

A brief introduction to the use of ORCA

In order to carry out a calculation of a molecule using ORCA, you need to specify the initial coordinates of the atoms and choose the method used for approximating the wave function of the electrons.

Generating initial coordinates of the atoms in the molecule

Some of the exercises in this course involve very simple molecules with just two or three atoms. Then, it is easy enough to write the coordinates in a file manually. For larger molecules, it is better to use the molecular builder feature of Chemcraft to generate the coordinates of the atoms. Sometimes, you might also want to use molecular structure generated from a previous ORCA calculation, visualize it in Chemcraft and make some modifications (e.g. to find a new conformer or substitute one chemical group for another).

If the molecule is too large or too complicated to be handled in Chemcraft, you can try to get the atom coordinates from another source such as a file created for a similar molecule that someone else calculated or a data base of structures containing calculated or experimentally determined structures.

Choosing the method for the calculation

In the lab handouts you will usually be told what method to use, but sometimes you should make that choice yourself. In research projects, the most challenging aspect of theoretical calculations is to make an intelligent choice of the level of theory (what approximation to the basic equations and what basis set to use). After taking this course, you should be able to make such choices but that requires that you understand the capabilities and limitations of the various levels of theory. Your choice will depend on the size of the molecule (namely the number of electrons) and the computational power you have access to. In many cases the task is to do a geometry optimization (or a single-point energy calculation on a previously optimized geometry) and it is good to start with a method that does not require large computational effort, such as Hartree-Fock (HF) or density functional theory (DFT). The basic rule is to start with rather low level and fast calculations and then later on move to more accurate and longer calculations.

0.1 Using Chemcraft to generate atomic coordinates

You can build a molecule atom by atom if you like but most of the time it is easier to find a fragment from the Chemcraft library and modify it to generate the molecule of interest. See the following Chemcraft tutorials on how to build molecules:

<https://www.chemcraftprog.com/help/constrmol.html>

<https://www.chemcraftprog.com/help/workwithmolfrag.html>

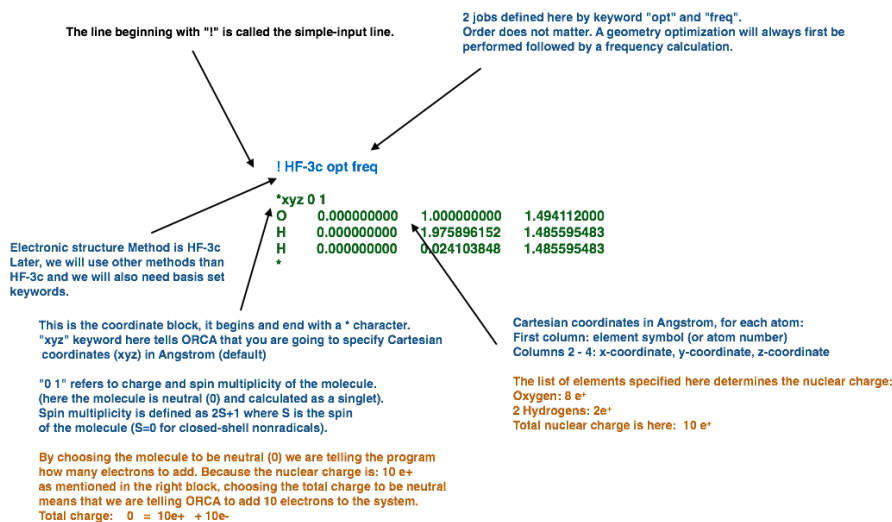
See also this page: <https://www.chemcraftprog.com/description.html>

Note that Chemcraft has some features that can be quite handy for building molecules: e.g. you can symmetrize your starting structures for a particular point-group by selecting Edit menu -> Set pointgroup. To get an improved estimate of bond lengths and angles select Edit menu-> Clean.

Once the initial structure of the molecule has been generated where the atoms are not too close to each other and also not too far, the coordinates can be exported to the computer cluster Jotunn. Note that it does not matter whether Chemcraft shows a single bond when you think there should be a double bond, or no bond when there should be a bond. Chemcraft just guesses the presence of bonds and bond order based on distances and often makes mistakes. Just make sure that your bond distances and bond angles are sensible (see e.g. Standard Bond Lengths and Bond Angles), otherwise ORCA may take long time solving the quantum mechanical equations and will need many iterations to optimize the structure. Use your chemical intuition!

Chemcraft only provides the Cartesian coordinates of the atoms. This information is obtained by clicking the "Coord" tab in the Chemcraft window. Then, you need to copy the coordinates into an ORCA input file, as described below.

0.2 Preparing an input file for ORCA



The figure above shows the structure of an ORCA input file (you can open a larger version of the figure in your browser at <https://notendur.hi.is/hj/reikniefnafr/input.png>). An ORCA input file always needs to specify the following:

- A line beginning with a ! symbol. This is where you give ORCA keywords that specify what kind of calculation should be carried out. In the example shown, 'HF-3c' refers to the theoretical method used to solve for the wave function, 'opt' specifies that the atoms should be moved iteratively so as to minimize the energy (optimization of the molecular geometry), and 'freq' specifies that vibrational frequencies should be calculated.
- A coordinate block beginning and ending with a * symbol. You also specify the charge and the spin multiplicity here, followed by the coordinates (usually Cartesian coordinates in units of Angstrom). The coordinates can for example come from Chemcraft or perhaps from a previous ORCA calculation.

There is a webpage explaining how to construct ORCA input files: The ORCA Input Library: (<https://sites.google.com/site/orcainputlibrary/generalinput>). It is recommended that you start by reading the "General Input" page. You can also download and use the ORCA manual at <https://orcaforum.cec.mpg.de/OrcaManual.pdf>