Spring 2018   **Chemistry 2000 Midterm #1**   _____/64 marks

1) Please read over the test carefully before beginning. You should have 6 pages of questions and a blank "overflow" page. A periodic table has also been provided.
2) **DO NOT WRITE ON THE QR CODE!!!** Work on pages without a QR code will not be graded.
3) If your work is not legible, it will be given a mark of zero.
4) Marks will be deducted for incorrect information added to an otherwise correct answer.
5) Calculators are not permitted.
6) 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 5:00 pm Mountain Time on <u>Friday</u>, February 19th, 2018. I understand that breaking this agreement would constitute academic misconduct. The minimum punishment would be a mark of 0/64 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: _____
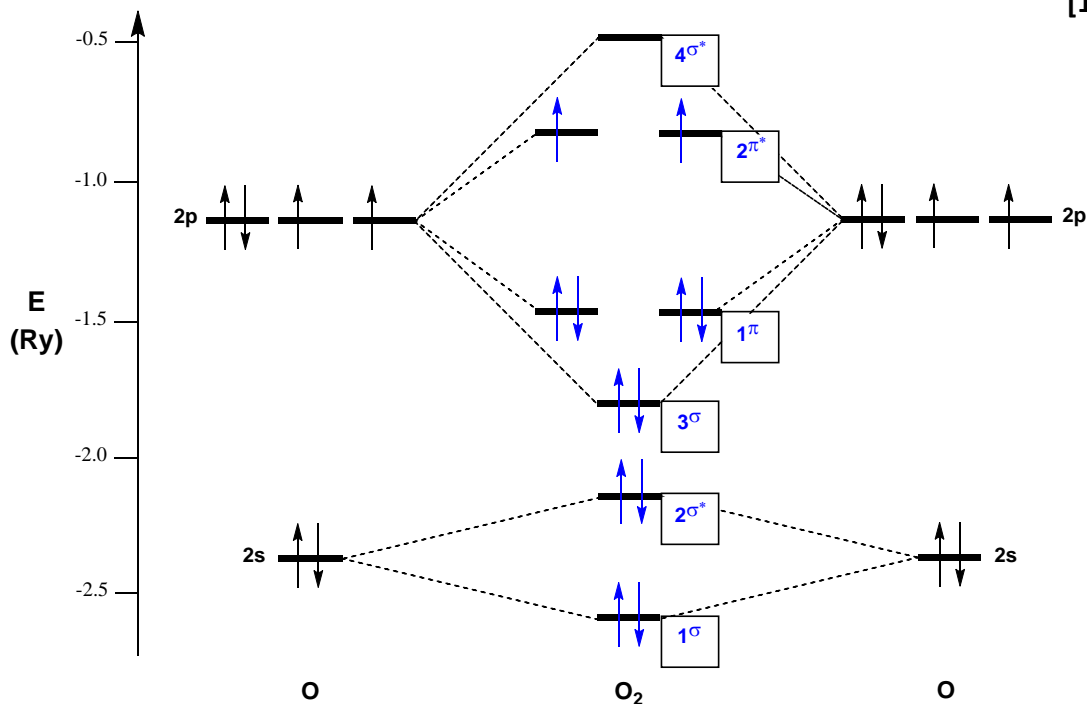Course: CHEM 2000 (General Chemistry II)
Semester: Spring 2018
The University of Lethbridge

Question Breakdown

| Q1	Q2	Q3	Q4	Q5	Q6				Total
/ 17	/ 4	/ 12	/ 17	/ 5	/ 9				/ 64

1. The diagram below shows an incomplete valence molecular orbital energy level diagram for O_2.

    [17 marks]

(a) Complete the diagram above by: *[4 marks]*
     - labeling the molecular orbitals in the boxes provided, clearly indicating if each molecular orbital is bonding, nonbonding or antibonding, and
     - placing the correct number of electrons in the molecular orbitals.

(b) In the space below, clearly identify which atomic orbitals combine to make each **sigma**-symmetric molecular orbital. For each sigma-symmetric molecular orbital, draw and name the atomic orbitals from which it is formed. Also, draw and name the molecular orbital itself.   *[8 marks]*
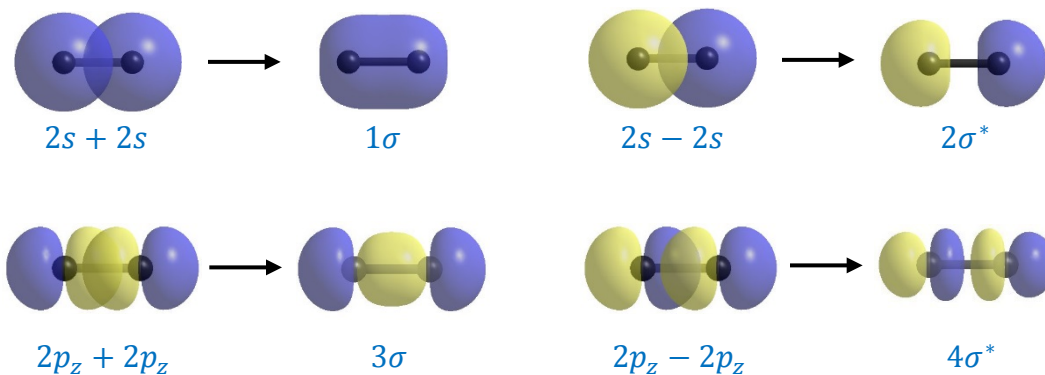
It is not necessary that the atomic orbitals be drawn overlapping (as shown here). It is not necessary that students show + or − between the atomic orbitals; however, the phases must be drawn to match the type of overlap (constructive or destructive).

1. *continued…*
(c) Is O_2 diamagnetic or paramagnetic? Justify your choice.   *[1 mark]*
    The mark is for the explanation. Answers without explanation will not get credit.
    O_2 is paramagnetic. It has two unpaired electrons.

(e) Write the valence orbital occupancy (electron configuration) for O_2.   *[1 mark]*
    $(1\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(2\pi^*)^2$

(f) Calculate the bond order for O_2.   *[1 mark]*
    $\frac{8-4}{2} = \frac{4}{2} = 2$

(g) Peroxide is the dianion formed from oxygen. It has the formula O_2^{2-}. Write the valence orbital
    occupancy for the peroxide ion **and** calculate the bond order in the peroxide ion.   *[2 marks]*
    The valence orbital occupancy for O_2^{2-} is $(1\sigma)^2(2\sigma^*)^2(3\sigma)^2(1\pi)^4(2\pi^*)^4$

    The bond order of O_2^{2-} is $\frac{8-6}{2} = \frac{2}{2} = 1$

2. The amount of *sp*-mixing observed in the homonuclear diatomic molecules varies dramatically
    across the periodic table.   **[4 marks]**
(a) Give an example of a homonuclear diatomic molecule (from the second period) in which you
    would expect to see a significant amount of *sp*-mixing.   *[1 mark]*
    Li_2, Be_2, B_2, C_2, or N_2

(b) Give an example of a homonuclear diatomic molecule (from the second period) in which you
    would expect to see a negligible* amount of *sp*-mixing.   *[1 mark]*
    The word "negligible" means "an insignificant amount" or "very little".
    O_2, F_2, or Ne_2

(c) What is the main factor influencing the amount of *sp*-mixing, and how does this factor relate to
    the amount of *sp*-mixing in a second period homonuclear diatomic molecule?   *[2 marks]*
   The main factor influencing the amount of *sp*-mixing is the size of the energy gap between the *s*
    and *p* orbitals in the valence shell. As the energy gap decreases, the amount of *sp*-mixing
    increases.
    Since the energy gap between the $2s$ and $2p$ orbitals increases from left to right across the
    periodic table, we expect homonuclear diatomic molecules for elements further left on the
    periodic table to have a significant amount of *sp*-mixing whereas homonuclear diatomics for
    elements further right on the periodic table will have very little *sp*-mixing.

3.

(a)   Draw a molecule orbital energy level diagram for $NaCl$. On your diagram: *[5 marks]*

- Label all atomic and molecular orbitals, clearly indicating if each molecular orbital is bonding, nonbonding or antibonding.
- Populate the molecular orbitals with the correct number of electrons.
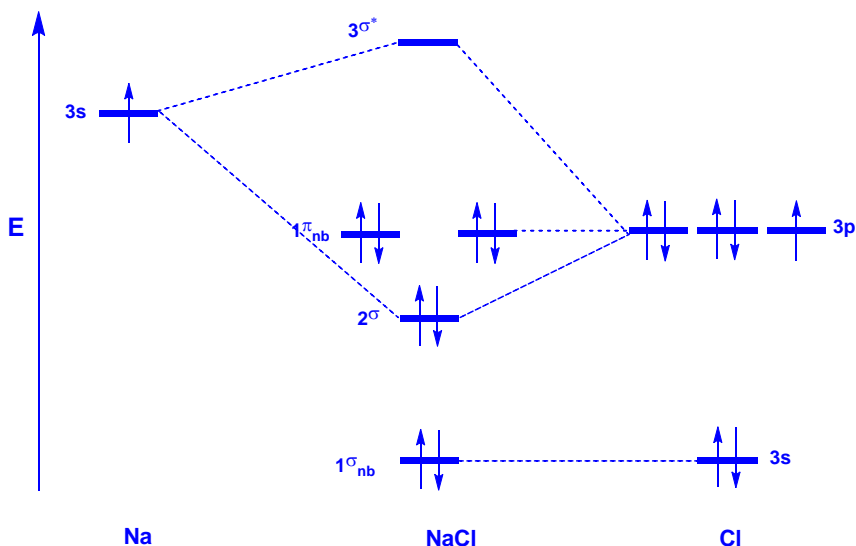
Since the 3s and 3p orbitals on Cl are within 1 Ry of each other, it is fine if you invoke some sp mixing and combine $3s(Na)$, $3s(Cl)$ and $3p_z(Cl)$ to make the three sigma-symmetric MOs.

(b)   Compare your molecular orbital energy level diagram to the Lewis diagram for $NaCl$. Briefly discuss similarities and/or differences. *Factors to consider include bond order, nonbonding electrons and bond polarity.*   *[4 marks]*

$$Na\!-\!\ddot{\underset{..}{Cl}}\!: \quad or \quad Na^{\oplus} \; :\!\ddot{\underset{..}{Cl}}\!:^{\ominus}$$
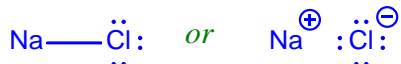
*The correlation between your MO energy level diagram and Lewis diagram will depend on which Lewis diagram you drew for NaCl.*

The MO energy level diagram suggests a bond order of 1 for the $Na - Cl$ bond (consistent with the Lewis diagram on the left). It also suggests that there are three pairs of nonbonding electrons (also consistent with the Lewis diagram on the left).

The 2σ MO is closer in energy to $3p_z(Cl)$ than to $3s(Na)$. As such, it will be polarized toward Cl (i.e. larger on the chlorine atom than on the sodium atom). This suggests that the $Na - Cl$ bond is polar, with Cl being the partially negative end and Na being the partially positive end. This is consistent with both Lewis diagrams (given that Cl is more electronegative than Na).

(c)   What would happen to the vibrational frequency of this molecule if we removed an electron from the HOMO? Would it increase, decrease or stay approximately the same? Explain briefly.
The HOMO is a nonbonding MO $(1\pi_{nb})$, so removing one or more electrons from it would not affect the $Na - Cl$ bond order. As such, we would expect the vibrational frequency to stay the same (since it increases if bond order increases and decreases if bond order decreases).

4. The atoms of N_2O (nitrous oxide, laughing gas) are connected: N—N—O. **[17 marks]**
(a) Draw all resonance structures for N_2O that have minimum formal charges. Explicitly show (using curved arrows) the electron movements that transform one resonance structure into the other. *You must explicitly show all non-zero formal charges.* *[5 marks]*
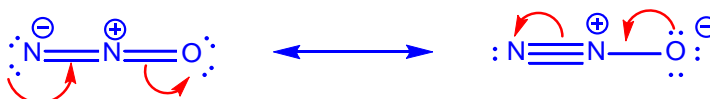

It is only necessary to show the curved arrows in one direction. Both are shown here since students may show either pair.

(b) What N—N and N—O bond orders would you predict from the Lewis diagrams drawn in part (a)?
[2 marks]

N—N bond order is _between 2 and 3_   N—O bond order is _between 1 and 2_

It would be fine to say "about 2.5" and "about 1.5". The resonance structures are not degenerate, so the bond orders are not exactly 2.5 and 1.5.

(c) While it is not obvious from the Lewis diagrams, there are **eight** π electrons in N_2O.
Draw a π molecular orbital energy level diagram for N_2O. On your diagram: *[5 marks]*
- Label all molecular orbitals.
- Populate the molecular orbitals with the correct number of electrons.
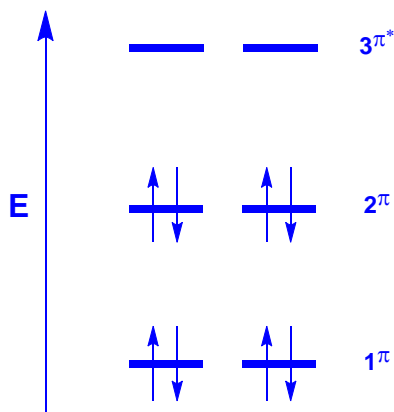
N_2O is linear therefore there are two degenerate pi systems – one made from the $2p_x$ orbitals and one made from the $2p_y$ orbitals. Each pi system consists of three molecular orbitals (made from three atomic orbitals – one from each of the three atoms).
Because the molecule is not symmetrical, it turns out that it is not safe to conclude that the middle energy level corresponds to nonbonding MOs. We can see this on the MO pictures on the next page. Those pictures show the 2π MO to have some bonding character. Similarly, it is acceptable to label the top MO as 3π instead of $3\pi^*$.

4.   *continued...*

(d)   The following images show some of the π molecular orbitals of N_2O. The images are not presented in any particular order. **<u>Underneath each image</u>**, write the correct orbital label.

[3 marks]

2π $3\pi^*$ 1π
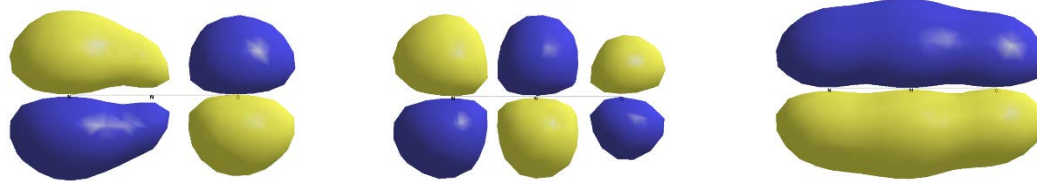
(e)   Correlate your Lewis diagram bond orders with these orbital images. In other words, can you (or not) rationalize the Lewis bond orders from the shapes of the π orbitals and your orbital occupancies?

[2 marks]

either   The orbital images show that 1π is bonding with respect to the $N - N$ bond and bonding with respect to the $N - O$ bond. They also suggest that 2π is bonding with respect to the $N - N$ bond and antibonding with respect to the $N - O$ bond.

Since there are four electrons in the two 1π orbitals (which are bonding for $N - O$) and four electrons in the two 2π orbitals (which are antibonding for $N - O$), that suggests that pi bonding does not significantly increase the bond order of the $N - O$ bond. It will therefore have a bond order only slightly higher than 1 (from sigma bonding).

Since there are four electrons in the two 1π orbitals (which are bonding for $N - N$) and four electrons in the two 2π orbitals (which are also bonding for $N - N$), that suggests that pi bonding is a significant contributor to the bond order of the $N - N$ bond. It will therefore have a bond order close to 3 (1 from sigma bonding + almost 2 from pi bonding).

Putting this together suggests that N_2O may more closely resemble the resonance structure below:
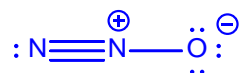

or   Another possible interpretation given the shape of the orbital is that the 2π orbital mostly consists of a p orbital on the end nitrogen atom, and of a p orbital on the oxygen, with only a minor contribution from the central p orbital. If we accept this interpretation, then this orbital is mostly non-bonding. Then the 1π orbital provides all of the π bonding. This would give us the equivalent of two π bonds, one between the N atoms, and one between the central N and O. This would be equivalent to the left-hand resonance structure.

It is noteworthy that the two feasible interpretations of the bonding character of the 2π orbital each correspond to one of the resonance structures. As with the Lewis resonance structures, where the truth lies somewhere between the two resonance structures, it is likely that the correct interpretation of the 2π orbital lies somewhere between the two extremes presented here.

5.   Boric acid has the following connectivity: **[5 marks]**
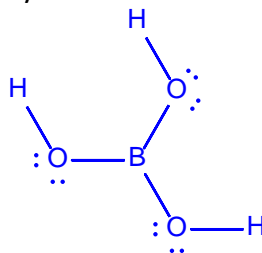

(a)   Convert the diagram above into a Lewis diagram by adding lone pairs where necessary.   *[1 mark]*

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

sp^2

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

sp^3

(d)   According to valence bond theory, how would we describe the B-O bond in boric acid?   *[2 marks]*

sigma bond between $sp^2(B)$ and $sp^3(O)$

6.   **[9 marks]**

(a)   Draw the band diagram for a p-type   (b)   Draw the band diagram for an n-type
       semiconductor, labeling all the relevant   semiconductor, labeling all the relevant
       bands.   *[3 marks]*   bands.   *[3 marks]*
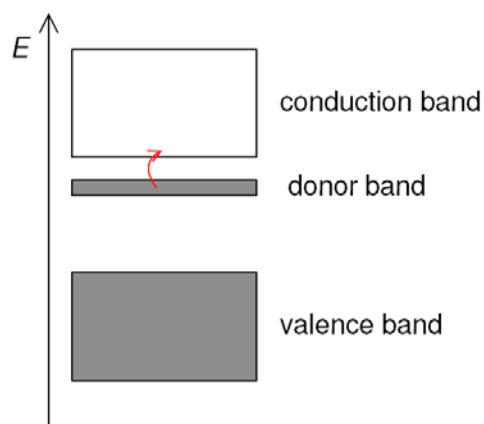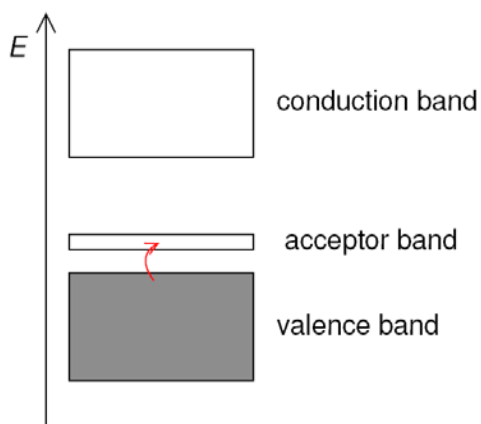
The red arrows are not necessary parts of the diagram; they were in the source image.

(c)   A diode is composed of an n-type and a p-type semiconductor connected to each other. Explain
        how this device restricts the flow of electrons in one direction.
        Your answer should include a diagram.   *[3 marks]*
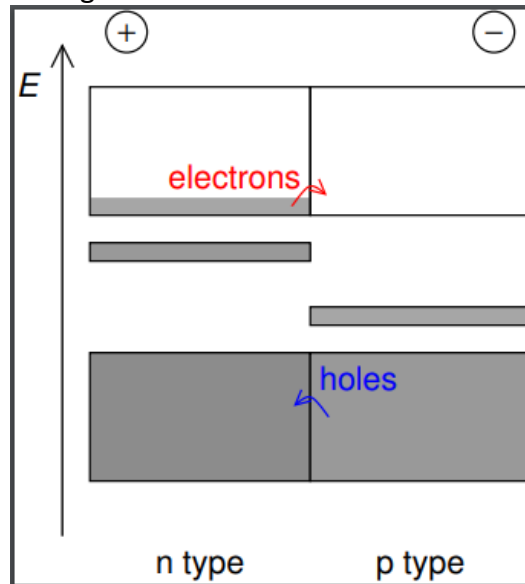
In a diode that has not been connected to a circuit, electrons diffuse (since this maximizes the entropy!)
from the partially filled conduction band of the n-type semiconductor, to the empty conduction band of
the p-type semiconductor. Holes also diffuse from the p-type valence band to the n-type valence band.
Both of these effects result in the n-type material becoming positively charged, while the p-type material
becomes negatively charged. An equilibrium is rapidly established in which electrons attracted back to
the positive n-type material from the p side balance the diffusion of electrons from the n side to the p side.

If we connect the negative pole of a battery to the n side and the positive pole to the p side, electrons can
flow easily because the excess electrons on the p side can exit the material and be replenished from the n
side. However, if we connect the negative pole to the p side, we are trying to push electrons into a
negatively charged material, which results in significant resistance to current flow. A current can be
established only if the applied voltage exceeds the potential difference between the n and p side due to the
charge separation.