

Lesson 1: The Single Electron Atom: Hydrogen

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Learning Objectives:

1. Utilize quantum numbers and atomic radii information to create input files and run a single-electron calculation.
2. Learn how to read the log and report files to obtain atomic orbital information.
3. Plot the all-electron wavefunction to determine where the electron is likely to be positioned relative to the nucleus.

Before doing this exercise, be sure to read through the Ins and Outs of Operation document.

So, what do we need to build an atom? Protons, neutrons, and electrons of course!

But the mass of a proton is 1800 times greater than that of an electron. **Therefore, based on de Broglie's wave equation, the wavelength of an electron is larger when compared to that of a proton.** In other words, the wave-like properties of an electron are important whereas we think of protons and neutrons as particle-like. The separation of the electron from the nucleus is called the Born-Oppenheimer approximation. So now we need the wave-like description of the Hydrogen electron.

Hydrogen is the simplest atom on the periodic table and the most abundant element in the universe, and therefore the perfect starting point for atomic orbitals and energies. The computational tool we are going to use is called OPIUM (silly name, right?). Before we get started, we should know what's needed to create an input file, which OPIUM calls a parameter files. Each parameter file consist of a sequence of "keyblocks", containing sets of related parameters. Let's examine the basic keyblocks and what they entail. We should be able to review the Ins and Outs of Operation tutorial to determine which keyblocks we need and the information they should contain.

Creating and Running Input Files

[Atom] is the first keyblock, and the most important one, as it hold the information for the atom we're dealing with! In the [Atom] keyblock, OPIUM needs to be told what specific atom

is being calculated, how many subshells it has and the electron filling for each subshell (don't worry, we'll show you examples).

1. *What are the n , l , m , quantum numbers used to describe Hydrogen's single orbital? How many electrons should it contain?*

The default eigenvalue guess "-" is entered after the filling.

[Atom]

H

1

100 1.00 -

2. *What forms of Hydrogen have you seen in discussed in class?*

The second keyblock, **[Pseudo]**, contains the number of valence orbitals and the cut-off radii for each pseudo orbital. Since Hydrogen has only 1 orbital, we have only a valence orbital, which is 1, and the cut-off radius (" r_c ") for the orbital (here 1.80 au). Remember, we care about the valence orbitals, because the electrons located there are responsible for how the atom reacts with other elements! Also, opt indicates that we want to use the optimized pseudopotential methods. Optimized is what we will be utilizing for all pseudopotentials we create.

[Pseudo]

1 1.8

opt

[Optinfo] is a mandatory key-block for the optimized method which indicates the cutoff wavevector q_c and the number of Bessel functions used in the pseudopotential construction. Refer to the Ins and Outs of Operation to review how q_c is determined. Remember, q_c should be larger than r_c ; a good starting point is $q_c = 2 * r_c$. The square of the cut off wavevector is your energy cutoff. Here if we have a value of 3.00 for q_c , that means our energy cutoff is 9 Ry ($q_c^2 = E$). Remember, these are technical components of the input file, you do not need to understand them completely to continue with the exercise.

[Optinfo]

3.00 10

The electron configuration for Hydrogen is $1s^1$. There is only one electron, so we only have a valence electron to worry about and no core electrons. Once we know the electron configuration of the atom of interest, the parameter file can be built. To design your pseudopotential, you need to start this file by typing **emacs H.param** or **emacs h.param**. Opium is case sensitive, so please pay attention to how you are naming your file. Emacs will open a blank window by this name for you and you can start writing the parameter file. If we assemble our keyblocks in order, the finished input file for hydrogen should look similar to this:

[Atom]

H

1

100 1.00 -

[Pseudo]

1 1.8

opt

[Optinfo]

3.00 10

Now the all-electron calculations can be obtained. To do this, type **./opium H H.log ae rpt** in the command line of the terminal. This will run the all-electron (ae) calculation. The rpt command tells Opium to summarize all of the results in a report file. By clicking enter after typing this into your command line, you run the calculations and generate .log and .rpt files.

Obtaining the Atomic Orbital Information from the Log or Report File

The h.log file will contain all of the output from the commands and indicate any errors or warnings. One needs to carefully look through the log files to look for errors. This can be done by typing **emacs h.log** and hitting the enter key. If no errors are found, close the .log file, and open

the report file **emacs h.rpt**.

AE report

AE:Orbital	Filling	Eigenvalues[Ry]	Norm
100	1.000	-0.4673245081	0.3760171534

$$E_{tot} = -0.8917869366 \text{ Ry}$$

When you open the .rpt file, first scroll down to the part of titled AE report. What do we find? We see each atomic orbital (only one for H), the number of electrons each orbital contains, and the eigenvalue (energy) of that particular atomic orbital. We also find the total energy. Remember, the total energy will *NEVER* equal the sum of the orbitals eigenvalues. And why not? The eigenvalues are the energy of each electron within an orbital. The total energy includes the eigenvalues (energies) of all electrons in every orbital, their repulsive forces between each other, and the attractive forces the electrons have for the nucleus.

Plotting All-electron Wavefunctions to Determine Electron Position

To plot the all-electron wavefunction, one types **opium h h.log all rpt plot wa** into the command line. This uses the information from our all-electron calculations to tell us where the electron is likely to be located relative to the nucleus.

The 1s peak is centered around 1.05 bohr, which is pretty far from the cut-off radius.

3. *What is this value in angstroms?*

Using the directions from the Radial Wavefunctions document, export the data for this wavefunction to a file called 1s.dat. We'll use this a bit later to determine how the all-electron wavefunctions change with principle quantum number.

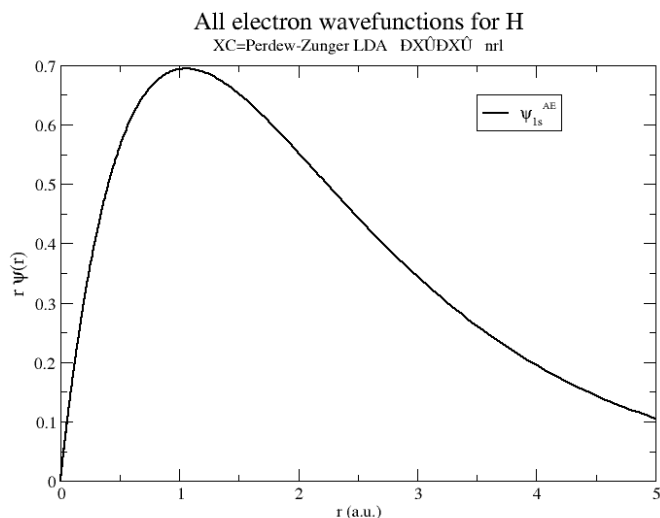


FIG. 1: Hydrogen all-electron wavefunctions.

4. Through examining the report file, find Hydrogen's atomic orbital and its energy. What is this orbital, its filling, and the energy?
5. Examine the all-electron wavefunction plot for Hydrogen. Does it have any nodes?

Let's move on to the next lesson, Carbon. **Don't forget to write your answers for the Carbon Lesson in your lab notebook!**

References

1. User's Guide. Opium-Pseudopotential Generation Project. opium.sourceforge.net
2. J.P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
3. J.P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
4. A.M. Rappe, K.M. Rabe, E. Kaxiras, and J.D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).

Answers to questions:

1. The quantum numbers used to describe Hydrogen's orbital are $n = 1$, $l = 0$ and $m = 0$. It should contain a single (1) electron

2. In class, diatomic hydrogen, the single atom, the cation and the anion have all been discussed.
3. 0.56 Angstroms
4. Hydrogens atomic orbital is the 1s orbital, and it contains one electron. It has an energy of -0.46732 Ry.
5. The all-electron wavefunction plot for Hydrogen does not contain any nodes, and peaks around 1.05 a.u. Refer to Figure 1.