

Chem 30324, Spring 2019, Homework 8

Due March 27, 2019

Variations on the hydrogen atom

The *variational principle* guarantees that the expectation value of the energy of a guessed wavefunction is always greater than that of the true lowest energy solution. Here you will apply the variational principle to the H atom. For this problem it is easiest to work in atomic units. In these units, \hbar , a_0 , and $4\pi\epsilon_0$ are all equal to 1 and the unit of energy is the Hartree, equivalent to 27.212 eV. In atomic units the H atom Schrödinger equation is written:

$$\left\{ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r} + \frac{l(l+1)}{2r^2} \right\} R(r) = ER(r)$$

1. Normalize the true 1s wavefunction, $R_{10}(r) = e^{-r}$. Do not forget to include the r^2 integration factor.
2. Is this 1s wavefunction an eigenfunction of the hydrogen Schrödinger equation? What is the eigenvalue? Recall that your answer will be in Hartree.
3. Suppose in a fit of panic you forget the 1s radial function when asked on an exam. Not wanting to leave the answer blank, you decide to guess something, and liking bell-shaped curves, you guess $R_{10}(r) = e^{-r^2}$. Normalize this guess.
4. Calculate the expectation value of the energy of your normalized guess. Is it greater or less than the true value?
5. What does the variational principle say about the expectation value of the energy of your guess as you vary a parameter γ in your guess, $R_{10} = e^{-\gamma r^2}$? Suggest a strategy for determining the "best" γ .
6. *Extra credit:* Determine the best value of γ . Show and carefully justify your work to receive credit.

Many-electron atoms:

Oxygen (O) is the eighth atom on the periodic table and has 6 valence electrons.

7. Write the ground state atomic configuration of oxygen.

8. Provide *one possible set* of quantum numbers (n, l, m_l, m_s) for each of the valence electrons in the atom. What is the ground state *spin multiplicity* of O?

9. *Qualitatively* compare the energies necessary to remove a 1s electron from O and from sulfur (S), one row below O in the periodic table. Explain your answer. (Note that the measurement of these energies is the basis of X-ray core-level spectroscopy.)

10. *Qualitatively* compare the ionization energies (energies to remove a valence p electron) from O and from S, one row below O in the periodic table. Explain your answer.

11. *Qualitatively* compare the ionization energies (energies to remove a valence p electron) from O and from fluorine (F), one column to the right of O in the periodic table. Explain your answer.

12. Show that a 2s hydrogenic orbital approaches closer to the nucleus than the 2p, by comparing the probability of finding either electron within 1 atomic unit of the nucleus. In atomic units, the 2s and 2p radial wavefunctions are given by:

$$R_{2,0} = \frac{1}{\sqrt{2}}(1 - r/2)e^{-r/2}$$
$$R_{2,1} = \frac{1}{2\sqrt{6}}re^{-r/2}$$

Remember to construct the radial probability functions correctly.

Multi-electron atoms and the self-consistent field.

Modern calculations on atom and molecules take advantage of the variational principle and are made with sophisticated computer programs that solve the many-electron Schrödinger equation. *Density functional theory* (DFT) is the most common set of approximations for the electron-electron interactions used today. In this problem you'll do a DFT calculation using the *Gaussian* program (<http://www.gaussian.com> (<http://www.gaussian.com>)).

Now, let's set up your calculation (you may do this with a partner if you choose):

1. Log into the Webmo server <https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi> (<https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi>) using "guest" as your username and password.
2. Select New Job-Creat New Job.
3. Use the available tools to draw an argon (Ar) atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Gaussian
6. Select "Molecular Orbitals" for the Calculation type, "B3LYP" for theory, "Minimal" for the basis set, "0" for the charge, and "Singlet" for the multiplicity.
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.

13. Write down the energies of the occupied molecular orbitals and identify them by their shell ($n = 1, 2, \dots$) and subshell (s, p, d, ...). For fun, click on the Magnifying Glass icons to see the molecular orbitals in 3-D. You may have to play around with the Display Settings and Preferences to get good views.

You are welcome to play around with other atoms. For anything other than the noble gases, be sure to set the Multiplicity to a sensible value.