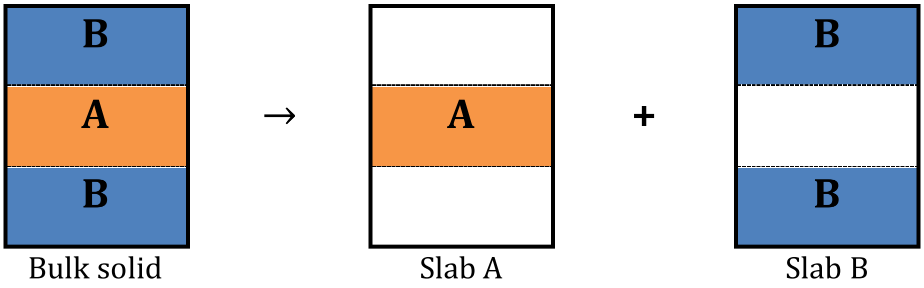
The total computing time of this calculation was 7 minutes on an Intel Core 2 Duo with 2 GHz, including relaxation of atoms in strained structures requires 10 minutes total.

J. Cleavage Energy of TiN

The purpose of this study is the computation of the cleavage energy of a material, i.e. the energy required to split a material into two parts. This could be a bulk material, a grain boundary, or an interface. To this end, one needs to compute the total energy of the bulk solid and the material with a free surface.

Outline of Approach

Within a supercell approach, the cleavage process is described as follows:

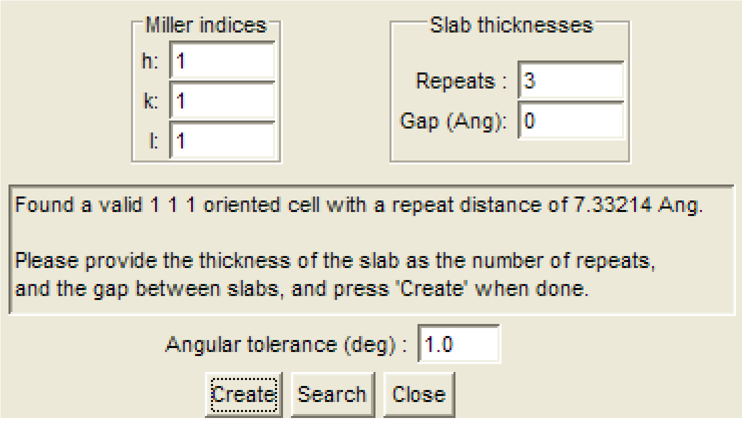


This process cleaves two A|B interfaces and leads to the formation of free surfaces of A and B.

1. Optimize Structure of Bulk TiN

The experimental crystal structure of TiN is retrieved with INFOMATICA. Using the search "**Formula is TiN**" gives several structures. We select ICSD.105128. Next, a cell optimization with VASP 4.6 is performed using "**Accurate**" precision. All other computational parameters are left at their defaults, *i.e.* **GGA-PBE**-**PAW** potentials with **Ti_pv** (the Ti-3*p* levels are treated as valence), a geometry **Convergence** of 0.02 eV/Å, a **k-spacing** of 0.5 Å^{-1}, and **Methfessel-Paxton** smearing with **Smearing width** σ =0.2 eV. The computed equilibrium lattice parameter is 4.2332 Å, which is 0.3 % smaller than the original experimental value of 4.2442 Å.

2. Construction of Slabs A and B



h: 1
k: 1
l: 1

Repeats : 3
Gap (Ang): 0

Found a valid 1 1 1 oriented cell with a repeat distance of 7.33214 Ang.

Please provide the thickness of the slab as the number of repeats, and the gap between slabs, and press 'Create' when done.

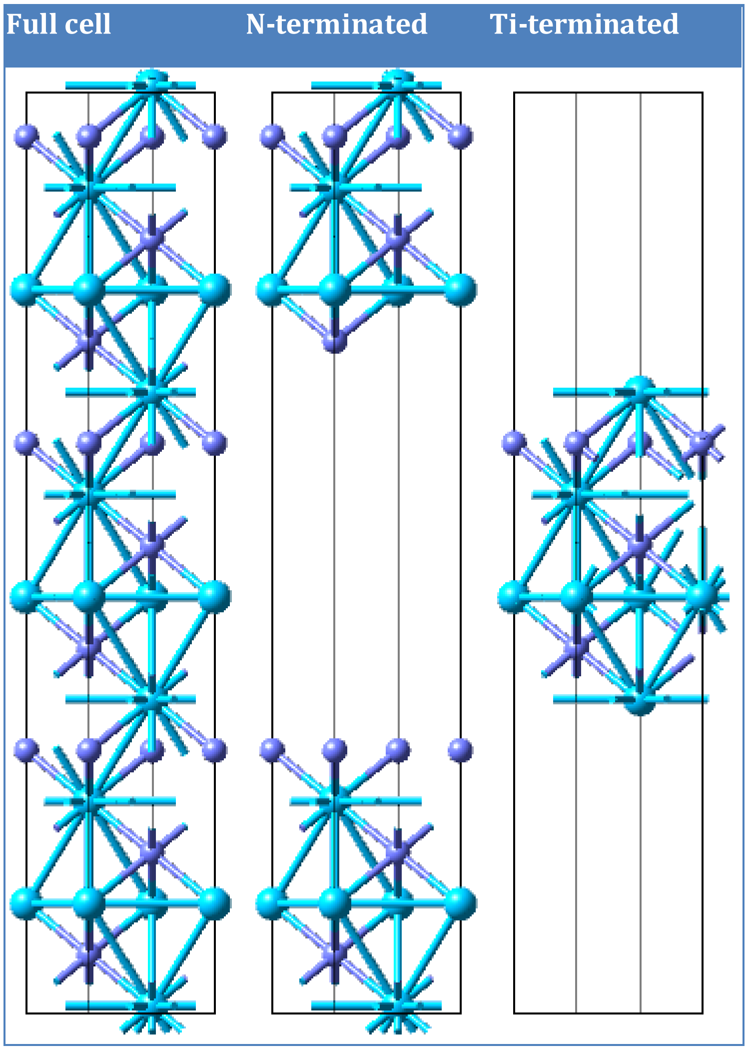
Angular tolerance (deg) : 1.0

Using the optimized unit cell of TiN, the surface builder is used to construct two slab models with one slab being terminated on both sides with Ti atoms and the other slab model terminated with N atoms.

Select **Edit**»**Build surfaces…**, enter "1 1 1" as Miller indices, then "**Search**" for possible cells. A cell is found with a thickness of 7.33216 Å.

Choose **Repeats**:3 with a **Gap (Ång)** of 0 and hit "**Create**".

This gives a full supercell as shown to the left Make two copies of this full cell using the command **Edit**≫**Copy**.



Full cell N-terminated Ti-terminated

Activate the window with the first copy of the full structure and use the ↖ icon in the upper left corner of the MEDEA tool bar and hold left mouse button and drag to select seven layers in the middle.

Right-click and hit **Delete selected atoms** or use the **DEL** key.

This will generate a N-terminated slab as shown in the figure in the middle panel.

You can also use the Spreadsheet button, sort atoms by z-position and delete the atoms in this manner.

Starting with the second copy of the full structure, delete the complementary atoms above and below.

This leads to a 7-layer slab model of a Ti-terminated surface as shown in the right-most panel.

3. Relax Slabs A and B and Compute Total Energy

Using VASP 4.6, relax the atom positions in the N-terminated and Ti-terminated slabs. To this end, select “**Normal**” precision, “Projection **Real space**” and leave the other parameters at their defaults. The **k-mesh** of 0.5 Å^{-1} leads to a 5x5x1 mesh, which is quite reasonable.

4. Calculate Reference Energy of Bulk TiN

The highest degree of error cancellation is achieved, when the energy for bulk TiN is computed with the full supercell using the same computational parameters as in the slab calculations rather than with the primitive cell of TiN. This is done by performing a single point energy calculation of the full cell.

5. Evaluate Cleavage Energy

The energy of cleaving a TiN crystal along a TiN(111) plane is obtained from the formula

$$E_{\mathrm{cleavage}}^{\mathrm{A|B}} = \frac{1}{2A}\left(E_{\mathrm{slab}}^{\mathrm{A}} + E_{\mathrm{slab}}^{\mathrm{B}} - E_{\mathrm{bulk}}^{\mathrm{AB}}\right) \tag{7-1}$$

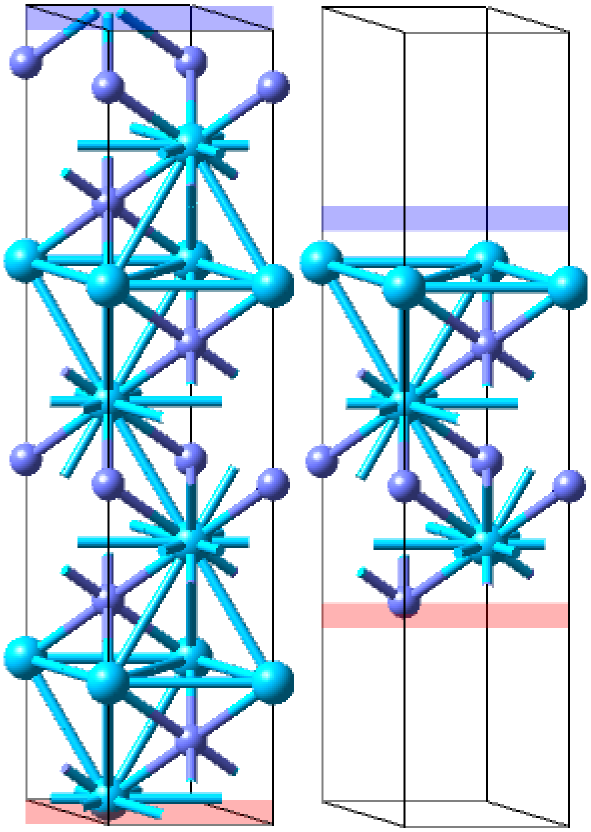
where A is the surface area in the supercell.

Analyze Results

The results of the calculation of the cleavage energy are shown in the table below.

Cleavage of TiN in (111) Plane	Value	Units
Total energy (eV) of full supercell, $E_{\mathrm{bulk}}(Ti_9N_9)$	-176.925	eV
Total energy of relaxed N-terminated slab, $E_{\mathrm{slab}}^{\mathrm{A}}(\mathrm{Ti_5N_6})$	-105.085	eV
Total energy of relaxed Ti-terminated slab, $E_{\mathrm{slab}}^{\mathrm{B}}\ (\mathrm{Ti_4N_3})$	-65.286	eV
Cleavage energy $E_{\mathrm{cleavage}} = \frac{1}{2}\left(E_{\mathrm{slab}}^{\mathrm{A}} + E_{\mathrm{slab}}^{\mathrm{B}} - E_{\mathrm{bulk}}\right)$	3.28 5.250×10^{-19}	eV J
Unit cell area (with a=2.993 Å): $A = \frac{1}{2}\sqrt{3}\,a^2$	7.758×10^{-20}	m^2
Cleavage energy	6.77	$\mathrm{J\ m^{-2}}$

6. Using a Stoichiometric Slab Model



Both slabs used above are symmetric in terms of their surface termination, but they are non-stoichiometric. Another option would be to choose stoichiometric slabs, but accept the fact that each slab has a dipole moment, because one side is terminated with Ti and the other side with N. To explore this alternative, load the optimized unit cell of TiN from the bulk calculation. Then invoke the surface builder, choose (1 1 1) as the Miller indices and hit **Search**. Leave the **Repeats** at 2 and change the **Gap (Ång)** to 0. Then build the structure by **Create**. This model, shown below on the left, consists of six layers of Ti and six layers of N. Use **Create Centered P1** to generate a model with the all atoms.

Moving the upper and lower planes as shown in the right panel in the figure, a slab is highlighted with three layers of each atom type. Now use **Create Centered P1** again to generate a slab model.

Perform a relaxation of the atoms on the slab model and a single point energy calculation with the full model using normal precision, real space projection, and leave all other parameters at their defaults.

Slab A and Slab B are identical, namely Ti_3N_3 slabs with one side Ti-terminated and the other side N-terminated. Hence the cleavage energy is

$$E_{\text{cleavage}} = \frac{1}{2A}\left(E_{\text{slab}}^{\text{A}} + E_{\text{slab}}^{\text{A}} - E_{\text{bulk}}\right) = \frac{1}{2A}\left(2E_{\text{slab}} - E_{\text{bulk}}\right) \qquad (7\text{-}2)$$

Using this alternative approach, we find E_{slab} = -55.665 eV and E_{bulk} = -117.969 eV.

This gives E_{cleavage} = (1/A) 3.32 eV = $(1/7.758)\times10^{20} \times 1.60219\times10^{-19} \times 3.32$ = 6.86 J/m^2.

The previous approach yielded a value of 6.77 J/m^{-2}. The values are close, but not identical, which is due to finite thickness effects of the slabs. However, the values are sufficiently similar to give confidence that the structural models are reasonable.

A similar study on the non-polar TiN(001) surface gives a cleavage energy of 2.60 J/m^2. This demonstrates that the non-polar surface is thermodynamically far more stable than the polar surface, at least as long as the surfaces are not covered, for example, by a polar liquid after cleavage.

K. Convergence of Total Energy with Plane Wave Cutoff and k-Mesh: Mo, Al, and LiF

The convergence of the total electronic energy as computed with VASP is determined by two key computational parameters, namely the number of basis functions (plane wave cutoff) and the number of k-points (k-spacing). In addition the integration of the states near the Fermi level is influenced by a smearing parameter. This case study demonstrates the automatic determination of these computational parameters for three systems, namely the transition metal molybdenum, the simple metal aluminum, and the ionic compound lithium fluoride.

Outline of Procedure

The computational procedure involves the following steps

- Retrieve a structure from database
- Choose desired convergence criterion
- Launch convergence job
- Analyze results

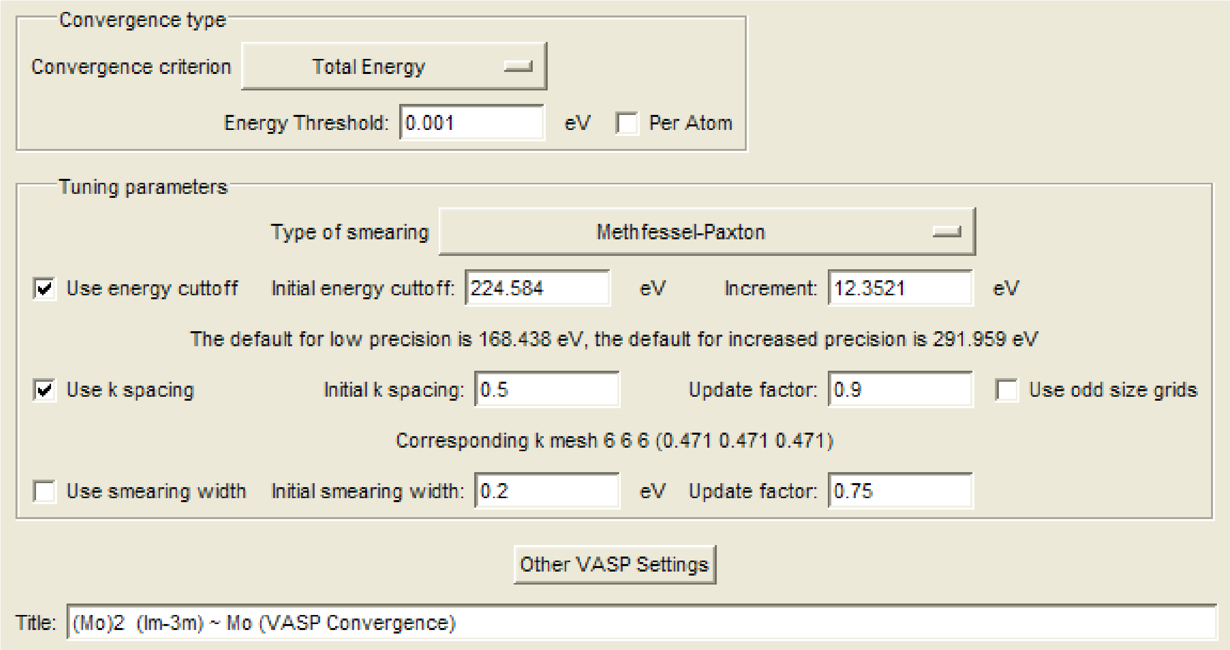
1. Molybdenum Metal

a. Load Structure

Searching INFOMATICA for structures and lattice parameters of elemental Mo results more than 50 entries in ICSD, Pearson and Pauling. The reported lattice parameters for the bcc structure with Im-3m space group symmetry range from 3.1403 Å to 3.1474 Å. Any entry with the right bcc structure is good, because for the actual lattice parameter is not critical for the convergence test, since a given set of computational parameters (plane wave cutoff and number of k-points) converges to the same structure for cases with similar lattice parameters.

b. Invoke Automated Convergence Tool

With the structure ICSD.76147 displayed in MEDEA as active window, the **Automated Convergence** module is selected from the **Tools** menu. A new menu item, **Convergence**, appears in the top menu bar, select **VASP Computation** to start.



Convergence type

Convergence criterion: Total Energy

Energy Threshold: 0.001 eV ☐ Per Atom

Tuning parameters

Type of smearing: Methfessel-Paxton

☑ Use energy cutoff Initial energy cutoff: 224.584 eV Increment: 12.3521 eV

The default for low precision is 168.438 eV, the default for increased precision is 291.959 eV

☑ Use k spacing Initial k spacing: 0.5 Update factor: 0.9 ☐ Use odd size grids

Corresponding k mesh 6 6 6 (0.471 0.471 0.471)

☐ Use smearing width Initial smearing width: 0.2 eV Update factor: 0.75

Title: (Mo)2 (Im-3m) ~ Mo (VASP Convergence)

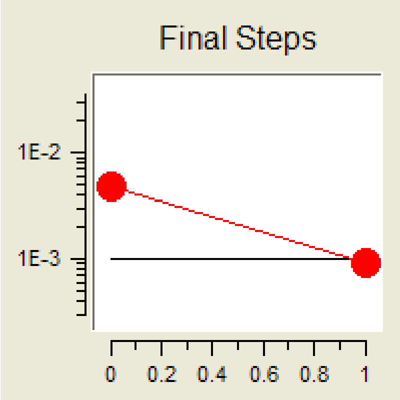
In the present case, a convergence of 0.001 eV in the total energy is requested as a function of two variables (**Tuning parameters**), namely the **☑ Use energy cutoff** (number of basis functions) and **☑ Use k spacing**, the density of the k-mesh (number of k-points for integration over Brillouin zone in the calculation of the charge density from the wave functions). The starting values and increments for these two parameters are chosen by the Convergence Module automatically depending on the system. These parameters are normally left unchanged as well as **Other VASP Settings**.

The convergence test is done for the two critical computational parameters, the plane wave cutoff and the k-mesh. For the integration of the one-electron densities over the first Brillouin zone, a **Methfessel-Paxton** smearing is selected with the default of σ=0.2 eV. For clarity, the convergence of the total energy as a function of the smearing parameters is done in a second step: **☐ Use smearing width** is unchecked. However, the Automated Convergence module allows the simultaneous optimization of all three parameters.

With all parameters for the convergence run selected, a job is launched with the **Run** button. This triggers the execution of a series of computational tasks.

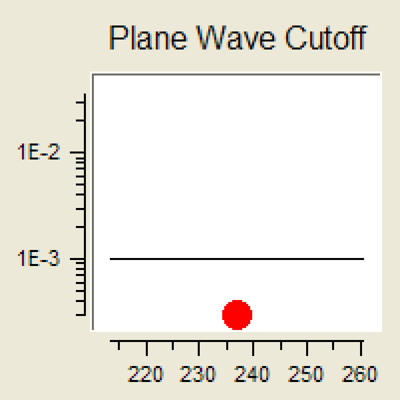
c. Monitor progress

The Convergence Monitor enables the user to follow the execution of the convergence process which starts with the initial parameters for the plane wave cutoff and the k-mesh and first pursues the convergence of both parameters independently. The results are plotted in the middle and right graph. The details of each computational task are reported in a list. Once each of the two parameters is converged independently, final steps are taken, where both parameters are increased. The results of the final steps are displayed in the left panel.

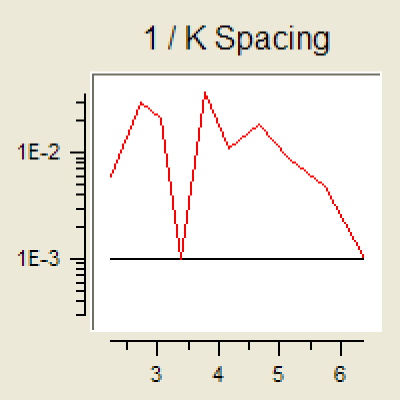


Convergence achieved.

Final step (1) confirms values.



Good starting values of PWC. Increase does not change results



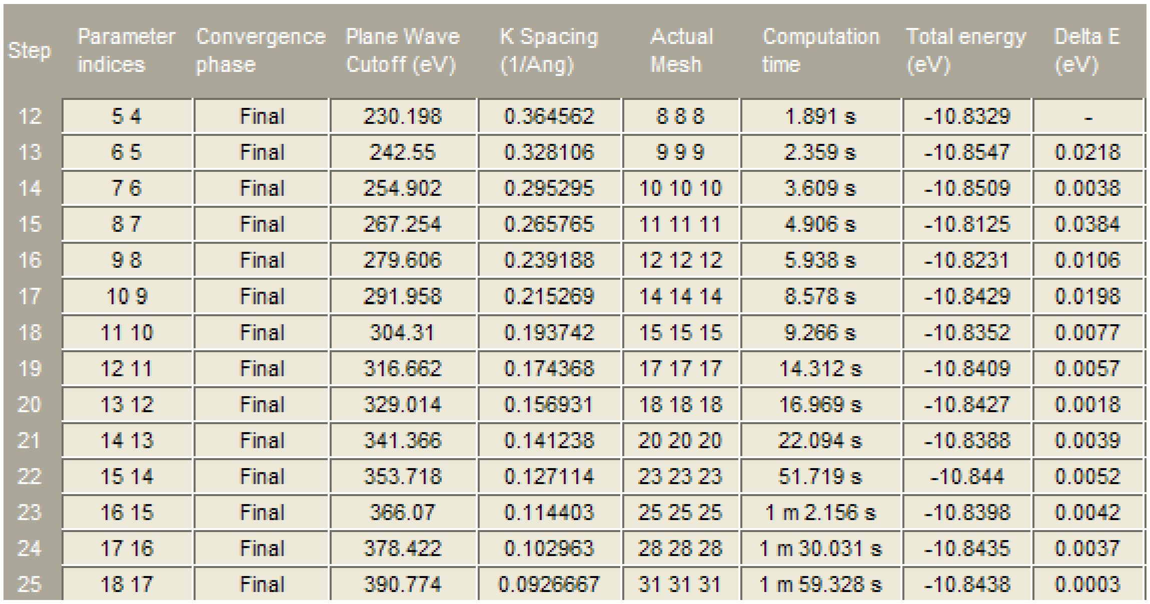
Erratic behavior for small values (<5) can lead to assume convergence (at 0.33).

The “Refresh” button updates the information in the Convergence Monitor by querying each computational node, which is working on the job. Note that one can change the size of the graphs and the central table by moving the little square just below the table on the right-hand side of the window.

d. Analyze Results

Step 0 is a calculation with the initial parameters. The first index labels the steps in the plane wave cutoff. The refinement of the k-spacing is done in a similar way with the actual k-mesh given in a separate column

The next column provides the computing time of each task, followed by the total energy and the change of the total energy of the entire system, and per atom. In the present case, the unit cell contains only one Mo atom and the last columns show the same numbers.

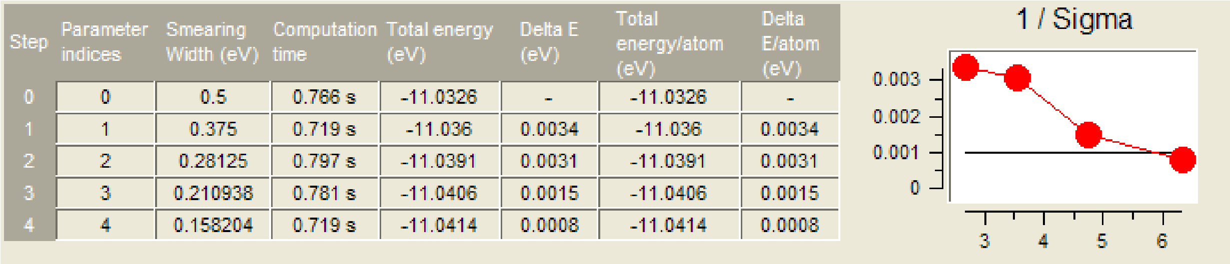


Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
12	5 4	Final	230.198	0.364562	8 8 8	1.891 s	-10.8329	-
13	6 5	Final	242.55	0.328106	9 9 9	2.359 s	-10.8547	0.0218
14	7 6	Final	254.902	0.295295	10 10 10	3.609 s	-10.8509	0.0038
15	8 7	Final	267.254	0.265765	11 11 11	4.906 s	-10.8125	0.0384
16	9 8	Final	279.606	0.239188	12 12 12	5.938 s	-10.8231	0.0106
17	10 9	Final	291.958	0.215269	14 14 14	8.578 s	-10.8429	0.0198
18	11 10	Final	304.31	0.193742	15 15 15	9.266 s	-10.8352	0.0077
19	12 11	Final	316.662	0.174368	17 17 17	14.312 s	-10.8409	0.0057
20	13 12	Final	329.014	0.156931	18 18 18	16.969 s	-10.8427	0.0018
21	14 13	Final	341.366	0.141238	20 20 20	22.094 s	-10.8388	0.0039
22	15 14	Final	353.718	0.127114	23 23 23	51.719 s	-10.844	0.0052
23	16 15	Final	366.07	0.114403	25 25 25	1 m 2.156 s	-10.8398	0.0042
24	17 16	Final	378.422	0.102963	28 28 28	1 m 30.031 s	-10.8435	0.0037
25	18 17	Final	390.774	0.0926667	31 31 31	1 m 59.328 s	-10.8438	0.0003

This automated convergence run demonstrates that the total energy of a Mo bcc unit cell is converged to 0.001 eV with a plane wave cutoff of 378.5 eV and a density of the k-mesh of 0.10 Å^{-1} corresponding to a 38×38×38 k-mesh of the bcc Mo unit cell. The large number of final steps indicates, that the choice of initial values for energy cutoff and k-spacing where lucky guesses, both seem to be converged when studied independently, but it turns out, that the k-spacing was not really converged, so there are many final steps till convergence.

Taking different starting values, notably a denser mesh, will reduce the demands on the plane wave cut-off. However, the k spacing is the more computationally demand parameter.

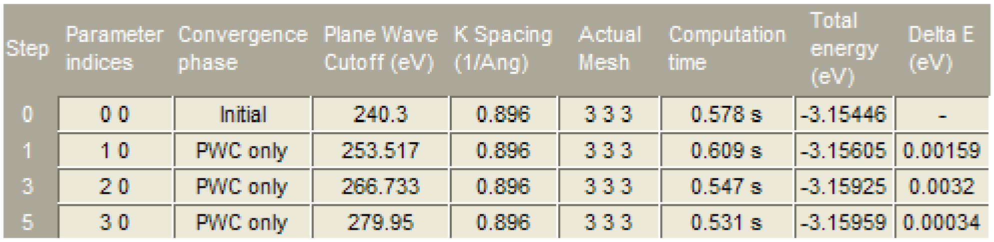
The convergence of the smearing width σ was tested in a separate run and it turn out, that the default setting of σ =0.2 is sufficient.



Step	Parameter indices	Smearing Width (eV)	Computation time	Total energy (eV)	Delta E (eV)	Total energy/atom (eV)	Delta E/atom (eV)
0	0	0.5	0.766 s	-11.0326	-	-11.0326	-
1	1	0.375	0.719 s	-11.036	0.0034	-11.036	0.0034
2	2	0.28125	0.797 s	-11.0391	0.0031	-11.0391	0.0031
3	3	0.210938	0.781 s	-11.0406	0.0015	-11.0406	0.0015
4	4	0.158204	0.719 s	-11.0414	0.0008	-11.0414	0.0008

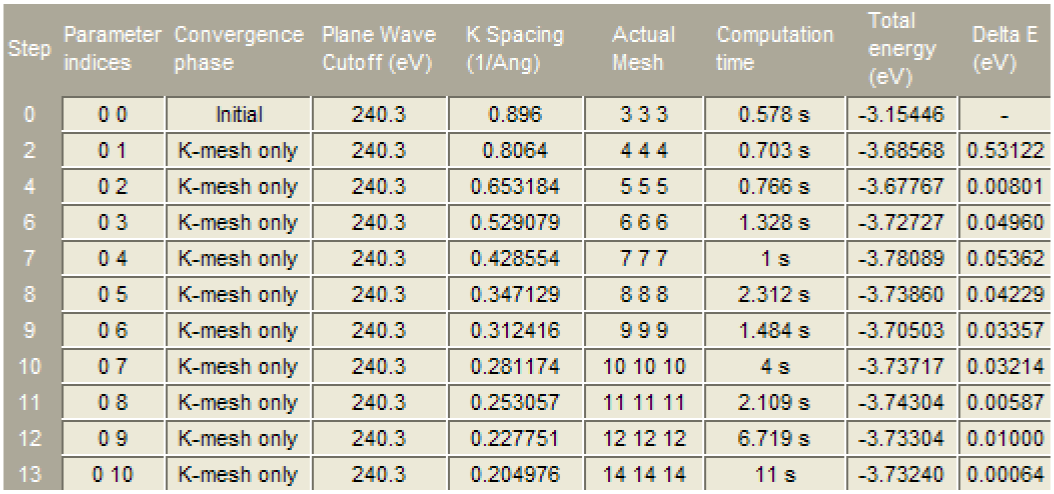
2. Aluminum Metal

The convergence behavior is demonstrated for two other cases, namely metallic aluminum, where the convergence is very sensitive to the k-mesh, but rather insensitive to the plane wave cutoff and lithium fluoride, where the sensitivity is different.



Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
0	0 0	Initial	240.3	0.896	3 3 3	0.578 s	-3.15446	-
1	1 0	PWC only	253.517	0.896	3 3 3	0.609 s	-3.15605	0.00159
3	2 0	PWC only	266.733	0.896	3 3 3	0.547 s	-3.15925	0.0032
5	3 0	PWC only	279.95	0.896	3 3 3	0.531 s	-3.15959	0.00034

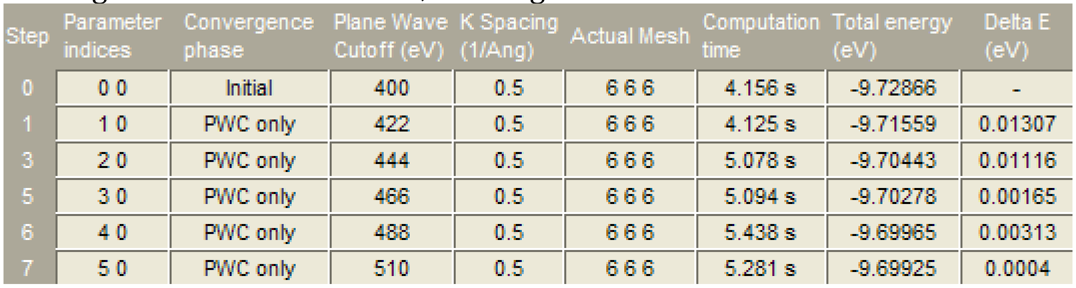
The convergence is dominated by the k-mesh. In order to reach the convergence criterion of 0.001 eV in the total energy, a k-mesh density of 0.2 Å^{-1} is required, while an energy cutoff of 267 eV is sufficient for convergence of the plane wave basis functions.



Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
0	0 0	Initial	240.3	0.896	3 3 3	0.578 s	-3.15446	-
2	0 1	K-mesh only	240.3	0.8064	4 4 4	0.703 s	-3.68568	0.53122
4	0 2	K-mesh only	240.3	0.653184	5 5 5	0.766 s	-3.67767	0.00801
6	0 3	K-mesh only	240.3	0.529079	6 6 6	1.328 s	-3.72727	0.04960
7	0 4	K-mesh only	240.3	0.428554	7 7 7	1 s	-3.78089	0.05362
8	0 5	K-mesh only	240.3	0.347129	8 8 8	2.312 s	-3.73860	0.04229
9	0 6	K-mesh only	240.3	0.312416	9 9 9	1.484 s	-3.70503	0.03357
10	0 7	K-mesh only	240.3	0.281174	10 10 10	4 s	-3.73717	0.03214
11	0 8	K-mesh only	240.3	0.253057	11 11 11	2.109 s	-3.74304	0.00587
12	0 9	K-mesh only	240.3	0.227751	12 12 12	6.719 s	-3.73304	0.01000
13	0 10	K-mesh only	240.3	0.204976	14 14 14	11 s	-3.73240	0.00064

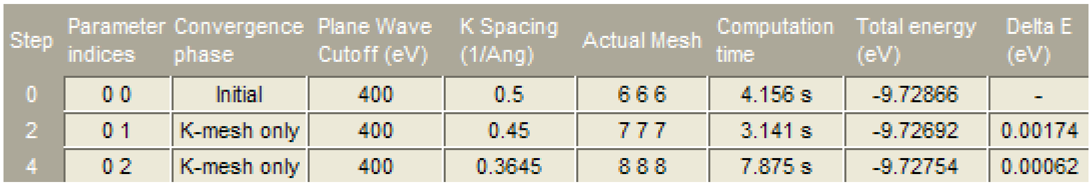
3. Lithium Fluoride

In the case of lithium fluoride, the convergence is dominated by the plane wave cutoff. Starting with a cutoff of 400 eV, convergence is reached at 488 eV.



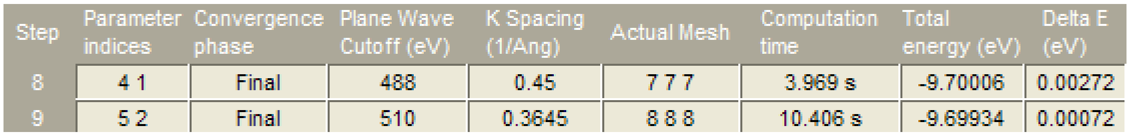
Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
0	0 0	Initial	400	0.5	6 6 6	4.156 s	-9.72866	-
1	1 0	PWC only	422	0.5	6 6 6	4.125 s	-9.71559	0.01307
3	2 0	PWC only	444	0.5	6 6 6	5.078 s	-9.70443	0.01116
5	3 0	PWC only	466	0.5	6 6 6	5.094 s	-9.70278	0.00165
6	4 0	PWC only	488	0.5	6 6 6	5.438 s	-9.69965	0.00313
7	5 0	PWC only	510	0.5	6 6 6	5.281 s	-9.69925	0.0004

The convergence in the k-spacing is much faster than for Mo or Al. A spacing of 0.45/Å is sufficient in this case.



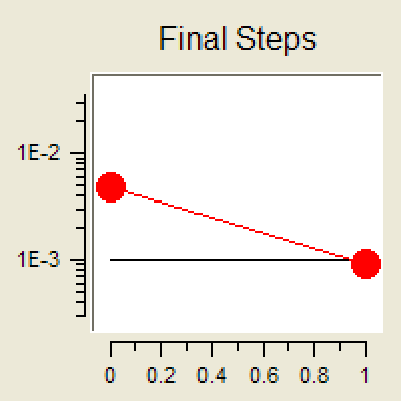
Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
0	0 0	Initial	400	0.5	6 6 6	4.156 s	-9.72866	-
2	0 1	K-mesh only	400	0.45	7 7 7	3.141 s	-9.72692	0.00174
4	0 2	K-mesh only	400	0.3645	8 8 8	7.875 s	-9.72754	0.00062

The final check shows that both parameters together are converged, when varied together.



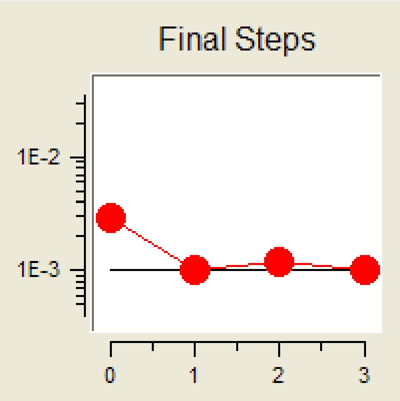
Step	Parameter indices	Convergence phase	Plane Wave Cutoff (eV)	K Spacing (1/Ang)	Actual Mesh	Computation time	Total energy (eV)	Delta E (eV)
8	4 1	Final	488	0.45	7 7 7	3.969 s	-9.70006	0.00272
9	5 2	Final	510	0.3645	8 8 8	10.406 s	-9.69934	0.00072

The values used as convergence goal should be used with a grain of salt. In the table above the middle graph should grazing convergence around 0.001 eV for three steps, the computational demands increase without much gain of precision.

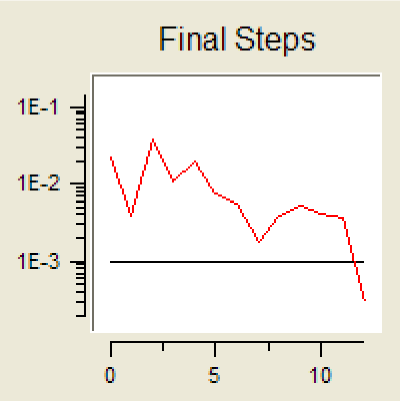


Convergence achieved.

Final step (1) confirms values.



Convergence nearly achieved with step (1).



Initial values seem to be quite converged, but not both parameters together.

L. PREDIBOND™ in Heterogeneous Catalysis: Predicting Activity Patterns

Introduction

The performance of catalytic materials depends on complex phenomena linked to chemical composition, preparation, activation procedures, and surface conditions under operational conditions. This complexity requires a comprehensive arsenal of R&D approaches including theoretical and computational methods. While many fundamental research efforts are currently directed at a detailed understanding of surface reaction mechanisms, PREDIBOND™ focuses on bond strength and local chemical environment as central descriptors of chemical reactivity. By combining in a unique and proprietary way experimental reactivity data on model systems with experimental structural data and computed information, PREDIBOND™ allows the classification of catalytic materials and thus the prediction of promising areas in the catalyst design space. This application note focuses on the application of PREDIBOND™ to a specific example in heterogeneous catalysis, namely hydrodesulphurization with catalytically active metal sulfide surfaces.

The problem

Consider the hydrodesulphurization reaction

$$C_nH_mS+H_2 \rightarrow C_nH_m+H_2S \qquad (7\text{-}3)$$

A set of known catalytic materials for this reaction is listed in the table on the right. Note that the catalysts with the highest activity contain rare and expensive metals. The obvious question arises, if there are more cost effective compounds with the same or possibly even higher catalytic activity. To this end, one could extend the search to include ternary and higher compounds, but apparently, one would face a huge combinatorial space to explore.

Catalyst	Activity [93]	Activity [94]
RuS_2	379.5	57.5
OsS_2	216.3	60.9
IrS_2	171.8	455.0
Rh_2S_3	106.1	813.0
ReS_2	39.4	34.3
PtS	16.0	15.5
PdS	12.5	20.1
MoS_2	8.0	21.1
Cr_2S_3	4.8	9.7
WS_2	3.2	7.2
NbS_2	1.7	3.5
Ni_3S_2	1.5	3.5
Co_9S_8	1.4	12.6
VS	1.1	7.3
FeS	1.1	1.2
TaS_2	1.1	2.2
MnS	0.6	0.3

Where do we start looking for new and improved catalysts?

Preparing sample structures and testing them is time consuming and costly. Criteria for prioritization are needed. PREDIBOND™ offers just these by exploiting the well-known Sabatier principle, which states in essence that

> *Catalytically active surfaces show intermediate bond strength with the reacting molecule*

While strong bonding of a molecule blocks the surface, weak bonding does not provide the interactions needed to retain reacting molecules at the surface and activate their bonds.

Bond Strength

Bond strength is a key concept to rationalize many complicated phenomena in areas as diverse as heterogeneous catalysis, sensor materials, and energy storage systems. The intuitive notion of the strength of a chemical bond is hard to express in a mathematically rigorous and practically useful scheme. In fact, crystallographers and theoretical chemists have developed a range of approaches to address this problem. For example, a very simple concept relates bond strength with bond distances. Shorter bond lengths are an indication of stronger bonds. The problem in this approach is a proper definition of a reference.

PREDIBOND™ applies a particularly useful definition and is the basis of a patent by Hervé Toulhoat from the French Petroleum Institute[13].

How does PREDIBOND™ work?

PREDIBOND™ uses a correlation between the bond strength and catalytic activity to predict candidates for specific reactions. No explicit surface models are involved in the derivation of the PREDIBOND™ descriptor. Therefore, it represents an efficient screening tool to prioritize the choice of starting materials for further investigations.

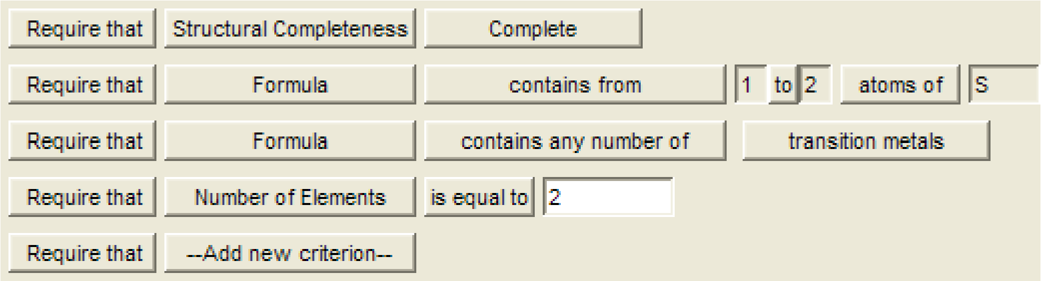
In essence, the bond strength of a particular target atom, for example sulfur, to its neighboring atoms is determined from experimental (or computed) stable crystal structures, which contain the bond type of interest. Three total energy calculations are performed, one for the full crystal structure and two calculations for hypothetical sub-lattices. The difference of the total energies of the full crystal and the two sub-lattices yields the interaction energy of the target atom with the surrounding atoms. This is accomplished by ab initio quantum mechanical methods. The bond energy follows from a normalization of the interaction energy by the number of nearest neighbors of the target atom in the full crystal structure. A detailed description of the approach is given in [95; 96].

PREDIBOND™ thus allows a ranking of the compounds according to bond strength. If the target atom does play a central role in the catalytic reaction of interest, then there exists a correlation between catalytic activity and the PREDIBOND™ bond strength in the form of a volcano curve. The PREDIBOND™ concept is implemented in the MEDEA technology platform as the PREDIBOND module. Its application is illustrated step-by-step in the following sections.

1. Build a PREDIBOND spreadsheet

In MEDEA choose **PrediBond** from the tool menu. If you do not have a license but wish to work with PREDIBOND, please contact info@materialsdesign.com. In the **PrediBond** submenu select **New**. An empty unnamed spreadsheet will come up. This spreadsheet is your starting point for building up a list of structures, defining parameters for PREDIBOND runs and launching your PREDIBOND jobs. As you go along and build up spreadsheets it is recommended to save them in MEDEA's internal database for later use.

Choose **Save As** from the PrediBond submenu and choose an appropriate name. In this example let us name the spreadsheet **TM-S**. Next we will add structures from the database to our worksheet. To this end, bring up InfoMaticA from the Tools menu and choose **Search** from its submenu. In the search window choose the following criteria to search the databases:



Require that Structural Completeness Complete
Require that Formula contains from 1 to 2 atoms of S
Require that Formula contains any number of transition metals
Require that Number of Elements is equal to 2
Require that --Add new criterion--

Launching a search with these criteria should give you more than 500 hits from ICSD and Pauling together .You can sort with respect to columns by right clicking on the column header: sort the **sum** column in the search result window by choosing **Sort ascending**.

Let's browse these entries for compounds listed with their activities in the above table. To run this example you should choose compounds showing high medium and low activities. You can select more than one entry at the time by holding down the **Ctrl**-key while left clicking on the entries. Copy selected structures using the **Copy** entry of the context sensitive menu (right-click).

As an example choose the following structures from InfoMaticA:

ID	Space group name H-M	sum	…	coordination number	PrediBond (kJ/mol)
ICSD.31704	P63MC	CdS			
CRYSTMET.56707	Pnma	IrS_2			
ICSD.2400	P63/MMC	$Mo\ S_2$			
CRYSTMET.85281	P63/mmc	$Nb\ S_2$			
ICSD.24187	PA3-	$Os\ S_2$			
ICCSD.26766	P42/M	PdS			
ICSD.15344	PBCN	$Rh_2\ S_3$			
ICSD.24186	PA3-	RuS_2			
CRYSTMET.56161	P63/mmc	TaS_2			
CRYSTMET.23344	P63/mmc	WS_2			
CRYSTMET.24330	P63/mmc	FeS			
CRYSTMET.86517	R32r	Ni_3S_2			

Select the worksheet and transfer the selected candidates with **Paste structures**

2. Configure and run a PREDIBOND job

Define Target atoms for which you would like to calculate the PREDIBOND energy:
You are going to calculate the energy per bond of "target" atom to the other elements in each compound on the list (obviously, each compound in the PREDIBOND spreadsheet must contain the target atom). PREDIBOND will apply the algorithm described above to each of the structures and derive the bond energy per bond. In the above example select **Target atoms** from the PREDIBOND menu and type **S** into the text field.

Select the computational tasks

Select Engine. You can perform a PREDIBOND with VASP or any other computational engine. In our example select VASP as an engine and choose **Structure optimization** from the VASP settings menu. Activate **Allow cell volume to change** and **Allow cell shape to change**. This will relax each structure to the theoretical lattice parameters and atomic positions before applying the vacancy method. Click **OK** to close the dialogue and choose **Run** from the PREDIBOND dialogue to launch the job.

As your job is being processed, MEDEA will import the key results from each run into your worksheet, which is then updated automatically. Once you have collected all data, you can sort with respect to columns by right clicking on the header cell of each column. In order to export to Excel, highlight a region of the spreadsheet and choose **Copy** from the context-menu (right click on highlighted region).

Below is an example of such a calculation presented in an Excel spreadsheet with experimental activities added. You can sort your results either directly in PREDIBOND or you can use Excel to sort and format your worksheets. PREDIBOND and MEDEA offer various units of energy, right-click on the corresponding column header to change units to kJ/mol or eV.

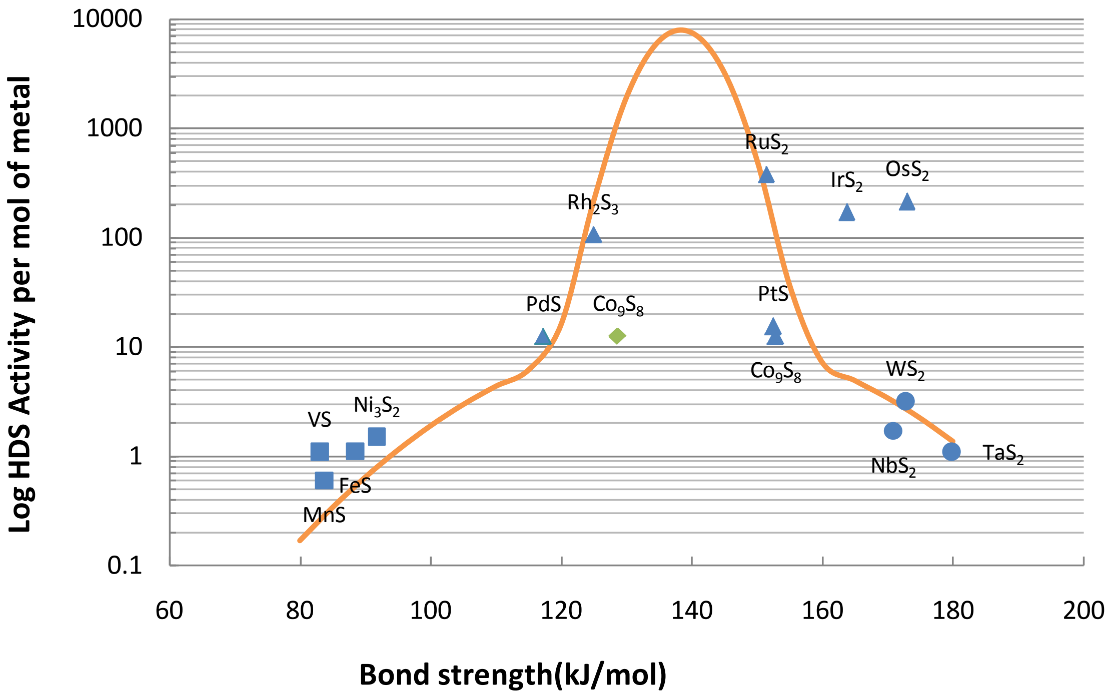
Space group name H-M	Formula	a (Å)	total (Ha)	E_{coh} (kJ/mol)	Coordination number n	$E_{PREDIBOND}$ (kJ/mol)	Activity
P63/mmc	VS	3.17	-1.04	1124.91	6	83.01	1.1
FM-3M	MnS	5.01	-0.52	770.45	6	83.72	0.6
P63mc	FeS	3.32	-0.94	821.98	6	88.44	1.11
R32	Ni_3S_2	5.70	-0.97	2131.76	6	91.78	1.5
P42/M	PdS	6.50	-2.95	894.17	4	117.21	12.5
PBCN	Rh_2S_3	8.55	-4.28	2413.12	4	124.88	106.80
PA-3	RuS_2	5.65	-2.78	1513.32	3	151.42	379.5
P42/MMC	PtS	3.51	-0.81	949.60	4	152.46	15.5
FM3-M	Co_9S_8	9.92	-3.82	7657.77	4	152.81	12.6
Pnma	IrS_2	20.01	-5.35	1490.34	3	163.74	171.8
P63/mmc	NbS_2	3.35	-1.57	1652.98	3	170.81	1.7
P63/mmc	WS_2	3.18	-1.72	1905.97	3	172.71	3.20
Pa3	OsS_2	5.66	-3.00	1611.04	3	172.94	216.30
P63/mmc	TaS_2	3.33	-1.70	1973.08	3	179.82	1.1

3. Analyzing results

Let us look at the volcano curve produced by correlating the above results with experimental activities. To do so, create an Excel graph relating PREDIBOND energies on the x-axis and the activities listed above on the (logarithmic) y-axis.

The plot represents the characteristic volcano shape, which is an expression of the Sabatier principle: Solids with extremely low or high TM-S bond strength show low activities while those with intermediate bond strength have higher activities. We have accomplished the mapping of a descriptor calculated from experimental bulk crystal structures onto experimental activity data for a highly complex heterogeneous catalyst.

The only input was the crystal structure from experiment. Based on this information, VASP "recreates" the chemical bonds and using the PREDIBOND descriptor we have succeeded in establishing a valuable activity pattern: the optimal metal-sulfur PREDIBOND energy for the given system is around 140 kJ/mol. In this region the bond energy of the metal-sulfur bond is favorable for activating the sulfur bond of a sulfur-containing molecule. Now the search for improved or new systems can rely on a clear steering principle.



Testing new candidates

Once the correlation is established with PREDIBOND, we can use a volcano plot to estimate activities of new candidates or materials, without experimental activity data at hand. To this end we have to calculate the corresponding PREDIBOND descriptor and use the above correlation curve as a gauge to predict the activity.

Navigating in the space of ternary compounds

Obviously the search is not limited to binary compounds! The concept of the volcano curve, allows us to navigate in the space of ternary compounds and to identify promising candidates by combining elements from the left and right side of the volcano curve. As a matter of fact, one of the actual industrial catalysts is MoS_2 doped with Co and Ni.[97] The volcano curve obtained with PREDIBOND gives a rationale for the activity of this system. The Mo-S, like the W-S bond, is too strong and needs to be moderated by elements with weak metal-sulfur bonds. The elements Ni and Co meet this requirement. Now the power of the approach becomes obvious: there are many other potential combinations between compounds from the right and the left side of the volcano curve!

Uncertainty of experimental data

The experimental activity data in the table above show significant variations between the two data sets. This uncertainty is due to the great difficulty in obtaining consistent experimental data series of catalytic activity. Therefore, one should not expect that correlations obtained with PREDIBOND are always perfect. One source for the deviation can be the uncertainty in the experimental data. Another critical point is the assumption about the target atom. If it turns out that no or only a poor correlation is found with a given target atom, then this may be an indication of important steps in the reaction, which involve other atoms or effects.

Inequivalent atoms in crystal structure

PREDIBOND™ calculates bond strength energies per chemical bond. The definition of what counts as a bond is not always unambiguous. As an example let us consider the above case of Co_9S_8 with 4 bonds between S and Co. This positions Co_9S_8 more to the right of the volcano curve, together with PtS. When analyzing the geometry of the crystal structure it becomes obvious that there are two symmetrically distinct S atoms in Co_9S_8. While one sulfur atom (S_1) has 4 Co neighbors at a distance of 2.127 Å, the other Sulfur (S_2) has 4 Co neighbors at 2.227 Å and one at 2.359 Å. PREDIBOND™ defines a coordination sphere around each target atom thus classifying atoms strictly as either **bonded** or **non-bonded**. In cases like the above this can lead to irregularities in the PREDIBOND™ energies. With the coordination number increased from 4 to 4.75 the bond energy is decreased and Co_9S_8 shifts (denoted by a green diamond) to the left side of the volcano curve.

M. Practical Thermochemistry: Sodium Metal, Chlorine Gas, and Solid Sodium Chloride

> *This case study covers the practical use of MEDEA to calculate thermochemical functions for solids, molecules and atoms. We will use VASP and PHONON for this, but the current document focuses on the thermochemistry and not the details of the calculations. As an example we will look into the heat of formation of sodium chloride* $NaCl_{(s)}$, *the cohesive energy of sodium* $Na_{(s)}$ *and the heat of formation and bond energy of the gas phase diatomic* $NaCl_{(g)}$ *and chlorine gas* $Cl_{2(g)}$. *This will give us a fairly complete view of how our theoretical methods do on a range of different systems.*

To start it is very useful to write down chemical reactions for the reactions defining the quantities that we are after. The heat of formation of $NaCl_{(s)}$ is defined by the reaction of the elements in their standard state to create $NaCl_{(s)}$:

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \rightarrow NaCl_{(s)} \tag{8-1}$$

The cohesive energy of $Na_{(s)}$ is defined as the energy to atomize the solid:

$$Na_{(s)} \rightarrow Na_{(g)} \tag{8-2}$$

Note that in this case, this is also the heat of formation of sodium atoms $Na_{(s)}$. The heat of formation of $NaCl_{(g)}$ is again defined by the reaction of the elements, but this time to form the diatomic molecule:

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \rightarrow NaCl_{(g)} \tag{8-3}$$

The bond energy of a diatomic is the energy needed to break the bond, producing atoms:

$$NaCl_{(g)} \rightarrow Na_{(g)} + Cl_{(g)} \tag{8-4}$$

For chlorine $Cl_{2(g)}$ the heat of formation is by definition 0 since it is the element in its standard state, but we can look at the bond energy:

$$Cl_{2(g)} \rightarrow 2\ Cl_{(g)} \tag{8-5}$$

Note that in this particular case this is also the definition of the heat of formation of $Cl_{(g)}$ atoms except for a factor of 2, since the reaction creates 2 atoms of Cl.

Now let us think about what information we need to calculate the heats of formation and bond energies. Clearly the chemical species that we are interesting are $Na_{(s)}$, $Na_{(g)}$, $Cl_{2(g)}$, $Cl_{(g)}$, $NaCl_{(s)}$ and $NaCl_{(g)}$ – but what properties do we need? Let's briefly review some thermodynamics so that we clearly understand what enthalpy is, since this is what a heat of formation or bond "energy" is. An overview of thermochemistry is available from NIST[1].

---

[1] http://www.nist.gov/compchem/irikura/docs/app_b2_rev.pdf

if you want a more in-depth look, but let us recap the main features here. Please note that different books use different symbols for the thermodynamic functions. The choices we use are in bold:

$\boldsymbol{T}$: Temperature

$P, \boldsymbol{p}$: Pressure

$\boldsymbol{V}, v$: Volume

$\boldsymbol{E}, U$: Internal Energy

$\boldsymbol{H}$: Enthalpy

$\boldsymbol{S}$: Entropy

$\boldsymbol{A}, F$: Helmholtz Free Energy

$\boldsymbol{G}, \boldsymbol{F}$: Gibbs Free Energy

The key equations defining these functions are

$$H = E + pV \tag{8-6}$$

$$A = E - TS \tag{8-7}$$

$$G = H - TS = E + pV - TS \tag{8-8}$$

The internal energy, E, of an atom, molecule or solid is the sum of various terms:

$$E(T) = E_{\text{elec}}(T) + E_{\text{vib}}(T) + E_{\text{trans}}(T) + E_{\text{rot}}(T) \tag{8-9}$$

where we emphasize that the internal energy is a function of temperature, T. The four terms are the electronic, vibrational, translational and rotational contributions. For a solid there are no translational and rotational terms but there are 3N_{atoms} vibrational terms. An atom has no vibrational or rotational terms but does have 3 translations. Finally, a molecule has all terms – nonlinear molecules have 3 translations, 3 rotations and 3N-6 vibrations. Linear molecules have 3 translations, 2 rotations and 3N-5 vibrations. Note that for all types of systems there are 3N degrees of freedom – just how they are partitioned into vibrations, rotations and translations differ.

Now let's work through each term to see what we can do – and what we can't!

Starting with the **electronic term**, the bulk of the electronic energy is indeed that which is calculated by a code such as VASP. There is a question of the reference for the energy, but in reactions this cancels so we don't need to be overly concerned. Some codes provide a total electronic energy, but others use a different reference. VASP, for example, uses the energy of non-spin-polarized atoms as the reference, so the energy reported by VASP ("VASP energy" in the MedeA Job.out) is close but not equal to the cohesive energy.

Now, MEDEA-VASP uses as reference energy the "Energy of Formation". Note that the energy of formation measured in experiment includes contributions other than just the (T=0) electronic contribution MEDEA lists as the "Energy of formation" in Job.out. However, there are many cases where the main contribution is in fact the electronic contribution, therefore the "Energy of formation" listed in Job.out is really a fairly good first approximation valid at lower temperature.

So where does MEDEA get these numbers from? MEDEA uses a database of calculated VASP energies for all elements in their standard state. When you run a calculation for an element or a compound MEDEA looks up the relevant reference energies and automatically calculates the heat of formation of the system in question. For more information on how the reference energies were calculated please refer to the corresponding section on standards and references in the MEDEA user guide.

The electronic energy also has a non-zero temperatures contribution due to the excitation of electrons from occupied levels or orbitals to unoccupied levels. Though in principle we can extract this information from VASP, the enthalpy terms at low temperatures – up to room temperature – are small so for the present we will ignore them.

Let's have a look at the vibration contribution to the enthalpy, which is exactly what PHONON calculates for solids. Indeed, for solids, we can directly use the PHONON results from Job.out.

For atoms there are no vibration contributions to the internal energy, but for molecules we need to be careful! For a molecular system the enthalpy due to vibrations is

$$E_{\text{vib}}(T) = E_{\text{vib}}(0) + RT \sum_i \frac{h\nu_i}{kT} \frac{e^{-\frac{h\nu_i}{kT}}}{1 - e^{-\frac{h\nu_i}{kT}}} \qquad (8\text{-}10)$$

R is the gas constant (8.314510 J mol^{-1} K^{-1}); k, Boltzmann's constant (1.38066x10^{-23} J K^{-1}); h, Planck's constant (6.626076x10^{-34} J s); and ν_i is the i^{th} vibrational frequency. At 0 K the second term in equation (8-10) is zero, leaving just $E_{\text{vib}}(0)$ which we can identify with the zero-point energy of the vibrations:

$$E_{\text{vib}}(0) = \frac{1}{2} h \sum_i \nu_i \qquad (8\text{-}11)$$

These are exactly the equations used by PHONON for solids, but for molecules we trick PHONON into thinking that it is dealing with a solid by putting the molecule in a periodic box. Currently PHONON doesn't realize this, so it merrily adds up **all** the vibrations that it finds – 3N of them. For a molecule-in-a-box, 6 of these "vibrations" (5 for a linear molecule) are actually approximations to the rotations and translations. For this reason, rather than use the PHONON results directly, we need to use the vibrational frequencies that PHONON reports for the gamma point and use equation (8-11). We'll see how to do this in a later section.

The translation contribution to equation (8-9) does not exist for solids. For molecules and atoms it is simply

$$E_{\mathrm{trans}}(T) = \frac{5}{2}RT \tag{8-12}$$

The rotational enthalpy term is also simple. For linear molecules it is

$$E_{\mathrm{rot,linear}}(T) = RT \tag{8-13}$$

and for general, nonlinear molecules,

$$E_{\mathrm{rot}}(T) = \frac{3}{2}RT \tag{8-14}$$

Finally we are in a position to put all this together:

- For each of the chemical species we need their electronic energy
- for molecules we need the vibrational frequencies (from PHONON)
- For solids we need the thermodynamic functions as produced directly by PHONON.
- We treat the atoms and molecules in pseudo-periodic systems by using a box of e.g. 11x12x13 Å so that we can run VASP on them.
- We pick the odd box to break any accidental symmetry and use only the gamma point in both the VASP and PHONON calculations.
- We need to optimize the geometries of the molecules and both the geometries and cells of the solids.

To summarize, these are the calculations we need to do:

Species	**VASP Calculation**	**PHONON**
$Na_{(s)}$	Geometry and cell optimization	✓
$Na_{(g)}$	Single point energy	
$Cl_{2(g)}$	Geometry optimization	✓
$Cl_{(g)}$	Single point energy	
$NaCl_{(s)}$	Geometry and cell optimization	✓
$NaCl_{(g)}$	Geometry optimization	✓

From the above set of calculations we need the following data:

For solids and gases: The electronic **energy of formation** in kJ/mol as listed in Job.out for single point energy calculations and geometry and cell optimizations. Note that PHONON also lists the energy of formation for the initial "undisplaced" calculation where it optimizes atomic positions in the supercell. However in the case of most solids the VASP geometry optimization done for the chemical unit cell will be more precise than the VASP supercell calculation done by PHONON as an initial step, simply because we tend to use less precision for these larger supercell calculations

```
Results for initial structural minimization of the supercell without displacements:
-----------------------------------------------------------------------------------
There are 4 symmetry-unique k-points
The plane wave cutoff is 280.00 eV

   VASP energy:    -216.695134 eV for Na32Cl32

Electronic contributions:

                          Empirical Formula         Cell
                                 NaCl          (NaCl)32
                          ---------------- ----------------
             VASP Energy        -653.372      -20907.897 kJ/mol
     Energy of formation         -354.598      -11347.129
                 PV term         -21.183         -677.861
   This is the electronic part of the formation energy with respect to the
   elements in their standard state. It is obtained from the total energy (above)
   and tabulated VASP energies for the elements in their standard state.
   See the documentation for more details.

   Details for NaCl:

                                                VASP energy (Etot):     -653.37 kJ/mol
       Standard state energy of 1.00 atoms of Cl  1.00 * -172.42:  -   -172.42
       Standard state energy of 1.00 atoms of Na  1.00 * -126.35:  -   -126.35
                                                                   ----------
                                          Energy of formation (Ef):     -354.60 kJ/mol
```

For solids: The **zero point energy** and **vibration energy** listed in the PHONON Job.out. The zero point energy is listed explicitly per formula unit just above the section tabulating the thermodynamic functions as a function of temperature. The vibration energy is tabulated as a function of temperature, labeled as E(T) – E(0) (third column). Provided we have done a very precise PHONON calculation we can use E(T=298) directly (6th column), which adds up the electronic energy, the zero point energy and the vibration contribution. However, in many cases we have a higher precision electronic calculation at our disposal, in which case we can use a more precise value for the electronic energy.

```
Electronic energy =  -354.60 kJ/mol (referenced to elements in the standard state)
          PV term =   -21.18 kJ/mol
Zero-point energy =     5.28 kJ/mol

     T        Cv        E(T)-E(0)      S(T)    -(A(T)-E(0))     E(T)        A(T)
     K      J/K/mol      kJ/mol      J/K/mol      kJ/mol       kJ/mol      kJ/mol
   ----- ----------- ----------- ----------- ----------- ----------- -----------
      0      0.0000      0.0000      0.0000      0.0000   -349.3181   -349.3181
      1      0.0000      0.0000      0.0000      0.0000   -349.3181   -349.3181
…
    275     47.3604      9.1511     66.2503      9.0677   -340.1670   -358.3857
    298     47.7235     10.2447     70.0694     10.6359   -339.0734   -359.9539
    300     47.7513     10.3402     70.3887     10.7763   -338.9779   -360.0944
```

For molecules: the **zero point energy** and **gamma point frequency** listed in the PHONON Job.out. When working with molecules however, we need to be careful as at this point, neither PHONON nor VASP “know” about non periodic systems. Below is an example listing for Cl_2 taken from a PHONON Job.out file: $Cl_{2(g)}$ being a linear diatomic molecule, we expect only a single frequency. In fact, for a linear diatomic molecule we should have 2 rotations, 3 translations and one vibration. The first (B3g R) and the forth (B2g R) vibration modes in the output actually correspond to rotations; the 3 degenerate “vibrations” with zero frequency are the translations; leaving the last frequency of 16.453 THz as the actual frequency that we are after.

```
Symmetry analysis of Gamma point phonon frequencies:
----------------------------------------------------
Crystal  Point  Group: D_2h  (mmm)
   Supercell Point Group: D_2h  (mmm)
    Table of irreducible representations of point group:
 ------------------------------------------
    IR     1  4  3  2 25 28 27 26
 ------------------------------------------
 Ag(R)     1  1  1  1  1  1  1  1   x^2, y^2, z^2
 B1g(R)    1  1 -1 -1  1  1 -1 -1   xy
 B2g(R)    1 -1  1 -1  1 -1  1 -1   xz
 B3g(R)    1 -1 -1  1  1 -1 -1  1   yz
 Au        1  1  1  1 -1 -1 -1 -1
 B1u(I)    1  1 -1 -1 -1 -1  1  1   z
 B2u(I)    1 -1  1 -1 -1  1 -1  1   y
 B3u(I)    1 -1 -1  1 -1  1  1 -1   x
 ------------------------------------------
    Wave vector= 0.0000  0.0000  0.0000    no macro. electric field
 Multi. Omega   Irreducible Representations
  1    -1.138     B3g(R)
  3     0.000     B1u(I) +  B2u(I) +  B3u(I)
  1     1.304     B2g(R)
  1    16.093     Ag(R)
Notation: (R)  Raman active mode
          (I)  Infrared active mode
          (RI) Raman and Infrared active mode
```

The next table presents a representative set of results using reasonable parameters for VASP (**Normal** precision, 280 eV energy cutoff, 1 k-point for atoms and molecules, otherwise **k-spacing** of 0.5 (Use **☑ Use odd mesh**), **GGA-PBE/PAW**, *Na_pv* potential for sodium) and PHONON (10 Ang interaction range, 3x3x3 k-mesh):

Species	Energy (kJ/mol)	ν(THz)	E^{vib}_{298} (kJ/mol)
$Na_{(s)}$	-0.11		7.55
$Na_{(g)}$	103.19		
$Cl_{2(g)}$	1.53	16.5	
$Cl_{(g)}$	162.20		
$NaCl_{(s)}$	-354.74		15.52
$NaCl_{(g)}$	-158.15	10.41	

Now we can put it all together to get the results we want. First, let's use the raw result to get the calculated enthalpy for each of the species:

Solids: This is as simple as adding together the electronic formation energy from and the vibration energy.

The volume term can be calculated, but is small enough that it can reasonably be ignored. For the pressure we are interested in (1 bar), the molar volume of for example sodium metal is about 0.24 L, which results in a pV term of 0.024 kJ/mol (2).

Atoms: For the atoms we need to add the translation enthalpy of $(5/2)RT$ = 6.20 kJ/mol to the electronic energy, following equation (8-12).

Molecules: For the molecules it is a bit more complicated:

1. The rotational and translational enthalpy from equations (8-12)and (8-13) yield $(7/2)RT$ = 8.68 kJ/mol.
2. From the vibration frequencies we must calculate and add the vibration term as defined in equation (8-10)
3. Finally we must add the pV term, which we can estimate from the ideal gas law: $pV = nRT$=2.48 kJ/mol for 1 mol of gas.

Putting this together gives the following value for the total enthalpy at 298K for our two diatomic molecules:

Now we can put it all together to get the results we want. First, lets use the raw result to get the calculated enthalpy for each of the species:

---

[2] Here we are looking at solid-gas reactions where the external pressure is assumed to be 1 atmosphere (1 bar). The pressure term reported by VASP in Job.out stems from the fact that we cannot optimize the lattice parameters of a solid to such a precision that the corresponding residual pressure would go to something in the order of 1 bar. For example the above geometry optimization for solid NaCl leads to a residual pressure of 720 bar. A very precise geometry optimization using 500eV cutoff and a 11x11x11 k-mesh changes the lattice by 0.041 Ang but still produces a residual pressure of 160 bar. This simply means that in a solid, a very small change in the lattice parameter results in a tremendous change of pressure. If we were to investigate a pressure induced phase transition, we would work at much higher pressures and consequently the pressure terms reported by VASP would become meaningful.

Species	H^0_{298} (kJ/mol)
Na(s)	2.74
Na(g)	101.61
Cl_2(g)	19.77
Cl(g)	168.40
NaCl(s)	-339.22
NaCl(g)	-141.88

For the solids this is as simple as adding together the electronic energy and the vibrational energy from PHONON. The volume term can be calculated, but is small enough that it can reasonably be ignored. For example, the molar volume of sodium metal is about 0.24 L, which results in a pV term of 0.024 kJ/mol.

For the atoms we need to add the translation enthalpy of 5/2 RT = 6.20 kJ/mol to the electronic energy, following equation (8-12).

For the molecules it is a bit more complicated. The rotational and translational enthalpy from equations (8-12) and (8-13) yield 7/2 RT = 8.68 kJ/mol.

We also need to add the vibrational term from equation (8-10)and remember the pV term. From the ideal gas law, pV = nRT, and hence for 1 mol gas the pV term is 2.48 kJ/mol. Putting this together gives the following for our two diatomic molecules:

Species	ν (cm^{-1})	ν(THz)	hν/kT	E_0(vib)	E_{298}(vib)	E_{form}	pV	$E_{\text{rot}} + E_{\text{trans}}$	H^0_{298}
Cl_2	550.38	16.5	2.66	3.29	3.79	1.53	2.48	8.68	19.77
NaCl	347.240	10.41	1.68	2.08	3.03	-158.15			-141.88

Finally we can get back to our chemical equations.

For reaction
$$\mathrm{Na}_{(s)} + \frac{1}{2}\ \mathrm{Cl}_2 \rightarrow \mathrm{NaCl}_{(s)} \qquad (8\text{-}1)$$

We have
$$\Delta_f H^0 \mathrm{NaCl(s)} = H\left(\mathrm{NaCl}_{(s)}\right) - H\left(\mathrm{Na}_{(s)}\right) - \frac{1}{2} H\left(\mathrm{Cl}_{2(g)}\right)$$
$$= -339.22 \text{—} 2.74 - {}^1\!/_2\ 19.77 = -351.85 \text{ kJ/mol} \qquad (8\text{-}15)$$

For reaction
$$\mathrm{Na}_{(s)} \rightarrow \mathrm{Na}_{(g)} \qquad (8\text{-}2)$$

We have
$$\Delta_f H^0\ \mathrm{Na(g)} = H\left(\mathrm{Na}_{(g)}\right) - H\left(\mathrm{Na}_{(s)}\ \right) = 101.61 - 2.74$$
$$= 98.87 \text{ kJ/mol} \qquad (8\text{-}16)$$

For reaction
$$\mathrm{Na}_{(s)} + \frac{1}{2} \mathrm{Cl}_{2(g)} \rightarrow \mathrm{NaCl}_{(g)} \qquad (8\text{-}3)$$

We obtain
$$\Delta_f H^0 \mathrm{NaCl(g)} = H(\mathrm{NaCl}_{(g)})\ - H(\mathrm{Na}_{(s)}) \text{-} \frac{1}{2} H(\mathrm{Cl}_{2(g)})$$
$$= -141.88 - 2.74 - \frac{1}{2}\ 19.77 = -154.51 \text{ kJ/mol} \qquad (8\text{-}17)$$

For reaction
$$\mathrm{NaCl}_{(g)} \rightarrow \mathrm{Na}_{(g)} + \mathrm{Cl}_{(g)} \qquad (8\text{-}4)$$

We have
$$\Delta H^0 \mathrm{NaCl(g)} = H\left(\mathrm{Na}_{(g)}\right) + H\left(\mathrm{Cl}_{(g)}\right) - H\left(\mathrm{NaCl}_{(g)}\right)$$
$$= 10.61 + 168.4 - (-141.88) = 411.89 \text{ kJ/mol} \qquad (8\text{-}18)$$

For reaction $$\mathrm{Cl}_{2(g)} \rightarrow 2\ \mathrm{Cl}_{(g)} \qquad (8\text{-}5)$$

We have $$\Delta H^0\ \mathrm{Cl}_2(g) = 2 \cdot H\left(\mathrm{Cl}_{(g)}\right) - H\left(\mathrm{Cl}_{2(g)}\right) = 2 \cdot 168.4 - 19.77 = 317.03\ \mathrm{kJ/mol} \qquad (8\text{-}19)$$

Well, we have calculated a lot of different enthalpies, plus geometries, etc. So how do they compare to experiment? Let's gather up all the results along with experiment:

Property	Calculated		Experiment			Difference
$\Delta_f\ H^0$ NaCl(s)	-351.85	kJ/mol	-411.121		[98]	-14.4%
$\Delta_f\ H^0$ Na(g)	98.87	kJ/mol	107.5	± 0.72	[99]	8%
$\Delta_f\ H^0$ NaCl(g)	--154.51	kJ/mol	-181.421		[98]	-14.8%
Bond energy of NaCl(g)	411.89	kJ/mol	412.1	±83	[100]	-0.1%
Bond Energy of Cl_2(g)	317.03	kJ/mol	242.580	±0.0043	[100]	31.0%
Vibrational frequency of NaCl(g)	345.7	cm^{-1}	3664		[101]	-5.5%
Vibrational frequency of Cl_2(g)	550.4	cm^{-1}	559.74		[101]	-1.7%
Bond length of NaCl(g)	2.3973	Å	2.360794		[101]	1.5%
Bond length of Cl_2(g)	1.994	Å	1.9884		[101]	0.3%
Lattice parameter of Na(s)	4.15	Å	4.2908	±0.00055	[102]	-3.3%
Lattice parameter of NaCl(s)	5.65	Å	5.6400	±0.00056	[103]	0.1%
H^0_{298} -H^0_0 Cl_2(g)	14.95	kJ/mol	9.181	± 0.0017	[99]	63%
H^0_{298} -H^0_0 Na(s)	2.08	kJ/mol	6.460	± 0.0207	[99]	-67%

N. Surface Energy of Molybdenum

The surface energy of a material is defined as the energy required to create a surface (h k l) from the bulk material. Surface energies are usually given in units of J m^{-2}. Surface energies can be determined with VASP by performing two calculations, namely one for a repeated slab representing the particular surface (h k l) and one for the bulk system as a reference.
For calculations using a slab model, the surface energy is given by

$$E_{\mathrm{surf}} = \frac{1}{2A}\left[E_{\mathrm{slab}}(n) - nE_{\mathrm{bulk}}\right]$$

Where E_{surf} is the surface energy, A the surface area, $E_{\mathrm{slab}}(n)$ is the energy of a slab containing n chemical formula units, and E_{bulk} is the energy per formula unit in the bulk material.
While the calculation of surface energies is conceptually straightforward, one needs to be careful in controlling the errors originating from the geometric models, e.g. layer thickness and spacing between layers, and various computational parameters, e.g. k-meshes. The following examples demonstrate these points.

1. Select bulk structure

In MEDEA, activate **INFOMATICA** under **Tools** and search the structure of Mo in the CRYSTMET database by using the command **Require that** **Formula** **is** **Mo** and **Require that** **Structural Completeness** to be **Complete**. Select, for example, ICSD.53799 and view the structure by right-clicking on the selected row.

2. Optimize lattice with VASP

The **lattice parameter** of bulk Mo is now optimized using VASP. To this end, the following computational parameters are chosen: **Structure Optimization**: **☑ Relax atom positions**, **☑ Allow cell volume to change**, **☑ Allow cell shape to change.**

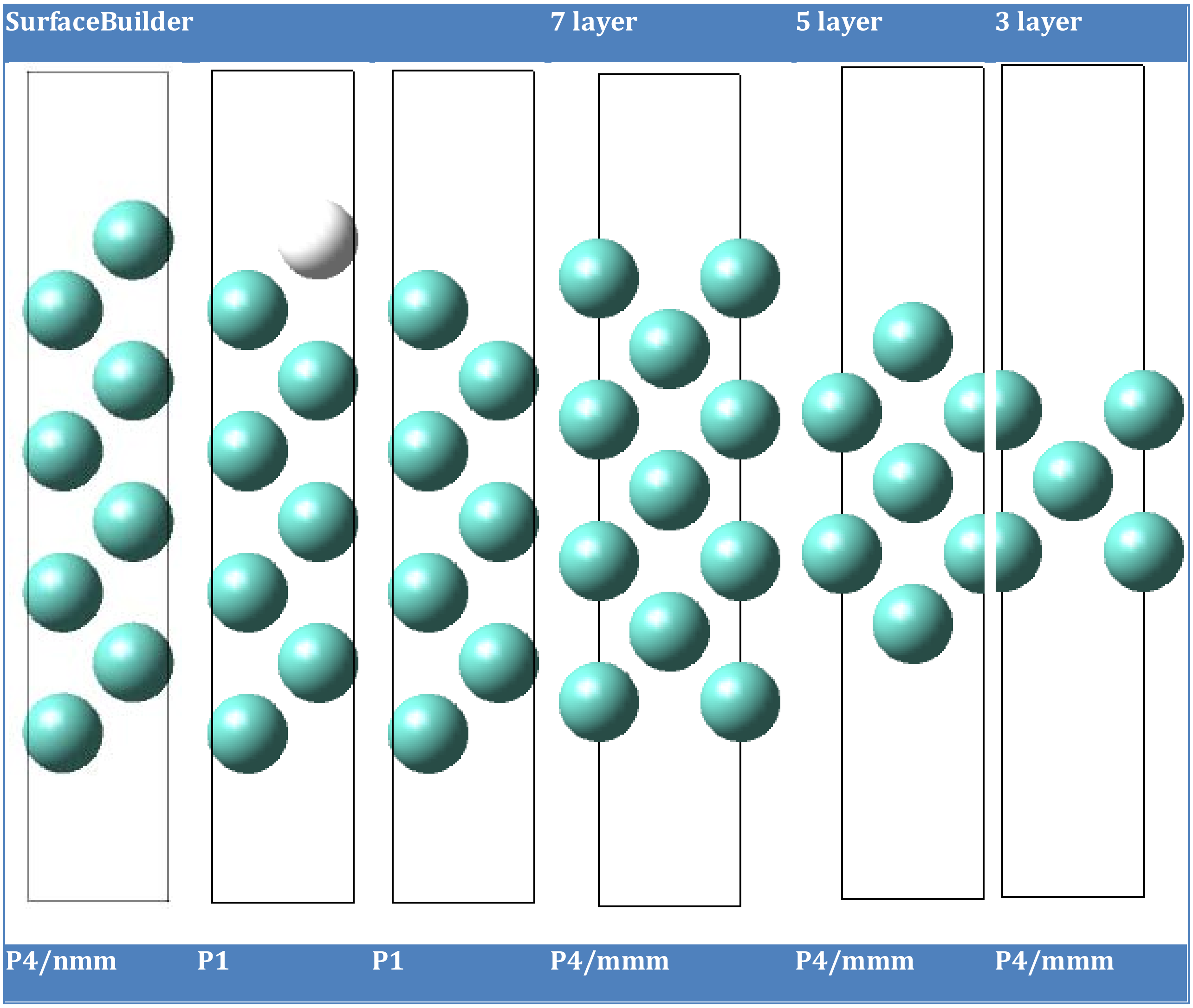
GGA-PBE-**PAW** with the default **Mo_pv** potential, **Accurate precision**, **☑ Increase planewave cutoff**, Projection: **Reciprocal space**

k-mesh spacing: 0.5/Å (6x6x6 mesh), **SCF convergence** of 10^{-6} in the SCF, and **Methfessel-Paxton** smearing. The optimized structure is taken as the starting point for the creation of surface models. To ensure consistency with the subsequent surface calculations, which are performed with medium precision, the total energy of the bulk unit cell is recalculated also with medium precision by a single point total energy.

> *Note 1: An increased-precision is chosen for the lattice optimization, because in this relies on the stress tensor, which requires a high-quality basis. In the subsequent surface calculations, the cell parameters are no longer optimized and thus a **Normal** level of accuracy is sufficient.*
>
> *Note 2: A k-mesh of 6x6x6 is reasonable, but still rather coarse for a small unit cell of a metal such as Mo. For a better converged calculation, a k-mesh of 10x10x10 or finer is recommended.*

3. Creation of a (001) Surface Model

The optimized structure of bulk Mo is loaded into the MEDEA window, e.g. by opening the results of previous calculations. Under the Edit pull-down menu, select **Build surfaces**. Enter 0 0 1 as the desired Miller indices, use **Search** and to choose4 **Repeats** and a **Gap (Ång)**of 6 Å. The result is a unit cell shown at the left. Select P1 symmetry and confirm with **Apply**. Now you can select one atom and delete it (**DEL**)to create the 7 layer cell. If you want, you can raise the symmetry with **Edit**»**Edit Structure**»**Symmetry** or right-clicking into the cell background and use **Edit Symmetry...** to **Raise Symmetry to P4/mmm**. The resulting surface is centered in the cell, as shown on the right.



4. Relaxation of the slab model

The atomic positions of the 7 layer model are now optimized with the following parameters for VASP changed: Uncheck **☐ Increase planewave cutoff**, **☐ Allow cell volume to change**, **☐ Allow cell shape to change**, but keep **☑ Relax atom positions**. We use now a 4×4×1 mesh (as the 0.5/Å spacing is the same and the cell shape changed). Note the value k_z=1 due to the elongated shape of the unit cell in the z-direction. In this step, all lattice parameters are kept constant, atoms will relax mostly in z direction with slight changes to the vacuum between slabs.

5. Evaluation of the surface energy

The evaluation of the surface energy is summarized in the spreadsheet below. Due to the choice of a primitive cell for the bulk bcc Mo calculation, a k-mesh of 6×6×6 corresponds most closely to the 4×4×1 k-mesh used in the slab calculations. To check the consistency, also the single-point total energy of a Mo 1×1×6 supercell is calculated, that's approximately the size of the cell for the 7 layer calculation.

Three different slab thicknesses are tested, namely 3-, 5-, and 7 layers. It can be seen that the 5-layer model is already close to the 7-layer model, thus indicating convergence in the thickness of the slab.

Another parameter to consider is the spacing between the slabs. The effect of different separation (thickness of vacuum) is tested here by calculating the total energy of a 5-layer slab model with a c-parameter of 14 and 18 Å, respectively. The difference is only 12 meV, which is insignificant in the present case. It should be noted that the dependence on vacuum thickness might be more critical for systems with a dipole moment or non-metallic systems.

For the (001) the area perpendicular to the elongated axis is $A = a^2$, but as we have two surfaces in the cell, we need to add the prefactor of 2. In `Job.out` we find besides the Vasp energy also the heat of formation for the formula unit and the cell. The heat of formation is with respect to the reference state of Mo and allows comparing the different layers at a glance. The surface energy is computed from either energies (E_{VASP})or heat of formations (E_{form}) by subtracting n-times the bulk reference for Mo (primitive cell), and dividing through the surface area. (1 eV=96.458 kJ/mol, N_A=6.022142·10^{23})

System		k-mesh	E_{VASP} (eV)	Comment	E_{form} [kJ/mol]	E_{surf} [J/m^2]
Mo bcc (optimization)	Mo	6×6×6	-10.79857	a=3.168 Å	4.69	
Mo bcc (P1)	Mo_2	4×4×4	-21.62101		7.08	
Mo primitive (P1)	Mo	6×6×6	-10.80283		4.28	
Mo 1x1x6 cell	Mo_6	4×4×2	-129.56473	c=19.00 Å	29.04	
Mo(001) 3 layers	Mo_3	4×4×1	-28.05031	c=18.67 Å	433.35	3.48
Mo(001) 5 layers	Mo_5	4×4×1	-49.97279	c=14.0 0Å	411.35	3.23
Mo(001) 5 layers	Mo_5	4×4×1	-49.96033	c=18.67 Å	412.55	3.24
Mo(001) 7 layers	Mo_7	4×4×1	-71.58431	c=18.67 Å	419.30	3.22

A point more subtle is the usage of energies from cell volume optimizations, there is a small difference of 0.4 kJ/mol. The rather coarse k-spacing also shows up when comparing the different Mo bulk cells; for surface energies, we used the primitive Mo cell.

Surface Reconstruction

The Mo(001) surface is known to undergo a reconstruction, forming zigzag chains of surface atoms with a c(2×2) periodicity. This reconstruction is not taken into account in the present calculations. The energy gained by this reconstruction, about 0.05 J/m^2, is small compared with the surface energy.

Cleavage Energy

In the case of a simple metal such as Mo, the surface energy is uniquely defined by the Miller plane such as (001), allowing the creation of a slab model with two equivalent surfaces. However, in the general case, it is not always possible to create a slab with two identical surfaces. In this case, one needs to be careful in the definition of a surface energy. In fact, in such a situation the concept of a “cleavage energy” may be more appropriate. In the present case of the Mo(001) surface, the cleavage energy would be exactly twice the surface energy.

6. Compute Energy of Mo (110) Surface

For comparison, we compute the (110) surface energy, as this is the most densely packed surface for a bcc structure. The same unit optimized unit cell is taken as the starting point for the surface builder to create a (100) surface model with 3 **Repeats** and a **Gap (Ång)** of 6 Å. We keep the settings from the surface optimizations and allow only for **☑ Relax atom positions**.

The resulting heat of formation is higher than for the (100) surface, but with the larger surface of the slab, $a = 4.4803, b = 3.1681$, the resulting surface energy is 25% lower. The actual number of k-points varies depending on the symmetry: 8×8×1 with Cmma, and 3×4×1 with P1 symmetry, both are based on a spacing of 0.5/Å, but the effective spacing for Cmma is 0.304×0.496×0.323, where for the P1 cell it is 0.467×0.496×0.323

System		k-mesh	E_{VASP} (eV)	Comment	E_{form} [kJ/mol]	E_{surf} [J/m^2]
Mo primitive	Mo	6×6×6	-10.80283		4.28	
Mo(110) 6 layer	Mo_{12}	8×8×1	-125.22086	c=19.44 Å	477.164	2.49
Mo(110) 6 layer	Mo_{12}	3×4×1	-124.28553	c=19.44 Å	567.409	3.02

Results

It takes less energy, 2.5 to 3 J/m^2, to create a (110) surface compared with 3.22 J/m^2 to create a (001) surface. So the Mo (110) surface is computed to be more stable than the (001) surface. This is consistent with experimental evidence.

The variation of surface energies with respect to the used k-mesh indicate that a denser k-mesh is necessary to reach convergence.

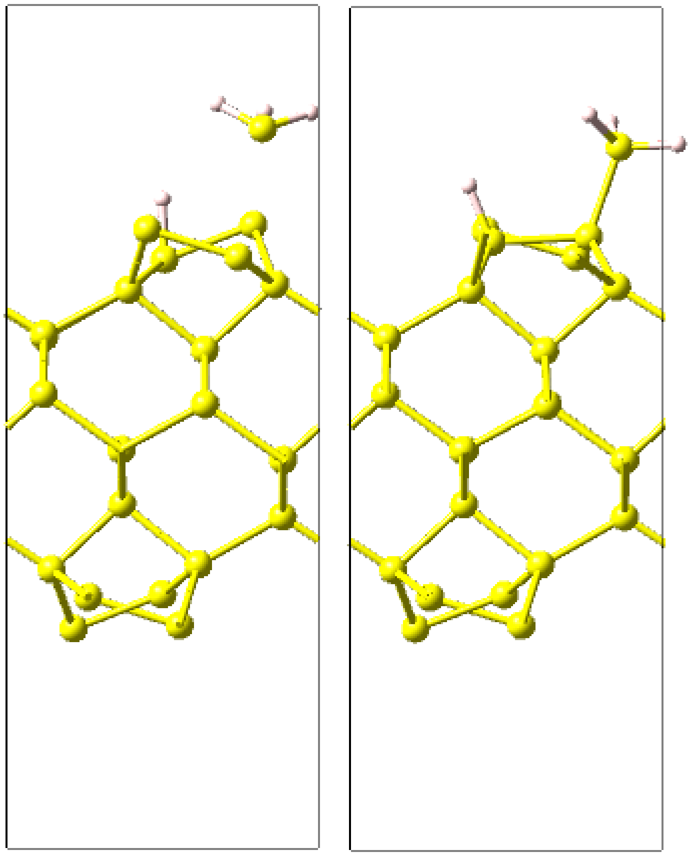
O. Energy of Dissociative Chemisorption of SiH_4 on Si (001) Surface

The energy of adsorption and dissociation of molecules on surfaces plays a critical role in technological processes such as chemical vapor deposition, catalysis, and corrosion. The present case shows the calculation of the energy of the dissociative chemisorption of a silane molecule on a Si (001) surface. This example is related to the previous case studies of the structure of a clean Si (001) surface and the structure of a dissociated silane molecule on this surface.

1. Construct Initial Structure

In a separate case study, V.E Surface Reconstruction of Si(001), we considered the reconstruction of the Si (001). Retrieve the minimized Si (001) structure from this case using **File**≫**Open**≫**Previous Calculation**.

2. Add Molecule to Surface


Initial structure Final structure

Select the structure of the pure reconstructed surface as the active window and right-click the mouse button to get the menu to add atoms.

Add one Si atom and four H atoms to the system. Use the **Move atom…** command and **Edit in molecular builder** to place these atoms approximately in the positions as shown on the left.

Place a Si atom with fourfold coordination and **Hydrogenate** to create a SiH_4 molecule. **Move** one H atom to about 1.5 Å away from the surface site.

Position the SiH_3 by selecting the Si atoms of the molecule and the adsorption site and use **Selection**≫**Distance** to move the Si atom, check **☑ Translate connected atoms** to move the SiH_3group about 2.4 Å away. Recreate the cell with **Create a periodic copy.**

3. Compute Structures and Energies

Select the structure of the silicon surface with the molecular fragments at the starting structure. Choose **VASP 4.6**≫**Run** and select **Structure Optimization**≫**Relax atom position.** Leave the other parameters at their defaults: **PBE-PAW** potentials, **k-spacing** 0.5 $Å^{-1}$, **Standard 500** precision, and **Methfessel-Paxton** smearing with 0.2 eV. Launch the calculation.

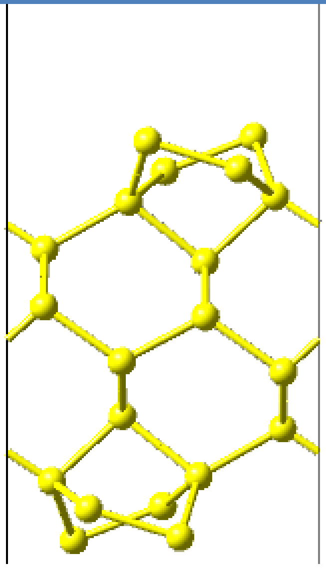
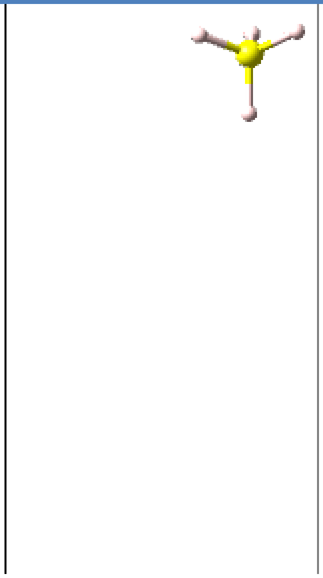
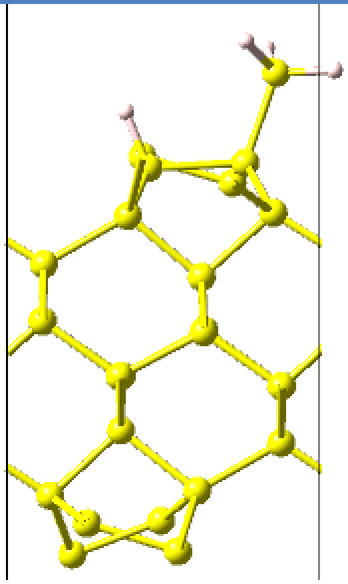
Construct a model of an isolated SiH_4 molecule in the same supercell as used for the surface. One way is to open the molecular spreadsheet and delete all bulk Si atoms. Move the absorbed H closer to the SiH_3 group, take the x and y coordinates of Si and set a distance in z direction of 1.5 Å or 0.07 fractional units.

We also need the clean Si surface with the nice reconstruction as a reference system. We compute the SiH_4 and the Si surface with the same computational parameters.

We choose **Standard 500** precision to avoid comparing systems with different energy cutoffs. If we took the **Normal** precision with **PBE-PAW**, for a system with Si and H atoms the cutoff is 250 eV, whereas for pure silicon 245.35 eV.

When optimizing structures, the differences in the plane wave basis sets are usually insignificant. However, when comparing total energies, it is very important to use consistent plane wave cut-off energies. The **Standard 500** precision is not the most efficient choice for structure relaxation, but great for energetics: The high cut-off value enables us to compare a wide range of absorbates and dopants without recalculation of the reference system.

Analyze Results

Si_{32} surface	SiH_4	$Si_{32}H\ SiH_3$
		
-15941.904 kJ/mol	-1822.840 kJ/mol	-17940.438 kJ/mol

The dissociative chemisorption of SiH_4 on a reconstructed Si (001) surface is exothermic. The electronic part of the reaction enthalpy is

$$\Delta E_{\text{elec}} = E\left(\text{HSi}_{32}\ \text{SiH}_3^{\text{chemisorbed}}\right) - E\left(\ \text{Si}_{32}^{\text{surface}}\right) - E\left(\text{SiH}_4^{\text{molecule}}\right) = -176.16\ \text{kJ/mol}$$

P. CO Adsorption on a TiO_2 Surface

As an example of molecular adsorption on a surface, this application shows the interaction of carbon monoxide with rutile. An answer is given to the question whether CO binds with the carbon or the oxygen molecule to the surface. Note that this case uses the VASP 4.4. Analogous computations with VASP 4.6 lead to very similar results.

1. Retrieve bulk TiO_2 (rutile)

The starting point is bulk TiO_2 in the rutile phase, optimized at the same computational level as used in the subsequent surface calculations. A search in the structural databases with INFOMATICA using the command **Require that Formula is TiO2** and **Require Structural Completeness Complete** gives more than 90 hits. For the present purpose, we select ICSD #63710, which is a representative and recent entry for rutile. The structure is loaded into MEDEA by right-clicking **View**.

2. Optimize Bulk Rutile with VASP

The cell is optimized with VASP using the following parameters: **Structure optimization** (all options checked) with a **convergence** of 0.02 eV/Å, **GGA-PBE**-**PAW** with standard O and Ti potentials (6 and 4 valence electrons for O and Ti, respectively), a **k-spacing** of 1.0 Å^{-1} (which gives a k-mesh of 2×2×3), **Standard 500** precision[3], and an SCF convergence of 1.0e-05. The optimization gives the following cell parameters:

```
Parameter   Original     change      Final        %
---------- ------------ ---------- ------------ -----
         a     4.593700   0.050731     4.644431   1.1
         b     4.593700   0.050731     4.644431   1.1
         c     2.958700   0.016755     2.975455   0.6
```

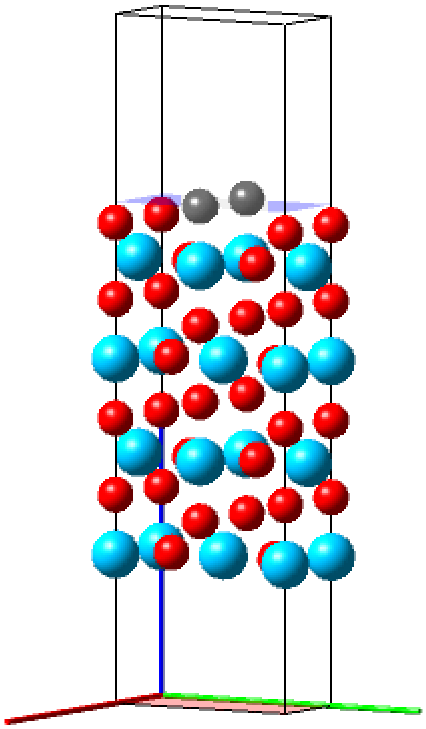
The symmetry of the rutile structure has one free internal degree of freedom for oxygen, which is optimized as follows.

```
Fractional Coordinates:
       Atom          Initial Coordinates              Final Coordinates
       -----      -------- -------- --------      -------- -------- --------
       Ti1          0.0000   0.0000   0.0000        0.0000   0.0000   0.0000
       O1           0.3048   0.3048   0.0000        0.3045   0.3045  -0.0000
```

---

[3] Normal and Accurate Precision have both a cut-off energy of 400 eV for TiO_2. So **Standard 500** is not much more expensive in terms of computing time, but allows us to reuse the energies for absorption energies.

3. Construct Model of a Clean TiO_2 (110) Surface



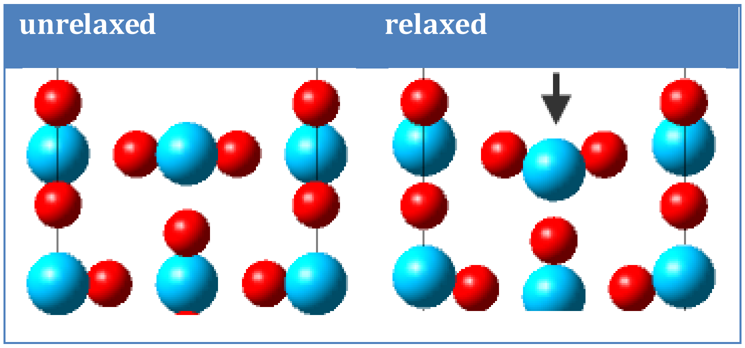
Using **File**≫**Open**≫**Previous Calculation**, the optimized structure of bulk rutile is loaded. Invoke the command **Edit**≫**Build surfaces** and set the parameters to (hkl) = (110), **Repeats:** 2 and **Gap (Ång):** 10.0 Ång. This produces the structure shown on the left.

The x-,y-, and z-axes (red, green, and blue) are displayed by setting **View**≫**Axes** from the MEDEA tool bar. Note that the length of each axis is exactly 1 nm (10 Å).

Now delete the appropriate atoms from structure shown in grey, just select the top-most oxygen atom with the mouse and press **Del** to remove it. The **Molecular Spreadsheet** is an alternative to find the atom based on its z-coordinate.

In the modified top surface we find surface Ti atoms with five-fold coordination; instead of the six-fold coordination in the bulk. This surface Ti atom is ready to react with CO molecules.

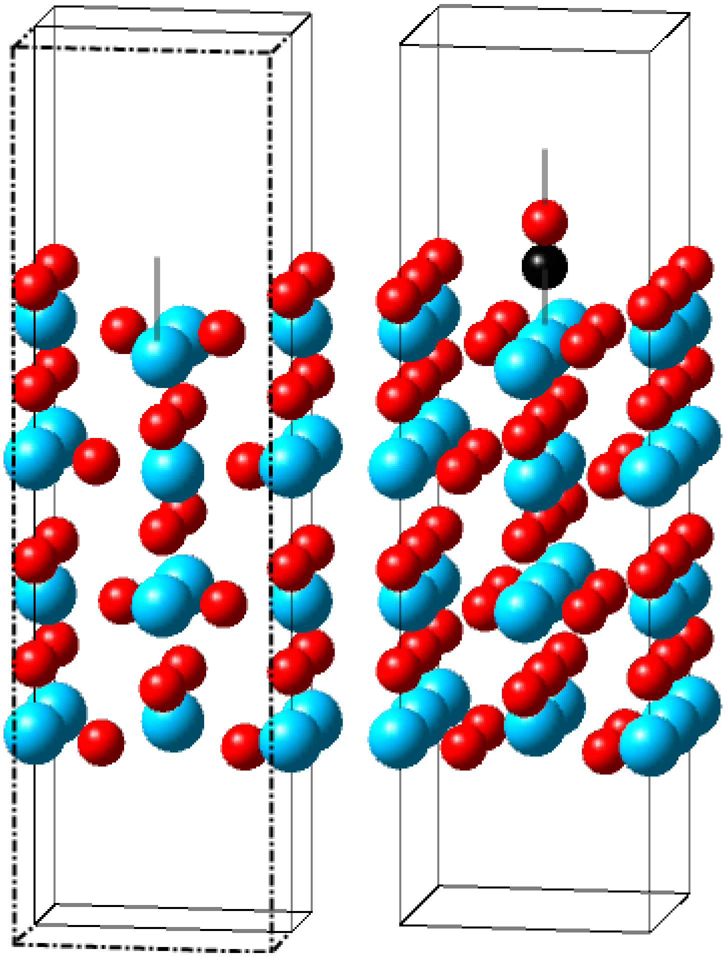
4. Relax the Clean TiO_2 (110) surface



The atom positions on the right side are relaxed using VASP with similar computational parameters as for the optimization of the bulk unit cell: **GGA-PBE**, **PAW** with standard potentials, a 1.0 Å^{-1} **k-spacing** (which now gives a k-mesh of 3×1×1, **Standard 500** precision, and **SCF convergence** of 1.0e-05. The **geometry convergence** criterion is set to 0.03 eV/Å in order to reduce the computing time. Only **☑ Relax atom positions** is checked. The upper halves of the unrelaxed and relaxed structures are shown in the figure to the left. The atoms at the surface move only slightly away from their bulk positions. Most significantly, the surface Ti atoms with five-fold coordination (see arrow) move towards the bulk thus leading to a slight corrugation of the TiO_2 (110) surface.

Note: If in the MEDEA view some atoms appear to be missing on the edges of the optimized structure, then this is because the atoms may have moved slightly parallel to the surface during the relaxation and are no longer displayed in the first unit cell. To show these atoms, select in View/Options/Cell a range from –0.1 to 1.1 for a and b.

5. Double the TiO_2 (110) Surface Unit Cell



The unit cell representing the clean (110) surface has the following dimensions: a=2.968 Å, b=6.513 Å and c=18.0 Å. Clearly, this is not much space for absorption:

Placing one CO molecule on top of the five-fold coordinated surface Ti atom in each unit cell, leads to a very crowded surface, as the distance between neighboring CO molecules would is only 2.968 Å. This will lead to strong intermolecular interactions and we want to focus at low coverage.

MEDEA makes it easy to double the surface area of our optimized surface unit cell: We load the optimized surface unit cell into MEDEA with **File**»**Open**» **Previous calculation** and using **Edit**»**Build supercell** to create a 2×1×1 supercell.

6. Add a CO molecule

To add the CO molecule we can use **Edit Structure**»**Add atom** to place a carbon atom at position (0.5,0.5,0.73) and an oxygen atom at (0.5,0.5,0.78) -all coordinates are fractional units of the cell parameters. That results in a CO molecule with C pointing to the surface.

7. Optimize Position of CO Molecule

a. CO bonded with C

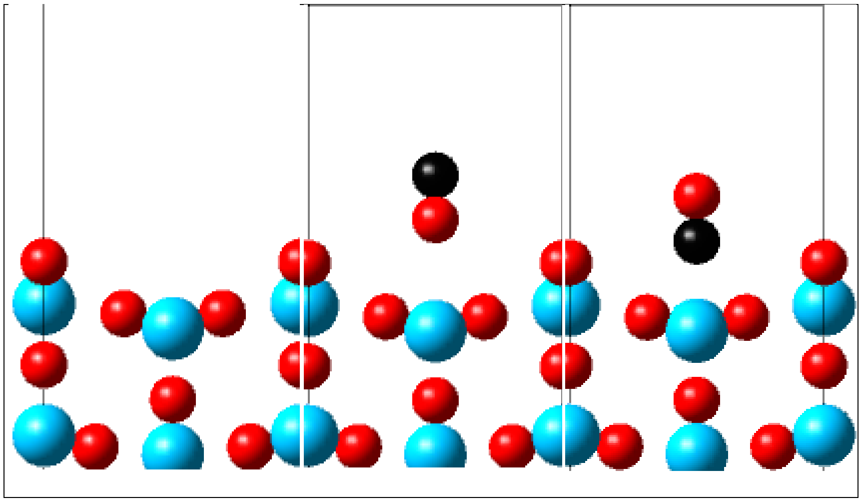
For an initial absorption study we want to restrict the optimization to the adsorbate and the top layers of the surface, so we freeze all atoms except the carbon and oxygen atoms of the CO molecule and the first layer of atoms in the TiO_2(110) surface. Freezing an atom is done by moving the cursor over an atom, right-clicking, and selecting the option **Freeze atom…** Once all the appropriate atoms are frozen, choose **VASP**»**Run** with the following computational parameters: **Structure optimization** as type of calculation with a convergence criterion of 0.02 eV/Å (only the relaxation of atoms should be checked), **GGA-PBE**, **PAW** and 1.0e-05 for the **SCF convergence**. A **k-spacing** of 1.0 Å^{-1} leads to a 2×1×1 k-mesh. A slight increase of the k-spacing to 1.1 $Å^{-1}$ leaves only one k-point, namely Γ. Since the Γ-only version of VASP is faster, a **k-spacing** of 1.1 $Å^{-1}$ is selected.

b. CO bonded with O

A second calculation is launched with the CO molecule turned upside down. Use **Edit Structure** and **Move Atom** or the **Molecular Spreadsheet** to exchange the atoms or switch the positions of O and C.

Analyze Results

A comparison of the total energies of the two calculations reveals that CO binds with the C atom to the Ti atom of a TiO_2 (110) surface. As can be seen from a quick analysis of the geometry the Ti-C bond distance is slightly shorter than the Ti-O bond, which illustrates the stronger bonding of Ti with carbon rather than the oxygen atom of the CO molecule.



This initial geometry optimization is a good starting point to calculate energies or refine the structure optimization with a finer k-mesh.

Q. Cohesive Energy of Diamond

The cohesive energy of a solid is defined as the energy required for separating the condensed material into isolated free atoms. Cohesive energies range from about 0.1 eV or 10 kJ/mol for inert gases up to about 8 eV or 800 kJ/mol per atom for strongly bound materials such as diamond or tungsten. The calculation of the cohesive energy requires a value of the total energy for the solid and of the free atoms. The energy difference between atoms and a solid is a measure of the bonding strength in the solid material. This appears to be a straightforward task. In practice, however, there are a number of subtleties, which are illustrated here for the case of a seemingly simple system, namely diamond.

Outline of Approach

In principle, the approach is very simple. One needs to compute the total energy of diamond and of an isolated C atom. The energy difference per atom is the cohesive energy. Now let us go through this process very carefully.

1. Get Structure

A search in the crystallographic databases with INFOMATICA gives a number of structures, most of them measured at room temperature. For simplicity, let's take the first entry, which is ICSD.66464 with a reported lattice parameter of a= 3.5667 Å.

2. Select Hamiltonian

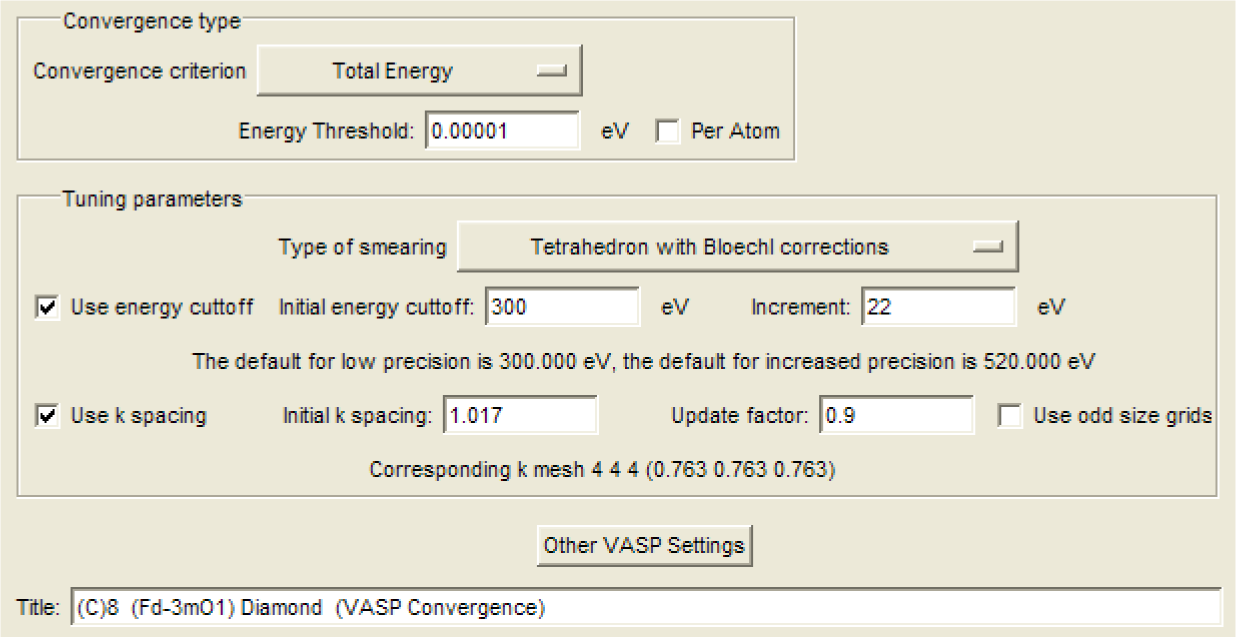
The Purdue-Burke-Ernzerhof form of the generalized gradient approximation is currently a widely used approach to treat exchange and correlation effects in electronic structure calculations. We follow this approach, but we should be aware that this is one particular choice. Diamond is non-magnetic, so we can use a non-spin-polarized Hamiltonian.

Furthermore, the atom is relatively light and relativistic spin-orbit effects can be neglected. For the case of the free C atom, the valence states have an electronic configuration of s^2p^2. There are unpaired electrons, so we need to perform the calculations for the atom with a spin-polarized Hamiltonian. Actually, atoms are more complicated and we will come back to this later.

3. Optimize VASP Parameters

It is well known that the total electronic energy converges rather slowly with the number of plane waves, i.e. with the cut-off energy in the basis-set expansion. The other major parameter in electronic structure calculations on solids is the number of k-points in the Brillouin zone, which determines the accuracy of the charge density and the potential.

MEDEA 2.0 offers a new capability to check the convergence of the total energy with respect to these parameters in an automated way. To this end, activate the window with the diamond structure and invoke **Tools**»**Automated Convergence** from the MEDEA tool bar. Choose "**Total Energy**" as convergence criterion and set the threshold at the rather stringent value of 0.0001 eV. In the VASP settings, choose "**Normal**" as precision.



Convergence type

Convergence criterion: Total Energy

Energy Threshold: 0.00001 eV ☐ Per Atom

Tuning parameters

Type of smearing: Tetrahedron with Bloechl corrections

☑ Use energy cuttoff Initial energy cuttoff: 300 eV Increment: 22 eV

The default for low precision is 300.000 eV, the default for increased precision is 520.000 eV

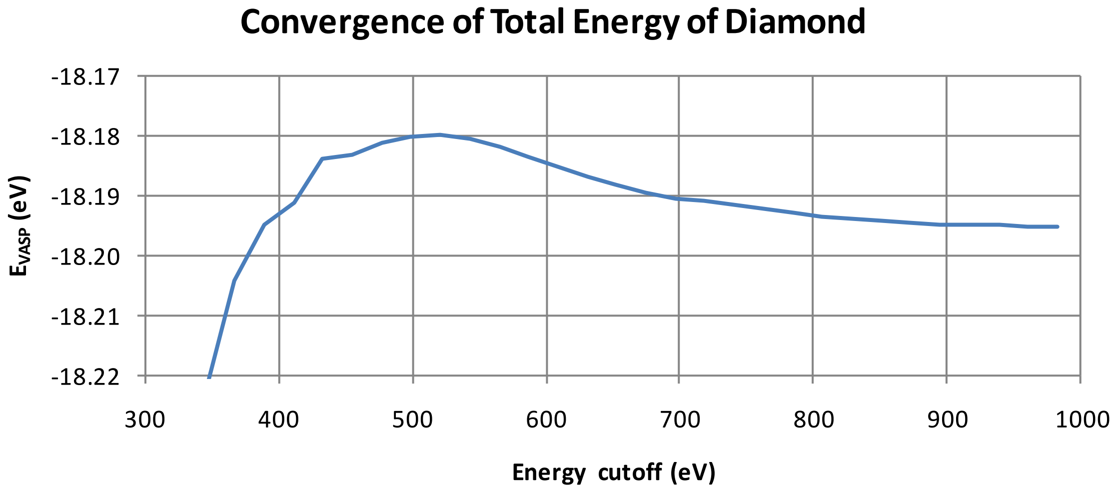
☑ Use k spacing Initial k spacing: 1.017 Update factor: 0.9 ☐ Use odd size grids

Corresponding k mesh 4 4 4 (0.763 0.763 0.763)

Other VASP Settings

Title: (C)8 (Fd-3mO1) Diamond (VASP Convergence)

Launch the convergence calculations and use the **Convergence**»**Monitor** to follow the convergence of the total energy with respect to the plane-wave cut-off and the k-mesh. In the present case, a rather large plane-wave cut-off of 938 eV and a k-mesh density of 0.18 Å^{-1} corresponding to a 17x17x17 Monkhorst-Pack mesh are needed to achieve a convergence of the total energy of less than 0.0001 eV. As can be seen from a plot of the total energy *vs.* the plane wave cut-off, the default value of 400 eV gives a total energy, which is actually very close to the converged value. However, the convergence is not monotonic. At lower values, the total energy increases and then diminishes gently for higher plane wave cut-off values.



4. Compute Lattice Parameters and Total Energies

Choose the diamond structure ICSD.66464 and use the following parameters for VASP 4.6: **Structure optimization** with all three boxes checked; **geometry convergence** 0.01 eV/Å, **Accurate precision**, **k-mesh spacing** 0.18 $Å^{-1}$, and **Tetrahedron with Blöchl corrections** as integration scheme. Leave the plane wave cut-off at 400 eV.

Then launch the calculations. The resulting lattice parameter is a=3.5623 Å, which is 0.1 % smaller than the experimental value used as input. The correspond total energy is

$$E_{VASP} = -18.186940 \text{ eV per } \mathrm{C}_2 \tag{8-1}$$

The value corresponds to a unit cell with 2 carbon atoms.
If we load the optimized structure from the JobServer's database and run a single-point energy with exactly the same parameters as in the previous lattice optimization, the total energy is

$$E_{VASP} = -18.186157 \text{ eV per } \mathrm{C}_2 \tag{8-2}$$

The two values are slightly different, because the single point energy uses a slightly different number of plane waves and Fourier meshes. The reason is that in an optimization of the lattice parameter, the meshes in reciprocal space are constructed from the dimensions of the input structure. Therefore, it is important to recompute the total energy after geometry optimizations to ensure consistency with subsequent calculations, where, for example, only internal parameters, such atomic positions in fractional coordinates, are optimized.

The energy E_{VASP} has a peculiar reference: E_{VASP} is relative to the total energy of a spherical atom, computed with a non-spin-polarized Hamiltonian. Therefore, E_{VASP} is not the total electronic energy of the system. In fact, this value would be much larger in magnitude.

To obtain a cohesive energy, we need the energy of an individual carbon atom. This is done in the next step.

5. Compute Energy of Carbon Atom

In MEDEA, use **File**≫**New** to create a supercell for a C atom. Use **Edit**≫**Cell** to set the cell parameters at a=10 Å, b=11 Å, and c=12 Å. Add a C atom at (0,0,0). Launch a VASP single-point energy calculation with "**Accurate**" precision, a k-spacing of 1, *i.e.* use only the Γ k-point. Set the k-integration to Methfessel-Paxton. The total energy is

$$E_{VASP}\,(\text{C,non-spin-polarized}) = -0.154091 \text{ eV} \tag{8-3}$$

An inspection of the OUTCAR.out file shows the following occupation of the electronic levels at the Γ-point (which is the only k-point used here):

```
k-point   1 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation
       1     -13.6874      2.00000
       2      -5.2097      0.66756
       3      -5.2097      0.66741
       4      -5.2094      0.66503
       5      -0.3463      0.00000
       6       0.7552      0.00000
```

The level of −13.6874 eV is the C-2*s* state, occupied with 2 electrons. The states # 2-4 are the C-2*p* levels. Each of them is occupied with 2/3 of an electron. This makes the atom spherical and represents an average configuration.

Now rerun the same calculation with a spin-polarized Hamiltonian. The total energy drops by 1.16 eV (or 112 kJ/mol) to

$$E_{VASP}(\text{C,spin-polarized}) = -1.315324 \text{ eV} \tag{8-4}$$

Now the occupation of the electronic levels is as follows:

***α* spin**

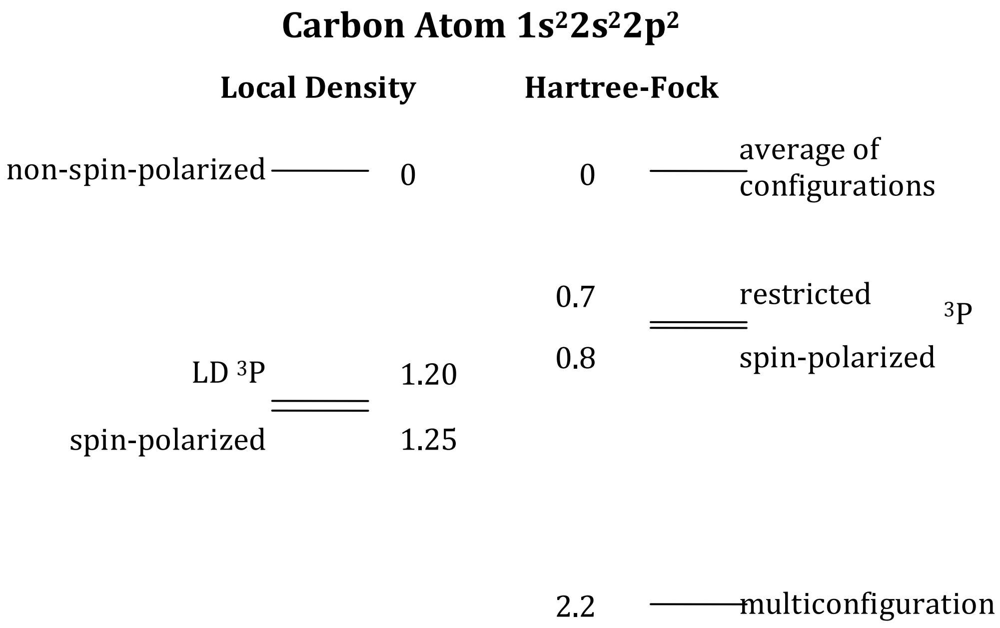
```
  band No.  band energies     occupation
       1     -14.5784      1.00000
       2      -6.0199      0.67576
       3      -6.0189      0.67171
       4      -6.0140      0.65253
       5      -0.3973      0.00000
       6       0.6728      0.00000
       7       0.7098      0.00000
```

***β* spin**

```
  band No.  band energies     occupation
       1     -11.8155      1.00000
       2      -3.5636      0.00000
       3      -3.5206      0.00000
       4      -3.5116      0.00000
       5      -0.0429      0.00000
       6       0.9993      0.00000
       7       1.0536      0.00000
```

In the C-2*s* states, one level is occupied with an electron with spin α and one with spin β. In the 2*p*-states, the computational approach occupies all three α-spin states with 2/3 of an electron. The corresponding 2*p* states with β-spin are empty. This amounts to a total of 2 unpaired electrons or a triplet state.

Spin-density functional theory predicts indeed the correct spin state of a C atom in its ground state. However, the electronic structure of a C atom is more complicated, since the coupling of the angular moments of the *p*-electrons leads to several configurations. The figure below shows the correspondence between density functional calculations and results from Hartree-Fock and configuration interaction results.[104]



The important point here is that the electronic energy obtained from standard density functional calculations on atoms is an average over configurations, and can differ from the energy of the electronic ground state of that atom by several hundreds of kJ/mol. Therefore, one needs to be really careful in making statements about the absolute value of cohesive energies. For closed-shell atoms such as Mg, the DFT calculations come close in describing the electronic ground state of that atom. In open shell systems, in particular transition metals, rare earth, and actinide atoms, the difference between the electronic ground state and the DFT results can be very large on the scale of chemical energies. Reference to spin-polarized atoms remedies some of these discrepancies, but multiplet splittings can play an important role.

6. Compute Cohesive Energy

With these warnings in mind, let us compute a cohesive energy of diamond. From the results of steps V.Q.4 Compute Lattice Parameters and Total Energies and V.Q.5 Compute Energy of Carbon Atom, we obtain

$$\begin{aligned} E_{\text{cohesive}}(\text{diamond}) &= E_{VASP}(\text{C}_{\text{atom}}) - E_{VASP}(\text{C}_{\text{bulk}}) \\ &= -1.3153\,\frac{\text{eV}}{\text{atom}} + \frac{18.1862}{2}\,\frac{\text{eV}}{\text{atom}} = 7.78\,\frac{\text{eV}}{\text{atom}} = 750.7\ \text{kJ/mol} \end{aligned} \quad (8\text{-}5)$$

The experimental value for the cohesive energy of diamond is 7.37 eV, compared with our calculated value of 7.78 eV. It is quite possible that the major source for this deviation comes from the present DFT calculations of the C atom rather than the solid.

R. Strength of Ni Grain Boundary and the Effect of Boron

Introduction

Interfaces are present in most materials and have a large impact on mechanical properties such as stiffness and yield strength. Given that the properties of an interface can radically change by the presence of even minute amounts of impurities, it is of great interest to predict the effect of segregated atoms at interfaces. As systematic experimental information on the impact of specific defect types on the grain boundary strength is hard to obtain, computational modelling is of great help.

In the present document, we will investigate the segregation of boron to a Σ5 Ni (001) twist grain boundary, and the resulting effect on the Ni grain boundary strength. It is known from experiments that B has in fact a strengthening effect in Ni based alloys.

The present application note describes how to build a Ni grain boundary and determine its strength in the presence/absence of segregated boron.

1. Construct and relax the pure grain boundary

Using the MEDEA interface builder, structure models of interfaces can be generated fast and easily and used as input to first-principles calculations. The construction of a Ni grain boundary consists of the following steps:

- Load and optimize the Ni bulk crystal structure
- Build a Ni surface from the optimized bulk system
- Construct the Ni grain boundary
- Optimize and relax the Ni grain boundary structure

a. Optimize the Ni bulk crystal structure

We start from Ni bulk and perform a full structure optimization in VASP where we allow for spin-polarization:

Retrieve the face centered cubic (Fm3-m) Ni structure from INFOMATICA.

Open VASP from the **Tools** menu, select **Vasp**≫ **Run** and choose **Structure Optimization** in the **Calculation** panel and check the boxes for **☑ Relax atom positions**, **☑ Allow Cell volume to change**, and **☑ Allow cell shape to change**. Set **Magnetism** to **Spin-polarized**, and finally, press **Run** to submit the job

Once the structure optimization finished, load the minimized structure (**File**≫**Load**≫**From Previous calculation**)

b. Build a Ni surface

Activate the window of the relaxed Ni structure and choose **Build surfaces** from the **Edit** menu.

To construct a Ni (001)/Ni (001) grain boundary, set **Miller Indices** (h, k, l)=(0, 0, 1) and click **Search**. Set the **Repeats** to 2 and **Gap thickness** to 10 Å, and click **Create**.

This yields a four-layer slab structure of Ni as displayed in the Surface Builder window.

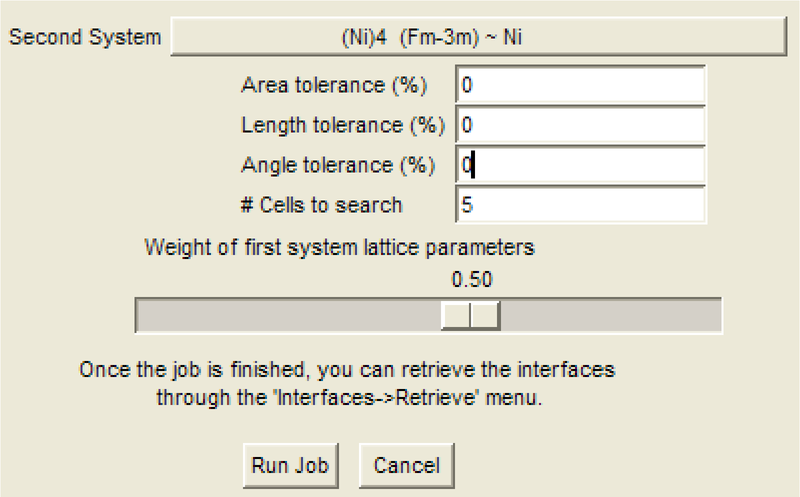
No further adjustments are needed, so click **Create Symmetric** to make use of the inherent symmetry.

c. Construct the Ni grain boundary

We will now use the Interface Builder (IB) to construct a Ni grain boundary:

Click on **Interfaces** in the **Tools** menu.

Activate the window of the Ni surface slab structure and choose **Define and run** in the Interfaces menu.



Second System: (Ni)4 (Fm-3m) ~ Ni

Area tolerance (%): 0

Length tolerance (%): 0

Angle tolerance (%): 0

Cells to search: 5

Weight of first system lattice parameters: 0.50

Once the job is finished, you can retrieve the interfaces through the 'Interfaces->Retrieve' menu.

In the **Interfaces Builder** dialogue the Ni surface is preset for both the first and second system. With this choice **Interfaces Builder** matches two identical Ni surfaces together to form a Ni grain boundary.

Set all tolerance values to 0 and **# Cells to search** to 5 and click on **Run Job**.

With tolerance values set to zero, we generate interfaces without strain to form the interface.

Submit the search for interface structures by clicking **Run** in the Interface Search Job window.

While the job is running, check its status via the **Job Control** menu. In `Job.out` you can follow the InterfaceBuilder's progress in identifying structures that match your search criteria.

When the search is completed, click **Retrieve** in the **Interfaces** menu to open the file selector. **Insert** the interface search calculation and click **OK**.

This will open the result window with a list of interfaces matching the search criteria.

ID	Identical Interfaces	nAtoms	Spacegroup	Area (Ang^2)	dArea	A (Ang)	dA	B (Ang)	dB	theta (degree)	dTheta	BedAngle (degree)
1.1	Yes	40	Pnna	31.04	0.0	5.572	0.0	5.572	0.0	90.0	0.0	0.00

1.2	Yes	40	P4/ncc	31.04	0.0	5.572	0.0	5.572	0.0	90.0	0.0	-18.43
2.1	Yes	104	Pnna	80.71	0.0	8.984	0.0	8.984	0.0	90.0	0.0	0.00
3.1	Yes	200	P4/ncc	155.21	0.0	12.459	0.0	12.459	0.0	90.0	0.0	-106.26
4.1	Yes	136	P4/nnc	105.55	0.0	10.274	0.0	10.274	0.0	90.0	0.0	0.00

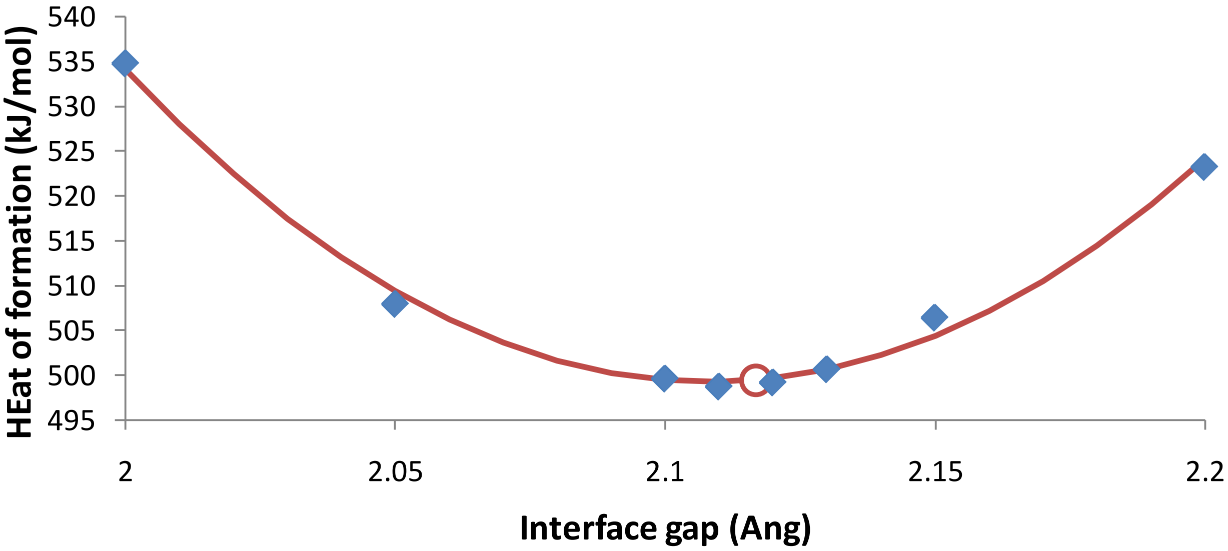
We find 5 structures in 4 classes which match the search criteria. The structure with ID 1.2 is appropriate for our purpose. It is reasonably sized with 40 atoms, which gives 5 atoms per layer and interface area 31.04 Å^2. This is a Ni Σ5 (001) twist grain boundary with two equivalent interfaces in the supercell.

Right-click on the line corresponding to ID 1.2 and select **Create Interface**.

In the following preview window, additional degrees of freedom can be specified.

d. Optimize and relax the Ni grain boundary structure

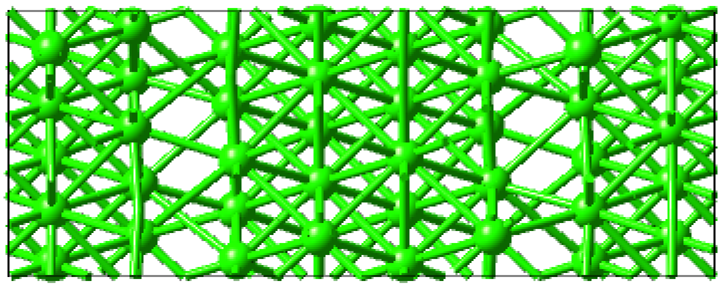
Next we would like to set the **Gap in Angstroms** between the two surface slab structures. To determine this value, a series of single point calculations with varying gap size can be performed to find the gap value that minimizes the energy. Note that this procedure, where no relaxation is performed, is a shortcut. A more precise procedure would be to optimize the atomic positions for each interface gap distance.



The minimum in energy is obtained for a gap distance of close to 2.12 Å.

Set **Gap in Angstroms** to 2.12, and confirm with **Apply** and OK.

Using this structure as a starting point we can now continue with a relaxation of the atomic positions: Activate the window with the Ni interface and open the VASP Run dialogue.



Choose **Structure Optimization** and check the box for **☑ Relax atom positions**, keeping the cell shape and volume fix. Submit the calculation and when it is finished, load the minimized structure into MEDEA.

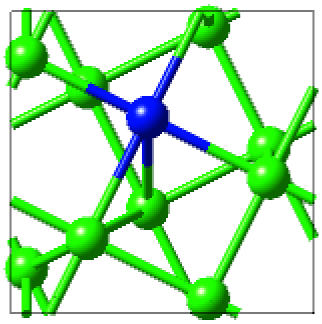
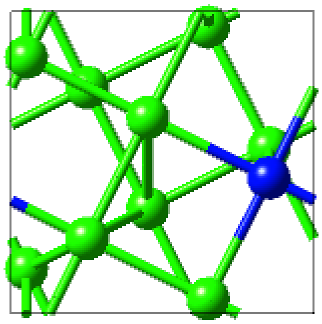
2. Introduce boron in grain boundary and relax new structure

In the general there are several positions at the interface where an impurity may be located. Often it is a substitutional site, where the impurity replaces one of the host atoms at the interface. Sometimes it is interstitial segregation, where the impurity occupies a position between host atoms. This requires the impurity to be small or the crystal structure to be open enough to accommodate an interstitial impurity atom. While for larger impurities interstitials are energetically unfavorable, it is a common scenario for smaller atoms like H, B, C, and N.

It is advisable to determine the most favored position for the impurity by comparing the energies of respective atomic structures. In this application note, we will study two interstitial and two substitutional positions.

a. Substitutional segregation

The impurities are introduced into the optimized grain boundary. Fig. 4 shows the relative positions of atoms at the interface (positions of the atoms at the second interface in the supercell are related via a 180 deg. rotation around the supercell z-axis (c-axis) followed by mirroring in the supercell xz-plane). For clarity, only the atoms in one atomic layer on each side of the interface are shown. (You can focus on the two layers by changing the limits in **View**»**Options...**»**View**»**View Limits**: **c** from **Min: 0.6** to **Max: 0.85.**

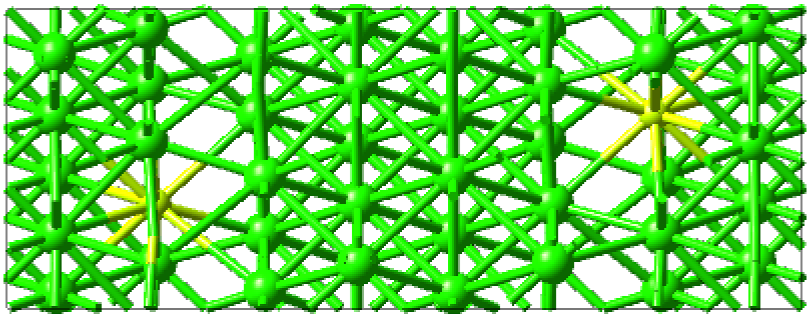
Coordinated to four atoms in the layer below	Coordinated to one atom in the layer below
	

Four of the five atoms in one interface atomic layer in the supercell are coordinated to predominantly one atom on the opposite side of the interface. The fifth atom is coordinated to four atoms on the opposite side of the interface. We will study both substitution of one-, and four-coordinated Ni atoms by boron. We start with the case of substituting the Ni atom in position 4:

Activate the window of the optimized grain boundary structure without impurities. Move the pointer over the interface atoms and read off the (Fractional) coordinates displayed in the bottom left corner of MEDEA. Right-click on the first Ni atom in pos 4 at one of the two interfaces in the supercell. The fractional coordinates are (0.25, 0.25, 0.31)

Select **Edit atom** from the pop-up menu. Choose B as **Element**, either from the periodic table or by typing in the entry box. Click on **Apply** and then **OK**. The Ni atom should now be substituted by Boron. Repeat the substitutional procedure for the Ni atom in pos 1 at the other interface in the supercell. The fractional coordinates are (0.75, 0.75, 0.69).

The supercell should now contain two boron atoms in the same Ni slab, one at each interface.



Next, optimize this grain boundary by performing a structural optimization of the atomic positions using VASP:

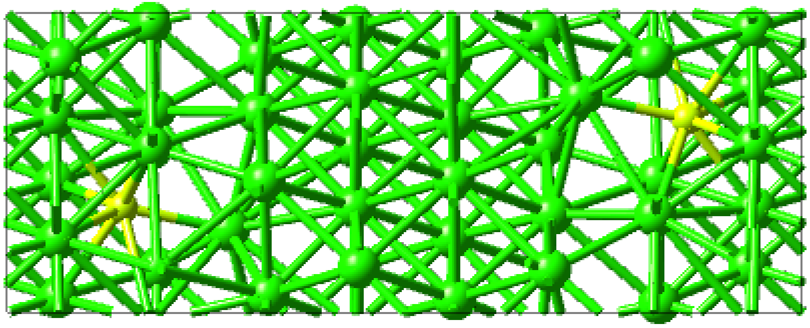
- Open VASP from the **Tools** menu, select **Vasp**≫**Run** and choose **Structure Optimization** in the **Calculation** panel
- Check the box for **☑ Relax atom positions**
- Press **Run** to submit the job

Using a single processor (Pentium D 1.83 GHz clock frequency) this may take about 50 hours. Check the progress of the calculation via the **Job Control** menu.

The energy (heat of formation) can be obtained from `Job.out`. It is calculated to be 585.7 kJ/mol. The computed heat of formation may vary slightly depending on the computational parameters. For all parameters, we have used the default values of VASP 4.6 as defined in MEDEA 2.1.

We now consider the case where instead the Ni atom in position 1 is substituted for B: Repeat the steps for constructing a grain boundary with substitutionally segregated boron as given above starting from the optimized structure without impurities. This time substitute the Ni atom in pos 1. The fractional coordinates for the two Ni atoms in the supercell are (0.66, 0.45, 0.32) and (0.34, 0.55, 0.68)

Perform a structural optimization where only the atomic positions are relaxed.



For substitution of Ni atoms in pos 1, we find the heat of formation 306.2 kJ/mol in `Job.out`. This is about 280 kJ/mol less than for substitution of Ni in pos 4. Thus, we can conclude that it is energetically more favorable for boron to substitute a Ni atom in pos 1 than in pos 4.

b. Interstitial segregation

Instead of substituting a Ni atom at the interface, it may be energetically more favorable for the impurity to be placed in the voids between the Ni atoms. In the present Ni/Ni grain boundary, we assume two interstitial positions for the impurity. In both these positions the B atom is placed in the middle of a square formed by four Ni atoms in one of the interface layers. Fig. 7 shows these two positions with the squares shadowed. In the general case it may be non-trivial to find interstitial positions in an interface. Sometimes symmetry considerations lead to good candidates for interstitial sites. Another option is to use the **Find empty space** tool in MEDEA under the **View** menu.

To generate and calculate the energy of the first interface structure with interstitial impurities: Activate the window of the optimized grain boundary structure without impurities

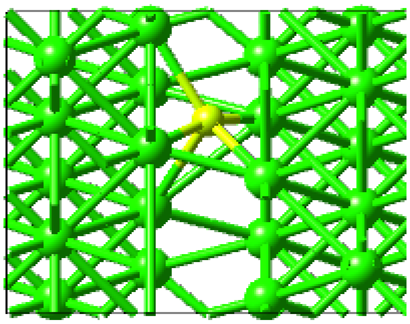
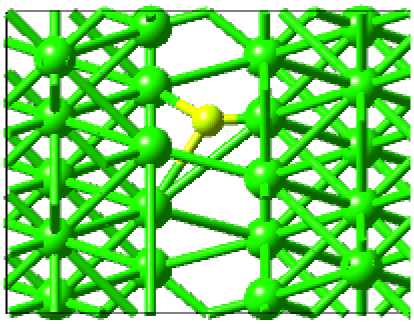
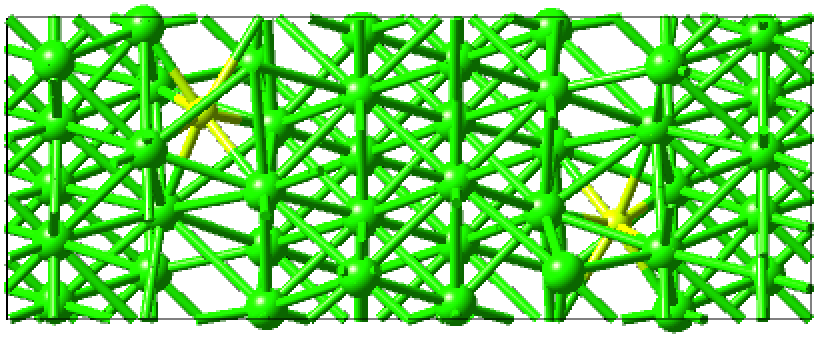
- Right-click and select **Add Atom** from the pop-up menu

Choose B as **Element**, either from the periodic table or by writing in the entry box

- Set **Atom Coordinates** to **X:** 0.36 **Y:** -0.64 **Z:** 0.25. Confirm with **Apply**
- Set **Atom Coordinates** to **X:** 0.64 **Y:** 0.36 **Z:** 0.75. Confirm with **Apply** and **OK**

This should result in a supercell with two interstitially placed B atoms, one at each interface in the supercell. (And the symmetry can be raised to P-1. Perform a structural optimization where the atomic positions are relaxed

Repeat the procedure for constructing the grain boundary structure with interstitial impurities as given above, but now insert the atoms at the fractional coordinates (0.45, 0.65, 0.25) and (0.65, 0.45,.75). Perform a structural optimization where only the atomic positions are relaxed.

Initial	final
 	

This results in the same final atomic configuration, with the same energy, as for the first interstitial position.

3. Cleave grain boundary and relax the free surfaces

To calculate the strength of the grain boundary as measured by the work of separation (see V.R.4 Calculating the energy required to cleave an interface), we need to separate the two grains forming the interface. We imagine the interface structure to be cleaved at the interface, and pulled apart so the resulting two surfaces have an infinite distance between them. From a computational point of view, the two resulting surface structures are treated independently in separate calculations.

We start with the optimized Ni grain boundary structure without any impurities. It is formed by matching two identical Ni slab structures with (100) surfaces together. Thus, it is enough to consider only one of the separated slab structures. On separation, the atomic positions at the free fracture surfaces will relax. We will therefore perform a structural optimization of one of the slab structures:

Activate the window of the optimized grain boundary structure without impurities

Right-click inside the window and choose **Select** from the pop-up menu

Select all atoms in one of the two Ni slabs on one side of the interface (half of the atoms in the cell) by clicking them

Right-click again and choose **Delete selected atoms** from the pop-up window

Note: In cases where the cell contains a lot of atoms it may be cumbersome to manually remove the atoms. It may then be more suitable to simply start from the surface structure from which the interface was constructed. Be careful to use the same basis set as for the interface in the calculation.

- Open VASP from the **Tools** menu, select **Vasp**≫**Run** and choose **Structure Optimization** in the **Calculation** panel
- Check the box for **☑ Relax atom positions**

All computational parameters should be the same as for the interface calculation. In particular, make sure the k-point densities and plane-wave cut-off energies are the same. Press **Run** to submit the job

The energy can be obtained from `Job.out`. We calculate it to be 822.9 kJ/mol.

The same procedure can be used for the Ni grain boundary where impurities have been included. When separating this boundary, the impurities are thought of as belonging to one of the Ni grains. Thus, in this case we need to calculate the energy of a Ni slab structure including the impurities. It is recommended to let the slab structure be symmetric, i.e. there should be an equal number of impurities on each side (surface) of the Ni slab structure.[4]

In this application note, we have three different surface systems including impurities to calculate: The interstitial one and the two substitutional ones. For each of these systems, we follow the same procedure to construct the surface and calculate its energy:

- Activate the window of the optimized grain boundary structure including impurities
- Right-click inside the window and choose **Select** from the pop-up menu
- Select all Ni atoms on one side of the interface by clicking them. Leave both impurity atoms
- Right-click again and choose **Delete selected atoms** from the pop-up window
- This should result in a Ni slab structure with impurity atoms on both sides of the slab.
- Use VASP to perform a calculation where the atomic positions are relaxed.

a. Calculate the energy required to cleave the boundary

We can now calculate the work of separation for the Ni grain boundary, with and without impurities. A quick overview over the basic theory behind calculating cleavage energies is given in the next section. In a gist, the work of separation is calculated by adding the energies of the surface systems, subtracting the energy of the interface system and dividing by the interface area.[105]

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[4] Otherwise, a dipole moment can be built up within the cell and we need to correct for this in some way. In principle, this can be done by specifying the VASP tool parameters IDIPOL and LDIPOL under **Add to input**. However, we do not do this in the present application note. Instead, we keep the supercell symmetric.

Remember that since we constructed symmetric surface slab structures, all impurities belong to only one slab. Separation of a grain boundary including impurities therefore results in one surface structure with impurities and another surface without impurities.

All energy values together with the resulting values of the work of separation are given in the table below:

Work of separation of the Ni grain boundary	Parameter	Value	Units
Interface area in supercell	A	3.063×10^{-19}	m^2
Without impurities			
Heat of formation of Ni/Ni grain boundary	$E_{interface}$	423.5	kJ/mol
Heat of formation of Ni surface	E_{surf}	822.9	kJ/mol
Work of separation of Ni/Ni grain boundary	W_{sep}	3.31	J/m^2
Substitutional segregation			
Heat of formation of Ni/Ni grain boundary + B [pos-4]	$E_{interface}$	585.7	kJ/mol
Heat of formation of Ni/Ni grain boundary + B [pos-1]	$E_{interface}$	306.2	kJ/mol
Heat of formation of Ni surface + B [pos-4]	E_{surf}	758.8	kJ/mol
Heat of formation of Ni surface + B [pos-1]	E_{surf}	759.1	kJ/mol
Work of separation of Ni/Ni grain boundary + B [pos-4]	W_{sep}	2.70	J/m^2
Work of separation of Ni/Ni grain boundary + B [pos-1]	W_{sep}	3.46	J/m^2
Interstitial segregation			
Heat of formation of Ni/Ni grain boundary + B	$E_{interface}$	152.1	kJ/mol
Heat of formation of Ni surface + B	E_{surf}	675.6	kJ/mol
Work of separation of Ni/Ni grain boundary + B	W_{sep}	3.65	J/m^2

The work of separation of the Ni/Ni grain boundary without boron is calculated to 3.31 J/m^2.

The energetically most favored situation for boron impurities is interstitial segregation. This results in stronger Ni/Ni grain boundaries, where the work of separation is increased by about 10 % to 3.65 J/m^2.

If Boron was to substitute Ni atoms at the grain boundary (a less likely scenario), the resulting effect on the grain boundary strength would depend on the atomic coordination: With boron coordinated to four Ni atoms in the interface layer on the opposite side of the interface, the strength would decrease by about 0.6 J/m^2. With boron coordinated to one Ni atom in the interface layer on the opposite side of the interface, the strength would increase by about 0.15 J/m^2.

4. Calculating the energy required to cleave an interface

The strength of an interface can be measured in terms of its *adhesion energy* (*work of adhesion*). The adhesion energy is defined as the reversible free energy change for forming free surfaces from the interface, whereby the surfaces are in equilibrium with their environment.

An explicit expression for the work of adhesion can be obtained by considering a closed, isothermal system, consisting initially of an interface with area A between two contacting solid phases. The interface is then supposed to be separated into free surfaces by applying the work W under constant pressure P in such a way that the chemical potentials remain uniform among all parts of the system which exchange mass with one another. Under these constraints, the reversible work $\mathbb{d}W$ can be written as

$$dW = \gamma_{\mathrm{surf}}^{(1)} dA_{\mathrm{surf}}^{(1)} + \gamma_{\mathrm{surf}}^{(2)} dA_{\mathrm{surf}}^{(2)} + \gamma_{\mathrm{int}} dA_{\mathrm{int}} \tag{9-1}$$

where $A_{\mathrm{surf}}^{(1)}$ and $A_{\mathrm{surf}}^{(2)}$are the areas of the free surfaces created during the process, and A_{int} is the remaining interface area. $\gamma_{\mathrm{surf}}^{(1)}$ and $\gamma_{\mathrm{surf}}^{(2)}$ are the associated free energies of the surfaces, and $\gamma_{\mathrm{int}}$is the free energy of the interface. As the two created surfaces grow at the same rate, with $\mathbb{d}A_{\mathrm{surf}} = -\,\mathbb{d}A_{\mathrm{int}}$, the cleaving process gives a change in Gibbs free energy of

$$\Delta G = \Delta W = \left(\gamma_{\mathrm{surf}}^{(1)} + \gamma_{\mathrm{surf}}^{(2)} + \gamma_{\mathrm{int}}\right) \mathbb{d}A \tag{9-2}$$

So the work per area unit is:

$$W = \gamma_{\mathrm{surf}}^{(1)} + \gamma_{\mathrm{surf}}^{(2)} + \gamma_{\mathrm{int}} \tag{9-3}$$

This result for the work of adhesion is known as the Dupré equation and applies directly to the case of fully equilibrated separation at constant potentials.

However, the adhesion energy is often not so easy to calculate. The reason for this is that there are many dissipative processes which are not straightforward to calculate. It is therefore common to simplify the computational model and omit such processes. The corresponding thermodynamic quantity is called the *ideal work of separation*, or sometimes just *work of separation*, W_{sep}. It is an ideal, theoretical quantity defined as the reversible work required to separate the interface into two free surfaces, whereby plastic and diffusion related degrees of freedom are suppressed. It is a useful measure of the strength of an interface, with the attractive quality of being easy to calculate. It is given by a modified Dupré equation:

$$W_{\mathrm{sep}} = \gamma'^{(1)}_{\mathrm{surf}} + \gamma'^{(2)}_{\mathrm{surf}} + \gamma_{\mathrm{int}} \tag{9-4}$$

where the primed surface energies indicate that they refer to non-equilibrated surfaces. That is, they give instantaneous values of the surface energies before any dissipative processes of chemical equilibrium have occurred.

This implies that the surface systems are kept intact during separation, maintaining the atomic composition from the interface. Thus, the work of separation can be obtained by calculating the free energy of the interface and the respective surface systems without any modifications of the atomic composition and structure apart from relaxation of the atomic positions.

Approximating the free energy with the heat of formation, as given by MEDEA-VASP, the work of separation can be obtained from

$$W_{\mathrm{sep}} = (E_{\mathrm{surf}}^{(1)} + E_{\mathrm{surf}}^{(2)} - E_{\mathrm{int}})/A \tag{9-5}$$

5. Comparing energies for segregation

In this application note we have calculated energies of the grain boundary and surface systems, with and without impurities. By comparing these energies, we can get an assessment of which is the preferred surface/interface site for the impurity.

Note that since we are only interested in relative energies of the interface systems including the impurity, we do not have to consider the reference state of the impurity (where the impurity is before it is introduced to the interface). That is, we do not have to calculate segregation energies to determine which the preferred site is.

All energies for the surface and interface systems are given in the table below. We start by looking at the interfaces with impurities: We find that the interstitial position gives the lowest heat of formation (152.1 kJ/mol) of the interface systems, and thus is the most favorable for the B atom.

Next we look at the surfaces with impurities:

Comparing the energies of surfaces with substitutional and interstitial boron (i.e. the surface with adsorbed impurities), we note that adsorption of boron on the surface position corresponding to the interstitial site is associated with a lower energy than surface substitution. This energy (675.6 kJ/mol) can also be compared to the energy of the grain boundary with impurities (152.1 kJ/mol). It is then found that the energy per B atom is about 262 kJ/mol higher for the surface structure compared to the grain boundary. Thus, the propensity for segregation of B is higher to the grain boundary than to the free surface.

S. Building and Analyzing Indium defects in GaAs

Introduction

The physics and chemistry of materials containing defects is of great interest in areas such as semiconductors, metal alloys and compounds, magnetic systems and optical materials. Destabilizing or stabilizing crystalline bulk systems, surfaces and interfaces through additives is a common technique, for example recent research into battery systems based on complex hydrides aims to tune the kinetics of the adsorption/desorption process by changing the stoichiometry and composition of the base materials.

Using systematic model building in combination with first-principle calculations, the impact and behavior of defects in a host lattice can be investigated: Local relaxation effects can be analyzed, relative stabilities can be assessed through formation energies and changes of the electronic structure can be studied.

When building atomistic models of defect systems we need to consider the stoichiometry and the local order imposed on the model by introduction of a defect. The MEDEA substitutional builder provides a tool to automatically

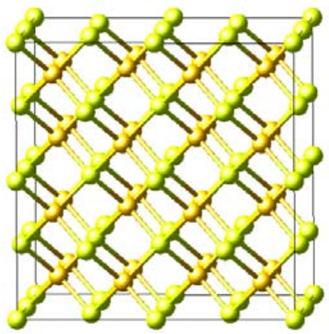
- build supercells with varying concentration of defects
- systematically analyze the changes in symmetry due to the introduction of multiple defects
- control the distance between defects to create dilute or clustered defect systems.

In this example we will analyze some structural aspects of substitutional Indium defects in GaAs.

1. Building the GaAs supercell

Start with the face centered cubic GaAs (F-43m) structure from INFOMATICA or build it from scratch: Start with an empty cell with F-43m symmetry, (a,b,c) = 5.653 Å, then add Ga at the a position (0,0,0) and As at the c position (0.25,0.25,0.25) - coordinates are in fractions of the lattice parameter.

The next step is building a (2x2x2) supercell from the unit cell. Use **Build Supercells** in the MEDEA **Edit** menu. In the pop-up dialogue, use the small arrows to select (a,b,c)=2 and click **OK** to create the model. Note that MEDEA constructs the supercell in P1 symmetry (raising the supercell symmetry will restore the original unit cell).



With the new structure window active, click on **Geometry Analysis** in the **Analysis** menu to verify that your cell has dimensions ~11.3 Å and 32 Ga and As atoms respective.

2. Introduce substitutional In defects

Choose **Substitutional Search** from the MEDEA **Edit** menu. In the Substitutional Builder Interface, select **As** from the **Replace Element** list and use the periodic table next to the **by** text field to select Indium (In) for substitution.

Next set the maximum number of substitutions to 3. This implies that you will create defect systems with In concentrations of $^{1}/_{64}$, $^{2}/_{64}$ and $^{3}/_{64}$. 64 is the total number of atoms in the original cell. Leave the other defaults and click **Run**

Let us look at the list of resulting structures step by step: First click on the **Symmetries** button to let MEDEA calculate the symmetries of the systems created through 3 subsequent substitutions of As by In. Next, check the box next to **Display results with only** and choose **1 substitutions.**

Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
1.0	1.00000	10	P-43m	-	-

The first substitution of As by In creates a system $InGa_{32}As_{31}$ of *P-43m* symmetry. You get this system by replacing any of the As atoms in the original supercell cell by using MEDEA's **Edit atom** function.

Now, set the filter to **2 substitutions** to display systems of type $In_2Ga_{32}As_{30}$:

You should now see 5 systems in the list. Right-click on the column header **Closest Substitutions** and select **Sort ascending** to sort by **Closest Substitutions**, i.e. the minimum distance between defects.

Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
2.4	0.38710	26	Cmm2	3.99727	2
2.1	0.09677	9	P-42m	5.653	2
2.3	0.38710	20	Cmc2_1	6.92348	2
2.2	0.09677	11	P-4m2	7.99455	2
2.0	0.03226	5	I-43m	9.79128	2

The **Weight** assigned to each structure corresponds to the multiplicity of the system. For example, the first line in figure 2 has a weight of 0.3871 (= 12/31), meaning that 12 out of 31 ways of substituting a second In atom for As in $InGa_{32}As_{31}$ result in a system having Cmm2 symmetry and an In-In distance of 3.99 Å.

The column **# Asymmetric Atoms** gives the number of symmetrically non-equivalent atoms per unit cell for each defect system.

 # Closest Distances gives the number of closest In-In distances. As only 2 In atoms are present in the cell, each of them has one (and the same) In neighbor. For more than 2 defect ions per cell this parameter tells about how closely defect atoms sit together (clustering).

Selecting **3 substitutions** you will yield a list of 14 structures classifying systems of type $In_3Ga_{32}As_{29}$.

Id	Weight	# Asymmetric Atoms	Symmetry	Closest Substitutions (Ang)	# Closest Distances
3.9	0.03871	26	Cmm2	3.99727	4
3.5	0.05161	20	R3m	3.99727	6
3.11	0.05161	40	Cm	3.99727	2
3.7	0.07742	36	P2	3.99727	4
3.10	0.07742	40	Cm	3.99727	2
3.3	0.07742	40	Cm	3.99727	2
3.12	0.10323	40	Cm	3.99727	2
3.13	0.15484	64	P1	3.99727	2
3.14	0.15484	64	P1	3.99727	4
3.1	0.01935	16	P-42m	5.653	2
3.2	0.01935	16	P-42m	5.653	4
3.8	0.07742	36	P2	5.653	2
3.6	0.03871	26	Cmm2	6.92348	4
3.4	0.05161	24	R3	6.92348	6
3.0	0.00645	10	P-43m	7.99455	6

Reset the search interface using the **Reset** button in order to initiate a new search.

Use the search criteria **Minimal distances between 2 substitutions** and **Maximal distances between 2 substitutions** to limit results to more (Id 3.5) or less (Id 3.11) clustered or diluted (Id 3.0) defect systems.

To view structures and consequently perform calculations on them, right-click on a result line and select **View** or **View as P1**. Note that when viewing in full symmetry, the unit cell shape and size can change.

T. Interface Energy of Metal-Ceramic Interface Co/WC Using ab initio Thermodynamics

Introduction

In many metal-ceramic composites the interface between the metallic and ceramic phases determines the mechanical properties of the material. A prominent example is the WC-Co composite, where the combination of high WC hardness and Co ductility results in advantageous mechanical properties for applications in the tool manufacturing industry. The outstanding performance of WC-Co can be explained by the low interface energies (high stability) of the contacting surfaces of WC and Co.

The present application note describes how to build a Co/WC interface and how to perform a computational study of the interface energy. You will learn how to:

- Search for interfaces using the MEDEA interface builder
- Set up computational procedures to calculate the interface energy
- Handle non-stoichiometry: The Co/WC interface built in the present application example has a differing number of C and W atoms and therefore requires the so-called "Ab Initio Thermodynamics" formalism to determine the interface energy.

Outline of procedure

- Construct the Co/WC interface
- Optimize the Co/WC interface structure
- Express the interface energy as a function of the carbon chemical potential
- Calculate the Co/WC interface energy

Geometric aspects of modeling interfaces

A number of geometrical aspects have to be considered when studying and modeling interfaces:

In most cases there are special requirements on how to match the two contacting materials: e.g. the use of periodic boundary conditions requires the lattice constants of the two materials to be commensurate

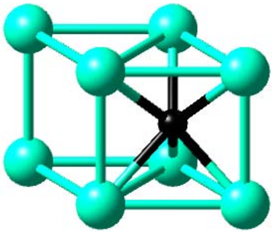
When modeling coherent structures using *ab initio* methods with periodic boundary conditions it is desirable to find geometries which minimize the elastic strain (misfit) at the interface. The reason is that with decreasing misfit, the coherent regions between misfit dislocations at an interface become larger. Consequently, for decreasing misfit, the interface model employed in the periodic approach becomes an increasingly realistic representation of the real systems.

In a composite material the two phases can differ in their elastic properties. You may want to account for this by adapting the lattice parameter of the softer material to the one of the harder material when building an interface.

Because periodic boundary conditions (slab model) are applied to model the interface, the resulting supercell contains two interfaces. In order to get a clear value of the interface energy you need to make sure both interfaces present in the cell are identical. Otherwise, an interface energy calculation gives an average value over the two interfaces.

1. Construct the Co/WC interface

1) Build a WC (001) surface

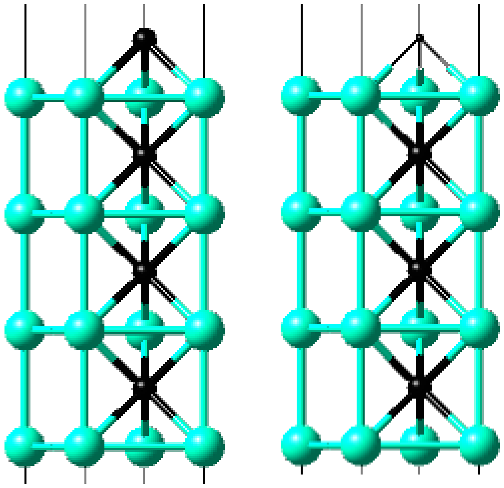


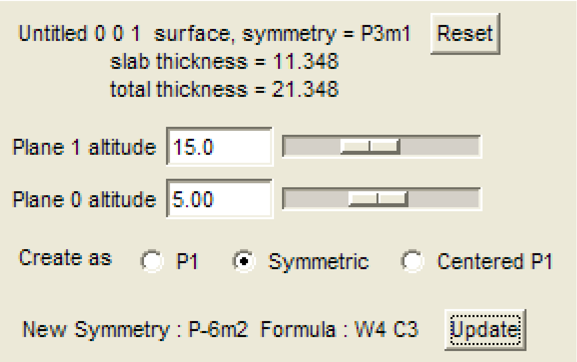
Retrieve the hexagonal WC (P-6m2) structure from InfoMaticA or build it from scratch by selecting a P-6m2 symmetry, (*a, c*) = (2.906, 2.837) Å, with W at the a-position (0, 0, 0) and C at the f-position (0.666, 0.333, 0.5), where the atomic coordinates are given relative to the lattice parameters.

In the MedeA Edit menu select **Build surfaces**. In the pop-up dialogue, choose the Miller indices (h, k, l) = (0, 0, 1) and click **Search** to find a stoichiometric model of a WC surface by cleaving the bulk parallel to the (xy) direction. Set the Number of **Repeats** to 4 and click **Create**

Note that the resulting preview model has both W- and C-terminated surfaces. To create W-terminated surfaces on both sides of the structure, adjust the altitude of one the cutting planes (blue or red) by using the slide bars, so that the outermost carbon atom is cut out. (Plane 1 at altitude 15) Click **Create Symmetric**

This results in a slab structure with 4 (001) layers of W and 3 (001) layers of C, terminated by W on both sides.





Untitled 0 0 1 surface, symmetry = P3m1

slab thickness = 11.348

total thickness = 21.348

Plane 1 altitude 15.0

Plane 0 altitude 5.00

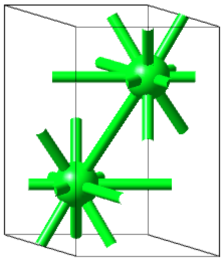
Create as ○ P1 ● Symmetric ○ Centered P1

New Symmetry : P-6m2 Formula : W4 C3

Note: Alternatively you could have created a slab structure with two C-terminated surfaces. In the remainder we will focus on the W-terminated structure. However, for completeness results for both W-, and C-terminated Co/WC interfaces are listed in the last section.

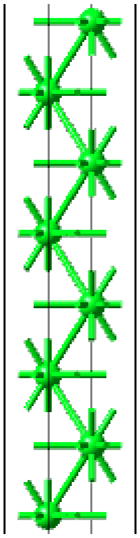
2) Build a Co (001) surface

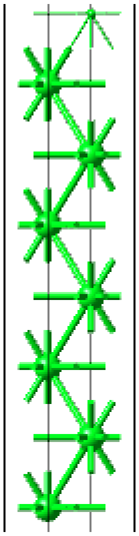
Next, build a Co (001) surface following the same procedure as for the WC (001) surface:

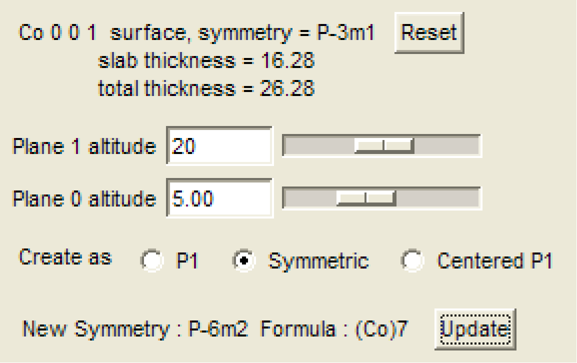


Retrieve the Co (P6_3/mmc) structure from InfoMaticA or build it from scratch by selecting a P-6m2 symmetry, (*a, c*) = (2.506, 4.069) Å, with Co at c-position (0.333, 0.666, 0.25) given relative to the lattice parameters.

Construct the (001) surface with 4 **Repeats** and cut out one atomic plane so that the resulting slab structure contains 7 layers. We cut off atoms to have Co and WC surfaces with specific properties: Top and bottom surface are identical and when we create a periodic WC|Co|WC|Co slab, we have only one WC|Co surface.







Co 0 0 1 surface, symmetry = P-3m1
slab thickness = 16.28
total thickness = 26.28
Plane 1 altitude 20
Plane 0 altitude 5.00
Create as ○ P1 ● Symmetric ○ Centered P1
New Symmetry : P-6m2 Formula : (Co)7

3) Build an interface between WC (001) and Co (001)

Select the **Interfaces** tool from the MedeA **Tools** menu

Activate one of the previously constructed surface structure windows (let it be the Co surface), and choose **Define and run** from the **Interfaces** menu, select the WC surface structure as **Second System.**

Set all tolerance values and **# Cells to search** equal to 3. To account for the fact that the Co metal is much more ductile than WC, put all **Weight of first system lattice parameter** to be on WC by adjusting the corresponding slider. In our case, the Co surface is the first system, so the weight should be 0.00. Press **Run Job** to submit a search for interface geometries.

The search algorithm uses Bravais lattice vectors in both surface planes to construct matching surfaces. From the many possibilities to match the surfaces, it lists those systems which fulfill the specified tolerance criteria. On a single Pentium D processor with 1.83 GHz clock frequency, this search takes about 20 seconds.

While the job is running, check its status through MEDEA’s **Job Control** menu

Once finished, click on **Retrieve** in the **Interfaces** menu and load the job in question through the file selection dialogue

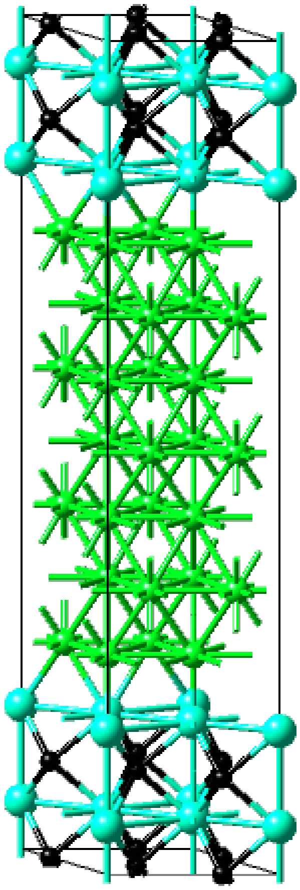
MEDEA displays a spreadsheet containing results of the interface search run. Given the above search criteria you should see the below result:

ID	Identical Interfaces	nAtoms	Spacegroup	Area (Ang^2)	dArea	A (Ang)	dA	B (Ang)	dB	theta (degree)	dTheta	BedAngle (degree)
1.1	Yes	49	P-6	21.94	-0.9	5.033	-0.5	5.033	-0.5	120.0	0.0	0.00

Select the entry by right-clicking and continue with **Create Interface**

In the builder window coming up, the distance between the WC (001) and Co (001) surface planes at the interface can be adjusted by setting the **Gap in Angstroms**. You can set the Total Gap to 4 Å or both **Upper Gap** and **Lower Gap** to 2 Å each, which is a reasonable starting value for optimizing the interface structure

Furthermore, the relative positions of the two slabs in the interface plane can be adjusted by specifying x-, and y-fractional shifts. For now, leave the default settings.



Create the interface by pressing the OK button

This procedure should result in a supercell containing two equivalent WC (001)/Co (001) interfaces. There are in total 49 atoms; 12 W, 28 Co, and 9 C atoms, respectively. Check with **Geometric analysis** in MEDEA's **Analysis** menu.

2. Optimize the Co/WC interface structure

Matching two phases together to form an interface the amount of strain and thereby the change in elastic energy stored in each phase depend on the interface misfit. Accounting for the effect of strain when calculating interface geometries and related interface energies can be achieved in a number of ways.

In the present application note, we perform a full structural relaxation of the interface, where the cell volume, cell shape, and atomic positions are relaxed simultaneously. In particular this means that the interface gap and the interlayer distances (i.e. perpendicular to the interface plane) are optimized for each phase. For our purpose, namely predicting the interface energy and atomic structure of an interface, this is reasonable.

Alternatively you can choose to fix the lattice parameters parallel to the interface. This corresponds to treating the in-plane lattice parameters as external, controllable parameters. Fixing the misfit of the two phases at the interface can be useful to investigate e.g. the impact on total energy, electronic-, optical-, and magnetic properties.

The latter method and conceptual differences between the two approaches are discussed below in section V.T.3.d Reference bulk phases and strain

1) Run a structure relaxation

Use VASP to optimize the atomic positions:

- Open VASP from the **Tools** menu, select **Vasp**≫**Run** and choose **Structure Optimization** in the **Calculation** panel
- Check the boxes for relaxation of atom positions, cell volume, and cell shape
- Choose **RMM-DIIS** as update algorithm in the optimization

Press **Run** to submit the job

All other parameters are left at their default values. To increase the accuracy of the total energy, the structure optimization should be followed by a single point calculation. The reason is that varying the volume of the unit cell during optimization implicitly changes the basis set.

Once the structure optimization has finished, load the minimized structure (MEDEA menu: File/Load/From Previous calculation)

Open VASP from the **Tools** menu, select **Vasp**≫**Run** and choose **Single Point** in the **Calculation** panel. Submit the job. Using a single Pentium D processor (1.83GHz), this takes about 80 CPU h.

Note: In this example Co is taken to be paramagnetic. This is a relevant case in e.g. liquid phase sintering of WC-Co, since the temperature exceeds the Curie temperature. Depending on the purpose of the study it may be important to probe the importance of Co spin-polarization.

2) Analysis

Use e.g. the geometric analysis to compare structural data between initial and minimized system (**Analysis menu**≫**Geometry analysis**). The main relaxation occurs for the Co atoms closest to the interface in the direction perpendicular to the interface. This gives an increase of the interface gap from our starting value of 2 Å by a few tenths of an Å.

The resulting heat of formation of the interface as given in `Job.out` is 574.90 kJ/mol.

3. Calculating the interface energy

a. Handling non stoichiometry

A general description of the formalism used in this section is given in [106].

The interface energy γ is the change in free energy associated with the formation of an interface from the bulk phases. Using the electronic contribution to the internal total energy E as an approximation of the Gibbs free energy and neglecting pressure and temperature terms, γ can be expressed as

$$\gamma = \frac{1}{A}\left(E_{\text{interface}} - N_{\text{W}}\mu_{\text{W}} - N_{\text{C}}\mu_{\text{C}} - N_{\text{Co}}\mu_{\text{Co}}\right) \qquad (10\text{-}1)$$

where A is the interface area, N_i and μ_i are the number of atoms and chemical potential of atom type i, respectively.

Given that the system is considered to be in chemical equilibrium, μ_{Co} is equal to the bulk chemical potential of the Co phase.

For the same reason, the chemical potentials of W and C at the interface are not independent, but related via the condition for chemical equilibrium with the bulk WC phase:

$$\mu_{\text{WC}} = \mu_{\text{W}} + \mu_{\text{C}} \qquad (10\text{-}2)$$

Using this relation, the expression for the interface energy can be written as

$$\gamma = \frac{1}{A}\left(E_{\text{interface}} - N_{\text{W}}\mu_{\text{WC}} + (N_{\text{W}} - N_{\text{C}})\mu_{\text{C}} - N_{\text{Co}}\mu_{\text{Co}}\right) \qquad (10\text{-}3)$$

For the supercell in this example: $N_{\text{W}} = 12$, $N_{\text{C}} = 9$, $N_{\text{Co}} = 28$ so that

$$\gamma = \frac{1}{A}\left(E_{\text{interface}} - 12\mu_{\text{WC}} + 3\mu_{\text{C}} - 28\mu_{\text{Co}}\right) \qquad (10\text{-}4)$$

In the following we use the MEDEA heat of formations to describe the relative electronic contributions to $E_{\text{interface}}$ and the chemical potentials μ[5]. The heat of formation of the interface was calculated in the previous step, and the heat of formations of WC and Co will be obtained from separate bulk calculations. For carbon the situation is different. Unlike WC and Co, C is not assumed to be in contact with a carbon bulk reservoir (graphite). Therefore the chemical potential of carbon is not directly related to its bulk value.

---

[5] Using the heat of formation as the electronic energy contributions to the internal energy corresponds to expressing energies with respect to the elements in their standard state. Alternatively we could express the electronic energy using the VASP energy. This is equivalent to taking VASP's internal energy reference, which is based on the non-spinpolarized energy of the atomic states. We recommend to use MedeA's heat of formation as this quantity is more physical, in particular it can be compared to experimental values and contains information about the compound's stability.

It remains to determine the allowed range for μ_{C}. This can be done by looking at the range of stability of the different phases present in the system:

b. Determining the range of the Carbon chemical potential

An upper bound of the carbon chemical potential is given by the condition that the chemical potentials of W and C must be lower than respective potentials in pure bulk phases of W and C. That is,

$$\mu_{\mathrm{C}} \leq \mu_{\mathrm{C}}^{\mathrm{bulk}} \text{ and } \mu_{\mathrm{W}} \leq \mu_{\mathrm{W}}^{\mathrm{bulk}} \tag{10-5}$$

Otherwise these bulk phases would start to precipitate, and WC would not be stable. Reformulated, an upper limit of the carbon chemical potential is:

$$\mu_{\mathrm{C}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} \leq 0 \tag{10-6}$$

The lower limit of μ_{C} can be obtained from the condition for chemical equilibrium

$$\mu_{\mathrm{WC}} = \mu_{\mathrm{W}} + \mu_{\mathrm{C}} \tag{10-2}$$

Solving for μ_{C}, we get

$$\mu_{\mathrm{C}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} = \mu_{\mathrm{WC}} - \mu_{\mathrm{W}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} \leq \mu_{\mathrm{WC}} - \mu_{\mathrm{W}}^{\mathrm{bulk}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} \equiv \Delta \mathrm{H}_{f,\mathrm{WC}}^{0} \tag{10-7}$$

where $\Delta \mathrm{H}_{f,\mathrm{WC}}^{0}$ is the heat of formation of WC.

Thus, we allow μ_{C} to vary in the interval given by

$$\Delta \mathrm{H}_{f,\mathrm{WC}}^{0} \leq \mu_{\mathrm{C}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} \leq 0 \tag{10-8}$$

Note that there might be other phases which are stable within the above internal. In this case the allowed interval for the carbon chemical potential may be smaller. In the W-C-Co system under study here, the interval is in reality half the size due to the occurrence of a $(\mathrm{W,Co})_6\mathrm{C}$ phase. However, in this example we will use the WC heat of formation as a lower bound.

c. Calculate the Co|WC interface energy

Now we have found that the Co/WC interface energy for our calculation is given by the expression

$$\gamma_{\mathrm{Co|WC}} = \frac{1}{A}\left(E_{\mathrm{interface}} - 12\mu_{\mathrm{WC}} + 3\mu_{\mathrm{C}} - 28\mu_{\mathrm{Co}}\right) \tag{10-4}$$

where μ_{C} is allowed to vary in the interval given by

$$\Delta \mathrm{H}_{f,\mathrm{WC}}^{0} \leq \mu_{\mathrm{C}} - \mu_{\mathrm{C}}^{\mathrm{bulk}} \leq 0 \tag{10-8}$$

The interface area A was given in the output of the MEDEA interface builder as 21.95 Å^2. We now need to calculate the energy of the bulk systems WC and Co:

Activate the WC structure window in MEDEA and perform a structural optimization in VASP, followed by a single point calculation. Use the same parameters as for the interface calculation.

From the converged run, the heat of formation of WC (`Job.out`) gives the lower bound of μ_{C}; the value is -34.29 kJ/mol.

MEDEA automatically calculates the heat of formation of WC from standard state energies of C and W. Because we are using heat of formations to express the chemical potentials,

$$\mu_{\mathrm{C}}^{\mathrm{bulk}} = \Delta H_{f,\mathrm{C}}^{0} = 0 \tag{10-9}$$

The only task remaining is a bulk calculation of Co:

Run a structural optimization and single point calculation of Co in the same way as for the interface structure. Make sure that all total energy calculations are performed with the same plane-wave cutoff.

In `Job.out` find the VASP energy of formation per empirical formula unit (Co) for Cobalt. Use this value for μ_{Co}.

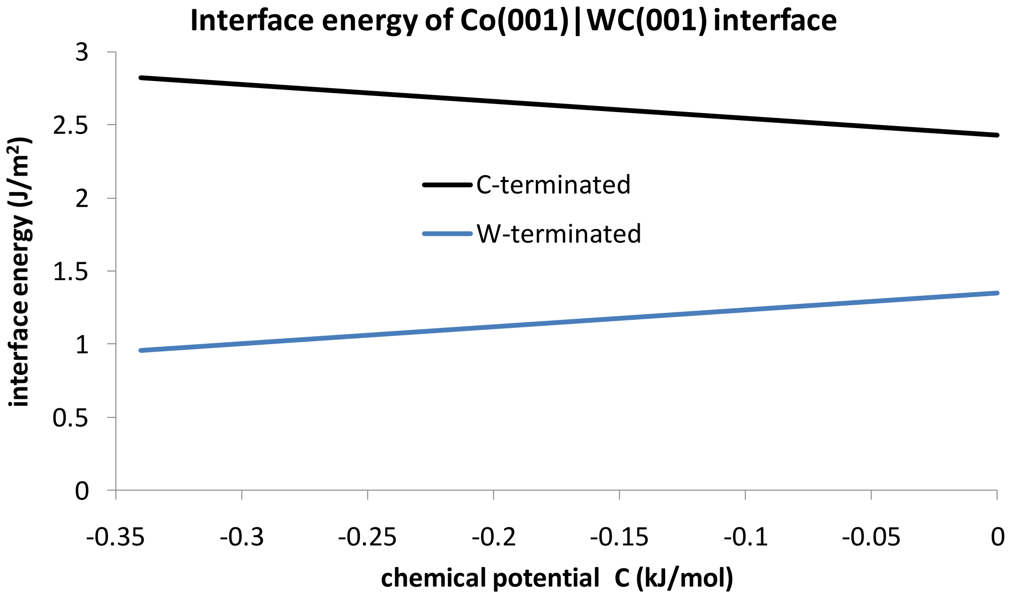
```
                    Empirical Formula         Cell
                              Co           (Co)2
                    --------------- ---------------
        VASP Energy        -663.214       -1326.427 kJ/mol
Energy of formation          22.452 ..       44.903
            PV term         -19.770         -39.540
```

Interface energy of Co/WC interface			
Interface area in supercell	A	2.195x10^{-19}	m^2
Energy (heat of formation) of interface supercell	$E_{\mathrm{interface}}$	574.90	kJ/mol
Heat of formation of WC	$\Delta\mathrm{H}_{f,\mathrm{WC}}^{0}$	-34.29	kJ/mol
Chemical potential of Co	μ_{Co}	22.45	kJ/mol
Interface energy Co|WC W-terminated	$\gamma_{\mathrm{Co\|WC}}$	0.96-1.35	J/m^2
Interface energy C-terminated WC|Co	$\gamma_{\mathrm{WC\|Co}}$	2.43-2.82	J/m^2

Plotting the interface energy as a function of the carbon chemical potential results in the below graph (W-terminated). For completeness it includes also the interface energy for the C-terminated Co|WC interface, here the expression for the interface energy becomes

$$\gamma_{\mathrm{WC|Co}} = \frac{1}{A}\left(E_{\mathrm{interface}} - 9\mu_{\mathrm{WC}} - 3\mu_{\mathrm{C}} - 28\mu_{\mathrm{Co}}\right) \tag{10-10}$$

A separate interface calculation is needed to get $E_{\text{interface}}$ for the C-terminated interface.



For the W-terminated interface, the energy increases linearly with increasing carbon chemical potential. For the C-terminated interface, the energy instead decreases with increasing carbon chemical potential. That is, interfaces with an excess of carbon in the interface become more stable when the carbon potential becomes higher. However, for all μ_C, the curve for the W-terminated interface is below the curve for the C-terminated interface. Thus, it can be concluded that the most stable Co (001)/WC (001) structure is W-terminated.

d. Reference bulk phases and strain

When building an interface structure the in-plane lattice parameters of the two phases can be adjusted by applying a weight factor (see also section II.C.8 Building Interfaces). With a full cell relaxation as outlined above **Weight of first system lattice parameters** merely represents a starting value for initializing the lattice parameters optimization:

Doing **a full relaxation**, the elastic energy of the interface structure is minimized. Therefore, in order to extract the interface energy, we compare the calculated VASP energy of the interface with separate fully relaxed bulk phases.

In doing so, we introduce a small error due to the fact that the relaxed interface and the corresponding bulk phases have differing lattice parameters.

To minimize this error, bulk calculations can be performed using the same lattice parameters as present in the interface. However, this is omitted in the present application note.

An alternative method is to fix the lattice vectors within the interface plane and consequently **optimize the structure in the direction perpendicular to the interface plane** only:

In this approach, the lattice parameters set by **Weight of first system lattice parameters** in the Interface Builder are maintained throughout the calculations. To perform a constraint optimization relaxing the structure only in the direction perpendicular to the interface plane, the interlayer distances and interface gap have to be varied manually. The recommended procedure for this is:

Starting from two bulk systems (phase 1 and phase 2), construct surfaces by selecting Miller indices to cleave the bulk in the direction of your choice (in this example we constructed a (001) WC surface and a (001) Co surface)

When building the interface, select a weight for the relative contribution of in-plane lattice parameters of both phases. For example, selecting 0.5 will create an interface where the in-plane lattice parameters of surface system 1 and surface system 2 are averaged with equal weight.

Run the interface search algorithm to determine a valid interface structure. Having selected an interface, note down the in-plane lattice parameters of the interface structure supercell

Now rebuild the two bulk phases, this time building a general cell for each bulk system: In doing so, you need to select lattice vectors and parameters matching the direction and value of the lattice parameters present in your interface system: The interface in-plane lattice parameters have to be equal to or a multiple of your new bulk lattice parameters

Next, for the bulk structures, determine the change in interlayer spacing perpendicular to what will be your interface plane: To do so you need to relax the interlayer distances by performing a series of calculations, varying distances between atomic planes parallel to the lattice planes matching the interface plane

Use these optimized bulk phases to construct a new interface where no adjustment of the in-plane lattice vectors is made (tolerance values set to zero in the Interface Builder)

- Optimize the interface gap by a series of calculations where the gap distance is varied
- Perform relaxation of the atomic positions of the interface structure

The interface energy is then calculated by comparing the energy of the interface structure with the energies of the bulk phases with corresponding strain. In this approach the elastic energy introduced by matching the two phases with lattice misfit is cancelled out to a large degree.

U. Heat of Formation of Ethyl Alcohol and Dimethyl Ether

Introduction

The molecular builder (Molecular Builder) is part of the MEDEA standard suite of building tools. This tutorial provides an overview of the Molecular Builder's basic functionality. You will learn how to

- Build simple molecules from scratch
- Build up and work with a library of molecule fragments
- Work with models of molecules in non-periodic and periodic representations
- Calculate the heat of formation of molecules

In this application note, we show how to build the isomers ethyl alcohol and di-ethyl ether and calculate their respective heats of formation.

A separate application note deals with positioning molecules on surfaces and calculating binding energies and related properties: V.V Dehydrogenation Energy of Ethyl Alcohol (Ethanol) on a Cu (111) Surface

The MolecularBuilder interface offers a range of features like coordinated drawing and translation/rotation of groups of atoms. It also allows building up fragment libraries of molecular building blocks, thus making it easy to assemble larger and more complex molecules and to position molecules with respect to e.g. a surface or an interface.

1. Building ethyl alcohol, C_2H_6O

In the MEDEA menu click **File** » **New Molecule** or alternatively press **Ctrl**-**M**

MEDEA opens a new window displaying the Molecular Builder graphical user interface.

a. Constructing the molecule

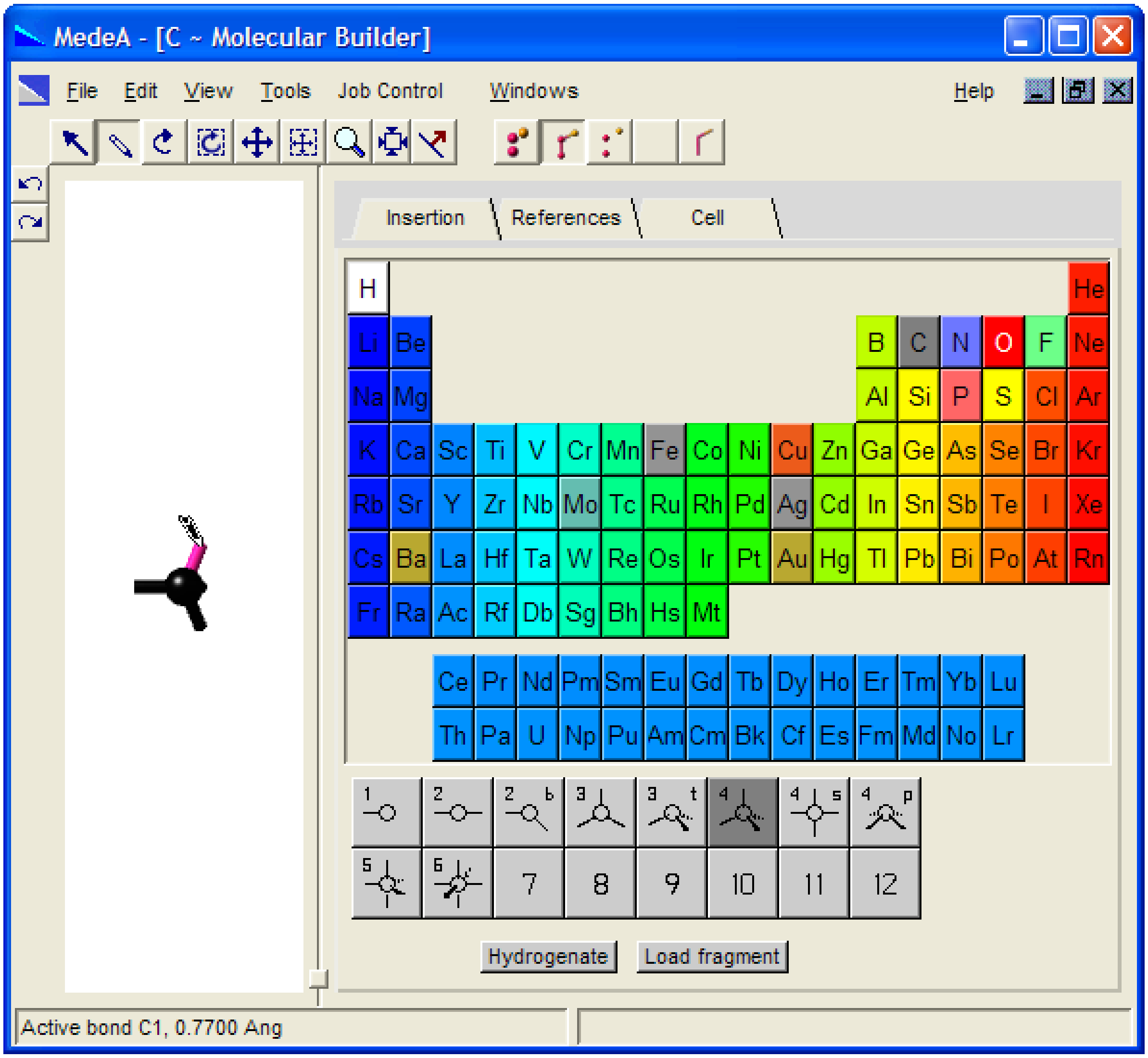
The Molecular Builder uses the concept of **active bonds**. Active bonds are used to make connections between atoms, using a default bond length given by the covalent radius of an element. For each element the Molecular Builder displays a default number of active bonds, e.g. four for Carbon and two for Oxygen.

Note that the number of active bonds (or coordination number) for a given element is not a well defined physical quantity but merely an empiric concept borrowed from chemistry (Lewis structure[6] and electron dot structure).

To construct a molecule, select an atom type from the periodic table, choose its connectivity and click on an active bond to form a connection. To build C_2H_5OH from scratch, start with Carbon.

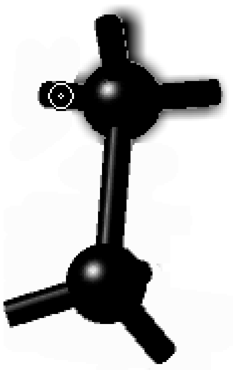
---

[6] Lewis structure: see also: http://en.wikipedia.org/wiki/Lewis_structure



Active bond C1, 0.7700 Ang

To insert Carbon atoms, select **C** from the periodic table in the Insertion panel. The default tetrahedral coordination for C is automatically highlighted in the coordination selector on the lower right. Leave this value at its default value **4**. Move the mouse cursor into the drawing

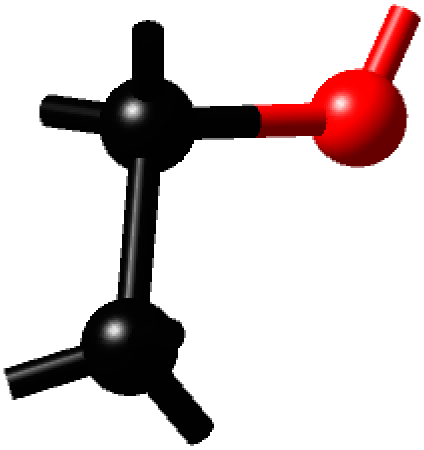


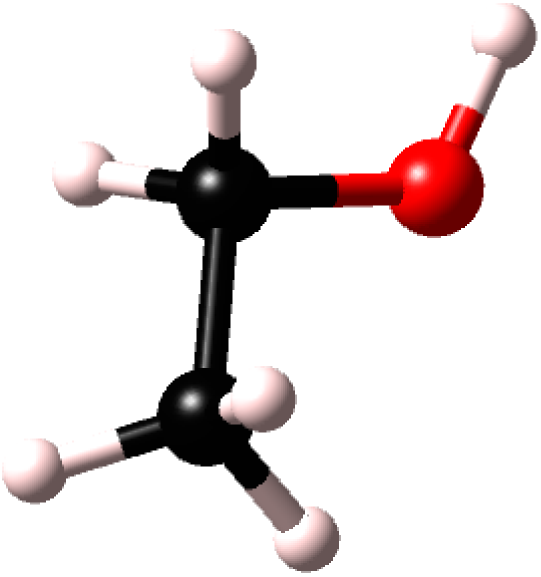
area on the left Note that the cursor shape changes to , indicating that the cursor is loaded with the selected element type

Left-click to deposit a C atom in the drawing area. Note that the cursor remains loaded. Move the mouse cursor over one of the active bonds of the C atom (active bonds turn pink when selected) and left-click one more time to add a second C atom.

While holding down the left mouse-button you can rotate the newly added atom around the bond.

To undo your last action click Ctrl-Z or the ↶ button on the left hand side of the MEDEA main window, to redo an action click the ↷ button. Next, select **O** from the periodic table. Note that when selecting O, the coordination selector changes to . Add an O atom to one of the C bonds by highlighting an active bond and left-clicking





To add hydrogen to the remaining active (dangling) bonds, select **H** and drop it atom by atom on each active bond, or simply click **Hydrogenate** in the lower right to put H atoms on all active bonds at once

To **rotate**, **zoom**, or **translate** the whole molecule, hold down the **r**,**z**,or **t** key and move your mouse cursor. To select an atom or a number of atoms, hold down the **s** key and click on the atoms(s) or hold down the **s** key, left-click-hold and draw a rectangle to select all atoms within its boundaries.

Repeated clicking on an atom in selection mode toggles the selection on and off

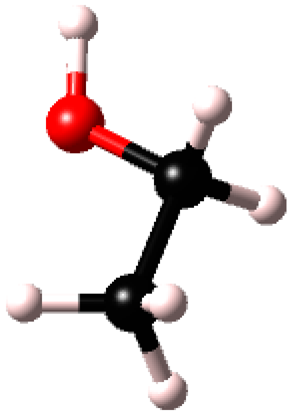
b. Creating a periodic model

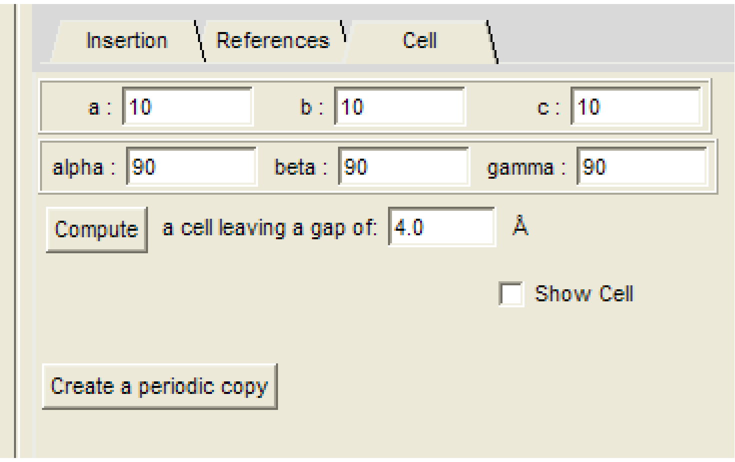
Now the next step is to create a periodic boundary box to make it a structure suitable for Vasp. Select the **Cell** panel to set size and shape of the bounding box: (a, b, c, α, β, γ). To change the amount of vacuum type in values for (a,b,c) directly, or **Compute** a cell leaving a gap of ☐ Ång.

In this example we are planning to compare the energies of two molecules. To minimize numerical errors, we should therefore work with identical box sizes

Check the button **Show Cell** to visualize the periodic cell. You can right-click the molecule and select **All**≫**Center to reference point** to center the molecule in the cell. In the field for **Bounding box cell** set box parameters (a,b,c) as (10,10,10) and select

Create a periodic copy.





a : 10 b : 10 c : 10

alpha : 90 beta : 90 gamma : 90

Compute a cell leaving a gap of: 4.0 Å

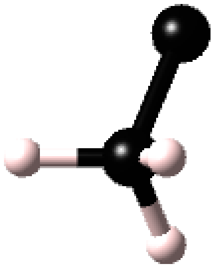
☐ Show Cell

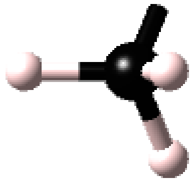
Submit a VASP job with atomic relaxation using a single k-point, real-space integration with defaults for all other settings.

c. Selecting, deleting multiple atoms, active bonds

Back in the Molecular Builder window, change to selection mode by clicking ↖ in the MEDEA panel (upper left) or by holding down the s-key. In selection mode, click atom per atom to mark as "selected" all atoms except for the two C atoms and the H atoms belonging to the CH_3. In selection mode, alternatively to selecting atoms by clicking on them, you can drag open a rectangle using your left mouse button to automatically select all atoms inside. Clicking on a selected atom toggles the selection off.

Next, right-click and use **Selection**≫ **Delete selected atoms** (Hotkey: **Del**) from the list of choices. You are left with $C\text{-}CH_3$.





Right click the single C atom and select **Atom**≫**Delete atom only** This leaves you with a methyl group CH_3, however as you will notice the remaining C atom preserves its fourth bond as an active bond (dangling bond)

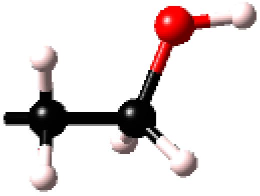
d. Saving structures to the fragment library

To save a molecule as a fragment the Molecular Builder requires an active bond to be present. You can also save a complete molecule to disc (**File**≫**Export**) or to MEDEA's internal database (**File**≫**Save**). Here, we have just created a fragment by deleting one of the C atoms and leaving a bond at the other one. To save the methyl group fragment right-click anywhere into the structure and select **Save as Fragment** from the menu. Select a descriptive name (e.g. the formula unit plus chemical name) and click OK. MEDEA saves the molecule to a temporary database.

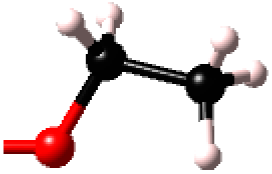
> **Note:** When saving a fragment, MEDEA saves a bitmap of the structure as-it-is-on-screen along with the structure data. By zooming in on the fragment arranging it in a well-to-look-at position before saving it to the library, you can improve the appeal and readability of the saved system.

For later use let’s create and save two more fragments, namely those of ethyl alcohol:

Replacing a H atom of the methyl group (CH_3)



Replacing the H atom of the OH group (OH)

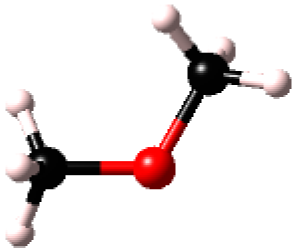


Right-click anywhere in the structure window and use **Save as Fragment** to keep it for further use in MEDEA's database.

To transfer fragments between computers, use the Insertion panel of the Molecular Builder, click **Load fragment**≫**Export library to file** to save it on disk. Library files can be imported (on a different computer).with **Import a library from a file.**

2. Building the isomeric di-methyl ether CH_3OCH_3

Next we will build the isomeric di-methyl ether. In the MEDEA file menu, select **New molecule** or type **Ctrl-M.** In the **Insertion** panel, select Oxygen with default coordination and drop one atom onto the drawing area. Click **Load fragment** in the **Insertion** panel, select the methyl group (CH_3) and click **OK**



Move the mouse cursor over each of the two active bonds on O and drop a CH_3 on each of them. Make sure the active bonds are highlighted before you left-click to drop the fragment, otherwise MEDEA will fail to make the connection O-C.

To undo an action click Ctrl-Z or the undo button in the MEDEA interface. Again select the box size (a,b,c) to be (10,10,10) as you did for ethyl alcohol and create a periodic model by selecting

Create periodic from the MEDEA **Edit** menu. Submit a VASP atomic relaxation using a single k-point, real-space integration and defaults otherwise

Results

An atomic relaxation using the VASP parameters **Normal precision**, **Real space integration**, 1 k-point, yields the following heats of formation:

molecule	heat of formation	difference
Dimethyl ether	-280.32 kJ/mol	+48.47 kJ/mol
Ethyl alcohol	-328.79 kJ/mol.	0 kJ/mol

This indicates ethyl alcohol as more stable than dimethyl ether by ~48 kJ/mol. The experimentally found value is~51 kJ/mol [7].

---

[7] Reference: NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/

V. Dehydrogenation Energy of Ethyl Alcohol (Ethanol) on a Cu (111) Surface

Introduction

The molecular builder (Molecular Builder) is part of the MEDEA standard suite of building tools. This document is the second part of a tutorial providing an overview of the Molecular Builder's basic functionality. You will learn how to

- Work with structure models in non-periodic and periodic representations
- Add molecules onto surfaces
- Translate/rotate molecules on surfaces
- Set up periodic slab models and compute adsorption energies

This application note deals with positioning molecules on surfaces. As an example we will investigate the adsorption of ethyl alcohol (ethanol) on a Cu (111) surface. In doing so we will consider two possible configurations for the adsorbed molecule: (1) adsorbed ethanol (2) dehydrogenated ethanol, i.e. an ethoxy group binding to a Cu (111) surface atom via the oxygen. Running structure relaxations using VASP we will produce a first estimate of the relative stability of these two systems.

A detailed description of the interface functionality of the molecular builder is available in section II.C.9 Molecular Builder

Note: In the present study we will perform VASP calculations for adsorbent-adsorbate systems containing ~ 40 atoms. Using lower/higher precision each of these structure optimizations may run for a couple of hours to 1-2 days, depending on the starting structure, parameters used and computing performance of your machine.

In our tests, on a parallel dual core Pentium Mobile with ~2GHz clock frequency and 2GBytes main memory the lower precision calculations took a couple of hours while the higher precision ones ran 1-2 days.

1. Creating a Cu (111) surface and positioning the molecule

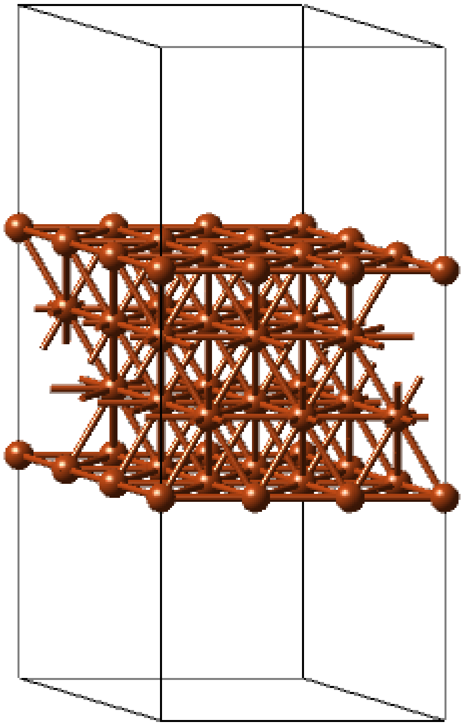
In order to place and position a molecular system on a surface you need to perform the following steps:

- Create a surface model large enough to accommodate the molecule
- Convert it to a non-periodic system
- Place and position the molecule(s)
- Convert the resulting system back to a periodic slab model

a. Creating a Cu (111) surface

Let's start by creating a simple Cu (111) surface with 3x3 atoms in the surface layer:

In the MedeA menu, click **File** ≫ **Open from disc** and select elemental Cu from the list of elements in the directory C:/MD/Structures/Elements



Invoke the surface builder (**Edit** ≫ **Build surfaces**) and create a (111) surface. In the Search window select a gap thickness of 6 Ang and click **Create**. In the preview window, use the sliders to reduce the number of Cu layers to 2. Click **Create P1** to build the surface model.

The resulting surface has only one Cu atom per layer. Even if we added only one atom as an adsorbate we had 100% coverage of the surface. Thus for our purposes we will work with a 3x3x1 supercell.

b. Building a 3x3 supercell

For the surface system, invoke the supercell builder and build a 3x3x1 supercell

The resulting structure model has 36 Cu atoms in 4 layers, 9 Cu atoms per layer.

c. Converting the surface to a non-periodic model

Next, convert the surface model to a non periodic model and add the molecules previously saved in the fragment library:

With the surface model of Cu active, click **Edit** ≫ **Create aperiodic** in the MedeA menu

In the resulting Molecular Builder window press the z-key and hold it while moving your mouse upwards on the screen. This will zoom up the image of the surface

Note that the default view of the aperiodic system is **Top**, in other words, you are looking down onto the Cu (111) surface along the z-axis.

Select **Show Cell** to view the bounding box

Select **View** ≫ **Axes** from the MedeA main menu to display (**x-red**, **y-green**, **z-blue**) axes.

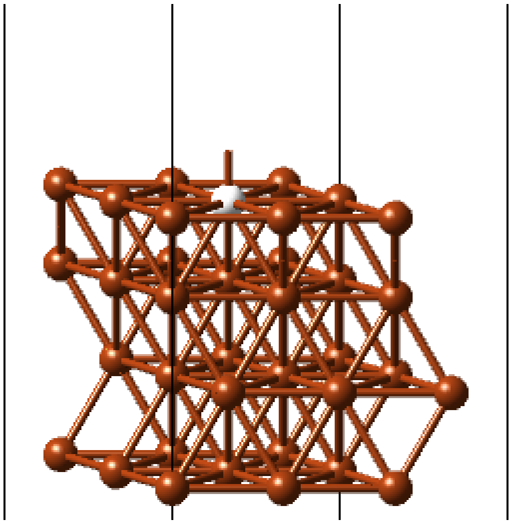
If at any point you would like to recenter the structure within the builder window, click the **Recenter** button to rearrange the cell in **Top** view.

d. Adding an active bond to the surface

Adding an active bond to one of the surface atoms creates a docking position for the adsorbate.

Right-click on one of the surface atoms and select **Add active bond**. To see which atom is a surface atom, you can check the z-coordinates by moving the mouse over an atom: the coordinates are displayed in the status line (lower left of MedeA main window)

Note that an active bond is by construction pointing towards you, i.e. it is parallel to the current view axis. To insert e.g. an active bond perpendicular to a surface, arrange to view the surface from above. To arrange the surface in “top” perspective, click the **Recenter** button



Press and hold down the r-key and repeatedly click the **up** key to rotate your structure upwards. In doing so you will notice a short bond sticking out of the surface.

e. Adding a fragment to the surface:

We will now add the ethoxy group saved as a fragment in the previous exercise, to the surface by docking its oxygen to a Cu surface atom. How to build the ethoxy group is covered in detail in section V.U Heat of Formation of Ethyl Alcohol and Dimethyl Ether

To add a molecule from the fragment library to the surface, do the following:

- In the Molecular Builder interface select the Insertion panel
- Click on **Load fragment** and select the ethyl alcohol fragment (ethoxy) having an active bond on the O atom
- Move the mouse cursor over the active Cu bond, left-click and hold down the mouse button to rotate the fragment into a convenient position above the surface

Note: The type of surface and adsorbate determine what is a good starting position for an atomic relaxation. For our ethoxy group a reasonable starting point may be a fcc hole or hcp hole position, a Cu-Cu bridge or a Cu top position.

f. Converting back to a periodic slab model

The resulting structure can be used as a starting point for an atomic relaxation. However, to submit a computation using a periodic code you need to convert the system back to a periodic cell.

In the MedeA Edit menu, select **Create periodic** to return to a periodic representation in form of a slab model

> Note: Changing the box size or shape while in the aperiodic representation will most likely destroy the periodic symmetry of your system. Therefore, when editing a periodic structure using the Molecular Builder make sure **never to change** the cell shape or size!

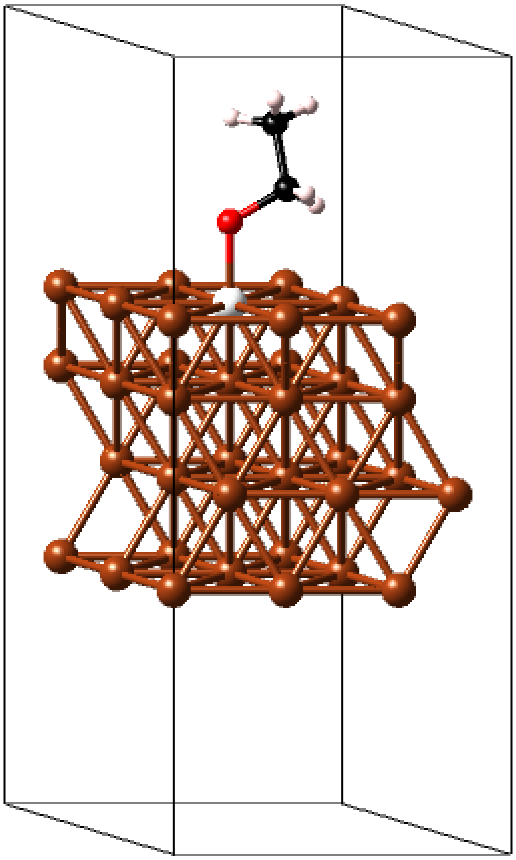
It may occur that when moving the molecule with respect to the surface, parts of the molecule end up outside the cell boundary. When creating a periodic system from such a model, the resulting 3D periodic structure will be correct but look “disrupted”. Simply keep the whole molecule within the cell to avoid this happening!

If you have enough compute power at your disposition, you are now ready to run an atomic relaxation on the system. Alternatively, you may want to continue modifying the position of the adsorbate with respect to the surface.

g. Submitting an atomic relaxation

Submit a low precision relaxation of atomic positions for the present system. Use the following parameters: Convergence for structure optimization 0.05 eV/Ang, Low precision (300 eV cutoff), Real space integration, 2x2x1 k-spacing, SCF convergence 1.0e-5, Algorithm **Fast** (Advanced panel)

h. Translating and rotating the fragment over the surface



You may want to modify the current position of the molecule with respect to the surface. You can do this by rotating and translating the adsorbate to set up a starting geometry based on your visual impression:

In doing so you should keep bond lengths close to defaults, avoid too close atoms as this may result in very large forces during the first relaxation steps, etc.

To rotate/translate a selected group of atoms you have a number of choices:

- Translate/Rotate a selection of atoms freely with respect/around the view axes. The view axes are invisible lines that define your viewing angle and distance, i.e. your perspective of the structure on the screen.
- Rotate around a bond
- Translate along a bond
- Rotate by a specific amount around a user-defined axis

If you know enough about the adsorbate position on the surface, the third method may be more accurate. If you simply want a reasonable starting geometry, the first one may suffice.

1) Rotating around view axes

Recenter the system (Press)

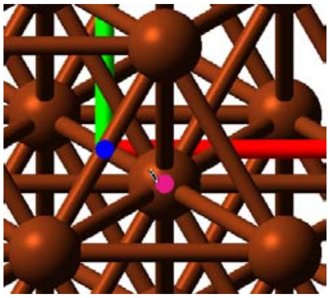
Hold down the r-key and click the up-arrow key until you see the surface and adsorbate from a side perspective (figure10). To translate **the whole** structure downwards/upwards/left/right hold down the t-key and press up-arrow/down-arrow/left/right key

Select the group of atoms you would like to rotate/translate. In selection mode you can left-click and draw a rectangle to select everything inside

Click on **Rotate Selection** ≫ **Translate selection** and next left-click and drag your mouse to actually rotate/translate the selected atoms

Note that **Translating** selected atoms will translate them in a plane perpendicular to your viewing axes, e.g. when in a Top position translation will happen in the surface plane.

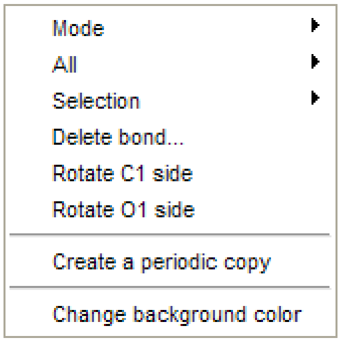
Let's imagine we want to position the ethoxy group with the O atom on a fcc hole position[8]:



Create a copy of your surface-adsorbate system. Remove the adsorbate molecule and recenter the surface. Zoom in and move the mouse cursor over sub surface atoms to see which hole has a direct sub surface atom (just check the z coordinate as you move the mouse over an atom). Right click on a subsurface atom and select **Add active bond**.

2) Translate along a bond

Change to insert mode, load the ethoxy fragment and drop it on the active bond. The ethoxy group is "inside" the Cu bulk. To move the molecule out of the bulk:



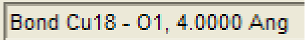
Press and hold down the **r** and left click and drag the mouse to slightly rotate the whole structure. Select both the O atom and the Cu atom bonded to it, right click and select **Selection**≫**Distance**: Set **New Distance** to 4 (all units in Ang). Make sure **Displace O1** and **Translate connected atoms** is checked. Click **OK**. Change the distance to ~4 Ang

Recenter the structure, press **r** and left-click and move the mouse to rotate the structure into a convenient position Press the **Esc** button to unselect all atoms

---

[8] A fcc hole has a Cu atom in the sub surface layer; a hcp hole has a Cu atom in the second sub surface layer.

3) Rotate around a bond

Move your mouse over the O-Cu bond until MEDEA shows a status message like  Bond Cu18 - O1, 4.0000 Ang in the lower left of the drawing area. Right-click and select **Rotate O side** from the menu. If you move over a bond and the bond information does not show up, it is likely that you still have one more atoms selected: unselect all atoms by **Esc** and try again.

The cursor changes to . You can now rotate the ethoxy group around the O-Cu bond by left-clicking and moving the mouse

Next, move your mouse over the O-C bond, select **Rotate C side** to rotate the group around the O-C bond

You may want to define rotation axes and perform rotations by precise amounts:

i. Rotating around a defined axis

You can define a vector of rotation and rotate a selection of atoms by a precise amount around the axis given by the vector. We have attached the O atom of the C_2H_5O molecule to the Cu surface. Now, let's say, in the above example we would like to rotate the CH_2-CH_3 group around the O-Cu bond by a specific amount:

- Right-click into the structure and select **Clear selection**.
- In selection mode , click on the Cu surface atom connected to the O atom to mark it as selected
- Click the **References** tab. Select **Point** - **Selection geometrical center** and click **Compute**

MEDEA takes the geometrical average of all selected points as the point of reference. Having selected only the Cu atom this yields the Cu positions as a starting point for our vector of rotation.

In selection mode, click on the O atom to mark it as selected. With both the O and Cu atom selected, right-click into the structure and choose **Selection**≫**Set as reference vector**.MEDEA chooses the vector connecting the two atoms as a reference vector. The starting point or offset is the previously selected Cu atom.

Select the rest of the alcohol molecule, right-click and choose **Selection**≫**Rotate selection.** In the dialogue, enter a rotation angle (e.g. 30°) and click **OK** to perform the rotation

MEDEA will rotate all selected atoms around the axis defined by our vector and offset. As Cu and O lie on this axis their positions do not change. The other atoms are rotated by 30.

In the same manner, you can perform a translation on a group of atoms. In this case the translation is defined by the vector you set. Note that all selected atoms will be translated by this vector, including selected surface atoms. You can multiply the vector by a factor to change its length (**Vector length**, **Multiply by**).

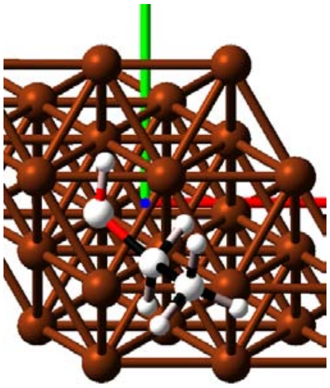
j. Constructing a second system with ethanol on Cu (111)

Next we create a copy of the present structure model and add a hydrogen atom to the active bond of the ethoxy group thus creating an ethanol molecule

With the Molecular Builder window active, select **Duplicate** from the MedeA **Edit** menu

In the new structure window right click on the O atom and select **Atom**≫**Delete atom only**.

Right click on the Cu active bond and select **Delete active bond…**.



Click on the Insertion tab on the upper right, select O and insert an oxygen atom binding it to the remaining active bond of Carbon

Click Hydrogenate to add hydrogen to the second O active bond.

Right click to select ethanol with **Molecule**≫**Select molecule**

Click on **Recenter** to go to Top view; Move the molecule such that the oxygen atom comes to sit over a hole position

2. Computing the dehydrogenation energy

The dehydrogenation energy of ethanol Cu (111) can be calculated by considering the formal reaction

$$\mathrm{Cu}_{36}^{(111)}\ \mathrm{HOC_2H_5} \ \rightarrow\ \mathrm{Cu}_{36}^{(111)}\mathrm{OC_2H_5}+\frac{1}{2}\mathrm{H_2} \tag{11-1}$$

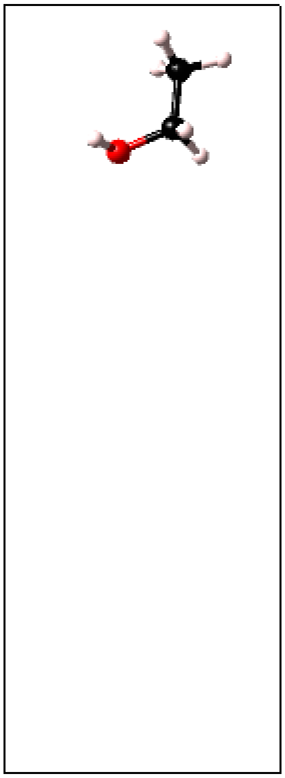
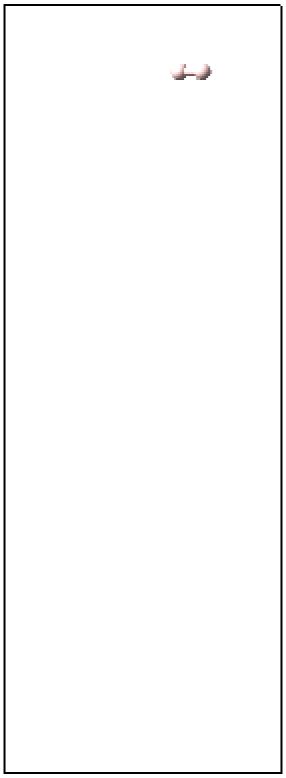
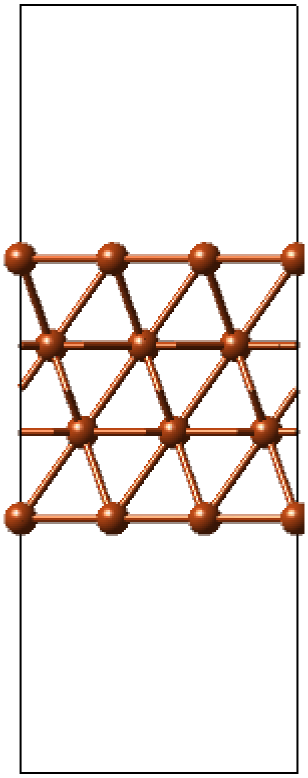
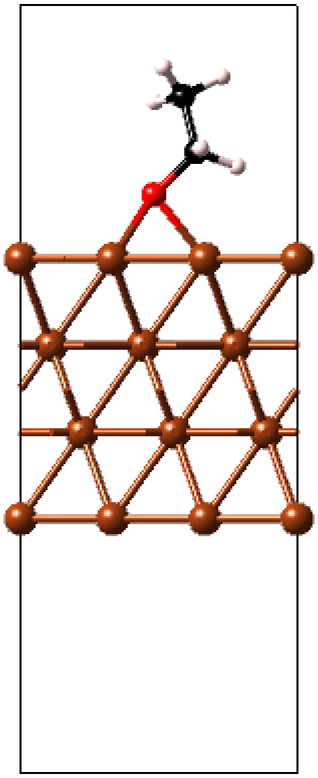
where wavy brackets around the left hand side indicate the ethanol molecule in an adsorbed state on the Cu (111) surface. We define the dehydrogenation energy to be the energy cost to rid the adsorbed ethanol molecule of an H atom hereby forming free hydrogen and a chemisorbed ethoxy group:

$$E^{\mathrm{dehydro}}=E^{F}\left(\mathrm{Cu}_{36}^{(111)}OCH_2CH_3\right)+\frac{1}{2}E^{F}(\mathrm{H_2})-E^{F}\left(\mathrm{Cu}_{36}^{(111)}+\mathrm{HOCH_2CH_3}\right) \tag{11-2}$$

E^F is the formation energy of a system given by MedeA in the `Job.out` file[9]. To compute the dehydrogenation energy via the above equation, a number of additional atomic relaxations need to be run:

---

[9] We could equally well use the VASP energies instead of the formation energies in order to calculate the binding energy. Using the formation energies reported by MedeA corresponds to using a different offset for the total energy calculations.

Ethanol molecule	H_2 molecule	Cu(111) surface	Absorbed ethoxy group on Cu (111)
			

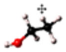
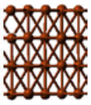
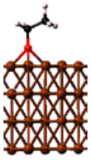
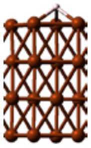
Ideally, to minimize numerical errors this is done using the same cell as was used for the adsorbate-surface system. In order to produce reliable results, convergence studies should be performed for the plane wave cutoff and - for the case of surface systems – the in-plane k-mesh spacing. For the purpose of this example study, we have used the below two sets of computational parameters:

Low precision: Precision=Low, cutoff=300eV, Real space integration, k-spacing=0.5 for slab models (i.e. the surface models); 1 single k-point for molecules, Algorithm=Fast

Higher precision: Precision=Normal, cutoff=400eV, Real space integration, k-spacing=0.5 for slab models; 1 single k-point for molecules, Algorithm=Fast.

Results and discussion

The formation energies and adsorption energies calculated this way are listed in table 1. All energies are given for both low precision and higher precision calculations (in brackets).

#	System	Picture	Energy of formation (kJ/mol)	ΔE (kJ/mol) based on Low (Normal) Precision
1	½ H_2		2.7 (1.01)	
2	$HOCH_2$-CH_3		-331.90 (-330.43)	
3	Cu_{36}(111)		676.9 (749.699)	
4	Cu_{36}(111)-OCH_2CH_3		359.9 (426.87)	Formation of chemisorbed ethoxy group and H_2:#4 + ½ #1 - #3 -#2 16.2 (8.1)
5	Cu_{36}(111) + $HOCH_2CH_3$		349.67 (409.89)	Ethanol adsorption: (#5 - #3 - #2) 4.67 (-9.41)
6	Cu_{36}(111)-H		672.79 (744.66)	H adsorption: #6 - #3 -½#1) -5.45 (-6.35)

a. Adsorption energy of ethanol

The adsorption of ethanol on Cu (111) is calculated by taking the difference between the adsorbed system (#5) and the free Cu (111) surface (#3) and free ethanol (#2).

While the low precision calculation produces an adsorption energy which is slightly positive, the more precise calculation indicates a negative value, i.e. an exothermic reaction. From these data we can conclude that ethanol is likely to be only weakly adsorbed on Cu (111).

b. Dehydrogenation energy

The energies of the chemisorbed ethoxy group and hydrogen gas are higher by ~ 13 (17) kJ/mol with respect to Cu adsorbed ethanol.

From the above data and equation (1) the dehydrogenation energy is calculated by doing the following subtraction: $E^{dehydro} = E^{F}$ (#4 + ½ #1 - #5) = 17.5 kJ/mol.

c. Adsorption of H on Cu (111)

Alternatively to forming the free hydrogen gas, one can formulate a dehydrogenation reaction were the hydrogen atom is also adsorbed on Cu (111) surface. We have computed the adsorption energy of hydrogen on a hole position in the above table. The value of -5.45 kJ/mol indicates that the dehydrogenation energy of ethanol will be further lowered, if both H and the ethoxy group are assumed to bind to the surface.

Comment

Please note, that the above study is meant as a tutorial on building and handling molecules on surfaces. It therefore lacks completeness as to the investigation of different adsorption sites for ethanol and hydrogen (top, bridge, fcc hole, hcp hole), alternative Cu surfaces directions and systematic convergence tests with respect to k-mesh and plane wave cutoff.

W. Chromium: Structure and Elastic Properties

Introduction

In Chromium and Chromium alloys antiferromagnetic ordering and spin-density-waves (SDW) states are at the origin of many physical properties like thermal expansion, elastic constants, and electrical resistivity among others.[107]

This document summarizes structural and elastic properties of Chromium, computed from first-principles using the MEDEA module MT in combination with VASP.

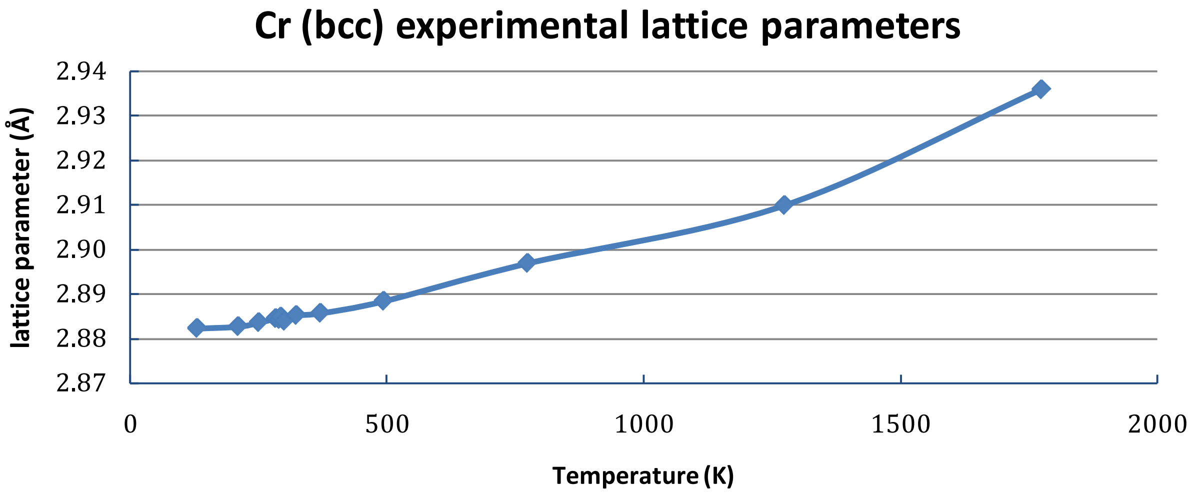
The MEDEA MT module provides an algorithm for performing fully automated stress-strain analysis for any type of crystal structure. In short, MT does the following:

- Analyze symmetry of input structure
- Apply strains required to calculate elastic coefficients for this symmetry
- Invoke VASP to compute the stress tensor for each strained systems
- Run a least square fit on stress tensor data to predict elastic coefficients
- Derive bulk modulus and other related thermo-mechanical data

In the following we discuss the experimental and computed lattice parameters of bcc Cr. We then summarize results for computed elastic coefficients and bulk moduli followed by a short discussion and conclusion.

1. Experimental structure:

For bcc Cr, measured lattice parameter vary mostly between **2.872 Å** and **2.89 Å** with some high temperature measurements yielding values up to 2.935 Å.[108]



Experimental structure data is usually measured at varying temperatures and pressures. Further, samples vary in their composition and magnetization thus yielding a range of data points rather than an absolute value for lattice parameters. The data from ICSD.44731 are plotted above –more references are in the ICSD database.

The most common representation of antiferromagnetic (AF) Cr has alternating layers of up and down directed spins with Pm-3m symmetry. In our calculations, for comparison, we can "turn off" magnetism and consider nonmagnetic (NM) Cr with *Im-3m* system.

Computational parameters

All present calculations were performed with MEDEA-MT-VASP using version 4.6.31 of VASP. The following computational settings, parameters and computed properties of relevance for both VASP and MT. (Unlisted parameters are at their default values.)

Structure

Chromium: *Pm-3m* (bcc), magnetic (AF) and non-magnetic

Structure optimization: **Conjugate Gradient** with **☑ Relax atomic positions**, **☑ Relax cell shape**, **☑ Relax cell volume**

VASP:

Precision: **S500** (cutoff=500eV, accurate), **k-mesh**: 0.2 odd, Projection: **Reciprocal space**, Potential: **GGA-PBE**-**PAW** *Cr_pv*, **Electronic SCF**: 1d-7, **Geometry convergence**: 0.001 eV/Å, Integration: **Tetrahedron /Blöchl correction**, **Extrafine augmentation grid** for forces

Results: Lattice parameter, Formation energy, Magnetic moments

MT:

Single strain=0.5%, **Relax internal degrees of freed**

Results: Elastic constants, Bulk/shear module

a. Results - lattice parameters

In order to clarify the role of magnetism for lattice parameters and elastic properties of Chromium, we perform cell optimizations for both AF and NM structures.

Bcc-Structure	Formation energy (kJ/mol)	Magnetic moment (μB)	Lattice parameter (Å)
Antiferromagnetic AF	0.0	±1.084	2.872
Paramagnetic NM	1.33	0	2.851
Experimental (77K)			2.879

The AF structure's formation energy is 1.33 kJ/mol lower than the paramagnetic phase and is thus more stable.

The AF magnetic moment is calculated to be ±1.084 μB, the AF ground state lattice parameter is 2.8716 Å compared to 2.8511 Å for the NM structure. In other words, the formation of a magnetic moment stabilizes the structure and increases the lattice parameter by approximately 1%.

We note that the computed AF lattice parameter lies closer to the experimental value than the one calculated non-magnetically. Considering thermal expansion of the experimental structures, a lower computed value within 0.5% can be considered an excellent result.

b. Results - Elastic constants

For bcc Chromium, the independent elastic constants are C_{11}, C_{12} and C_{44}.

2. Magnetic calculation

For AF Cr we find C_{11} = 428, C_{12} = 52 and C_{44} = 96 (all in GPa). The computed C_{11} is ~10% larger than the experimental value, which can be explained by thermal expansion. C_{44} is ~7% below the experimental value and C_{12} is more than 50% off!

a. Sensitivity to computational parameters

Testing for sensitivity with respect to k-mesh and plane wave cutoff brings about only minor changes to the elastic constants.

b. Sensitivity to lattice parameter

In order to test the sensitivity to the lattice parameter we repeat the calculation using the experimental lattice parameter 2.8792Å.

We find a significant drop in C_{11} and a smaller drop in C_{44}, both towards the measured values. C_{12} however decreases further away from the experimental value. In addition we note that the magnetic moment increases by ~10% as the structure expands!

3. Non-magnetic calculations

Next we run a NM calculation using the magnetic lattice parameter a=2.8716Å.

We find a ~10% increase in both C_{11} and C_{44} with respect to the AF calculation (C_{44} matches perfectly with the experimental value!) and a huge increase in C_{12} from former 51.5 GPa to 124.9 GPa.

a. Sensitivity to lattice parameter

Running a NM calculation using the experimental lattice parameter, we find a somewhat smaller increase with respect to the AF calculation except for C_{12} that is now 116.5 GPa.

Structure	Lattice parameter (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	Bulk module (GPa)	Magnetic moment (μB)
AF	2.8716	428.10 ±4.52	51.50 ±4.52	96.20 ±6.39	177.03	±1.083
NM	**2.8716**	460.60 ±2.92	124.90 ±2.92	103.80 ±4.12	236.80	0
AF	**2.8792**	412.90 ±4.22	43.80 ±4.22	94.20 ±5.97	166.83	±1.136
NM	2.8792	445.60 ±3.02	116.50 ±3.02	101.20 ±4.27	226.20	0
Experiment (77K)	2.8792	391	90	103.2	191	

Discussion and Conclusion:

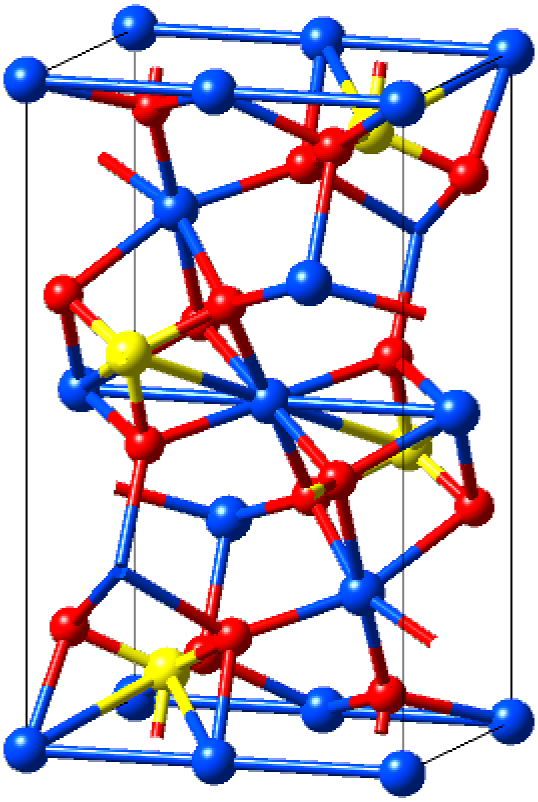
For C_{11} the deviation between experimental and computed elastic coefficients can be explained in terms of thermal expansion.

The computed shear constant C_{44} is in overall good agreement with experiment, where the NM calculation yields results slightly closer to the value measured at 77K.

C_{12} however is very sensitive to the lattice parameter and type of calculation, i.e. NM or AF. Experimentally Chromium is known to show an anomaly for C_{12} at around 120K, attributed to a transition between two states of different anti-ferromagnetic ordering.[109] The sensitivity of our results for C_{12} to the type of calculation, namely antiferromagnetic or nonmagnetic, seems to point in a similar direction.

X. MEDEA-MT in Depth: Forsterite Mg_2SiO_4

Introduction



MEDEA's-MT-Elastic Properties[55; 56] (hereafter "**MT**") automates the calculation of elastic properties from first-principles.

For a given input system, MT applies symmetry–relevant strains and computes the resulting stress tensor for each deformed structure. The elastic properties are derived by a multi dimensional least-square fit of the strain-stress data.

The present document aims to give a detailed summary of MT's text output (Job.out) using the Forsterite Mg_2SiO_4 (Pearson. 1406391) as an example.

Results in detail

The first section of Job.out consists of

- Title section
- Status line
- Type of calculation (here "Elastic properties")
- Details on how many independent "first principle" steps are needed to complete the calculation
- Details on each computational step

```
Job.out output for 2:
(Mg2SiO4)4 (Pnma) MT 0.01eV/A, Acc520, RSp, km=577, xfG

Status: finished

Opening the database
Elastic properties calculation using a strain of 0.005

Need to run a total of 10 calculations, 1 for the unstrained system
and 9 strained systems for each of the 1 strain levels.

The atom positions will be relaxed in structures where the atoms are not fixed by
symmetry, i.e. where the number of degrees of freedom (DOF) is greater than zero.
The convergence criterion is 0.01 eV/Ang.
```

MT proceeds to list space groups and degrees of freedom (DOF) for each strained system followed a representation of the elastic constant matrix:

```
         Strain          Spacegroup      DOF
        -----------    ----------------- ---
        unstrained:    Pnma              11

                 plus for each strain

              +e1:     Pnma              11
              -e1:     Pnma              11
              +e2:     Pnma              11
              -e2:     Pnma              11
              +e3:     Pnma              11
              -e3:     Pnma              11
              +e4:     P2_1/c            18
              +e5:     P2_1/m            22
              +e6:     P2_1/c            18
Symbolic elastic constant matrix:

         C11 C12 C13   0   0   0
         C12 C22 C23   0   0   0
         C13 C23 C33   0   0   0
           0   0   0 C44   0   0
           0   0   0   0 C55   0
           0   0   0   0   0 C66
```

The next section summarizes VASP computational parameters. VASP (Vienna Ab-Initio Simulation Package) is MEDEA's main first-principles code. VASP computes the total energy of a given input crystal lattice and the analytic derivative of the total energy with respect to changes of the lattice parameters a,b,c,α,β,γ (stress tensor) from first principles.

Vasp parameters

VASP uses a number of computational parameters relevant to speed of execution and precision of a given calculation. Key parameters are:

- The precision of the basis set, also called ***plane wave cutoff***
- The convergence criterion for convergence of the electronic charge (***electronic iteration convergence***)
- The *k-mesh*, or k-point mesh: An internally used integration mesh
- The type of integration algorithm
- Convergence criterion for geometry optimizations (***ionic relaxations***)
- The type of potential used to describe the core electronic states (here ***PAW***) and the level of density functional theory used (here ***GGA-PBE***)

```
VASP parameters
===============

This is a non-magnetic calculation using 'accurate' precision and an increased planewave
cutoff energy of 520.000 eV (for cell optimizations).

The electronic iterations convergence is 1.00E-006 eV using the Normal (blocked Davidson)
algorithm and real space projection operators.
```

```
The requested k-spacing is 0.2 per Angstrom, which leads to a 5x7x7 mesh.
This corresponds to actual k-spacings of 0.122 x 0.149 x 0.187 per Angstrom.
The k-mesh is forced to have an odd number of points in each direction.

Using the linear-tetrahedron method with Bloechl corrections to the energy.

Other non-default parameters:

       Extrafine augmentation grid for accurate forces is TRUE
       Convergence criterion for ionic relaxations is 0.01 eV/Ang
------------------------------------------------------------------------
Using GGA-PBE / PAW potentials:
       O
       Mg
       Si
Results for initial structural minimization
------------------------------------------------------------------------
```

Results for the initial (unstrained) system:

MEDEA uses the electronic energy calculated by VASP to produce an estimate of the heat of formation of the compound in question (here Mg_2SiO_4). This is done by comparing the computed energy to a database of energies calculated for the elements in their standard state. In the present example these are hcp Magnesium (P6_3/mmc), molecular Oxygen (½ O_2) and Silicon (Fd-3m).

Note that these are only the electronic contributions to the heat of formation, i.e. zero-point contributions and contributions from lattice vibration are not included. For heavier elements (small zero-point energy) and lower temperatures this is a good first approximation.

```
There are 48 symmetry-unique k-points
The plane wave cutoff is 520.00 eV

   VASP energy:    -192.795419 eV for Mg8Si4O16

Electronic contributions:
                          Empirical Formula          Cell
                               Mg2SiO4      (Mg2SiO4)4
                          --------------- ---------------
             VASP Energy        -4650.481      -18601.926 kJ/mol
      Energy of formation       -1927.564       -7710.256
                  PV term          -0.403          -1.612

This is the electronic part of the formation energy with respect to the elements in their
standard state. It is obtained from the total energy (above) and tabulated VASP energies
for the elements in their standard state.

See the documentation for more details.
   Details for Mg2SiO4:
                                       VASP energy (Etot):    -4650.48 kJ/mol
       Standard state energy of 2.00 atoms of Mg  2.00 * -148.64:  -  -297.28
       Standard state energy of 4.00 atoms of  O  4.00 * -475.56:  - -1902.23
       Standard state energy of 1.00 atoms of Si  1.00 * -523.41:  -  -523.41
                                                                  ----------
                                 Energy of formation (Ef):    -1927.56 kJ/mol
```

Structural parameters, pressure and stress tensor for the initial or unstrained system:

In the present example the structure was relaxed before starting the MT calculation. Therefore the pressure and stress tensor elements are rather small (9-40 MPa). These values provide an idea of how far the structure is from perfect equilibrium given that we are working with a finite basis set and that we are using a convergence criterion to stop the structure relaxation after a “reasonable” amount of steps. In the present solid, the above pressure/stress values correspond to changes of the lattice parameters smaller than 0.001 Ang.

```
Cell parameters:
 Parameter    Value
---------- ------------
         a    10.292894
         b     6.029448
         c     4.791239
     alpha    90.000000
      beta    90.000000
     gamma    90.000000

      Density:     3.143 Mg/m^3

     Pressure:    -9.000 MPa
            =    -90.000 bar
       Stress:    29.000    37.000   -38.000     0.000     0.000     0.000 MPa
            =    290.000   370.000  -380.000     0.000     0.000     0.000 bar

The pressure and stress include only electronic terms, i.e. the vibrational,temperature
and other terms are not included here.

Fractional Coordinates:
       Atom          Initial Coordinates            Final Coordinates
       -----      -------- -------- --------      -------- -------- --------
       O1           0.3370   0.0324   0.2232        0.3370   0.0324   0.2232
       O2           0.0535   0.2500   0.2773        0.0535   0.2500   0.2773
       Mg1          0.2228   0.2500   0.5083        0.2228   0.2500   0.5083
       Si           0.4063   0.2500   0.0738        0.4063   0.2500   0.0738
       O3           0.4084   0.2500   0.7331        0.4084   0.2500   0.7331
       Mg2          0.0000   0.0000   0.0000        0.0000   0.0000   0.0000
------------------------------------------------------------------------
```

Strain-stress analysis.

For each deformation $\boldsymbol{e}_i$ the resulting stress is calculated and listed together with the stress value of the unstrained system and the change between unstrained and strained system. Based on a least square fit residual strains and thereby new or “improved” lattice parameters are predicted. Note that the changes in the lattice parameters (Delta) are small. This indicates that the initial system had well relaxed lattice parameters.

```
                             --------- Stress (MPa) ---------
      Strain    Amount       Unstrained  Strained    Change
     ---------- ------       ---------- ---------- ----------
     unstrained
            +e1 0.500%            29        931        902
            -e1 0.500%            29       -963       -992
            +e2 0.500%            37       1136       1099
            -e2 0.500%            37      -1078      -1115
            +e3 0.500%           -38       1470       1508
            -e3 0.500%           -38      -1580      -1542
            +e4 0.500%             0        385        385
            +e5 0.500%             0        365        365
            +e6 0.500%             0        329        329
Results for strains 0.005:

Least squares converged in 1 iterations to a residual of 2.18%

Residual strain:
            Residual    Original               Predicted
     Param   Strain       Value      Delta        Value
     ----- ---------- ----------- ----------- -----------
         a  -0.000003   10.292894    0.000027   10.292921
         b   0.000247    6.029448   -0.001489    6.027960
         c  -0.000184    4.791239    0.000884    4.792122
```

Elastic constants

Next, the elastic constants are printed, together with a delta value for the errors stemming from the least square fit. In the present example we applied only one strain (0.5%). Using more than one strain can reduce the error of the least square fit.

```
Elastic constants (GPa):
                Least-sq
        ---------------
     C11  189.40 ± 2.89
     C12   69.20 ± 2.04
     C13   60.50 ± 2.04
     C22  221.40 ± 2.89
     C23   65.35 ± 2.04
     C33  305.00 ± 2.89
     C44   77.00 ± 4.09
     C55   73.00 ± 4.09
     C66   65.80 ± 4.09
The errors are from the least-squares fit and only give the numerical uncertainty.
```

Elastic constants and compliance matrices

In addition MT reports the elastic constant matrix and elastic compliance matrix

```
Elastic constant matrix (GPa):
     |     1         2         3         4         5         6
-----|------------------------------------------------------------
   1 |   189.40     69.20     60.50      0.00      0.00      0.00
   2 |    69.20    221.40     65.35      0.00      0.00      0.00
   3 |    60.50     65.35    305.00      0.00      0.00      0.00
   4 |     0.00      0.00      0.00     77.00      0.00      0.00
   5 |     0.00      0.00      0.00      0.00     73.00      0.00
   6 |     0.00      0.00      0.00      0.00      0.00     65.80
Elastic compliance matrix (1/GPa) (x 1000):

     |     1         2         3         4         5         6
-----|------------------------------------------------------------
   1 |   6.1671   -1.6723   -0.8650    0.0000    0.0000    0.0000
   2 |  -1.6723    5.2751   -0.7985    0.0000    0.0000    0.0000
   3 |  -0.8650   -0.7985    3.6214    0.0000    0.0000    0.0000
   4 |   0.0000    0.0000    0.0000   12.9870    0.0000    0.0000
   5 |   0.0000    0.0000    0.0000    0.0000   13.6986    0.0000
   6 |   0.0000    0.0000    0.0000    0.0000    0.0000   15.1976
```

Eigenvalues and moduli

Eigenvalues and eigenvectors of the elastic constant matrix, followed by Bulk, Shear, Young's and Longitudinal moduli, as well as the velocity of sound estimation:

```
The following are eigenvalues and corresponding eigenvectors of the elastic constant
matrix, including pressure terms. Negative eigenvalues indicate instability.
See G VSin'ko and N A Smirnov, J. Phys.: Condens. Matter 14 (2002) 6989-7005.

                                  Eigenvector

Eigenvalue           exx      eyy      ezz      eyz      exz      exy
----------         -------- -------- -------- -------- -------- --------
    134.01           0.8033  -0.5928  -0.0576   0.0000   0.0000   0.0000
    201.06           0.4229   0.6358  -0.6457   0.0000   0.0000   0.0000
    380.76           0.4194   0.4943   0.7614   0.0000   0.0000   0.0000
    308.04           0.0000   0.0000   0.0000   1.0000   0.0000   0.0000
    292.04           0.0000   0.0000   0.0000   0.0000   1.0000   0.0000
    263.24           0.0000   0.0000   0.0000   0.0000   0.0000   1.0000

   Modulus      Voigt      Reuss      Hill

------------ --------- --------- ---------
        Bulk    122.88    119.16    121.02 GPa
       Shear     77.88     75.28     76.58
     Young's    192.88    186.56    189.72
Longitudinal                        223.13

Velocity of sound

       Calculated from Hill moduli:
         transverse waves:     4936 m/s
       longitudinal waves:     8426 m/s
                     mean:     5316 m/s
```

Thermodynamic properties based on Debye theory

The last section of Job.out gives a number of thermodynamic properties calculated based on Debye theory where a fixed Grüneisen parameter of 2 was used. As mentioned in the output these data are derived from an approximation to the full spectrum of lattice, therefore the data represent a mere first estimate of thermodynamic properties at lower temperatures. An analysis of the full spectrum of lattice vibrations including high frequency PHONON contributions can be performed using MEDEA-PHONON.

All thermodynamic expressions used are described in the output below.

```
Debye temperature: 575.2 K

Thermodynamic Properties and Coefficient of Linear Expansion for empirical formula Cr

The following results are obtained from the Debye model.
Definitions:
      Cv            : vibrational heat capacity at constant volume
E_vib(T)=E(T)-E(0)  : the change in vibrational internal energy from 0 K
                      E(0) is the zero point energy (ZPE)
      S(T)          : the vibrational entropy at temperature T
   -(A(T)-E(0))     : the change in the vibrational Helmholtz free energy from 0 K
      E(T)          : the electronic plus vibrational energy of formation, so this
                      term is E_elec + ZPE + E_vib(T)
      A(T)          : the electronic plus vibrational Helmholtz free energy,
                      E(T) - T.S(T)
     alpha          : the thermal coefficient of linear expansion (x 10^6)

Note that the electronic energy, which is part of the enthalpy and free energies, is
referenced to the elements in their standard state.

Finally, these results are appropriate for the solid, crystalline material below its
melting point. Since the melting point of your compound is unknown (to us), the following
table extends to high temperatures, probably well above the melting point of your
compound. The results near and above the melting point are not physical, but the table
extends to those temperatures for e.g. high-melting point oxides.

Electronic energy of formation =     0.04 kJ/mol (referenced to elements in the standard
state)

                       PV term =    -9.70 kJ/mol
             Zero-point energy =     5.38 kJ/mol
```

Values of thermodynamic functions

The last part of the output lists thermodynamic functions (partial listing below), followed by timing data for the MT job.

```
   T        Cv       E(T)-E(0)      S(T)   -(A(T)-E(0))    E(T)         A(T)       alpha
   K     J/K/mol      kJ/mol      J/K/mol     kJ/mol      kJ/mol       kJ/mol      x 10^6
 -----  ----------- ----------- ----------- ----------- ----------- ----------- ----------
     1      0.0000      0.0000      0.0000      0.0000      5.4243      5.4243     0.0000
     2      0.0001      0.0000      0.0000      0.0000      5.4243      5.4243     0.0000
     3      0.0003      0.0000      0.0002      0.0000      5.4243      5.4243     0.0001
     4      0.0007      0.0000      0.0004      0.0000      5.4243      5.4243     0.0002
     5      0.0013      0.0000      0.0007      0.0000      5.4243      5.4243     0.0004
    10      0.0102      0.0000      0.0060      0.0000      5.4243      5.4242     0.0029
    15      0.0345      0.0001      0.0201      0.0002      5.4244      5.4241     0.0097
    20      0.0817      0.0004      0.0477      0.0005      5.4247      5.4237     0.0229
    30      0.2757      0.0021      0.1608      0.0028      5.4263      5.4215     0.0773
    40      0.6528      0.0065      0.3810      0.0087      5.4308      5.4156     0.1829
    50      1.2640      0.0159      0.7397      0.0211      5.4402      5.4032     0.3542
    60      2.1283      0.0327      1.2555      0.0427      5.4569      5.3816     0.5964
    70      3.2186      0.0592      1.9258      0.0756      5.4835      5.3487     0.9020
    80      4.4733      0.0976      2.7297      0.1208      5.5218      5.3035     1.2536
    90      5.8193      0.1490      3.6372      0.1783      5.5733      5.2459     1.6308
   100      7.1908      0.2141      4.6168      0.2476      5.6383      5.1766     2.0152
   125     10.4379      0.4353      7.2129      0.4664      5.8595      4.9579     2.9251
   150     13.1718      0.7316      9.8126      0.7403      6.1558      4.6839     3.6913
   175     15.3475      1.0892     12.2895      1.0615      6.5134      4.3628     4.3010
   200     17.0467      1.4950     14.6039      1.4258      6.9192      3.9985     4.7772
   225     18.3719      1.9384     16.7531      1.8311      7.3627      3.5932     5.1486
   250     19.4123      2.4112     18.7484      2.2759      7.8355      3.1484     5.4401
   273     20.1778      2.8668     20.4610      2.7191      8.2911      2.7052     5.6546
   275     20.2372      2.9072     20.6047      2.7591      8.3315      2.6652     5.6713
   298     20.8508      3.3800     22.2031      3.2366      8.8042      2.1877     5.8432
   300     20.8986      3.4217     22.3375      3.2795      8.8460      2.1447     5.8566
   350     21.8747      4.4927     25.4858      4.4274      9.9169      0.9969     6.1302
   400     22.5434      5.6041     28.2846      5.7098     11.0284     -0.2855     6.3176
   450     23.0189      6.7438     30.8020      7.1171     12.1681     -1.6928     6.4508
   500     23.3678      7.9039     33.0887      8.6405     13.3282     -3.2162     6.5486
   550     23.6309      9.0792     35.1832     10.2716     14.5034     -4.8473     6.6223
   600     23.8338     10.2660     37.1153     12.0032     15.6902     -6.5789     6.6792
   650     23.9935     11.4618     38.9082     13.8285     16.8861     -8.4043     6.7239
   700     24.1213     12.6648     40.5808     15.7417     18.0891    -10.3175     6.7598
   750     24.2250     13.8735     42.1481     17.7375     19.2978    -12.3132     6.7888
   800     24.3105     15.0870     43.6226     19.8111     20.5113    -14.3868     6.8128
   850     24.3816     16.3044     45.0147     21.9581     21.7286    -16.5339     6.8327
   900     24.4414     17.5250     46.3331     24.1748     22.9492    -18.7506     6.8495
   950     24.4922     18.7483     47.5853     26.4577     24.1726    -21.0334     6.8637
  1000     24.5357     19.9741     48.7775     28.8035     25.3983    -23.3792     6.8759
  1050     24.5732     21.2018     49.9154     31.2093     26.6261    -25.7850     6.8864
  1100     24.6058     22.4313     51.0035     33.6725     27.8556    -28.2483     6.8955
  1150     24.6343     23.6623     52.0461     36.1907     29.0866    -30.7665     6.9035
  1200     24.6593     24.8947     53.0469     38.7616     30.3189    -33.3373     6.9105
  1250     24.6814     26.1282     54.0090     41.3831     31.5525    -35.9588     6.9167
  1300     24.7010     27.3628     54.9354     44.0533     32.7870    -38.6290     6.9222
  1350     24.7186     28.5983     55.8286     46.7703     34.0225    -41.3461     6.9271
```

```
  1400   24.7343   29.8346   56.6909    49.5327   35.2589   -44.1084      6.9315
  1450   24.7484   31.0717   57.5244    52.3387   36.4959   -46.9144      6.9355
  1500   24.7611   32.3094   58.3309    55.1869   37.7337   -49.7627      6.9391
  1550   24.7726   33.5478   59.1121    58.0760   38.9720   -52.6518      6.9423
  1600   24.7831   34.7867   59.8696    61.0048   40.2109   -55.5805      6.9452
  1650   24.7926   36.0261   60.6048    63.9719   41.4503   -58.5476      6.9479
  1700   24.8013   37.2659   61.3189    66.9763   42.6902   -61.5520      6.9503
  1750   24.8093   38.5062   62.0132    70.0169   43.9304   -64.5926      6.9526
  1800   24.8166   39.7468   62.6886    73.0927   45.1711   -67.6684      6.9546
  1850   24.8234   40.9878   63.3462    76.2027   46.4121   -70.7784      6.9565
  1900   24.8296   42.2292   63.9869    79.3460   47.6534   -73.9218      6.9583
  1950   24.8353   43.4708   64.6116    82.5219   48.8950   -77.0976      6.9599
  2000   24.8407   44.7127   65.2210    85.7294   50.1369   -80.3051      6.9614
  2050   24.8456   45.9548   65.8159    88.9678   51.3791   -83.5435      6.9627
  2100   24.8502   47.1972   66.3969    92.2363   52.6215   -86.8120      6.9640
  2150   24.8545   48.4399   66.9647    95.5342   53.8641   -90.1100      6.9652
  2200   24.8585   49.6827   67.5198    98.8610   55.1069   -93.4367      6.9664
  2250   24.8622   50.9257   68.0629   102.2158   56.3500   -96.7916      6.9674
  2300   24.8657   52.1689   68.5944   105.5982   57.5932  -100.1739      6.9684
  2350   24.8690   53.4123   69.1148   109.0075   58.8365  -103.5832      6.9693
  2400   24.8720   54.6558   69.6245   112.4431   60.0801  -107.0188      6.9702
  2450   24.8749   55.8995   70.1241   115.9045   61.3237  -110.4803      6.9710
  2500   24.8776   57.1433   70.6138   119.3913   62.5675  -113.9670      6.9717
  2550   24.8802   58.3872   71.0941   122.9028   63.8115  -117.4785      6.9724
  2600   24.8826   59.6313   71.5654   126.4386   65.0556  -121.0144      6.9731
  2650   24.8849   60.8755   72.0278   129.9983   66.2997  -124.5741      6.9737
  2700   24.8870   62.1198   72.4819   133.5814   67.5440  -128.1571      6.9744
  2750   24.8890   63.3642   72.9279   137.1875   68.7884  -131.7632      6.9749
  2800   24.8910   64.6087   73.3660   140.8161   70.0329  -135.3918      6.9755
  2850   24.8928   65.8533   73.7966   144.4669   71.2775  -139.0426      6.9760
  2900   24.8945   67.0980   74.2198   148.1395   72.5222  -142.7152      6.9765
  2950   24.8962   68.3427   74.6360   151.8334   73.7670  -146.4092      6.9769
  3000   24.8977   69.5876   75.0453   155.5485   75.0118  -150.1242      6.9774

** Currently assuming a Gruneisen constant = 2

Job completed on Tue 29 April 2008 at 17:49:51 after 2761 s (0:46:01)
```

Y. MedeA Gibbs: Liquid - Vapor Pressure Curve of Methane

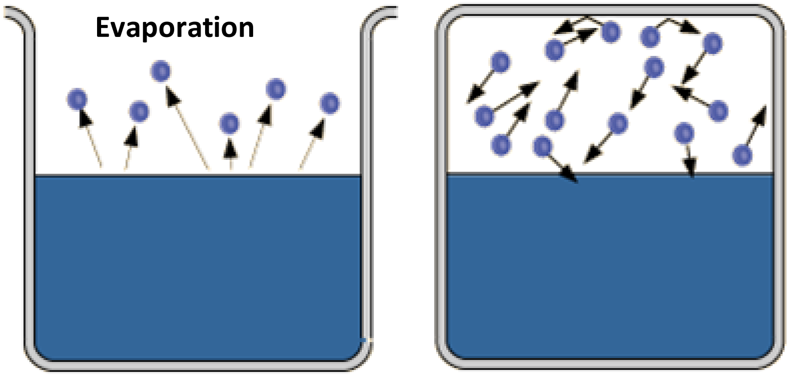
Introduction

MedeA Gibbs calculates equilibrium properties of fluids either pure or mixed, in a single phase or in multiple phases, using a force field based Gibbs ensemble Monte Carlo technique. The present application note focuses on the vapor pressure curve of methane, in other words we will deal with a one-component two-phase system. For such a system the Gibbs phase rule, with the number of components C and the number of phases π,

$$F = C + 2 - \pi \tag{12-1}$$

States that there is only one degree of freedom, F, so we can control either temperature or pressure. Defining the temperature as an initial condition, we can thus calculate the corresponding equilibrium pressure for the liquid-gas system. Doing this for a range of temperatures we get the equilibrium vapor pressure of the liquid-gas system.

Now, how does MedeA Gibbs model the two phases and what does it do to find the equilibrium? The figure below illustrates the condition of liquid-vapor equilibrium. At a given temperature, particles in the liquid phase evaporate into the gas phase until saturation, i.e. a number balance between particles in both phases is reached.



Evaporation which has reached equilibrium with the liquid surface is said to have reached saturation

In modeling this system we are limited to a rather small number of particles, typically a few hundred to keep computational efforts within limits. In MedeA Gibbs we therefore define two boxes containing the liquid and the gas phase respectively. Technically this means that we squeeze many more particles into a volume unit for the liquid phase than we do for the gas phase resulting in a higher starting density of articles in the box representing the liquid.

During the computation, we allow for random moves of the particles, i.e. translations, rotations and moves between the boxes. For each move into a new configuration a "penalty" function is calculated using force fields and over the duration of the simulation a minimum energy configuration is established.

In this final or equilibrium configuration, particles are distributed over both the liquid and the gas phase, provided that the initial temperature lies in the range of liquid-vapor coexistence.

Before we start working with MEDEA GIBBS, a few words about force fields: Force fields are system specific parameterizations of interatomic forces that hold a number of atoms together in a specific arrangement, e.g. a molecule or a crystalline structure. While force-field parameters can be more or less complex and very sophisticated parameterizations exist, they typically only work for the class of systems they were designed for.

Therefore, whenever using force fields we need to make sure they are appropriate in describing the physical interactions we are looking to model!

Now, let us get started with the MEDEA GIBBS code. In the rest of this document you will learn how to:

- Assign a force field to a molecule using the MEDEA interface
- Extract experimental liquid-vapor equilibrium data from the NIST webbook
- Run MEDEA GIBBS to calculate the liquid-vapor curve of methane

Outline of procedure

- Build methane (CH_4) and assign a force field
- Get experimental data from NIST webbook
- Set up the conditions of the run in the GIBBS interface
- Analyze the result

1. Build methane (CH_4) and assign a force field

MEDEA comes with a number of structures already carrying force fields in the *.sci* structure file (including methane CH_4). These systems are located in *C:/MD/Structures/Gibbs* (standard installation path). To load any of these structures simply invoke **File**≫**Open from disk** in the MEDEA main menu.

In the following, we will first build the molecule and then attach a force field to it.

Build a CH_4 molecule

We will build a CH4 molecule from scratch using the MEDEA molecule builder.

In the MEDEA **File** menu select **New Molecule**.

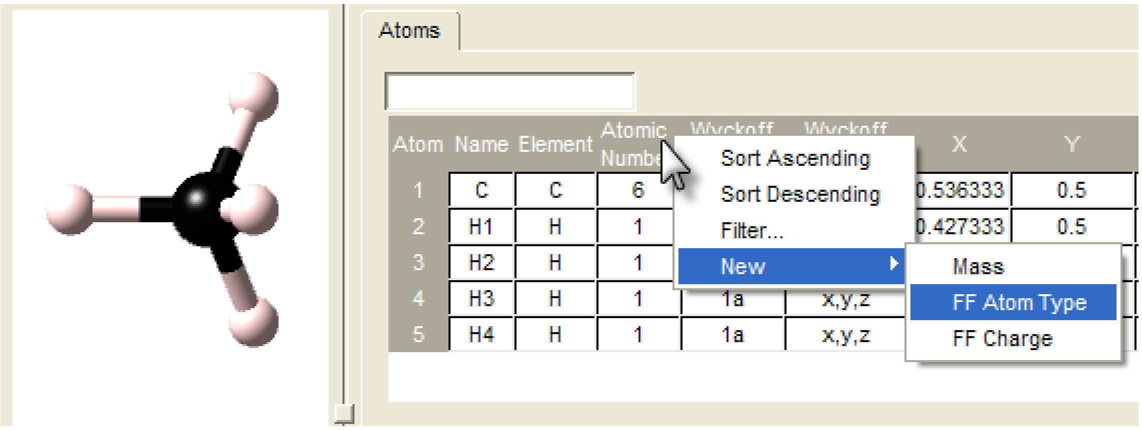
Select ***C*** in the periodic table of the elements on the right and subsequently click into the center of the drawing area to drop a C atom in its standard fourfold coordination. Finish with **Hydrogenate** to attach hydrogen atoms to each of the carbon bonds. Right-click into the drawing area and select **All**≫ **Center to origin** from the context menu

In the MEDEA **Edit** menu select **Create a periodic copy** and close the molecule builder window

Attach a force field to the CH_4 molecule

With the windows focus on the new CH_4 structure window, click on the spreadsheet icon to invoke the detailed view of atomic properties of CH_4

You can resize the window and use the slider at the bottom to see more of the spreadsheet. Right click in the title bar and select **New**»**FF Atom Type**, which will create a new column on the right. You may have to use the scroll bar to see it. In the first row, click into the FF Atom Type column to select the cell, right click in the selected cell and select **CH4-Moller** from the list of force fields. Now you have assigned this force-field to the carbon atom. Do not assign anything to the H atoms.



Atom	Name	Element	Atomic Number	Wyckoff	Wyckoff	X	Y
1	C	C	6			0.536333	0.5
2	H1	H	1			0.427333	0.5
3	H2	H	1				
4	H3	H	1	1a	x,y,z		
5	H4	H	1	1a	x,y,z		

Toggle off the detailed view by clicking once more on the spreadsheet icon

2. Get experimental data from NIST webbook

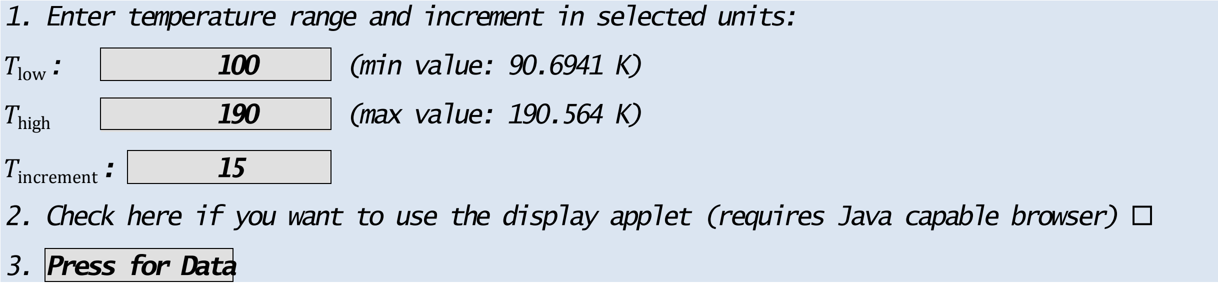
We now have an appropriate CH_4 molecule to use with the GIBBS module. However, before calculating the liquid-vapor equilibrium curve, we will have a look at the NIST webbook to obtain experimental data describing the liquid-vapor equilibrium properties of methane.

Open a web browser and go to the URL: http://webbook.nist.gov/chemistry/fluid/

Please follow the steps below to select the data required.

1. Please select the species of interest: ***Methane***
2. Please choose the units you wish to use:
…
3. Choose the desired type of data: **◉ *Saturation properties – temperature increments***
4. Please select the desired standard state convention: ***Default***
5. ***Press to Continue***

This will direct you to another web page titled *Saturation properties for Methane – Temperature Increments*. On this page:



1. Enter temperature range and increment in selected units:

T_{low} : 100 (min value: 90.6941 K)

T_{high} 190 (max value: 190.564 K)

$T_{increment}$: 15

2. Check here if you want to use the display applet (requires Java capable browser) ☐

3. Press for Data

The NIST webbook will display two tables containing data for the liquid and vapor phases of methane. The first seven columns of each table should look like

Liquid Phase Data

Data on Saturation Curve

Temperature (K)	Pressure (MPa)	Density (mol/l)	Volume (l/mol)	Internal Energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/mol*K)
100.00	0.034376	27.357	0.036554	-0.64728	-0.64603	-6.0856
115.00	0.13221	26.021	0.038431	0.18241	0.18749	1.6440
130.00	0.36732	24.562	0.040714	1.0379	1.0529	8.6383
145.00	0.82322	22.917	0.043636	1.9317	1.9676	15.154
160.00	1.5921	20.964	0.047702	2.8887	2.9647	21.462
175.00	2.7765	18.384	0.054394	3.9734	4.1244	28.021
190.00	4.5186	12.515	0.079902	5.7074	6.0685	38.000

Vapor Phase Data

Data on Saturation Curve

Temperature (K)	Pressure (MPa)	Density (mol/l)	Volume (l/mol)	Internal Energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/mol*K)
100.00	0.034376	0.042048	23.782	7.0469	7.8644	79.019
115.00	0.13221	0.14457	6.9171	7.3680	8.2825	72.036
130.00	0.36732	0.37278	2.6825	7.6403	8.6256	66.890
145.00	0.82322	0.80691	1.2393	7.8406	8.8608	62.693
160.00	1.5921	1.5821	0.63206	7.9306	8.9369	58.789
175.00	2.7765	3.0268	0.33038	7.8184	8.7357	54.371
190.00	4.5186	7.8027	0.12816	6.7850	7.3641	44.819

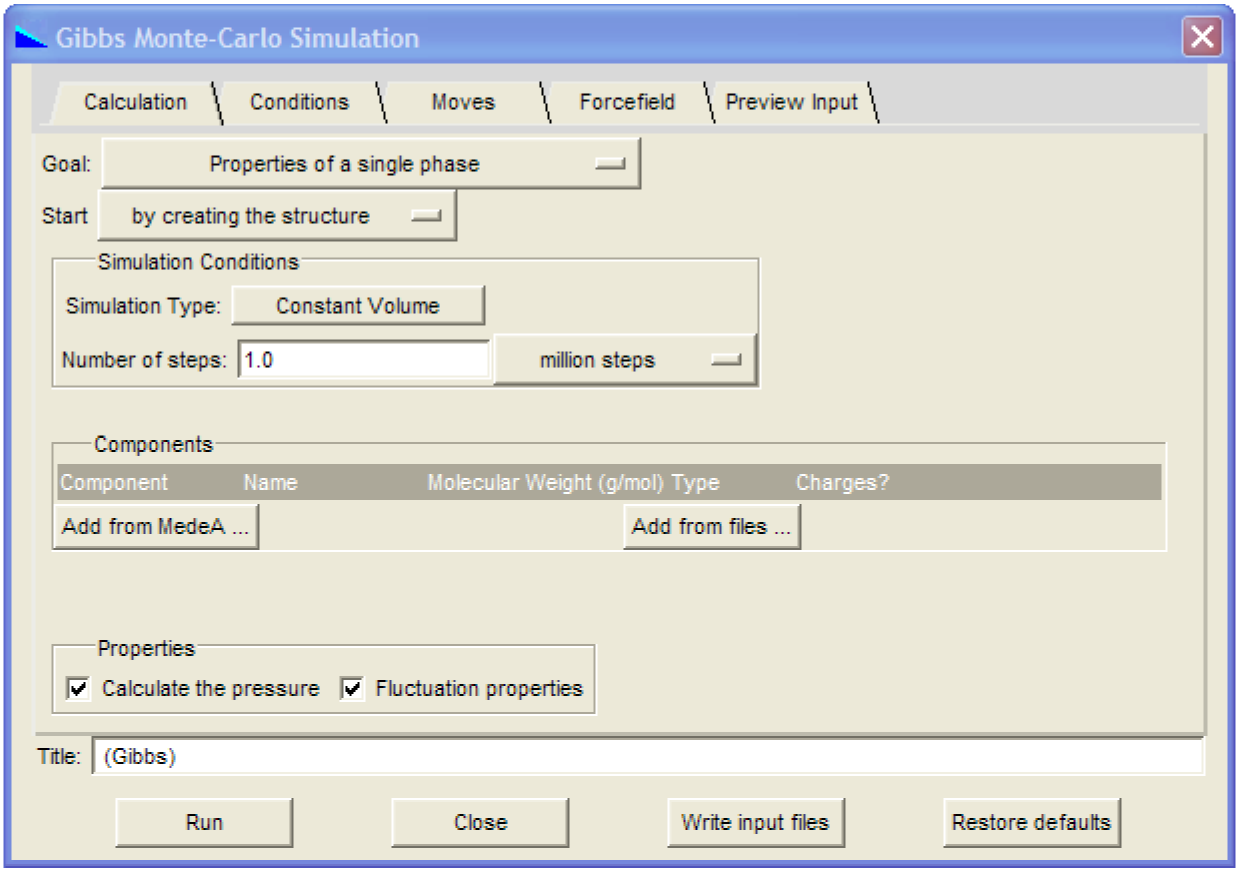
The data gives the experimental values of pressure, density and volume of the liquid and vapor phases of methane at the chosen temperatures.

3. Use MEDEA GIBBS to calculate the liquid vapor saturation curve of methane

We will now employ the MEDEA GIBBS module to calculate the liquid vapor saturation curve of methane.

Open the **Tools**>> **Gibbs** menu and select **Run**.

This will bring up the GIBBS interface in MEDEA. The computational setup and parameters are specified under the tabs **Calculation**, **Conditions**, **Moves**, and **Forcefield**.



Goal: Properties of a single phase

Start by creating the structure

Simulation Conditions

Simulation Type: Constant Volume

Number of steps: 1.0 million steps

Components

Component	Name	Molecular Weight (g/mol)	Type	Charges?

Properties

☑ Calculate the pressure ☑ Fluctuation properties

Title: (Gibbs)

Calculation tab

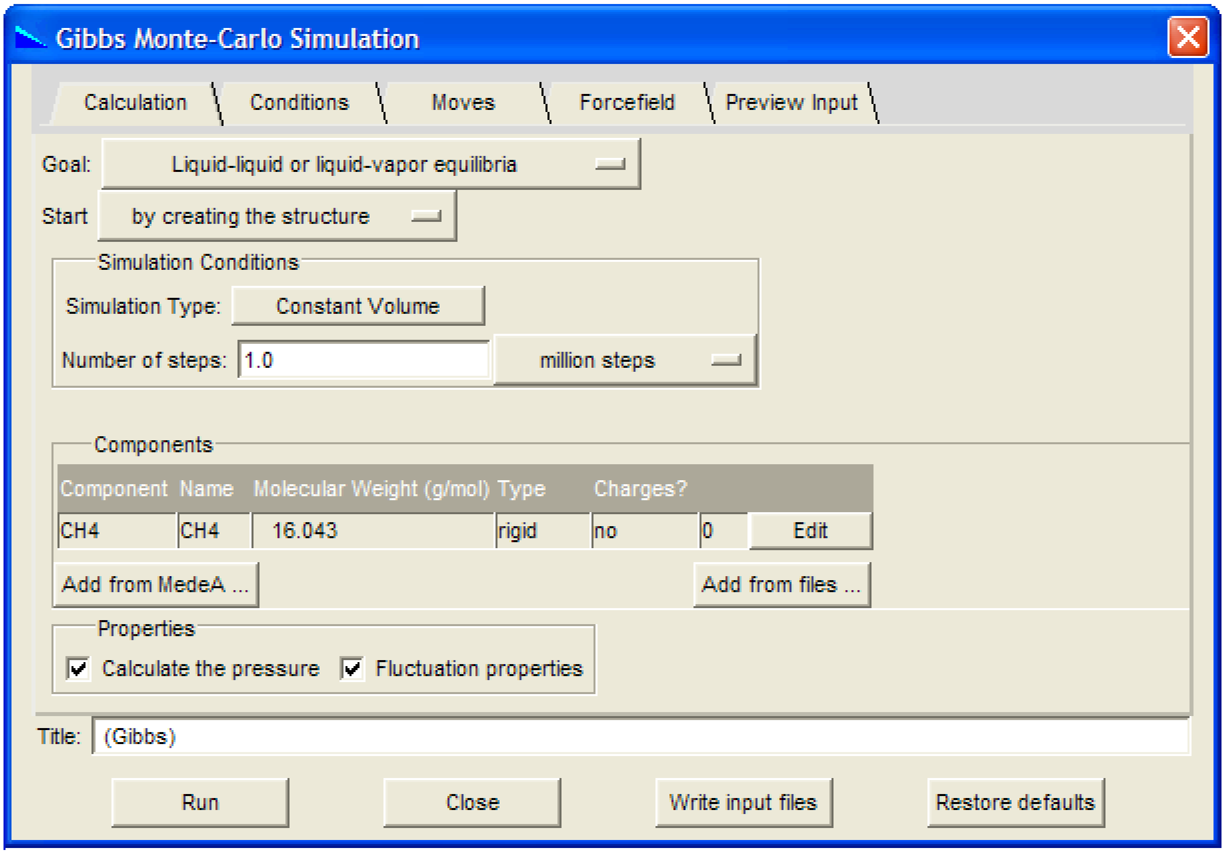
Here, we need to specify the type of calculation and system to study:

Set **Goal** to **Liquid-liquid or liquid-vapor equilibria**.

In the **Components** field, add methane by clicking **Add from MedeA**, in the **Add Component** file selector, select and **Insert»** the CH$_4$ structure (its structure window must be open in MEDEA) and confirm with **OK**.

In **Simulation Conditions** we leave the **Number of steps** unchanged at 1 million steps for sampling the statistical ensemble in each temperature run.

The Calculation tab should now look like this:



Goal: Liquid-liquid or liquid-vapor equilibria

Start by creating the structure

Simulation Type: Constant Volume

Number of steps: 1.0 million steps

Component	Name	Molecular Weight (g/mol)	Type	Charges?		
CH4	CH4	16.043	rigid	no	0	Edit

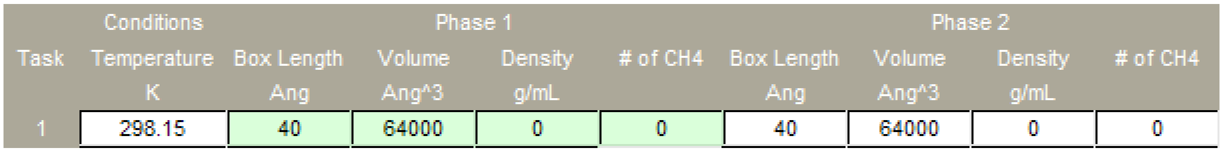
☑ Calculate the pressure ☑ Fluctuation properties

Title: (Gibbs)

Conditions tab

Let us now set the initial conditions for the liquid and vapor phase of methane.

Click the **Conditions** tab and then click into the table to select it. Right click and select **Add phase**



	Conditions		Phase 1				Phase 2		
Task	Temperature K	Box Length Ang	Volume Ang^3	Density g/mL	# of CH4	Box Length Ang	Volume Ang^3	Density g/mL	# of CH4
1	298.15	40	64000	0	0	40	64000	0	0

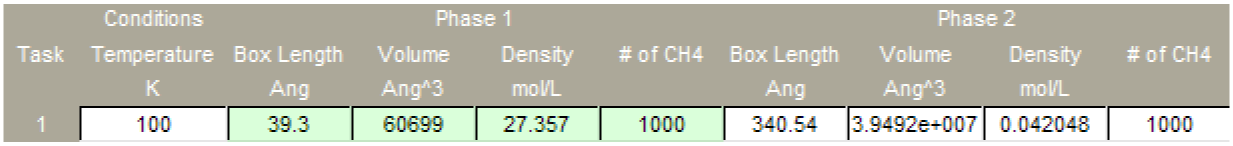
We have created two phases, one for the liquid and one for the gas phase of CH_4. For each of these phases, we now need to define values for the number of particles and starting density Note that the box size for each phase is adjusted by the program based on input number of particles and input density. We will work with 1000 particles in each phase and we will use starting values for the density taken from the NIST web book. In order to run at temperatures T=100 K, T=115 K, T=130 K, T=145 K, T=160 K, T=175 K, and T=190 K we create additional rows, each of them corresponding to one GIBBS simulation at fixed temperature where equilibrium pressure between the two phases will be calculated.

Let's have Phase 1 represent the liquid and Phase 2 the vapor phase.

The NIST webbook gives in units of **mol/L**, so let's adjust to these units:

- Right click on both ***Density*** column headers and select **Units** and change the units to **mol/L**
- Click in the first cell in the table and change the temperature to 100 K
- Change the number of molecules in both phases (***# of CH4***) to 1000

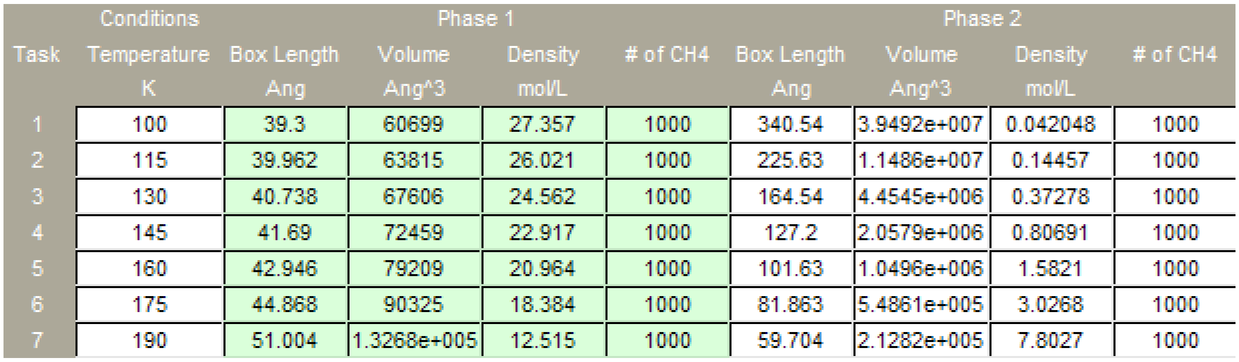
Type in the experimental value for the density of the liquid phase (27.357) and for the density of the vapor phase (0.042048) at T=100 K in the ***Density*** columns for Phase 1 and Phase 2, respectively.



	Conditions	Phase 1				Phase 2			
Task	Temperature K	Box Length Ang	Volume Ang^3	Density mol/L	# of CH4	Box Length Ang	Volume Ang^3	Density mol/L	# of CH4
1	100	39.3	60699	27.357	1000	340.54	3.9492e+007	0.042048	1000

Note that the values for the density are only starting values. We will check the sensitivity of results to these values later in this work.

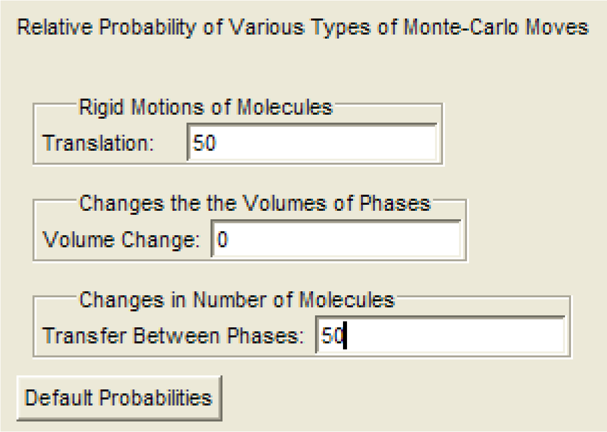
With the cursor anywhere in the last row, press **Down arrow** or **Enter** to create additional rows and fill in the experimental values. For each temperature, set ***# of CH4*** to 1000 and add the densities of the liquid and vapor phase.



	Conditions	Phase 1				Phase 2			
Task	Temperature K	Box Length Ang	Volume Ang^3	Density mol/L	# of CH4	Box Length Ang	Volume Ang^3	Density mol/L	# of CH4
1	100	39.3	60699	27.357	1000	340.54	3.9492e+007	0.042048	1000
2	115	39.962	63815	26.021	1000	225.63	1.1486e+007	0.14457	1000
3	130	40.738	67606	24.562	1000	164.54	4.4545e+006	0.37278	1000
4	145	41.69	72459	22.917	1000	127.2	2.0579e+006	0.80691	1000
5	160	42.946	79209	20.964	1000	101.63	1.0496e+006	1.5821	1000
6	175	44.868	90325	18.384	1000	81.863	5.4861e+005	3.0268	1000
7	190	51.004	1.3268e+005	12.515	1000	59.704	2.1282e+005	7.8027	1000

Moves tab

Next, the relative probability of the different types of Monte-Carlo moves in each simulation step needs to be specified.



Relative Probability of Various Types of Monte-Carlo Moves

Rigid Motions of Molecules

Translation: 50

Changes the the Volumes of Phases

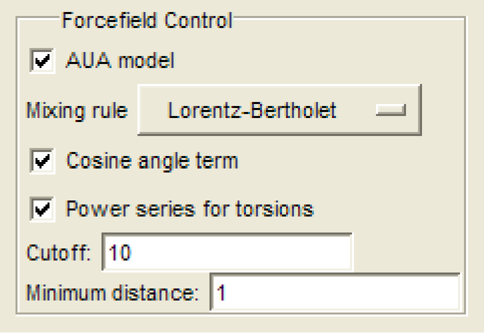
Volume Change: 0

Changes in Number of Molecules

Transfer Between Phases: 50

Go to the **Moves** tab,
set **Translation** to 50,
set **Volume change** to 0
set **Transfer Between Phases** to 50.

Forcefield tab



Forcefield Control

☑ AUA model

Mixing rule: Lorentz-Bertholet

☑ Cosine angle term

☑ Power series for torsions

Cutoff: 10

Minimum distance: 1

A good value for the cutoff radius of the intermolecular potential is 10Å, as it generally leads to a reliable evaluation of the Lennard-Jones interactions. In any event the cutoff should be smaller than half the box size used in the simulation.

The default (zero) uses half the size of the box, however, this option may result in longer computational time if large simulation boxes are used.

Go to the **Forcefield** tab and set **Cutoff** to 10.

Submit the calculation

Enter an appropriate job name in the **Title** field at the bottom of the GIBBS interface, let's use **Methane vapor-liquid,** and submit the job by **Run**

4. Analyze the result

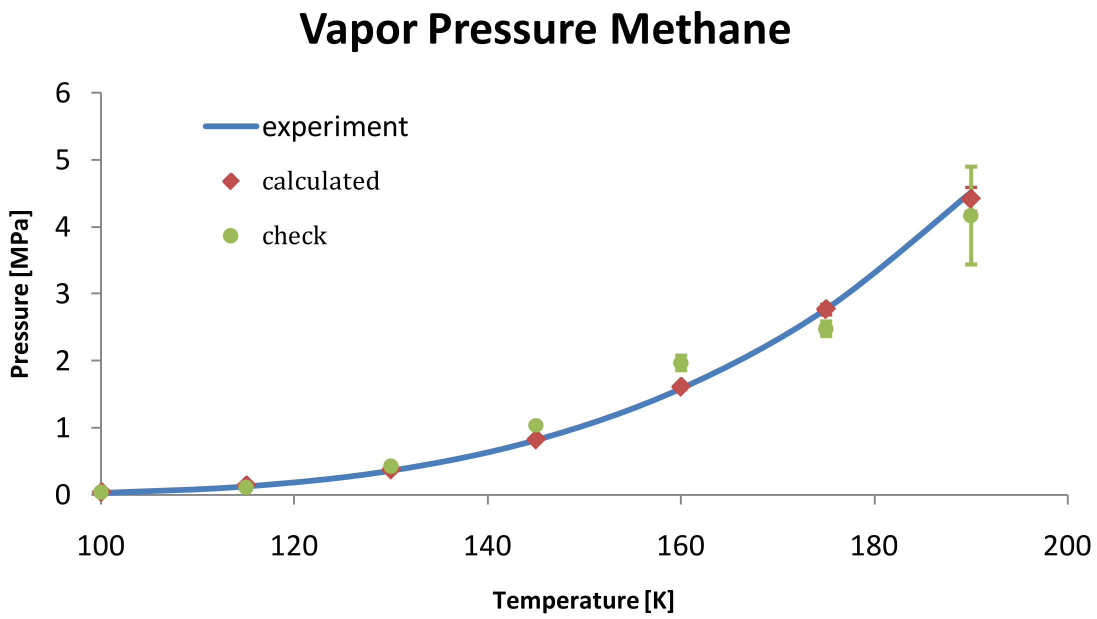
After completion, the calculated equilibrium properties are summarized in the file *job.out*. Similar to all other MEDEA jobs, you can access the output files through **View and Control Jobs** in **the Job Control** menu.

For a liquid vapor equilibrium calculation, *job.out* gives both initial and calculated values of the properties of the two phases. In our calculations we assigned phase 1 and phase 2 to be the liquid phase and gas phase respective. Now we are interested in the vapor pressure as a function of temperature, and thus need the calculated pressures of phase 2.

In *job.out*, scroll to the Calculated Results for Phase 2

pressure			volume			density			# mol of CH4		
bar			Ang^3			mol/L					
0.3701	±	0.0061	39492000	±	0	0.04441	±	0.00019	1056.3	±	4.5
1.39	±	0.037	11487000	±	0	0.14588	±	0.00038	1009.2	±	2.6
3.749	±	0.061	4454700	±	0	0.3691	±	0.0013	990.4	±	3.4
8.229	±	0.077	2058100	±	0	0.8015	±	0.0044	993.6	±	5.5
16.09	±	0.38	1049700	±	0	1.5444	±	0.0093	976.4	±	5.9
27.66	±	0.8	548610	±	0	2.88	±	0.056	952	±	18
44.1	±	1.8	212820	±	0	5.47	±	0.13	701	±	16

The calculated vapor pressure is listed in *job.out* for each of the temperatures. The pressures are given in units of bar. The calculated values (converted in MPa) are plotted below together with the experimental values from the NIST webbook. The agreement is very good, but we were using excellent initial conditions: the experimental values.



Sensitivity analysis

Initial pressure:

To check the sensitivity of the computed equilibrium pressure on the initial density we rerun with initial pressures for the liquid/vapor phase randomly deviating up to 26 % from the experimental equilibrium pressures. We change the initial density of the vapor phase from {0.042, 0.144,0.372,0.806,1.582,3.027,7.803} to {0.05,0.12,0.4,0.9,2,2.5,7} mol/L respectively. In addition we reduce the number of Monte Carlo steps per temperature to 100000. Apart from that we start with identical parameters to the first set of calculations.

The resulting vapor pressure curve is shown above. Even though quite large deviations from experimental values of the initial pressures of the two phases were introduced, the calculated vapor pressure curve is in good agreement with experiment. Not surprising, the most difficult temperature to obtain good computed values for methane is 190 K since this is close to the critical point of methane.

VI. References

A. Frequently Asked Questions

If you cannot find an answer to your problem, check out our online FAQ on www.materialsdesign.com or email us at support@materialsdesign.com (Japan: medea@rsi.co.jp).

1. System related

a. Upgrade DVD

I cannot use the **Update from the web**. Can I get the Upgrade on DVD? Yes, of course. Please contact us at support@materialsdesign.com (Japan: medea@rsi.co.jp).

b. Do subnet mask and gateway change affect MEDEA settings?

No, there is no need to modify your MEDEA settings.

c. Sharing violation when moving C:\MD\Databases\ folder

The Microsoft SQL server is using the file. Stop the programs/services SQLServer and mdJobServer before moving the directory. From version 2.2 onwards backup the job directory and database by making a backup copy of the directory Jobs. For each job there is a `db.backup` file, so the need for a backup of the database file is obsolete.

d. Which files do we need to backup?

From MEDEA 2.2 onwards, all you need to backup is the Jobs directory (`C:/MD/2.0/Jobs` by default) [19]

2. MedeA

a. I cannot start up MEDEA

Please check if you have a valid license file in `C:/MD/2.0` or in your installation directory. If you do not have a license file or if MEDEA fails to read your license file, please contact support@materialsdesign.com.

If MEDEA stops during startup, there may be a problem connecting to the databases. To check which databases are currently installed on your machine and attached to the SQL server, start the **Materials Design Maintenance** tool from the Windows start menu (**Start** ≫ **All Programs** ≫ **MaterialsDesign2** ≫ **Maintenance**) and select Manage databases. Make sure all your licensed databases are installed and attached to the SQL server.

b. MEDEA shows a message "The databases are not ready yet. Please try again in a minute"

On startup MEDEA needs to access the databases which can take some seconds. While doing so, MEDEA indicates progress in the lower left message bar.

c. The bonds of a structure displayed by MEDEA look strange

You may have to update the bonds. To do so, click **Edit bonds** .in the **Edit** menu and reapply the settings by clicking **OK**.

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[19] In older versions of MEDEA you should backup the Jobs directory and also the files MDJob.mdf and MDJob.ldf. For version 2.0, these files are located `in C:/MD/Databases`.

d. How can I display the charge density computed by VASP?

Since MEDEA 2.4 use **Analysis** ≫ **Valence Charge Density** to visualize charge densities.[20]

e. Can MEDEA display VASP Charge Densities for core electrons?

No, MEDEA cannot display charge densities for core electrons.

f. How can I draw the electronic/phonon dispersion relation/density of states (DOS) using Excel?

From MEDEA2.2 onwards, click on **Analysis** ≫ **Export** ≫ **Bandstructure** ≫ **DOS** menu entry to select a band structure/DOS job to be written to an Excel spreadsheet.

g. Can I save a PHONON animation as a movie file?

Currently not. You need to run the animation in MEDEA and use a screen grabber program like Snagit to capture a movie file like *.avi*

h. How do I create a vacancy?

You can edit a structure by right-clicking in the structure window. To delete an atom, first select the atom, then use **Delete selected atom**.

A more systematic way of analyzing substitutional sites with respect to symmetry and inserting vacancies or defects is using the **Substitutional Search** Tool. To use this tool, select the structure you want to edit and, from the MEDEA **Edit** menu, select **Substitutional Search**. More information on how the module works can be found in section II.C.7 Substitutional Search.

3. Job Control

a. How do we check the progress of a running job?

To check the progress of a running job, select **Job Control** ≫ **View and Control Jobs** from the MEDEA menu. Click on a task number to see the output files. For a VASP calculation, you can check the progress in the *OSZICAR* file.

b. What are JobServer and TaskServer?

MEDEA uses a (tiered) client-server model to distribute computational tasks throughout a network. You can think of the jobserver as the central place (middle tier) where all computational tasks are configured and where all result files end. A TaskServer (end tier) is a machine that receives a specific task (e.g. a VASP single point run), performs the calculation and returns all result files to the jobserver. The JobServer controls computational jobs which can consist of many separate tasks. MEDEA connects to a JobServer machine to start jobs and retrieves results. In most cases you only work with one JobServer and multiple TaskServers.

c. I cannot access JobServer with Internet Explorer?

The JobServer and/or TaskServer machines which MEDEA tries to access might be down. Check whether the machine starts-up and if there are network problems.

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[20] In older versions Vaspview was used to visualize charge densities.

On the machine with the jobserver, check if the jobserver is actually running: Click **Ctrl**-**Alt**-**Delete** to bring up the Windows Task Manger and in the Processes tab click on the column header **Image Name** to sort the list of processes alphabetically. Look for a process `mdJobserver`. If it is not present you need to start the jobserver, either as a normal program (click **Start** » **All Programs** » **MaterialsDesign2** » **JobServer 2.0**) or as a service (click **Start** » **All Programs** » **MaterialsDesign2** » **Maintenance** and then **Manage Services**)

Maybe the network IP address of your jobserver has changed or the port number for the Job Server was changed. Check your settings in the server configuration file, located in `C:\MD\2.0\servers.dat`. For each jobserver configured in MEDEA there should be one uncommented line. Make sure the settings for your machine agree with your network configuration.

d. The Job Server claims a job is running, but it seems to be finished on that machine?

A network failure might have occurred. Check if all tasks of the job have finished. If you think all tasks have finished, select the **Restart** button and then select **Just get files again** and click **Restart**. The jobserver will reattempt to bring back files from the taskserver.

If the above operation produces an error, on the job page click **Restart** one more time and select **Rerun task** for the tasks indicated as incomplete. Click the **Restart** button to submit the calculation.

e. Can I remove a job that has failed from the Job Server?

You can remove a Job and all its associated files by clicking in the checkbox next to a Job entry in the job list of the Job server and then click **Delete Selected** at the bottom of the page.

f. Can I transfer my Jobs directory and database to a new machine?

Make completely sure that the databases are detached before moving them, otherwise they will be corrupted.

Example: MEDEA is located on both machines, called *XP32* and *XP64*, in `c:\MD\`

1) Install MEDEA on *XP64*, but do not install JobServer and TaskServer as services yet.

The installer asks you to do that (after installing MEDEA and databases, creating shortcuts…)

> ***Setup the Job and Task Servers as Services***
>
> *The job and task servers can be run manually, or can be set up as Windows services if you have administrator privileges.*
>
> *Use the following buttons to set up the services*
>
> ***Both Job and Task Servers***
>
> ***Job Server***
>
> ***Task Server***

Just continue without selecting any of the three options.

2) Stop JobServer on XP32

Start » **All Programs** » **Materials Design 2** » **Maintenance** » **Manage Services**:
Click on **Stop Service**

Or use the Windows Task Manager: Stop process *`mdJobserver.exe`*

3) Verify that JobServer is not running on XP64:

Windows Task Manager: Look for (and stop process) *`mdJobserver.exe`*

4) Make sure that the MD2Jobs database is detached from MSDE on XP32.

Stop SQL Server / MSDE or

Start » **All Programs** » **Materials Design 2** » **Maintenance** » **Manage Databases**

If MD2Jobs says **Detach** click the button. If it says **Attach** it is already detached, so leave it alone.

5) Copy (and don't move) *`MD2Jobs.mdf`* and *`MD2Jobs.ldf`*

`[XP32]c:\MD\Databases\MD2Jobs.*df` to *`[XP64]c:\MD\Databases\`*

6) Copy (including subdirectories) *`[XP32]c:\MD\Jobs\dir0`* to *`[XP64]c:\MD\Jobs\`*

7) Start service on new machine [XP 64]

Start » **All Programs** » **Materials Design 2** » **Maintenance** » **Manage Services**:
Click on **Create Service** for JobServer and TaskServer

8) On XP64 open in Internet Explorer "http://localhost:32000" to look at imported jobs on the JobServer. If everything worked as expected, you can delete the files on the old machine.

4. Vasp

a. How can I see the results of a VASP calculation?

Job.out summarizes the computational settings and results of a specific calculation. To access the file via the MEDEA menu, click on **Job Control** ≫ **View and Control Jobs** (brings up your default web browser) ≫ **Jobs** ≫ **Job #** ≫ **Job.out**.

To load a minimized structure, select **File** ≫ **Open** ≫ **From previous calculation** from the MEDEA menu.

To display graphical results such as band structures, select the corresponding entry from the Analysis menu.

b. How can I preview an INCAR file to be used in a VASP calculation in MEDEA?

In the VASP interface, select **Preview Input** and choose **INCAR** from the File menu.

c. How do I add extra VASP parameters?

You can do this via the **Add to Input** tab in the VASP interface window. Please note that only the first occurrence of a keyword in INCAR will be used by VASP. To perform a constrained minimization, right click an atom in MEDEA and freeze its degrees of freedom.

d. How can I see the initial parameters of already calculated jobs?

In MEDEA click on Job Control and select View and control jobs. Click on the job number of the job you want to check parameters for and next click on **Job.out**. `Job.out` summarizes all settings used in the calculation.

e. Is there a detailed description of the VASP parameters?

For a detailed description refer to the MEDEA user guide or to the VASP manual. You can get a short explanation for each parameter by right-clicking next in the VASP interface.

f. When is a VASP calculation converged?

Single point: A single point calculation is converged when the electronic energy difference between two self-consistent steps changes less than the SCF convergence criterion demands. Default for the SCF convergence is 10^{-5} eV.

Structure relaxation: A structure relaxation is converged when the residual forces on the atoms are smaller than the convergence criterion. The default value for structure relaxation is 0.02eV/Å.

Note: A MEDEA job may finish although a calculation is not converged!

For example if a calculation does not converge within the maximum number of steps defined in the VASP interface, MEDEA will finish the job anyway.

Defaults for the number of steps are: SCF: 60 steps; Structure optimization: 100 geometry steps.

g. What is the typical accuracy of a VASP calculation?

For a structure calculation, the deviation from experimental lattice parameter is typically within a 2-3 percent.

h. What is different between Real space and Reciprocal space?

Real space and reciprocal space refer to different numerical techniques of performing integrals. Real space is recommended for "larger" unit cells (one dimension larger than 5 Ång) where it is faster than the reciprocal space integration scheme. For smaller cells reciprocal space is recommended.

If you would like to perform a very accurate calculation, use reciprocal space in any case.

i. How do I select the right smearing method?

Please consult the detailed description of the MEDEA-VASP user interface panels in section II.D.5.b Integration Scheme of the User's Guide.

j. I feel the values of the partial charges in Job.out are somewhat strange?

VASP evaluates charges only within a specific radius - the Wigner-Seitz (WS) radius. The total charge is the sum of all WS spheres and the contribution from the interstitial space. You can set the WS radius for each atom by specifying the parameter *RWIGS* in the Add to Input panel.

k. Why are the RWIGS values in DOS_INCAR file different from POTCAR?

MEDEA uses VASP which evaluates charges only within a specific radius, the Wigner-Seitz (WS) radius. The total charge is the sum of all WS spheres and the contribution from the interstitial space. You can set the WS radius for each atom by specifying the parameter *RWIGS* in the Add to Input panel.

l. I get an error trying to perform a VASP calculation on a hexagonal system?

In the VASP interface SCF tab, try **Shift origin to Gamma** or **Use odd size grids**.

m. Error when performing a DOS and Band structure calculation with VASP?

Check the Job.out for the following message:

```
Can't use empty string as operand of "*" while executing.
```

If this error occurs, divide the band structure calculation into a number of tasks. To do so, edit the Number of k-points per task on the Band structure tab of the VASP interface.

5. Phonon

a. How come a PHONON calculation can give imaginary frequencies in a system which might be stable?

PHONON calculates the Eigen frequencies from the dynamical matrix. The dynamical matrix is made from the second derivative of the energy with respect to atomic displacements. Imaginary frequencies (negative in a MEDEA PHONON dispersion plot) can occur even though the system is thermodynamically stable if the forces are not calculated precisely enough. How precisely the forces need to be calculated for a given system depends on the shape of the energy hyper surface.

Therefore a general answer is difficult. However we recommend to check the following settings if negative modes occur for a system which might be stable:

Geometry Optimization: Make sure the undisplaced system is really in equilibrium regarding the atomic positions: Run the initial atomic relaxation separately with VASP before running PHONON. Choose a force convergence of 0.001-0.005 eV/Ång and for the electronic (SCF) convergence choose 10^{-6}, or 10^{-7} eV.

k-points sampling: You might need more k-points. Even for large supercells Gamma-point only is not recommended.

Accuracy of forces: Try the following parameters for a more accurate calculation

> **Projection**: Reciprocal space; **Precision**: Accurate; Check **Extrafine** augmentation grid for accurate forces in the **Advanced** ≫ **Restart tab** (ADDGRID = .TRUE.)

Allow for **+** /**-** **displacements** if this option has not already been set.

B. Release Notes

1. MEDEA release 2.4

Main features and changes:

- Pearsons data file added
- ICSD data file updated
- Improved indexing and Search for Pauling and Pearson's
- New vastly improved version of interface builder algorithm and interface
- FERMI module added
- VASP licensing added
- JobServer raw file access added
- Charge density analysis added
- Molecular spreadsheets added
- Added option to edit atomic masses
- Added savable color schemes for atoms and background
- Added graphics export to a number of picture formats

Detailed release notes:

MEDEA 2.4b2

Fixed problem with batch jobs using Windows security in SQL Server
Renamed to "valence" charge density throughout

MEDEA 2.4b1

Renamed 2.3.5.11

MEDEA 2.3.5.11

Adding support for Windows security in SQL Server
Fixed problem in PHONON with long, or identical, site names

MEDEA 2.3.5.10

Added mass to molecular spreadsheet, used in e.g. PHONON
The "Add to Input" tab in VASP is red if there is added input
INFOMATICA

- Apparently fixed the flickering window when starting
- Searches on title, author, mineral, systematic name and remarks
- The scroll wheel now scrolls the table
- Use the hourglass cursor and don't allow actions while the detail is updating when browsing the results, avoiding e.g. viewing too quickly causing an error
- Fixed browsing NCD structures

- Fixed sorting of tables to ignore blanks, placing them at the end (or beginning for decreasing sort)

Added Mass tab to edit dialog and atom/edit mass to popup

PHONON

- Uses masses on system if they are set
- interface improved to allow summing of individual DOS, etc.
- Fixed factor of 3 problem in energies for Rxxx spacegroups DOS

MEDEA 2.3.5.9

New version of PHONON, removing the limit on the number of displacements

Internal version of transition state searching

MEDEA 2.3.5.8

Fixing problem opening structures from older JobServers

JobServer 2.3.7

Small corrections to interface to make it more clear

MEDEA 2.3.5.7

GIBBS can now show convergence data from task subdirectories

Modes for atom display: small atoms, and no atoms at all. This is intended for charge density plots

Minor fix to MPM menus

JobServer 2.3.6

- Support for getting files from subdirectories
- Added selection on job number
- Provide size of files
- Allow listing of subdirectories
- immediate link to raw files
- Limit the formatted output to files < 10 MB in size, since the formatting consumes considerable memory and may crash the server

MEDEA 2.3.5.6

Fix for PHONON / supercell bug is included this time!

New console include in MEDEA

MEDEA 2.3.5.5

Atoms Colors Schemes: The Atom color editor now offer the possibility to save the current atom colors to a file whit extension *.mdacs_* (MD Atoms Colors Scheme). You can read in such a file, and you can also reset to MEDEA default colors. Each time you modify your ACS, it's saved in a file: *~/MedeA/Setting/default.mdacs*. This file is loaded when you first open a structure. So if you change the ACS, quit MEDEA, restart it, you keep your ACS through this default file

View Options: The **Change background color** in the View menu has been moved to the **General** tab of the View Options dialog, from a button below the **Change elements colors**. The frame is simply renamed **Colors**.

Color Schemes: Fixed and adapted the new colors scheme scale in the slice viewer (Select any number of section, types, etc....)

Export structure windows as picture

Iso-Surfaces exported to POVRAY

Fermi Surfaces: The side triangles (at the BZ limits) rendering improved

MEDEA 2.3.5.4

Updated job server to version 2.3.5 since it has a new TclLib that is needed

Corrected problems with multiple windows and molecular spreadsheet

Add widgets in molecular spreadsheet for fixing atoms via check boxes

MEDEA 2.3.5.3

Fixed problem switching from a structure window involving 'sys_periodicity'

Molecular spreadsheet: pasting now works

MEDEA 2.3.5.2

Fixed remaining problems with licensing

Moved new MT to Restricted license

Molecular spreadsheet

Added menu bar button to activate/deactivate

Fixed naming and element/atomic number editing, spin and partially have fixing atoms working

MEDEA 2.3.5.1

3-D Contour plots (charge density, etc) plus 2-D slices

Complete revamp of interface builder

FERMI module

MEDEA 2.3.3

Added Pearson

Fixes in PHONON for rhombohedral systems

MEDEA 2.3.2

VASP licensing

New VASP executables statically linked and considerably faster on Intel chips

MEDEA 2.3.1.4

Improved Licensing

MEDEA 2.3.1.3

Fixed problem in licensing in PHONON jobs

MEDEA 2.3.1.2

GIBBS:

- Fixed bug writing csv file Results.csv :-(
- Corrected problem with wrong factors (prefixes) for units when swapping phases
- Made units consistent between phases, keeping them the same as the conditions

MEDEA 2.3.0.18

Writing the exported results in a comma separated value (csv) format and file

JobServer, version 2.3.1:

- Adding csv files to the results, allowing them to be downloaded directly rather than as HTML
- Added a link for direct access to the job directory.

MEDEA 2.3.0.17

GIBBS:

- Fixed crash in constant pressure runs indicating 'PUnits' could not be found
- Corrected roundoff problems with probabilities
- Added branched and cyclic molecule input data
- Fixed problem with printing statistics for individual calculations

MEDEA 2.3.0.16

GIBBS:

- Fixed problem changing pressure units in Conditions panel
- Added Structures/GIBBS with a sample of structures
- O2, N2 to the forcefield
- Added preliminary parameters for Zn MOF's to the forcefield

MEDEA 2.3.0.15

GIBBS: Fixed problem with band indexing of Bonds array in default probabilities

MEDEA 2.3.0.14

GIBBS: Fixed problem with headers in adsorption calculations

MEDEA 2.3.0.13

GIBBS: fixed bug in density as mol/L

MEDEA 2.3.0.12

GIBBS: Reorganized interface to support multiple tasks for single job, so can do e.g. a set of isotherms at once

MEDEA 2.3.0.11

GIBBS:

- Fixed bug putting number of molecules in component in the electrostatic column
- Fixed bug identifying rigid and semi-flexible molecules
- bug in default probabilities

MEDEA: Started atom number in molecular spreadsheet from 1, not 0

MEDEA 2.3.0.10

Fixed problem with molecular spreadsheet requiring GIBBS Batch

MEDEA 2.3.0.9

Added edit / molecular spreadsheet to edit menu for systems

Added ability to add forcefield columns to a system

Added ability to select forcefield atom types guided by the atom in question

Added general ability to run adsorption in solids to GIBBS

MEDEA 2.3.0.8

Updating the setup program for GIBBS

MEDEA 2.3.0.7

GIBBS

- Implemented flexible molecules such as propene
- restart capability expanded

Improvements to export of band structure that may help it work with Excel 2007

MEDEA 2.3.0.5

Enhancements to GIBBS

MEDEA 2.3.0.3

Enhancements to GIBBS for restart.

MEDEA 2.3.0.2

Fixed problem reading atomic properties file for MPM

Updated job and task server versions to 2.3

MEDEA 2.3.0.1

Fixed problem in Windows 32 VASP executables that would not run on older hardware -- Athlon XP/MP and Pentium III

Fixed issues with installer not working on eg. Windows 2000

Corrected problem with atom correspondence in animation of PHONON dispersion for A, B and C centered cells

2. MEDEA release 2.3

Molecular builder added to standard builder suite

Pauling File added to databases

New VASP executables for all platforms

Fixed DOS/band structure bug

Improved 64bit compatibility under Windows

PHONON version 4.28

- Significantly improved performance
- Changed default displacement in PHONON to from 0.01 to 0.02
- Changed default number of points in the PHONON dispersion from 400 to 100 (to save memory)

MEDEA structure handling and editing

- New bond algorithm implemented, which is significantly faster, in particular for large systems
- Added Accelrys car file reader
- Added CIF reader
- Implemented Selection by dragging a rectangle
- Changed Open File to allow selecting multiple files

Added functionality to interface builder

- Indicate if interfaces are equivalent
- Control gaps separately
- Added functionality to split an interface into separate surfaces

Updated documentation

- Improved layout
- New section on molecular builder
- Updated section on interface/surface builder
- Added application notes on molecular builder

General clean-up

- Reorganized surface builder preview
- Reorganized context sensitive menus
- Reorganized Edit bonds dialogue; Added Edit bonds to right-click menu
- Added shortcuts for viewing modes
- Made rendering quality a function of the number of atoms

Bug fixes

- Fixed error when applying trigonal symmetry to a new, empty system
- Fixed problem that prevented displaying bonds from e.g. ICSD
- Fixed bug with points for 'e' Wyckoff position in Add Atom

- Cleaned up Move Atom when switching to a window with no atoms
- Cleaned up the Wyckoff coordinate display in Add and Move Atom
- Fixed bug when checking symmetry after e.g. straining a system
- Corrected bug in handling of nonstandard settings
- Fixed problem running calculation on a structure in a nonstandard setting such as *Amma*. VASP calculations died immediately because of an inability to find the Wyckoff position
- Fixed problem with constraints on the VASP k-mesh for e.g. orthorhombic systems with primitive cells
- Fixed problem in trajectory animation for centro-symmetric systems

3. MEDEA release 2.2

The MEDEA 2.2.2 release provides a complete set of serial/parallel 32/64bit VASP binaries with preinstalled mpi support for both Windows and Linux. To configure the TaskServer to run in parallel mode, please see section III.G TaskServer administration and configuration

In addition a number of new features and bug fixes are included in this release.

JobServer

- Added ability to edit restart information in the job server. After the update, you will need to restart the job server to access the new functionality. It should function fine until you do restart it, so you may wait until a convenient time.
- Fixed a problem in the job server where it occasionally did not realize that a job had finished.
- Allow 'holding' running jobs. This does not stop running tasks but prevents new tasks being started until the hold is removed.
- Corrected a problem when editing the name or comments for a job that resulted in braces {} being placed around the text.
- Added a backup of the database — each job directory contains a file *db.backup* with the backup for that one job.
- Improved the performance of the job server when getting structures or results from previous calculations into MEDEA. This was quite slow when there was a large number of jobs.
- The job server now brings the PROCAR back when running a bandstructure calculation.
- Added ability to change queues and priority of jobs.
- Fixed a problem in the job server that caused it to be extremely slow when a task server was down. The job server now checks task servers every 5 minutes to see if they are up.

TaskServer

- Fixed problems with the special characters in PHONON tasks displaying incorrectly.
- Added a button in Administration / TaskServer page for manually checking the status of task servers.
- Added the ability to stop or restart a running task locally on the job server, to be used if a task server is dead. This is accessed through the Control button of the task on the detailed page for the job.

MEDEA

- Corrected serious problem that occurred when the empty space panel was closed while coordination lines were still displayed.
- Added stoichiometry and spacegroup automatically to the titles of windows
- Corrected a problem introduced recently with building surfaces: the error referenced the bonds.

- Fixed occasionally problem with 'lcd' not defined while handling chemical formulas
- Fixed an error in the empty space finder when moving the mouse that lead to a message 'Error: Must have two sets of points!'.
- Fixed an error in the geometry analysis if the distance for the bond cutoff was less than the shortest distance
- Added the angle analysis that was in MEDEA 1.8. Also added the ability in geometry analysis to look at just one atom
- Corrected misleading graphs in Geometry Analysis > Coordination tab for low symmetry systems. The lines for symmetrically different atoms of the same element were placed on top of each other, rather than added up. Now they are added, so e.g. the pattern for a $2 \times 2 \times 2$ supercell in $P1$ looks identical to the parent cell in symmetry.
- Fixed a problem in the supercell builder that caused MEDEA to hang when building a general cell.

VASP

- Fixed the bug pasting into the summary line in the VASP input
- Replacing the Windows VASP executables with faster ones and including parallel.
- Fixed problems with k-meshes for VASP. For some spacegroups with primitive cells, the code did not correctly constrain the k-mesh to abide by the symmetry.
- Roundoff in the cell parameters when finding symmetry could cause problems in VASP calculations with messages like "VERY BAD NEWS! internal error in subroutine IBZKPT: Reciprocal lattice and k-lattice belong to different class of lattices". This is fixed.
- Enhanced error checking for VASP calculations.
- Added export of DOS and band structure to Excel, both electronic and PHONON.
- Add an indication in the unit conversion tool about errors (or incomplete) unit expressions
- Fixed a severe crash in MEDEA when stopping e.g. a PHONON animation and then starting a second animation without deleting the first window.

PHONON

- Changed PHONON animation so that after stopping the animation the distorted, rather than original, structure is left. This is convenient for following modes.
- Removed the yellow balloon help from animation since it tended to remain displayed.
- Corrected problem in PHONON with triclinic systems with $\alpha \neq \beta$.

Note on running Vasp on Windows versions dating from before 2005

Some versions of Windows dating from earlier than 2005 and not subject to regular operating system updates may require a Microsoft Visual C++ runtime library to be installed. This library can be downloaded from Microsoft's website[21] for both 32bit and 64bit architectures:

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[21] http.://www.microsoft.com/downloads/details.aspx?familyid=32bc1bee-a3f9-4c13-9c99-220b62a191ee

C. Standards and Reference Energies

1. The MEDEA Standard_500

MEDEA2.1 introduces a standard plane wave cutoff of 500 meV for VASP4.6 calculations. *Standard_500* is recommended in cases where an overall precise plane cutoff is required for a single system or for a range of systems with varying constituent elements. Using a standard cutoff of 500eV within a project has the advantage of facilitating the comparison of data from compounds containing different elements like e.g. in the calculation of heat of formations or defect energies.

2. Reference energies for the calculation of the heat of formation

From MEDEA2.1 onwards, the electronic contribution to the heat of formation of compounds is provided for most elements and potentials available for VASP4.6. To this end all model structures of all elements in their standard state were built and consequently optimized. For solids, cell parameters and internal degrees of freedom were relaxed. For molecules the atomic positions were relaxed within a fixed box of dimensions 10 × 10 × 10 Ång.

Element	Structure	Correction
H	H2 molecule	
He	He atom	
Li	bcc	
Be	α-Be, hcp	
B	α-B, R-3m	
C	diamond, Fd-3m	-1.897 kJmol-1 = graphite
N	N2 molecule	
O	O2 molecule, FM	
F	F2 molecule	
Ne	Ne atom	
Na	bcc	
Mg	hcp	
Al	fcc	
Si	Fd-3m	
P	black phosphorus,	
S	S8 molecule	-13.04875 kJmol-1 for condensation
Cl	Cl2 molecule	
Ar	Ar atom	
K	bcc	
Ca	α-Ca, fcc	
Sc	α-Sc, hcp	

Element	Structure	Correction
Ti	α-Ti, hcp	
V	bcc	
Cr	α-Cr, bcc,	
Mn	γ-Mn, P4/mmm,	-4.348 kJ/mol
Fe	α-Fe, bcc,	
Co	β-Co, hcp,	
Ni	fcc, FM	
Cu	fcc	
Zn	hcp	
Ga	α-Ga, Cmca	
Ge	Fd-3m	
As	grey metallic R-3m	
Se	grey metallic P3121	
Br	Br2 molecule	-22.85 kJ/mol for condensation
Kr	Kr atom	
Rb	bcc	
Sr	α-Sr, fcc	
Y	hcp	
Zr	α-Zr, hcp	
Nb	bcc	
Mo	bcc	
Tc	hcp	
Ru	hcp	
Rh	fcc	
Pd	fcc	
Ag	Silver 3C,	
Cd	hcp	
In	I4/mmm	
Sn	α-Sn, Fd-3m	(transition temperature T=286K)
Sb	R-3m	
Te	P3121	
I	Cmca	
Xe	Xe atom	
Cs	bcc	
Ba	bcc	
La	α-La, dhcp	
Ce	γ-Ce, fcc	
Pr	dhcp	

Element	Structure	Correction
Nd	dhcp	
Pm	dhcp	
Sm	R-3m	
Eu	bcc	
Gd	hcp	
Tb	hcp	
Dy	hcp	
Ho	hcp	
Er	hcp	
Tm	hcp	
Yb	fcc	
Lu	hcp	
Hf	hcp	
Ta	α-Ta, bcc	
W	α-W, bcc	
Re	hcp	
Os	hcp	
Ir	fcc	
Pt	fcc	
Au	fcc	
Hg	R-3m	2.3 kJ/mol for melting (JANAF)
Tl	α-Tl, hcp	
Pb	fcc	
Bi	R-3m	
Po	no potential	
At	no potential	
Rn	no potential	
Fr	no potential	
Ra	no potential	
Ac	fcc	
Th	α-Th, fcc	
Pa	I4/mmm	
U	α-U, Cmcm	
Np	no potential	
Pu	work in	

VASP parameters:

- Precision accurate
- Planewave cutoff 500eV (900 eV for hard potentials with ENMAX > 450 eV)
- Reciprocal space projection
- Convergence criterion for SCF cycle: 10^{-7} eV
- Convergence criterion for geometry optimization: 0.001 eV/Ang
- Conjugate gradient geometry optimization

Nonmagnetic in general, however, spin-polarized Hamiltonian for O_2,Cr(AF), γ-Mn(AF), Fe, Co, Ni, and lanthanides heavier than Ce for potentials including *f* electrons as valence states

For crystalline reference structures:

- k-spacing of 0.2 $Å^{-1}$, odd size grids
- Tetrahedron method including Blöchl corrections

For molecular reference structures:

- Cubic box of 10 Ang, for S_8 molecules a cubic box of 15 Ang
- Γ-point only
- FERMI Release Notes

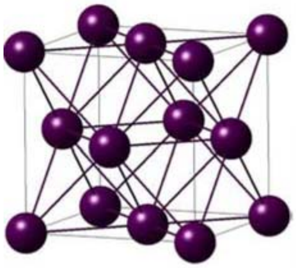
Unresolved potentials:

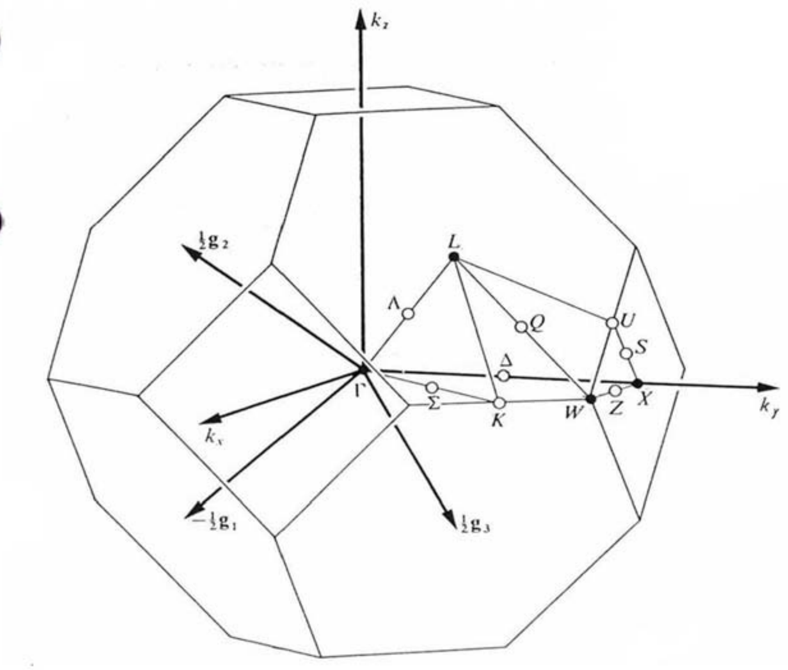
For the following potentials reference energies are not yet available:

Atom	PBE	GGA	LDA
Na		GGA-US-Na pv	
K			LDA-US-K s
Sr		GGA-US-Sr	LDA-US-Sr
Pm	PBE-PAW-Pm	GGA-PAW-Pm	
Sm	PBE-PAW-Sm	GGA-PAW-Sm	
Tm	PBE-PAW-Tm	GGA-PAW-Tm 3 , GGA-PAW-Tm	
Lu	PBE-PAW-Lu		
Os		GGA-PAW-Os pv	
Pb			LDA-US-Pb d
Pu	PBE-PAW-Pu,PBE-PAW-PU_s	GGA-PAW-Pu, GGA-PAW-Pu_s	LDA-US-Pu, LDA-US_Pu_s

D. Brillouinzones

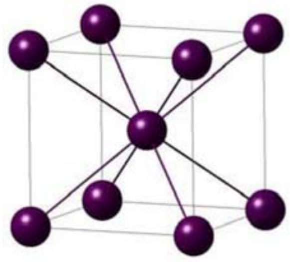
1. Face centered cubic

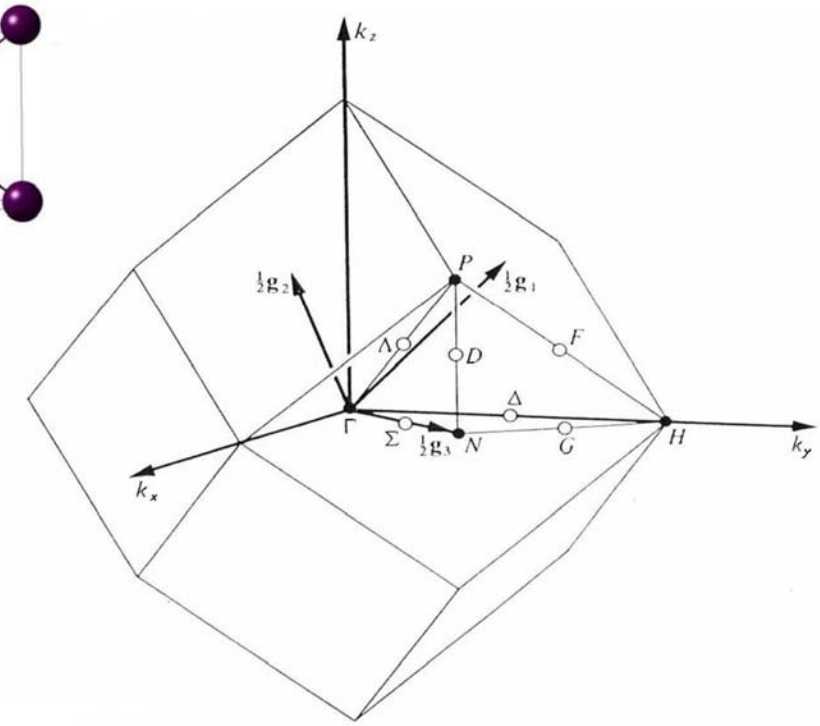




Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
L	$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$
X	$\frac{1}{2} \quad 0 \quad \frac{1}{2}$
W	$\frac{1}{2} \quad \frac{1}{4} \quad \frac{3}{4}$
K	$\frac{3}{8} \quad \frac{3}{8} \quad \frac{3}{4}$

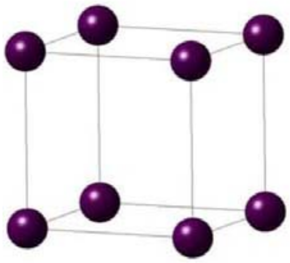
2. Body centered cubic

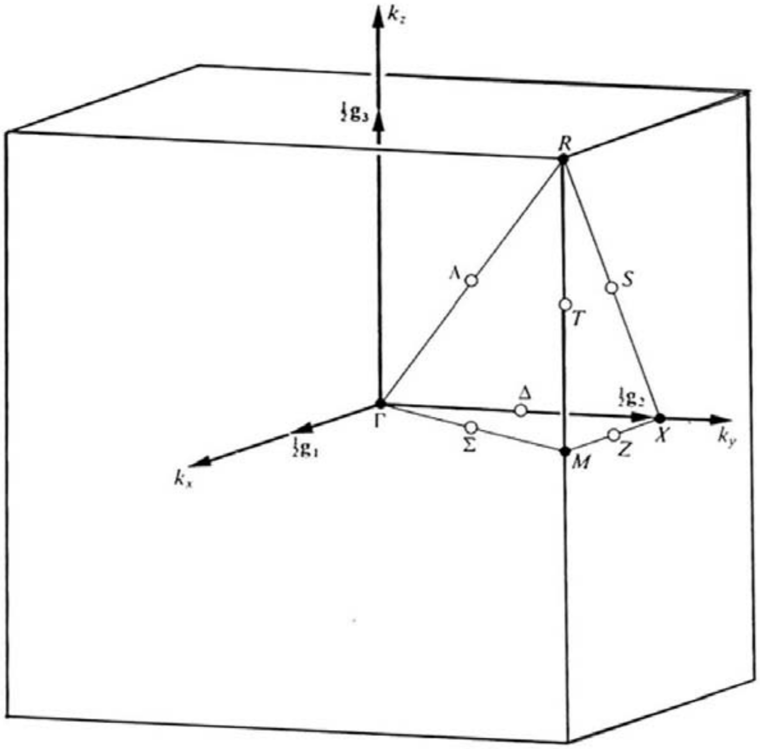




Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
H	$\frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2}$
P	$\frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4}$
N	$0 \quad 0 \quad \frac{1}{2}$

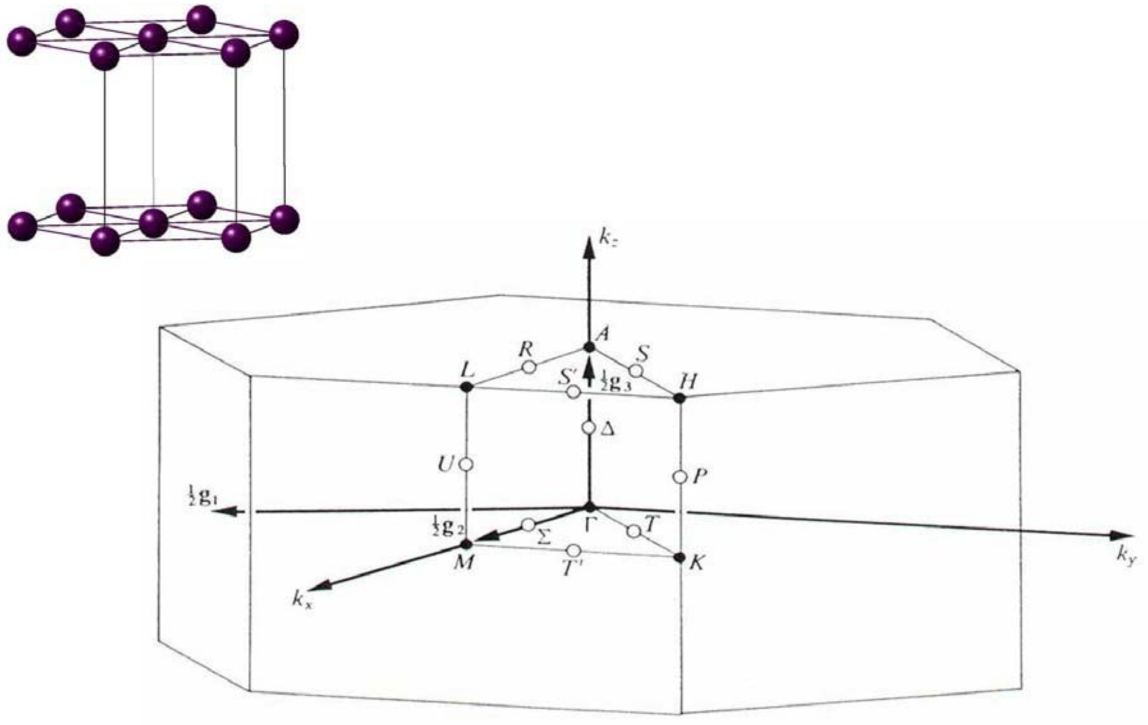
3. Simple cubic





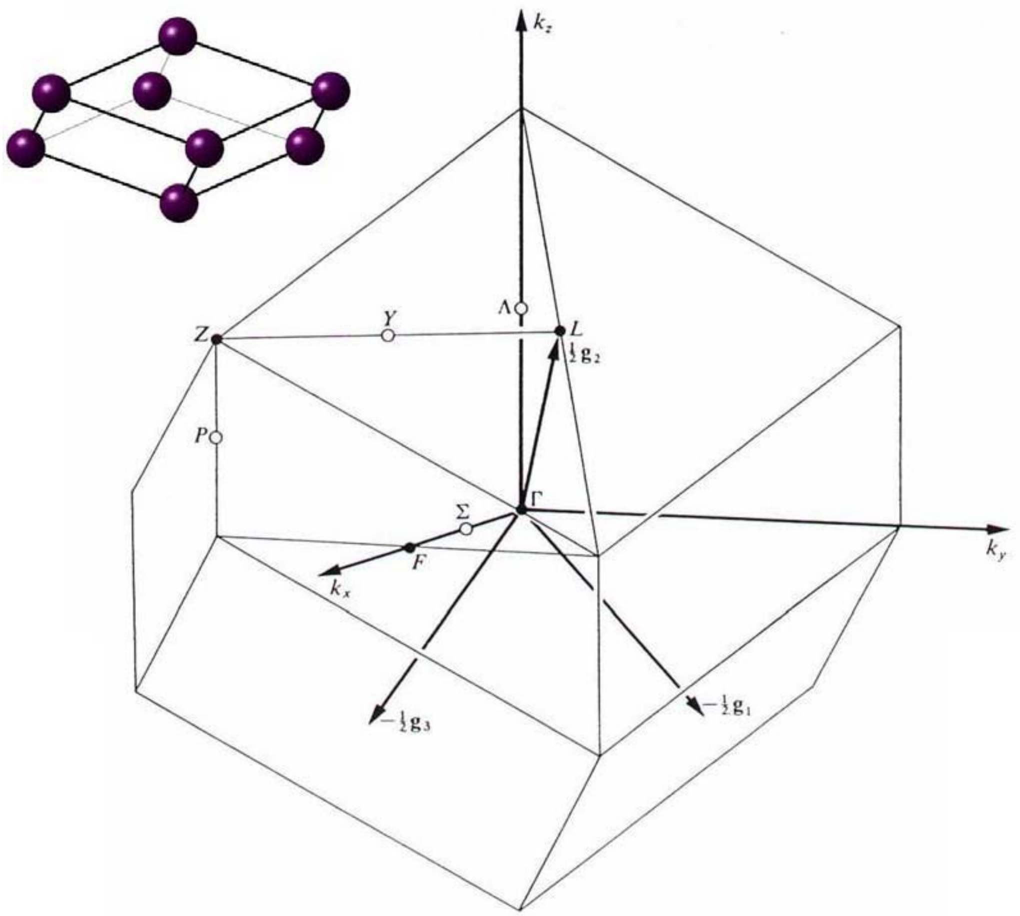
Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
X	0	$\frac{1}{2}$	0
M	$\frac{1}{2}$	$\frac{1}{2}$	0
R	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

4. Hexagonal



Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
A	$0 \quad 0 \quad \frac{1}{2}$
M	$0 \quad \frac{1}{2} \quad 0$
L	$0 \quad \frac{1}{2} \quad \frac{1}{2}$
K	$-\frac{1}{3} \quad \frac{2}{3} \quad 0$
H	$-\frac{1}{3} \quad \frac{2}{3} \quad \frac{1}{2}$

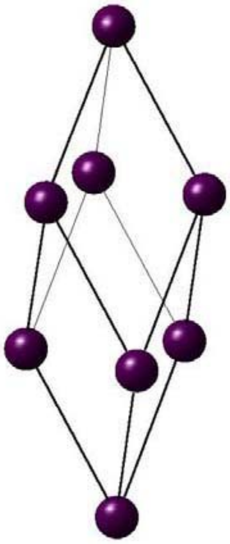
5. Rhombohedral for √2c<a

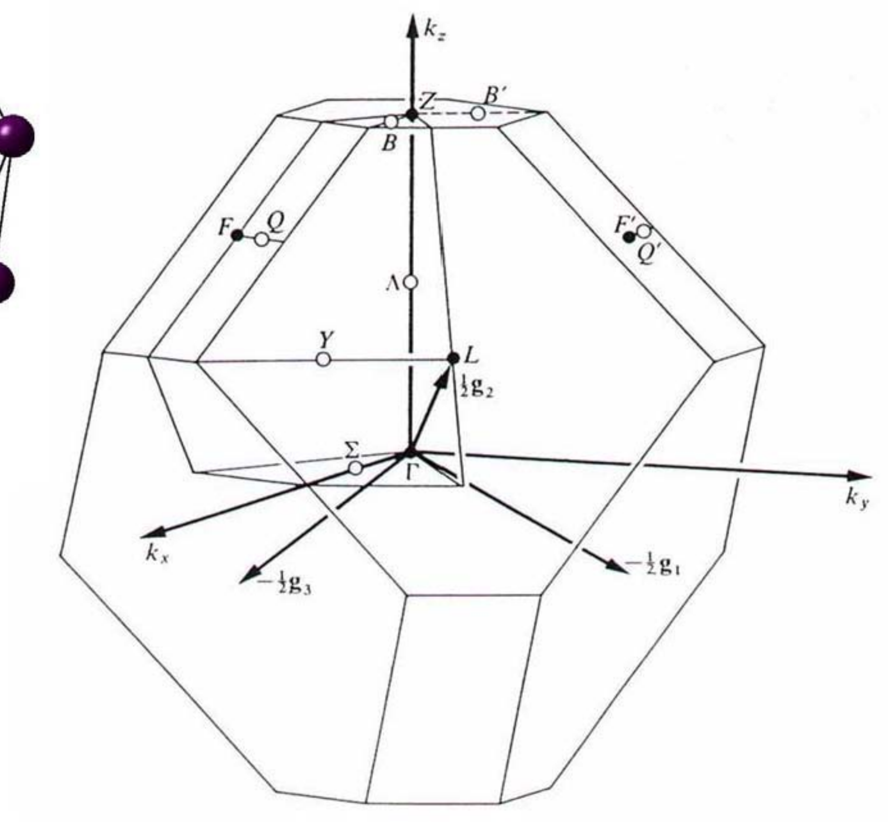


Condition: $\sqrt{2}c < a$

Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
Z	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
L	0	$\frac{1}{2}$	0
F	0	$\frac{1}{2}$	$\frac{1}{2}$

6. Rhombohedral for √2c>a

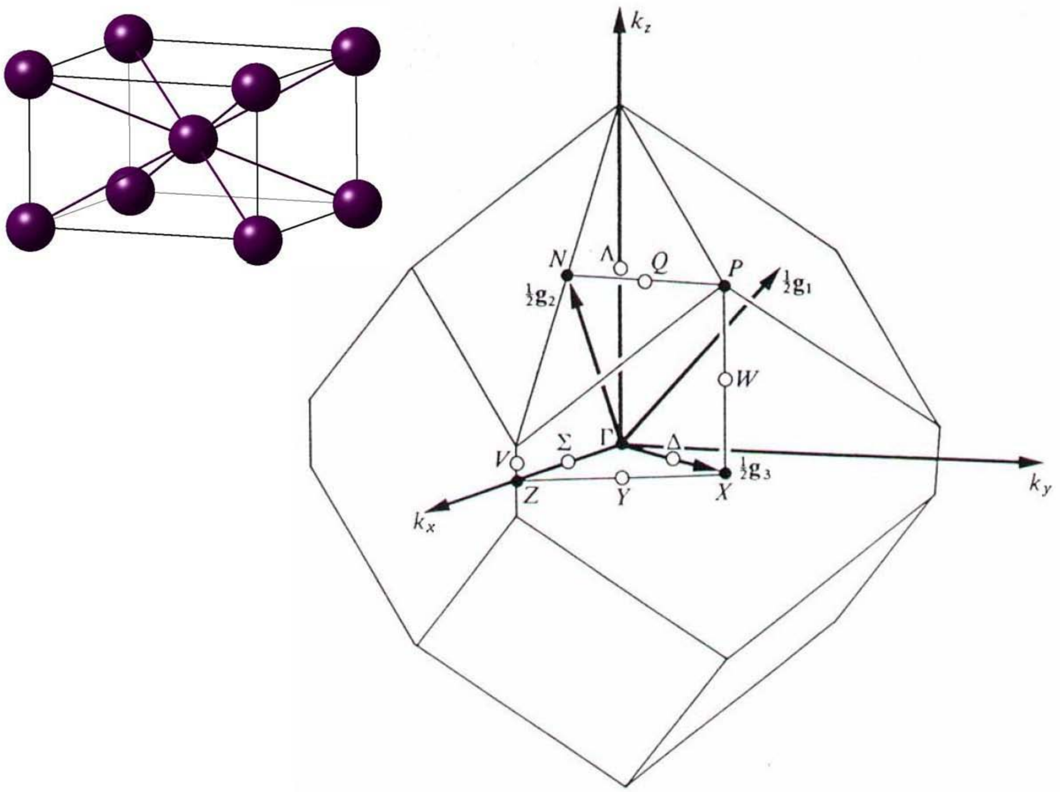




Condition: $\sqrt{2}c > a$

Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
Z	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
L	0	$\frac{1}{2}$	0
F	$\frac{1}{2}$	$\frac{1}{2}$	0

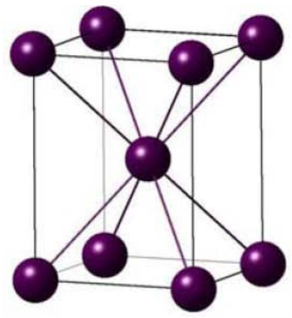
7. Body centered tetragonal c<a

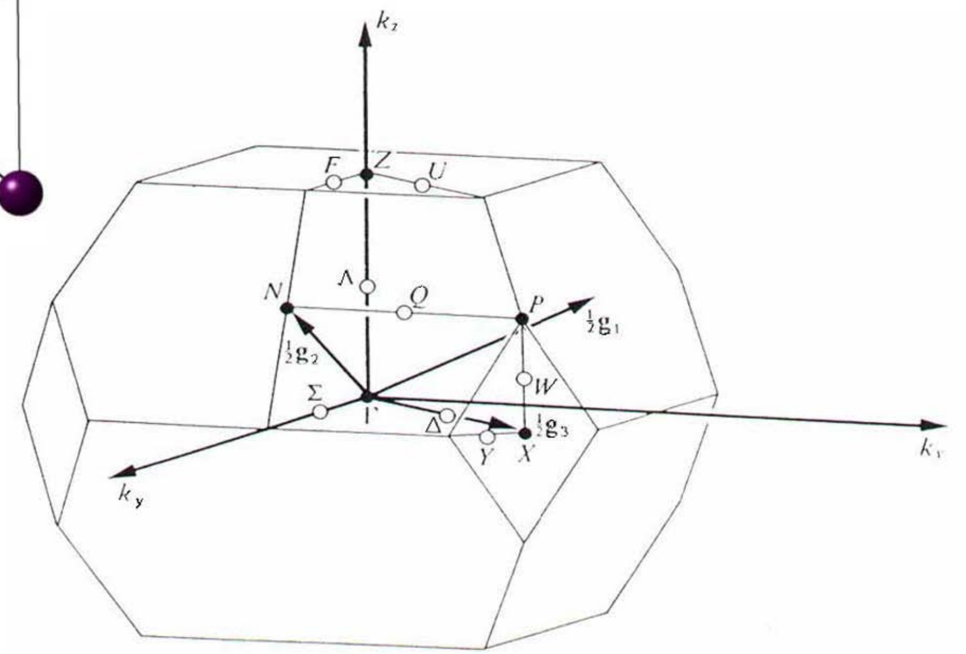


Condition: $c < a$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
N	$0 \quad \frac{1}{2} \quad 0$
X	$0 \quad 0 \quad \frac{1}{2}$
Z	$-\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$
P	$\frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4}$

8. Body centered tetragonal c>a

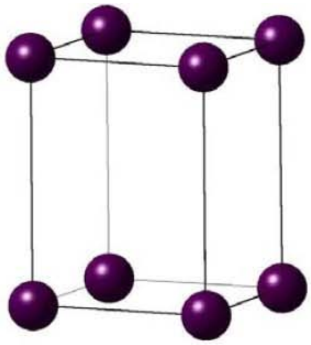


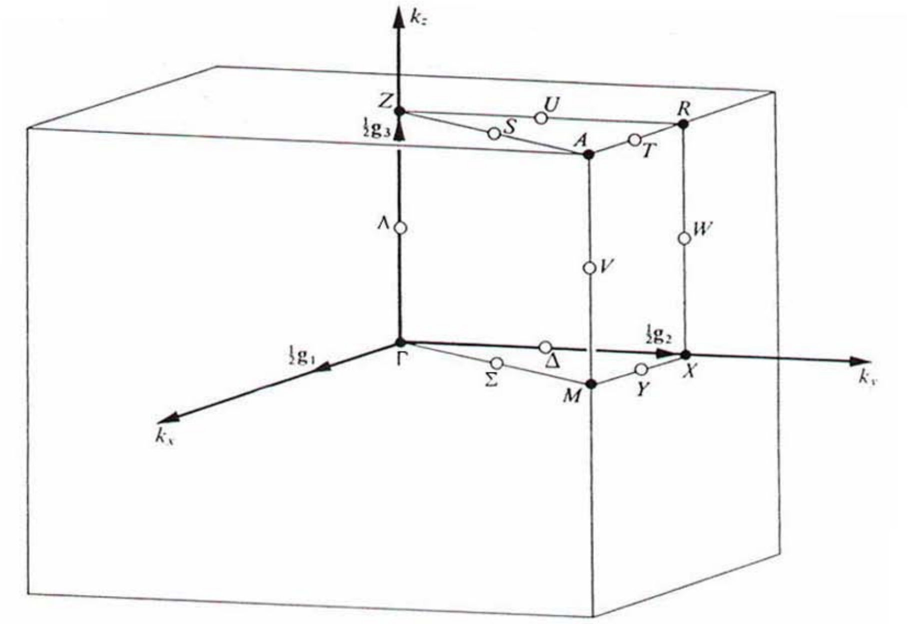


Condition: $c > a$

Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
N	0	$\frac{1}{2}$	0
X	0	0	$\frac{1}{2}$
Z	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
P	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$

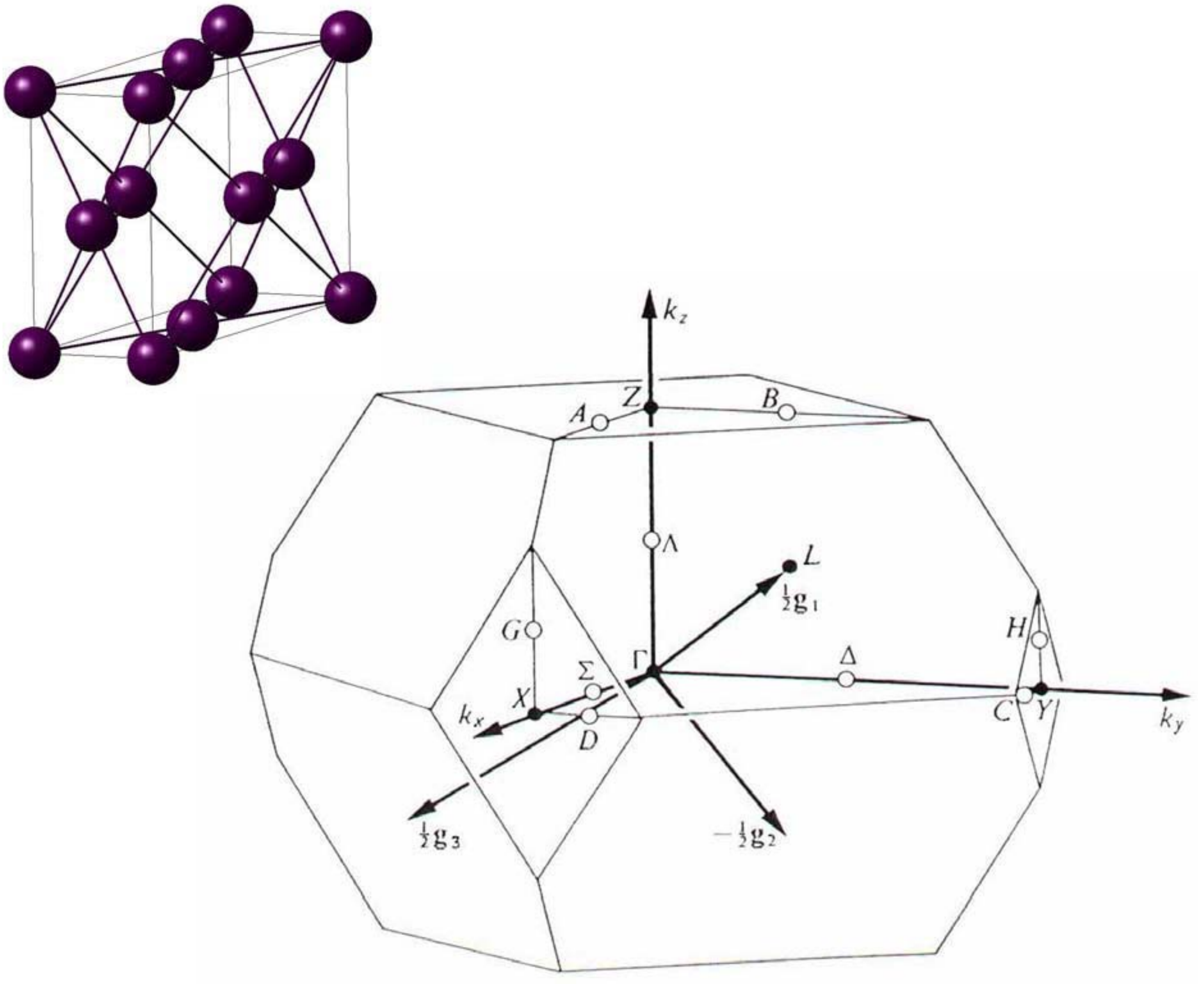
9. Simple tetragonal





Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
M	$\frac{1}{2}$	$\frac{1}{2}$	0
Z	0	0	$\frac{1}{2}$
A	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
R	0	$\frac{1}{2}$	$\frac{1}{2}$
X	0	$\frac{1}{2}$	0

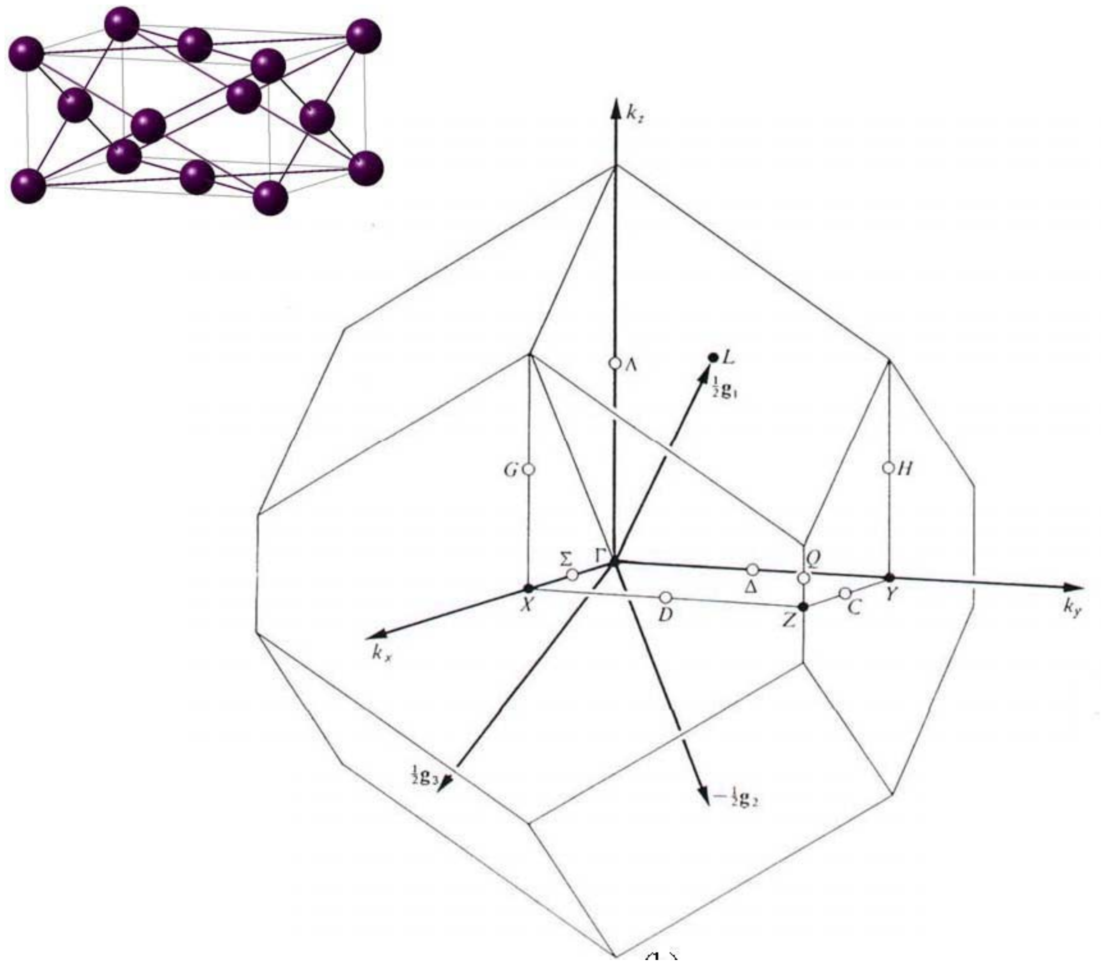
10. Face centered orthorhombic $1/a^2 < (1/b^2+1/c^2)$, $1/b^2 < (1/c^2+1/a^2)$, and $1/c^2 < (1/a^2+1/b^2)$



Condition: $\frac{1}{a^2} < \left(\frac{1}{b^2} + \frac{1}{c^2}\right)$, $\frac{1}{b^2} < \left(\frac{1}{c^2} + \frac{1}{a^2}\right)$, and $\frac{1}{c^2} < \left(\frac{1}{a^2} + \frac{1}{b^2}\right)$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
Y	$0 \quad \frac{1}{2} \quad \frac{1}{2}$
X	$\frac{1}{2} \quad 0 \quad \frac{1}{2}$
Z	$\frac{1}{2} \quad -\frac{1}{2} \quad 0$
L	$\frac{1}{2} \quad 0 \quad 0$

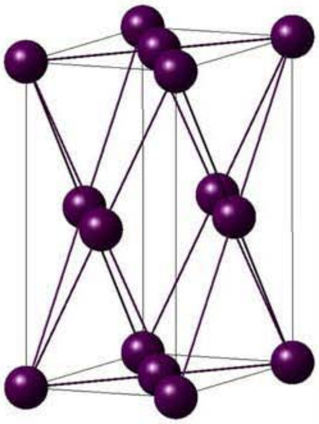
11. Face centered orthorhombic with $1/c^2 < (1/a^2+1/b^2)$

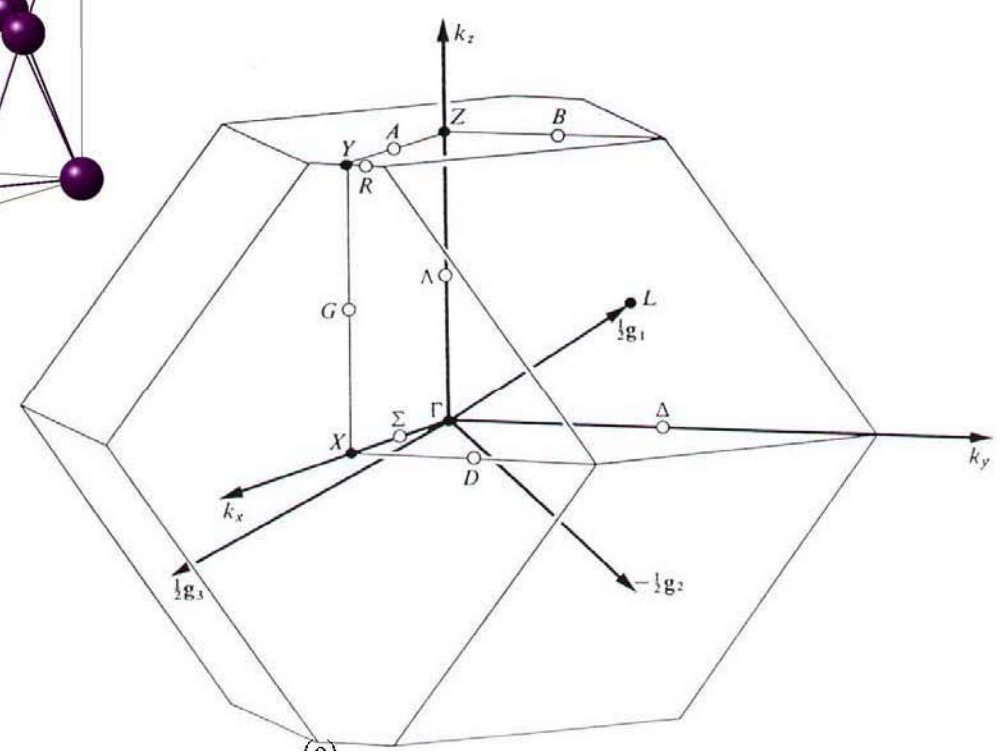


Condition: $\frac{\mathbf{1}}{\boldsymbol{c}^{\mathbf{2}}} > \left(\frac{\mathbf{1}}{\boldsymbol{a}^{\mathbf{2}}} + \frac{\mathbf{1}}{\boldsymbol{b}^{\mathbf{2}}}\right)$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
Y	$0 \quad -\frac{1}{2} \quad -\frac{1}{2}$
X	$\frac{1}{2} \quad 0 \quad \frac{1}{2}$
Z	$\frac{1}{2} \quad \frac{1}{2} \quad 0$
L	$\frac{1}{2} \quad 0 \quad 0$

12. Face centered orthorhombic with $1/b^2 < (1/a^2+1/c^2)$

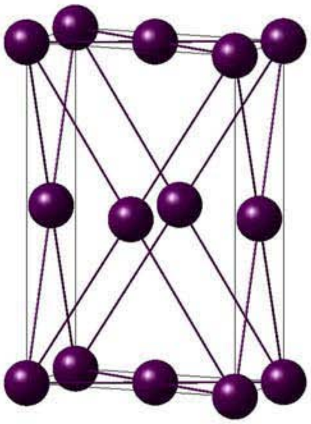


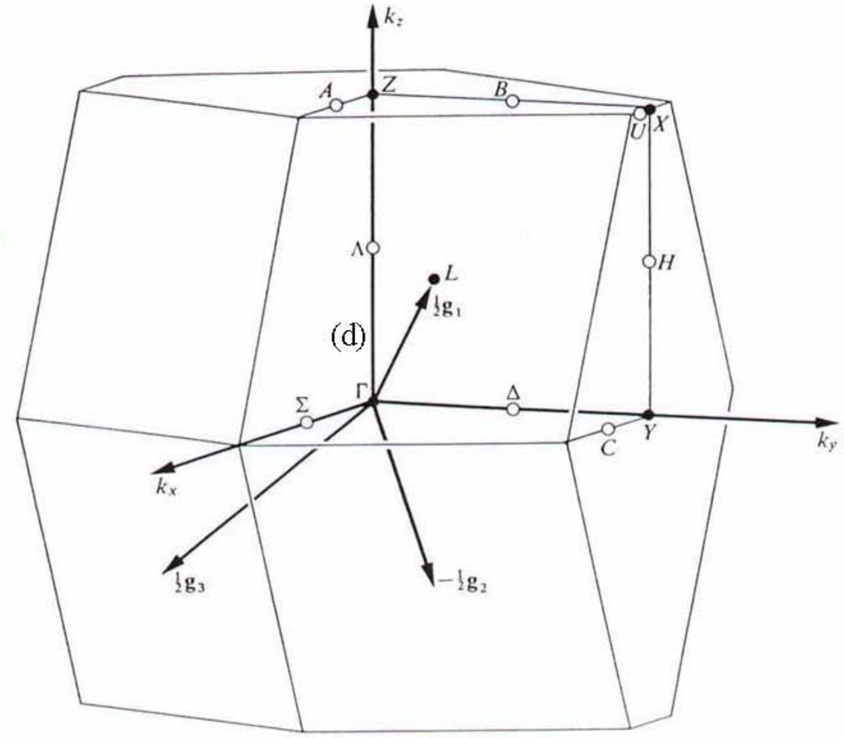


Condition: $\frac{\mathbf{1}}{\boldsymbol{b}^2} > (\frac{\mathbf{1}}{\boldsymbol{a}^2} + \frac{\mathbf{1}}{\boldsymbol{c}^2})$

Point	Coordinates (g_1, g_2, g_3)
Γ	0 0 0
Y	$1 \quad -\frac{1}{2} \quad -\frac{1}{2}$
X	$\frac{1}{2} \quad 0 \quad \frac{1}{2}$
Z	$\frac{1}{2} \quad \frac{1}{2} \quad 0$
L	$\frac{1}{2} \quad 0 \quad 0$

13. Face centered orthorhombic with $1/a^2 < (1/b^2+1/c^2)$

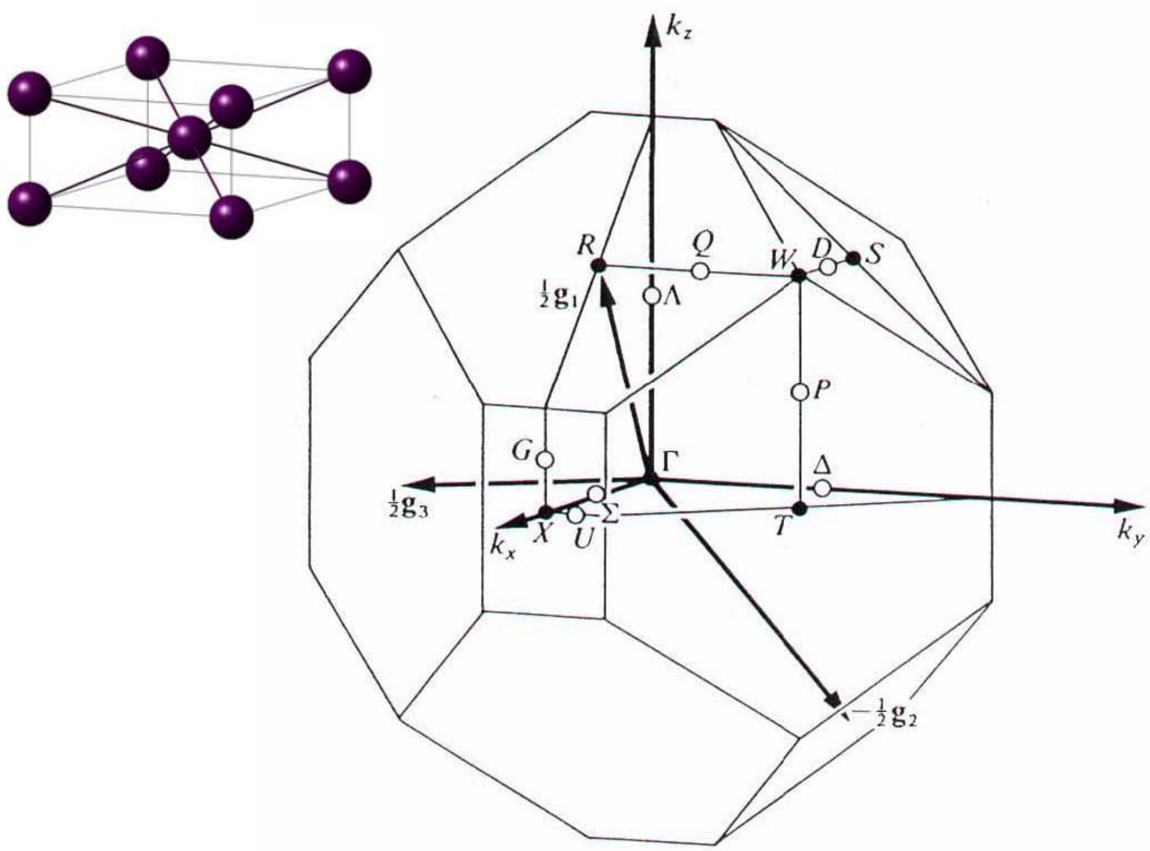




Condition: $\frac{\mathbf{1}}{\boldsymbol{a}^2} > (\frac{\mathbf{1}}{\boldsymbol{b}^2} + \frac{\mathbf{1}}{\boldsymbol{c}^2})$

Point	**Coordinates (g_1, g_2, g_3)**
Γ	$0 \quad 0 \quad 0$
Y	$0 \quad -\frac{1}{2} \quad -\frac{1}{2}$
X	$\frac{1}{2} \quad 0 \quad -\frac{1}{2}$
Z	$\frac{1}{2} \quad \frac{1}{2} \quad 0$
L	$\frac{1}{2} \quad 0 \quad 0$

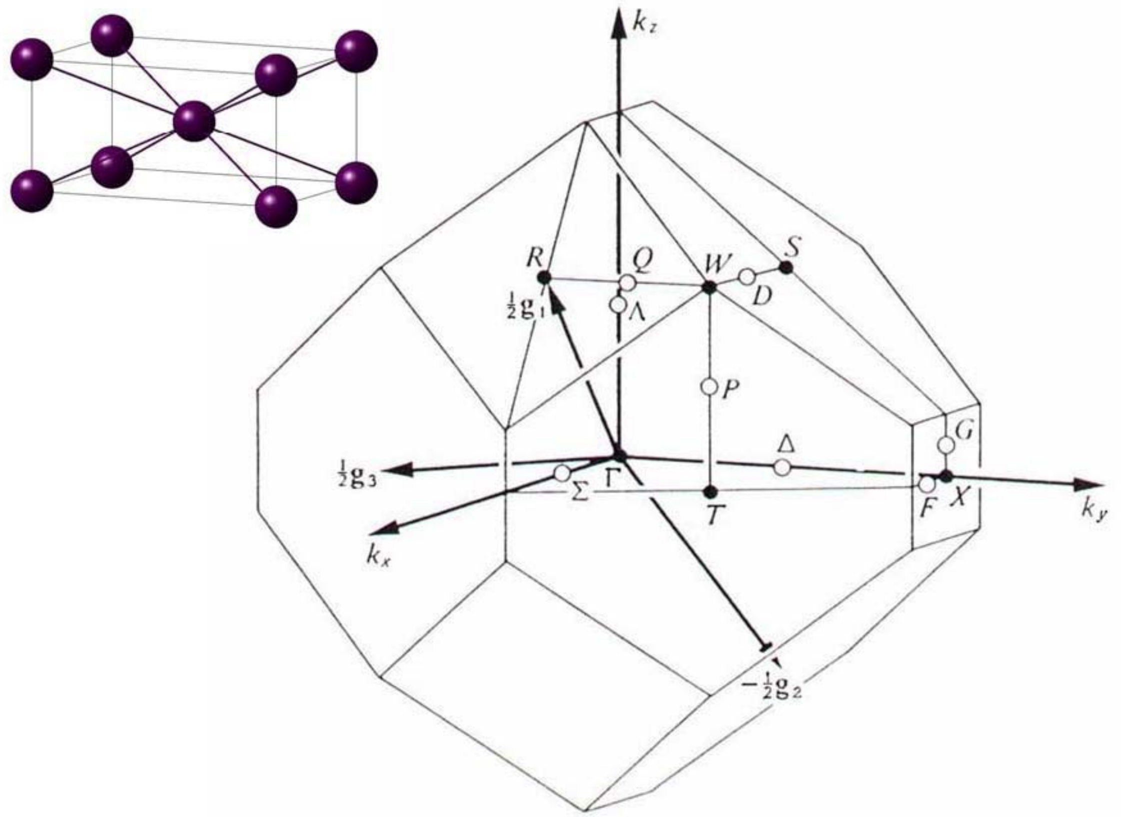
14. Body centered orthorhombic for a>b>c or a>c>b



Condition: $a > b > c$ or $a > c > b$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
X	$\frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2}$
R	$\frac{1}{2} \quad 0 \quad 0$
S	$\frac{1}{2} \quad 0 \quad -\frac{1}{2}$
T	$\frac{1}{2} \quad -\frac{1}{2} \quad 0$
W	$\frac{3}{4} \quad -\frac{1}{4} \quad -\frac{1}{4}$

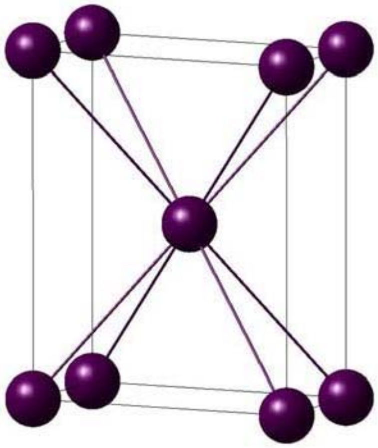
15. Body centered orthorhombic for b>a>c or b>c>a

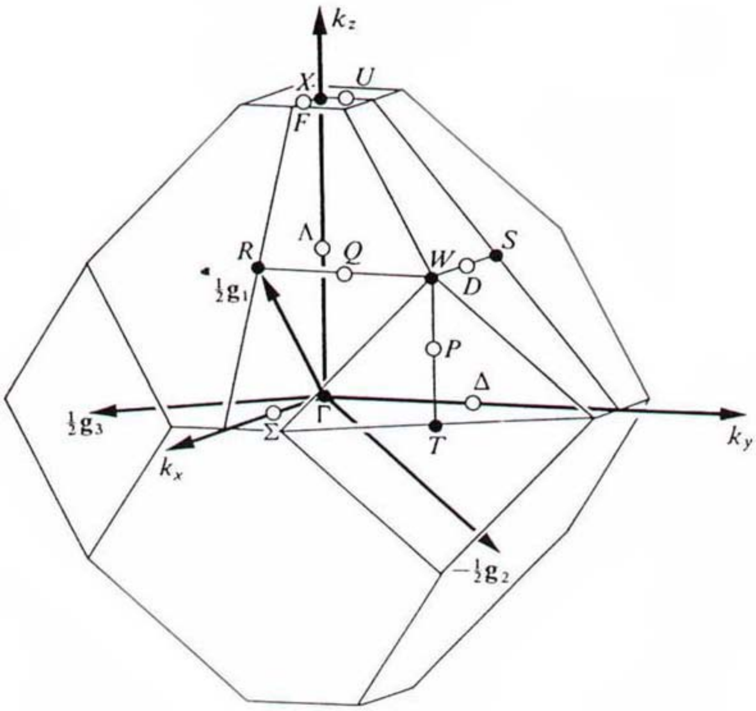


Condition: $b > a > c$ or $b > c > a$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
X	$\frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2}$
R	$\frac{1}{2} \quad 0 \quad 0$
S	$\frac{1}{2} \quad 0 \quad -\frac{1}{2}$
T	$\frac{1}{2} \quad -\frac{1}{2} \quad 0$
W	$\frac{3}{4} \quad -\frac{1}{4} \quad -\frac{1}{4}$

16. Body centered orthorhombic for c>b>a or c>a>b

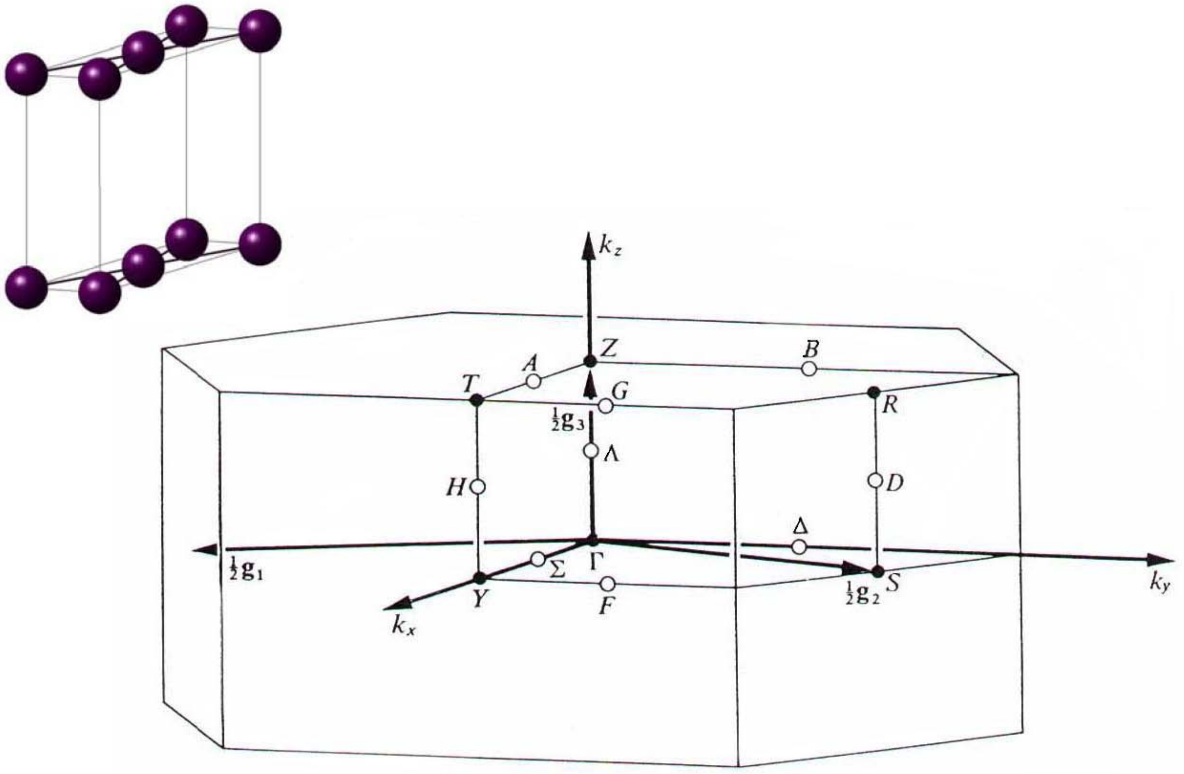




Condition: $c > b > a$ or $c > a > b$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
X	$\frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2}$
R	$\frac{1}{2} \quad 0 \quad 0$
S	$\frac{1}{2} \quad 0 \quad -\frac{1}{2}$
T	$\frac{1}{2} \quad -\frac{1}{2} \quad 0$
W	$\frac{3}{4} \quad -\frac{1}{4} \quad -\frac{1}{4}$

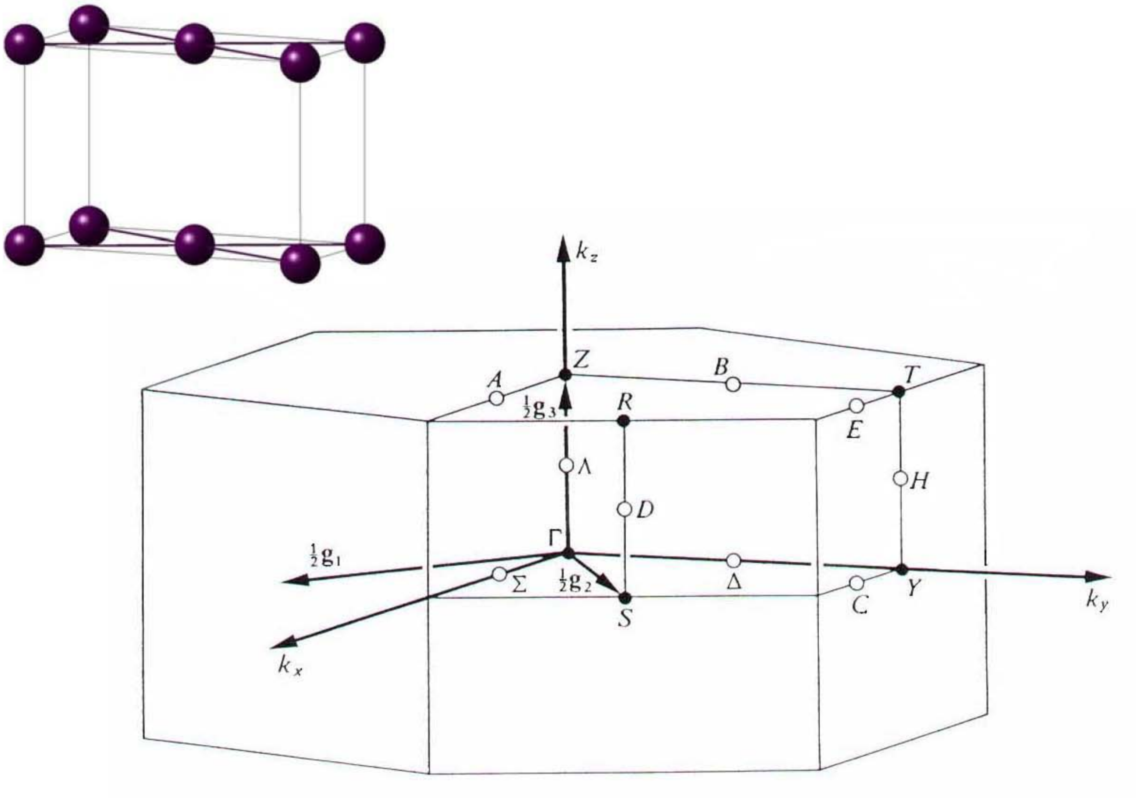
17. Base centered orthorhombic a>b



Condition: $a > b$

Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
Y	$\frac{1}{2}$	$\frac{1}{2}$	0
Z	0	0	$\frac{1}{2}$
T	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
S	0	$\frac{1}{2}$	0
R	0	$\frac{1}{2}$	$\frac{1}{2}$

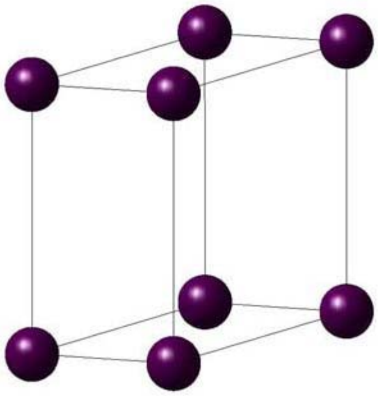
18. Base centered orthorhombic b>a

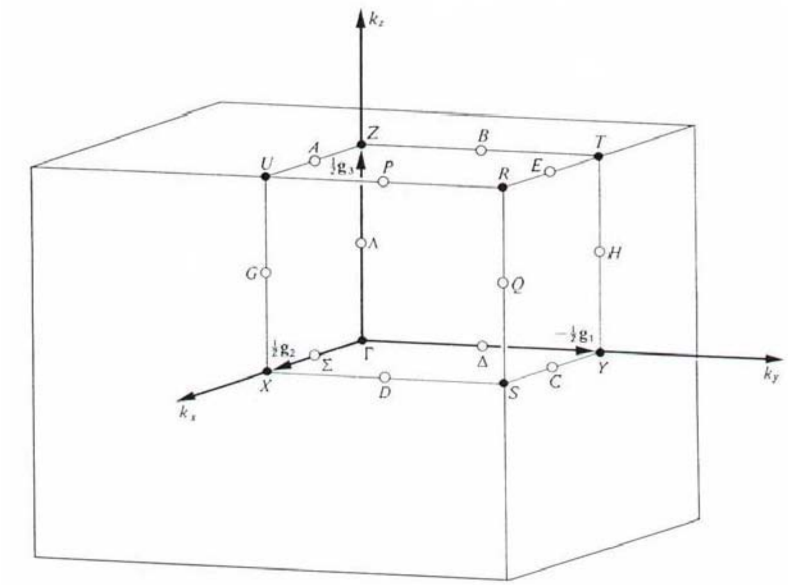


Condition: $b > a$

Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
Y	$-\frac{1}{2} \quad \frac{1}{2} \quad 0$
Z	$0 \quad 0 \quad \frac{1}{2}$
T	$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$
S	$0 \quad \frac{1}{2} \quad 0$
R	$0 \quad \frac{1}{2} \quad \frac{1}{2}$

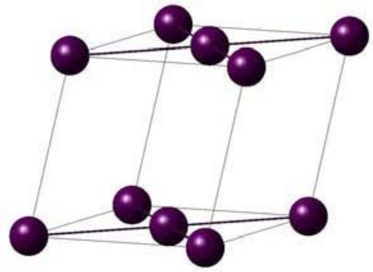
19. Simple orthorhombic

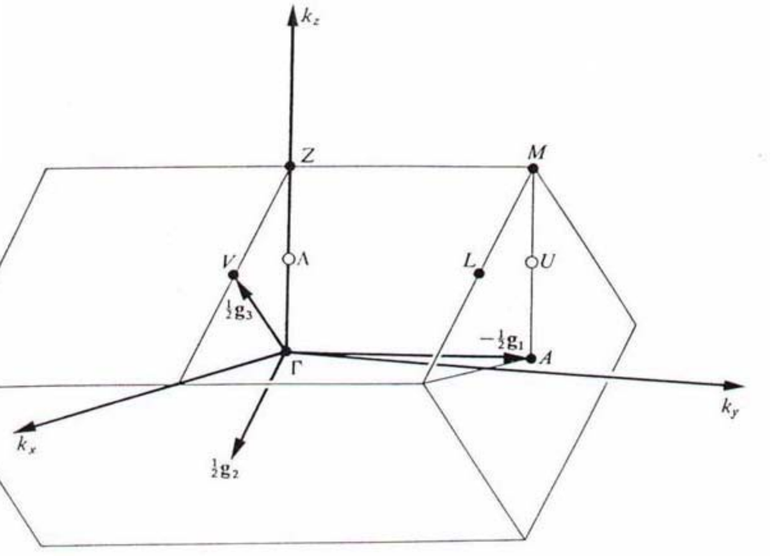




Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
Y	$-\frac{1}{2} \quad 0 \quad 0$
X	$0 \quad \frac{1}{2} \quad 0$
Z	$0 \quad 0 \quad \frac{1}{2}$
U	$0 \quad \frac{1}{2} \quad \frac{1}{2}$
T	$-\frac{1}{2} \quad 0 \quad \frac{1}{2}$
S	$-\frac{1}{2} \quad \frac{1}{2} \quad 0$
R	$-\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$

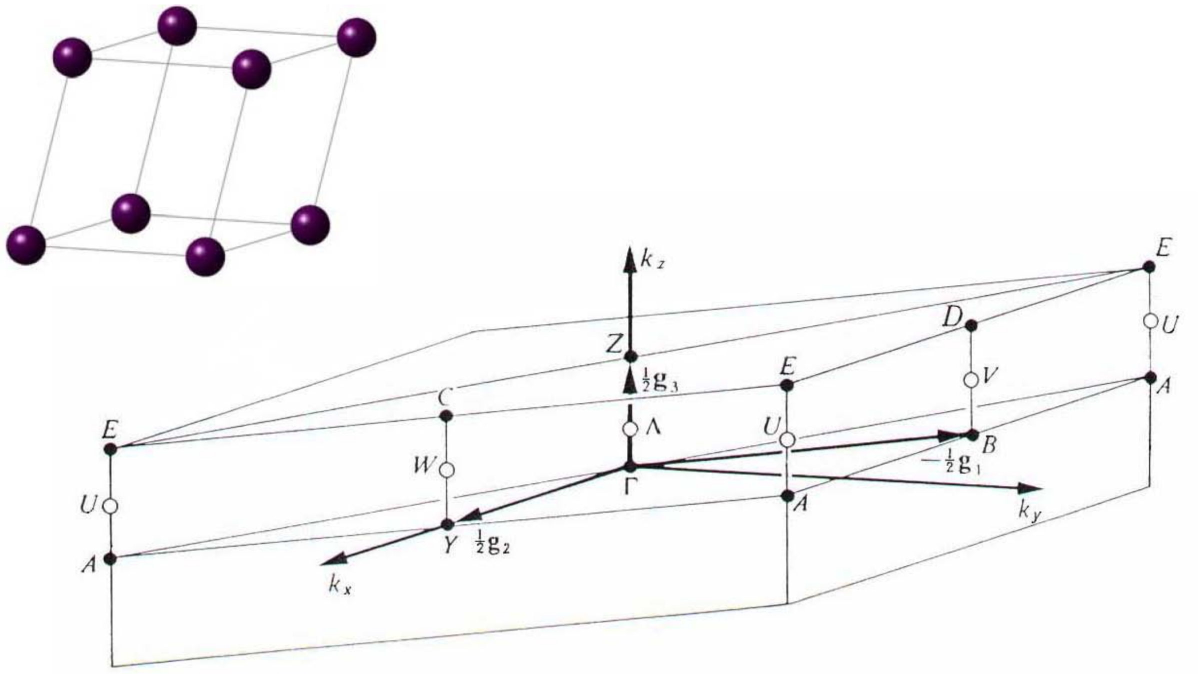
20. Base centered monoclinic





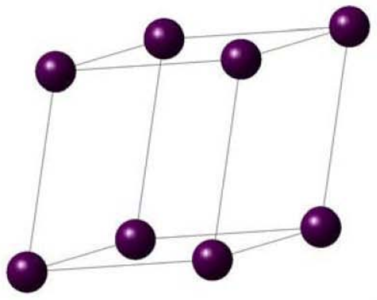
Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
A	$-\frac{1}{2} \quad 0 \quad 0$
Z	$0 \quad -\frac{1}{2} \quad \frac{1}{2}$
M	$-\frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2}$
L	$-\frac{1}{2} \quad 0 \quad \frac{1}{2}$
V	$0 \quad 0 \quad \frac{1}{2}$

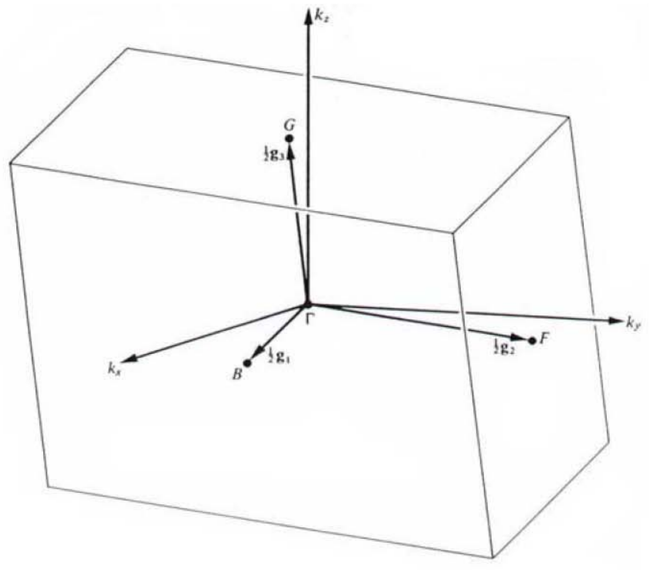
21. Simple monoclinic



Point	Coordinates (g_1, g_2, g_3)
Γ	$0 \quad 0 \quad 0$
B	$-\frac{1}{2} \quad 0 \quad 0$
Y	$0 \quad \frac{1}{2} \quad 0$
Z	$0 \quad 0 \quad \frac{1}{2}$
C	$0 \quad \frac{1}{2} \quad \frac{1}{2}$
D	$-\frac{1}{2} \quad 0 \quad \frac{1}{2}$
A	$-\frac{1}{2} \quad \frac{1}{2} \quad 0, -\frac{1}{2} \quad -\frac{1}{2} \quad 0, \frac{1}{2} \quad \frac{1}{2} \quad 0$
E	$-\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}, -\frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2}, \frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2}$

22. Triclinic





Point	Coordinates (g_1, g_2, g_3)		
Γ	0	0	0
B	$\frac{1}{2}$	0	0
F	0	$\frac{1}{2}$	0
G	0	0	$\frac{1}{2}$

E. Bibliography

1. **Barber, C B, Dobkin, D P and Huhdanpaa, H T.** The Quickhull algorithm for convec hulls. *ACM Trans. on Mathematical Software.* 1996, Vol. 22, 4, pp. 469-483. http://www.qhull.org.

2. **Kresse, G and Furthmüller, J.** *Phys. Rev. B.* 1996, Vol. 54, p. 11169.

3. **Kohn, W and Sham, L.** *Phys. Rev. A.* 1965, Vol. 140, p. 1133.

4. **Kresse, G and Joubert, D.** *Phys. Rev. B.* 1999, Vol. 59, p. 1758.

5. **Kresse, G and Furthmüller, J.** *Comput. Mat. Sci.* 1996, Vol. 6, p. 15.

6. **Blöchl, P E.** *Phys. Rev. B.* 1994, Vol. 50, p. 17953.

7. **Perdew, J B and Wang, Y.** *Phys. Rev.* 1992, Vol. B 45, p. 13244.

8. **Perdew, J B, Burke, K and M, Ernzerhof.** *Phys. Rev. Lett.* 1996, Vol. 77, p. 3865.

9. **Dudarev, S L, et al.** *Phys. Rev. B.* 1998, Vol. 57, p. 1505.

10. **Liechtenstein, A I, Anisimov, V I and Zaanen, J.** *Phys. Rev. B.* 1995, Vol. 52, p. R5467.

11. **Becke, A D and Edgecombe, K E J.** 1990, J. Chem. Phys., Vol. 92, p. 5397.

12. **Parlinski, K, Li, Z Q and Kawazoe, Y.** *Phys. Rev. Lett.* 1997, Vol. 78, p. 4063.

13. **Toulhoat, Hervé.** *Conception de nouveaux materiaux dont l'usage fait intervenir une liaison chimique au moyen d'un descripteur de ladite liaison. FR2810113* France, 12 13, 2001.

14. —. *Design of new materials whose use produces a chemical bond with a descriptor of said bond. 6799089* US, 9 28, 2004.

15. —. *Design of novel material having method of use to give rise to chemical bond by using descriptor of chemical bond. 2003053197* Japan, 2 25, 2003.

16. **Ungerer, P, et al.** 2000, J. Chem. Phys., Vol. 112, p. 5499.

17. **Bourasseau, E, Ungerer, P and Boutin, B.** 2002, J. Phys. Chem. B, Vol. 106, p. 5483.

18. **Möller D, Oprzynski J, Müller A, Fischer J.** 75, 1992, Mol. Phys., p. 363.

19. **Smit, B and Siepmann, J I.** 5162, 5 1994, Science, Vol. 264, pp. 1118--1120.

20. **Bourasseau, E, et al.** 7, 2003, J. Chem. Phys., Vol. 118, p. 3020.

21. **Contreras, O.** *Ph.D. Thesis.* Taragona : Departament d'Enginyeria Quimica de la Universitat Rovira i Virgili, 2002.

22. **Lachet, V, et al.** 106, 1997, Faraday Discuss, p. 307.

23. **Harris J G, Yung K H.** 1995, J. Phys. Chem., Vol. 99, p. 12021.

24. **Poling, B E, Prausnitz, J M and O'Connell, J P.** *The properties of gases and liquids, 5th Edition.* New York : Mac Graw Hill, 2001.

25. **Delhommelle, J, et al.** 104, 2000, Journal of Physical Chemistry B, pp. 4745–4753.

26. **Kranias, S, et al.** 5, 2003, Phys. Chem. Chem. Phys., p. 4175.

27. **Dang, L X and Kollman, P A.** 1995, J. Phys. Chem., Vol. 99, pp. 55-58.

28. **Di Lella, A, et al.** 46, 2006, Phys. Chem. Chem. Phys., Vol. 8, p. 5396.

29. **Hohenberg, P and Kohn, W.** *Phys. Rev.* 1964, Vol. B 136, p. 864.

30. **Thomas, L H.** *Proc. Camb. Phil. Soc.* 1926, Vol. 23, p. 542.

31. **Fermi, E.** *Z. Phys.* 1928, Vol. 48, p. 73.

32. **Hartree, D R.** *Proc. Camb. Phil. Soc.* 1928, Vol. 24, p. 89.

33. **Fock, V.** *Z. Phys.* 1930, Vol. 62, p. 795.

34. **—.** *Z. Phys.* 1930, Vol. 61, p. 126.

35. **Slater, J C.** *Phys. Rev.* 1951, Vol. 385, p. 385.

36. **—.** *Quantum Theory of Molecules and Solids.* New York : McGraw-Hill, 1974.

37. **Hedin, L and Lundqvist, B I.** *J. Phys. C.* 1971, Vol. 4, p. 2064.

38. **Hedin, L and Lundqvist, S J.** *J Phys (France).* 1972, Vol. 33, pp. C3-73.

39. **Ceperley, D M and Alder, B J.** *Phys. Rev. Lett.* 1980, Vol. 45, p. 566.

40. **Gáspár, R.** *Acta Phys Acad Sci Hung.* 1954, Vol. 3, p. 263.

41. **Janak, J F.** *Phys. Rev. B.* 1978, Vol. 18, p. 7165.

42. **Hybertsen, M S and Louie, S G.** *Phys. Rev. Lett.* 1985, Vol. 55, p. 1418.

43. **Schulte, F K.** *Z. Phys.* 1977, Vol. B27, p. 303.

44. **von Barth, J and Hedin, L.** *J. Phys. C.* 1972, Vol. C5, p. 1629.

45. **Gunnarson, O, I, Lundqvist B and S, Lundqvist.** *Solid State Communications.* 1972, Vol. 11, p. 149.

46. **Perdew, J P.** *Phys. Rev.* 1986, Vol. B 33, p. 8822.

47. **Becke, A D.** Density-functional exchange-energy appromixmation with correct asymptotic behavior. *Phys. Rev. A.* 1988, Vol. 38, pp. 3098-3100.

48. **Andzelm, J and Wimmer, E.** *J.. Chem. Phys.* 1992, Vol. 96, p. 1280.

49. **Bjorken, J D and Drell, S D.** *Relativistic Quantum Mechanics.* New York : McGraw-Hill, 1965.

50. —. *Relativistic Quantum Fields.* New York : McGraw-Hill, 1964.

51. **Messiah, A.** *Quantum Mechanics Vol. II.* Amsterdam : North-Holland, 1970.

52. **Koelling, D D and Harmon, B N.** *J. Phys. C.* 1977, Vol. C 10, p. 3107.

53. **Kirkwood, J G and Oppenheim, I.** *Chemical Thermodynamics.* New York : McGraw-Hill, 1961.

54. **Gibbs, J W.** Vol. *The Collected Works of J Willard Gibbs.* 1957, Vol. 1, Thermodynamics.

55. **Le Page, Y and Saxe, P.** *Phys. Rev.* 2001, Vol. B 63, p. 174103.

56. —. *Phys. Rev.* 2002, Vol. B 65, p. 104104.

57. **Anderson, O L.** *J. Phys. Chem. Solids.* 1963, Vol. 24, pp. 909-917.

58. **Grüneisen, E.** *Handbuch der Physik.* Berlin : Springer Verlag, 1928, Vol. X.

59. **Mayer, B, et al.** *Intermetallics.* 2003, Vol. 11, 1, pp. 23-32.

60. **Ashcroft, N and Mermin, N D.** *Solid State Physics.* s.l. : Saunders College Publishing, 1976. p. 458.

61. **Born, M and Huang, K.** *Dynamical Theory of Crystal Lattices.* Oxford : Oxford University Press, 1954.

62. **Dick, B G and Overhauser, A W.** *Phys. Rev.* 1958, Vol. 112, p. 90.

63. **Cochran, W.** *Phys. Rev. Lett.* 1959, Vol. 2, p. 495.

64. **Schröder, U.** *Solid State Commun.* 1966, Vol. 4, p. 347.

65. **Keating, P N.** *Phys. Rev.* 1966, Vol. 145, p. 637.

66. **Martin, R M.** *Phys. Rev.* 1969, Vol. 186, p. 871.

67. **Weber, W.** *Phys. Rev. B.* 1977, Vol. 15, p. 4789.

68. **Pick, R, Cohen, M H and Martin, R.** *Phys. Rev. B.* 1970, Vol. 1, p. 910.

69. **De Cicco, P D and Johnson, F A.** *Proc. R. Soc. London.* 1969, Vol. Ser. A 310, p. 111.

70. **Rahman, A.** *Phys. Rev. A.* 1964, Vol. 136, p. 405.

71. **Martyna, G J, Klein, M L and Tuckerman, M.** *J. Chem. Phys.* 1992, Vol. 97, p. 2635.

72. **Lawrence Marple Jr, S.** *Digital Spectral Analysis with Applications.* Engelwood Cliffs, NJ : Prentice-Hall, 1987.

73. **Kohanoff, J and Andreoni, W, Parinello, M.** *Phys. Rev. B.* 1992, Vol. 46, p. 4371.

74. **Kohanoff, J.** *Comput. Mater. Sci.* 1994, Vol. 2, p. 221.

75. **Gonze, X and P, Vigneron J.** *Phys. Rev. B.* 1989, Vol. 39, p. 13120.

76. **Baroni, S, Giannozzi, P and Testa, A.** *Phys. Rev. Lett.* 1987, Vol. 58, p. 1861.

77. **Giannozzi, P, et al.** *Phys. Rev. B.* 2001, Vol. 43, p. 7231.

78. **Baroni, S, et al.** *Rev. Mod. Phys.* 2001, Vol. 73, p. 515.

79. **Yin, M T and Cohen, M L.** *Phys. Rev. B.* 1982, Vol. 26, p. 3259.

80. **Kunc, K and Martin, R M.** *Phys. Rev. Lett.* 1982, Vol. 48, p. 406.

81. **Wei, S and Chou, M Y.** *Phys. Rev. Lett.* 1992, Vol. 69, p. 2799.

82. —. *Phys. Rev. B.* 1994, Vol. 50, p. 2221.

83. **Kresse, G, Furthmüller, J and Hafner, J.** *Europhys. Lett.* 1995, Vol. 32, p. 729.

84. **Frank, W, Elsässer, C and Fähnle, M.** *Phys. Rev. Lett.* 1995, Vol. 74, p. 1791.

85. **Kresse, G and Hafner, J.** *Phys. Rev. B.* 1994, Vol. 49, p. 14251.

86. —. *Phys. Rev. B.* 1993, Vol. 47, p. 558.

87. **Pavone, P.** *J. Phys.: Condens. Matter.* 2001, Vol. 13, p. 7593.

88. **Ackland, G J, Warreny, M C and Clark, S J.** *J. Phys.: Condens. Matter.* 1997, Vol. 9, p. 7861.

89. **Press, W H, et al.** *Numerical Recipes.* Cambridge : Cambridge University Press, 1992. p. 670.

90. **Finnis, M W, Lozovoi, A Y and Alavi, A.** *Annu. Rev. Mater. Res.* 2005, Vol. 35, p. 167.

91. **Gilman, J J and Robert, B W.** *J Appl Phys.* 1961, Vol. 32, p. 1405.

92. **Spoor, P S, et al.** *Appl. Phys. Lett.* 1997, Vol. 70, p. 1959.

93. **Peroraro, T A and Chianelli, R R.** *J. Catalysis.* 1989, Vol. 67, p. 430.

94. **Ledoux, M J, et al.** *J. Catalysis.* 1986, Vol. 102, p. 275.

95. **Toulhoat, H, et al.** *Catalysis Today.* 1999, Vol. 50, pp. 629-636.

96. **Toulhoat, H and Raybaud, P.** *J. Catalysis.* 2003, Vol. 216, 1-2, pp. 63-72.

97. **Schweiger, H, Raybaud, P and Toulhoat, H.** *J. Catalysis.* 2002, Vol. 212, pp. 33-38.

98. *NIST-JANAF thermochemical tables.* **Chase, M W.** Gaithersburg, MD : AIP for NIST, 1998, J Physical and Chemical Reference data, Vol. 9.

99. **Cox, J D, Wagman, DD and Medvedev, V A.** *CODATA Key Values for Thermodynamics.* New York : Hemisphere Publishing, 1084.

100. **Kerr, R M.** [ed.] D R Lide. *CRC Handbook of Chemistry and Physics.* Boca Raton : CRC Press, 1999.

101. **Huber, K P and Herzberg, G.** *Molecular Spectra and Molecular Structure.* New York : Von Nostrand, Reinhold, 1979. Vol. IV Constants of Diatomic Molecules.

102. **Aruja, E and Perlitz, H.** *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* 1939, Vol. 100, p. 157.

103. **Wallace, W E and Barrett, W E.** *J Am Chem Soc.* 1954, Vol. 76, p. 366.

104. **Weinert, M, Wimmer, E and Freeman, A J.** *Phys Rev B.* 1982, Vol. 26, p. 4571.

105. *An Atomistic Modeling Study of Alloying Element, Impurity Element, and Transmutation Products on the Cohesion of a Nickel Σ5 {001} Twist Grain Boundary.* **Young, G A, Jr., et al.** Stevenson, WA : s.n., 2003. 11th International Conference on Environmental Degradation of Materials in Nuclear Power System - Water Reactors.

106. **Christensen, M and Wahnström, G.** Effects of Cobalt intergranular segregation on interface energetics in WC-Co. *Acta Materialia.* 2004, Vol. 53, pp. 2199-2207.

107. **Fawcett, E, et al.** *Rev Mod Phys.* 1994, Vol. 66, pp. 25-127.

108. **Dutchak, Y I and Checkh, V G.** High Temperature X-ray Diffraction Study of Cr-V and Cr-Mo Solid Solution. 1982, pp. 169-174.

109. **Bolef, D I and de Klerk, J.** Anomalies in the Elastic Constants and Thermal Expansion of Chromium Single Crystals. *Phys. Rev.* 1963, Vol. 129, pp. 1063-1067.

110. **Nosé, S.** *Proc. Theor. Phys. Suppl.* 1991, Vol. 103, 1.

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