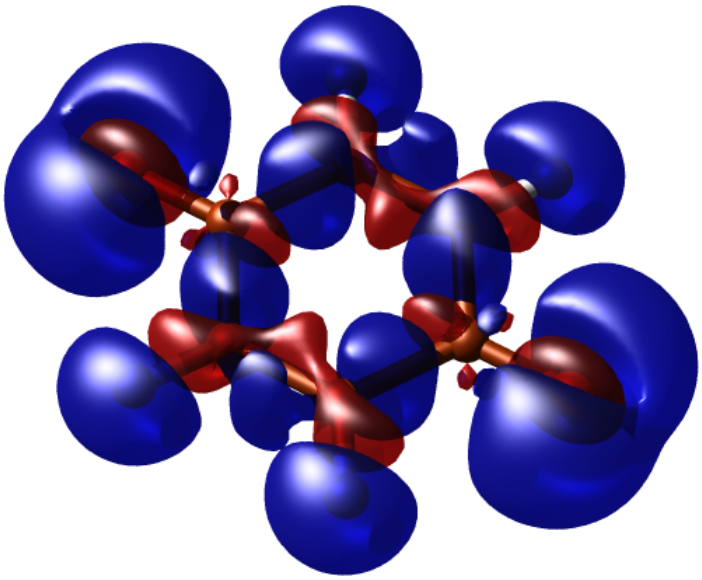
Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

Los Angeles, July 21 - August 1, 2014



Tutorial I: Basics of Electronic-Structure Theory
Manuscript for Exercise Problems

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A quick summary of the exercises

A guideline through the tutorial

This tutorial aims to give a basic introduction to electronic structure calculations for very simple systems. As every DFT code has its own philosophy, this tutorial should also familiarize you with fundamental aspects of using FHI-aims.
The goal of the first section is to explain the basic inputs of FHI-aims and to demonstrate that DFT calculations can have predictive power for many observable quantities. The second part introduces geometric optimization of a molecule and how to assess the reliability of the result. The third part is dedicated to efficiently obtaining and visualizing electronic structure derived data. Some exercises are marked with a red exclamation mark (!). These exercises demonstrate pitfalls or limitations of the approach.
The practice session consists of three parts:

Part I: Basic electronic structure with FHI-aims

- Problem I: The hydrogen atom
- Problem II: Hydrofluoric acid (HF): bond length and dipole moment
- Problem III: Molecular oxygen - a critical look !

Part II: Local structure optimization

- Problem IV: Planar hydronium cation H_3O^+
- Problem V: A vibrational analysis of planar H_3O^+
- Problem VI: Getting H_3O^+ right
- Problem VII: Pyramidal H_3O^+
- Problem VIII: Infra-red spectrum

Part III: Electron density mixing and visualising electron densities and eigenstates

- Problem IX: Efficiently converging the SCF
- Problem X: Visualizing density differences of *para*-benzoquinone

For every exercise, we also provide solutions, including sample input files. They can be found in $HANDSON/hands-on-2014-tutorials/tutorial_1/reference/solutions. The input files are also attached in this pdf and can be assessed by clicking on . [1] 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. For the tutorials, an executable of FHI-aims will be provided on your workstation.

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. This can confuse FHI-aims and yield to strange errors which are difficult to find.

The very basics of FHI-aims

Each calculation should be done in a separate directory containing the two mandatory input files `control.in` and `geometry.in`. FHI-aims is then called in this directory.

[1] Currently, only Acrobat Reader supports this functionality

In short:

- **Each calculation in a separate directory**
- **2 input files:**
  - `control.in`
  - `geometry.in`
- **Start calculation**
  `aims.x | tee output`

The above starts a calculation on a single processor, shows the main output on the screen and, at the same time, pipes it to the `output` file. The `output` file contains the basic information and results of the calculation such as the total energy, atomic forces, and so forth. Additional output files might be generated according to the specified settings.

Nuclear positions: geometry.in

The `geometry.in` file contains all information concerning the atomic structure of the system. This includes the nuclear coordinates, which are specified by the keyword `atom`, followed by cartesian coordinates (in units of Å) and the name of the element, called "species" in FHI-aims. In addition, comments can be added using a preceding hash symbol. Fig. 1 shows an example `geometry.in` file for a hydrogen atom.

```
#The hydrogen atom
atom 0.0 0.0 0.0 H
```

Figure 1: An example `geometry.in` file for a hydrogen atom positioned at the origin.

For periodic calculations, lattice vectors can also be given in this file. This will be covered in the next tutorial. In the present tutorial, however, we will stick to non-periodic systems.

Choosing the method: control.in

This file contains all physical and computational settings for the calculation. Fig. 2 shows a minimal example of a `control.in` file, which can be used as a template during the tutorial. These basic settings should be used as default for part I of this tutorial, unless specified otherwise.

In this example, the following options are set:

- `xc`
  This keyword sets the method to be used. For example you can choose the option `hf`, which requests a Hartree-Fock calculation.
- `charge`
  Set the total charge of the system in units of $|e|$. For a neutral system, this is zero.
- `spin`
  This keyword governs the spin treatment. It can be set to `none`, which requests a spin-restricted calculation, or to `collinear`, which requests a spin-unrestricted (polarized) calculation. In a spin-restricted calculation, α and β spins are assumed to be equal. Only one spin-channel is treated and hence, the number of electrons is effectively halved. This accelerates the calculations significantly.
- `default_initial_moment hund`
  Sets the initial spin of the atoms. The value "hund" requests an initial moment taken from

```
#Sample input file for the calculation of a H atom
#####################################################

xc  hf
charge 0.0
spin collinear
default_initial_moment hund

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

########Species#####################################
```

Figure 2: Default physical and computational settings for `control.in`.

Hund's rule, but it is often more sensible to provide a reasonable guess by hand. Only necessary for `spin collinear` calculations.

The other lines determine the convergence criteria of the self-consistency cycle regarding

- `sc_accuracy_rho` the change of the density
- the sum of orbital eigenvalues: `sc_accuracy_eev`, and
- the total energy `sc_accuracy_etot` between two consecutive cycles.

In addition to these keywords, the `control.in` file must contain the definition of the computational parameters for each species that is specified in `geometry.in`. The order of the species in the listing is irrelevant. FHI-aims is shipped with pre-defined settings for all species which govern the key parameters regarding the numerical accuracy. They include, *inter alia*, the specification of all real-space integration grids, the accuracy of the Hartree potential and, of course, the basis set. For all elements, defaults are provided for three different levels of accuracy: *light*, *tight*, and *really tight*. They can be found in the directory

`$HANDSON/aimsfiles/species_defaults`

and should be copied and pasted into `control.in`, e.g. via the command

`cat $HANDSON/aimsfiles/species_defaults/really_tight/01_H_default » control.in`

which pastes the really_tight settings of the H-atom into the `control.in` file. Already the *tight* species_defaults are rather safe and *really tight* settings are overconverged for most purposes. In addition the number of basis functions can be varied, as well as the basis functions themselves. The basis functions associated with a given species are tabulated at the end of these default settings, as shown in Fig. 3

The idea of keeping the species defaults out in the open is that, even if they are not modified, these are the critical accuracy parameters which one might look at to ensure numerical convergence. Each line denotes a specific basis function. They can be read as follows: The first keyword denotes the "type" of the basis function. *Hydro* means that this is a hydrogen-like basis functions. Some basis functions are of the type *ionic*. They are described in more detail in the manual. The next two symbols correspond to the first two quantum numbers (principal quantum number n, orbital quantum number l) of the basis functions, and the final number corresponds to the "effective nuclear charge" for which this basis function is created. `hydro 1 s 0.85` corresponds to the exact solution for the 1 s basis function of a hydrogen atom if it had a nuclear charge of only 0.85.

The basis functions are classified in "tiers". Not all basis functions are enabled by default. Rather, some are commented out using the " # " symbol. They can be included in the calculation by removing the hash symbol from the corresponding lines. Systematically improved calculations can be performed by enabling additional tiers one after another.

```
################################################################################
#
#  FHI-aims code project
#  VB, Fritz-Haber Institut, 2007
#
#  Suggested "safe" defaults for H atom (to be pasted into control.in file)
#
################################################################################
  species        H
#     global species definitions
    nucleus             1
    mass                1.00794
#
    l_hartree           8
#
    cut_pot             4.0  2.0  1.0
    basis_dep_cutoff    0.d0
#
    radial_base         24 7.0
    radial_multiplier   2
    angular_grids       specified
      division   0.2783  110
      division   0.3822  194
      division   0.5626  302
      division   0.5922  434
      division   0.6227  590
#      division   0.7206  770
#      outer_grid  770
      outer_grid  590
################################################################################
#
#  Definition of "minimal" basis
#
################################################################################
#     valence basis states
    valence      1  s   1.
#     ion occupancy
    ion_occ      1  s   0.5
################################################################################
#
#  Suggested additional basis functions. For production calculations,
#  uncomment them one after another (the most important basis functions are
#  listed first).
#
#  Basis constructed for dimers: 0.5 A, 0.7 A, 1.0 A, 1.5 A, 2.5 A
#
################################################################################
#  "First tier" - improvements: -1014.90 meV to -62.69 meV
     hydro 2 s 2.1
     hydro 2 p 3.5
#  "Second tier" - improvements: -12.89 meV to -1.83 meV
#     hydro 1 s 0.85
#     hydro 2 p 3.7
#     hydro 2 s 1.2
#     hydro 3 d 7
#  "Third tier" - improvements: -0.25 meV to -0.12 meV
#     hydro 4 f 11.2
#     hydro 3 p 4.8
#     hydro 4 d 9
#     hydro 3 s 3.2
```

Figure 3: Tabulated basis functions for hydrogen. The basis functions are classified in "`tiers`". In this example only the `tier 1` and minimal basis functions are enabled.

Additional tools and programs

Scripts: For some exercises, scripts are required for dedicated tasks, such as the manipulation of cube files. All scripts you will need for this tutorial can be found in

`$HANDSON/hands-on-2014-tutorials/tutorial_1/utilities`

Visualization tools: To visualize structures, vibrational modes, charge density plots, etc., several programs including molden, avogradro, vmd, jmol, and gdis are installed on your work stations.

Plotting and Editing:

To plot data, gnuplot, qtiplot, and xmgrace are provided. Also several editors are available, including gedit, emacs, and vi. The simplest one to handle is probably gedit.

Part I: Basic electronic structure with FHI-aims

Problem I: The hydrogen atom

In this exercise, we aim to convey the basics of FHI-aims using the hydrogen atom. The hydrogen atom is the simplest non-trivial system possible and the only one for which the exact analytic solution is known. By the end of the first exercise, we will see how various computational methods compare to each other and to the exact solution. From a technical perspective, we will learn how to generate input files, read the standard FHI-aims output, and perform basis set convergence tests.

Getting started - the hydrogen atom

Eductational Objectives:

- Become aquainted with running FHI-aims calculations
- Learn how to do systematic basis set convergence

Tasks

1. Generate a simple `geometry.in` file by hand, which contains only a single hydrogen atom, using the example shown in Fig. 1 . This corresponds to a single hydrogen atom in a hypothetical ideal gas phase. It is located at the origin of the coordinate system, although its position does not matter here.

2. Generate a simple `control.in` file by hand, using the example `control.in` file given in Fig. 2 . Systems with only a single electron can be solved exactly (within the Born-Oppenheimer approximation) using Hartree-Fock. Finally, append the "*really_tight*" species data of H to the end of the `control.in` file, e.g. via the command
   ```
   cat $HANDSON/aimsfiles/species_defaults/really_tight/01_H_default >> control.in
   ```

3. Now, run FHI-aims:
   ```
   aims.x | tee output
   ```

   One the calculation has finished, open the `output` file. If you find the line "`Self-consistency cycle converged`" near the end, then your calculation is converged. We are now interested in the total energy. Search for the block

   ```
   | Total energy uncorrected   :   -0.136054662652353E+02   eV
   | Total energy corrected     :   -0.136054662652353E+02   eV
   | Electronic free energy     :   -0.136054662652353E+02   eV
   ```

   In this special case, all energies are equal, but this will not be the case if fractionally occupied orbitals were found! For non-metallic systems, as in this tutorial, always use the **Total energy uncorrected** value. (You will learn what the other two values mean in a future lecture.) Compare it with the exact result for the hydrogen atom (0.5 Hartree $\approx$ 13.6057eV).

   TIP:
   In later exercises, to find this value fast and efficiently, use the command
   ```
   grep 'Total energy uncorrected' output
   ```

4. Redo the calculation with different basis sets (`minimal`[2] , `tier1`, `tier2`, `tier3`) by (un)commenting the basis functions at the end of the control.in file. Calculations with minimal basis set are

[2] Here we do not use parallelization because it is not required. You will learn how to start FHI-aims in parallel in Tutorial 2

performed by removing all basis functions that are listed in the file. Search the output file to find out how many basis functions are actually used in the calculations. Then, plot the total energy as function of the basis set size. At which tier does total energy converge?

TIP:
To plot the results, simply create a text file (e.g., *results.dat*) with two columns, the number of basis functions and the obtained total energy. This file can be plotted directly using the command
`xmgrace results.dat`

Optional: Method performance

To learn about the performance of difference exchange-correlation functionals, repeat for different methods. Replace `hf` in control.in with

- `pw-lda`
- `pbe`
- `pbe0`

Do all methods converge with basis set size? Do all converge to the same result?

Optional: An optimal basis set

Optional part: If you browse through the hydrogen basis set, you will note that the hydrogen 1s function is not included. Change that by adding the line

```
hydro 1 s 1
```

at the end of the `control.in` file. Comment out all other basis functions and run the Hartree-Fock calculation again. How close does it get to the exact result?

Problem II: Hydrofluoric acid (HF): bond length and dipole moment

Hydrofluoric acid (HF)

One of the most influential papers in chemistry for systematic investigation of the performance of DFT was Johnson et al.[1], in which several properties of a large number of diatomic systems were consistently computed and compared to experimental values. In the style of this work, we will calculate the binding curve, atomization energy (ΔH_{at}), and the dipole moment for hydrogen fluoride (HF) with two methods. From a technical perspective, this exercise teaches how simple shell scripting can be used to make your (computational) life easier.

Eductational Objectives:

- Become acquainted with shell scripting.
- Learn how to compute dipoles and atomic charges.
- Find the equilibrium bond distance of a simple diatomic molecule.
- Assess the reliability of charge partition schemes.

Tasks:

1. The first task of this exercise will be to find the equilibrium bond distance of HF from a series of calculations. Start by creating a `geometry.in` file which contains a H and a F atom, as shown in Fig. 4 .

```
#HF at variable bond distances
atom 0.0 0.0 0.0 H
atom 0.0 0.0 Dist F
```

Figure 4: The geometry data for a HF molecule. H is put on the origin and F is located `Dist` Å away from the origin along the z-axis.

In this example, H is put on the origin and F is located `Dist` Å away from the origin along the z-axis. Hereby, `Dist` is a placeholder which will be replaced by the actual distance later using a script.

2. Create a `control.in` file, and specify a `hf` calculation for a neutral system. Feel free to copy the file from the previous exercise, but remove the *really tight* species setting for hydrogen. Instead, please paste the *tight* setting for H **and** F into the `control.in` file. We also want to compute the electronic dipole moment, which is requested using the keyword `output dipole`. Note that although it doesn't matter where you put the keyword, it is recommended to put all manually set keywords *before* the species tags. Alternatively, you can use this file

3. Next, create a bash script which runs FHI-aims for a series of bond distances (ideally between 0.7Å and 1.3Å with 0.1Å steps, and a denser step width of 0.02 Å between 0.85 Å and 0.95 Å).

   For each distance, it should

   - create a unique directory
   - create the `control.in` and `geometry.in` file from templates
   - replace the bond distance place holder `Dist` with the bond distance and
   - start FHI-aims.

   Appendix I holds a short sample bash script (fig. 8) for this task. Alternatively, you may also use the script we provide in

   `$HANDSON/hands-on-2014-tutorials/tutorial_1/reference/exercise_02_HF/templates/Run.sh`

   Run the script and plot the total energies vs. the bond length. This can be scripted as well. An example script is also provided in

   `$HANDSON/hands-on-2014-tutorials/tutorial_1/reference/exercise_02_HF/templates/PP_Energies.sh`

   Which bond length corresponds to the lowest energy? How does the bond length compare to the experimental bond length of 0.917Å?

4. To compare with experimental values, we compute the atomization energy (ΔH_{at}). In order to calculate ΔH_{at}, we will also need the total energy of the isolated H and F atoms. Compute the total energies for the single atoms using the methods `hf`. Check the result carefully - is Hund's rule fulfilled? Does the electronic configuration correspond to what you expect from the aufbau principle?

Note:
Atoms are highly symmetric systems, often with multiple degenerate solutions. In the case of fluorine, for example, the unpaired p-electron might sit in the p_x, p_y, or p_z orbital. All three solutions are equivalent. If the calculation is started unbiased, it might converge to a superposition of these three cases, which is a saddle point on the potential energy surface and results in partial electron occupations. Although in DFT non-integer occupations are in principle allowed, one should be very suspicious when obtaining such a solution for non-metallic systems. Typically, solutions exist that are lower in energy. They can be found by breaking the inherent symmetry of the problem, for example by applying a small external field at the beginning of the SCF cycle.

To break the inherent symmetry of an atom and ensure integer occupation, set the keyword `switch_external_pert 10 safe`. This means that for 10 iterations, a small external field in the z-direction is applied and then switched off. Usually, this is sufficient to perturb the SCF out of the symmetric solution and towards the correct electronic structure. Calculate the atomization energy (ΔH_{at}) of HF by subtracting the free-atom energies from the predicted total energy of HF (i.e. the minimum total energy found when varying bond distances).

$$\Delta H_{at} = E_{tot}^{HF} - E_{atom}^{H} - E_{atom}^{F} \tag{1}$$

How does this compare to the experimental value of $\Delta H_{at} = 135.2$kcal mol^{-1} (5.86 eV)?

5. Now, let us look at the dipole moment. Search for the corresponding line in the output file. Does the dipole differ much between the two methods used? How does the dipole at the equilibrium distance compare with the experimental value of 1.82 Debye? Plot the dipole moment vs. the bond distance. You will find a (mostly) linear correspondence. Do you expect this trend to continue at large distances? Why or why not?

6. **Optional:** Repeat the bond length determination using `pbe0`. How does the optimal bond length change? How much does the total energy change? Are the dipole moments the same?

Optional: Charge partition schemes.

Chemical reactivity and many physical properties are often explained in terms of atomic charges. However, atomic charges are not physical observables, since no unique operator exists to determine this quantity. They rather depend on the chosen charge partition scheme. The charge partition schemes that is probably most commonly used is Mulliken [2]. In FHI-aims, you can request it by specifying `output mulliken` in `control.in`.

For the equilibrium structure of HF, compute the atomic charges with this scheme using `pbe0`. Use the charges to calculate the dipole moment μ in the point dipole approximation. In this approximation, for a two atom system, the dipole moment is defined as:

$$\mu = q \cdot |\vec{r_H} - \vec{r_F}| \tag{2}$$

where q is the atomic partial charge and $\vec{r_H}$ and $\vec{r_F}$ are the atomic positions of the atoms. The absolute value of the difference $|\vec{r_H} - \vec{r_F}|$ is the distance between hydrogen and fluorine. Compare the dipole moment to the one computed by FHI-aims. How do they compare?

Problem III: Molecular oxygen - a critical look !

An important part of every calculation is to always look critically at the output and ensure that the result is reasonable. For some systems, defaults may not be adequate, or assumptions which commonly work well may prove to be wrong. A prime example is the the treatment of spin in systems with degenerate orbitals, such as O_2.

[**Eductational Objectives:**]

- Do not trust default settings blindly
- See the effect of an incorrect spin-treatment

Tasks

1. Set up a calculation for O_2 similar to the previous exercise, but leave out the `spin` keyword in `control.in` . Look at the output file to find out which spin treatment is used by default.

2. Look at the output file and find the occupation numbers of the Kohn-Sham orbitals. Does this make sense here? Is Hund's rule fulfilled?

3. Using `pbe` and `pbe0`, calculate the binding curve in the interval $[0.8, 1.6]$ Å with a stepwidth of 0.1 Å as before. Also, calculate the atomization energy (ΔH_{at}).

4. Repeat the calculation with `spin collinear` - is Hund's rule now fulfilled? Compare the results: Do both spin settings yield the same equilibrium bond length? Calculate the difference in the total energy at the equilibrium bond length. Which one is lower? How does it compare to the experimental value of 1.21 Å? How does the atomization energy (ΔH_{at}) compare to the experimental value of 5.18 eV?

Note: The oxygen atom is a notoriously difficult case to converge. If you have problems with it, try using the linear mixer for the SCF by including the keyword `mixer linear` in `control.in`. The linear mixer is guaranteed to converge, but usually requires much more iterations than the default (Pulay) mixing scheme.

Part II: Local structure optimisation

Problem IV: 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 in FHI-aims
- Visualize the relaxation.

1. Fig. 5 shows a `geometry.in` file, which can also be found in $HANDSON/hands-on-2014-tutorials/tutorial_1/reference/exercise_04_H3O+_planar/templates . 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 5: 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. 6.

```
# 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 6: 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 $HANDSON/aimsfiles/species_defaults/light/01_H_default  >> control.in
cat $HANDSON/aimsfiles/species_defaults/light/08_O_default  >> control.in
```

3. Run FHI-aims.

```
aims.x | tee H3O+_planar_relaxation.out
```

4. To visualize the results, copy the tool `create_relax_movie.pl` from $HANDSON/hands-on-2014-tutorials/tutorial_1/utilities into the working directory. Apply it to the output and pipe the result to a new file using the command
   `./create_relax_movie.pl H3O+_planar_relaxation.out > H3O+.xyz`
   Open the file `H3O+.xyz` with a visualizer, e.g. molden or avogadro.
   `molden H3O+.xyz`

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

Problem V: 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 wrapper `aims.vibrations.pl` in a folder that contains a control.in and geometry.in file.

1. Use the same control.in as in Problem IV . Next copy the optimized geometry from the previous exercise. This should be contained in the file geometry.in.next_step.

2. Run the vibrational script.
   `> aims.vibrations.pl  H3O+_planar`
   (The argument is used to name the output, i.e. the suffix `H3O+_planar` labels your calculation output.)

3. Inspect the `H3O+_planar.vib.out` file.

The script `aims.vibrations.pl` produces several output files - most importantly the `H3O+_planar.vib.out` and the `H3O+_planar.xyz` file. The `H3O+_planar.vib.out` file contains basic information regarding vibrational frequencies, zero point energies and infrared (IR) intensities. In addition, the `H3O+_planar.xyz` file contains geometrical information about the vibrational modes.

If the Hessian (the matrix of second derivatives of total energy with respect to 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 $\sim \pm 15$ 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.

To visualize the eigenmodes of the molecule, the FHI-aims output needs to be converted. We provide a script called "troublemaker" in the utilities folder, which converts the `*xyz` file to the molden format: `> ./troublemaker.pl -xyz2molden H3O+_planar.xyz > H3O+_planar.molden`
These files can also be visualized with some other programs, such as avogadro.

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

Problem VI: 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 transistion states to find the nearest energetic minimum structure

1. Take the `H3O+_planar.xyz` file from Problem V and distort the planar geometry along the imaginary mode using the script
   `> ./troublemaker.pl H3O+_planar.xyz`
2. For the distorted geometry, optimize the structure again (as described in Problem IV).
   `> aims.x | tee aims.H3O+_distorted_relaxation.out`

What does the optimized structure look like?
How does the energy compare to the planar optimized structure of Problem IV?

Problem VII: Pyramidal H_3O^+

Check whether the 3D geometry of H_3O^+ is stable by performing a vibrational analysis as described in Problem V.

Tasks:

- Perform a vibrational analysis of the pyramidal H_3O^+ cation.
- Is it stable?

Problem VIII: IR spectrum

Besides information about the structural stability, a vibrational calculation also gives the IR spectrum. In this exercise we will compare the IR spectrum for the planar and pyramidal geometry 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 V and Problem VII. Compare the vibrational frequencies obtained in both problems.

- The IR-spectrum can be visualized using `molden`
  MOLDEN Tutorial
- Repeat the same thing for the vibrational analysis of the planar structure.

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.

- Perform convergence tests with respect to light, tight and really tight settings for the infrared spectrum and for the 3D geometry (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 trm 1E-3`.
  If set, the vibrational script optimizes the geometry before doing the actual calculation for the vibrations.

- For light settings, compute the PBE IR spectrum and compare it with the pw-lda spectrum.
- Compare your obtained spectrum with the experimentally obtained vibration frequencies. You can look them up online at the NIST webbook:
  http://webbook.nist.gov/cgi/cbook.cgi?ID=C13968086&Mask=800#Electronic-Spec

Part III: Electron density mixing and visualizing electron densities and eigenstates

Italian chef Antonello Colonna said in an interview with an American newspaper: "Garlic is the king of the kitchen, to eliminate it is like eliminating violins from an orchestra."
The garlic bulb releases a number of low-molecular-weight organosulfur compounds rarely encountered in nature [3]. One of them is the molecule Allicin (see Fig. 7). Allicin is responsible for the characteristic smell of freshly crunched garlic.
In this part of the exercise, we will use this molecule to compare the influence of different electron density mixing settings.

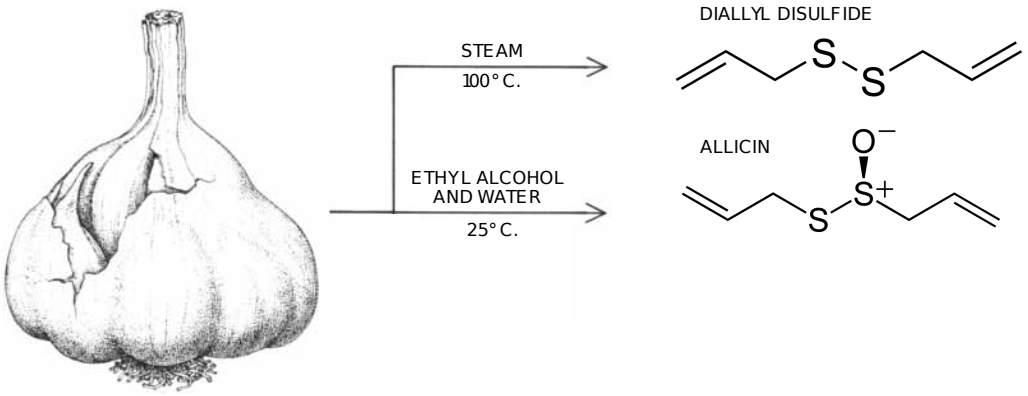


Figure 7: The allicin molecule features a thiosulfinate functional group (R-S(O)-S-R), which gives freshly crunched garlic its unique smell. (Figure adapted from Block [3])

Problem IX: Converging efficiently

During the self-consistent solution of the calculation, it is beneficial to use a history of densities from previous SCF cycles. FHI-aims provides two mainstream density mixing algorithms, linear and Pulay (also known as Direct Inversion in Iterative Subspace, DIIS).

Educational Objectives

- Obtain a first impression of the performance of different mixing schemes and parameters.

The geometry of the molecule for this exercise, as well as a sample `control.in` file, can be found in the `$HANDSON/hands-on-2014-tutorials/tutorial_1/reference/Templates` directory.

1. First create a directory for a calculation using the `linear` mixer. In the template `control.in` file you will find three new keywords:

   ```
   mixer TYPE
   charge_mix_param PARA
   n_max_pulay NUM
   ```

   For now ignore the keywords `charge_mix_param` and `n_max_pulay` – add a hash (#) in front of these two lines to deactivate them. The `mixer` keyword specifies the electron density mixing algorithm used. Here we use the *t*ype `linear`, so replace the place holder `TYPE` by `linear`.

2. Run the calculation and open the FHI-aims output file. How many SCF cycles were needed to reach self-consistency? Do you think this many SCF cycles are necessary to converge a rather small molecule?

3. Next we will use a more advanced mixing scheme, the `Pulay` mixer.
   This mixer also takes into account the history of the self-consistent calculation. For this algorithm, `n_max_pulay` n and `charge_mix_param` v have to be specified, n determines the number of past iterations $\mu - k$ $(k = 1, \cdots, n)$ to be mixed with the Kohn-Sham output density of iteration μ. The value v for the keyword `charge_mix_param` determines an additional (system-dependent) linear factor that is multiplied with the output density change of the Pulay mixer.
   We will try three different settings:

   - ```
     mixer pulay
     n_max_pulay 3
     charge_mix_param 0.1
     ```
   - Use the FHI-aims default settings:
     ```
     mixer pulay
     n_max_pulay 8
     charge_mix_param 0.2
     ```
   - Finally use the settings specifically optimised for Allicin.
     ```
     mixer pulay
     n_max_pulay 5
     charge_mix_param 0.3
     ```

4. Compare the number of SCF cycles and computational time with the linear mixer. Did the choice of mixer speed up your calculation? How do the optimized settings compare to the previous calculations?

This exercise can be nicely scripted by automatically replacing the place holder `TYPE, PARA, NUM`. Have a look at the example script in the Appendix I: Sample bash scripts.

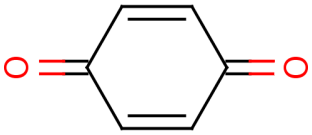
Problem X: Visualization of Kohn-Sham orbitals and electron densities

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

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 (see the appendix on how this can be done with `molden`) or use the provided input file from the Templates folder.
     ```



2. Create a control.in input file for a spin-unpolarized, uncharged PBE calculation of the molecule . 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 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`
   to the `control.in` file. By default, FHI-aims will figure out the region to plot into the cube files by itself.

   However, you are also free to choose the cube region yourself by adding the following lines after the `output cube` keyword:
   The line
   `cube origin` ***`x y z`***
   sets the center of the space to be plotted, with x y z being its cartesian coordinates in Å. The edges of the cube file can be configured using the syntax
   `cube edge` ***`n dx dy dz`***,
   where n indicates the number of steps of a particular edge (voxel), and dx, dy, dz indicate the length of each individual step in x, y, and z direction, respectively. Note that each cube file, being a 3D object, requires 3 edges to be completely defined. A complete definition of a cube file could look like
   `output cube total_density`

```
cube filename total_density_uncharged.cube
cube origin 0 0 0
cube edge 100 0.1 0.0 0.0
cube edge 150 0.0 0.1 0.0
cube edge 50 0.0 0.0 0.1
```

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? Next, use your favourite tool to plot the cube files. (See appendix on how this is done with molden.) Do HOMO and LUMO both have π character?

4. 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 charge. Remember that the total number of electrons is odd, and therefore, `spin collinear` should be used.

   Obtain the electron addition and removal energies by subtracting the total energy of the charged system 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?

5. The change in the electron density upon charging 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
   `> python subtract_cubes.py total_density_uncharged.cube total_density_charged.cube chargediff.cube`
   to subtract the file given as second argument from the file given as first argument. 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?

We like to thank you for participating in the first tutorial of this workshop. We wish you an interesting and inspiring time here at the 'Density functional theory and beyond' workshop.

Appendix

Appendix I: Sample bash scripts

Sample script for Exercise 2

Below, you find a sample script to calculate a molecule with pre-defined bond distances.

```
#############################################################################
# This is a simple example how to run a series of distances                 #
# Note: To run this script, you must be in a directoy which contains        #
#  /  geometry.template file with HF, where the distance between H and F#
#     is determined by a variable named DIST                                #
#                                                                           #
#  /  a control.template file which contains                                #
#     the correct method and basis set specifications.                      #
# Example input files are provided in the same directory as this script     #
#############################################################################

#!/bin/bash -l
ulimit -s unlimited

#Variable defintion:
#This variable should point to your local FHI-aims executable
AIMSBIN=$HANDSON/bin/aims.x


#Loop over the distances
for Distance in 0.7 0.8 0.85 0.87 0.89 0.91 0.93 0.95 1.0 1.1 1.2 1.3 ;
 do
   echo $Distance
   # Create directory with the distance as name
   mkdir $Distance;
   # copy the control file into the new directoy
   cp control.template $Distance/control.in
   # the the geometry template  and
   # replace the term DIST by the current distance and
   # copy the new file into the directory
   sed "s/Dist/$Distance/g" geometry.template > $Distance/geometry.in
   # Change directory
   cd $Distance;
   # Run aims and pipe the output into a file named "output"
   $AIMSBIN | tee output;
   # Go back to the original directory
   cd ..
done;
```

Figure 8: This is a sample bash script for calculating a molecule with different pre-defined bond distances.

Sample script for Exercise 9

Below, you find a sample bash script that adapts the `control.in` file from the `Templates` directory, to test different settings for the density mixing scheme (`linear` and `pulay`).

```
#!/bin/bash -l

AIMS_BIN=$HANDSON/bin/aims.x
#################################################################
MIXER='linear pulay'
N_MAX='3 5 8'
PARAM=(0.1 0.3 0.2)

echo "*****************************************************"
echo "EXERCISE IX:"
echo "*****************************************************"

for type in $MIXER; do

  mkdir $type
  cd $type

  if [ $type != 'linear' ]; then
     for num in $N_MAX; do
        if [ $num == '3' ];then
           para=${PARAM[0]}
        elif [ $num == '5' ];then
           para=${PARAM[1]}
        elif [ $num == '8' ];then
           para=${PARAM[2]}
        fi
        mkdir $num-$para
        cd $num-$para
        cp ../../Templates/geometry_template.in geometry.in
        cp ../../Templates/control_template.in control.in
        sed -i "s/TYPE/$type/g" control.in
        sed -i "s/PARA/$para/g" control.in
        sed -i "s/NUM/$num/g" control.in
        $AIMS_BIN | tee aims.out
        cd ..
     done
  else
     cp ../Templates/geometry_template.in geometry.in
     cp ../Templates/control_template.in control.in
     sed -i "s/TYPE/$type/g" control.in
     sed -i "s/charge_mix_param/#charge_mix_param/g" control.in
     sed -i "s/n_max_pulay/#n_max_pulay/g" control.in
     $AIMS_BIN | tee aims.out
  fi
  cd ..
done
```

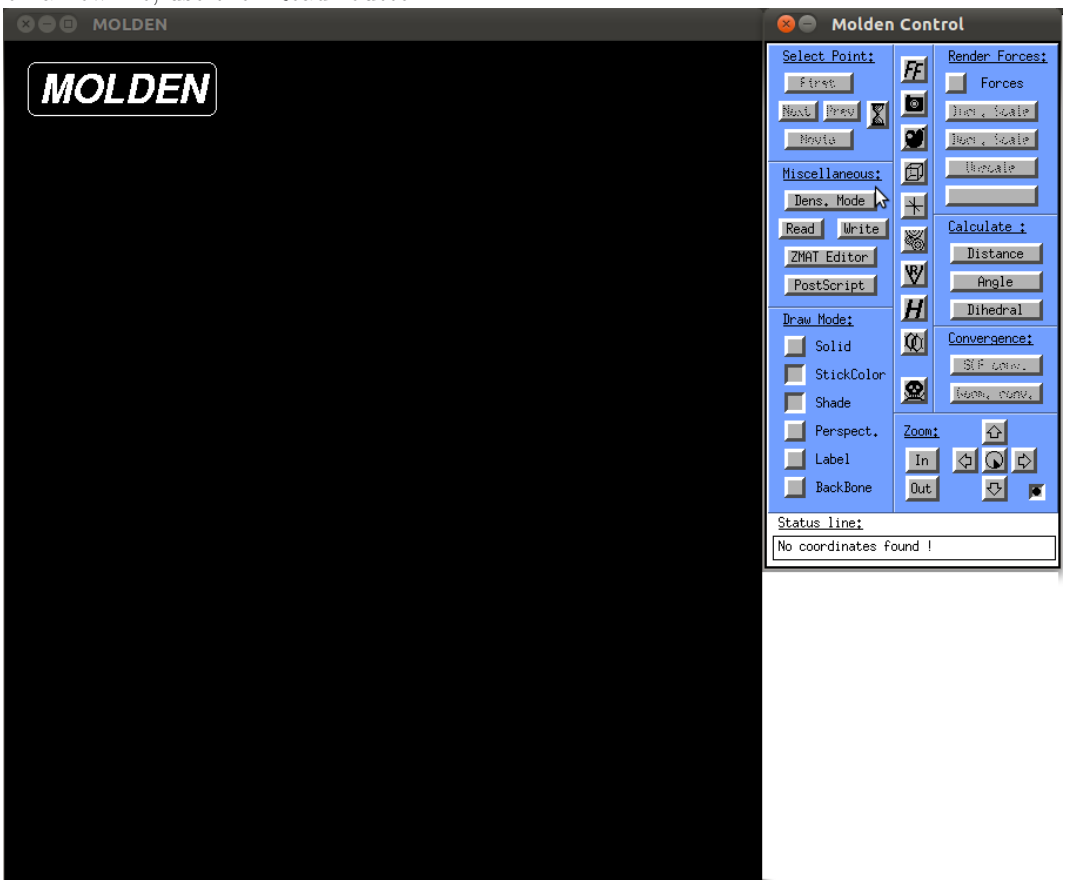
Figure 9: This is a sample bash script that tests different settings for the density mixing schemes.

Appendix II: 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 appyling 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

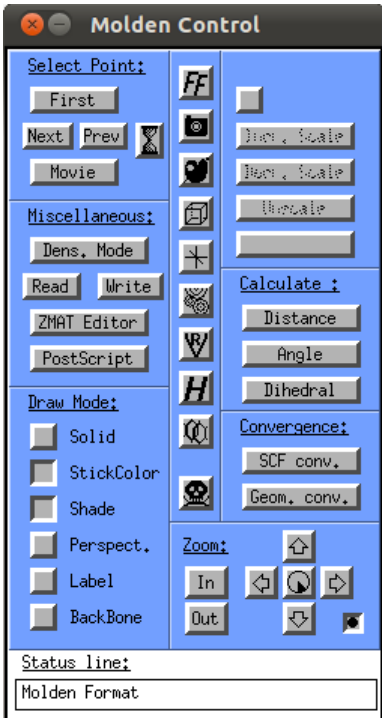
1. Create a molden file by applying the script `create_relax_movie.pl` to the FHI-aims output of a geometry relaxation.

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 though each point of the geometry optmisation 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.

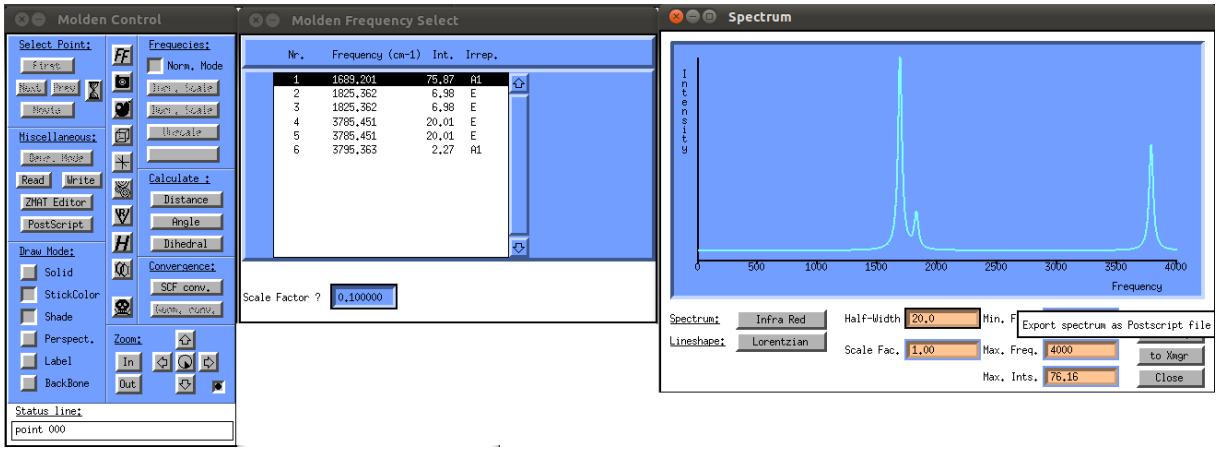


Vibrations

1. Create a molden file by applying the script `> ./troublemaker.pl -xyz2molden H3O+.xyz > H3O+.molden` to the FHI-aims output `H3O+.xyz` of a vibration (`troublemaker.pl` can be found in the `$HANDSON/hands-on-2014-tutorials/tutorial_1utilities` folder). calculations.

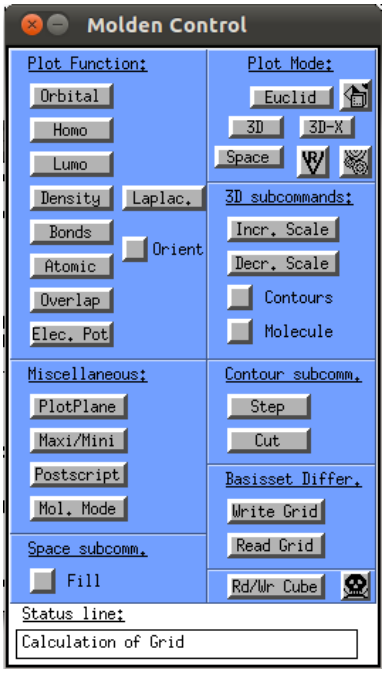
2. Open the file typing `molden` *`filename`*. On the top right corener fo the Molden Control Window, the "Norm. Mode" button should be active now, as highlighted in the picture.

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.



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-benzoquione, the molecule used in the last part of Tutorial 1, and shown in the picture below.

1. Open molden 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.

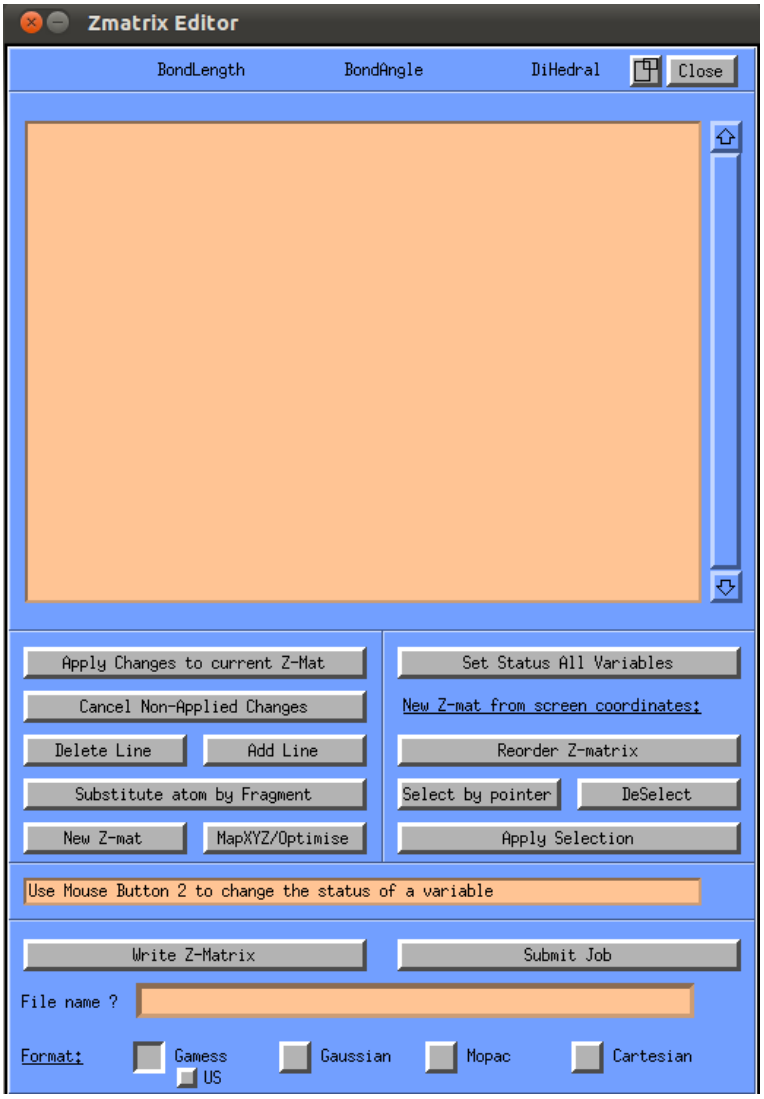
3. The fastest way to proceed is to mark the carbon atom, choose 'Substitute atom by fragment' from the Zmatrix Editor, and select -Phenyl. This will turn the atom into a completed ring, saturated with hydrogen atoms on all carbon atoms but one. The formally empty box will now contain a list of all atoms. 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.


Zmatrix Editor
BondLength
BondAngle
DiHedral
Close
Apply Changes to current Z-Mat
Set Status All Variables
Cancel Non-Applied Changes
New Z-mat from screen coordinates:
Delete Line
Add Line
Reorder Z-matrix
Substitute atom by Fragment
Select by pointer
DeSelect
New Z-mat
MapXYZ/Optimise
Apply Selection
Use Mouse Button 2 to change the status of a variable
Write Z-Matrix
Submit Job
File name ?
Format:
Gamess
US
Gaussian
Mopac
Cartesian

Acknowledgments

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References

[1] B. G. Johnson, P. M. W. Gill and J. A. Pople, *The performance of a family of density functional methods*, The Journal of Chemical Physics **98**, 5612 (1993).

[2] R. S. Mulliken, *Electronic Population Analysis on LCAO-MO Molecular Wave Functions. II. Overlap Populations, Bond Orders and Covalent Bond Energies*, The Journal of Chemical Physics **23**, 1841 (1955).

[3] E. Block, *The Chemistry of Garlic and Onions*, Scientific American **252**, 114 (1985).