Chemistry 1480, Final Exam, April 28, 2007.

This exam consists of seven (7) problems. Please work them all, and provide brief descriptions of your reasoning as appropriate. GOOD LUCK!

1) [15%] A particle of mass *m* is confined to a one dimensional box of length *L* (with one end at *x=0* and the other at *x=L*). Recall that the allowed quantum energy levels are given by:

$$E_n = \frac{h^2 n^2}{8mL^2} \quad , \ n = 1, 2, 3, ...$$

a) Consider a system prepared in the *n=1* (ground) state of this box. It can absorb a photon of light and make a transition to the *n=2* (1^{st} excited) state of the box. What frequency photon would this entail? (State your answer in terms of the frequency unit $\frac{h}{8mL^2}$.)

b) The intensity of an absorption transition from state *i* to *f* of this one dimensional particle in a box system is given (to within irrelevant proportionality constants) by:

$$I_{fi} = \left[\int_0^L \psi_f(x) x \psi_i(x) dx \right]^2 \quad ,$$

where $\psi_i(x)$ is the unit-normalized energy eigenfunction corresponding to state *i*, and analogously for $\psi_f(x)$. Calculate I_{21}, that is, the intensity of light absorbed in the transition from *n=1* (ground state) to *n=2* (1^{st} excited state) of the system.

Notes: i) Your answer should have units of $(\text{length})^2$.

ii) The following integral identity should prove useful: For positive integers *i,j* such that *i-j* is an odd integer:

$$\int_0^L x \sin(\tfrac{i\pi x}{L}) \sin(\tfrac{j\pi x}{L}) dx = \frac{-L^2}{\pi^2} \left[\frac{1}{(i-j)^2} - \frac{1}{(i+j)^2} \right]$$

2) [15%] Consider a particle of mass m moving in a one-dimensional harmonic oscillator potential $V(x) = \frac{1}{2}kx^2$.

(a) Write down the formula for the normalized ground state eigenfunction and sketch it. Write down the formula for the corresponding energy eigenvalue.

(b) The same as (a), but for the first excited state. [Be sure to identify any nonstandard symbols that appear in your eigenfunction formula.]

(c) Suppose the particle is prepared in the superposition state $\psi = 0.949\varphi_0 + 0.316\varphi_1$, where φ_0, φ_1 are the normalized ground and first excited state energy eigenfunctions considered in parts (a) and (b).

What is the probability that a measurement of energy will yield the ground state energy eigenvalue? The first excited state eigenvalue? The second excited state eigenvalue?

3) [15%] Suppose we wish to approximate the ground state energy and wavefunction of the two-electron atom Li^+. As in Problem Set 9, we adopt a variational trial function of the form

$$\psi_T(\vec{r}_1, \vec{r}_2) = \varphi_{ls}(r_1;\xi)\varphi_{ls}(r_2;\xi),$$

where $\varphi_{ls}(r;\xi)$ is a normalized hydrogenic orbital corresponding to effective nuclear charge ξ. Following the same procedure used in Problem Set 9, it can be shown that

$$E(\xi) \equiv < \psi_T \left| \widehat{H} \right| \psi_T > = \frac{e^2}{8\pi\varepsilon_0 a_0}\{-2\xi^2 + 4(\xi - 3)\xi + 5\xi/4\},$$

where $\widehat{H}$ is the two-electron Hamiltonian operator appropriate to Li^+. [As usual, e is the magnitude of the electron's charge and a_0 is the Bohr radius.]

(a) Find the value of ξ for which $E(\xi)$ is a minimum.

(b) Is $\xi < 3$ or $\xi > 3$? Interpret your result.

4) [20%] In this problem, we will consider π-bonding in the (linear) allyl radial C_3H_3, whose carbon backbone is shown in Figure 1. If the π MO's are written as $\psi = c_A\varphi_A + c_B\varphi_B + c_C\varphi_C$, where $\varphi_{A,B,C}$ are the indicated $2p_z$ orbitals, then Hückel theory implies the secular equations:

$$\begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix} \begin{bmatrix} c_A \\ c_B \\ c_C \end{bmatrix} = E \begin{bmatrix} c_A \\ c_B \\ c_C \end{bmatrix} \qquad (1)$$

(a) (i) Define the symbols α, β and E that appear in this expression.

(ii) Why are two of the elements of the matrix on the left hand side equal to zero?

(b) The eigenvectors of the matrix in Equation (1) are

$$\begin{bmatrix} 1 \\ 2^{1/2} \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ -\ 2^{1/2} \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ -\ 1 \end{bmatrix}$$

Sketch the molecular orbitals associated with each eigenvector.

(c) What are the associated molecular orbital energies?

(d) (i) Use the results of part (c) to make an energy level diagram. [Remember: β<0.]

(ii) Indicate the ground state configuration of the π electrons in the allyl radical.

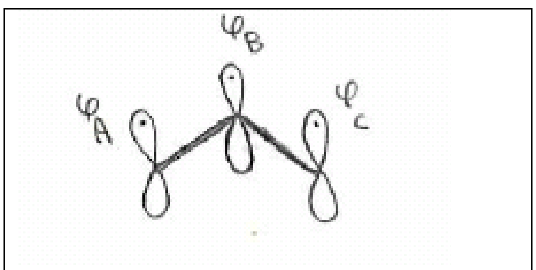

Figure 1: π-bonding in the allyl radical.

5) [10%] Use qualitative molecular orbital theory to compute the bond order of (i) NO and (ii) NO^+. Assume that the same molecular orbital diagram holds as in the case of homonuclear second row diatomic O_2; the only consequence of the fact that the molecules considered here are composed of two different atoms is in the number of electrons in the molecule.

6) [10%] Suppose that the Pauli Exclusion Principle required that acceptable electronic wavefunctions be <u>symmetric</u> with respect to exchange of any two electron labels. If so, which of the following wavefunctions would provide acceptable descriptions of the $1s^1 2s^1$ configurations of helium (ignoring normalization)?:

(i)	[ls(1)2s(2)	-	ls(2)2s(1)]$\alpha(1)\alpha(2)$
(ii)	[ls(1)2s(2)	+	ls(2)2s(1)]$\alpha(1)\alpha(2)$
(iii)	[ls(1)2s(2)	+	ls(2)2s(1)][$\alpha(1)\beta(2) - \alpha(2)\beta(1)$]
(iv)	[ls(1)2s(2)	+	ls(2)2s(1)][$\alpha(1)\beta(2) + \alpha(2)\beta(1)$]
(v)	[ls(1)2s(2)	-	ls(2)2s(1)]$\alpha(1)\beta(2)$

Briefly explain your reasoning.

7) [15%] A heteronuclear diatomic molecule with moment of inertia *I* can absorb radiation that excites its rotational motion, which is well-described as that of a three dimensional rigid rotator corresponding to moment of inertia *I*.

a). The relative intensity of the $J \to J+1$ transition is given approximately by the formula

$$I_{J\to J+1} = (2J+1)\exp\{-J(J+1)B/k_B T\}$$

where $B \equiv \hbar^2/2I$, k_B is Boltzmann's constant, and T is the absolute temperature.

Assuming that the intensity of absorption is proportional to the equilibrium population of the initial state J in a given experimental sample, briefly explain the origin of this formula.

(b) Show that the absorption frequency ν of the transition from $J \to J+1$ is given by $h\nu = 2B(J+1)$.

(c) Deduce the value of J for which the intensity $I_{J\to J+1}$ is maximum. State your answer in terms of the dimensionless ratio $k_B T/B$.

Note: Recall from class that

i) the energy levels of a rigid rotator are given by $E_J = BJ(J+1)$, $J = 0,1,2,...$

ii) the degeneracy of level J is $(2J+1)$.