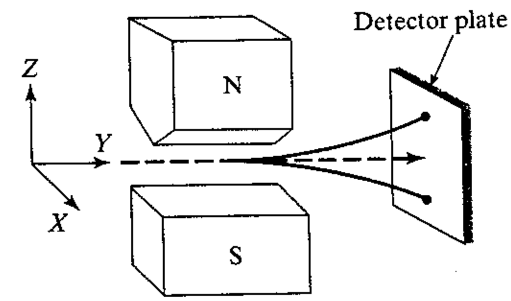
Name________________________________

Chemistry 344

Exam II
Monday November 12, 2001
2:00 -2:50 PM



NO CALCULATORS PERMITTED. Additional information, integrals, etc. are given on last page. Where a calculator is required, you do not need to provide a final numerical answer. Just carry through all the way up to the complete numerical expression, ready for punching numbers into the calculator.

1. Suppose we are in a universe in which the spin quantum number for the electron is s = 3/2 instead of s = 1/2, as it is in our universe.

(a) Describe in qualitative terms what would be observed when the ground state hydrogen atom is passed through an inhomogeneous magnetic field in the hypothetical universe.

(b) What are the possible values for S_z for the electron in that universe? What is the value of S^2 for the electron in that universe?

S_z:
S^2:

(c) With s = 1/2, there are 10 *elements contained in each transition metal series* in the periodic table. *How many* would there be, if s for the electron were 3/2? *Explain.*

2. (a) Muonium is a transient atom with a proton nucleus and a negative muon. The muon is an elementary particle with a charge of -e and a mass 206.77 times as great as that of the electron. Calculate the ground state energy of muonium in eV.

(b) Students Victor and Joyce have a demonstration (this question courtesy of Prof. Lionel Raff; student names have been changed to protect their privacy). Victor: "Joyce and I each have a dewar. One is filled with liquid N_2, the other with liquid O_2. As you see, we also have two large, powerful permanent horseshoe magnets on the table in front of us. I'm going to pour the contents of my dewar over this magnet while Joyce pours the contents of the dewar over the magnet in front of her. Watch what happens!" *The contents of Victor's dewar pour over his magnet without sticking to it. The liquid hits the tabletop and runs over the surface, where it rapidly vaporizes. In contrast, most of the contents of Joyce's dewar stick to the magnet, completely filling the space between the magnet's poles with liquid that is held suspended in the air. Only a small amount of the liquid reaches the table top.*

Joyce: "Isn't that amazing! Our questions are:

(1) *Which dewar held the liquid oxygen,* Victor's or mine?

(2) *How can we use simple molecular orbital theory to explain the results* of the experiment we have just witnessed?"

(c) A rigid rotor is known to be in a state whose eigenfunction is $Y_{43}(\theta,\phi)$. *What is the rotational energy* of the rotor in terms of the moment of inertia = μR^2 and $\hbar$?

What is the magnitude of the rotational angular momentum of the rotor?

Determine the z component of the rotational angular momentum.

3. Suppose we use the central field approximation, and suppose that we had a table or formulas to obtain the effective charge seen by each electron [$Z_{eff}(i)$ for the ith electron] in a many-electron atom.

(a) *Write down the Hamiltonian for the lithium atom in this central field approximation,* after the center-of-mass motion has already been separated out.

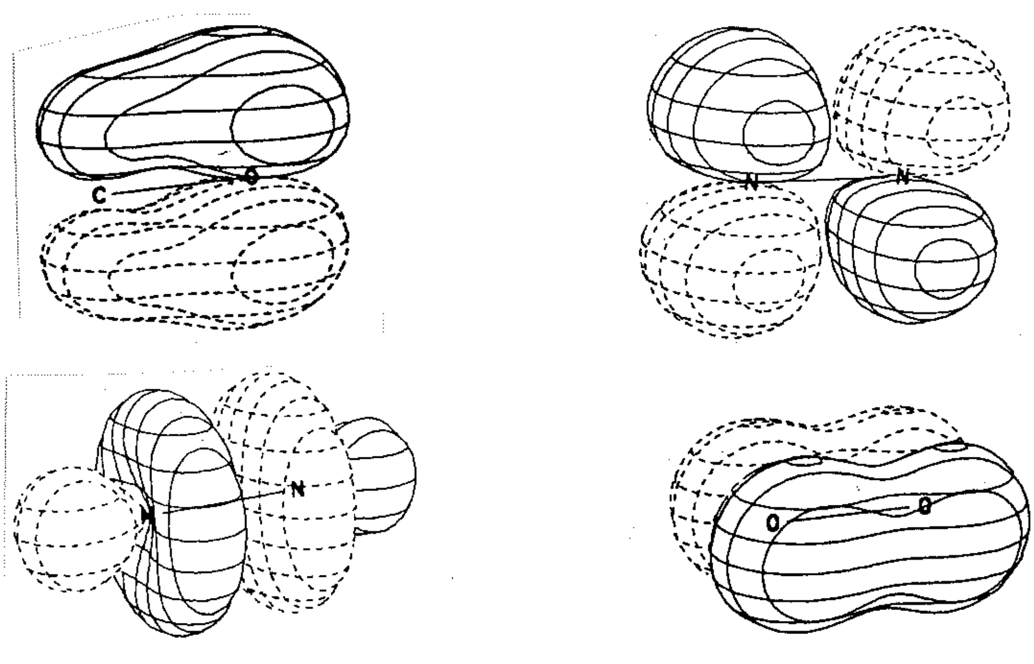
(b) *Explain, with equations, how the eigenfunctions and eigenvalues of this hamiltonian operator can be found.*

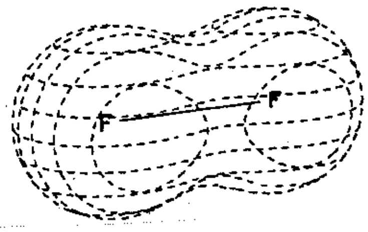
(c) Consider the lithium atom in its ground state. Use Slater's rules (attached) to find the $Z_{eff}(i)$. *What is the energy of the lithium atom in its ground state* (in addition to translational energy)?

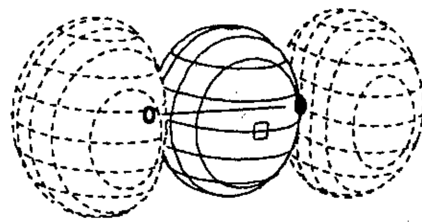
(d) *What is the energy of the ground state of the Li^+ ion?*

(e) *What is the first ionization energy of lithium atom?*

4. *Assign the appropriate molecular orbital designation to each of the following one-electron functions.* Designate the plane of the paper as xz plane







(b) When the Born-Oppenheimer separation is carried out, *what are the two equations to be solved? Answer by writing out the two equations explicitly* for a diatomic molecule AB, using symbols that have the standard meanings as used in class. Define completely all symbols used for eigenvalues.

BONUS QUESTION (to go beyond 100 points on this exam):

5. A particle of mass m in a potential well (with infinitely high walls) of length L in the x dimension is known to have eigenfunctions $\psi_n(x) = (2/L)^{1/2} \sin [n\pi x/L]$ and eigenvalues $n^2h^2/8mL^2$. Consider a particle in a one-dimensional potential box *as a model* for *four non-interacting pi electrons* of butadiene. Let the box be of length L such that $h^2/8mL^2 = 0.1$ in some energy unit.

(a) *Write down the hamiltonian for one electron in the box.*

(b) *Write down the Schrödinger equation for the model system of 4 pi electrons in the box as explicitly as you can.*

(c) *Draw the energy level diagram for <u>one</u> electron in this system,* in the energy units specified above. Your diagram should show, to scale, at least the lowest 4 levels and should be labeled with energy values.

(d) If not more than two electrons can be assigned the same quantum number n, *calculate the lowest possible energy for the four pi electrons* in this model for butadiene.

(e) *Write down the explicit wavefunction for this state* (ground state) of the four pi electrons, excluding spin.

List of possibly useful integrals that will be provided with each exam

$\int \sin(ax)dx = -(1/a)\cos(ax)$

$\int \cos(ax)dx = (1/a)\sin(ax)$

$\int \sin^2(ax)dx = ½\, x - (1/4a)\sin(2ax)$

$\int \cos^2(ax)dx = ½\, x + (1/4a)\sin(2ax)$

$\int \sin(ax)\sin(bx)dx = [1/2(a-b)]\sin[(a-b)x)] - [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$

$\int \cos(ax)\cos(bx)dx = [1/2(a-b)]\sin[(a-b)x)] + [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$

$\int x \sin(ax)dx = (1/a^2)\sin(ax) - (x/a)\cos(ax)$

$\int x \cos(ax)dx = (1/a^2)\cos(ax) + (x/a)\sin(ax)$

$\int x^2 \cos(ax)dx = [(a^2x^2 - 2)/a^3]\sin(ax) + 2x\cos(ax)/a^2$

$\int x^2 \sin(ax)dx = -[(a^2x^2 - 2)/a^3]\cos(ax) + 2x\sin(ax)/a^2$

$\int x \sin^2(ax)dx = x^2/4 - x\sin(2ax)/4a - \cos(2ax)/8a^2$

$\int x^2 \sin^2(ax)dx = x^3/6 - [x^2/4a - 1/8a^3]\sin(2ax) - x\cos(2ax)/4a^2$

$\int x \cos^2(ax)dx = x^2/4 + x\sin(2ax)/4a + \cos(2ax)/8a^2$

$\int x^2 \cos^2(ax)dx = x^3/6 + [x^2/4a - 1/8a^3]\sin(2ax) + x\cos(2ax)/4a^2$

$\int x \exp(ax)dx = \exp(ax)\,(ax-1)/a^2$

$\int x \exp(-ax)dx = \exp(-ax)\,(-ax-1)/a^2$

$\int x^2 \exp(ax)dx = \exp(ax)\,[x^2/a - 2x/a^2 + 2/a^3]$

$\int x^m \exp(ax)dx = \exp(ax) \sum_{r=0 \text{ to } m} (-1)^r\, m!x^{m-r}/(m-r)!a^{r+1}$

$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1} \qquad a > 0$, n positive integer

$\int_0^\infty x^2 \exp(-ax^2)dx = (1/4a)(\pi/a)^{½} \qquad a > 0$

$\int_0^\infty x^{2n} \exp(-ax^2)dx = (1\cdot 3\cdot 5\cdot \ldots \cdot(2n-1)/(2^{n+1}a^n)(\pi/a)^{½} \qquad a > 0$

$\int_0^\infty x^{2n+1} \exp(-ax^2)dx = n!/2a^{n+1} \qquad a > 0$, n positive integer

$\int_0^\infty \exp(-a^2x^2)dx = (1/2a)\,(\pi)^{½} \qquad a > 0$

$\int_0^\infty \exp(-ax)\cos(bx)dx = a/(a^2+b^2) \qquad a > 0$

$\int_0^\infty \exp(-ax)\sin(bx)dx = b/(a^2+b^2) \qquad a > 0$

$\int_0^\infty x \exp(-ax)\sin(bx)dx = 2ab/(a^2+b^2)^2 \qquad a > 0$

$\int_0^\infty x \exp(-ax)\cos(bx)dx = (a^2-b^2)\,/(a^2+b^2)^2 \qquad a > 0$

$\int_0^\infty \exp(-a^2x^2)\cos(bx)dx = [(\pi)^{½}/2a]\cdot\exp[-b^2/4a^2] \qquad ab \neq 0$