

Tutorial 1: Getting to know nanoHUB and Ab-initio Calculations

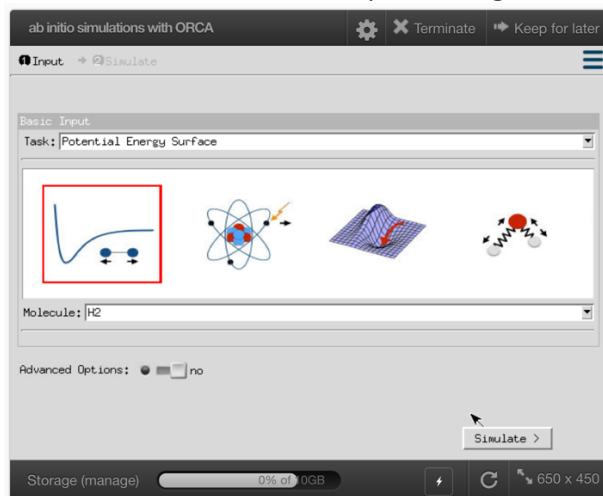
Goal: The goal of these activities is for you to get comfortable with running electronic structure calculations. We will be using the ORCA GUI housed on nanoHUB to start. ORCA can be run from the command line too.

To get credit for doing this tutorial, there are a number of activities (underlined) that you must complete and submit your answers/work. **Tasks** or results to submit are indicated with bold.

Continue after you sign up for nanoHUB!

To start, we'll click on all the buttons (except for simulate) to see what kind of control we have over the simulation.

First: Switch on Advanced Options to get more tabs/control!



Basic Input – you can choose from 4 types of simulations.

Task i: Describe (write a definition) of these simulation types.

- Potential Energy Surface
- Geometry Optimization
- Ionization Energy
- Normal Mode Analysis

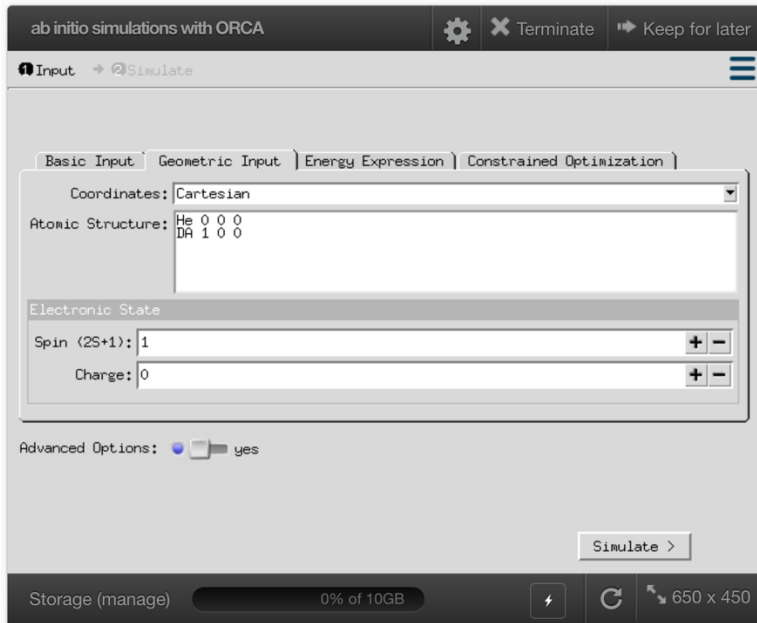
ORCA has some pre-built molecules

Molecule: pick from drop down or use Geometric Input

There is always a 'default', so you need to edit the default if you don't want that molecule.

Use the Geometric Input tab to make your own molecules (or atoms).

The picture/screenshot below shows me editing the Atomic Structure to simulate a He atom.



Activity 1: Set up simulation - Select Potential Energy Surface and the H₂ molecule.

Task ii: Write down what you see in the Geometric Input. The coordinates will be given in the form of a Z-matrix. Please go read the Wikipedia article on it! It is easier to use Cartesian when we build our own molecules.

Atomic Structure:
H 0 0 0 0.0 0.0 0.0
H 1 0 0 1.0 0.0 0.0

Task ii: Write down what you see in the Electronic State for the

- Spin (2S+1):
- Charge:

Spin and charge controls are important for simulating molecules like H-He⁺.

Energy Expression – We will try out all of the methods for electronic structure calculation, but we will start with Hartree-Fock.

Method:

- Hartree-Fock
- Density Functional Theory
- Hartree-Fock + Perturbation (MP2)
- Coupled-Clusters (SD)
- Complete Active Space SCF

Task iii: Write down the method and basis set (the default) that you will use for your first simulation. A short description of all the possible basis sets is given below. We will discuss basis sets in lecture eventually.

Basis Set:

Example: 3-21G, page 623, The 3 indicates that each nonvalenced orbital is represented by a sum of three Gaussian functions, which as a whole is called a contracted Gaussian function. The dash indicates that the basis set is a split-valence basis set; the 21 indicates that each valence orbital is represented by two contracted Gaussian functions, one consisting of two primitive Gaussian functions and the other consisting of only (not a contraction really).

- a) STO-3G: minimal basis set (atoms H-I?)
Contracted Gaussian functions fit to Slater Type Orbital. A contraction of 3 Gaussian functions to represent one Slater-type orbital is given the term STO-3G. Any number of Gaussians can be chosen, N, indicated using STO-NG basis set.
- b) 6-31G: Pople 6-31G and its modifications (H-Ar)
- c) 6-31+G*: one set of first polarization (on d orbitals?) functions on all atoms except H, with diffuse functions on all atoms except H
- d) 6-311+G*: Pople 6-311G and its modifications (H-Br)
- e) SVP: Ahlrichs basis set – polarized valence double-zeta
- f) TZVP: polarized valence triple-zeta basis set
- g) cc-pVTZ: Dunning correlation-consistent polarized triple-zeta
- h) cc-pVQZ: Dunning correlation-consistent polarized quadruple-zeta
- i) aug-cc-pVTZ: (n=D,T,Q,5,6) Augmented with diffuse functions
- j) aug-cc-pVQZ: same as above but for quadruple-zeta

For now, we are going to ignore the constrained optimization tab.

Activity 2: Click 'Simulate' and the job will start running. The output will pop up!

Task iii: Click on Result: Relaxed Potential Energy Surface and sketch the result (turn it in).

Answer the following questions:

- a) What is the equilibrium bond length found by the simulation? Compare it to the experimental bond length. What experiments can be done to find the experimental bond length?
- b) What is the minimum energy for the molecule? Convert that number to Hartree and eV.
- c) What is the meaning of the minimum energy found on the potential energy surface?
- d) What is the bonding energy for this molecule? Describe why your estimate from the plot might be inaccurate.

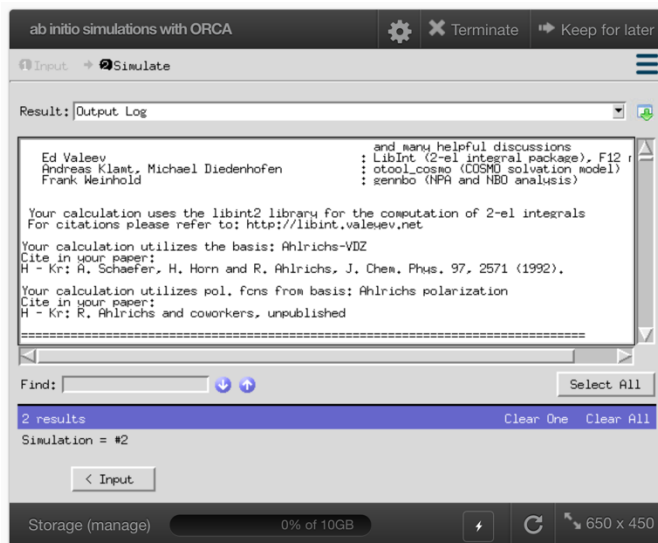
The output of a simulation contains A LOT of information and should include all the parameters that you set in the input (file).

Click on Result: Output Log and start to scroll through the text.

Task iv (a-d):

- a) What is the first piece of information about the actual simulation that you did?

Hint from my screenshot:



- b) Copy out the format of the input file for ORCA simulations. Note that the GUI input is much easier to set-up.
- c) Which line tells the simulation to run the Potential Energy Surface calculation? Match up with information with your sketch (or open the Potential Energy Surface image).
- d) How many bond distances are tested to form the potential energy surface?

Task v (a-f): The output is difficult to read in the GUI (while scrolling). A text editor, like VIM, is much better for finding the useful information. Thus, download the output!

- a) Go to the bottom of the file and determine if the simulation finished (or crashed). What information tells you that the simulation finished? How long did it take for the simulation to run?
- b) Find all the locations where information about the SCF convergence is reported. What does SCF stand for? What does the Tolerance indicate? What are the units for the Tolerance?
- c) What was the bond distance for the first SCF calculation? What was the energy in Hartrees? In eV?
- d) How many cycles were needed to converge for the first SCF calculation?

- e) Find the location where the ORBITAL ENERGIES are reported. Describe what is given in the four columns. Why are there a bunch of zeros?
- f) Find where the MULLIKEN REDUCED ORBITAL CHARGES are reported. Describe what is given in the three columns. Why aren't there a bunch of zeros?

Ten "atomic orbitals" are used to build the molecular orbitals in the SVP, using 5 from each atom. Let's ignore the p orbitals when examining the two lowest energy states, since they only contribute a small amount.

The molecular orbital is made of a wavefunction that is a linear combination of these orbitals:
 $\varphi = c_{01}(1s_0) + c_{11}(1s_1) + c_{02}(2s_0) + c_{12}(2s_1) + p \text{ orbitals}$

Task vi: The section labeled MOLECULAR ORBITALS gives the energy and the population of each orbital and the coefficients.

- a) Write out the first two orbitals for the SVP calculation you just did, substituting the coefficients with actual numbers from the output. Only include the contributions from the 1s and 2s "atomic orbitals".
- b) What is the occupation and energy of these two lowest orbitals?
- c) It turns out there is a "significant" contribution from one of the p orbitals for the ground state. Which one? Justify why this orbital contributes to the ground state wavefunction.
- d) How many excited states were calculated in this simulation?

Congratulations! You finished your first ab-initio calculations using ORCA.