

HW 2 (Problems 1-6,8,10,14-19)
CHEM 362

Available: Jan. 25, 2008

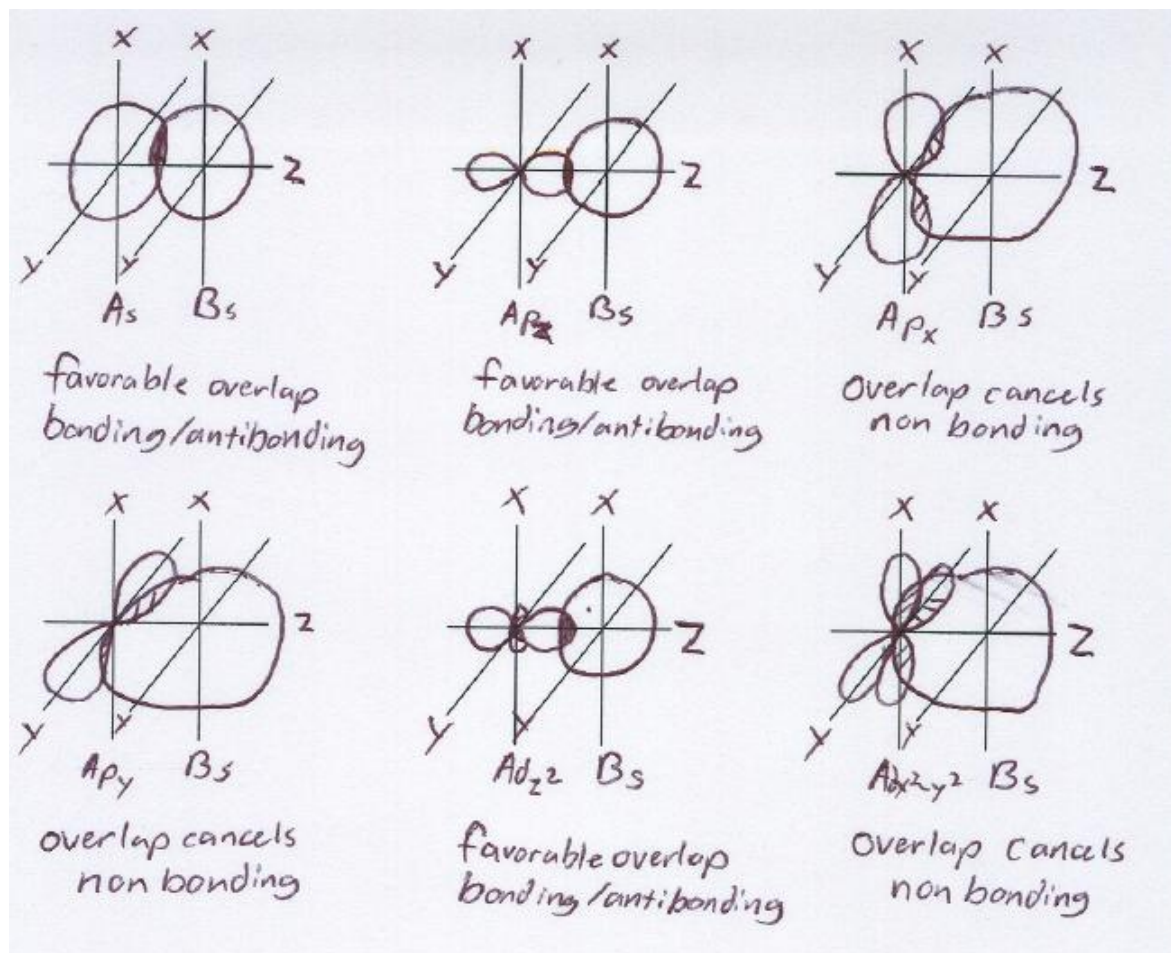
Due: Feb. 1, 2008

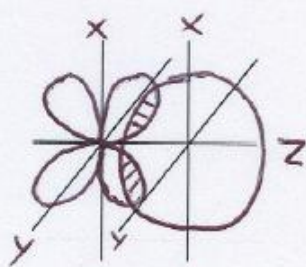
- Why are the sign and magnitude of overlap between orbitals on adjacent atoms good indications of whether atoms are bonded and how strongly they are bonded?

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 the overlap 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. (s orbitals overlap better than p in sigma bonds).

- 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)

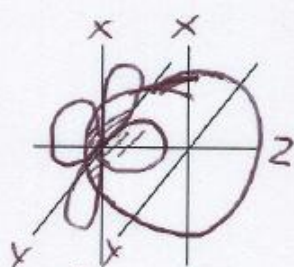
Be certain to label your coordinate axes on Atoms A and B (which must be the same).





$A_{x^2} B_s$

Overlap cancels
non bonding



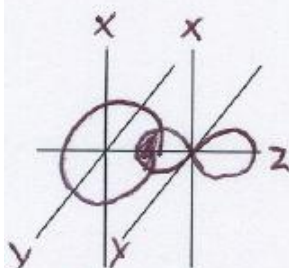
$A_{xy} B_s$

Overlap cancels
non bonding



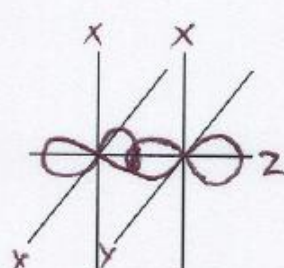
$A_{yz} B_s$

Overlap cancels
non bonding



$A_s B_{p_z}$

Favorable overlap
bonding/antibonding



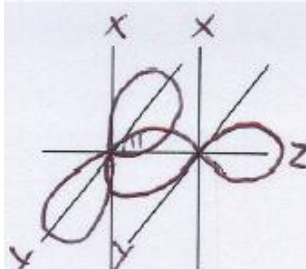
$A_{p_z} B_{p_z}$

Favorable overlap
bonding/antibonding



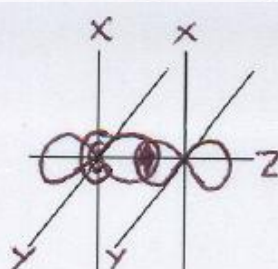
$A_{p_x} B_{p_z}$

Overlap cancels
non bonding



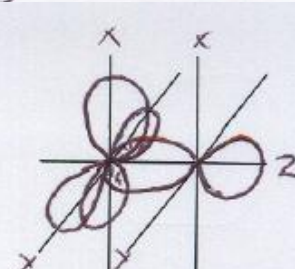
$A_{p_y} B_{p_z}$

Overlap cancels
non bonding



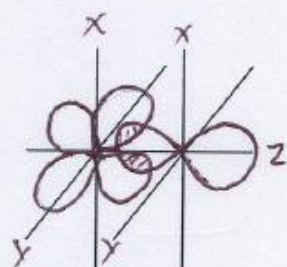
$A_{d_{z^2}} B_{p_z}$

Favorable overlap
bonding/antibonding



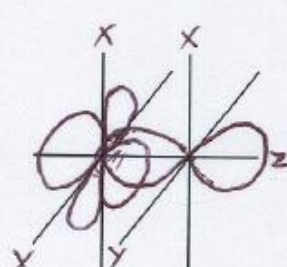
$A_{x^2-y^2} B_{p_z}$

Overlap cancels
non bonding



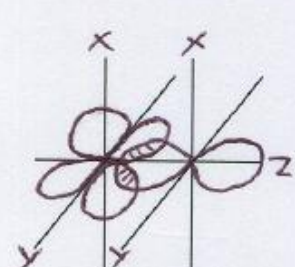
$A_{d_{x^2}} B_{p_z}$

Overlap cancels
non bonding



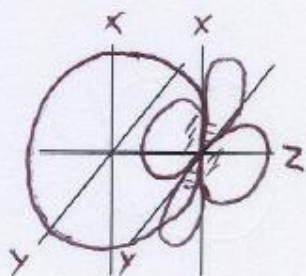
$A_{d_{xy}} B_{p_z}$

Overlap cancels
non bonding

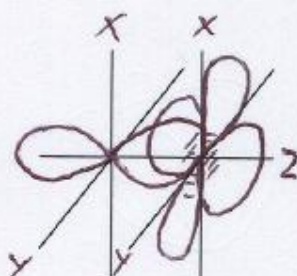


$A_{d_{yz}} B_{p_z}$

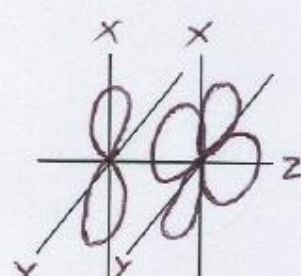
Overlap cancels
non bonding



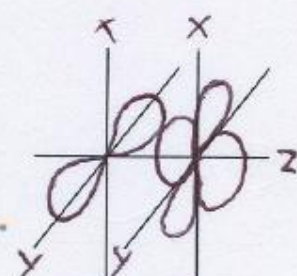
A_s B_{dx}
overlap cancels
non bonding



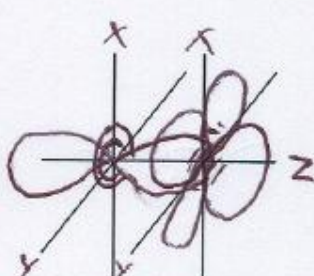
A_{pz} B_{dx}
overlap cancels
non bonding



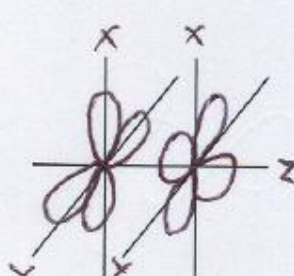
A_{px} B_{dx}
no overlap
non bonding



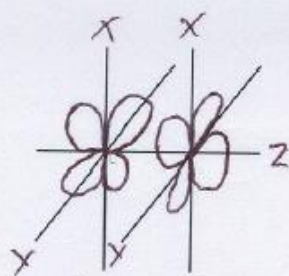
A_{py} B_{dx}
no overlap
non bonding



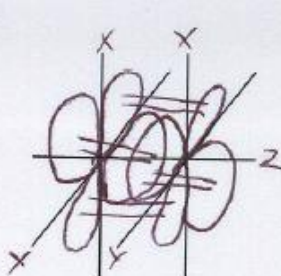
A_{dz^2} B_{dx}
overlap cancels
non bonding



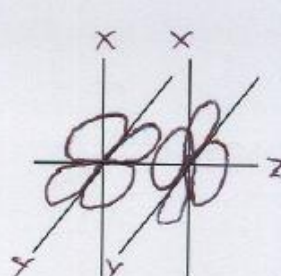
$A_{dx^2-y^2}$ B_{dx}
no overlap
non bonding



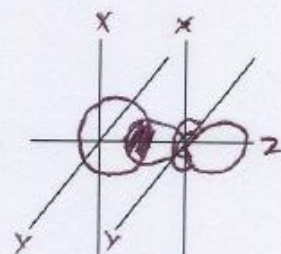
A_{dxz} B_{dx}
no overlap
non bonding



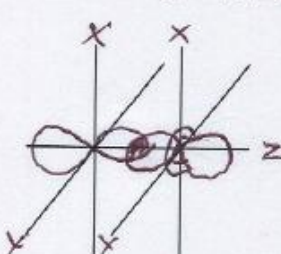
A_{dxy} B_{dx}
favorable overlap
(all 4 lobes indicated by \Rightarrow)
bonding/antibonding



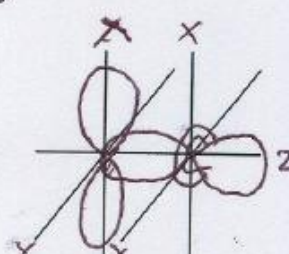
A_{dyz} B_{dx}
no overlap
non bonding



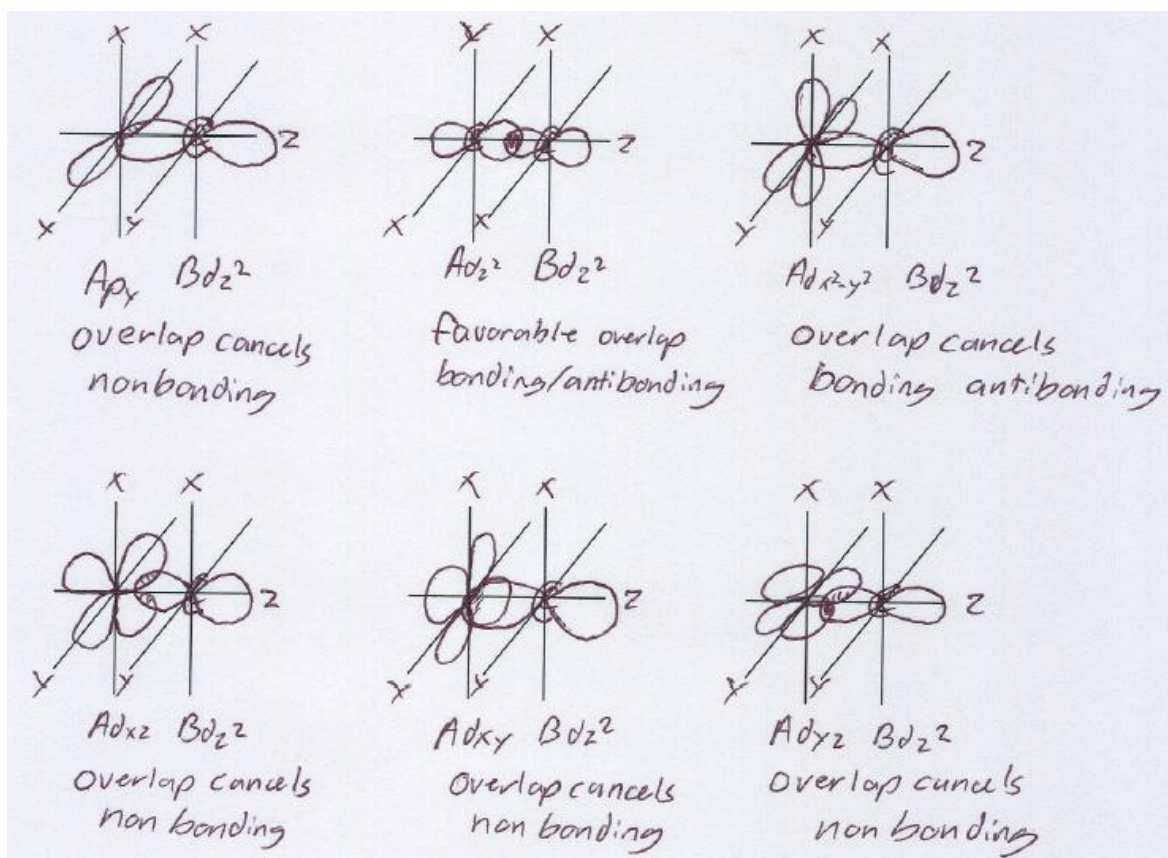
A_s B_{dz^2}
favorable overlap
bonding/antibonding



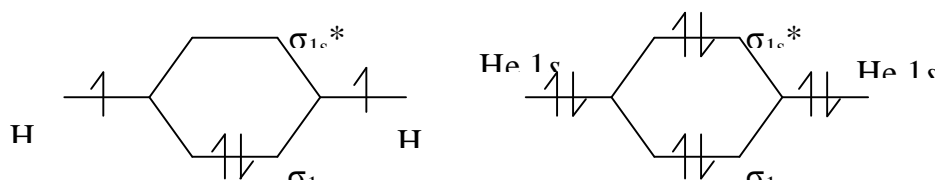
A_{pz} B_{dz^2}
favorable overlap
bonding/antibonding



A_{px} B_{dz^2}
overlap cancels
non bonding



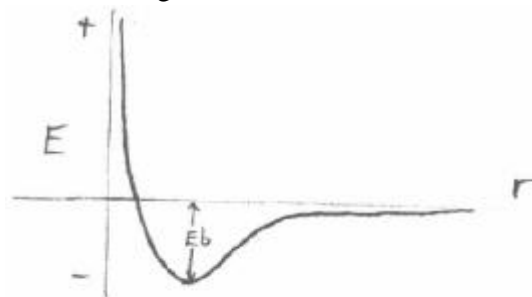
3. Draw an energy-level diagram for the interaction of two atoms that both have an s orbital. Show how the M.O.'s would be occupied if the two atoms in question were H atoms and if they were He atoms. What conclusions are to be drawn about the formation of bonds in the two cases?



H_2 has a σ_{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 σ , π and δ 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 σ orbital has no nodal planes, a π orbital has one nodal plane and a δ has two nodal planes.

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

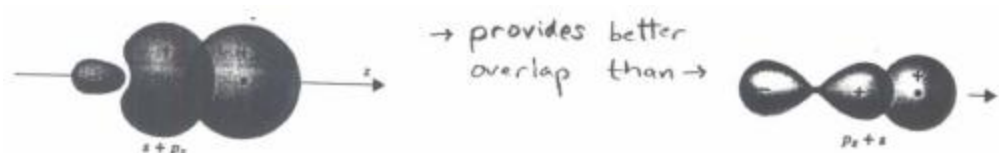
$$\text{B.O.} = (1/2)(\# \text{ of bonding electrons} - \# \text{ of antibonding electrons})$$

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 , $d_{x^2-y^2}$

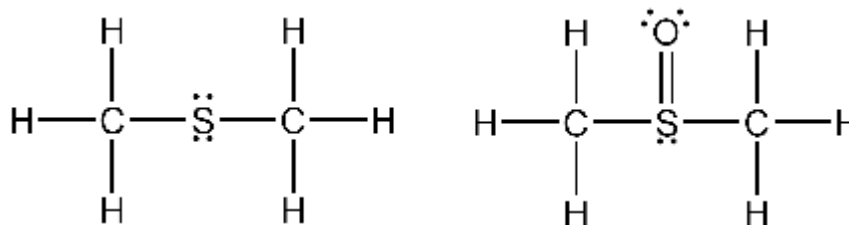
10. Why is the use of hybrid orbitals preferable to the use of single atomic orbitals in forming bonds? Illustrate.

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



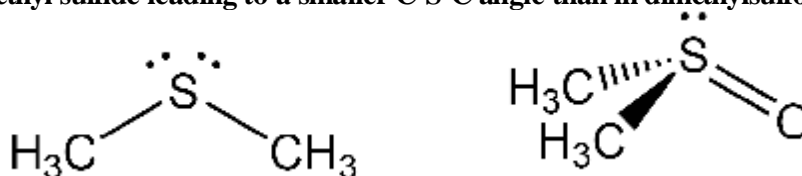
Note: On the left is an sp (formed from the s and p_z orbitals) overlapping with an s orbital. On the right is just the p_z orbital overlapping with the s . The sp orbital has a lobe that is comparable in size to the s orbital allowing for greater overlap than just the p_z by itself.

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?

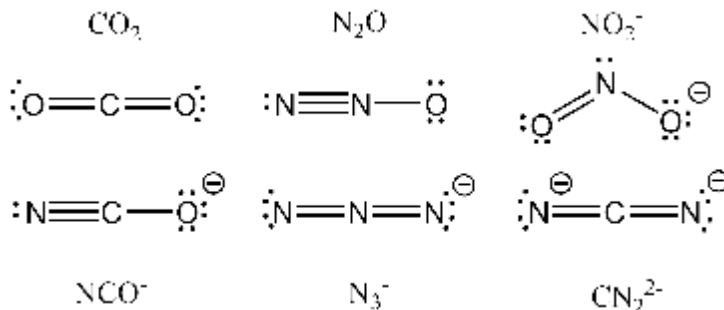


Overall, both molecules have an occupancy of four, giving rise to a tetrahedral arrangement around the sulfur atom. With two lone pairs dimethyl sulfide is an AB_2E_2 molecule and adopts a bent shape. Dimethylsulfoxide on the other hand only has 1 lone pair, making it an AB_3E molecule, and adopts a pyramidal shape. (see next page) The

two lone pairs present on dimethyl sulfide will experience more repulsion than the lone pair – double bond on dimethylsulfoxide. This will force the S-C bonds closer together on dimethyl sulfide leading to a smaller C-S-C angle than in dimethylsulfoxide.



15. Draw Lewis Diagrams for each of the molecules or ions in the series: CO_3 , NNO , ONO^- , NCO^- , NNN^- and NCN^{2-} . What is the same in all of these molecules?



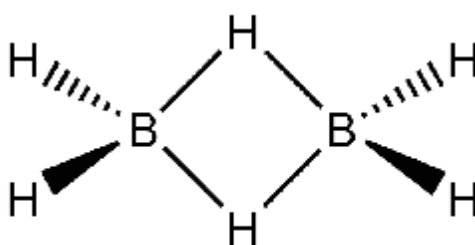
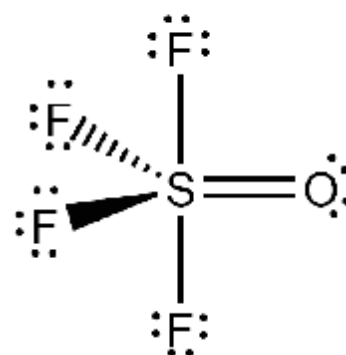
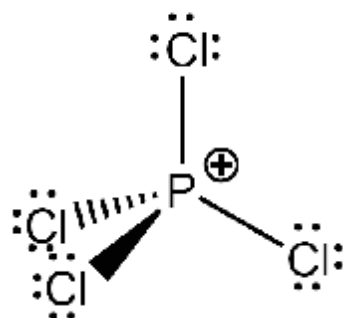
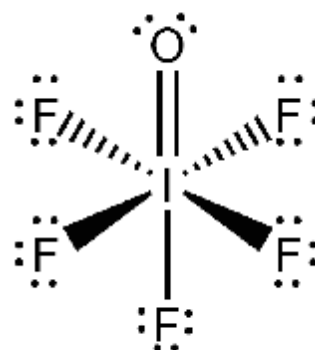
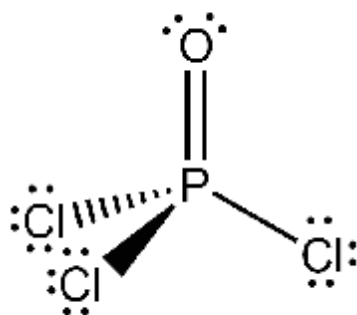
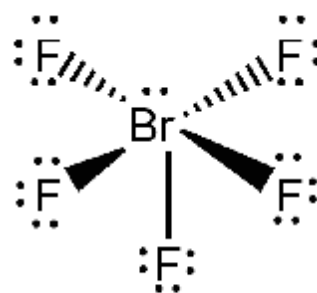
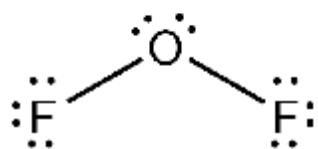
All of the compounds are linear except for NO_2^- . The central atom of all compounds except NO_2^- is sp hybridized. NO_2^- has an sp^2 hybridized central atom and is a bent molecule. All compounds have π bonds as well.

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

$[\text{PtCl}_6]^{2-}$ has an 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:
- OF_2 – AB_2E_2 – bent – F-O-F angle $> 104^\circ$
 - BrF_5 – AB_5E – square pyramid – $\text{F}_{\text{eq}}\text{-Br-F}_{\text{axial}}$ angle $< 90^\circ$
 - OPCl_3 – AB_4 – tetrahedron – O-P-Cl angle $> 109^\circ$
 - OIF_5 – AB_6 – octahedron – O-I-F_{eq} angle $> 90^\circ$
 - PCl_4^+ – AB_4 – tetrahedron – Cl-P-Cl angle $= 109^\circ$
 - OSF_4 – AB_5 – trigonal bipyramid – O-S-F_{eq} angle $> 90^\circ$
 - B_2H_6 – AB_4 – tetrahedron – H-B-H angle $= 109^\circ$

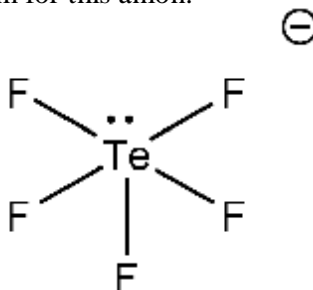
The structures are drawn on the next page.



18. Identify the molecules in problem 17 that are:
- electronically saturated – OF_2 , BrF_5 , PCl_4^+
 - electronically unsaturated – OPCl_3 , OIF_5 , OSF_4
 - electron deficient – B_2H_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.)
- What is the oxidation state of Te in this anion?



- Draw the Lewis Diagram for this anion.



- Determine the occupancy and formula AB_xE_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 AB_5E molecule. The F-Te-F bond angles are not the idealized 90° for a square pyramid. They are $< 90^\circ$, due to the electron-electron repulsion from the lone pair on the tellurium atom.