

### Practice Test Questions 3

#### Molecular Orbital Theory: Heteronuclear Diatomic Molecules

1.

**Energy Values for the Atomic Orbitals of Hydrogen and Helium Atoms**

	Hydrogen	Helium
1s	-1.00 Ry	-1.81 Ry

- (a) Use the energy values in the table above to help you develop a valence molecular orbital energy level diagram for the helium protonate ion ( $HHe^+$ ).

Label all orbitals on your diagram, and include electrons in the AOs and MOs.

You **MUST** draw sketches of the MOs as well as the energy levels.

Include the effects of **polarization**.

- (b) According to your MO diagram, what is the bond order for this ion?  
 (c) Would you expect  $HHe^+$  to be paramagnetic or diamagnetic?

Justify your answer (*in one sentence or less...*)

2. In the gas phase, it is possible to make exotic diatomic molecules like  $LiF$  (which normally exists in a lattice rather than as a diatomic molecule).

**Atomic Orbital Energies**

Li		F	
1s	-4.77 Ry	1s	-51.2 Ry
2s	-0.40 Ry	2s	-2.95 Ry
		2p	-1.37 Ry

\*1 Ry =  $R_H = 2.179 \times 10^{-18}$  J

- (a) The above energies were determined experimentally. Name and briefly describe the technique used to make these measurements.  
 (b) Develop the MO energy level diagram for  $LiF$ . Clearly indicate which atomic orbitals mix to make which molecular orbitals. Write the orbital occupancy for  $LiF$ , and estimate the bond order.  
 (c) We would expect  $LiF$  to have substantial ionic character. Does your MO work agree with this expectation? Explain.  
 (d) Does your MO work agree with a Lewis diagram for  $LiF$ ?

3. **Energy Values for the Atomic Orbitals of Oxygen and Fluorine Atoms**

	<b>Oxygen</b>	<b>Fluorine</b>
1s	-39.9 Ry	-51.2 Ry
2s	-2.38 Ry	-2.95 Ry
2p	-1.17 Ry	-1.37 Ry

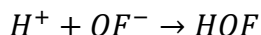
- (a) Use the energy values in the table above to help you develop a valence molecular orbital energy level diagram for the hypofluorite ion ( $OF^-$ ).

Label all orbitals on your diagram, and include electrons in the AOs and MOs.

It is not necessary to draw pictures of the orbitals for this part of the question.

- (b) On your diagram, clearly label the HOMO(s) of  $OF^-$ . Draw a picture of this/these molecular orbital(s), clearly indicating the relative amount of electron density on each atom.

- (c) Draw a Lewis diagram for the product of the following reaction:



- (d) Use MO theory to justify the location of the hydrogen atom in HOF.

*No credit will be given for answers not involving molecular orbitals.*

4. **Table 1: Energy Values for the Atomic Orbitals of Hydrogen and Chlorine Atoms**

	<b>Hydrogen</b>	<b>Chlorine</b>
1s	-1.0 Ry	-208 Ry
2s		-21 Ry
2p		-16 Ry
3s		-2.3 Ry
3p		-1.0 Ry

- (a) Why is there such a dramatic difference in energy between the 1s orbital of hydrogen and the 1s orbital of chlorine?

- (b) Use the energy values in the table above to help you develop a **valence** molecular orbital energy level diagram for hydrochloric acid ( $HCl$ ).

Label all orbitals on your diagram, and include electrons in the AOs and MOs.

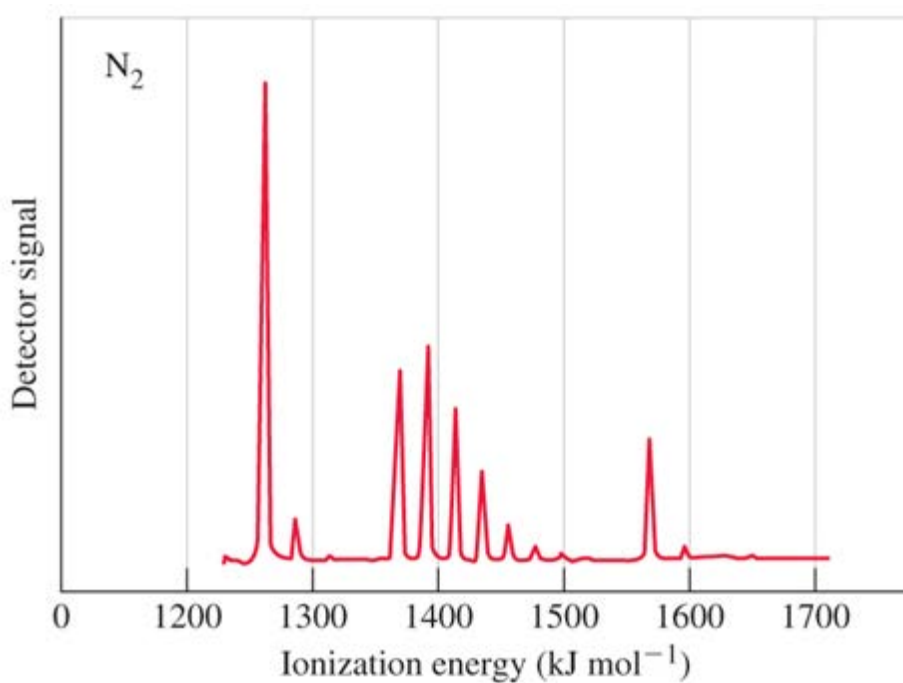
It is not necessary to draw pictures of the orbitals for this question.

- (c) Draw a Lewis diagram for HCl.

- (d) Compare your Lewis diagram for HCl to your MO diagram for HCl. What are the bond orders? How many nonbonding electrons? Where are the nonbonding electrons?

5.

- (a) Construct a valence molecular orbital energy level diagram for  $N_2$ . Label all atomic and molecular orbitals on your diagram, and include tie lines to show the linear combinations that form each molecular orbital. Place the correct number of valence electrons into the atomic orbitals as well as the molecular orbitals. It is not necessary to draw pictures of the orbitals for this part of the question.
- (b) Calculate the bond order of  $N_2$  using MO theory.
- (c) Label the signals of the UV-photoelectron spectrum of  $N_2$  (depicted below) with the appropriate MO labels.

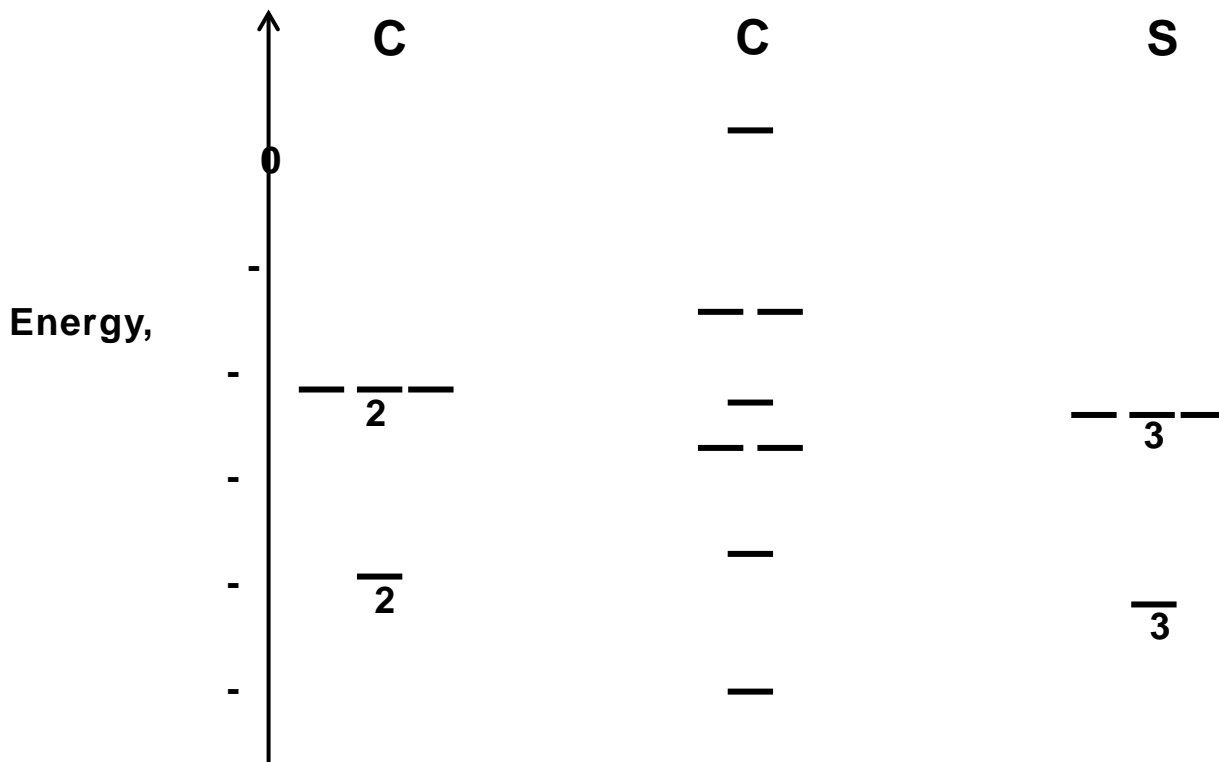


- (d) Briefly explain what information about each orbital is provided by the UV-photoelectron spectrum, and how this information can be deduced.

6.

(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 valence molecular orbital energy level diagram for CS below by:

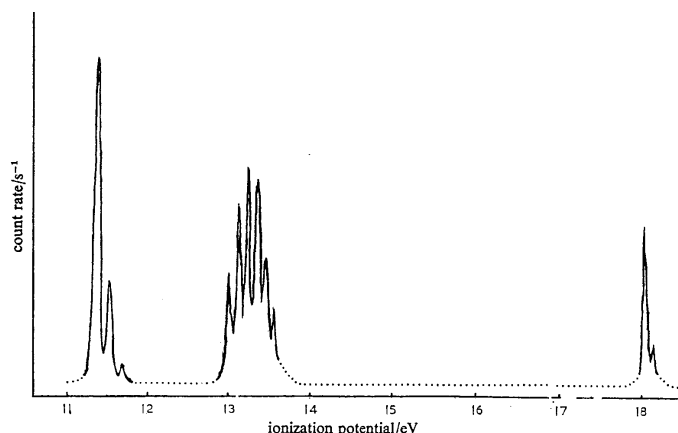
- Sketching and naming only the molecular orbitals (MOs).
- Adding the correct # of valence electrons only to the MOs for the ground electronic state of CS.



(b) Write the valence orbital occupancy for CS.

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

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

7.

- (a) Construct a valence molecular orbital energy level diagram for  $NO^+$ . Label all atomic and molecular orbitals on your diagram, and include tie lines to show the linear combinations that form each molecular orbital. Place the correct number of valence electrons into the atomic orbitals as well as the molecular orbitals. It is not necessary to draw pictures of the orbitals for this part of the question.
- (b) On your diagram, clearly label the HOMO(s) of  $NO^+$ . Draw a picture of this/these molecular orbital(s). Clearly indicate the phase, location of the nuclei, and relative amounts of electron density on each atom.
- (c) On your diagram, clearly label the LUMO(s) of  $NO^+$ . Draw a picture of this/these molecular orbital(s). Clearly indicate the phase, location of the nuclei, and relative amounts of electron density on each atom.
- (d) Write the valence orbital occupancy for  $NO^+$ .
- (e) Provide a molecular formula for one neutral diatomic molecule that is isoelectronic with  $NO^+$ .
- (f) Draw a Lewis diagram for  $NO^+$ . What  $N - O$  bond order does your Lewis diagram predict?
- (g) What bond order does your MO treatment predict for  $NO^+$ ? Does it agree with the bond order from the Lewis diagram?
- (h) What is the bond order if we add an electron to  $NO^+$  (i.e. what is the bond order in neutral  $NO$ )?
- (i) Is the  $N - O$  bond strengthened or weakened in  $NO$  versus  $NO^+$ ? Briefly explain why or why not.
- (j) Which of the following species is/are paramagnetic:  $NO^+$ ,  $NO$ ,  $NO^-$ ?