Lesson 2: Carbon; A Multi-Electron Atom

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Introduction

Carbon is the most important element to all living things, making it highly studied. Building upon what we learned from the Hydrogen Tutorial, we'll take a look at Carbon to gain a better understanding of some of the keyblocks utilized in the first tutorial and how they can be adjusted to include more electrons.

Learning Objectives:

1. **How to deal with atoms containing degenerate orbitals and what that means for our atomic orbitals.**

2. **To plot all-electron potentials and wavefunctions.**

Preliminary Questions

What do we need to start building our parameter file? If your answer is the electron configuration, you're correct! Previously, we looked at Hydrogen, the simplest atom on the periodic table, which has a configuration of $1s^1$. Carbon has five more electrons than hydrogen when in the neutral state. **Write your answer to the prelab questions in your lab notebook.** It may help to refer back to the chapter on Electronic Structure in your textbook.

1. What is the electron configuration for a neutral carbon atom?

2. How many orbitals does carbon contain?

3. How does our angular momentum quantum number, l change as we increase the principle quantum number, n?

4. What do you think the numerical notations should be for these orbitals in nlm?

5. Which electrons do you think are core electrons? Valence electrons?

6. What are nodes, and do you think we'll see any in our plots? If so, where? Refer to the electronic structure in your textbook as needed.

Degenerate orbitals

We know from Hydrogen that $1s$ is given the number 100 to correspond to the n, l, and m_l values. This means the $2s$ should be 200, but what about the $2p$? If we refer back to our numerical notation in general chemistry, the p orbitals are assigned a number of 1, so $2p$ would be 210. our m_l quantumn number ranges from $-l$ to l, but the orientation of our orbitals does not affect the energy. This means all of the p orbitals are degenerate–meaning the electrons in these orbitals will all have the same energy. The last value for the nlm entry for each orbital will never change from a 0 since OPIUM enforces spherical symmetry, meaning the electrons will always be centered around the origin.

Which four keyblocks should be used to build a carbon atom?

[Atom]
C
3
100   2.00   -
200   2.00   -
210   2.00   -

[Pseudo]
2   1.4   1.4
opt

[Optinfo]
7.07   10
7.07   10

[XC]
lda

As a reminder, the [Atom] keyblock should include the symbol of the element, the total number of orbitals (s, p, d, and f as needed), and the occupation of each orbital(how many electrons the orbital contains). The [Pseudo] keyblock specifies the number of valence states,

the cutoff radius (r_c) for each valence state, and the method of pseudopotential construction. **How many valence orbitals does carbon have?** When using the Optimized function, the third keyblock [Optinfo] is mandatory and will include your cutoff wavevector and the number of bessel functions for each valence orbital. The cutoff wavevector in the input here should be the square root of your energy cutoff. If our desired energy cutoff is 50 Ry, the keyblock should have a value of 7.07 for q_c.

In the terminal window, execute the command **./opium C C.log ae** once your param file has been completed and saved.

Once our calculation has completed, open up the log file and find the atomic orbital energies **Where do we find this information again?**

To do this, type **cat C.log** or **emacs C.log** and scroll down until you see the AE part of the calculation.

```
===============================================================================
Begin AE calculation
===============================================================================
Performing non-relativistic AE calculation...
————Eigenvalue guesses————


1s        -36.00000000
2s         -2.25000000
2p         -2.25000000
```

iter	Etot	Ebs	Ehxc	de$_{max}$	dv$_{max}$
1	-78.0101223	-46.1066343	-31.9034880	0.73E+00	0.20E+01
2	-76.9630569	-44.6770656	-32.2859913	0.10E+00	0.10E+01
3	-75.3373196	-42.8552064	-32.4821132	0.18E+00	0.14E+00
...					
27	-74.8485240	-42.5925069	-32.2560171	0.52E-08	0.18E-07

27 iterations: (units are Ry and bohr)

Energy: -74.84852399,   Ebs: -42.59250694,   Ehxc: -32.25601705

Eh : 35.24955639,   Exc: -9.45350358,

Orbital	Filling	Eigenvalues	Norm(rc− > ∞)	Peak
$|100>$	2.000	-19.895705		
$|200>$	2.000	-1.001950	0.542895	1.224346
$|210>$	2.000	-0.398599	0.589443	1.192923

The first section of the all-electron portion of the log file shows that this calculation was performed using a non-relativistic (the velocity is small with respect to that of light) Hamiltonian. Next, we see the convergence of both the energy and potential. We can see that the largest change in any eigenvalue ($de_{\max}$) and potential ($dv_{\max}$) [2] is smaller than $1 * 10^{-7}$ Ry. Finally, the last section under AE calculation shows the total energy and eigenvalues for the electronic configuration. The eigenvalues provide us with the energy of each atomic orbital in carbon. We can use this information, along with the atomic orbital energies from other elements to determine how they will form bonds and molecular orbitals. Also, for the valence states, the norm of the wavefunction beyond the cutoff radius and the position of the outermost peak is shown. **What is the energy of the atomic orbitals in carbon? How has the energy of the 1s orbital changed when compared to hydrogen? What information do you think this can tell you about the location of the electrons with respect to the nucleus?**

In the terminal window, plot the all-electron wavefunction: **./opium C C.log plot wa**

Xmgrace will open up the completed plot when the calculation finishs, and from both the plot and the log file, we can see the outermost peaks of the valence wavefunctions are slightly more than 1 a.u. from the nucleus. It's normal to place the pseudopotential r_c at or somewhat beyond the outermost wavefunction peak. Also, the r_c's should be less than roughly 45% of the smallest bond length in the target calculation. **What are some of the bond lengths of carbon? (Hint: Check your textbook)**

Pseudopotential Construction and Convergence Check

Now, we can construct the pseudopotential by typing **opium C C.log ps**. Inspect the C.log file
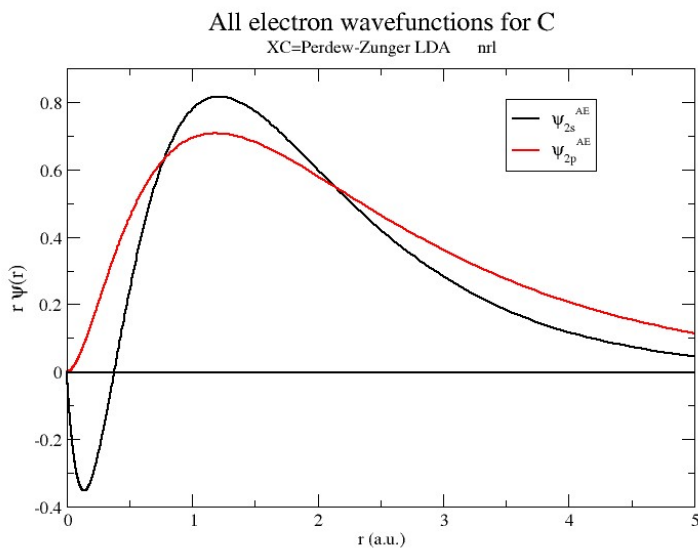
FIG. 1: Carbon all-electron wavefunctions.

to see if the calculation converged without any errors. If so, we'll move on to plotting potentials.

Plotting Ionic Potentials

Ionic potential can be obtained when one takes a ratio of electric charge to the radius of an ion, giving one a measure of the ion's density. This gives an idea of how strongly or weakly the ion will be attracted to ions of opposite charge and to what degree it will repel ions of similar charge. To find the ionic potential for the element of interest, in the terminal window, plot the all-electron and pseudo ionic potentials using the following command: **./opium C C.log all plot vi**
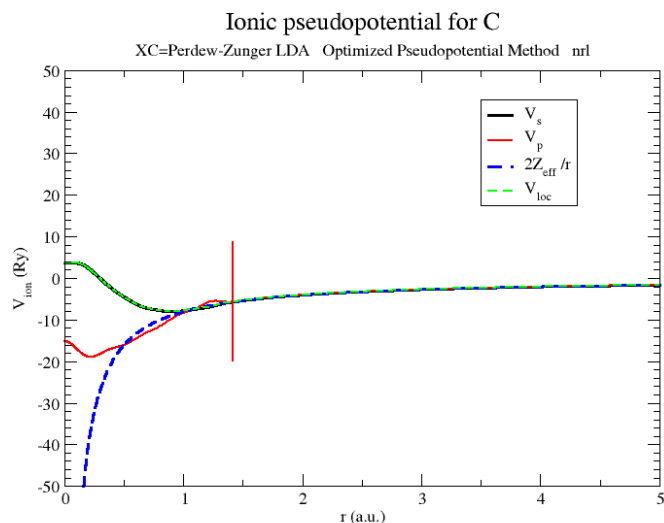
 Data Analysis questions

FIG. 2: Carbon ionic potentials.

1. Run and open the report file for Carbon. What atomic orbitals does carbon have and what are their energies? How has the 1s orbital energy changed between Hydrogen and Carbon? Which orbitals are core orbitals and which ones are valence?

2. Plot the all-electron wavefunction for carbon. Which orbital contains nodes and how many? How does it differ from Hydrogens wavefunction?

Additional Post Lab Problems

1. **Utilize your textbook to help you determine the screening potential for carbon. How does your calculated value compare to the one found in by OPIUM? (Hint: This can be found in the PS construction portion of your log file.)**

2. **Compare your Z_{eff} and OPIUM's to the literature value for Carbon. What is the percent error for each method? Please cite the literature values.**

3. **Tabulate your energy values for the electrons in each orbital and create an energy diagram. Do these agree with the energy diagram and trends discussed in class?**

References

1. J.P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

2. dv_{max} is the largest change at any grid point in the self-consistent potential

3. A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990)

4. L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).

Answers to data analysis questions:

1. Carbon contains three orbitals, the 1s, the 2s, and the 2p. The 1s orbital is the only core orbital and has an energy of -19.89571 Ry. The 2s and 2p orbitals are valence orbitals; the 2s has an energy of -1.00195 Ry and the 2p an energy of -0.39860 Ry. The 1s orbital in Carbon is much lower in energy compared to Hydrogens 1s orbital.

2. The 2s orbital in carbon contains 1 node. The 2p orbital does not contain any. Carbon has two wavefunctions, one for each valence state, and the peaks or each of these are slightly further away (1.20 a.u.) from the origin than the peak (1.05 a.u.) in the Hydrogen wavefunction.