Name: ________________________ **Student Number:** ___________________

CHM 2311
Final Exam
April 24, 2006
Professor Darrin Richeson

There are 18 pages in this exam (including supporting materials and tables). Please count the pages to make sure none are missing.

You may *carefully remove* the last three pages of the exam and use them for scratch work.

Please write legibly and show your work to receive credit for your answers. Partial marks ***may in some cases*** be awarded for partially correct work.

Question	Mark	Question	Mark
1	**/5**	**8**	**/6**
2	**/ 6**	**9**	**/4**
3	**/ 7**	**10**	**/5**
4	**/ 18**	**11**	**/16**
5	**/ 6**	**12**	**/12**
6	**/3**	**13**	**/12**
7	**/3**	**14**	**/10**
		Total	**/113**

Good luck and have a great summer!

1. (**5 points**) A hydrogen orbital has the following ***complete*** wave function (both angular and radial portions of the wave function are included and the angular part is written in Cartesian coordinate form):

$$\psi(r,\theta,\varphi) = R(r)\{Y(\theta,\varphi)\} = \frac{1}{81\sqrt{3}}\left(\frac{2Z}{a_o}\right)^{3/2}(6-\rho)e^{-\rho/3}\left\{1/2\sqrt{\frac{3}{\pi}}\frac{z}{r}\right\}$$

where $\rho = \dfrac{Zr}{a_o}$ and Z = 1 for a hydrogen atom

$a_o = 52.9$ pm

a. Determine the distance from the nucleus in picometers at which **all** ***radial*** nodes occur.

The radial component becomes zero (has a node) when $6-\rho = 0$ *or*
$\rho = 6 = Zr/a_o$
$r = 6a_o = 6(52.9pm) = 317.4\ pm$

b. Determine the quantum numbers n and l for this orbital. ***Clearly*** show the process by which you determined these values. Identify the orbital (1s, 2s, $2p_x$, etc...).

In part (a) we determined that there is one radial node.

The number of angular nodes can be determined from the angular part of the wavefunction. From the equation, $\psi = 0$ *for* $z = 0$ *(and all values for x and y). This is an angular node. Thus there is one angular node which corresponds to* $l = 1$

The equation for the number of radial nodes is given by $n-l-1$ = *number of radial nodes. Since* $n-l-1 = 1$ *then* $n = 1+1+1 = 3$

Therefore this is a 3p orbital and specifically the $3p_z$ *orbital.*

2. **(6 points)** a. Calculate Z_{eff} for an electron in the 3p orbital of the phosphorus ***anion***, P^-.

$$P^- \; Z_{actual} = 15$$

$$(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^4)$$

$$Z_{eff} = Z_{actual} - s$$

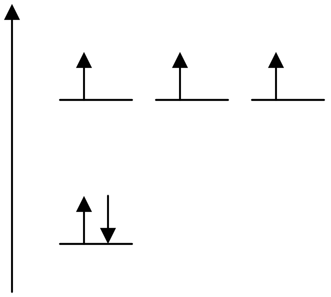
$$s = (2 \times 1.00) + (8 \times 0.85) + (5 \times 0.35) = 10.55$$

$$Z_{eff} = 15 - 10.55 = 4.45$$

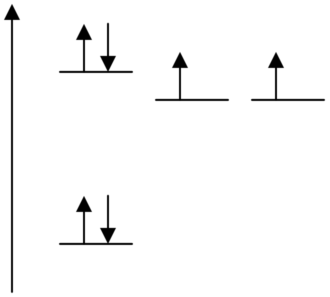
b. The Z_{eff} for an electron in the 3p orbital of the silicon ***anion***, Si^-, is ***less than*** 4. Taking this into account, provide a justification for the fact that the electron affinity for silicon is ***more negative*** than the electron affinity for phosphorus.

Since Si^- has a lower Z_{eff} than P^-, we would expect it to be easier to add an electron to P than to Si. However the fact that silicon has a more negative electron affinity means that it is easier to add an electron to Si! (The reverse of the prediction based on Z_{eff}!) This unexpected result occurs because an electron added to P has to go into an already occupied orbital (see below). The resulting electron-electron repulsions are energetically unfavorable. An electron added to Si, on the other hand will not have to share an orbital, and thus avoids the electron pairing repulsions experienced by P. This makes addition of an electron to Si more favorable.

Si^-



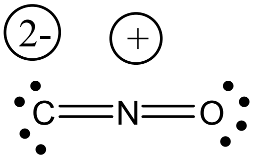
P^-

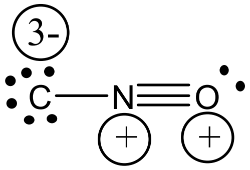


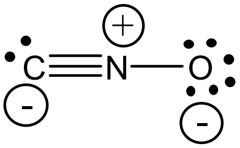
3. **(7 points)** The fulminate ion, CNO$^-$, forms only a few salts, and these salts are unstable and explosive. (Much of the explosive power comes from a re-arrangement to the more stable NCO$^-$ ion).

Draw *all* of the valid Lewis dot structures for the fulminate ion, CNO$^-$ and indicate the formal charges for each atom in each structure. Use this information to explain the instability of fulminates.

The anion has 16 electrons (4+5+6+1)





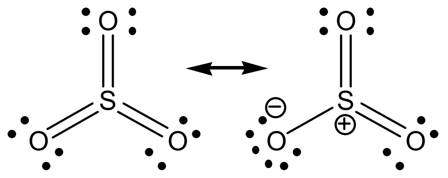


Notice that the formal charges are unlikely for all of the structures!

4. **(18 points)** Draw the most stable Lewis structure and all ***significant*** resonance contributors for each of the molecules below. In your final answer, show all bonded pairs of electrons as lines between the bonded atoms and show all non-bonded electrons as dots. Indicate any ***non-zero formal charges*** on every element where they occur.

a. SO_3

Final Answer: ***(24 electrons)***



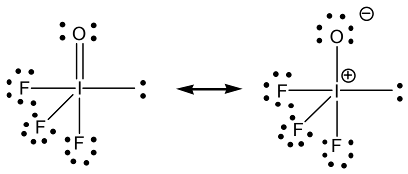
Geometry: ___Trigonal planar________

Shape: ___Trigonal planar________

Hybridization of S: _____sp^2___

b. IOF_3 (I is central atom, O and F are terminal)

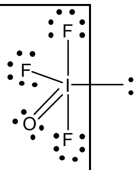
Final Answer: ***(34 electrons)***



Geometry: ___Trigonal bipyramidal

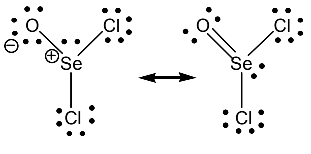
Shape: ____seesaw_

Hybridization of I: ___sp^3d____



c. $SeOCl_2$ (Se is central atom, O and Cl are terminal)

Final Answer: ***(26 electrons)***

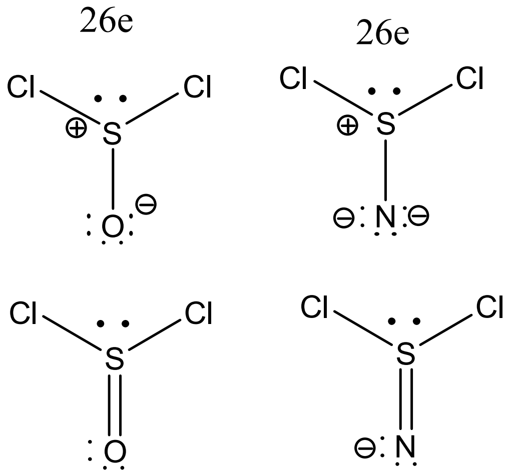


Geometry: __Tetrahedral_

Shape: ____pyramidal_______

Hybridization of Se: __sp^3__

5. (**6 points**) Thionyl dichloride $OSCl_2$ and thiazyl dichloride $NSCl_2^-$ have both been isolated.
Which of these species has the smallest Cl-S-Cl angle? Explain.
Which do you predict to have the long S-Cl bond? Why?



Smaller for $^-NSCl_2$. Less electronegative substituent (nitrogen) leads to smaller bond angle (larger role of S lp)
Longer in $NSCl_2^-$ - reasoning is similar.

6. (**3 points**) Given the three molecules SH_2, SeH_2, and OH_2, answer the questions below:

a. Arrange them in order of increasing bond ***length***:

_____OH_2______ < _______SH_2________ < _______SeH_2_______

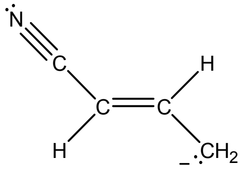
b. Arrange them in order of increasing bond ***strength***:

_____SeH_2_____ < ______SH_2_________ < ______OH_2_________

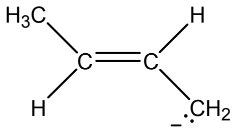
c. Arrange them in order of increasing bond ***angle***:

_____SeH_2_____ < _______SH_2________ < _____OH_2__________

7. **(3 points)** Predict which anion, **1** or **2**, will be a stronger base. Explain your answer.



1



2

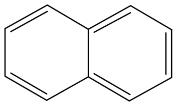
(1) has more resonance structures (I came up with 2) and one of those resonance structures allows the negative charge to be delocalized onto a more electronegative atom (N). This delocalization stabilizes the anion.

(2) has fewer resonance structures (only 1 besides the one drawn), and that resonance structure does not have the benefit of placing the negative charge on a more electronegative atom. Thus, anion (2) is less stabilized than anion (1).

The less stabilized anion (2) will be more reactive – more basic.

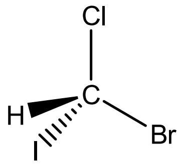
8. **(6 points)** Determine the point group for each of the following molecules.

A.

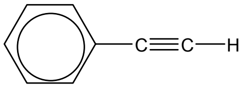


(resonance structures, planar)

B.

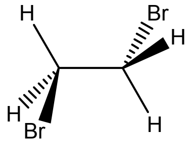


C.



Point Group: A.___D_{2h}___ B. ___C_1______ C.___C_{2v}_____

D.



E. PF_5

F. dz^2

Point Group: D.___C_{2h}___ E. _____D_{3h}_____ F. _____$C_{\infty v}$______

9. **(4 points; ½ point per blank)** In the questions below you will determine the irreducible representations for specific orbitals on a central atom of a molecule in a given point group. You may use the back of one of the exam pages for your scratch work. It is ***not necessary to determine the symmetry labels.***

   a. A d_{xy} orbital on the central atom of a molecule in the S_4 point group (the tricky point here is that the S_4 axis is oriented along z)

S_4	E	S_4	$S_4^2 = C_2$	S_4^3	
	1	***-1***	***1***	***-1***	d_{xy}

   b. A d_{yz} orbital on the central atom of a molecule in the C_{2v} point group

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	
	1	***-1***	***-1***	***1***	d_{yz}

10. **(5 points; ½ point per blank)** Given the symmetry labels for the following irreducible representations, fill in the missing characters:

C_{3v}	E	$2C_3$	$3\sigma_v$
A_2	***1***	***1***	***-1***

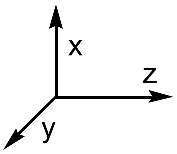
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1"	***1***	***1***	***1***	***-1***	-1	-1

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
A_{2g}	1	***1***	***-1***	***1***	1	-1

11. **(16 points)** a.**(10 points)** In this problem we will derive the complete MO energy-level diagram for hypochlorite anion ClO$^-$. ClO$^-$ should be placed in the Cartesian coordinate system shown below with the principal axis of rotation corresponding to the z-axis.

You only need to consider the valence orbitals of chlorine and oxygen.

You can neglect secondary orbital mixing.



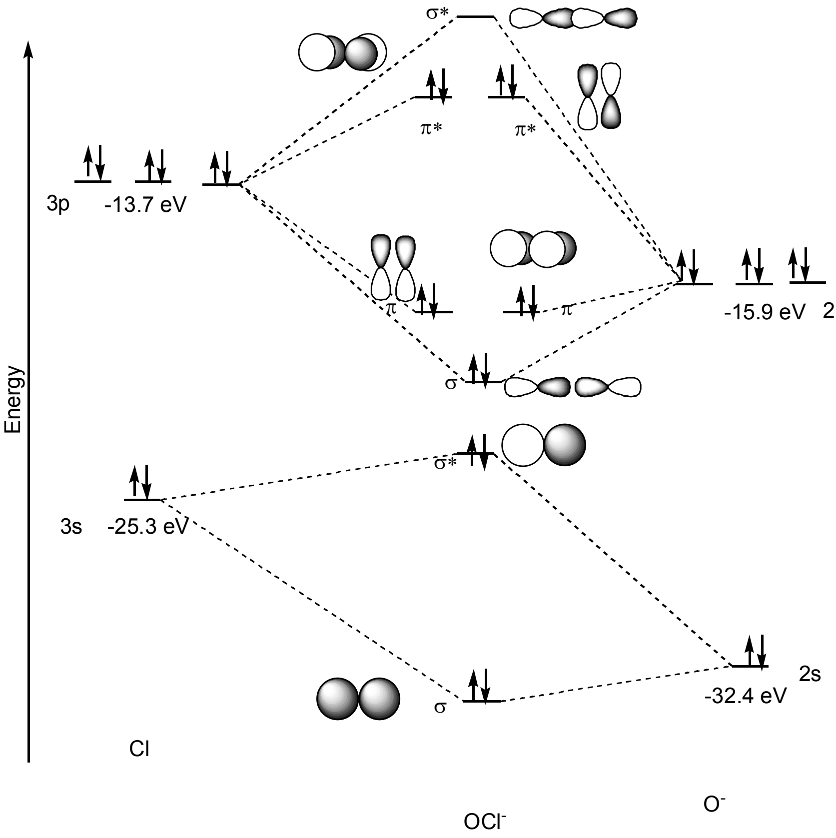
<u>Your diagram should include the following:</u>

Atomic orbitals shown at the appropriate energies

Molecular orbitals shown at the appropriate energies (include sketches)

Assignment of numerical labels (e.g. 3σ) to distinguish between orbitals of similar symmetry

Electrons placed in appropriate orbitals of the molecule

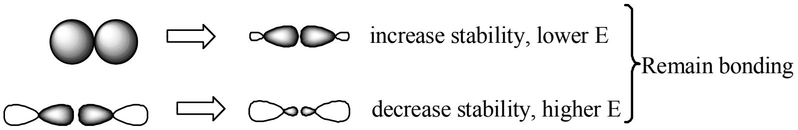


The anion has 7+6+1 electrons = 14 e$^-$

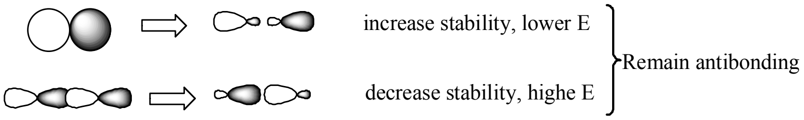
b. **(4 points)** In part (a) we neglected secondary orbital mixing. In the space below, discuss how secondary orbital mixing would effect the orbital energies and shapes in ClO^-. (Feel free to use point form rather than paragraph form in providing your answer.)

Secondary orbital mixing involves the combination of MOs of the same symmetry. The net effect is to lower the energy of the lower (often filled) MO and raise the energy of the upper (often empty) MO. This mixing will change the shapes of the orbitals.

In the case of ClO^- *the orbital mixing that will have the most profound effect on the diagram will be that between the* $\sigma\,(s+s)$ *and the* $\sigma(p_z + p_z)$*. This will lower the first and raise the second. This could lead to the* $\sigma(p_z + p_z)$ *being raised in energy above the* π *orbitals. As for the effects on the orbital shapes, this mixing will give new MOs that have s and p character mixed. A pictorial representation of this is given by:*



Of course the antibonding combinations will also mix to look like this:

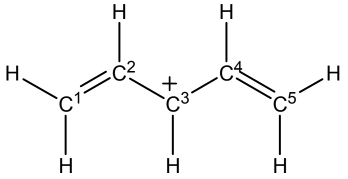


Note: secondary mixing does not change the bond order of this molecule.

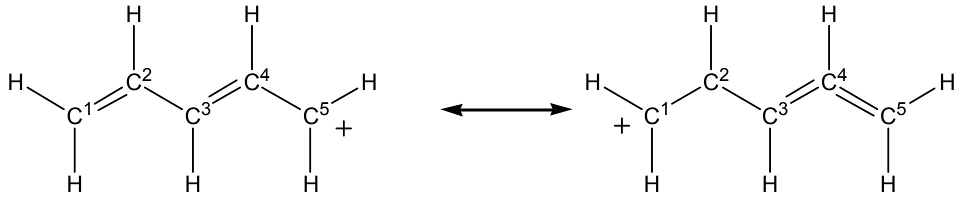
c. **(2 points)** Determine the bond order of ClO^-

$$(6-4)/2 = 1$$

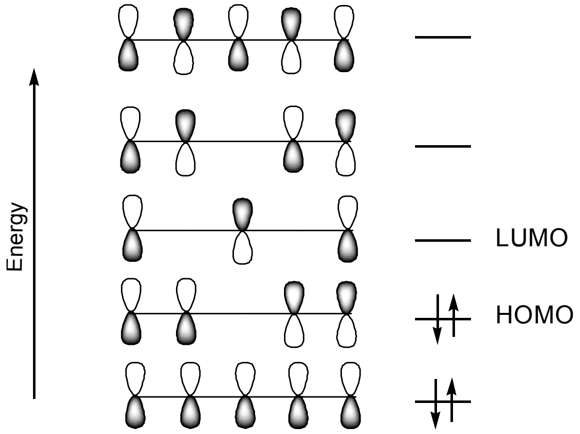
12. **(12 points)** One resonance structure of the pentadienyl carbocation is shown below. (The carbon atoms are numbered for purposes of the discussion in part (c).)



a. Draw all other energetically reasonable resonance structures.



b. **(6 points)** Draw all of the π molecular orbitals for the pentadienyl cation in the appropriate vertical position on the energy axis below and **show electrons** in the appropriate molecular orbitals. **Label the HOMO and LUMO.**



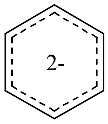
c. A nucleophile is a reagent that seeks out a site of positive charge on another molecule. Nucleophiles possess a reactive pair of electrons.
A nucleophile can successfully attack pentadienyl cation at C1, C3, or C5, but not at C2 or C4. This can be explained according to resonance theory concepts or by MO Theory concepts. Please provide *both* explanations. If diagrams or sketches will enhance your explanation, please feel free to include them (but they are not necessary).

(2 points) Resonance Theory Explanation (Your explanation should not exceed the space provided below)
As shown in the resonance structures (part a), the positive charge is delocalized over C1, C3, and C5 making these carbons good targets for nucleophilic attack.

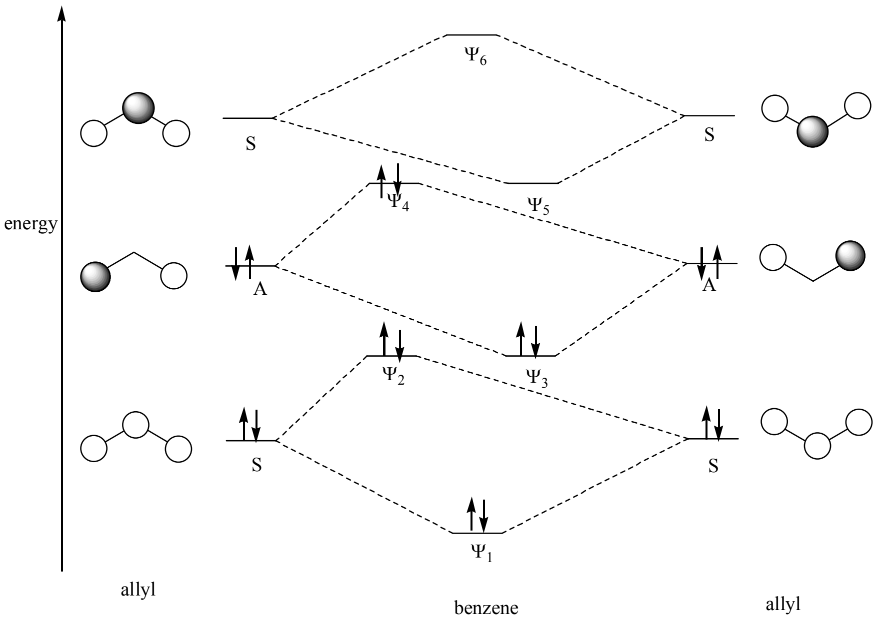
There is no positive charge on C2 or C4, as shown by the resonance structures. Thus, a nucleophile is not likely to attack C2 or C4.

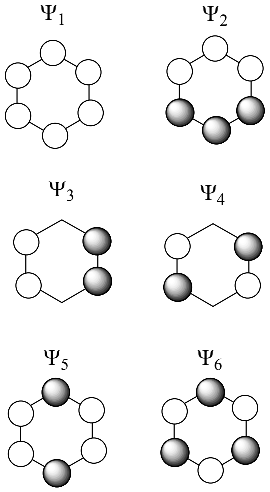
(2 points) MO Theory explanation (Your explanation should not exceed the space provided below)
A nucleophilic attack requires the nucleophile (HOMO) to interact with the cation LUMO (good orbital overlap is necessary). The LUMO's orbital resides on C1, C3, and C5, but there are nodes at C2 and C4. Attack at C2 and C4 would not be possible because there would be no HOMO/LUMO overlap

13. **(12 points)** a. **(10 points)** In the space below, draw a MO diagram for the ***dianion*** of benzene using allyl π-orbitals as your basis orbitals. Your diagram should include the following:



i. Sketches of all orbitals (allyl fragments ***and*** benzene)
ii. Symmetries of allyl orbitals (S or A) with respect to the central mirror plane
iii. Relative energy levels of all orbitals indicated by appropriate placement of orbitals on the vertial energy axis.
iv. Electrons in the appropriate molecular orbitals





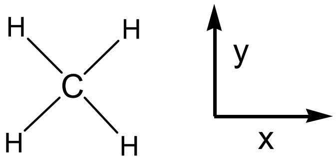
b. **(2 points)** Does Huckel's rule predict that the benzene dianion will be aromatic or antiaromatic? Is your MO diagram consistent with this prediction? Explain.

4n π electrons: Huckel's rule predicts antiaromaticity

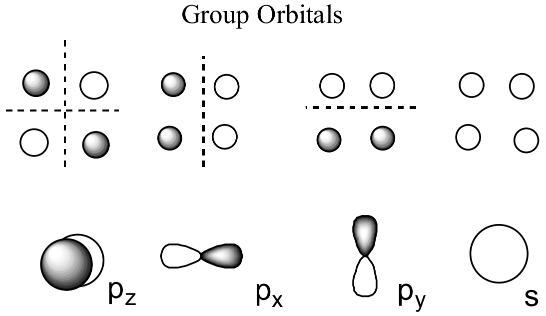
As shown in the MO diagram above, the highest-occupied orbital of the benzene dianion are higher in energy than the HOMOs of the allyl cations. This indicates the delocalization in the ring results in destabilization, which is consistent with the prediction of Huckel's rule

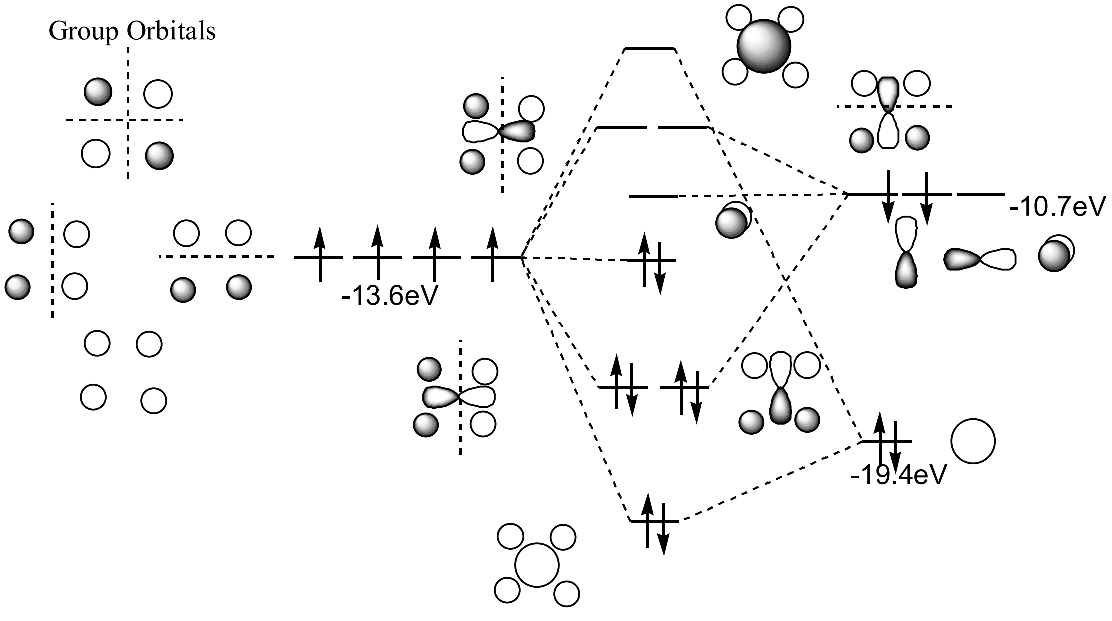
14. **(10 points)** In this problem you will attempt to construct a molecular orbital energy diagram for a hypothetical *square planar* CH_4.

NOTE: Neatness of the diagram will be important for receiving full marks.



(a) Sketch the group orbitals that you will use in this diagram and clearly indicate their nodal structure.
(b) Indicate how **all** of the orbitals of carbon might interact with these group orbitals.
(c) Sketch the MO energy diagram and put in the appropriate number of electrons. Include labels for the atomic (e.g. s, $2p_x$, $3d_{xy}$ etc.) and molecular (σ, π, σ^* etc.) orbitals. Comment on the magnetic properties that you would expect for this species.
(d) Is the highest occupied molecular orbital localized on a particular atom? If so, which one?





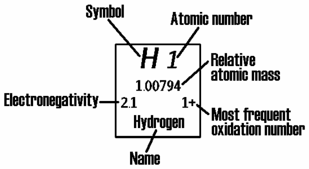
This species should be diamagnetic.
The HOMO is purely hydrogen centered group orbital (not localized on an individual atom)

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		-14.0	-8.3				
C		-19.5	-10.7				
N		-25.5	-13.1				
O		-32.4	-15.9				
F		-46.4	-18.7				
Ne		-48.5	-21.6				
Na				-5.2			
Mg				-7.7			
Al				-11.3	-6		
Si				-15.0	-7.8		
P				-18.7	-10.0		
S				-20.7	-12.0		
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	-11.0
Br						-24.1	-12.5
Kr						-27.5	-14.3

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	σ(xy)	σ(xz)	σ(yz)	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z, x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	x^2-y^2
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(x,y) (R_x, R_y) (xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	*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	(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)



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	*H 1* 1.00794 2.1 1+ Hydrogen																	*He 2* 4.002602 - - Helium
2	**Li 3** 6.941 1.0 1+ Lithium	**Be 4** 9.012182 1.5 2+ Beryllium											**B 5** 10.811 2.0 3+ Boron	**C 6** 12.011 2.5 4+,4- Carbon	*N 7* 14.00674 3.0 3+,3- Nitrogen	*O 8* 15.9994 3.5 2- Oxygen	*F 9* 18.9984032 4.0 1- Fluorine	*Ne 10* 20.1797 - - Neon
3	**Na 11** 22.989768 0.9 1+ Sodium	**Mg 12** 24.3050 1.2 2+ Magnesium											**Al 13** 26.981539 1.5 3+ Aluminum	**Si 14** 28.0855 1.8 4+ Silicon	**P 15** 30.973762 2.1 5+ Phosphorus	**S 16** 32.066 1.8 4+ Sulfur	*Cl 17* 35.4527 3.0 1- Chlorine	*Ar 18* 39.948 - - Argon
4	**K 19** 39.0983 0.8 1+ Potassium	**Ca 20** 40.078 1.0 2+ Calcium	**Sc 21** 44.955910 1.3 3+ Scandium	**Ti 22** 47.88 1.5 4+ Titanium	**V 23** 50.9415 1.6 5+ Vanadium	**Cr 24** 51.9961 1.6 3+ Chromium	**Mn 25** 54.93805 1.5 2+ Manganese	**Fe 26** 55.847 1.8 3+ Iron	**Co 27** 58.9332 1.8 2+ Cobalt	**Ni 28** 58.6934 1.8 2+ Nickel	**Cu 29** 63.546 1.9 2+ Copper	**Zn 30** 65.39 1.6 2+ Zinc	***Ga 31*** 69.723 1.6 3+ Gallium	**Ge 32** 72.61 1.6 4+ Germanium	**As 33** 74.92159 2.0 3+,3- Arsenic	**Se 34** 78.96 2.4 4+ Selenium	***Br 35*** 79.904 2.8 1- Bromine	*Kr 36* 83.80 - - Krypton
5	**Rb 37** 85.4678 0.8 1+ Rubidium	**Sr 38** 87.62 1.0 2+ Strontium	**Y 39** 88.90585 1.3 3+ Yttrium	**Zr 40** 91.224 1.4 4+ Zirconium	**Nb 41** 92.90638 1.6 5+ Niobium	**Mo 42** 95.94 1.8 6+ Molybdenum	Tc 43 98.9063 1.9 7+ Technetium	**Ru 44** 101.57 2.2 3+,4+ Ruthenium	**Rh 45** 102.9055 2.2 3+ Rhodium	**Pd 46** 106.42 2.2 2+ Palladium	**Ag 47** 107.8682 1.9 1+ Silver	**Cd 48** 112.411 1.7 2+ Cadmium	**In 49** 114.82 1.7 3+ Indium	**Sn 50** 118.71 1.8 4+ Tin	**Sb 51** 121.757 1.9 3+,3- Antimony	**Te 52** 127.60 2.1 4+ Tellurium	**I 53** 126.90447 2.5 1- Iodine	*Xe 54* 131.29 - - Xenon
6	***Cs 55*** 132.90543 0.7 1+ Cesium	**Ba 56** 137.327 0.9 2+ Barium	**La 57** 138.9055 1.1 3+ Lanthanum	**Hf 72** 178.49 1.3 4+ Hafnium	**Ta 73** 180.9479 1.5 5+ Tantalum	**W 74** 183.85 1.7 6+ Tungsten	**Re 75** 186.207 1.9 7+ Rhenium	**Os 76** 190.2 2.2 4+ Osmium	**Ir 77** 192.22 2.2 4+ Iridium	**Pt 78** 195.08 2.2 4+ Platinum	**Au 79** 196.96654 2.4 3+ Gold	***Hg 80*** 200.59 1.9 2+ Mercury	**Tl 81** 204.3833 1.8 1+ Thallium	**Pb 82** 207.2 1.8 2+ Lead	**Bi 83** 208.98037 1.9 3+ Bismuth	**Po 84** 208.9824 2.0 2+ Polonium	**At 85** 209.9871 2.2 1- Astatine	*Rn 86* 222.0176 - - Radon
7	***Fr 87*** 223.0197 0.7 1+ Francium	**Ra 88** 226.0254 0.9 2+ Radium	**Ac 89** 227.0278 1.1 3+ Actinium	Rf 104 261.11 - - Rutherfordium	Db 105 262.11 - - Dubnium	Sg 106 263.12 - - Seaborgium	Bh 107 262.12 - - Bohrium	Hs 108 264 - - Hassium	Mt 109 266.1378 - - Meitnerium	Uun 110 269 - - Ununnilium	Uuu 111 272 - - Unununium	Uu 112 277 - - Ununbium		Uuq 114 289 - - Ununquadium		Uuh 116 289 - - Ununhexium		Uuo 118 293 - - Ununoctium

6	**Ce 58** 140.115 1.1 3+ Cerium	**Pr 59** 140.90765 1.1 3+ Praseodymium	**Nd 60** 144.24 1.1 3+ Neodymium	Pm 61 144.9127 1.1 3+ Promethium	**Sm 62** 150.36 1.2 3+ Samarium	**Eu 63** 151.965 1.2 3+ Europium	**Gd 64** 157.25 1.2 3+ Gadolinium	**Tb 65** 168.92534 1.2 3+ Terbium	**Dy 66** 162.50 1.2 3+ Dysposium	**Ho 67** 164.93032 1.2 3+ Holmium	**Er 68** 167.26 1.2 3+ Erbium	**Tm 69** 168.93421 1.2 3+ Thulium	**Yb 70** 173.04 1.1 3+ Ytterbium	**Lu 71** 174.967 1.2 3+ Lutetium
7	**Th 90** 232.0381 1.3 4+ Thorium	**Pa 91** 231.03588 1.5 5+ Protactinium	**U 92** 238.0289 1.4 6+ Uranium	Np 93 237.082 1.3 5+ Neptunium	Pu 94 244.0642 1.3 4+ Plutonium	Am 95 243.0614 1.3 3+ Americium	Cm 96 247 1.3 3+ Curium	Bk 97 247.0703 1.3 3+ Berkelium	Cf 98 251.0796 1.3 3+ Californium	Es 99 252.03 1.3 - Einsteinium	Fm 100 257.0951 1.3 - Fermium	Md 101 258.01 1.3 - Mendelevium	No 102 259.1009 1.3 - Nobelium	Lr 103 260.1053 - - Lawrencium

Under normal conditions, bold symbols correspond to solid state, bold italic correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.