Chemistry 115 (Crim)
Fall, 2000

Name Key

Section________ **T.A.**____________

Examination II

Instructions

1. This examination contains 9 pages of questions and instructions, two blank pages, a page of equations, a page of one-electron wavefunctions, and a periodic table. If a page is missing, take the examination to a proctor ***immediately***.

2. ***Print*** your name ***now*** in the spaces at the top of ***all*** of the examination pages.

3. There are some potentially useful equations at the back of the exam and some potentially useful conversion factors and constants on the back of the periodic table.

4. *Read each question carefully* before beginning your work.

5. *Show your work and make your reasoning clear.* The goal is to produce an answer that the reader can follow to understand your reasoning. We must be able to follow your reasoning to give you partial credit. *Make your work legible and be concise.* If you continue an answer elsewhere, mark it clearly.

4. You have two hours to work on the examination.

1.	**/12**
2.	**/12**
3.	**/7**
4.	**/14**
5.	**/20**
6.	**/20**
7.	**/15**
8.	**/20**
TOTAL	**/120**

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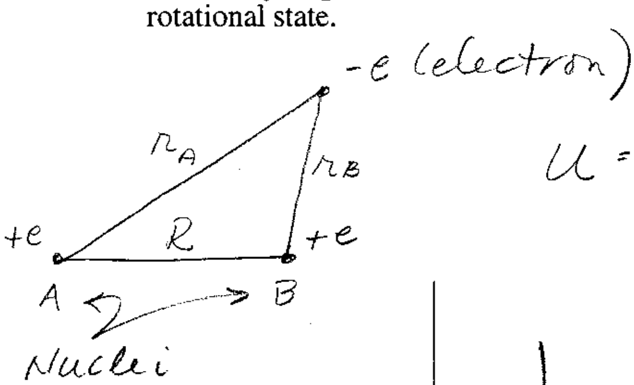
1. *(12 Points)* Write out the potential, U, that goes into the 3-D Schrödinger equation,

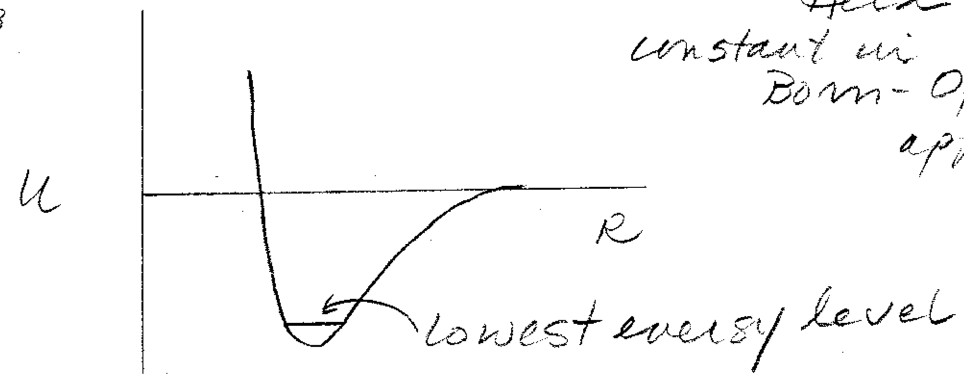
$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi$$

for the H_2^+ molecular ion. Identify the term(s) one holds constant when making the Born-Oppenheimer approximation. Sketch the energy of the ion as a function of the distance between the two hydrogen nuclei, and indicate the energy of H_2^+ in its lowest electronic, vibrational and rotational state.



$$U = -\frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}$$

Held constant in Born-Oppenheimer approximation



2. (*12 Points*) Imagine a universe in which the spin quantum number has three possible values (m_s = 0, +1/2, -1/2). Work out the atomic numbers of the first three noble-gas atoms in such a situation.

"$1s^3$" $Z = 3$

"$1s^3 2s^3 2p^9$" $Z = 15$

"$1s^3 2s^3 2p^9 3s^3 3p^9$" $Z = 27$

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3. *(7 Points)* Arrange the following seven atoms or ions in order of size from the smallest to the largest

K, F^+, Rb, Co^{25+}, Br, F, Rb^-

Co^{25+}, F^+, F, Br, K, Rb, Rb^-

smallest → → → → → → → → largest

4. (*14 Points*) We observed the red emission line at 656.1 nm in H as it made a transition from n=3 to n=2. Explain whether the corresponding transition in Li^{2+} would be at a shorter or longer wavelength and calculate the wavelength of the transition. (*Hint: Make life easy on yourself - you are comparing the energy of two transitions.*)

The transition should be at a shorter wavelength. The energies of the levels in a one-electron atom are $E_n = -\frac{\hbar^2}{2ma_0^2}\frac{Z^2}{n^2}$

The larger Z in Li^{2+} makes them further apart in energy, giving a shorter wavelength transition

$$\Delta E = -\underbrace{\left(\frac{\hbar^2}{2ma_0^2}\right)\left(\frac{1}{n_u^2}-\frac{1}{n_e^2}\right)}_{\text{CONSTANT FOR } n_u=3,\ n_e=2} Z^2 = h\nu = \frac{hc}{\lambda}$$

$$\therefore \lambda = \frac{hc}{\text{CONSTANT} \cdot Z^2}$$

$$\therefore \frac{\lambda^{Li^{2+}}}{\lambda^H} = \frac{Z_H^2}{Z_{Li^{2+}}^2} \; ; \; \lambda^{Li^{2+}} = \left(\frac{Z_H}{Z_{Li^{2+}}}\right)^2 \lambda_H = \left(\frac{1}{3}\right)^2 656.1\,nm$$

$$\lambda^{Li^{2+}} = 79.20\,nm$$

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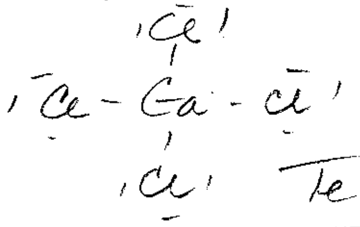
5. (*20 Points*) Mixing $SbCl_3$ and $GaCl_3$ in a one-to-one molar ratio (using liquid sulfur dioxide as a solvent) gives a solid, ionic compound of empirical formula $GaSbCl_6$. On the basis of this information, one cannot be certain whether the compound is

$(SbCl_2^+)(GaCl_4^-)$ *or* $(GaCl_2^+)(SbCl_4^-)$

(a) Predict the geometries of the two possible *anions* $GaCl_4^-$ and $SbCl_4^-$.

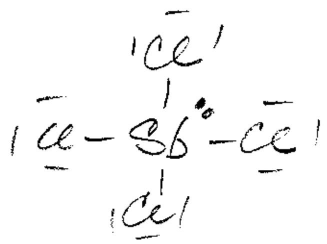
$GaCl_4^-$ $3+4(7)+1 = 32e^-$



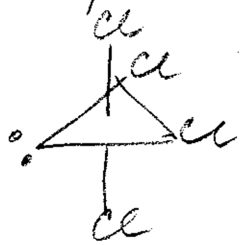
SN=4

Tetrahedral structure

$SbCl_4^-$ $5+4(7)+1 = 34e^-$



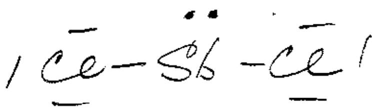
SN=5



Seesaw structure

(b) Assume that one learns through experiment that the *cation* in the actual compound is *bent*. Using that additional information, explain which of the two formulations is most likely the correct one.

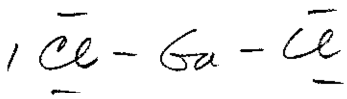
$SbCl_2^+$ $5+2(7)-1 = 18e^-$



SN=3

∴ Bent

$GaCl_2^+$ $3+2(7)-1 = 16e^-$



SN=2

∴ Linear

The bent cation is $SbCl_2^+$ thus the best formulation is $(SbCl_2^+)(GaCl_4^-)$

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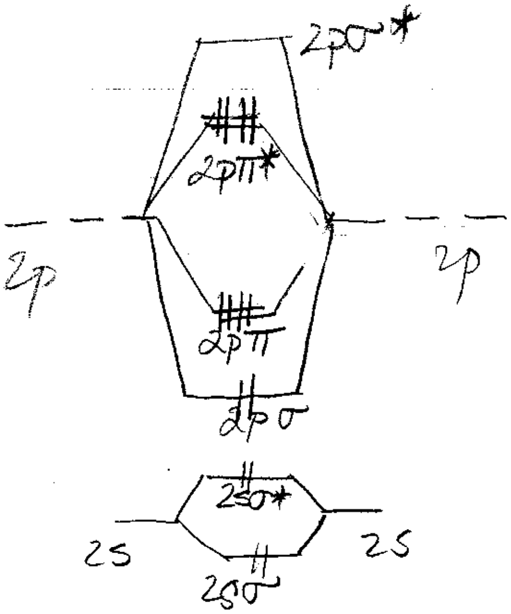
6. (*20 Points*) The following list gives you two choices for the bond length (R_e), dissociation energy (D_e), and vibrational frequency of the molecule (ν). (The frequency here is expressed in wavenumber units, cm^{-1}.)

	Set 1 (F_2)	Set 2 (F_2^-)
Bond Length (R_e)	1.411 Å	1.900 Å
Dissociation Energy (D_e)	1.60 eV	1.31 eV
Vibrational Frequency (ν)	917 cm^{-1}	450 cm^{-1}

(a) Assign one set of quantities to the molecule F_2 and one to the ion F_2^-. Explain your reasoning about each of the quantities.

MO diagram



F_2 : 14e⁻ $(2s\sigma)^2(2s\sigma^*)^2(2p\sigma)^2(2p\pi)^4(2p\pi^*)^4$

BO : 1

F_2^- : 15e⁻ $\ldots(2p\sigma)^2(2p\pi)^4(2p\pi^*)^4(2p\sigma^*)^1$

Extra antibonding orbital : BO = ½

Set 1 is F_2 and Set 2 is F_2^-.

The higher bond order in F_2 makes its bond shorter and stronger. For similarly shaped potentials, the corresponding vibrational frequency is higher

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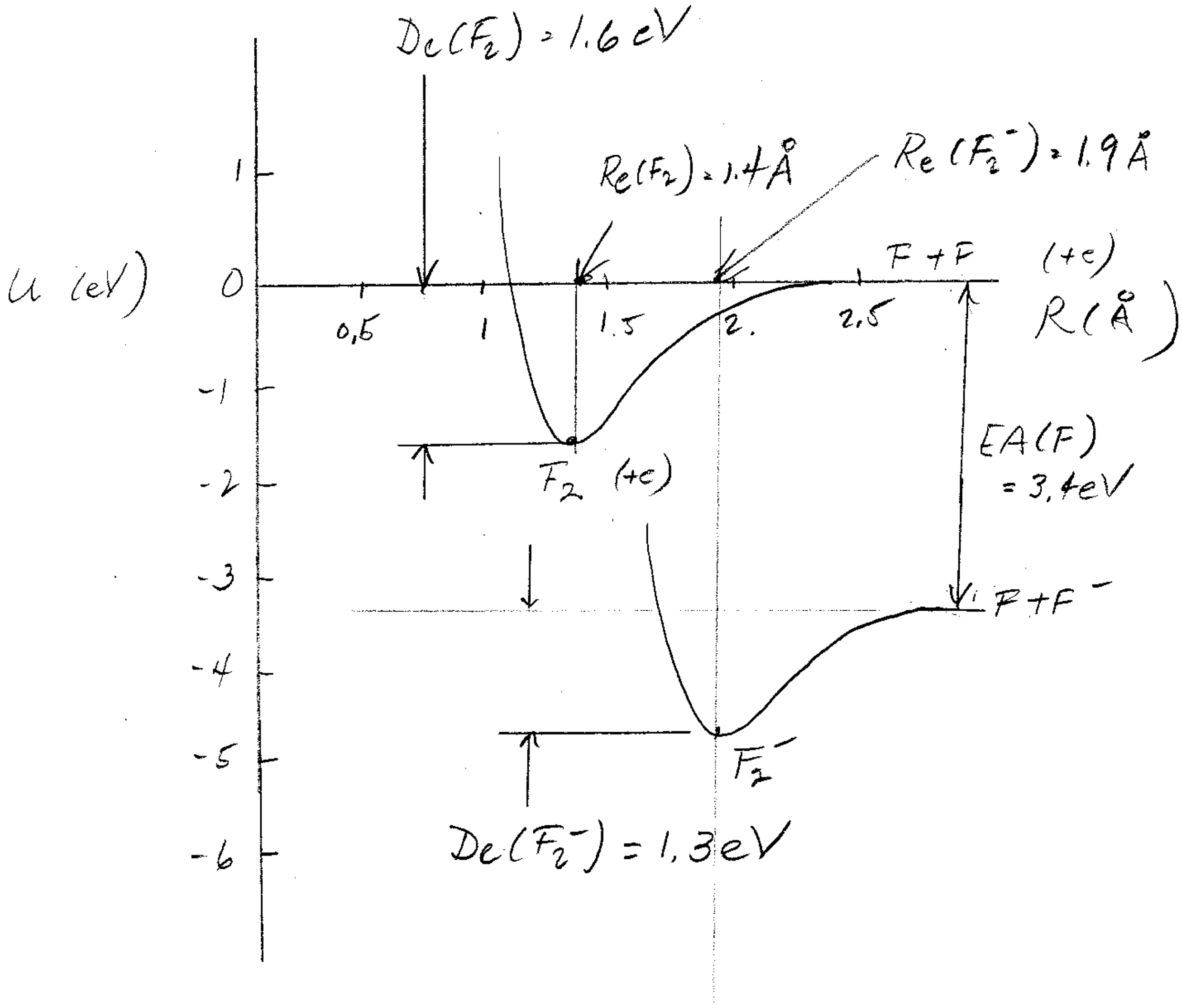
(b) Sketch the potential curves as a function of the internuclear distance for F_2 and F_2^-. Label the vertical and horizontal axes as completely as you can and place the curves in their proper relative position. (*Hint: The species F_2^- dissociates into F + F^-, whose energy is different than that of the nuetral products F + F formed in the dissociation of F_2. The electron affinity of F is 3.4 eV.*)



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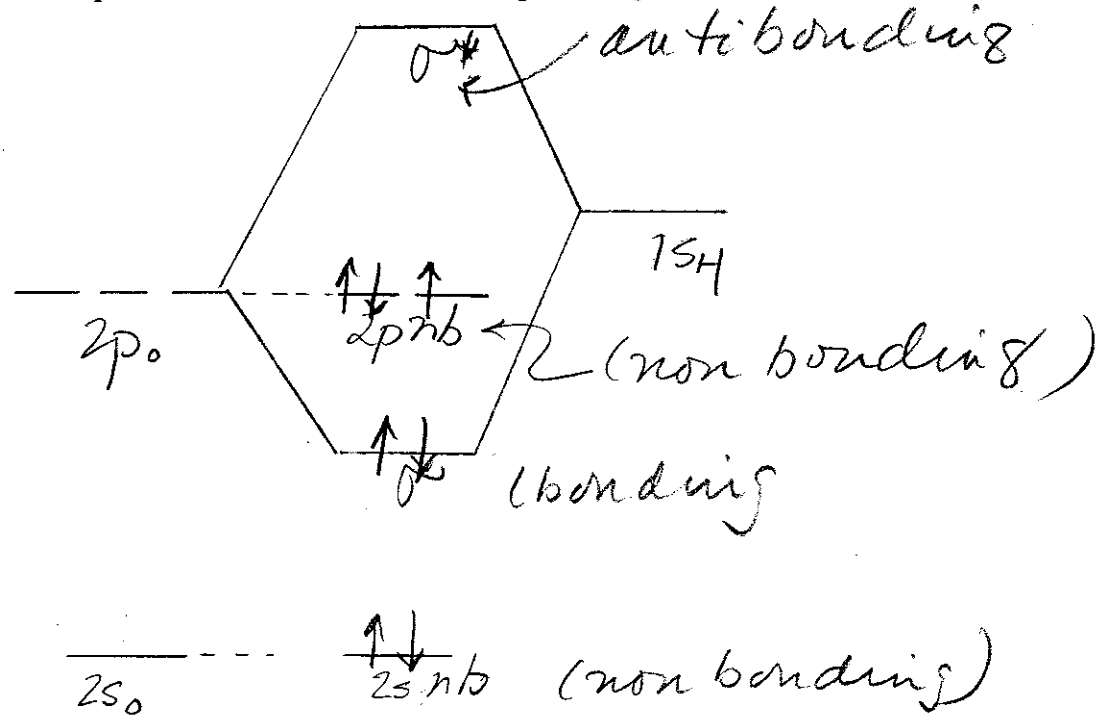
7. *(15 Points)* The molecular orbital diagram for OH is very similar to that for HF. The 2*s* orbital in oxygen is too low in energy to mix with 1*s* orbital from hydrogen. Rather the bonding comes from the interaction of the 2*p* orbitals on oxygen with the 1*s* orbital on hydrogen.

   (a) Sketch the molecular orbital diagram for OH, label the orbitals according to the contribution they make to the bonding in the system (bonding, antibonding, nonbonding), and denote the occupation of the levels with arrows representing electrons.



OH 7e⁻

   (b) Estimate the bond order in OH. Predict how the length of the bond in OH^+ compares to that in OH?

The bond order of OH is 1.
The bond length in OH^+ should be about the same since one makes the ion by removing an electron from a non-bonding orbital –

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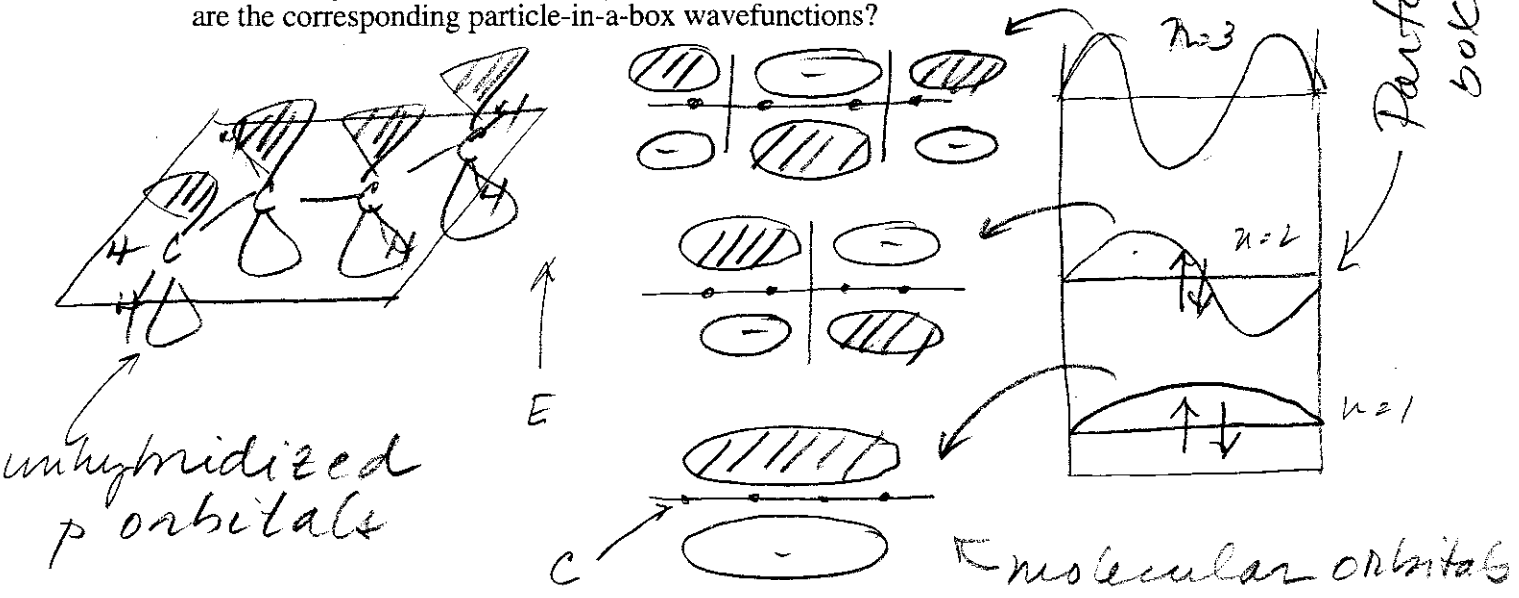
8. *(20 Points)* The *free electron molecular orbital* theory for spectra of polyenes is a fancy name for a 1-D particle in a box model. In butadiene (H_2C=CH-CH=CH_2), we can use the nodal pattern of the molecular orbitals formed from the unhybridized *p* orbitals to assign them to particle-in-a-box states.

Particle-in-a box levels

(a) Sketch the unhybridized *p* orbitals in butadiene and identify the lowest three molecular orbitals they can form. How many of these orbitals are occupied by the π electrons? What are the corresponding particle-in-a-box wavefunctions?



(b) Identify the lowest energy transition one of these electrons can make between particle-in-a-box levels. Write the expression for the energy of the transition.

The lowest two contain electrons

Lowest E transition is

$n=2 \rightarrow n=3$

$$\Delta E = E_3 - E_2 = \frac{h^2}{8mL^2}(n_3^2 - n_2^2)$$

$$\Delta E = \frac{h^2}{8mL^2}(9-4) = \frac{5h^2}{8mL^2}$$

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(c) The lowest energy electronic transition in butadiene occurs at a wavelength of λ=2100 Å. Calculate the corresponding length of box needed in this model. Does the result make physical sense given what you know about the size of atoms and lengths of bonds?

$$\Delta E = \frac{5h^2}{8mL^2} = \frac{hc}{\lambda}; \quad L^2 = \frac{\lambda}{hc}\frac{5h^2}{8m}$$

$$L^2 = \frac{5h\lambda}{8mc}$$

$$\therefore L = \left(\frac{5h\lambda}{8mc}\right)^{1/2} = \left(\frac{5 \cdot 6.62\times10^{-34} \cdot 2100\times10^{-10}}{8 \cdot 9.11\times10^{-31} \cdot 3\times10^{8}}\right)^{1/2}$$

$$\underline{\underline{L}} = 5.6\times10^{-10}\,m = \underline{\underline{5.6\,Å}}$$

This is a reasonable result since we have 3 C-C bonds, which have a length of about 1.4 Å.