

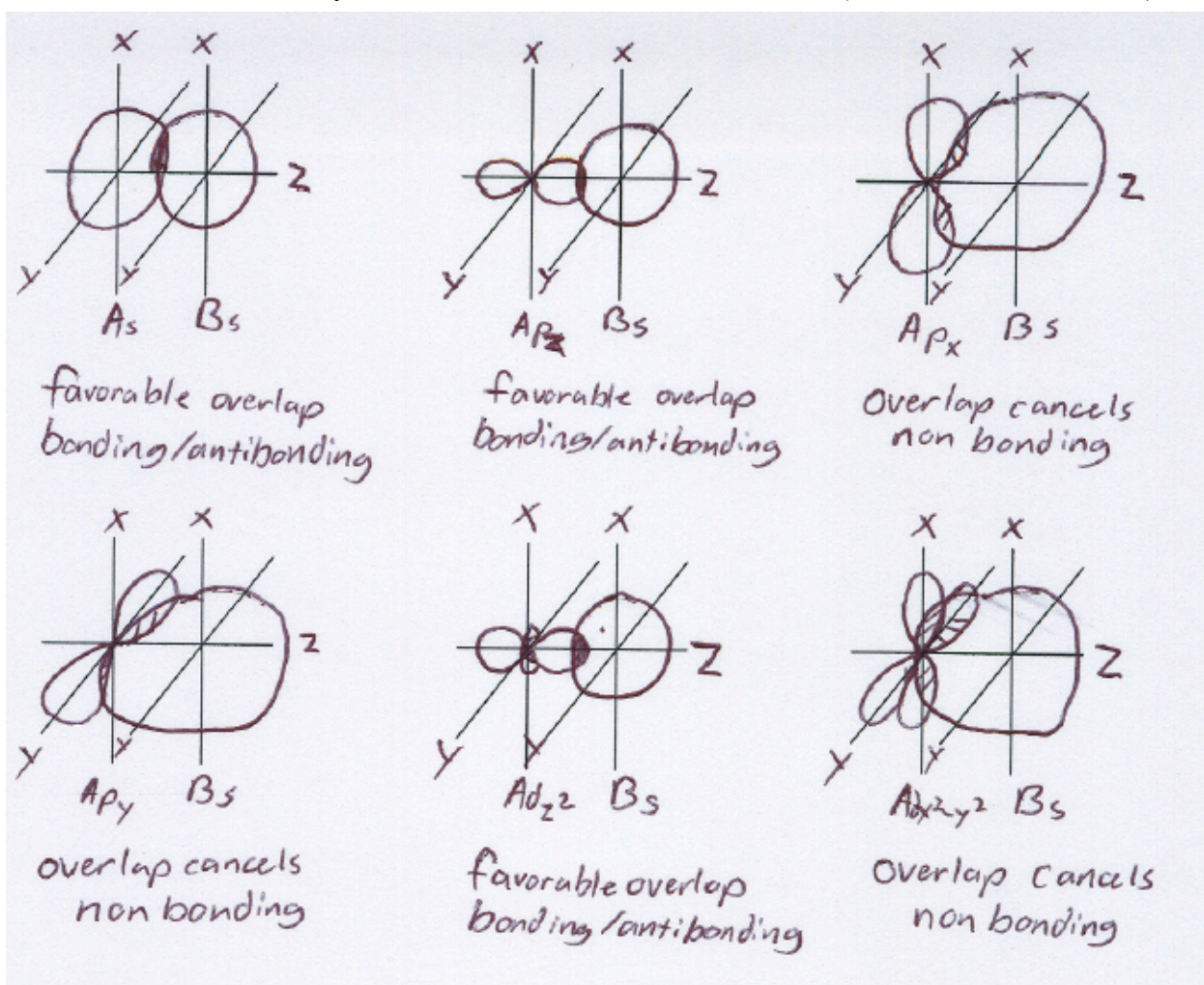
HW 2  
CHEM 362

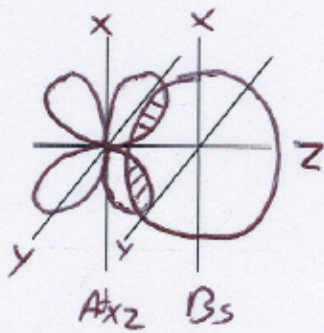
1. Why are the sign and magnitude of overlap between orbitals on adjacent atoms good indications of whether atoms are bonded and how strongly they are bonded?

**The sign is indicative of the nature of orbital overlap. If the orbitals are bonding, meaning the orbital overlap is between two orbitals of the same phase (+, + or -, -), then the sign of the overlap is positive. Antibonding orbitals are formed when the two orbitals are out of phase (+, -), indicated by a negative sign. If the overlap is 0, then the orbitals are non-bonding. The magnitude of is a direct indication of the degree of orbital overlap. The larger the magnitude, the more overlap exists between any two orbitals and the more strongly they interact.**

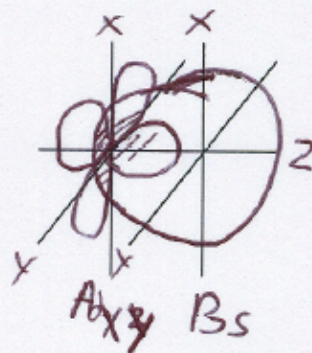
2. Take Atom A with one  $s$  orbital, three  $p$  orbitals and five  $d$  orbitals and show with drawings how each of these orbitals overlaps with:
- an  $s$  orbital located on atom B (nine drawings)
  - the  $p_x$  orbital located on atom B (nine drawings)
  - the  $d_{xy}$  orbital located on atom B (nine drawings)
  - the  $d_{z^2}$  orbital located on atom B (nine drawings)

Be certain to label your coordinate axes on Atoms A and B (which must be the same).

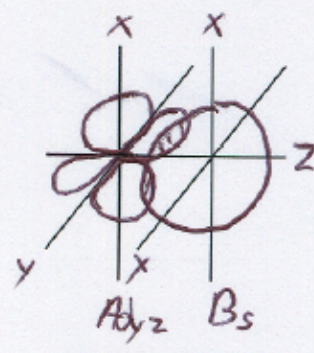




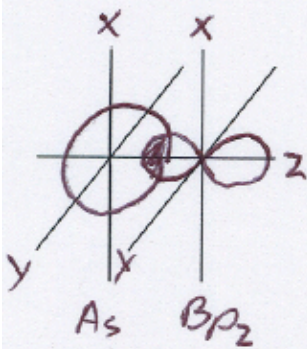
Overlap cancels  
non bonding



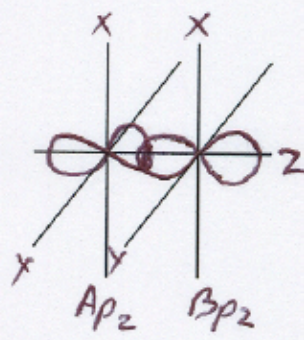
Overlap cancels  
non bonding



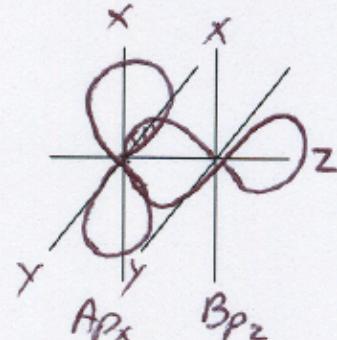
Overlap cancels  
non bonding



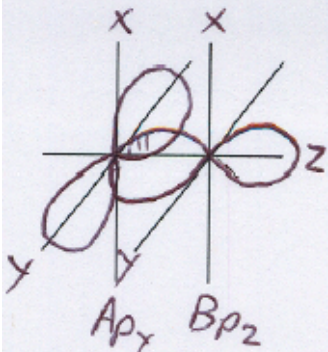
Favorable overlap  
bonding/antibonding



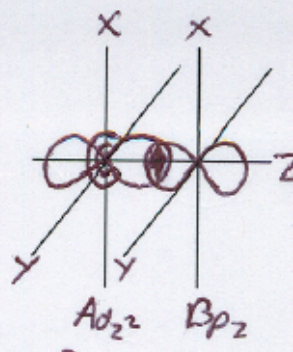
Favorable overlap  
bonding/anti bonding



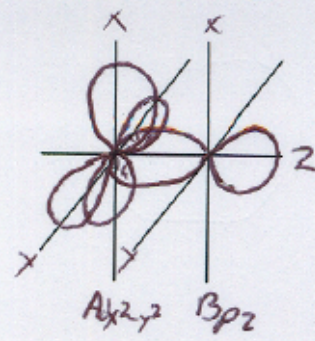
Overlap cancels  
non bonding



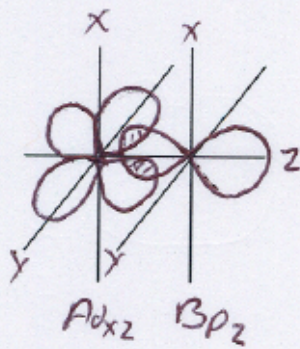
Overlap cancels  
non bonding



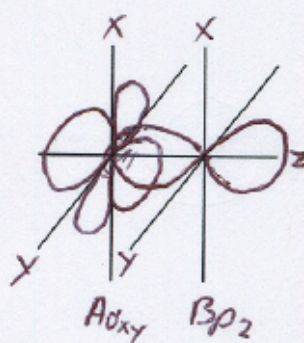
Favorable overlap  
bonding/antibonding



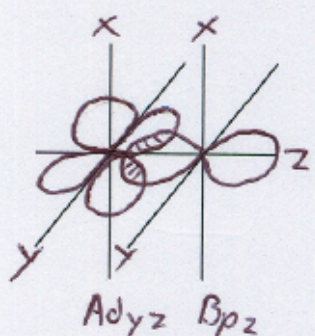
Overlap cancels  
non bonding



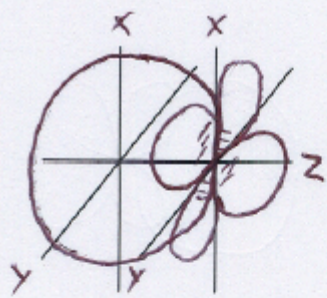
Overlap cancels  
non bonding



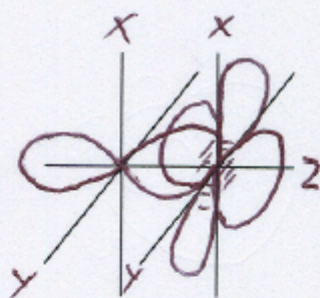
Overlap cancels  
non bonding



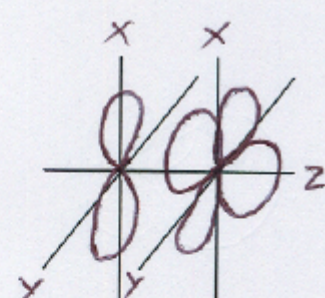
Overlap cancels  
non bonding



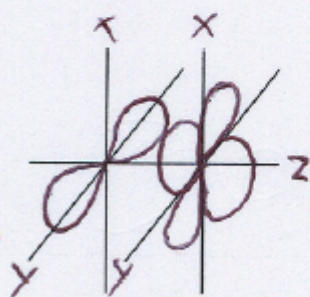
$A_s$   $B_{d_{xy}}$   
 overlap cancels  
 non bonding



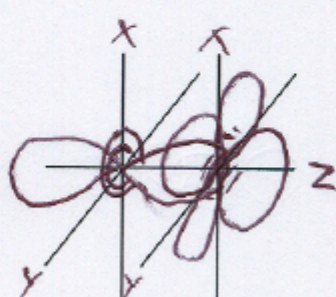
$A_{d_{z^2}}$   $B_{d_{xy}}$   
 overlap cancels  
 non bonding



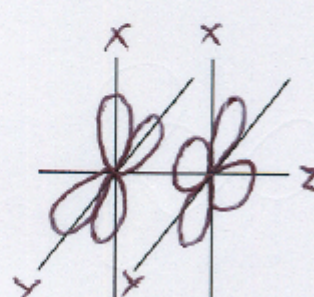
$A_{d_{x^2-y^2}}$   $B_{d_{xy}}$   
 no overlap  
 non bonding



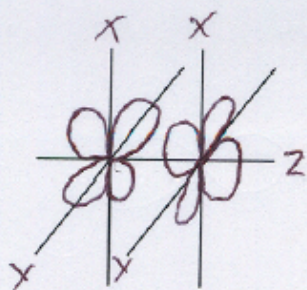
$A_{p_y}$   $B_{d_{xy}}$   
 no overlap  
 non bonding



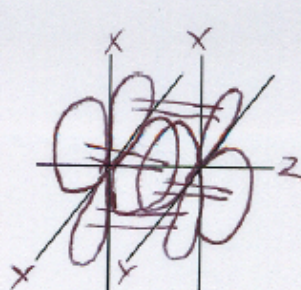
$A_{d_{z^2}}$   $B_{d_{xy}}$   
 overlap cancels  
 non bonding



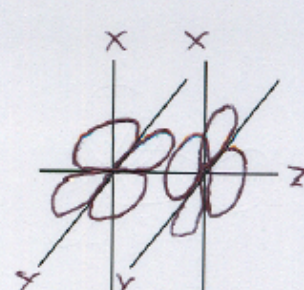
$A_{d_{x^2-y^2}}$   $B_{d_{xy}}$   
 no overlap  
 non bonding



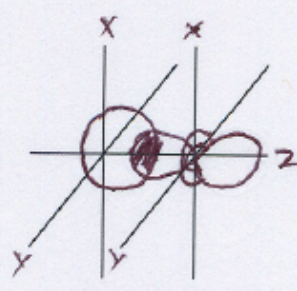
$A_{d_{xz}}$   $B_{d_{xy}}$   
 no overlap  
 non bonding



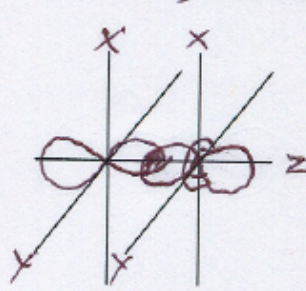
$A_{d_{xz}}$   $B_{d_{xy}}$   
 favorable overlap  
 (all 4 lobes indicated by  $\Rightarrow$ )  
 bonding/antibonding



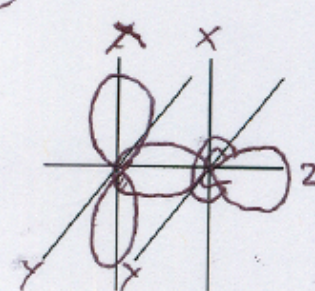
$A_{p_y}$   $B_{d_{xy}}$   
 no overlap  
 non bonding



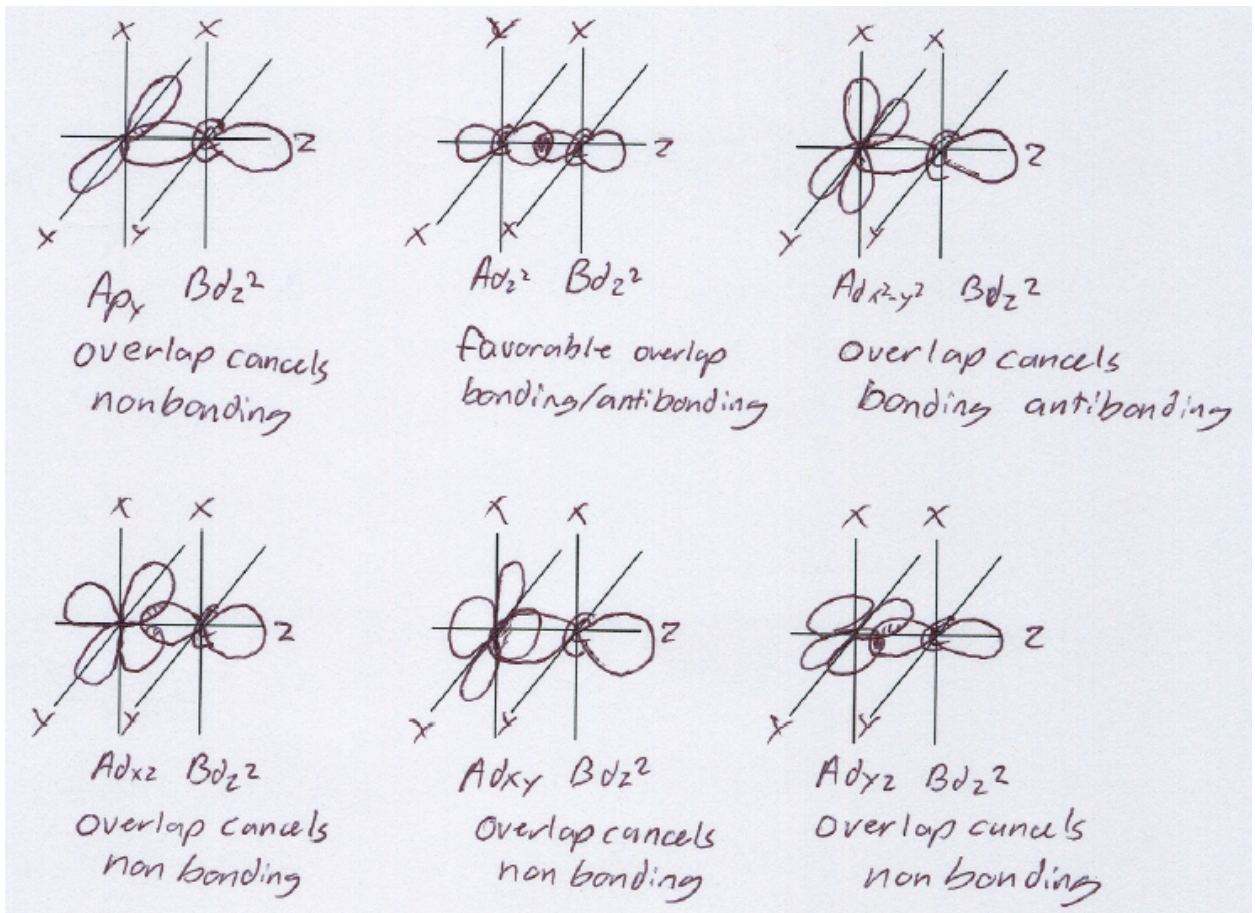
$A_s$   $B_{d_{z^2}}$   
 favorable overlap  
 bonding/antibonding



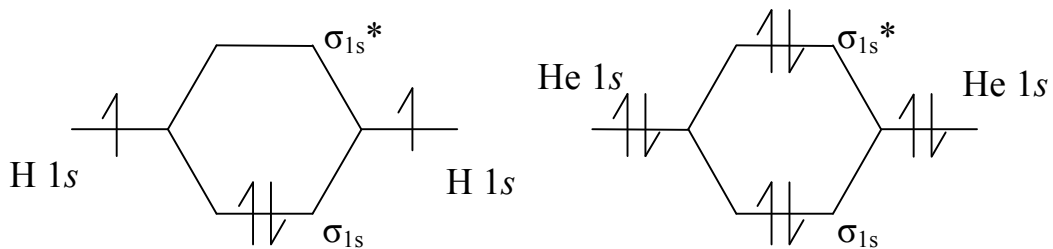
$A_{p_z}$   $B_{d_{z^2}}$   
 favorable overlap  
 bonding/antibonding



$A_{p_x}$   $B_{d_{z^2}}$   
 overlap cancels  
 non bonding



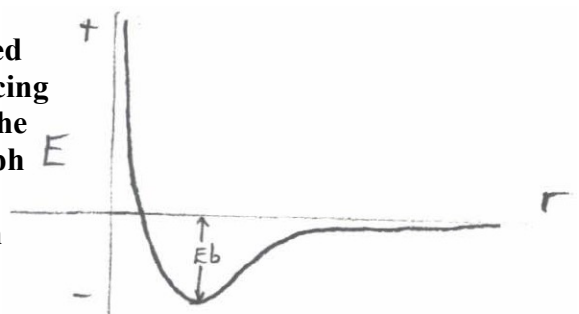
3. Draw an energy-level diagram for the interaction of two atoms that both have an  $s$  orbital. Show how the M.O.'s would be occupied if the two atoms in question were H atoms and if they were He atoms. What conclusions are to be drawn about the formation of bonds in the two cases?



$H_2$  has a  $\sigma_{1s}^2$  configuration giving rise to a bond order of 1.  $H_2$  has a single bond and is a stable molecule.  $He_2$  has a  $\sigma_{1s}^2\sigma_{1s}^{*2}$  configuration giving rise to a bond order of 0 ( $2e^-$  in a bonding and  $2e^-$  in an antibonding orbital).  $He_2$  is not a stable molecule and does not form,

4. When a bond is formed between two atoms, they are drawn together. What limits their internuclear distance so that they do not coalesce into one big atom?

The repulsion of the two positively charged nuclei prevent the two atoms from coalescing into one large atom. This is observed in the plot to the right (left hand side of the graph shows a dramatic increase in energy as the two nuclei are drawn too close to each other).



5. What is meant by a node and a nodal plane? How do these terms relate to the characteristics of  $\sigma$ ,  $\pi$  and  $\delta$  bonding?

**A node refers to a point on the radial wavefunction,  $R(r)$ , where the function changes sign. A nodal plane refers to a plane where the electron probability for a given orbital drops to zero. A  $\sigma$  orbital has no nodal planes, a  $\pi$  orbital has one nodal plane and a  $\delta$  has two nodal planes.**

6. How is a bond order defined for a diatomic molecule in MO theory?

**B.O. = (1/2)(# of bonding electrons - # of antibonding electrons)**

7. Are the  $2s$  and  $2p$  orbitals in a N atom *higher* or *lower* than those of O? Explain your answer.

**The  $2s$  and  $2p$  orbitals on the N atom are higher than those of O. An O atom has 1 more proton than a N atom and thus has a higher effective nuclear charge. This lowers the energy of the  $2s$  and  $2p$  orbitals by holding them closer to the nucleus (consider the trend for atomic radii to decrease as you go from left to right across the periodic table).**

8. State the geometric arrangement of bonds produced by each of the following sets of hybrid orbitals:  $dsp^2$ ,  $d^2sp^3$ ,  $dsp^3$ . For each one, state explicitly which d and p orbitals are required for each geometric arrangement.

**$dsp^2$  – square planar using the  $s$ ,  $p_x$ ,  $p_y$  and  $d_{x^2-y^2}$**

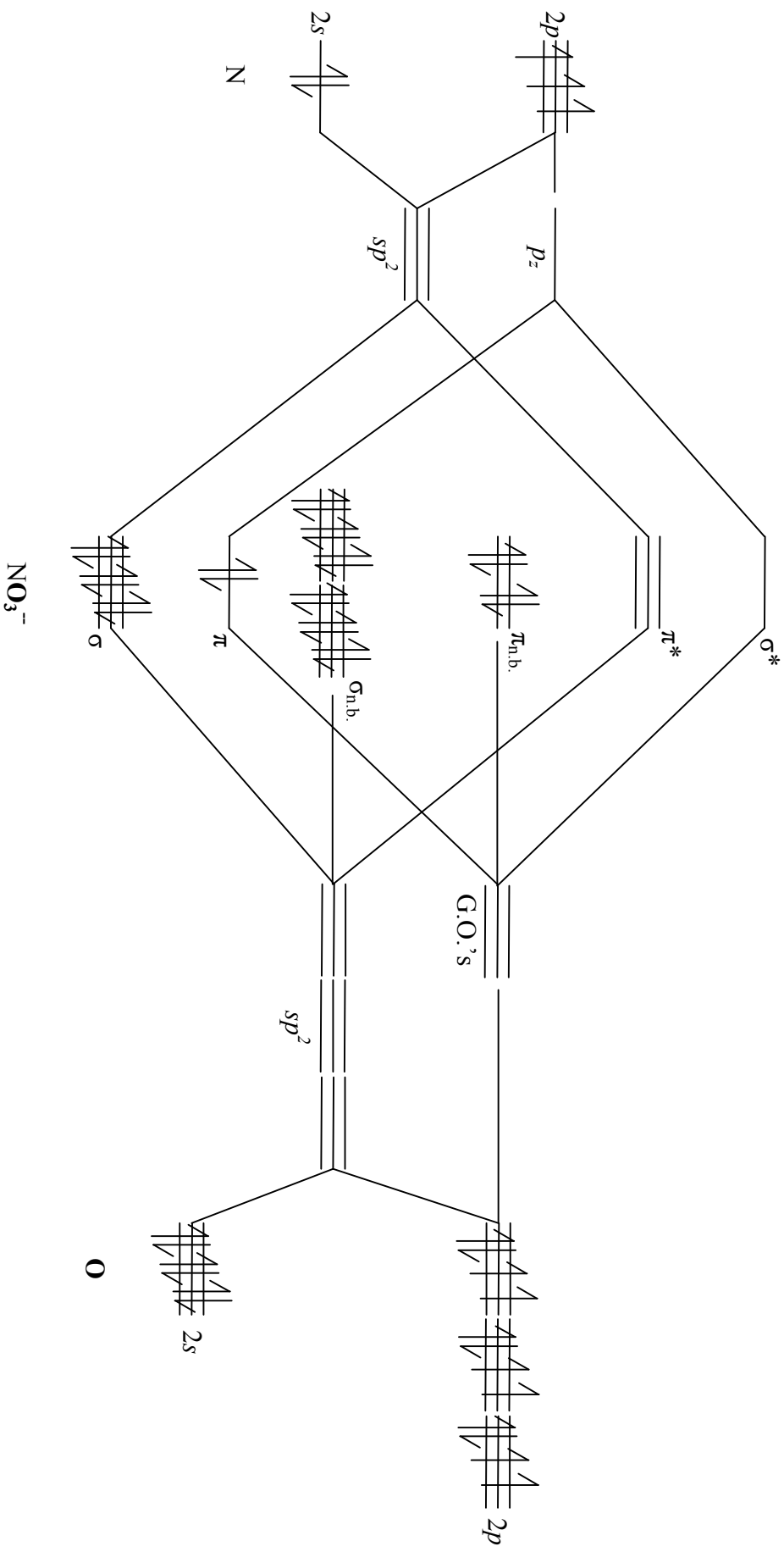
**$d^2sp^3$  – octahedral using the  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$**

**$dsp^3$  – trigonal bipyramidal using the  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$  and  $d_{z^2}$   
or square pyramidal using the  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{x^2-y^2}$**

9. Explain by M.O. theory why the NO bonds in  $\text{NO}_3^-$  have a bond order of  $1\frac{1}{3}$ .

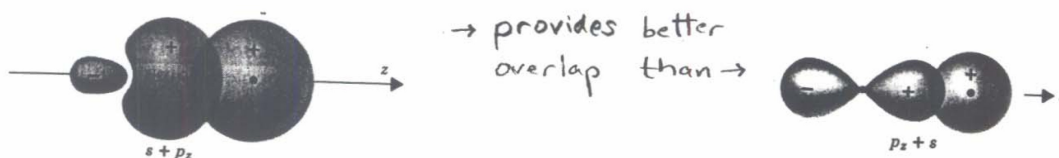
**$\text{NO}_3^-$  is a trigonal planar molecule and in molecules of this type the all the atoms can be treated as  $sp^2$  hybridized atoms.  $\text{NO}_3^-$  has  $24e^-$ , each  $sp^2$  hybrid contains  $2e^-$ . This accounts for the 3  $\sigma$  bonds between the N atom and the O atoms ( $6e^-$ ) and 2 lone pairs for each O ( $12e^-$ ). This leaves 6 of the  $24e^-$  unaccounted for. These electrons go into the unhybridized  $p_z$  orbitals that we can use to form 3 G.O's (group orbitals) on the oxygen atoms. One of these orbitals forms a  $\pi$  bond with the unhybridized  $p_z$  orbital on N, while the other two form nonbonding orbitals. The sum of  $\sigma$  and  $\pi$  bonding electrons in  $\text{NO}_3^-$  is  $8e^-$  (and there are no antibonding electrons) giving 4 bonds over 3 atoms with a B.O. of  $1\frac{1}{3}$  for each**

**See the MO diagram on the following page.**



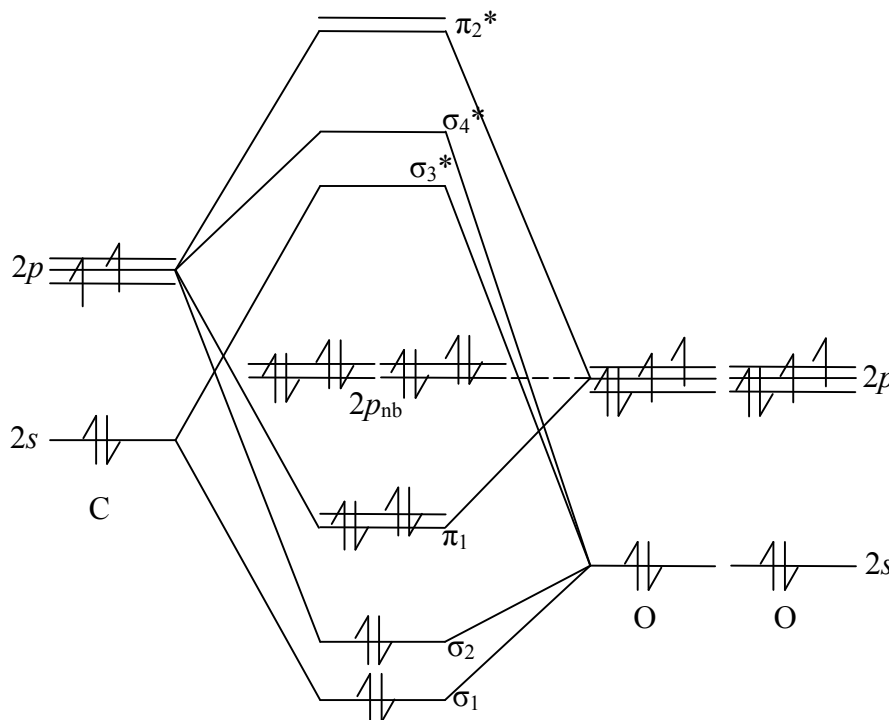
10. Why is the use of hybrid orbitals preferable to the use of single atomic orbitals in forming bonds? Illustrate.

**Hybrid orbitals have a shape and direction that allows for significantly better orbital overlap between two atoms.**



**Note: On the left is an  $sp$  (formed from the  $s$  and  $p_z$  orbitals) overlapping with an  $s$  orbital. On the right is just the  $p_z$  orbital overlapping with the  $s$ . The  $sp$  orbital has a lobe that is comparable in size to the  $s$  orbital allowing for greater overlap than just the  $p_z$  by itself.**

11. Draw a qualitatively correct energy-level diagram for the  $\text{CO}_2$  molecule. Show that it accounts correctly for the presence of double bonds.

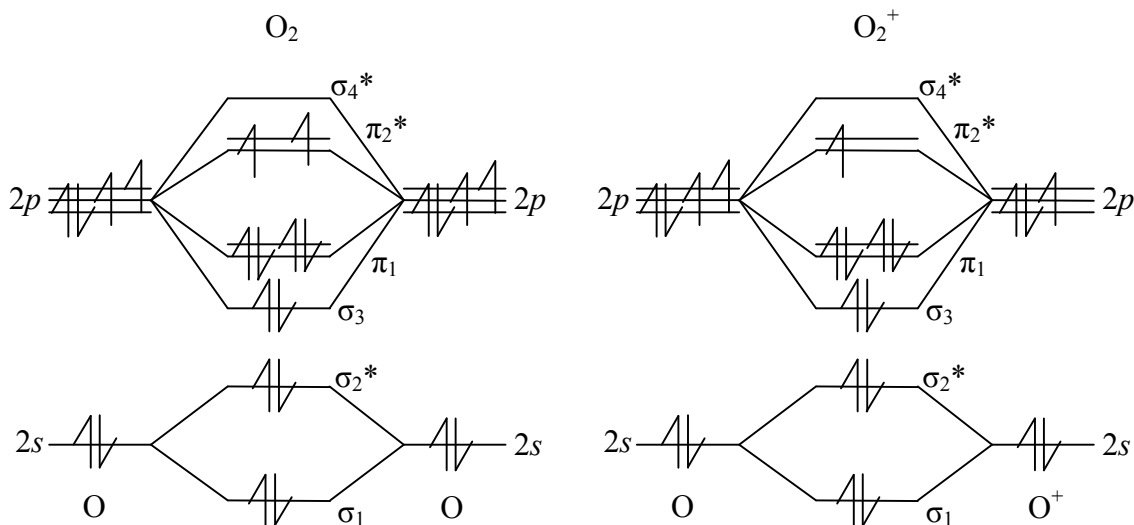


**The diagram predicts that there will be two sigma bonds and two pi bonds between the carbon atom and the oxygen atoms and four lone pairs on the oxygen atoms.**

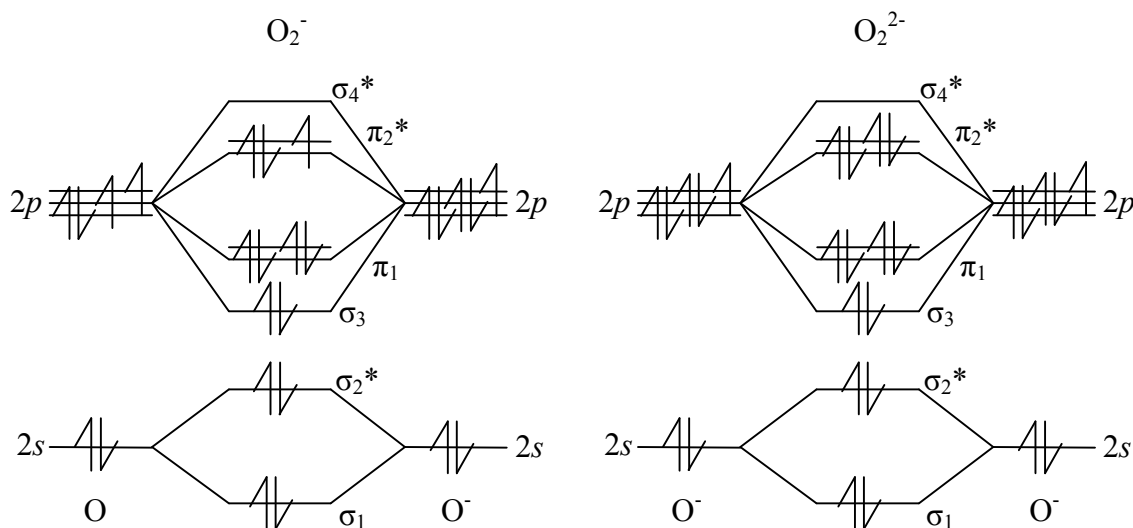
12. Explain why there is  $2s$ - $2p$  mixing in the M.O. energy-level diagram of  $\text{Li}_2$ , but none for  $\text{F}_2$ .

**As you move from left to right across the periodic table the energy gap between the  $2s$  and  $2p$  increases. At  $\text{Li}$ , the  $2s$  and  $2p$  are close enough in energy to allow for some  $s$ - $p$  mixing. But by the time you reach  $\text{F}$ , the  $2p$  orbital is so much higher in energy than the**

13. For the series of diatomics:  $O_2^+$ ,  $O_2$ ,  $O_2^-$ ,  $O_2^{2-}$ , determine from an M.O. diagram how the bond lengths will vary and how many unpaired electrons each will have.



$O_2$  will have 2 unpaired electrons (B.O. = 2)     $O_2^+$  will have 1 unpaired electron (B.O. = 2.5)

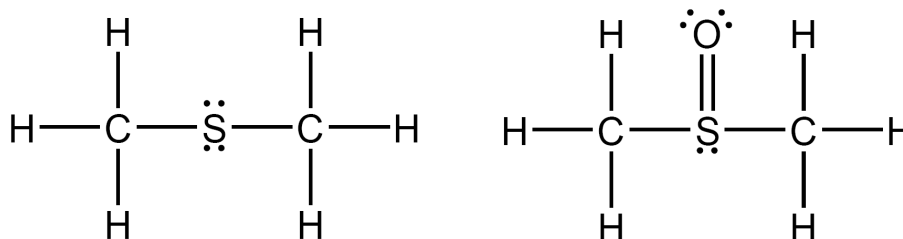


$O_2^-$  will have 1 unpaired electron (B.O. = 1.5)     $O_2^{2-}$  will have 0 unpaired electrons (B.O. = 1)

From shortest bond to longest bond:  $O_2^+ < O_2 < O_2^- < O_2^{2-}$

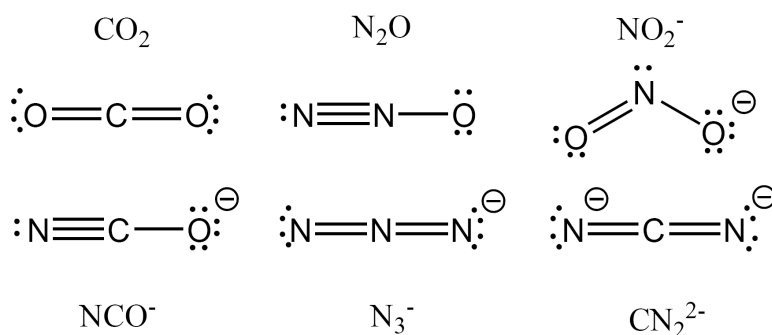


14. Draw Lewis Diagrams and predict the structures of  $(\text{CH}_3)_2\text{S}$  (dimethyl sulfide) and  $(\text{CH}_3)_2\text{SO}$  (dimethylsulfoxide). How will the C-S-C bond angles differ?



Withough considering the carbon to sulfur bonds dimethyl sulfide has 2 lone pairs on the central atom compared to 1 lone pair and one double bond on the sulfur. Dimethyl sulfide will have greater electron repulsion forcing the S-C bonds closer together giving a smaller C-S-C angle than in dimethylsulfoxide

15. Draw Lewis Diagrams for each of the molecules or ions in the series:  $\text{OCO}$ ,  $\text{NNO}$ ,  $\text{ONO}^-$ ,  $\text{NCO}^-$ ,  $\text{NNN}^-$  and  $\text{NCN}^{2-}$ . What is the same in all of these molecules?



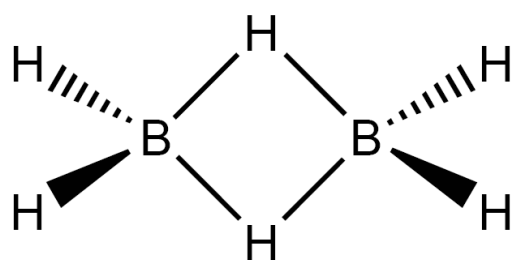
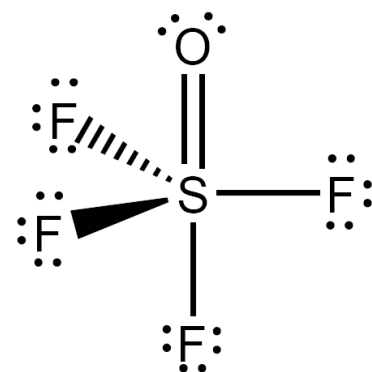
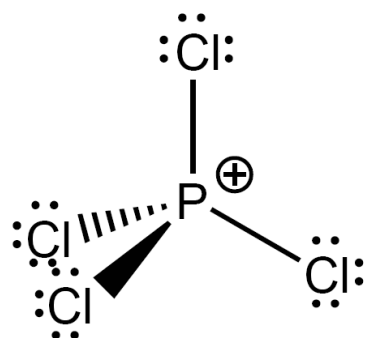
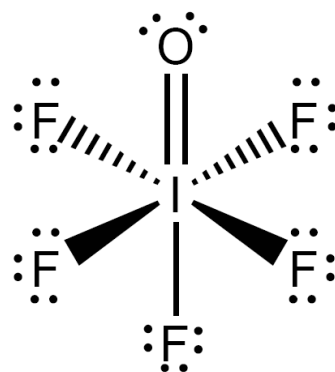
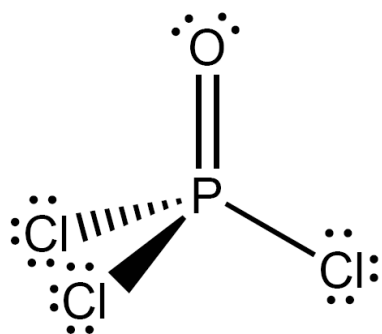
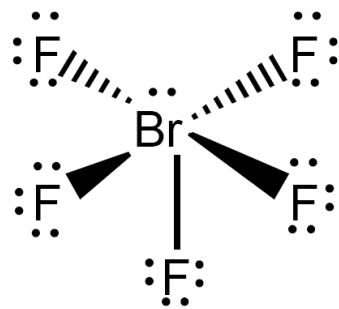
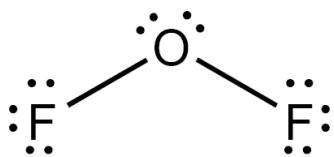
All of the compounds are linear except for  $\text{NO}_2^-$ . The central atom of all compounds except  $\text{NO}_2^-$  is  $sp$  hybridized.  $\text{NO}_2^-$  has an  $sp^2$  hybridized central atom and is a bent molecule. All compounds have  $\pi$  bonds as well.

16. Describe the geometry and hybridization in  $[\text{PtCl}_6]^{2-}$ .

$[\text{PtCl}_6]^{2-}$  has an  $\text{AB}_6$  type formula and thus it has to adopt an octahedral geometry. The hybridization is the  $d^2sp^3$ .

17. Use VSEPR to predict the shapes (bond angles) in the following:
- $\text{OF}_2 - \text{AB}_2\text{E}_2 - \text{bent} - \text{F-O-F angle} > 104^\circ$
  - $\text{BrF}_5 - \text{AB}_5\text{E} - \text{square pyramid} - \text{F}_{\text{eq}}-\text{Br}-\text{F}_{\text{axial}} \text{ angle} < 90^\circ$
  - $\text{OPCl}_3 - \text{AB}_4 - \text{tetrahedron} - \text{O-P-Cl angle} > 109^\circ$
  - $\text{OIF}_5 - \text{AB}_6 - \text{octahedron} - \text{O-I-F}_{\text{eq}} \text{ angle} > 90^\circ$
  - $\text{PCl}_4^+ - \text{AB}_4 - \text{tetrahedron} - \text{Cl-P-Cl angle} = 109^\circ$
  - $\text{OSF}_4 - \text{AB}_5 - \text{trigonal bipyramid} - \text{O-S-F}_{\text{eq}} \text{ angle} > 90^\circ$
  - $\text{B}_2\text{H}_6 - \text{AB}_4 - \text{tetrahedron} - \text{H-B-H angle} = 109^\circ$

The structures are drawn on the next page.

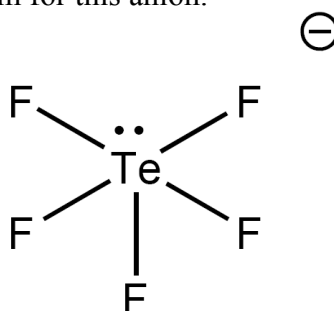


18. Identify the molecules in problem 17 that are:
- electronically saturated –  $\text{OF}_2$ ,  $\text{BrF}_5$ ,  $\text{PCl}_4^+$
  - electronically unsaturated –  $\text{OPCl}_3$ ,  $\text{OIF}_5$ ,  $\text{OSF}_4$
  - electron deficient –  $\text{B}_2\text{H}_6$
19. The structure of the pentafluorotellurate monoanion,  $[\text{TeF}_5]^-$ , has been determined by X-ray techniques (see attached journal article: S. H. Mastin *et. al. Inorg. Chem.*, **1970**, *9*, 2100-2103.)

- a. What is the oxidation state of Te in this anion?



- b. Draw the Lewis Diagram for this anion.



- c. Determine the occupancy and formula  $\text{AB}_x\text{E}_y$  for Te in this anion and explain any deviations from ideal geometry using VSEPR theory.

**$[\text{TeF}_5]^-$  has an occupancy of 6 and is an  $\text{AB}_5\text{E}$  molecule. The F-Te-F bond angles are not the idealized  $90^\circ$  for a square pyramid. They are  $< 90^\circ$ , due to the electron-electron repulsion from the lone pair on the tellurium atom.**