Winter 2025 **Chemistry 2000 Midterm #1** ____/60 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2000 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/60 on this exam.

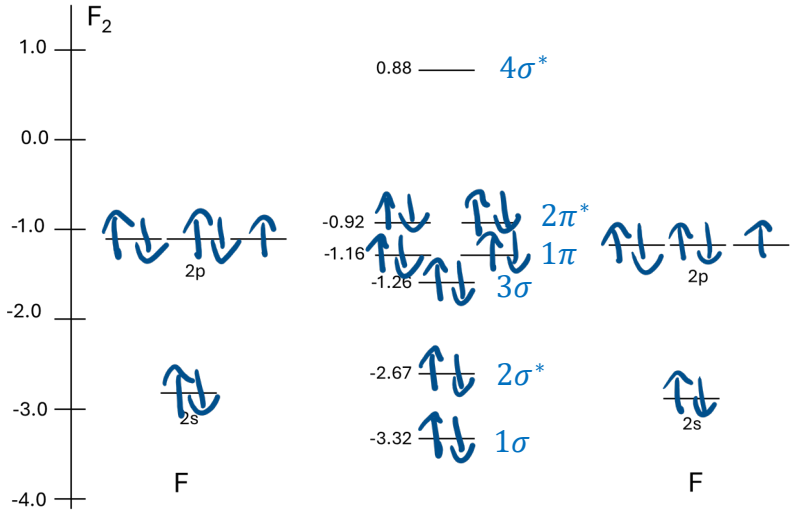
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 6 pages of questions (3 pages double-sided).
2) You have also been given a data sheet. It does not have a QR code, so nothing written on it will be graded.
3) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
4) Neither calculators nor any other electronic devices may be used while writing this test.
5) If your work is not legible, it will be given a mark of zero.
6) Show your work. Answers without supporting reasoning or calculations will not get full credit
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 90 minutes to complete this test.

Question Breakdown

Q1	**Q2**	**Q3**	**Q4**	**Q5**									**Total**
/ 12	/ 14	/ 14	/ 10	/ 10									/ 60

1. A valence molecular orbital energy level diagram ("MO diagram") for F_2 is provided below. **[12 marks]**



(a) State the number of valence electrons in one molecule of F_2. *[1 mark]*

14

(b) Draw a Lewis diagram for F_2. *[1 mark]*



(c) Which atomic orbitals give rise to sigma symmetric molecular orbitals (MOs) in F_2? Be specific. *[1 mark]*

$2s$ and $2p_z$

(d) Which atomic orbitals give rise to pi symmetric molecular orbitals (MOs) in F_2? Be specific. *[1 mark]*

$2p_x$ and $2p_y$

(e) Label each MO on the MO diagram provided. Labels must identify both symmetry (pi or sigma) and bonding character (bonding, nonbonding or antibonding) of the MO. *see diagram* *[3 marks]*

(f) Complete the MO diagram provided by populating atomic orbitals and molecular orbitals with the appropriate number of electrons. *see diagram* *[2 marks]*

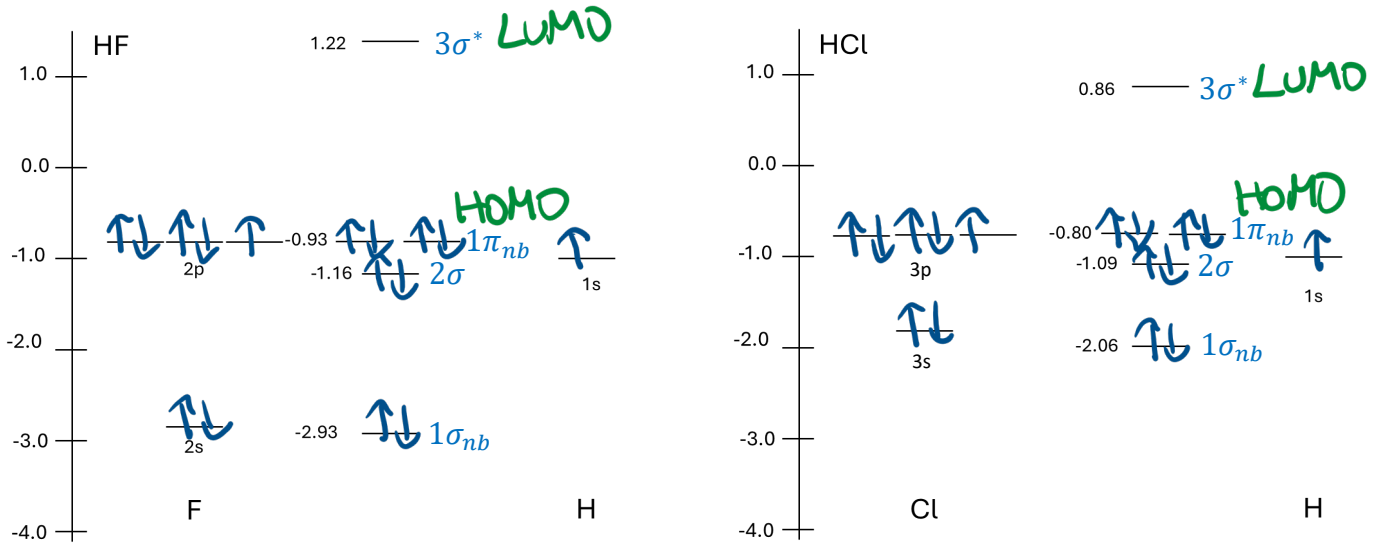
(g) Write the orbital occupancy (electron configuration) for F_2. *[1 mark]*

$(1\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(2\pi^*)^4$

(h) Calculate the bond order for F_2 based on your MO diagram. Is this value consistent with the Lewis diagram you drew in part (b)? *[2 marks]*

$BO = \frac{8-6}{2} = 1$ This is consistent with the single bond in the Lewis diagram.

2. Valence molecular orbital energy level diagrams ("MO diagrams") for HF and for HCl are provided below. Energies are in Rydberg units (Ry). **[14 marks]**



(a) Label each molecular orbital (MO) on each diagram. Labels must identify both symmetry (pi or sigma) and bonding character (bonding, nonbonding, antibonding). *see diagram* *[4 marks]*

(b) Complete the MO diagrams provided by populating atomic orbitals and molecular orbitals with the appropriate number of electrons. *see diagram* *[2 marks]*

(c) Label the HOMO and LUMO on each MO diagram. *see diagram* *[2 marks]*

(d) Draw a picture of the LUMO of HF. Your drawing must clearly show relative phases and must clearly show toward which atom this MO is polarized. *[2 marks]*

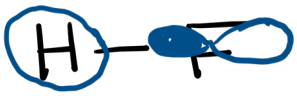


Diagram should show destructive (out-of-phase) overlap between $1s(H)$ and $2p_z(F)$ and should show polarization toward H (larger lobe on H)

(e) With reference to your answer to part (d), explain why a base such as HO^- deprotonates HF. Your answer must address both the atom at which the reaction occurs and any change to bond order. *[2 marks]*

When a base reacts with an acid, it donates an electron pair into the LUMO of the acid.

Adding an electron pair to $3\sigma^*$ adds two antibonding electrons which decreases the $H-F$ bond order from 1 to 0 so the bond breaks.

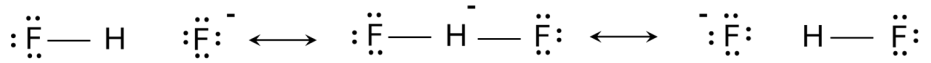
The base attacks H rather than F because $3\sigma^*$ is polarized toward H.

(f) With reference to the MO diagrams provided, explain why HCl is a stronger acid than HF. *[2 marks]*

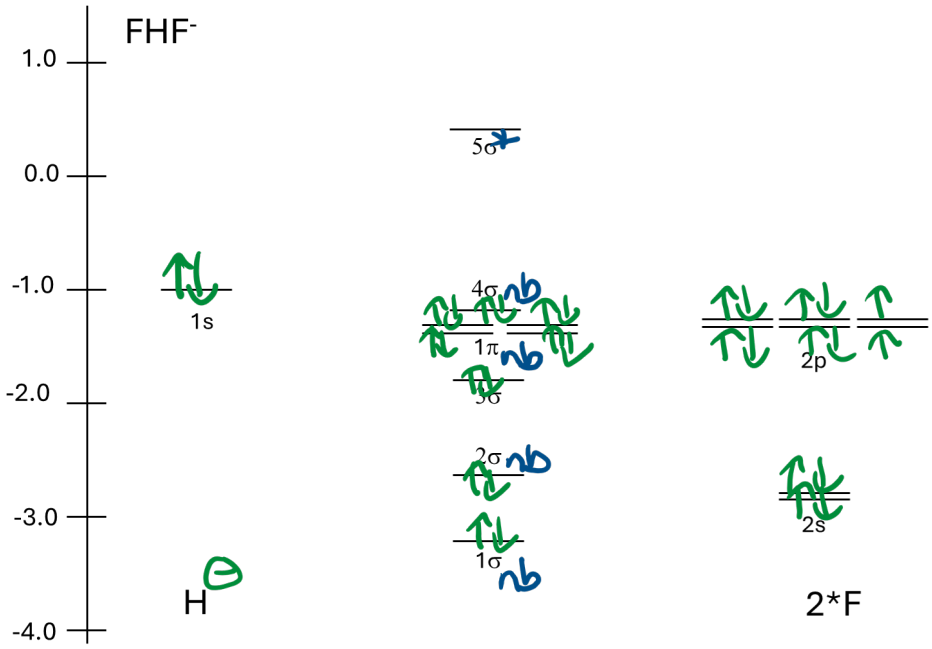
The LUMO $(3\sigma^*)$ in HCl is lower in energy than the LUMO $(3\sigma^*)$ in HF.

As such, it is more favourable for a base to donate its electron pair to HCl.

3. The bifluoride anion (FHF^-) anion can be considered to have the following resonance structures: **[14 marks]**



A valence molecular orbital energy level diagram ("MO diagram") for FHF^- is provided below.



(a) State the number of valence electrons in one FHF^- ion. *[1 mark]*

16

(b) Complete the MO diagram provided by populating orbitals with electrons. *see diagram* *[2 marks]*

(c) Use VSEPR theory to predict the molecular geometry of FHF^-. *[1 mark]*

linear

(d) Complete the label for each MO so that it identifies bonding character. If appropriate notation is used for nonbonding and antibonding, MOs without such notation will be treated as labeled 'bonding'. *[3 marks]*

There are a few viable assignments for 1σ and 2σ.

- *The energy gap between $1s(H)$ and $2s(F)$ is larger than 1 Ry so if we conclude that $2s(F)$ can only interact with each other (and not with $1s(H)$), both MOs would be nonbonding.*
- *The diagrams at the top of the next page show that it could also be reasonable to assign 1σ as bonding, leaving 2σ as nonbonding.*
- *One might argue that 1σ is bonding while 2σ is antibonding based on 1σ having significantly lower energy than $2s(F)$ and 2σ having significantly higher energy than $2s(F)$.*

(e) Calculate the average $F-H$ bond order for FHF^- based on your MO diagram. Is this value consistent with the resonance structures provided? Why or why not? *[2 marks]*

If $1\sigma_{nb}$ and $2\sigma_{nb}$ or if 1σ and $2\sigma^*$: $F-H$ bond order is $\frac{1}{2}\left(\frac{2-0}{2}\right)=\frac{1}{2}$ or $\frac{1}{2}\left(\frac{4-2}{2}\right)=\frac{1}{2}$ (consistent with a weighted averaging of all three resonance structures given that the central one is not degenerate with the other two)

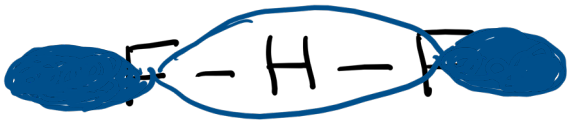
If 1σ and $2\sigma_{nb}$: $F-H$ bond order is $\frac{1}{2}\left(\frac{4-0}{2}\right)=\frac{2}{2}=1$ (consistent with middle resonance structure)

For full marks, a detailed explanation referencing all three resonance structures was required.



3. *…continued from previous page*

(f) Draw a picture of 3σ. Your drawing must clearly show relative phases. *[1 mark]*



Drawing must clearly show constructive interference (in-phase overlap) between $2p_z(F)$, $1s(H)$ and $2p_z(F)$. There should be two nodes perpendicular to the bond axis, one through each fluorine nucleus.

Because there is significant electron density between each pair of adjacent atoms this is clearly a bonding MO.

(g) Draw a picture of 4σ. Your drawing must clearly show relative phases. *[1 mark]*



Drawing must clearly show destructive interference (out-of-phase overlap) between $2p_z(F)$ and $2p_z(F)$ with no contribution from $1s(H)$. There should be three nodes perpendicular to the bond axis, one through each fluorine nucleus and one through the hydrogen nucleus.

Because this MO does not contain any interaction between AOs on adjacent atoms, it is likely nonbonding.

(h) Draw a picture of 5σ. Your drawing must clearly show relative phases. *[1 mark]*



Drawing must clearly show destructive interference (out-of-phase overlap) between $2p_z(F)$, $1s(H)$ and $2p_z(F)$. There should be four nodes perpendicular to the bond axis, one through each fluorine nucleus and one through each $F-H$ bond.

Because there is a node through each bond, this is clearly an antibonding MO.

(i) Where are the lone pairs localized? Clearly reference the relevant MOs. *[2 marks]*

The lone pairs are localized on the two fluorine atoms.

They can be found in the nonbonding MOs: $1\pi_{nb}$ (four degenerate MOs containing a total of eight electrons), $4\sigma_{nb}$ (two electrons), $2\sigma_{nb}$ (two electrons) and $1\sigma_{nb}$ (two electrons).

4. Consider a form of boron in the solid state that has a planar shape at the lattice positions forming sheets of hexagonal shapes as shown below. The valence electron configurations of B, B_2, B_4 and so forth to B_N are shown for this planar arrangement. **[10 marks]**



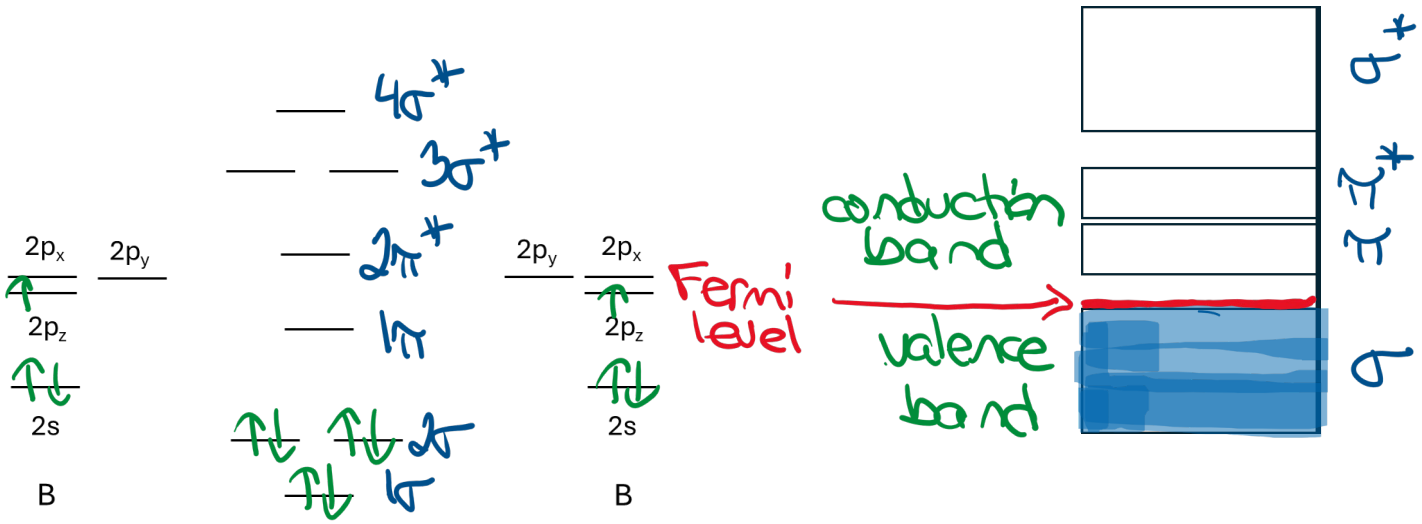
B $2s^2 2p^1$

B_2 $1\sigma^2 2\sigma^4 1\pi^0 2\pi^{*0} 3\sigma^{*0} 4\sigma^{*0}$

B_4 $1\sigma^2 2\sigma^2 3\sigma^4 4\sigma^4 1\pi^0 2\pi^0 3\pi^{*0} 4\pi^{*0} 5\sigma^{*0} 6\sigma^{*0} 7\sigma^{*0} 6\sigma^{*0}$

B_N $[\sigma's]^{3N}[\pi's]^0[\pi^{*}'s]^0[\sigma^{*}'s]^0$

(a) A valence molecular orbital energy level diagram ("MO diagram") for B_2 is provided below showing energy levels consistent with those observed for the solid-state boron shown above. Complete this diagram by labeling each MO (based on the electron configuration provided) and by populating orbitals with the appropriate number of electrons. *[3 marks]*



(b) Beside the MO diagram, a band diagram is provided for B_N. Based on the trends shown by the valence electron configurations for B_2 to B_N, complete the band diagram by: *[5 marks]*

i. labeling the bands (using the notation from the electron configurations),

ii. adding shading to show which bands are occupied by electrons,

iii. labeling the valence band and conduction band, and

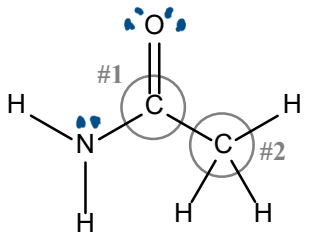
iv. labeling the Fermi level.

(c) Comment on the size of the band gap and indicate whether this form of boron is a conductor, semiconductor or insulator. *[2 marks]*

Boron is known to be a semiconductor, so it's likely that the band gap is of moderate size.

5. Consider the following molecule according to valence bond theory. **[10 marks]**

The carbon atoms have been circled and numbered so that they can be referenced clearly.



(a) Complete the diagram above by adding lone pairs to the appropriate atoms. *[1 mark]*

see diagram

(b) According to valence bond theory, what is the hybridization of the nitrogen atom? *[1 mark]*

Answer based on the resonance structure drawn above.

sp^3

(c) According to valence bond theory, what is the hybridization of carbon **#1**? *[1 mark]*

Answer based on the resonance structure drawn above.

sp^2

(d) According to valence bond theory, what is the hybridization of carbon **#2**? *[1 mark]*

Answer based on the resonance structure drawn above.

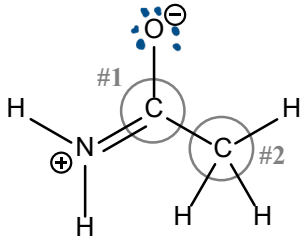
sp^3

(e) Describe the $C - O$ bond using valence bond terminology. Your answer must identify both how many sigma bonds and/or how many pi bonds are present between the two atoms and which atomic and/or hybrid atomic orbitals interact to give each of those bonds. *[4 marks]*

σ: $sp^2(C) + 2p_x(O)$ *There is a sigma bond between sp^2 on carbon and $2p_x$ on oxygen. It would also be acceptable to say that oxygen bonds via $2p_y$ or via sp^2 (instead of $2p_x$)*

π: $2p_z(C) + 2p_z(O)$ *There is a pi bond between $2p_z$ on carbon and $2p_z$ on oxygen.*

(f) Another resonance structure for this molecule is shown below. Complete it by adding lone pairs to the appropriate atoms and explain how your answers to questions (b), (c) and (d) would (or wouldn't) change if you answered based on the resonance structure below instead of the one at the top of the page. *[2 marks]*



According to this resonance structure, the nitrogen atom would become sp^2 while the two carbon atoms would still be sp^2 and sp^3 respectively.