

# Chem 30324, Spring 2020, Homework 7

**Due March 27, 2020**

## 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. 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. Do not forget to include the  $r^2$  Jacobian integration factor.

2. Calculate the expectation value of the energy of your normalized guess. Is it greater or less than the true value?

3. What does the variational principle say about the expectation value of the energy of your guess as you vary a parameter  $\gamma$  in your guess,  $R_{10} = e^{-\gamma r^2}$ ? Suggest a strategy for determining the "best"  $\gamma$ .

**3.5 Extra credit:** Determine the best value of  $\gamma$ . Show and carefully justify your work to receive credit.

## Many-electrons means many troubles

Helium (He) is only one electron larger than hydrogen, but that one more electron makes a big difference in difficulty in setting up and solving the Schrödinger equation.

4. Write down in as much detail as you can the exact Schrödinger equation for the electrons in a He atom.

5. This equation is conventionally solved within the "independent electron" approximation, by writing an effective one-electron Schrödinger equation with approximate potentials (shown below in atomic units). Briefly, what does it mean to solve this equation "self-consistently"?

$$\left\{ -\frac{1}{2}\nabla^2 - \frac{2}{r} + \hat{v}_{\text{Coul}}[\psi_i] + \hat{v}_{\text{ex}}[\psi_i] + \hat{v}_{\text{corr}}[\psi_i] \right\} \psi = \epsilon\psi$$

6. How many solutions are needed to describe the electrons in a He atom? Provide a possible set of quantum numbers  $(n, l, m_l, m_s)$  for each electron.

7. The Schrödinger equation has five terms, or operators, on the left. Identify the physical meaning of each term and the *sign* of the expectation value when it is applied to one of the solutions.

Sophisticated computer programs that solve the many-electron Schrödinger equation are now widely available and powerful tool for predicting the properties of atoms, molecules, solids, and interfaces. *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 *Orca* program (<https://www.its.hku.hk/services/research/hpc/software/orca> (<https://www.its.hku.hk/services/research/hpc/software/orca>)).

**Now, let's set up your calculation (you may do this with a partner or two 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 atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Orca
6. Select "Molecular Orbitals" for the Calculation type, "PBE" for theory, "def2-SVP" for the basis set, "0" for the charge, an appropriate value for the "Multiplicity", and check "Unrestricted."
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.
9. 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.

**8. Perform calculations across the first row of the periodic table (B, C, N, O, F, Ne). Make a table of energies of the occupied orbitals and identify them by their shell ( $n = 1, 2, \dots$ ) and subshell (s, p, d, ...).**

**9. Contrast the energies of the 1s electrons across the series. Determine the wavelength of light necessary to remove each 1s electron. What range of the spectrum is this light in?**

**10. Why, qualitatively, do the energies vary as they do?**

**11. Compare the energies of the highest-energy (valence) electrons compare across the series. Determine the wavelength of light necessary to remove each valence electron. What range of the spectrum is this light in?**

**12. Why, qualitatively, do the energies vary as they do?**