V25.0109: General Chemistry I (Honors)

Problem set #6: due 10/30

Practice problems from Chapter 4: 1,6,9,20,21

Graded problems

1. Show that the Hartree-Fock guess wave function for helium

$$\Psi_g(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \psi_{1s(Z)}(\mathbf{r}_1)\psi_{1s(Z)}(\mathbf{r}_2) \left[\psi_\uparrow(S_{z,1})\psi_\downarrow(S_{z,2}) - \psi_\uparrow(S_{z,2})\psi_\downarrow(S_{z,1})\right]$$

   is properly normalized. Note that you must integrate over the coordinates *and* sum over the two values each S_z variable can assume.

2. In a particular Hartree-Fock calculation of the Lithium ($Z = 3$) atom, we allow the effective value of Z vary for each electron. Such a calculation yields, for the spatial part of the guess wave function, two orbitals of $1s$ character with an effective charge $Z_1 e$. These orbitals can be denoted as $\psi_{1s(Z_1)}$. The third orbital has $2s$ character with a different effective charge $Z_2 e$ and is denoted $\psi_{2s(Z_2)}$.

   Write down the complete guess wave function including both the spatial orbitals and the correct spin wave functions. You do not need to write out the explicit expressions for the ψ_{1s} and ψ_{2s} functions; you can simply use the notation $\psi_{1s(Z_1)}(\mathbf{r})$ and $\psi_{1s(Z_2)}(\mathbf{r})$ in your overall wave function. Be sure that your wave function has the correct normalization factor.

3. Recall that an electron pinned in space interacting with a magnetic field of strength $\mathbf{B}$ has two energy levels given by

$$E_{m_s} = \frac{eB\hbar}{m_e c} m_s$$

   where $m_s = \pm 1/2$.

   a. If the magnetic field strength is 13.2 Tesla, what frequency would a photon need to have to excite the electron from the spin-down energy level to the spin-up energy level?

   b. An experiment is performed on the electron such that it is prepared in a particular state and its energy is measured. When this experiment is repeated many times, it is found that 2/3 of the time, the energy is $E_{-1/2}$ and 1/3 of the time, the energy is $E_{1/2}$. What is the wave function of the electron just before the energy measurement is made?

   c. If, in one of these measurements, the outcome of the energy measurement is $E_{-1/2}$, what is the wave function of the electron just *after* the energy measurement is made?

   d. Now consider a very large number of electrons in the magnetic field. Assume they are all at fixed spatial locations far enough apart that we can neglect the (constant) Coulomb interaction between them. Suppose the system is as temperature T. Then, thinking back to the Planck's analysis of the blackbody radiation, in particular, making use of the Boltzmann relation, find a general expression for the probability that a randomly chosen electron will be in the spin-down state.

4. A simple model of the helium atom consists of two electrons attached by harmonic springs to a nucleus of zero charge at the origin. If we label the two electrons as 1 and 2, and assign them coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, then the classical energy for this "helium" atom is

$$E = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}$$

where k is the spring constant, $p_1 = |\mathbf{p}_1|$, $p_2 = |\mathbf{p}_2|$, $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$, and ϵ_0 is the permittivity of free space.

a. The energy cannot be expressed as a sum $E_1 + E_2$ for electrons 1 and 2. However, However, consider making the following change of coordinates to the center-of-mass $\mathbf{R}$ and relative position $\mathbf{r}$ of the two electrons:

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

We also have to change the momentum variables to center of mass momentum $\mathbf{P}$ and relative momentum $\mathbf{p}$ according to

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 \qquad \mathbf{p} = \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2)$$

Show that if the classical energy is expressed in terms of the variables $\mathbf{r}$, $\mathbf{R}$, $\mathbf{p}$ and $\mathbf{P}$, the energy becomes a simple sum $E_{\rm COM} + E_{\rm rel}$ of only center-of-mass energy terms (kinetic and potential energies) and relative energy terms (kinetic and potential energies). Determine the expressions for $\varepsilon_{\rm COM}$ and $\varepsilon_{\rm rel}$.

b. Let $F(\mathbf{R})$ be a function of $\mathbf{R}$ and $G(\mathbf{r})$ be a function of $\mathbf{r}$. In terms of $F(\mathbf{R})$ and $G(\mathbf{r})$, propose a general form for the spatial part of the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ of the two electrons and provide a justification for the form you propose.

c. How do the variables $\mathbf{R}$ and $\mathbf{r}$ change if an exchange of the electron coordinates, $\mathbf{r}_1 \to \mathbf{r}_2$ and $\mathbf{r}_2 \to \mathbf{r}_1$, is performed?

d. Let $\mathbf{x}_1$ denote the position $\mathbf{r}_1$ and spin $s_{z,1}$ of electron one, and let $\mathbf{x}_2$ be the analogous variable for electron 2. The complete wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ for the wave function must satisfy the Pauli exclusion principle. Suppose that the two electrons are in spin-up states. Based on your proposed wave function for part b, and considering your answer to part c, what conditions must be imposed on $F(\mathbf{R})$ and $G(\mathbf{r})$ in order to satisfy the Pauli exclusion principle? Write down the full wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ in terms of $F(\mathbf{R})$, $G(\mathbf{r})$ and the appropriate spin wave functions.

e. Suppose now that one of the electrons is a spin-up electron and the other is a spin-down electron. Based on your proposed wave function for part b, and considering your answer for part c, what conditions must be imposed on $F(\mathbf{R})$ and $G(\mathbf{r})$ in order to satisfy the Pauli exclusion principle? Write down the full wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ in terms of $F(\mathbf{R})$, $G(\mathbf{r})$ and the appropriate spin wave functions.

N.B. There are two possible answers to this question! Give both of them.