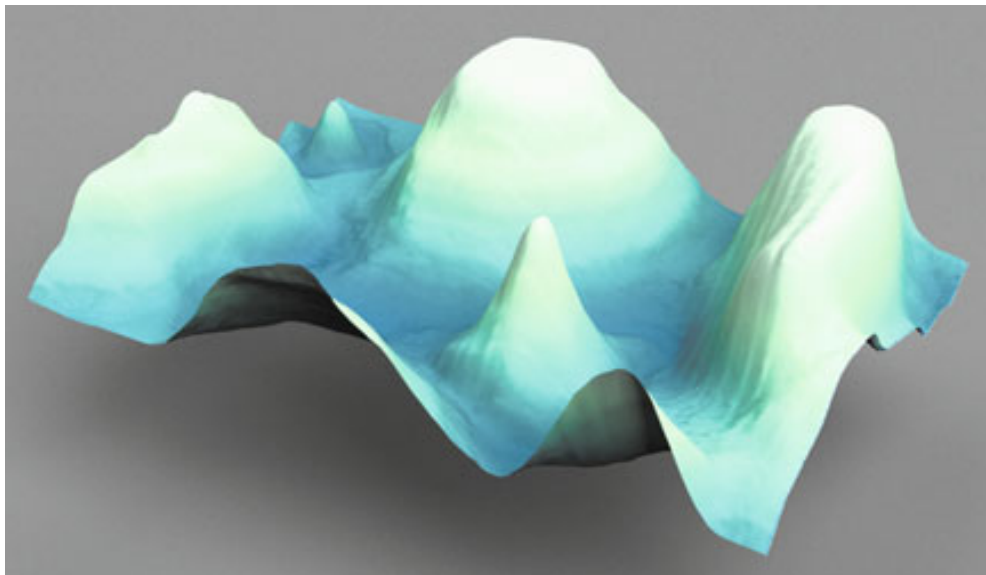

**Special Course in Theoretical Physics
PHYS-E0546: DFT for Practitioners**

Aalto University, September 2022



**Tutorial 2: Energy surface: structure optimisation
Manuscript for Exercise Problems**

Prepared by Ondřej Krejčí, Orlando Silveira and Adolfo Fumega
Developed by Patrick Rinke, Milica Todorović,
Department of Applied Physics
Aalto University, 2022

A quick summary of the exercises

This tutorial will give you a practical understanding of the potential energy surface concept, and familiarise you with one of the most popular uses of DFT - determination of ground state structures. The first part introduces geometric optimization of a molecule and how to assess the reliability of the result. In the second part, you will learn how to build a molecular structure and consider the problem of local minima. The third part is dedicated to efficiently obtaining and visualizing electronic structure derived data.

Part I: Local structure optimization

- Problem I: Planar hydronium cation H_3O^+
- Problem II: A vibrational analysis of planar H_3O^+
- Problem III: Getting H_3O^+ right
- Problem IV: Pyramidal H_3O^+
- Problem V: Infra-red spectrum

Part II: Exploring conformers and the potential energy surface

- Problem VI: Building alanine with a molecular editor
- Problem VII: Relaxing alanine with DFT

Part III: Visualising electron densities and eigenstates

- Problem VIII: Outputting molecular orbitals
- Problem IX: Visualising orbitals

For every exercise, we also provide solutions and sample input files. They can be found in `$TUTORIALS/` directory. However, we strongly recommend to use the provided input files only in case of time shortage. You will maximize your learning progress by trying to generate the input files on your own. In case you get stuck with a particular problem, do not hesitate to ask one of the tutors. An executable of FHI-aims, as well as species files and utility scripts, are provided in the `$COURSE/` directory.

Note: Please do not copy and paste the description in this pdf into your input files. Typically, invisible characters from the formatting are copied, too. FHI-aims will revoke these characters and your calculations will not start.

Additional tools and programs

- **Speed up with parallel FHI-aims calculations:**

```
To launch a parallel FHI-aims calculation type:  
mpirun -np 4 aims.x | tee "output-file"
```

- The `mpirun -np 4` command starts FHI-aims in parallel on four cores.
- **ATTENTION:** do not start another FHI-aims run simultaneously. That would slow down **BOTH** calculations considerably.

- **Molecular building tools:**

Out of the several atomistic model building tools widely available, Avogadro is a very intuitive molecular editor and straight forward to learn. We will provide instructions throughout the tutorial whenever necessary.

- **Visualization tools:**

To visualize structures, vibrational modes, charge density plots, etc., several programs including `molden`, `vmd`, and `jmol` are installed on your workstations. In [Appendix I](#) you will find instructions on how to use `Molden` and `VESTA`.

- **Utility scripts:**

DFT output files are complex, so we use utility scripts to extract important data. In the `$COURSE/CODE/utilities` directory you will find tools like `aims-SCF_convergence.awk` and `get_relaxation_info.pl` to monitor the simulation, as well as `create_xyz_movie.pl` to track the geometry optimisation. In this tutorial, additional scripts can be found in `$TUTORIALS/Tutorial_2/utilities`.

Part I: Local structure optimisation

Problem I: Planar H_3O^+

This exercise covers how to perform geometry optimizations. Specifically, we will relax the H_3O^+ molecule starting from an initial planar guess for the geometry.

Educational Objectives

- Learn how to perform a geometry optimization (structural relaxation) in FHI-aims
- Visualize molecular structures and molecular relaxations.

Tasks

1. Figure 1 shows a `geometry.in` file, which can also be found in the `$TUTORIALS/` directory. Please use this as the starting point for your structure relaxation.

```
# Initial guess for planar H3O+
atom 0.00 0.00 0.00 O
atom 0.92 -0.53 0.00 H
atom -0.92 -0.53 0.00 H
atom 0.00 1.06 0.00 H
```

Figure 1: This `geometry.in` file gives a starting point for the planar H_3O^+ cation.

2. Create a `control.in` file, using the `control.in` file from the previous exercises as a template. For your xc functional (i.e. `method`), specify `pw-lda`. This time, use `spin none` and, as we are interested in a cation, `charge 1.0`. Finally, add the keyword `relax_geometry trm 1E-3` to request structural relaxation. Your `control.in` should look similar to the example shown in Fig. 2.

```
# Sample input file for the relaxation
# of the H3O+ molecule
#####
xc pw-lda
charge 1.0
spin none

#####SCF Accuracy#####
sc_accuracy_eev 1E-2
sc_accuracy_etot 1E-5
sc_accuracy_rho 1E-4
sc_accuracy_forces 5E-4
sc_iter_limit 100

#####Relaxation#####
relax_geometry trm 1E-3
```

Figure 2: The `control.in` file used for the structure relaxation of the cation H_3O^+ .

As in the exercises before, the basis set must be included in the `control.in` file. Use the “*light*” species defaults for O and H atoms.

```
cat $SPECIES/light/01_H_default >> control.in
cat $SPECIES/light/08_O_default >> control.in
```

- Run FHI-aims.

```
aims.x | tee H30+_planar_relaxation.out
```
- To visualize the results, copy the tool `create_relax_movie.py` from `$TUTORIALS/Tutorial_2/utilities` into the working directory. Apply it to the output and pipe the result to a new file using the command

```
python3 create_relax_movie.py H30+_planar_relaxation.out > H30+.xyz
```

 Open the file `H30+.xyz` with a visualizer.

```
molden H30+.xyz
```

 or

```
jmol H30+.xyz
```

What does the fully relaxed structure look like? Do you believe that this could be the actual total energy minimum?

Problem II: A vibrational analysis of planar H_3O^+

Now we will check whether our obtained geometry is a **local minimum** or **saddle point** by performing a vibrational analysis.

Educational Objectives

- Learn to calculate vibrations in FHI-aims
- Recognize transition states

We will use the python script `get_vibrations.py` in a folder that contains a `control.in` and `geometry.in` file. The script is located in `$TUTORIALS/Tutorial_2/utilities`.

Tasks

- Use the same `control.in` as in [Problem I](#). Next, copy the optimized geometry from the previous exercise. This should be contained in the file `geometry.in.next_step`.
- Run the vibrational script.

```
>python3 get_vibrations.py -r aims.x -x -p -w -d 0.002 H30+_planar 2 > H30+_planar.vib.out
```

 This will create folders containing the single calculations and calculate the vibrational frequencies. For information about the python script and its options type:

```
>python3 get_vibrations.py -h
```
- Inspect the `H30+_planar.vib.out` file and check which other files were obtained.

The script `get_vibrations.py` produces several output files - most importantly the `H30+_planar.vib.out` and the `H30+_planar.xyz` file. The `H30+_planar.vib.out` file contains basic information about the vibrational frequencies, zero point energies and infrared (IR) intensities. In addition, the `H30+_planar.xyz` file contains geometrical information about the vibrational modes.

If the Hessian (the matrix of the second derivatives of the total energy with respect to the atomic positions) is positive definite (i.e., there are only positive eigenvalues), the structure is in a local minimum. If not we, found a saddle point or a maximum. Formally, in this case the Hessian will have imaginary vibrational frequencies. However it is also common to output them as negative numbers. There are $3N-6$ non-zero modes ($3N-5$ for linear molecules), where N is the number of atoms. Due to numerical errors you will typically find the remaining 6 (5) 'zero' frequencies to be in the range of $\sim \pm 15 \text{ cm}^{-1}$. They may be negative, but as their values are numerical errors and not physical, these zero modes should be ignored when decided if the structure is in a local minimum.

Visualize the eigenmodes of the molecule:

Create a molden file by applying following the script to the FHI-aims output `H30+_planar.xyz` of

the vibration calculation (`troublemaker.pl` can be found in the `$TUTORIALS/Tutorial_2/utilities` folder):

```
> ./troublemaker.pl -xyz2molden H3O+_planar.xyz > H3O+_planar.molden.  
Visualize the eigenmodes in the molden file:  
> molden H3O+_planar.molden
```

In this example, H_3O^+ has one imaginary frequency. What does the corresponding mode look like (see [MOLDEN tutorial](#))?

Problem III: Getting H_3O^+ right

An imaginary frequency indicates that the curvature of the potential energy surface (PES) along that mode is negative. In other words, following that mode leads to a structure with lower energy. Therefore, a reasonable guess would be to distort the geometry along this direction and optimize the structure again. This is what we are going to do next!

Educational Objectives:

- Use the vibrational analysis of transition states to find the nearest energetic minimum structure

Tasks

1. Take the `H3O+_planar.distorted.vibration_1.geometry.in` file from the previous exercise. It contains the planar geometry distorted along the imaginary mode.
2. For the distorted geometry, optimize the structure again (as described in [Problem II](#)).
> `aims.x | tee H3O+_distorted_relaxation.out`

What does the optimized structure look like? How does the energy compare to the planar optimized structure of [Problem I](#)?

Problem IV: Pyramidal H_3O^+

Check whether the 3D geometry of H_3O^+ is stable by performing a vibrational analysis as described in [Problem I](#).

Tasks

1. Perform a vibrational analysis of the pyramidal H_3O^+ cation and check if this structure is stable.

Problem V: Infrared spectrum

In addition to the information about the structural stability, a vibrational calculation also gives the infrared (IR) spectrum. In this exercise we will compare the IR spectrum for the planar and pyramidal geometry, and optionally, for different numerical settings and different functionals.

Educational Objective

- Visualize the IR-spectrum of the H_3O^+ cation
- Compare experimental and calculated results.

To get started, we can use the data calculated in [Problem II](#) and [Problem IV](#). Compare the vibrational frequencies obtained in both problems.

Tasks

1. The IR-spectrum can be visualized using `molden`, see [MOLDEN Tutorial](#).
2. Repeat the same steps for the vibrational analysis of the planar structure.
3. Compare your spectra with the experimental vibrational frequencies. You can look them up online at the NIST web book:
<http://webbook.nist.gov/cgi/cbook.cgi?ID=C13968086&Mask=800#Electronic-Spec>

Note:

As you see, the IR-spectrum is very sensitive to the structure. Comparing a calculated IR-spectrum to an experimental one can shed light on the structure that is predominantly present in experiment.

Optional: Convergence of numerical settings and performance of different methods.

Tasks

1. Perform convergence tests going from light, to tight and then to really tight settings for the infrared spectrum and for the 3D geometry (use `pw-lda` functional).

Important:

Since a harmonic IR-spectrum only makes sense for an optimized geometry, make sure that you request a geometry optimization in your `control.in` file, i.e. set `relax_geometry tnm 1E-3`.

If set, the vibrational script optimizes the geometry before doing the actual calculation for the vibrations.

2. For light settings, set the xc-functional (i.e. `method`) to the PBE functional you used in the first tutorial. Compute the IR spectrum again and compare it to the `pw-lda` spectrum.
3. Compare again with the experimental vibrational frequencies.

Part II: Exploring conformers and the potential energy surface

Educational Objectives:

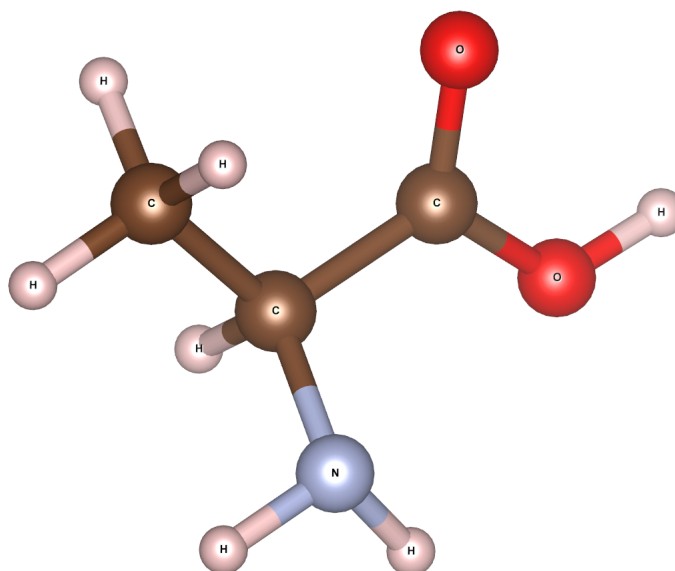
- Learn how to use a molecular editor
- Continue to build up expertise to visualize molecular structures
- Experience molecular conformers first-hand

As the second smallest amino-acid and a key building block of organic biomolecules, alanine has been the subject of intense experimental and theoretical characterisation. After some confusion over its ground-state geometry, it has now been established that alanine can assume different stable configurations that are very close in energy. These conformers of alanine represent different local minima, each of them stabilised by internal dispersion bonds between the functional groups of the molecule. Different conformers can be realised by rotating the functional groups around key molecular bonds, without breaking any of the bonds.

Problem VI: Building alanine with a molecular editor

Tasks

1. Open Avogadro by typing `avogadro2` in command line.
2. Make sure you are in *Tool Settings* mode and you can see the *Draw Settings*. The *Element* drop down menu lets you select the atomic species you would like to place. Uncheck the tick-box *Adjust Hydrogen*. Now you can select your first atom type and place an atom in the editor. When you place a second atom you can create a bond between the two atoms by keeping the left mouse button pressed and dragging the cursor to the first atom. Clicking on the bond changes it from single to double to triple and back to single. A right mouse button click should remove the bond.
3. Use the Avogadro editor to build an alanine molecule as attached to the tutorial document.



4. Click on *Extensions* in the top bar of the Avogadro program. This brings up the force-field structure relaxation tool box *Open Babel*. Using the default settings, press the *Optimize Geometry* button to launch the structure relaxation. Avogadro will now minimize the forces acting on all atoms until the optimal structure is reached.

You now have an alanine molecule in front of you on the computer screen. You can use Avogadro's view features to rotate the alanine molecule on the screen or zoom in and out. The equilibrium structure of your alanine molecule has been determined with a force field. Next we will check what DFT will do to this structure.

Problem VII: Relaxing alanine with DFT

Tasks

1. In Avogadro, output the final geometry as xyz file by going to *File*→*Save As*.
2. Generate an FHI-aims `geometry.in` file by hand, based on the xyz file output.
3. Adjust the `control.in` from the previous exercise to alanine, e.g. add the correct basis functions using the light Tier 1 setting. Switch back to the PBE functional.
4. To describe the van der Waals effects in alanine correctly, you need a better exchange-correlation functional than PBE. This can also be achieved with the Tkatchenko-Scheffler van der Waals corrections (Phys. Rev. Lett., **102**, 073005 (2009)). To activate them, add: `vdw_correction_hirshfeld`.
5. Launch a parallel FHI-aims calculation to relax your alanine molecule (5min):
`mpirun -np 4 aims.x | tee output-file`
6. Apply a utility script (`create_relax_movie.py`) on the "output-file" to generate the xyz file as in Problem I, visualize the relaxation process in Molden and take note of the final structure.
7. Create a postscript file (alanine.ps) of your relaxed molecule. Can you spot any differences in the pre- and post-relaxation geometries?
8. Take note of the initial and final total energy and report the final total energy that you obtain to the white board at the front of the class.

NOTE: the convergence settings here are set to average values to speed up calculations during the practical class. In real calculations, convergence parameters are typically benchmarked and assigned tighter settings.

Part III: Visualizing electron densities and eigenstates

Chemical reactions and many important physical effects (such as the formation of interface dipoles) are triggered by electron rearrangement. They are often associated with filling or emptying of molecular frontier orbitals. In this exercise, we will demonstrate how charge distributions are visualised and investigate how well the “actual” filling of a molecular orbital corresponds to the associated eigenstate of the neutral molecule.

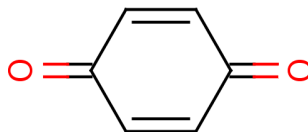
Educational Objectives

- Visualization of charge distributions
- See how orbitals (wave functions) and charge-density differences compare
- Understand the difference between orbital eigenvalues and ionization energies

Problem VIII: Outputting and visualizing molecular orbitals

Tasks

1. The molecule for the present example is para-benzoquinone, a readily available small molecule that is a strong electron acceptor. You can either create the geometry input for this molecule yourself (using Avogadro) or use the provided input file from the Templates folder.



2. Create a control.in input file for a spin-polarized, uncharged PBE calculation of the molecule. Use `spin collinear` and `switch_external_pert 10 safe`. We want to visualize the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in form of a standard cube file. Request the output of the wave functions in the `control.in` file using the keywords:

```
output cube eigenstate homo
cube filename HOMO.cube
output cube eigenstate lumo
cube filename LUMO.cube
```

We also want to look at charge density differences, so we need the total density of the molecule. Add:

```
output cube total_density
cube filename total_density_uncharged.cube
```

By default, FHI-aims will figure out the region to plot into the cube files by itself (to change this, see FHI-aims User Manual).

3. Run the calculation and look at the output. In the final occupation numbers, search for the energies of the HOMO and the LUMO. How do these energies compare to the experimental values of 10.7 eV for the ionisation potential and 1.9 eV for the electron affinity?
4. Next, use your favourite tool to plot the cube files (see appendix on how this is done with molden, but you may use vmd or vesta). Do HOMO and LUMO both have π character?
5. To see how well the eigenvalues and eigenstates correspond to the physical situation of charging a molecule, prepare and run two more inputs for the molecule with one negative and one positive charge.

6. Check the total number of electrons in neutral and charged calculations. Obtain the electron addition and removal energies by subtracting the total energy of the charged systems from the total energy of the uncharged system. This is also known as the ΔSCF approach. Compare the values with the HOMO and LUMO eigenvalue of the neutral molecule. How much do they differ?
7. The change in the electron density upon charging (positive and negative) can be obtained by subtracting the total density of the charged system from the total density of the uncharged system. To that end, a python-script called `subtract_cubes.py` is provided in the utilities folder. Copy this script and the `total_density.cube` files into a separate folder and execute

```
> python3 subtract_cubes.py total_density_uncharged.cube
total_density_charged.cube chargediff.cube
```

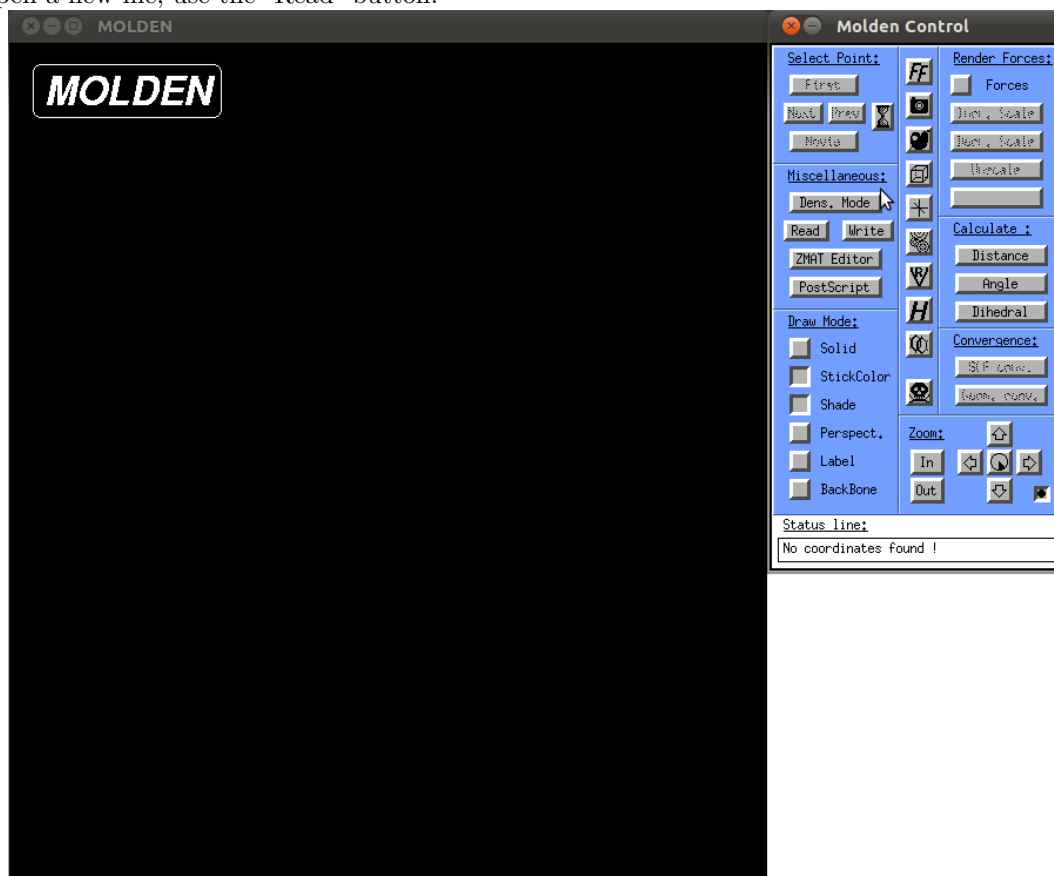
This will subtract the file given as second argument from the file given as first argument (adjust the file names accordingly). The result will be written to the file provided as final argument. Note that the cube files need to be generated with the same cube file settings in `control.in`. Visualise the density differences. Do you see qualitative differences to the eigenstates? Can you explain (or at least speculate) on the reasons for them?

Appendix I: Molden

Molden is a small, free tool which allows visualization of non-periodic structures, geometry optimizations, vibrations, and cube files. It can be used for all visualisations during tutorial 1. In the utilities folder, we provide several scripts which convert the output from FHI-AIMS to the molden format.

To open molden, simply type
`molden` or `molden filename`
in the command line.

Two windows will open, one named "MOLDEN", which contains the structure (and is empty if you didn't provide a file), and one named "MOLDEN Control" which contains several buttons. To open a new file, use the "Read" button.



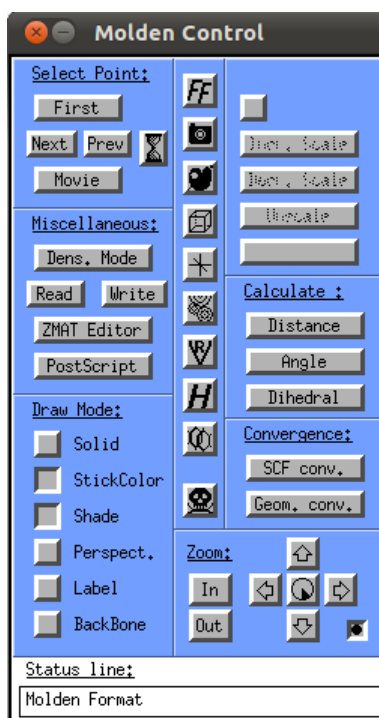
Below, we will describe how to visualize the output from the individual task. Of course, molden can do much more than what is shown here - feel free to play around. If you want to close molden, please use the skull icon in the middle of the control window.

Geometry single points

1. Create a molden file by applying the script `create_relax_movie.pl` to the FHI-aims output of a single point calculation
2. Open the file typing `molden filename`. On the top left corner of the Molden Control Window. The geometry of the system should appear in the Molden Window.
3. You can change the display options by playing around with the Draw Options in the bottom left corner of the Molden Control Window. Good results are often achieved by disabling shade and setting "Solid" to "Ball and Stick". Feel free to experiment!

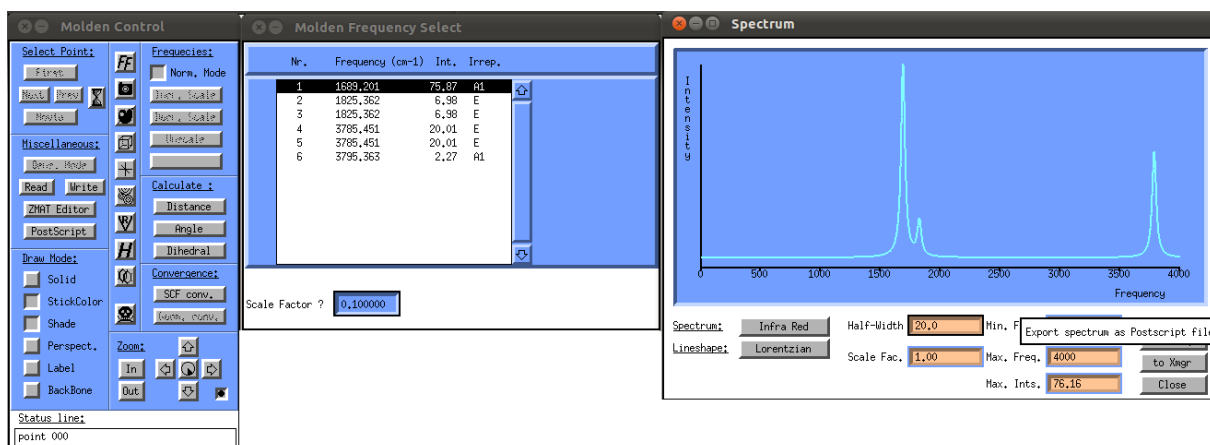
Geometry relaxations

1. Create a molden file by applying the script `create_relax_movie.pl` to the FHI-aims output of a geometry relaxation.
2. Open the file typing `molden filename`. On the top left corner of the Molden Control Window, the “Select Point” field should be active now. (See picture)
3. Watch a movie of the relaxation by clicking on the “Movie” button. If the movie is too fast, use the “sand-clock” button to set a delay between the individual frame.
4. You can also walk through each point of the geometry optimisation using the “Next” and “Prev” buttons.
5. Clicking on the “Geom. Conv” button in the bottom right corner of the Molden Control window will open a new window with information about the change of energy, maximum force, and maximum step size for each step.



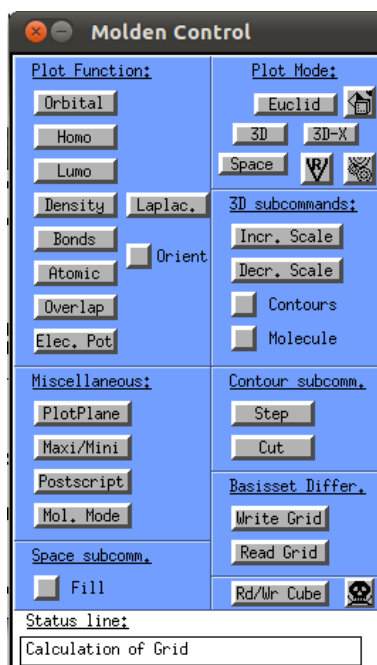
Vibrations

1. Create a molden file by applying the script `> ./troublemaker.pl -xyz2molden H30+.xyz > H30+.molden` to the FHI-aims output `H30+.xyz` of a vibration calculation (`troublemaker.pl` can be found in the `$TUTORIALS/Tutorial_2/utilities` folder).
2. Open the file typing `molden filename`. On the top right corner for the Molden Control Window, the “Norm. Mode” button should be active now, as highlighted in the picture.
3. Click on the button. Two more windows will open. The window called “spectrum” will provide you with an simulated infra-red spectrum based on the eigenvalues and their intensity. The bottom of this window provides several possibilities to alter the appearance of the spectrum or print it. The second window is called “Molden Frequency Select” and contains a list of all eigenmodes along with their frequency and IR intensity. By choosing one of these, the geometry in the molden window becomes animated and displays the corresponding eigenmode. The box scale factor at the bottom of the window can be used to amplify or damp the movement of the atoms.



Cube files

1. Cube files are generated directly by FHI-AIMS using the `output cube` syntax (see manual section 3.19).
2. Open molden without any filename by typing `molden`.
3. Click on the “Dens Mode” button in the left central panel. The Molden control window will change and show different buttons, see picture.
4. Click on the “Rd/Wr Cube” button in the bottom right corner. Choose read, Gaussian and give input the file name of your cube file when asked.
5. When the file opens, use the “Space” button in the top right corner to choose an isovalue for the display of the cube file. Try value 0.01.



Creating geometries

Besides pure visualization, molden also efficiently generates and saves geometries for molecular structures. Molden uses a z-matrix editor. A detailed explanation of z-matrices is beyond the scope of this work, but can be found online, e.g. under <http://www.cmbi.ru.nl/molden/zmat/zmat.html>. Even for people not familiar with z-matrices, generating input structures is usually easy and intuitive. This function is briefly explained here for the example of para-benzoquinone, the molecule used in the last part of Tutorial 1, and shown in the picture below.



1. Open molten and go to the z-matrix editor. A new window will appear which contains an empty field and several buttons, as shown in the picture below.
2. Begin by clicking on the "Add Line" button and select a carbon atom. A green circle should appear on your screen now.
3. The fastest way to proceed is to mark the carbon atom, choose "Substitute atom by fragment" from the Zmatrix Editor, and select -Phenyl. This will turn the atom into a completed ring, saturated with hydrogen atoms on all carbon atoms but one. The formerly empty box will now contain a list of all atoms. The first row is for bond distance, the second row is bond angles and the forth row is dihedral angle.
4. To add additional atoms, select the "Add Line" button again. Choose "double" as bond length, and an oxygen atom from the periodic table. Molden will now ask you to select 3 atoms to define the connectivity. These are the atoms to which bond length, angle and dihedral angle are defined. Click on the only carbon atom which has no hydrogen on it, and sub-sequentially on 2 neighbouring carbon atoms. A new line should appear.
5. If you made a mistake and want to delete the atom, click on the "delete line" button. If you were successful, delete the hydrogen atom opposite to the oxygen atom. Then, add another oxygen atom in its place, the same way you added the first one.
6. Once you are done, save the geometry by clicking on "Cartesian" in the lower right corner of the Zmatrix Editor, choose "XYZ" and provide a file name. Save by pressing return, and

quit molden via the Skull icon.

7. Use an editor or an script to adjust the xyz-format to the FHI-aims `geometry.in` format.

Appendix II: Visualization with VESTA

Visualizing your results from density functional calculations is useful and important for a couple of reasons. First, you can visualize the structure **as it was read by FHI-aims** and check its accuracy. This is a fool-proof way to check that the geometry handled by the code is actually the one you want. Second, you can view ‘volumetric data’ superimposed on the structure of whatever system you are dealing with. Volumetric data can be any kind of data written to a real-space grid including charge densities, wave functions, potentials, etc. Visualization of volumetric data can help you extract meaningful physics from your calculation. This document is a quick-start guide to visualizing output from FHI-aims with VESTA.

VESTA is a public, easy-to-use application for visualization of atomic structures and volumetric data. You can find it here: <http://jp-minerals.org/vesta/en/>

The complete manual for VESTA is here:

http://www.geocities.jp/kmo_mma/crystal/download/VESTA_Manual.pdf

Visualizing crystal structures

It is difficult to understand what a bulk, three-dimensional crystal structure looks like just by reading atomic coordinates. Luckily, VESTA will read the `geometry.in` file needed for FHI-aims and visualize the crystal for you. Type `vesta` to launch.

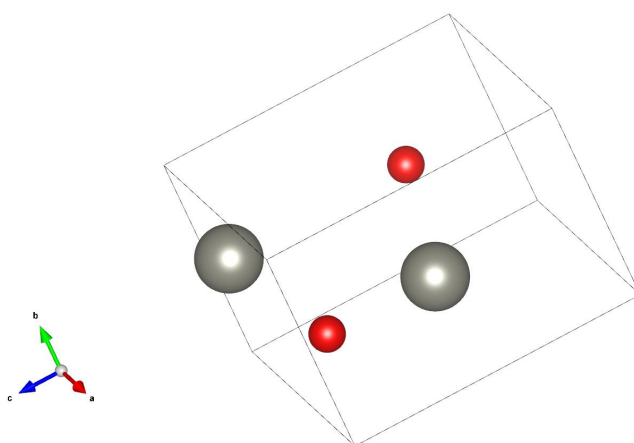


Figure 3

Now navigate to **File** and open your `geometry.in` file for FHI-aims. It should show the crystal structure you are interested in. An example `geometry.in` file for wurtzite ZnO and its appearance in VESTA are shown below and in Fig. 3.

```
lattice_vector 3.27534473 -0.07200997 -0.00749503
lattice_vector -1.57091511 2.87405204 -0.05082762
lattice_vector 0.01006313 0.10435241 5.29125719
atom 0.04290507 1.88121444 -0.06093020 Zn
atom 1.66090983 0.94898484 2.59987036 Zn
atom 0.04188438 1.91975639 1.94486746 O
atom 1.66718882 0.99019168 4.60509159 O
```

You can rotate the structure just by clicking and dragging the mouse. If you lose track of what direction you are looking at, click the ‘a,’ ‘b,’ or ‘c’ buttons on the top left. These will automatically orient the camera with the first, second, or third crystallographic direction. Notice the three crystallographic directions are given by the axes in the bottom left corner. If you click on ‘Tools’ at the top left of Fig. 7, you can select the ‘Animation’ rotation mode. With this selected, the crystal will slowly rotate in the direction you choose.

Fig. 3 looks ok, but it can be improved a lot. When looking at a periodic structure, it is helpful to increase the number of unit cells displayed so that you can see how different cells meet at their

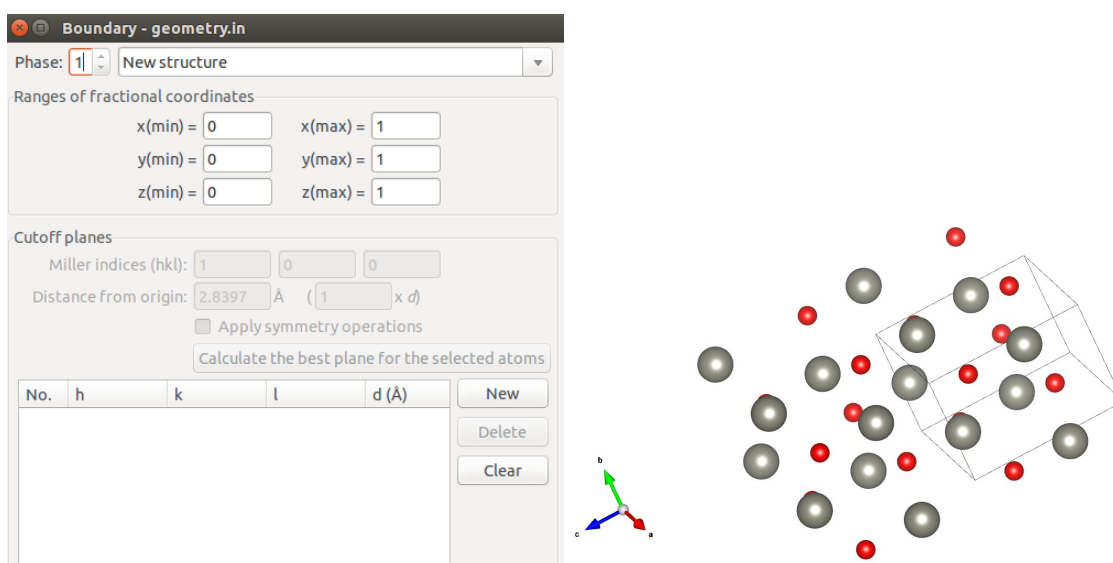


Figure 4

boundary. Click on **Objects** → **Boundary** to get the menu shown in Fig. 4. The boundaries of the displayed structure are set by 'xmin' and 'xmax' in reduced coordinates (and likewise for y and z). Setting the boundaries to 0 and 1 shows one cell. Try setting all of the maximum boundaries to 2.

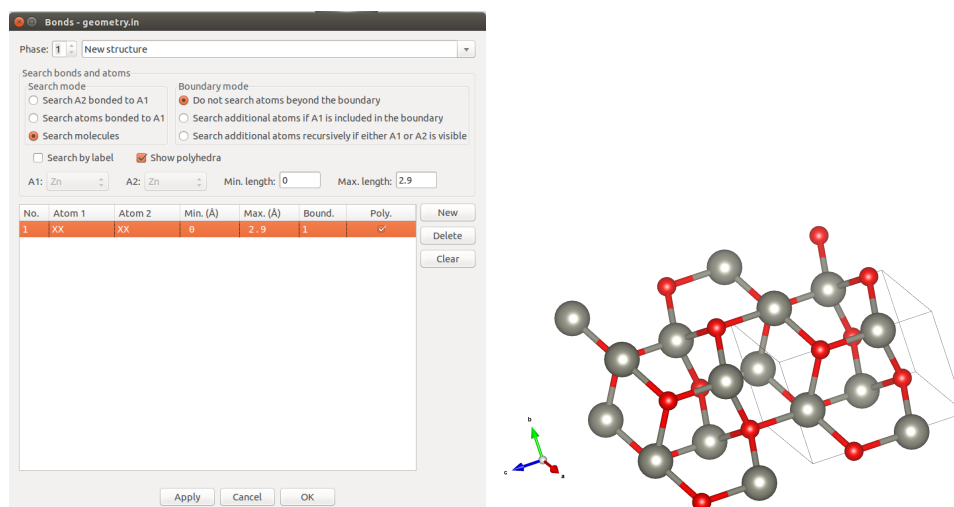


Figure 5

That looks better, but it is still difficult to see how the material is bonded. To fix that, click on **Edit** → **Bonds**. You should see the menu shown in Fig. 5. You have a few choices on how VESTA will search for bonds. The simplest, catch-all method is to click on 'New', choose 'Search molecules,' check 'Do not search atoms beyond the boundary,' and then set a maximum bond length. This choice will draw a bond for any two atoms that are less than the maximum bond length away from each other. You need to determine a reasonable maximum bond length for your structure. By searching atoms bonded only to 'A1' and/or 'A2,' you can search for bonds only involving those one or two chemical species. Now that the bonds are drawn, it is much easier to visualize the crystal and how the atoms are arranged when you rotate the crystal. For reference, a single unit cell is still outlined in black by VESTA.

Visualizing cube files

Navigate to **File** and open your **.cube** file from FHI-aims. It should show the atomic structure and some colored surfaces, something like Fig. 6. The yellow surfaces are called **isosurfaces** – surfaces of constant value. In the case of plotting ρ or ρ_i , they are surfaces of constant charge density. These isosurfaces are analogous to reading a topographic map in 2D. Instead of lines at constant value in the 2D case, we now visualize surfaces. Try clicking the different options under ‘Style’ on the left to change the appearance of the structure (Fig. 7). You can turn isosurfaces on or off by clicking the ‘Show isosurfaces’ box. And you can change the isosurface style by choosing a different option under ‘Style’ (the second ‘Style’ panel). The ‘Show sections’ box is probably also checked. Sections are cuts through the charge density on the boundary of your plotting box. They appear as contour plots on the sides of the plotting box. These can be useful for periodic systems, but for molecular systems, the density near the edges of your plotting box is so low, there is not much meaningful information there.

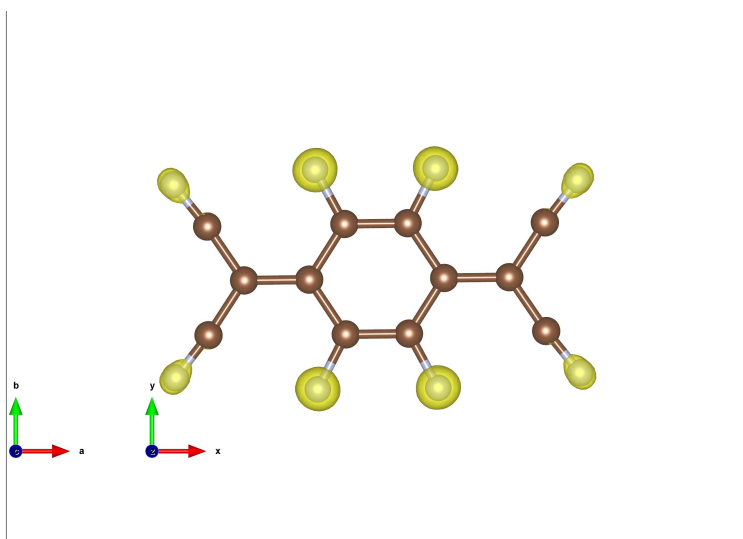


Figure 6

The tools on the left side of the screen (very left side of Fig. 7) allow you to measure bond lengths, angles, etc. with your mouse. For example, click the one with the little arrow between two atoms, then click on two atoms in the structure. In the output dialogue on the bottom, VESTA should tell you the distance between those two atoms. The next tool down the list will allow you to measure bond angles. Click it, then click on three atoms in the structure. The angle formed by these three should be printed in the output dialogue.

If you navigate to **Objects** → **Properties** → **Isosurfaces**, you should see the ‘Properties’ menu shown in Fig. 7. Here, you can change the isosurface value by clicking on the number underneath the ‘level’ label. You can also change the color or add multiple isosurfaces by selecting ‘New.’ Try selecting a reasonable isosurface value that allows you to see the character of the charge density. Selecting isosurface values is subjective and can be tricky, as different values can show very different shapes. One possibility is to select isosurface values that are a certain percentage of the maximum value on the grid, which is conveniently reported by VESTA. Always selecting the same percentage of the maximum offers some plotting consistency between different molecules.

Under the ‘General’ tab (Fig. 8), you can change the overall appearance of the viewer. You can turn on/off the outline of the plotting box, remove the coordinate axes, or adjust the material appearance. Under ‘Atoms,’ you can change the color of each species, the size of each atom, etc. There are lots of customizable aspects to create exactly the look you want. Explore all the options!

Images can be exported by going to **File** → **Export Raster Image** or **File** → **Export Vector Image**. Either of these will save a snapshot of the viewing window. Be sure to zoom in and orient the molecule correctly for the best quality image. That’s it! Now you can visualize your results

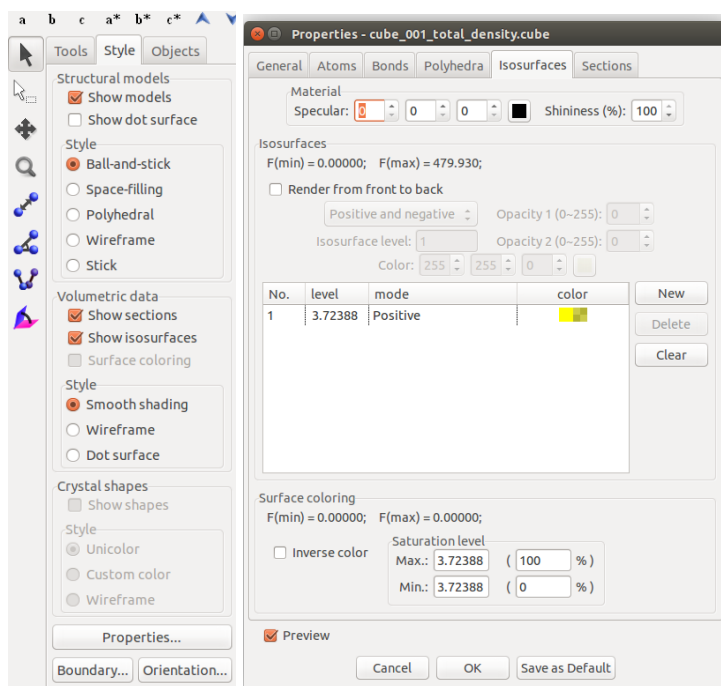


Figure 7

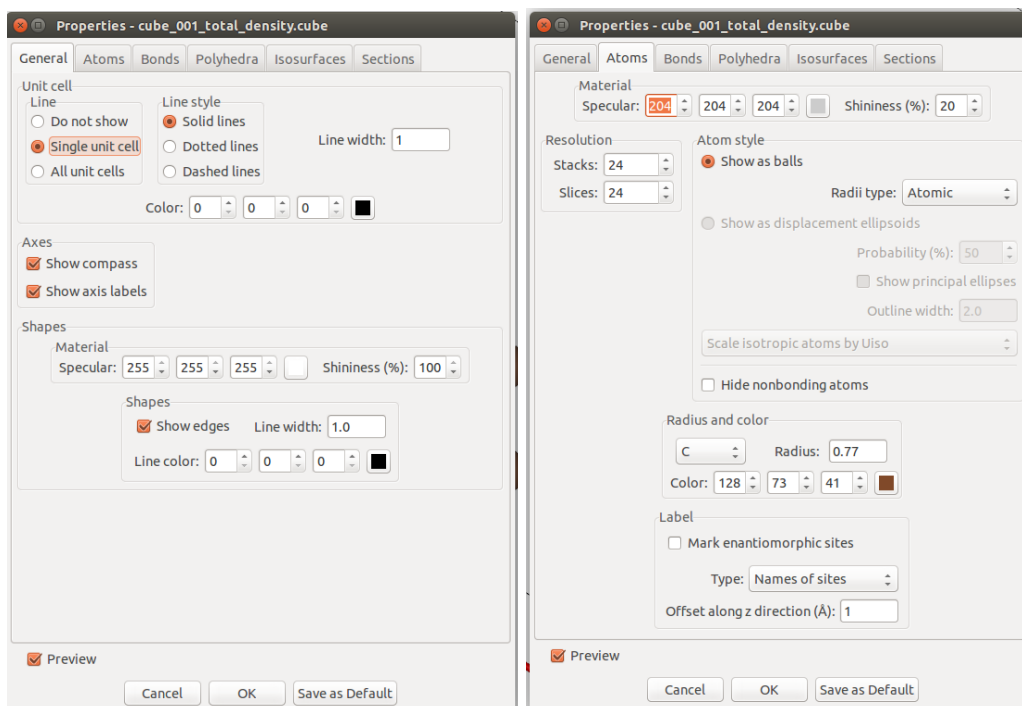


Figure 8

from FHI-aims.

VESTA also has a 2D display mode. Sometimes, making a 2D contour plot on a slice through a certain plane looks better than an isosurface in 3D. To start the 2D mode, click on **Utilities** → **2D Data Display**. You should see the menu shown in Fig. 9.

First, you must select which plane you want to make your 2D slice through. Click on 'Slice' to

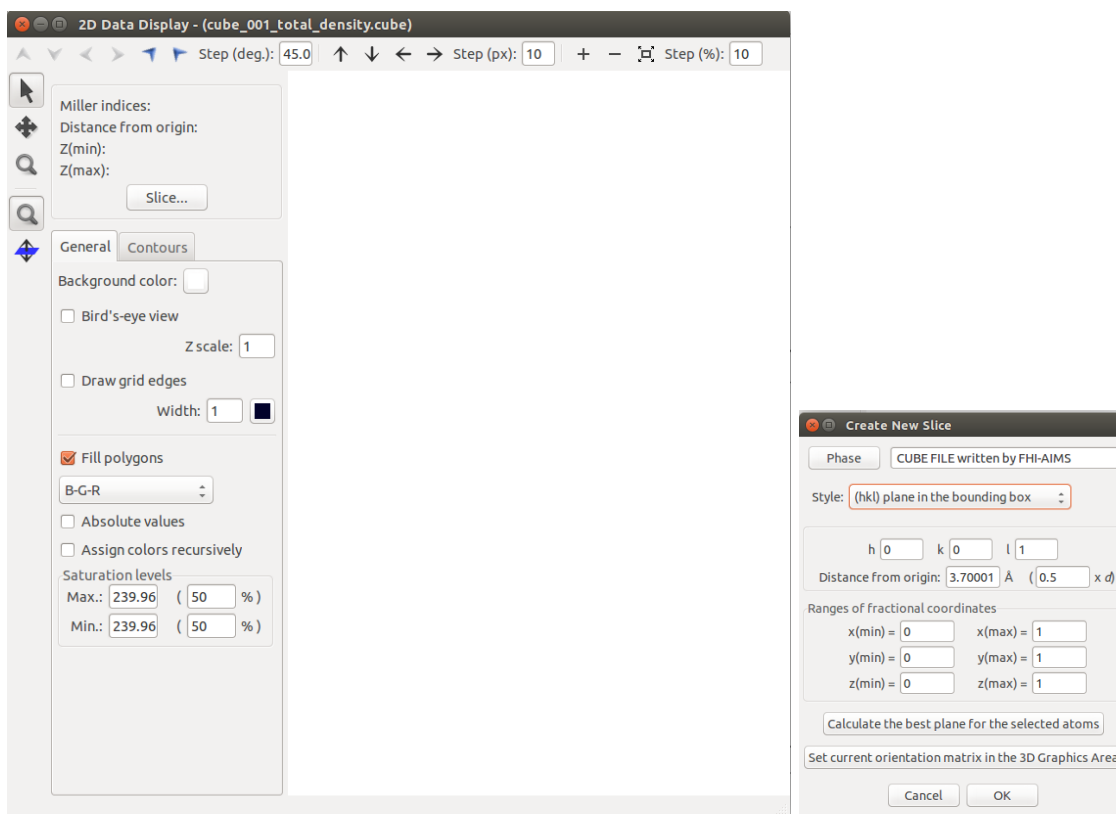


Figure 9

get the second menu shown in Fig. 9. Set a plane based on its (hkl) index. Don't worry about setting the distance from the origin - you will be able to visualize data in *all* planes parallel to the one set by (hkl) . The default setting is $(hkl) = (001)$. If your molecule is planar and oriented in the xy -plane, this is a good choice. Click 'Ok.'

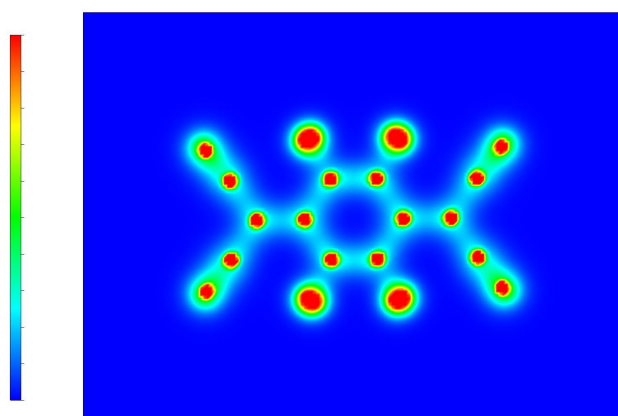


Figure 10

Now you need to set the saturation levels for the color scale. The maximum value will be the grid value that appears red, and the minimum value will appear blue. These do *not* have to be 100% and 0%. Usually, the maximum and minimum values on the grid are very far apart, with most of the grid points taking a value much closer to the minimum than the maximum. If you

simply set the maximum and minimum to 100% and 0%, you probably won't be able to see much. The majority of the data points will be in a very narrow color band, and you won't be able to see much detail at all. Next to 'Max,' set the saturation level to something around 3%. Then set the 'Min' level to 0%. This will probably take some tuning to get a nice image – you can reset these later. Now click on the blue plane with an arrow going through it and scroll with the wheel on the mouse. You should see a new image with every wheel click as you scroll through different planes parallel to the one you set, something like Fig. 10. Each plot is a slice through the density parallel to the (hkl) plane that you set. Try setting different saturation levels and a different (hkl) plane. Again, you can export an image by navigating to **File** → **Export Raster Image**.

Now check the 'Bird's-eye view' box. As long as the blue plane with the arrow going through it is checked, you can still scroll through different plane levels. Now, though, click and drag the plotting area. You should be able to rotate the plotting plane, and the plot now has depth. The colors correspond to the height of the features out of the plotting plane. To see more dramatic features, you might want to increase the maximum saturation level. Now you can generate a surface corresponding to the density through a single plane. 2D displays can be easier to look at than 3D isosurfaces, especially for planar molecules.