Chemistry 60649 — Fall 2008
Professor J. Daniel Gezelter — Due Wed. 11/12/2008

Problem Set 6

These problems will concentrate on the Hydrogen atom and on the approximate methods that we have been covering in class after the mid-semester break.

1. Show explicitly that ψ_{2p_x} and ψ_{2p_y} are orthonormal. (This requires doing three integrals).

2. By evaluating the appropriate integrals, compute $\langle r \rangle$ in the $2s$, the $2p$ and the $3s$ states of the hydrogen atom; compare your results to the general formula

$$\langle r_{n\ell} \rangle = \frac{a_0}{2}[3n^2 - \ell(\ell+1)]$$

3. Calculate the radius of the sphere that encloses a 50% probability of finding a hydrogen $1s$ electron. Repeat the calculation for a 90% probability.

4. When an electron moves in some orbit it has a magnetic moment $\underline{\mu}$ given by

$$\underline{\mu} = -\frac{|e|}{2m_e}\underline{\hat{L}}$$

which results in an interaction energy with an external magnetic field $\underline{B}$ of

$$V = -\underline{\mu} \cdot \underline{B}$$

   a) Find the energy levels for the H atom in a magnetic field given by $\underline{B} = B_z \hat{z}$.
   b) Calculate the splitting (in cm^{-1}) of the hydrogen $3p$ level in a magnetic field of strength $B_z = 1000$ gauss (1 gauss $= 10^{-4}$ Tesla).
   c) Predict the form of the absorption spectrum for the $2s \rightarrow 3p$ transition, and calculate the energies of the lines (in cm^{-1}).

5. Any two particle system with only central forces of the form

$$V(r) = ar^{n+1}$$

obeys a generalized virial theorem

$$\langle T \rangle = \frac{n+1}{2}\langle V \rangle$$

   a) Compare the form of the virial theorem for the H atom to the form for a harmonic oscillator.
   b) Show that the virial theorem is obeyed for the ground state of the H atom.

6. The square well potential with infinite walls at $x = -a/2$ and $x = a/2$ has energy eigenvalues $E_n = n^2h^2/8ma^2$, and eigenfunctions

$$\langle x|n\rangle = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right)$$

if n is odd and

$$\langle x|n\rangle = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

if n is even.

Let the perturbing potential $V = kx^2/2$ be added to this square well, with

$$\frac{ka^2}{8} << \frac{\hbar}{8ma^2} - E_1.$$

a) Show that the first order correction to the energies of the states is

$$E_n^{(1)} = \frac{1}{2}ka^2\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)$$

b) Suppose one were to calculate the first order correction to the ground state wave function $\langle x|1\rangle$. Which of the matrix elements $H_{j,1}^{(1)}$, if any, would vanish? Explain your answer