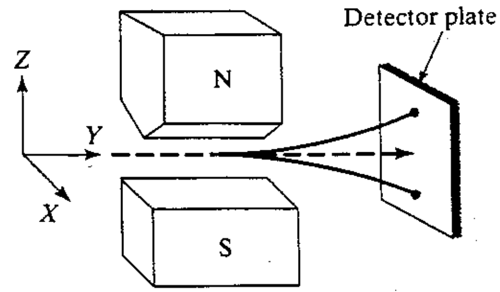


Name______________________________________

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.

Instead of splitting into two beams and arriving at the detector in two spots corresponding to $+\frac{1}{2}$ and $-\frac{1}{2} = m_s$ there will be 4 beams arriving at the detector in 4 spots corresponding to $m_s = +\frac{3}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ and $-\frac{3}{2}$

(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: $\frac{3}{2}\hbar$ $\frac{1}{2}\hbar$ $-\frac{1}{2}\hbar$ $-\frac{3}{2}\hbar$
S^2: $\frac{3}{2}\left(\frac{3}{2}+1\right)\hbar^2$

(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.*

The 10 come from $nd^1, nd^2, \cdots nd^{10}$ configurations, which arise from $m_\ell = 2, 1, 0, -1, -2$ and $m_s = +\frac{1}{2}, -\frac{1}{2}$
Instead there will the same m_ℓ going with 4 different m_s leading to 20 elements in each transition metal series

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.

For a proton nucleus and a real electron, the eigen ~~ground state~~ values for an H atom is $-\frac{Z^2 e^2}{2a_0}$ $a_0 = \hbar^2/m_e e^2$ can be used because $m_e \ll m_p$ in which case the reduced mass is given by $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p} \simeq \frac{1}{m_e}$
For muonium this is no longer true. We have to use the correct μ: $\frac{1}{\mu} = \frac{1}{1836 m_e} + \frac{1}{206.77 m_e} = \frac{206.77+1836}{1836(206.77)m_e}$

$\therefore a = \underbrace{\frac{\hbar^2}{m_e e^2}}_{a_0} \times \frac{206.77+1836}{1836(206.77)}$ $\therefore$ Ground state muonium $= -\frac{1^2}{1^2}(13.6057) \times \frac{(206.77)(1836)}{(1836+206.77)} = -13.6(185.8)$ 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 ~~my~~ 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?

Joyce's

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

O_2 is paramagnetic ($S=1$) whereas N_2 is not ($S=0$)

N_2 has $14e^-$ with electronic configuration

$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2 \underbrace{(\sigma_g 2p_z)^2(\pi_u 2p_{x,y})^4}_{\text{triple bond}}$

all spins paired closed shell $S=0$

O_2 has $16e^-$ with electronic configuration

$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_{x,y})^4(\pi_g^* 2p_{x,y})^2$

$S=1$ ground state of O_2 since $|\Lambda|=1$ is doubly degenerate

This configuration gives rise to both $S=0$ and $S=1$

(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 $\hbar$?

Rotational energy = $\frac{J(J+1)\hbar^2}{2\mu R^2}$ for $J=4$ it is $\frac{4(4+1)\hbar^2}{2\mu R^2} = \frac{10\hbar^2}{\mu R^2}$

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

$\sqrt{4(4+1)}\ \hbar$ since the eigenvalue for the square is $4(4+1)\hbar^2$

Determine the z component of the rotational angular momentum.

$3\hbar$

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.

$$H = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right) - \frac{\hbar^2}{2m_e}\underbrace{\left(\frac{\partial^2}{\partial x_3^2}+\frac{\partial^2}{\partial y_3^2}+\frac{\partial^2}{\partial z_3^2}\right)}_{\text{or } \nabla_3^2}$$

$$- Z_{eff}(1)\frac{e^2}{r_1} - Z_{eff}(2)\frac{e^2}{r_2} - Z_{eff}(3)\frac{e^2}{r_3}$$

where x_i, y_i, z_i are coordinates of electron i with respect to the nucleus as origin

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

To find eigenfunctions and eigenvalues of the hamiltonian operator we need to solve the following equation

$$H(\vec{r}_1, \vec{r}_2, \vec{r}_3)\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = E\,\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \qquad (1)$$

where $\vec{r}_i$ represents the vector position (x_i, y_i, z_i) of electron i with respect to the nucleus as origin. We need to find E and Ψ.

This is an equation in 9 variables. Let us use the method of separation of variables.

Let $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = F(\vec{r}_1)\cdot G(\vec{r}_2)\cdot P(\vec{r}_3)$

Substitute this product function into eqn (1)

where we have $H(\vec{r}_1, \vec{r}_2, \vec{r}_3) = H_1(\vec{r}_1) + H_2(\vec{r}_2) + H_3(\vec{r}_3)$

where

$$H_1(\vec{r}_1) = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right) - Z_{eff}(1)\frac{e^2}{r_1}$$

$$[H_1(\vec{r}_1) + H_2(\vec{r}_2) + H_3(\vec{r}_3)]\,F(\vec{r}_1)\cdot G(\vec{r}_2)\cdot P(\vec{r}_3) = E\,F(\vec{r}_1)\cdot G(\vec{r}_2)\cdot P(\vec{r}_3)$$

and then divide by the product function, to get

$$\frac{[H_1(\vec{r}_1)F(\vec{r}_1)]\cdot\cancel{G(\vec{r}_2)\cdot P(\vec{r}_3)}}{F(\vec{r}_1)\cdot\cancel{G(\vec{r}_2)\cdot P(\vec{r}_3)}} + \frac{[H_2(\vec{r}_2)G(\vec{r}_2)]\cdot\cancel{F(\vec{r}_1)\cdot P(\vec{r}_3)}}{\cancel{F(\vec{r}_1)}\cdot G(\vec{r}_2)\cdot\cancel{P(\vec{r}_3)}}$$

$$+ \frac{[H_3(\vec{r}_3)P(\vec{r}_3)]\cdot\cancel{F(\vec{r}_1)\cdot G(\vec{r}_2)}}{\cancel{F(\vec{r}_1)\cdot G(\vec{r}_2)}\cdot P(\vec{r}_3)} = E$$

Leaving

$$\underbrace{\frac{H_1(\vec{r}_1)F(\vec{r}_1)}{F(\vec{r}_1)}}_{E_1} + \underbrace{\frac{H_2(\vec{r}_2)G(\vec{r}_2)}{G(\vec{r}_2)}}_{E_2} + \underbrace{\frac{H_3(\vec{r}_3)P(\vec{r}_3)}{P(\vec{r}_3)}}_{E_3} = E$$

E is a number, an eigenvalue and since the 3 variables in $F(\vec{r}_1)$ can be assigned any set of values, and the same can be said of the 3 variables in $G(\vec{r}_2)$ and in $P(\vec{r}_3)$ the sum of the three expressions can always equal the same number if and only if each expression is itself equal to a constant, ~~such~~ that the sum of the 3 constants is the number E. Therefore, we need to solve 3 equations each in 3 variables instead of one equation in 9 variables, and they all have the same form:

$$\left(\frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-Z_{eff}(1)\frac{e^2}{r_1}\right)F(\vec{r}_1) = E_1\, F(\vec{r}_1) \qquad (2)$$

This is the same mathematical equation as for a hydrogen-like atom excepting only that instead of the actual Z of the nucleus we instead have $Z_{eff}(1)$ which can be different for each electron.

Therefore, we already know the solutions of this eq (2) are $F(\vec{r}_1) = R_{n_1 \ell_1}(r_1)\cdot Y_{\ell_1 m_1}(\theta_1,\phi_1)$ and $E_1 = -\frac{(Z_{eff}(1))^2}{n_1^2}\frac{e^2}{2a_0}$

Therefore the solutions to eqn (1) are

$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = R_{n_1\ell_1}(r_1)\cdot Y_{\ell_1 m_1}(\theta_1,\phi_1)\cdot R_{n_2\ell_2}(r_2)\cdot Y_{\ell_2 m_2}(\theta_2,\phi_2)\cdot R_{n_3\ell_3}(r_3)\cdot Y_{\ell_3 m_3}(\theta_3,\phi_3)$

and $E = \left[-\left(\frac{Z_{eff}(1)}{n_1}\right)^2 - \left(\frac{Z_{eff}(2)}{n_2}\right)^2 - \left(\frac{Z_{eff}(3)}{n_3}\right)^2\right] e^2/2a_0$

(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)?

Ground configuration $1s^2 2s$ $\quad Z=3$

$E = E_1 + E_2 + E_3 \qquad E_i = \frac{Z_{eff}(i)^2}{n_i^2}(13.6\,eV)$

$E_1 = -\frac{(3-0.30)^2}{1^2}(13.6\,eV) \qquad E_2 = -\frac{(3-0.30)^2}{1^2}(13.6\,eV)$

$E_3 = -\frac{[3-0.85(2)]^2}{2^2}(13.6\,eV)$

$$E = \left\{-\frac{(3-0.30)^2}{1^2} - \frac{(3-0.30)^2}{1^2} - \frac{[3-0.85(2)]^2}{2^2}\right\}(13.6\,eV)$$

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

Configuration Li^+ : $1s^2$

$$E = E_1 + E_2 = -\frac{(3-0.30)^2}{1^2}(13.6\,eV) - \frac{(3-0.30)^2}{1^2}(13.6\,eV)$$

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

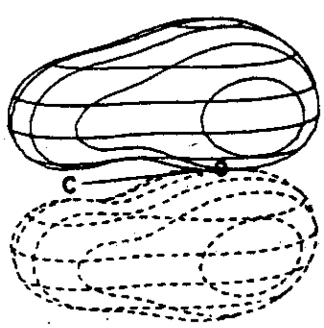
First ionization energy = $E(Li^+ \text{ion}) - E(Li \text{ atom})$

We note that in this case $E_1 + E_2$ for ion and ground state atom happen to be identical (not usually the case!)

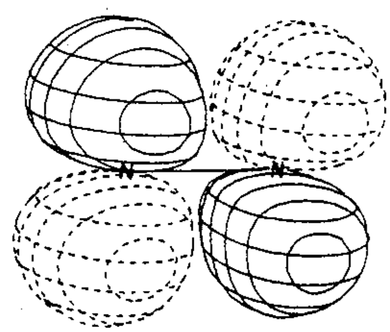
so

$$1^{st} \text{ ionization energy} = +\frac{(3-2\times 0.85)^2}{2^2}(13.6\,eV)$$

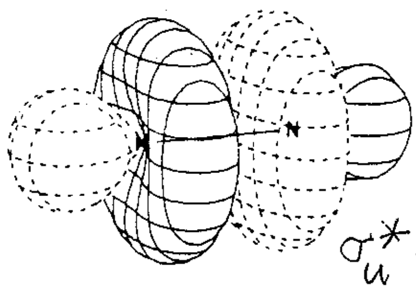
4. *Assign the appropriate molecular orbital designation to each of the following one-electron functions.* Designate plane of paper as xz plane



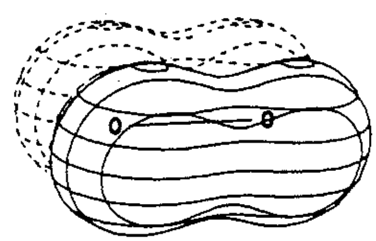
$\pi\ 2p_x$



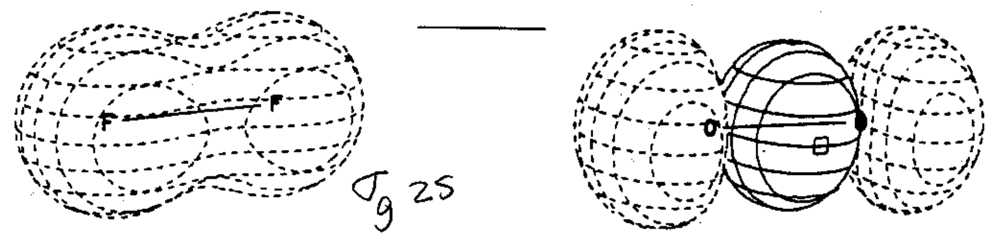
$\pi_g^*\ 2p_x$



$\sigma_u^*\ 2p_z$



$\pi_u\ 2p_x$



(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* using symbols that have the standard meanings as used in class. Define completely all symbols used for eigenvalues. For a diatomic molecule AB

Need to solve eqns (1) and (2):

At fixed nuclear positions, i.e. nucleus A and nucleus B at fixed points in the laboratory frame, R_{AB} = constant

(1) $$\left[-\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2+\dots) - \frac{Z_A e^2}{r_{1A}} - \frac{Z_A e^2}{r_{2A}} - \dots - \frac{Z_B e^2}{r_{1B}} - \frac{Z_B e^2}{r_{2B}} - \dots + \frac{e^2}{r_{12}} + \dots\right]\psi(\vec{r}_1,\vec{r}_2,R_{AB}) = \mathcal{U}(R_{AB})\,\psi(\vec{r}_1,\vec{r}_2,R_{AB})$$

Eqn (1) is solved for each R_{AB} value.

The points that are individual eigenvalues $\mathcal{U}(R_{AB})$ for $R_{AB} = 0$ to ∞ are collectively used as a potential energy in the variable R_{AB} for each electronic state

(2) $$\left[-\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 + \mathcal{U}(R_{AB})\right]F(\vec{R}_A,\vec{R}_B) = E\,F(\vec{R}_A,\vec{R}_B)$$

$E = E_{translation} + E_{vibration\text{-}rotation} + E_{electronic}$

Eqn (2) is solved for each electronic state

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.*

$-\frac{\hbar^2}{2m_e}\frac{d^2}{dx^2}$

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

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial x_3^2}+\frac{\partial^2}{\partial x_4^2}\right)F(x_1,x_2,x_3,x_4) = EF(x_1,x_2,x_3,x_4)$$

(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

———— $+4^2(0.1)$

———— $+3^2(0.1)$

———— $+2^2(0.1)$

———— $+0.1$

(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.

$E = E_1+E_2+E_3+E_4 = 2(0.1)+2(2^2\times 0.1)$

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

$$F(x_1, x_2, x_3, x_4) =$$

$$\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x_1}{L}\right) \cdot \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x_2}{L}\right) \cdot \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x_3}{L}\right) \cdot \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x_4}{L}\right)$$