Your name _____ Grade this page___

Chem 104A - Midterm II Total Exam Score ____

closed text, closed notes, no calculators

There are 100 total points. General advice - if you are stumped by one problem, move on to finish other problems and come back later if time permits. You may use the whole class period.

A. General (10 points) 2 Points Each _____

True or false (Enter T or F on line) next to statement:

_T_ 1. A linear molecule has 3N-5 normal modes, where N is the number of atoms.

_T_ 2. Nuclear excitations often involve gamma rays.

_T_ 3. Vibrations of molecules with inversion centers are not both Raman & IR active.

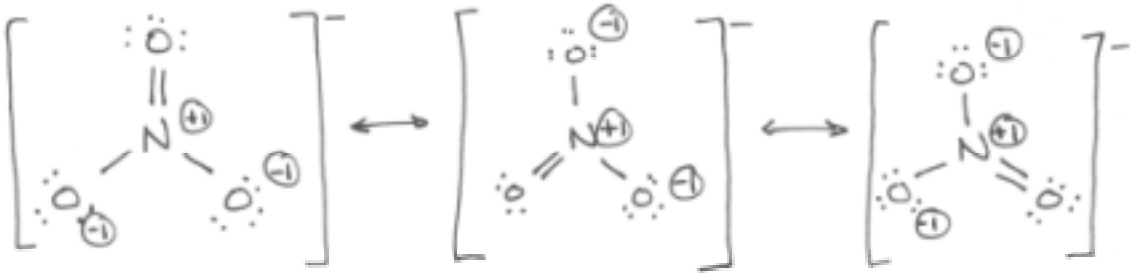
_F_ 4. Molecules are free to rotate at any velocity.

_T_ 5. Electronic excitations often involve energies of several eV.

B. Lewis Diagrams (10 points) 2 Points Each _____

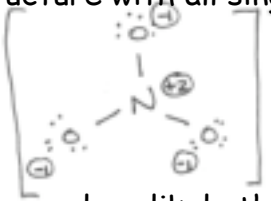
1. Complete a Lewis diagram for one resonance structure of NO_3^- (include a double bond, and identify formal charges):

electrons = 5 + 3(6) = 24



2. Do more resonance structures make for greater or less stability? **_greater_**

3. Draw a resonance structure with all single bonds, and identify the formal charges.



4. Is this structure more or less likely than the first structure you drew?
less

5. Why? **The first structure minimizes the number of non-zero formal charges**

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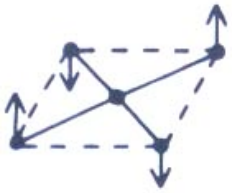
C. Vibrational Spectroscopy (30 points) 2 Points each answer._____

Shown below are some vibrational modes for XeF_4.

a.

b.

c.



d.

1. How many vibrational modes will this molecule have? **_3N-6 = 9_**

2. What is the point group for this molecule? **_D_{4h}_**

3. Based on the character table supplied in the appendix, what are the irreducible representations for the above modes ?

a. **_A_{1g}__** b. **_A_{2u}__** c. **_B_{1g}__** d. **_B_{2u}__**

4. For each mode, fill in IR, R, or 'both' on the adjacent line, depending on whether the mode is IR-active, Raman-active, or IR- and Raman-active.

a. **__R___** b. **__IR__** c. **__R___** d. **_neither_**

5. It turns out one of the above modes is neither Raman nor IR active.

a. Which one do you think it is? (insert letter on line) **__d (B_{2u})____**

b. Why? **The character table shows no IR or Raman activity for vibrations with a B_{2u} representation.**

c. Suggest another technique to see this mode: **inelastic neutron scattering**

d. Would NRVS using the Xe nucleus be an option? Why or why not? **No, because vibration d. does not include any Xe motion.**

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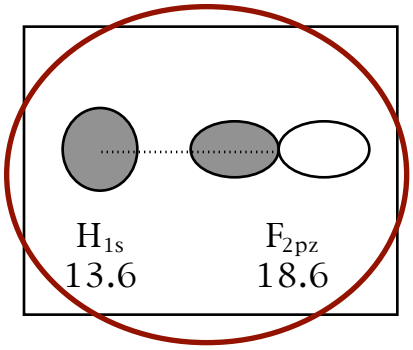
D. MO Theory 30 Points _____

1. (4 points each) In MO theory, we know that the bond energy depends on two things -- overlap (S) between the atomic orbitals and the atomic orbital energy difference (E):

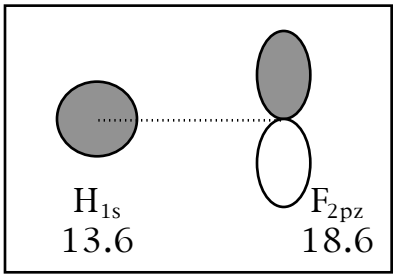
$$\text{bond energy} \quad \frac{S^2}{\Delta E}$$

For the sketches below, circle the case with the higher bond energy, **and briefly state why (in the margin)**.

a.

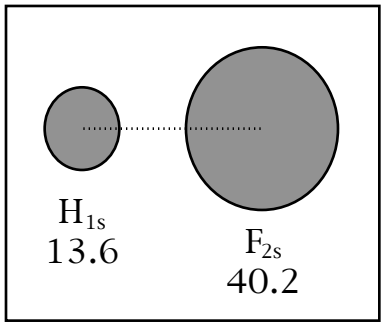


or

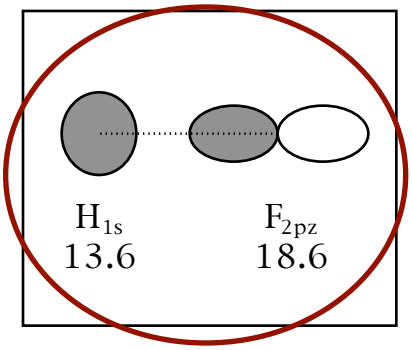


more overlap (big S)

b.

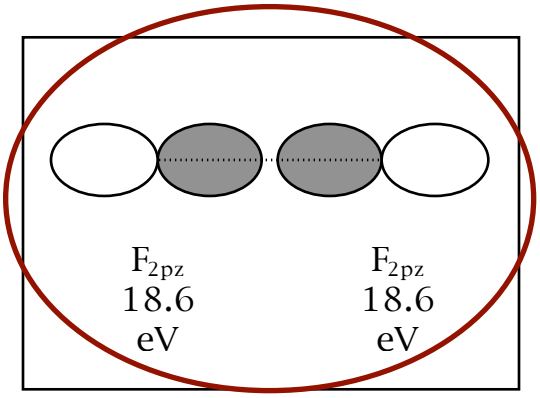


or



Atomic orbital energies are closer (small E)

c.



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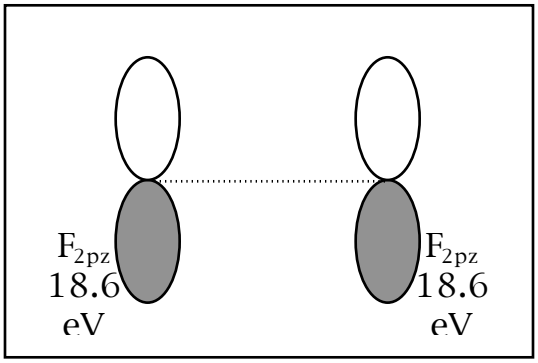

π bonds have better overlap than σ bonds (big S)

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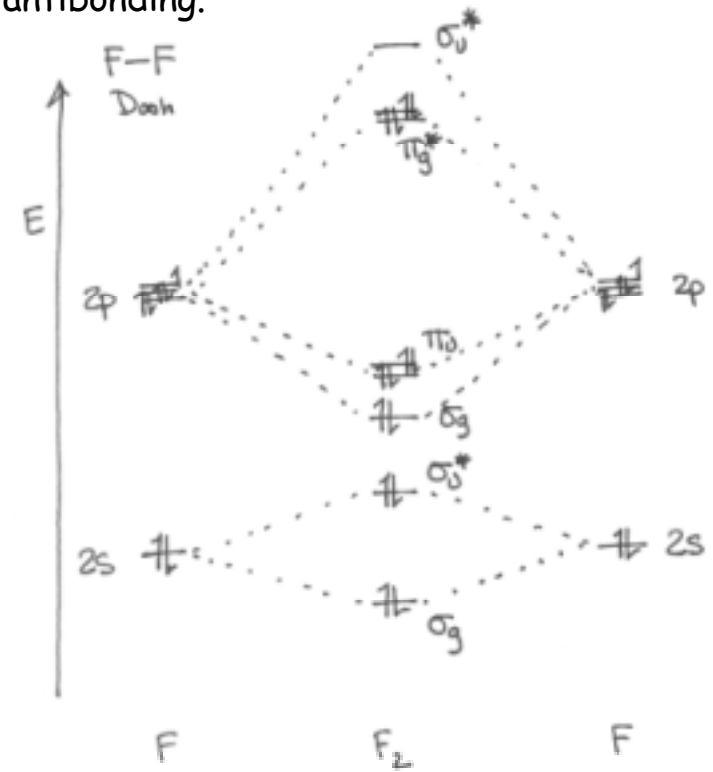
2. In class we frequently discussed the O_2 molecular orbital diagram. F_2 has a similar diagram, but of course with 2 more electrons.

a. (10 points) Draw a MO energy level diagram for F_2, including the atomic orbitals. You need not include the core electrons. Be sure to draw an energy axis and draw in arrows for the electrons. Include labels for □, □, bonding, and antibonding.



b. (10 points) Using the MO from part a, fill in this table of bond orders and number of electrons for molecules similar to F_2.

Molecule	F_2^-	F_2	F_2^+	F_2^{+2}	F_2^{+3}
Total number of electrons	15	14	13	12	11
Bond order	1/2	1	3/2	2	5/2

c. (2 points) Which molecule in part b has the shortest bond and why?
F_2^{+3} because it has the highest bond order (least antibonding of any choice)

d. (2 points) Which molecule in part b has the weakest bond and why?
F_2^- because the bond order is the lowest, so the atoms are not held tightly together (most antibonding character)

e. (2 points) Which molecule(s) in part b are paramagnetic?
F_2^-, F_2^+, F_2^{+2}, F_2^{+3} (all except F_2)

f. (2 points) What happens when you pour a paramagnetic liquid near a magnet?
The liquid is attracted to the magnet.

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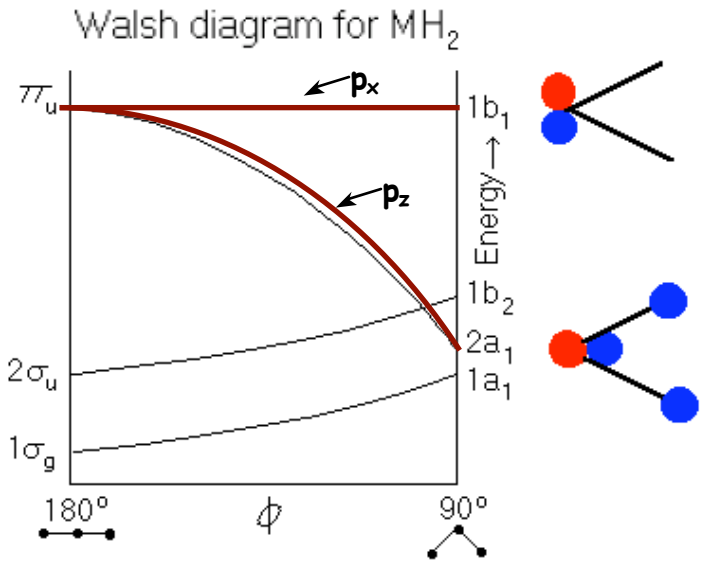
E. Walsh diagram (10 points) (2 Points Each) Points _____

Consider this Walsh diagram for an MH_2 molecule.



1. Call the axis perpendicular to the plane of the bent molecule 'x', and label the line in the diagram that corresponds to the orbital with a p_x component.

2. Call the axis bisecting the H-M-H angle 'z', and label the line in the diagram that corresponds to the orbital with a p_z component.

3. What is the point group of the molecule when at far left and right ?

far left :_$D_{\infty h}$_ right: _C_{2v}_

4. Where does BeH_2 fall on this diagram? **_linear_**

5. Why does the $2a_1$ energy drop as you bend the molecule?

The overlap increases as the hydrogens move to bond with the p_z orbital.

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F. Matching Problems – (Dead Guys) (10 points) 1 points each Points _____

Place letter of phrase on right next to number of person(s) on left that matches best.
Only use each letter once.

1. h	1. Kekulé	a. UCB professor
2. c	2. Werner	b. proposed tetrahedral carbon
3. e	3. Heitler & London	c. synthesized chiral Co complexes
4. f	4. Roald Hoffman	d. UC Davis professor (still alive)
5. a	5. G. N. Lewis	e. invented valence bond theory
6. b	6. van't Hoff	f. still alive; really likes MO theory
7. i	7. Mullikan	g. Stanford professor (for a while)
8. d	8. Cramer	h. constant valence
9. g	9. Pauling	i. invented molecular orbital theory
10. j	10. a gift	j. you're finished!

G. Constructive suggestions always welcome here or by e-mail.

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H. Appendix – Character Tables

1. D_{4h}

D_{4h}	E	$2C_4$	C_2	$2\,C_2'$	$2\,C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

2. C_{3v}

C_{3v}	E	$2\,C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y), (R_x, R_y)$	(x^2-y^2), (xy, xz, yz)

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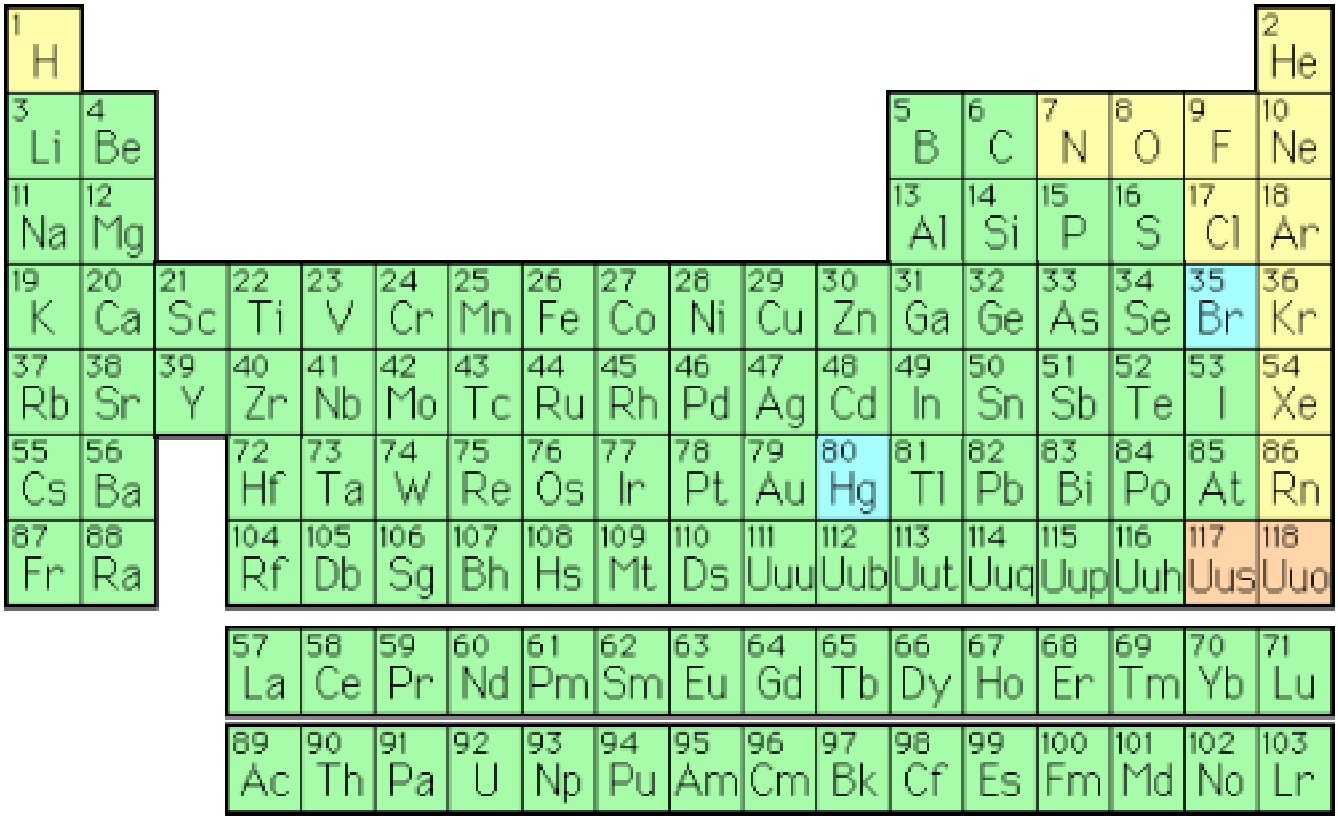
I. Appendix - VOIE's and periodic table



Valence Atomic Orbital Energies

Element	Orbital Potential Energy (eV) 1s	2s	2p	3s	3p	4s	4p
H	-13.6						
He	-24.5						
Li		-5.5					
Be		-9.3					
B		-14	-8.3				
C		-19.5	-10.7				
N		-25.5	-13.1				
O		-32.4	-15.9				
F		-40	-18.7				
Ne		-48.5	-21.6				
Na				-5.2			
Mg				-10.7			
Al				-13.1	-6		
Si				-15	-7.8		
P				-18.7	-10		
S				-20.7	-12		
Cl				-25.3	-13.7		
Ar				-29.3	-15.9		
K						-4.3	
Ca						-6.1	
Zn						-9.4	
Ga						-12.6	-6
Ge						-15.6	-7.6
As						-17.6	-9.1
Se						-20.8	-11
Br						-24.1	-12.5
Kr						-27.5	-14.3