

Chem 30324, Spring 2017, Homework 8

Due April 3, 2017

Quantum mechanics of an H atom:

Consider an excited hydrogen atom with a $2s^1$ electron configuration. The $2s$ radial wavefunction is given by

$$R_{2,0} = \frac{1}{\sqrt{2a_0^3}}(1 - \rho/2)e^{-\rho/2}, \rho = r/a_0$$

where a_0 = bohr radius. (*Hint: It's easiest to solve the following using a_0 as the unit of length.*)

1. Provide a hand sketch of the 3-D shape of a $2s$ wavefunction ("orbital"). Be sure to indicate the *sign* of the wavefunction in each region and the location(s) of nodes. How many radial and how many angular nodes does a $2s$ electron orbital have?
2. Plot the radial probability function $P_{20}(r) = r^2 |R_{2,0}(r)|^2$. Be sure to label both axes appropriately. (*Hint: Stick with a_0 as the length unit.*)
3. Determine and indicate on your plot $\langle r \rangle$, the expectation value of the distance of the electron from the nucleus.
4. Determine and indicate on your plot r_{MP} , the most probable distance of the electron from the nucleus.
5. Determine and indicate on your plot the maximum classical distance of the electron from the nucleus in this orbital.
6. What is the probability of finding the electron beyond the classical distance? (Evaluate the necessary integral numerically.)

7. Can a 2s electron undergo an allowed transition to a lower energy electronic state? If so, what frequency (in cm^{-1}) of light would be emitted?

Variations on the hydrogen atom

The *variational principle* allows us to develop approximate solutions to the Schrödinger equation numerically. 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:

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

8. Normalize the true 1s wavefunction, $R_{10}(r) = e^{-r}$. Do not forget to include the r^2 integration factor.

9. Is this 1s wavefunction an eigenfunction of the hydrogen Schrodinger equation? What is the eigenvalue? Recall that your answer will be in Hartree.

10. Suppose in a fit of panic you forget the 1s radial function when asked on an exam. Now wanting to leave the answer blank, you decide to guess something, and liking bell-shaped curves, you guess $R_{10}(r) = e^{-\gamma r^2}$. Normalize this guess.

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

12. 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 .

13. *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.

14. Write the ground state atomic configuration of oxygen.

15. 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?

16. *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.)

17. *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.

18. *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.

19. 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.

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