INSTRUCTIONS:
1) Please read over the test carefully before beginning. You should have 6 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.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on <u>Wednesday</u>, February 13th, 2013. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/47 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____   Date: _____

Course: CHEM 2000 (General Chemistry II)
Semester: Spring 2013
The University of Lethbridge

Question Breakdown

Q1	/ 12
Q2	/ 5
Q3	/ 4
Q4	/ 15
Q5	/ 11

Total	/ 47

1.   **[12 marks]**

(a)   Draw a valence molecular orbital diagram for C_2. Your diagram must include labeled atomic and molecular orbitals and include electrons in the appropriate orbitals.   *[3 marks]*
        You do <u>not</u> need to draw pictures of the orbitals.
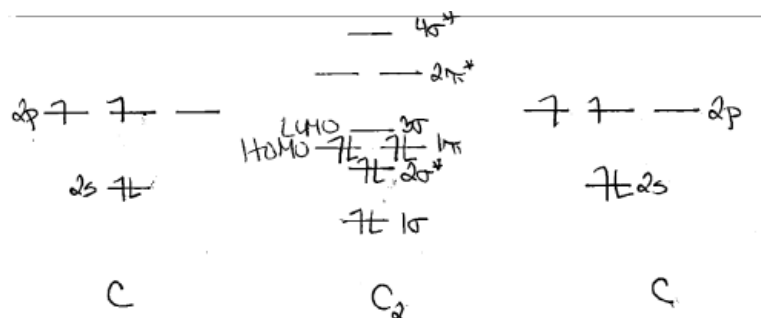
(b)   Draw a valence molecular orbital diagram for F_2. Your diagram must include labeled atomic and molecular orbitals and include electrons in the appropriate orbitals.   *[3 marks]*
        You do <u>not</u> need to draw pictures of the orbitals.
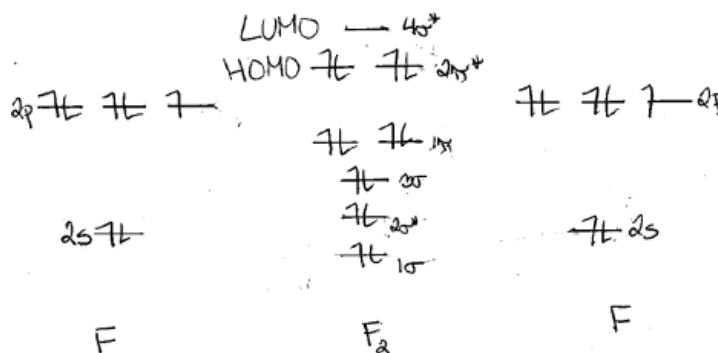
(c)   On each of your answers to part (a) and (b) of this question, clearly label the HOMO and LUMO.
                                                                                                    [2 marks]

(d)   Calculate the bond order for F_2.   *[1 mark]*
        bond order = ½ (8 - 6) = 1

(e)   Does the bond order change when an electron is removed from F_2? If so, how?   *[1 mark]*
        Yes.
        The electron is removed from an antibonding orbital ($2\pi^*$) so the bond order increases to 1½.

(f)   Does the bond order change when an electron is added to F_2? If so, how?   *[1 mark]*
        Yes.
        The electron is added to an antibonding orbital ($4\sigma^*$) so the bond order decreases to ½.

(g)   Of the following species, which (if any) are paramagnetic: F_2, F_2^+ and F_2^- ?   *[1 mark]*
        F_2^+ and F_2^- are paramagnetic.

2. A photoelectron spectrum of C_2 is obtained using an ultraviolet lamp producing a single wavelength of light. The electrons ejected with the highest kinetic energy have a kinetic energy of 9×10^{-19} J. **[5 marks]**

(a) From what orbital are the electrons with the highest kinetic energy being ionized? *[2 marks]*
*Hint: You drew a valence MO diagram for C_2 in question 1(a)*

1π

The electrons ejected with the highest kinetic energy will be the electrons which require the least energy to eject from the molecule. These are the electrons in the HOMO (highest energy occupied molecular orbital). In the case of C_2, the HOMO is 1π.

(b) What effect would the ionization process have on the vibrational spacing of the ion relative to the neutral molecule? *[3 marks]*

1π is a bonding orbital so removing an electron from 1π will lower the C-C bond order, weakening the bond. This will decrease the vibrational spacing of the ion relative to the neutral molecule.

3. The best Lewis structure for formamide is shown below. **[4 marks]**
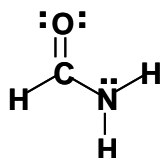
(a) Draw another Lewis structure for formamide that also obeys the octet rule. *Your Lewis structure should have atoms with nonzero formal charges. Show those charges.* *[2 marks]*
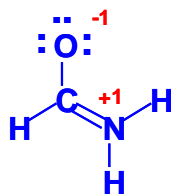
(b) A typical C=O bond has a stretching frequency (expressed as a wavenumber*) of 1700 cm^{-1} on an infrared spectrum. Would you expect the C=O stretching frequency for formamide to be larger or smaller than 1700 cm^{-1}? Explain briefly. *[2 marks]*

Given that the true picture of a molecule is a weighted average of all valid resonance structures, the resonance structure drawn in part (a) suggests that the C-O bond order in formamide is less than 2.
Since the bond order in formamide is less than in a typical C=O bond, the vibrational spacing will be smaller and it is therefore expected that the C-O stretching frequency in formamide will be less than 1700 cm^{-1}.

*wavenumber: 1 cm^{-1} = 2.997925×10^{10} Hz

4. The valence atomic orbital energies for Be and Cl are as follows: **[15 marks]**

	Be	Cl
$2s$	-0.69 Ry	
$2p$	+0.08 Ry	
$3s$		-1.86 Ry
$3p$		-1.01 Ry

While the $2p$ orbital is unoccupied in a Be atom, we can still get molecular orbitals involving this atomic orbital since it is relatively low in energy.

(a) Draw the Lewis structure for $BeCl_2$. Predict the geometry of this molecule as well as the Be-Cl bond order. *[3 marks]*

$$\ddot{\underset{..}{Cl}} - Be - \ddot{\underset{..}{Cl}}$$
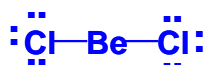
This is a linear molecule.
The Lewis structure indicates a Be-Cl bond order of 1.

(b) Classify each of the atomic orbitals of Be and Cl as sigma or pi type. *[2 marks]*

σ
2s(Be)
$2p_z$(Be)
3s(Cl) × 2
$3p_z$(Cl) × 2

π
$2p_x$(Be)
$2p_y$(Be)
$3p_x$(Cl)× 2
$3p_y$(Cl)× 2

(c) Indicate which (if any) of the atomic orbitals would not be expected to participate in bonding. *[1 mark]*

The 3s orbitals on the chlorine atoms are not expected to participate in bonding because the difference in energy between them and any sigma-symmetric atomic orbital on beryllium is more than 1 Ry.

One can make a similar argument for all of the pi-symmetric atomic orbitals ($3p_x$ and $3p_y$ on the chlorine atoms; $2p_x$ and $2p_y$ on the beryllium atom) as the energy difference between 3p(Cl) and 2p(Be) is 1.09 Ry. Recall that 1 Ry is not a 'hard' cut-off, though, and the pictures in part (e) of this question show that there is still some interaction between these orbitals.

(d) Sketch the combination of atomic orbitals that produces the lowest-energy bonding sigma orbital of $BeCl_2$ in LCAO-MO theory. Also, show the final shape of that molecular orbital. *[2 marks]*

4.   …*continued*

(e)   A sketch of the valence molecular orbital diagram of $BeCl_2$ is shown below, along with pictures of all but the bottom three orbitals. The diagram is not entirely drawn to scale. In particular, the two orbitals at the bottom are closer in energy than suggested by this graphic. In the orbital pictures, approximate locations of nuclei are marked by heavy dots.
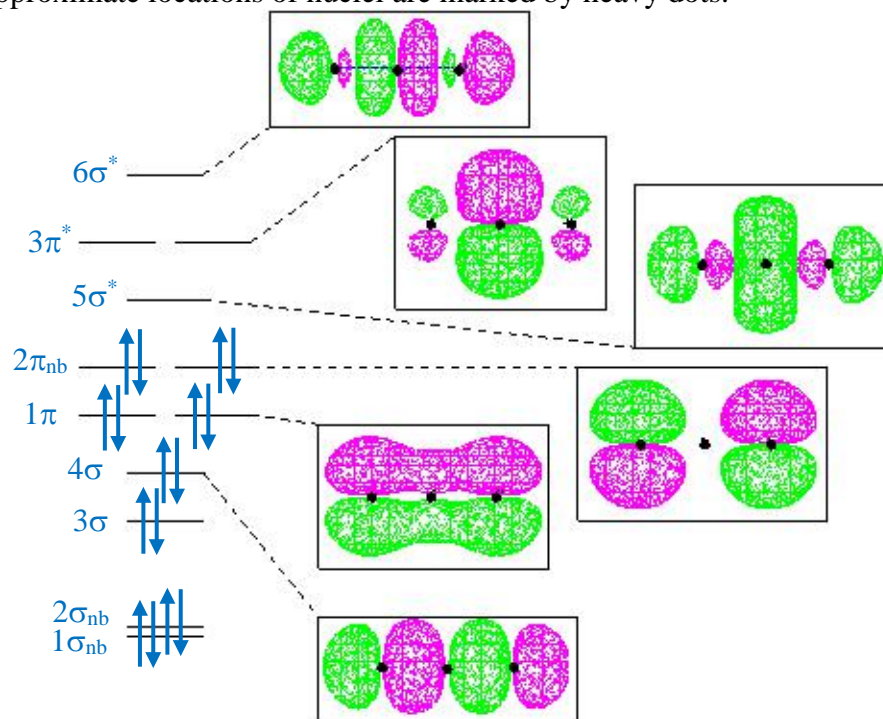
i.   One of the orbitals for which a picture isn't shown is the bonding orbital you sketched in part (d). Which of the bottom three lines in the molecular orbital diagram corresponds to your bonding orbital?   *[1 mark]*
3σ *(third from the bottom)*

ii.   What are the other two orbitals for which a picture isn't shown?   *[1 mark]*
The two lowest energy orbitals are nonbonding orbitals from the 3s orbitals on the chlorine atoms.

iii.   Label all orbitals in the diagram using our usual numbering scheme (1σ, 2σ, 1π, etc.). Clearly label any nonbonding orbitals with a subscript nb.   *[2 marks]*

iv.   Show the ground state orbital occupancy on the diagram using up/down arrows to symbolize electrons.   *[1 mark]*

v.   Use the completed valence molecular orbital diagram to estimate the Be-Cl bond order. Does it agree with the bond order from your Lewis structure in part (a)?   *[2 marks]*

total bond order = ½ (8 - 0) = 4 = 2
                                   2   2

This does not agree with the bond order from the Lewis structure.

5.   **[11 marks]**

Table 1: Atomic Orbital Energy Values for Hydrogen, Fluorine and Bromine

	Hydrogen	**Fluorine**	**Bromine**
$1s$	-1.0 Ry	-51.2 Ry	-993.0 Ry
$2s$		-3.0 Ry	-131.7 Ry
$2p$		-1.4 Ry	-115.6 Ry
$4s$			-1.8 Ry
$4p$			-0.93 Ry

(a) Why is the difference in energy between the $1s$ orbital of hydrogen and the $1s$ orbital of bromine much larger than that between hydrogen and fluorine?   *[1 mark]*

A bromine atom has many more protons in its nucleus so the core 1s electrons are much more strongly attracted to the nucleus in bromine. As such, their energy is much lower.

(b) Complete the valence molecular orbital energy level diagram for HBr by adding electrons to the appropriate orbitals and labeling the orbitals as bonding, nonbonding or antibonding.   *[2 marks]*
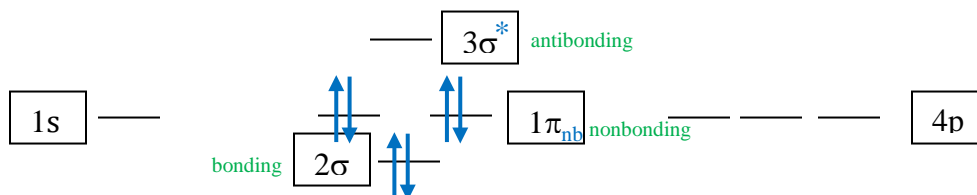
(c) Sketch a picture of each molecular orbital and clearly indicate which atomic orbitals were used to generate it.   *[4 marks]*
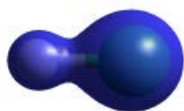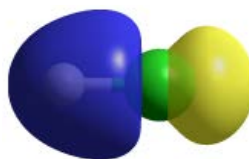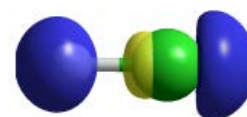
π MOs:

$1\pi_{nb}$
from $4p_x(Br)$

$1\pi_{nb}$
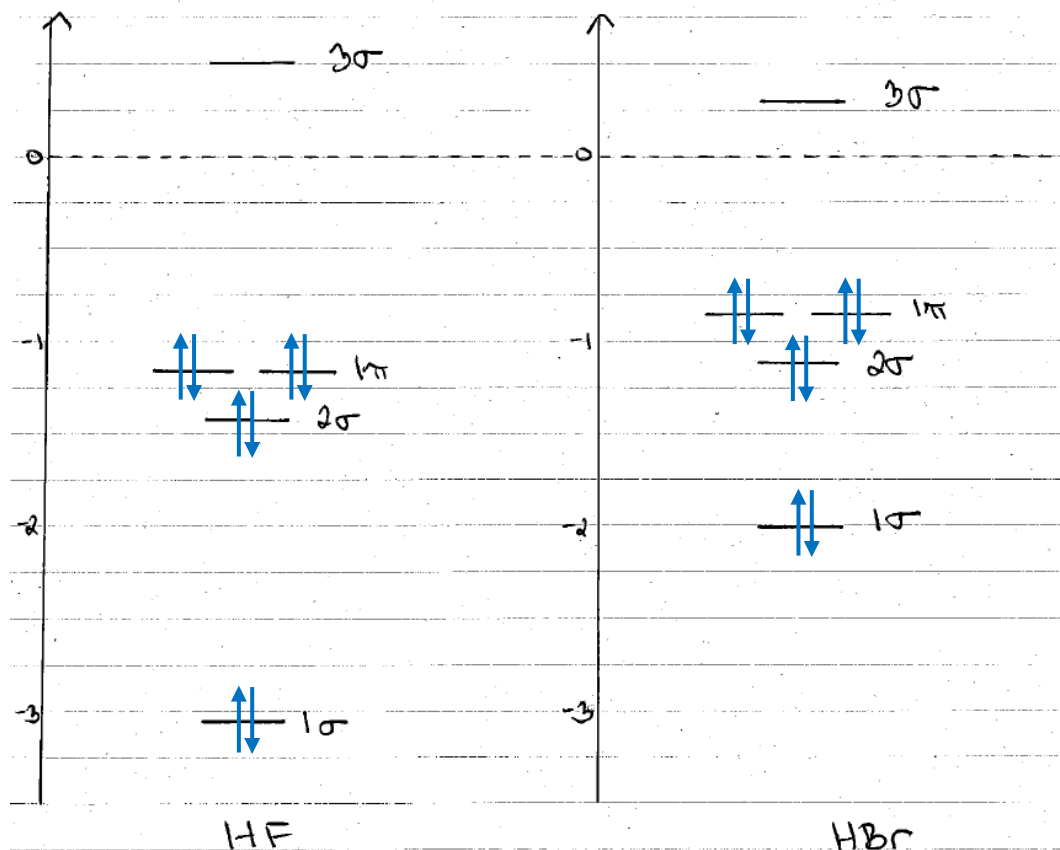from $4p_y(Br)$

σ MOs:

$1\sigma_{nb}$
primarily from $4s(Br)$

2σ
from $1s(H)+4p_z(Br)$

$3\sigma^*$
from $1s(H)+4p_z(Br)$

5.   *…continued*

(d)   The valence molecular orbital energy level diagram for HBr has been redrawn below. To its left is the valence molecular orbital energy level diagram for HF. You will need to add the electrons again.

Use these two diagrams to explain why HBr is a stronger Lewis acid than HF.   *[4 marks]*

A Lewis acid is an electron pair acceptor, so it will accept electrons into its LUMO.

The LUMO of HBr is lower in energy than the LUMO of HF, so electrons will more readily be accepted by HBr.

This makes HBr a stronger Lewis acid than HF.