CHEM 550 Problem Set #7

Problem Set 7A and 7B both Due Mon Dec 3 at NOON – order problems as listed below

Set 7A

Levine Exercises:

10.18 Spin functions

Additional Problems

Spin

1) a) Write out all of the allowed wave functions for the first **excited** state of the He atom as proper antisymmetric products of spatial and spin functions so that your functions correspond to triplet states and to singlet states (identify which is which). Demonstrate which are eigenfunctions of S^2_{total} and $S_{z\text{-}total}$? What are the eigenvalues?

2) The Mhz value on an NMR is the frequency of electromagnetic radiation needed to induce a transition between the upper and lower states of a proton in the NMR's magnetic field. Calculate the field strength of the 900Mhz wide-bore NMR that was installed at PNNL in 2002 (http://www.pnl.gov/news/2002/02-08.htm) (now that's a big magnet!)

Qualitative Material – Keep the Answers SHORT and CONCISE (2-3 sentences)

4) a) Explain why the Hartree-Fock SCF method doesn't obtain the exact ground state energy even though it incorporates an interelectron repulsion term into the Hamiltonian.

b) Explain why the energy of an orbital depend on *l* for electrons in atoms other than hydrogen? Annotate your discussion with a *sketch* of the radial wave functions for 3s, 3p and 3d.

c) Rationalize why, all other things being equal, parallel (unpaired) spins *generally* (not always) produce states of lower energy than states with antiparallel (paired) (*Hund's rule*)

d) Complete this sentence: Hartree-Fock is a variational theory that approximates the wave function as a ____________________ using _____________________ as trial functions. (I bet its been a long time since you had a fill-in-the-blank homework problem—that's my holiday gift to you!)

Freshman Chemistry Revisited

3) When UV radiation of wavelength 58.4 nm from a He lamp is directed on to a sample of Krypton gas, electrons are ejected with a maximum speed of 1.59×10^6 m/s. What is the ionization energy of Krypton?

Problem Set 7B
Levine Problems:
13.28 – review MO diagrams

Additional Problems:

1) Atomic emission spectroscopy can be used to detect the presence of certain metals at very low concentration. The basic concept is simple enough, and you may have even done this in some form or another in a chemistry lab: heat the sample until it is hot enough to emit light and see what color the flame is glowing. Sodium makes the flame glow yellow because of an electronic transition from the (3p) $^2P_{3/2}$ to the (3s) $^2S_{1/2}$ level. Calculate the percentage of atoms in the relative populations of these levels in thermal equilibrium in flames at temperatures of 1500, 2500 and 3500K.

2) This is a fun problem (honestly!): Choose a MO wave-function for the H_2^+ ground state using 1s-like orbitals with the exponent (nuclear charge) as the variational parameter (Levine eqns 13.43 and 13.44). Set up the coordinate system as suggested in lecture so that you won't need to learn confocal elliptical coordinates.

2A) Evaluate the overlap integral (S) for the H_2^+ MO wave function.

2B) Evaluate the Coulomb (H_{aa}) and Exchange (H_{ab}) integrals for H_2^+ MO wave function.

2C) Using your results from 2 and 3, plot minimized E (as a function of the variational parameters, k) as a function of R for the H_2^+ ion for the bonding and antibonding molecular orbitals. Optional: Plot E vs R for the orbitals with k=1.

2D) Use your calculation to find the equilibrium bond length, and the dissociation energy, of the H_2^+ molecule. Use your calculation to find the energy required to excite the molecule from the n=0 to n=1 vibrational level.

Tips: Make sure you use the 'assume' command to tell the computer everything you know about parameters such as a_0 , R_{AB} (are they positive, real, etc.) or you won't get a correct answer.