NAME:_____   Section:_____   Student Number:_____

Spring 2015   **Chemistry 2000 Midterm #1A**   ____/ 55 marks

INSTRUCTIONS: 1) Please read over the test carefully before beginning. You should have 5 pages
                          of questions, a blank "overflow" page and a periodic table page.
                     2) If your work is not legible, it will be given a mark of zero.
                     3) Marks will be deducted for incorrect information added to an otherwise
                          correct answer.
                     4) Calculators are not permitted.
                     5) You have 90 minutes to complete this test.

_____

Question Breakdown

Q1	/ 6
Q2	/ 4
Q3	/ 15
Q4	/ 14
Q5	/ 9
Q6	/ 3
Q7	/ 4

Total	/ 55

1.   Fill in each blank with the word or short phrase that best completes the sentence.   **[6 marks]**

(a)   An exact solution to the Schrödinger wave equation can be derived for H_2^+ by "freezing" the separation of the two H nuclei, an approach which is known as the _____ _____ approximation.

(b)   The parameter defined in order to correlate the degree of bonding in MO theory with the number of bonds counted from a Lewis diagram is called the _____.

(c)   Electron density in a molecule is expected to be *highest* in what location? _____.

(d)   The frontier molecular orbital (FMO) that is associated with a molecule's ability to act as a *donor* (i.e. as a Lewis base) is known by the following acronym: _____.

(e)   In *linear* and *planar* molecules, the _____ separation can be used to simplify the treatment of bonding in MO theory.

(f)   In the MO description of bonding in the molecule hydrogen fluoride (HF), the $2p_x$ and $2p_y$ orbitals of fluorine have 100% _____ character.

2.   Draw <u>and</u> label the correct *shape* of the LCAO-MO for the indicated interaction. Include correct shading.   **[4 marks]**
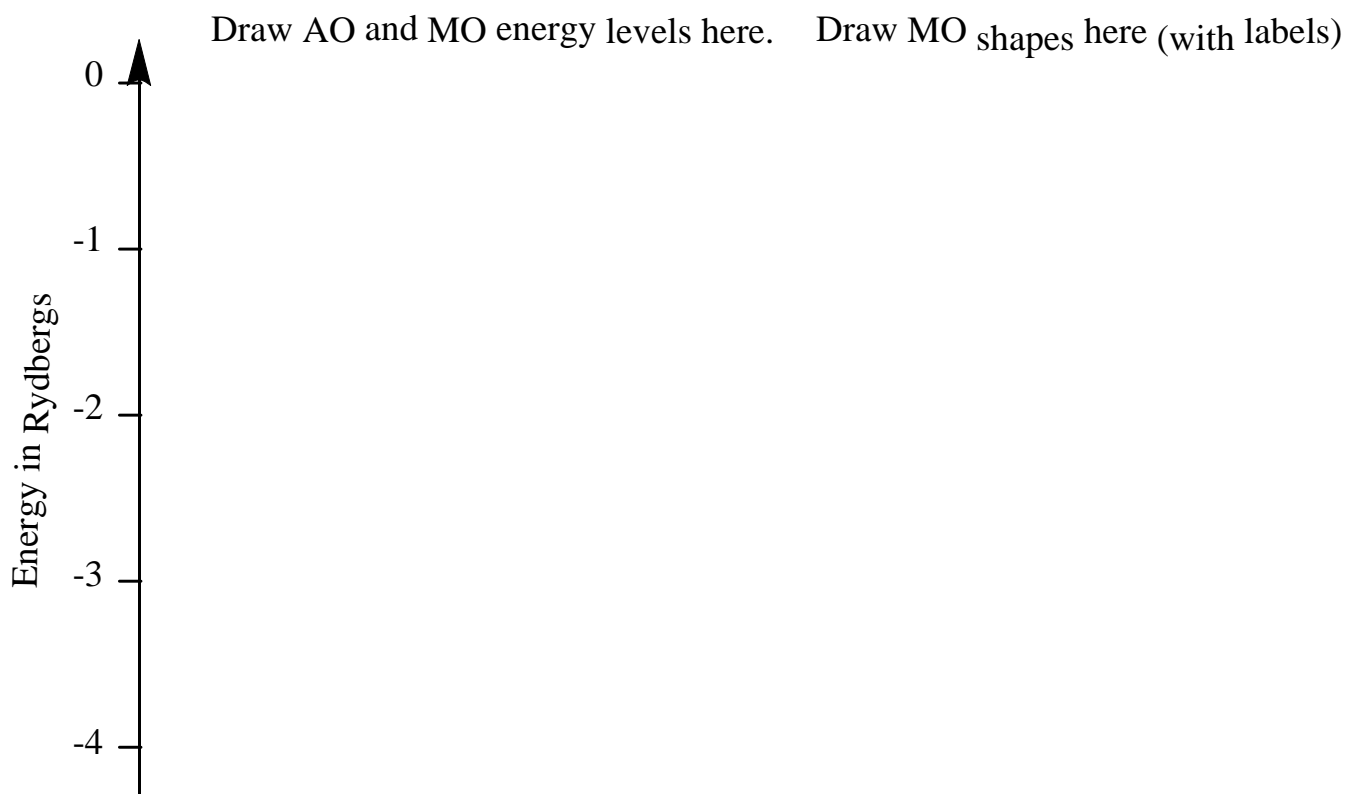
(a)   Destructive overlap.   (b)   Constructive polarized overlap.
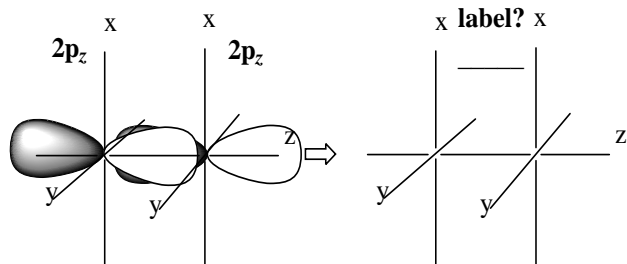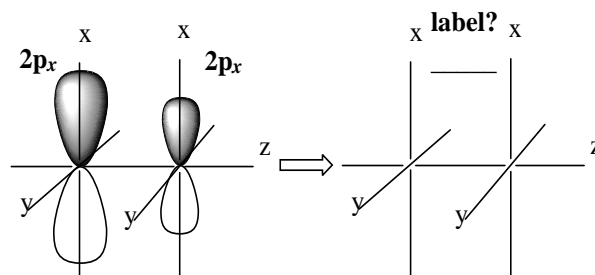
3.   Construct an **atomic orbital – molecular orbital** interaction diagram for difluorine (F_2).

[15 marks]

(a)   Write the atomic electron configuration for a neutral atom of F <u>and</u> identify the valence electrons.

(b)   How many valence electrons does *the difluorine molecule* (F_2) possess?

(c)   Which valence AOs of F have σ symmetry?

(d)   Which valence AOs of F have π symmetry?

(e)   Show energy levels at left as indicated and sketch the resultant LCAO-MOs that are correct in shape and in phase (shading) at right. Be sure to label all the MOs. Make use of the provided energy scale and show both the atomic and molecular energy levels in your diagram. Where possible assign the *dominant bonding character of each MO* using the usual label markers.

Populate your MO diagram with the correct no. of electrons!

Draw AO and MO energy levels here.   Draw MO shapes here (with labels)

Energy in Rydbergs

0 —

-1 —

-2 —

-3 —

-4 —

(f)   Determine the *bond order* in F_2. Show your work clearly.

(g)   Explain clearly, with reference to the MO diagram, why the molecular ion F_2^{2-} cannot exist. What alternative form of this anion does exist and why?

4.   **[14 marks]**

(a)   Carbon monosulfide (CS) is an analogue to carbon monoxide that has been investigated in detail. It forms many interesting metal coordination complexes. Complete the AO-MO interaction diagram for CS by:

   i.   Sketching and naming _only_ the molecular orbitals (MOs).

   ii.   Adding the correct # of valence electrons _only to the MOs_ for the ground electronic state of CS.
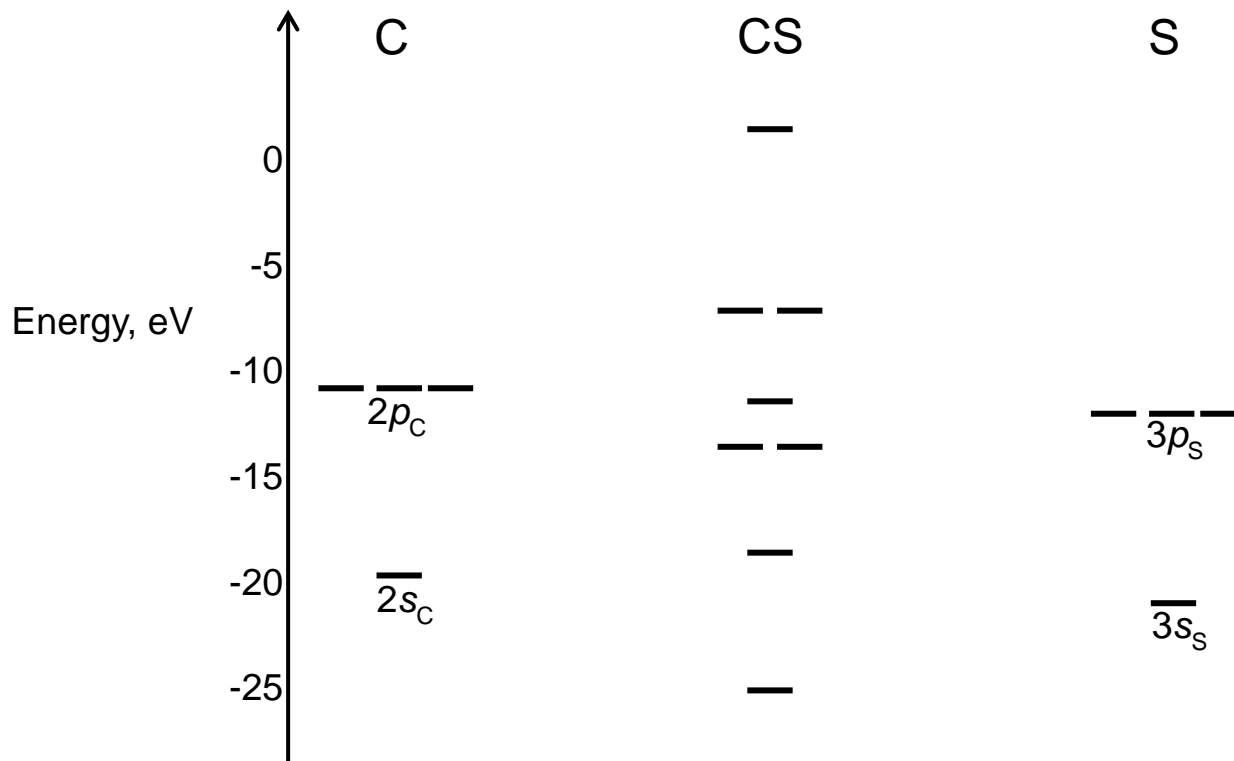
(b)   Write the valence molecular electron configuration of CS in the standard format for diatomics:

(c)   Consider the UV-PES diagram for CS shown at right. _Assign_ the ionization processes to the MO diagram _by labelling the peaks with the corresponding MO labels from your diagram above._

i.   Which peak corresponds to ionization from the highest occupied molecular orbital (HOMO)?

ii.   Which peak(s) correspond to electrons ionized from bonding MOs? Explain.
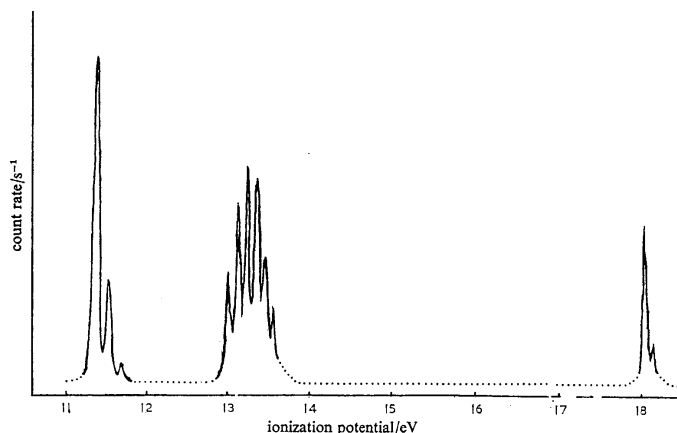
Simplified UV-PES spectrum of carbon monosulfide (22.2 eV photons)

iii.   Which peak(s) correspond to electrons ionized from non-bonding MOs? Explain.

5. **[9 marks]**

(a) Use the "Frost circle" approach to generate an approximate valence π-MO energy-level diagram (energy levels only!) for cyclic hydrocarbon species of the form $[C_5H_5]^x$. Be sure to label each molecular energy level on your diagram with the correct label. Indicate the *dominant* bonding character with the usual symbols. Pay attention to multiplicity of levels!
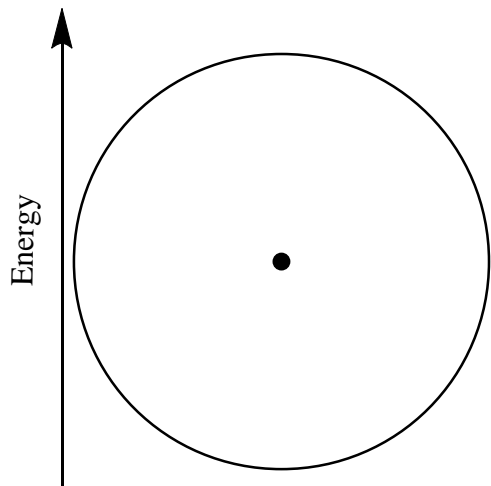
(b) Sketch approximate orbital shapes for each of the π-MOs in your MO diagram. *Fill in as many of the rings as required to complete this project.* Clearly label each MO you decide to draw. Show the resultant $\perp$ nodes.

It is sometimes easier just to draw the atomic p_z orbitals with the correct relative shading (phase).
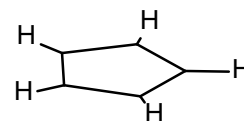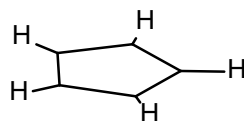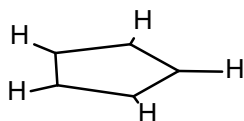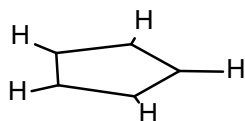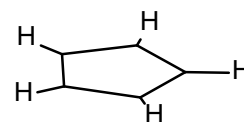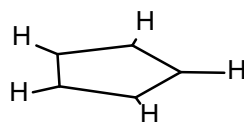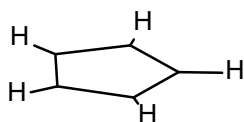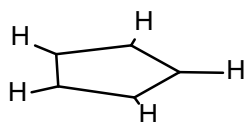
(c) Which value of "x" (i.e. which charge of $[C_5H_5]^x$) will provide the *optimal π-bonding* in this type of hydrocarbon? Show your work or explain your reasoning.

6.   Use Valence Bond theory to consider the bonding in acetonitrile (CH_3CN).   **[3 marks]**

(a)   Draw the best Lewis structure for CH_3CN.

The three larger atoms are connected C-C-N with three H attached to the terminal C.

(b)   What is the hybridization of each of the following atoms in CH_3CN:

C (of CH_3) = _____   C (of CN) = _____

7.   *Please answer (a) and (b) side by side so that the relative scales are obvious.*   **[4 marks]**

(a)   Draw the band structure of potassium   (b)   Draw the band structure of silicon.

(c)   One of these two elements is an insulator. Which one? Explain your choice.

NAME:_____ Section:_____ Student Number:_____

Overflow Page

If you use this page for any answers, please clearly indicate which question is being answered and make sure you note on the page for the question itself that the answer continues here.

CHEM 1000 Standard Periodic Table

1																	18
1.0079 **H** 1	**2**											**13**	**14**	**15**	**16**	**17**	**4.0026** **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Uut** 113	(289) **Fl** 114	(288) **Uup** 115	(293) **Lv** 116	(294) **Uus** 117	(294) **Uuo** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2014)

Table of atomic orbital energies. All energies are in Ry.

	1s	2s	2p
H	-1.00		
He	-1.81		
Li	-4.77	-0.40	
Be	-8.9	-0.69	
B	-14.5	-1.03	-0.42
C	-21.6	-1.43	-0.79
N	-30.0	-1.88	-0.95
O	-39.9	-2.38	-1.17
F	-51.2	-2.95	-1.37
Ne	-64.0	-3.56	-1.59
		3s	**3p**
S		-1.54	-0.86

All energies are from J.C. Slater, *Physical Review* (1955) **98**, 1039-1045.
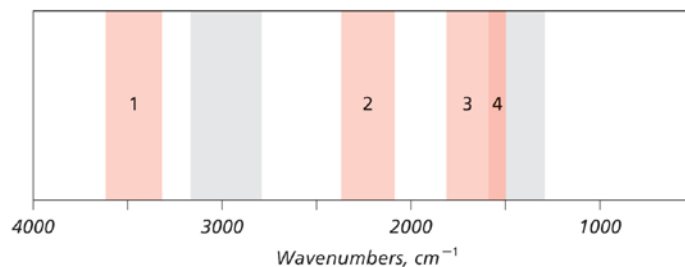
Region	Frequency range, (cm^{-1})	Bond types	Functional groups
1	3500 – 3200	O—H N—H	Alcohol, phenol Amine, amide
2	2300 – 2100	C≡C C≡N	Alkyne Nitrile
3	1800 – 1650	C=O	Aldehyde Amide Anhydride (2 bands) Carboxylic acid Acid chloride Ester
4	1650 – 1500	C=C C=C C=N N=O	Alkene Arene Imine Nitro compound