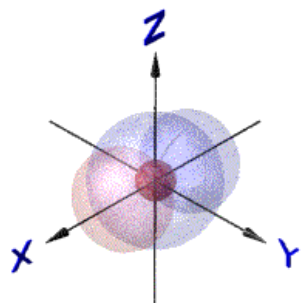


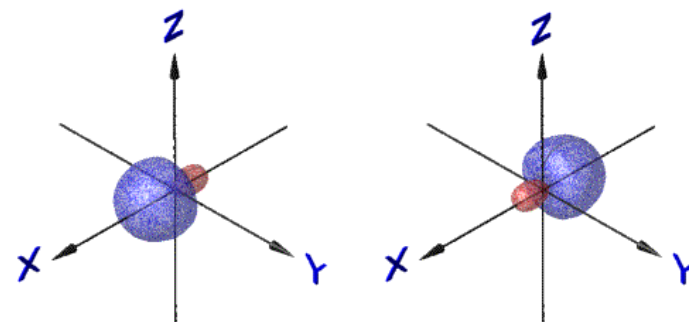
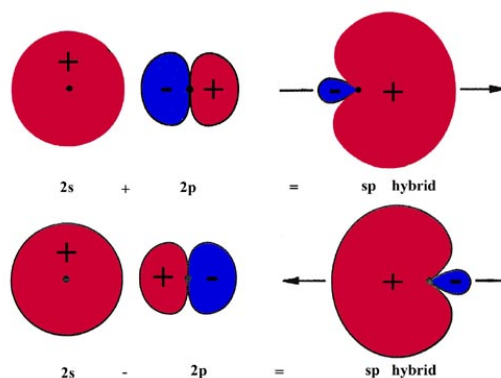
Hybridization

The problem of accounting for the true geometry of molecules and the directionality of orbitals is handled using the concept of *hybrid* orbitals. Hybrid orbitals are mixtures of atomic orbitals and are treated mathematically as **Linear Combinations** of the appropriate s, p and d **Atomic Orbitals** (LCAO).

Linear sp hybrid orbitals



A 2s orbital superimposed on a 2p_x orbital



The two resultant sp hybrid orbitals that are directed along the X-axis (in this case)

$$\Psi_1 = \frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p$$

The $1/\sqrt{2}$ are normalization coefficients.

Chem 59-250 Orthogonality and Normalization

Two properties of acceptable orbitals (wavefunctions) that we have not yet considered are that they must be *orthogonal* to every other orbital and they must be *normalized*. These conditions are related to the probability of finding an electron in a given space.

Orthogonal means that the integral of the product of an orbital with any other orbital is equal to 0, i.e.:

$$\int \Psi_n \Psi_m d\tau = 0$$

where $n \neq m$ and $d\tau$ means that the integral is taken over “all of space” (everywhere).

Normal means that the integral of the product of an orbital with itself is equal to 1, i.e.:

$$\int \Psi_n \Psi_n d\tau = 1$$

This means that we must find normalization coefficients that satisfy these conditions. Note that the atomic orbitals (ϕ) we use can be considered to be both orthogonal and normal or “*orthonormal*”.

$$\Psi_1 = \frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p \quad \Psi_2 = \frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p$$

$$\int \Psi_1 \Psi_2 \partial\tau = \int \left(\frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p \right) \left(\frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p \right) \partial\tau$$

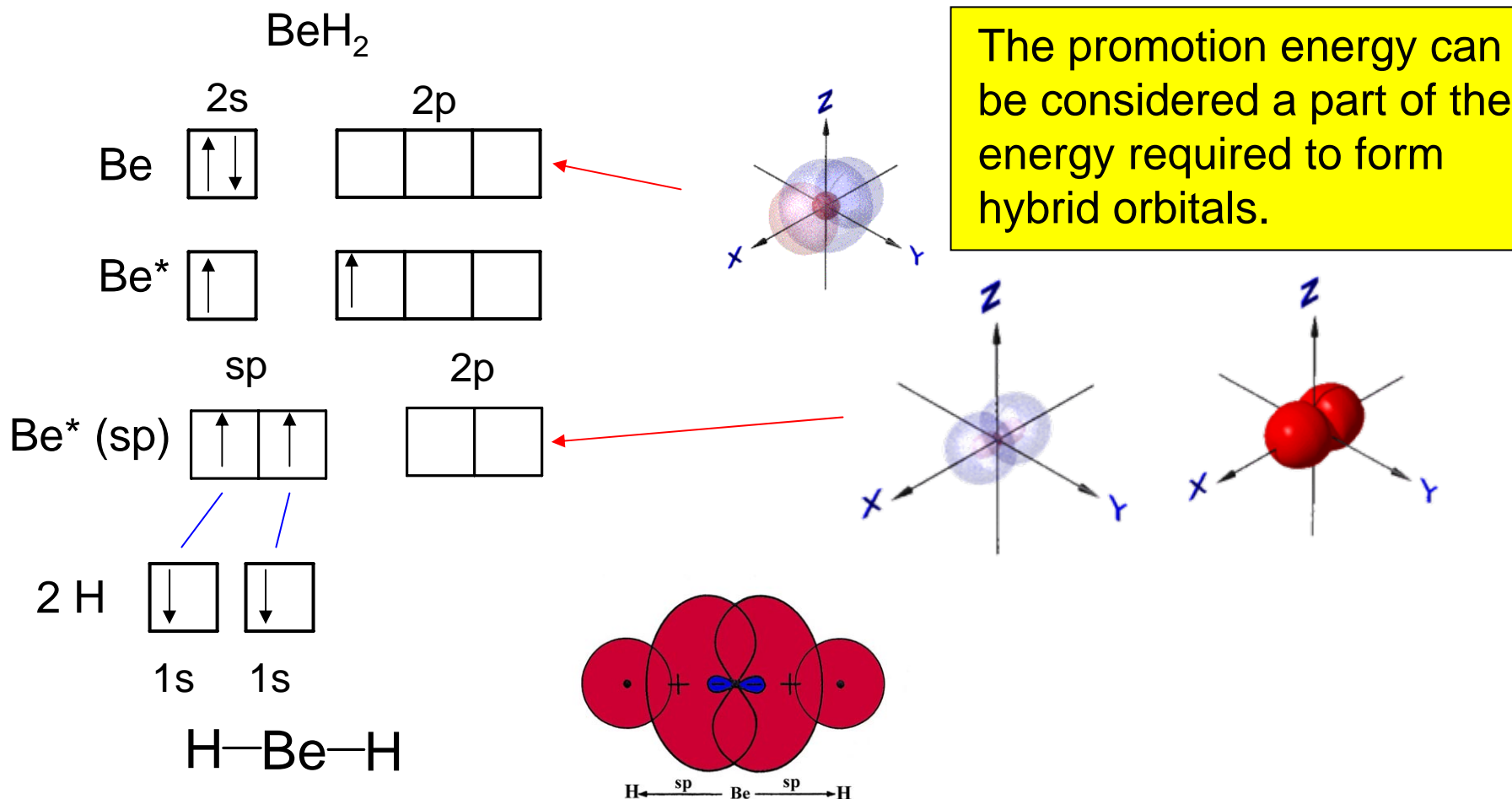
$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2} \int (\phi_s \phi_s) \partial\tau - \frac{1}{2} \int (\phi_s \phi_p) \partial\tau + \frac{1}{2} \int (\phi_s \phi_p) \partial\tau - \frac{1}{2} \int (\phi_p \phi_p) \partial\tau$$

$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2}(1) - \frac{1}{2}(0) + \frac{1}{2}(0) - \frac{1}{2}(1)$$

$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2} - \frac{1}{2} = 0$$

Thus our hybrid sp orbitals are orthogonal to each other, as required.

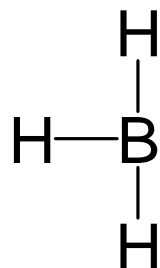
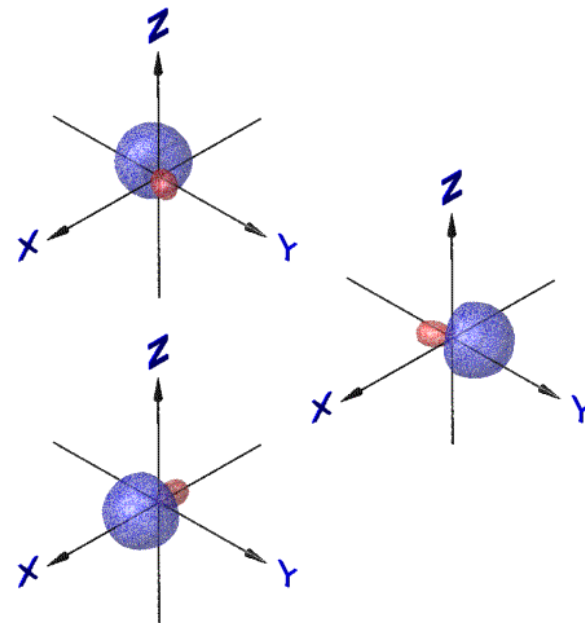
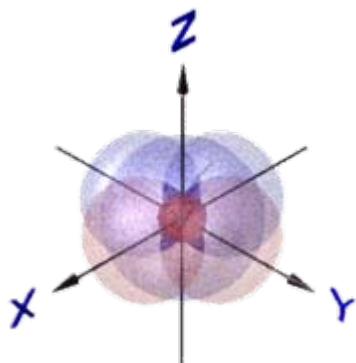
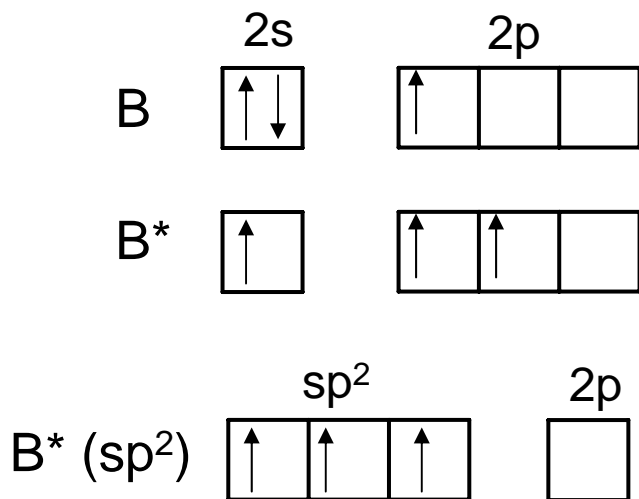
Valence bond theory treatment of a linear molecule: the bonding in BeH_2



The promotion energy can be considered a part of the energy required to form hybrid orbitals.

The overlap of the hybrid orbitals on Be with the 1s orbitals on the H atoms gives two Be-H (sp)-1s σ bonds oriented 180° from each other. This agrees with the VSEPR theory prediction.

Valence bond theory treatment of a trigonal planar molecule: the bonding in BH_3



This gives three sp^2 orbitals that are oriented 120° apart in the xy plane – be careful: the choice of axes in this example determines the set of coefficients.

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} + \frac{1}{\sqrt{2}} \phi_{p_y} \\ \Psi_2 &= \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} - \frac{1}{\sqrt{2}} \phi_{p_y} \\ \Psi_3 &= \frac{1}{\sqrt{3}} \phi_s + \frac{2}{\sqrt{6}} \phi_{p_x} \end{aligned}$$

The coefficients in front of each atomic wavefunction indicate the amount of each atomic orbital that is used in the hybrid orbital. The sign indicates the orientation (direction) of the atomic orbitals. Remember that you have to use each atomic orbital completely (**columns**) and that each hybrid must be normal (**rows**). Check this by summing the squares of the coefficients.

$$\Psi_1 = \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} + \frac{1}{\sqrt{2}} \phi_{p_y}$$

$1/3 + 1/6 + 1/2 = 1$
So this hybrid is normal

$$\Psi_2 = \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} - \frac{1}{\sqrt{2}} \phi_{p_y}$$

$1/3 + 1/6 + 1/2 = 1$
So this hybrid is normal

$$\Psi_3 = \frac{1}{\sqrt{3}} \phi_s + \frac{2}{\sqrt{6}} \phi_{p_x}$$

$1/3 + 4/6 = 1$
So this hybrid is normal

$1/3 + 1/3 + 1/3 = 1$
So the entire s orbital
has been used

$1/6 + 1/6 + 4/6 = 1$
So the entire p_x orbital
has been used

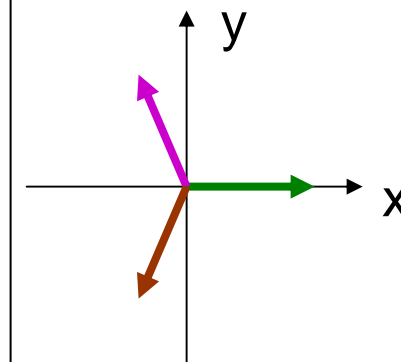
$1/2 + 1/2 = 1$
So the entire p_y orbital
has been used

The signs in front of the coefficients indicate the direction of the hybrid:

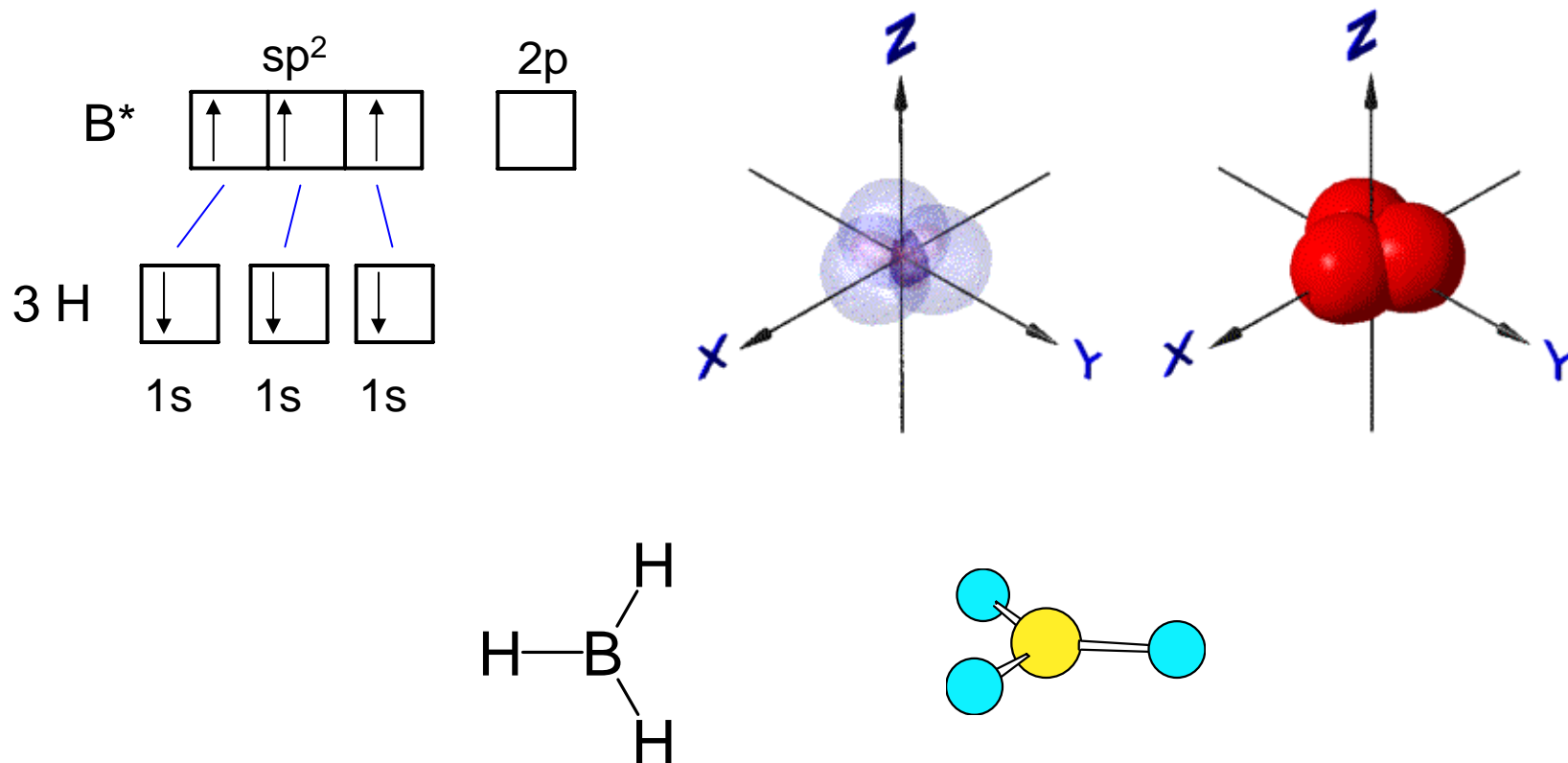
Ψ_1 : -x, +y

Ψ_2 : -x, -y

Ψ_3 : +x, 0y

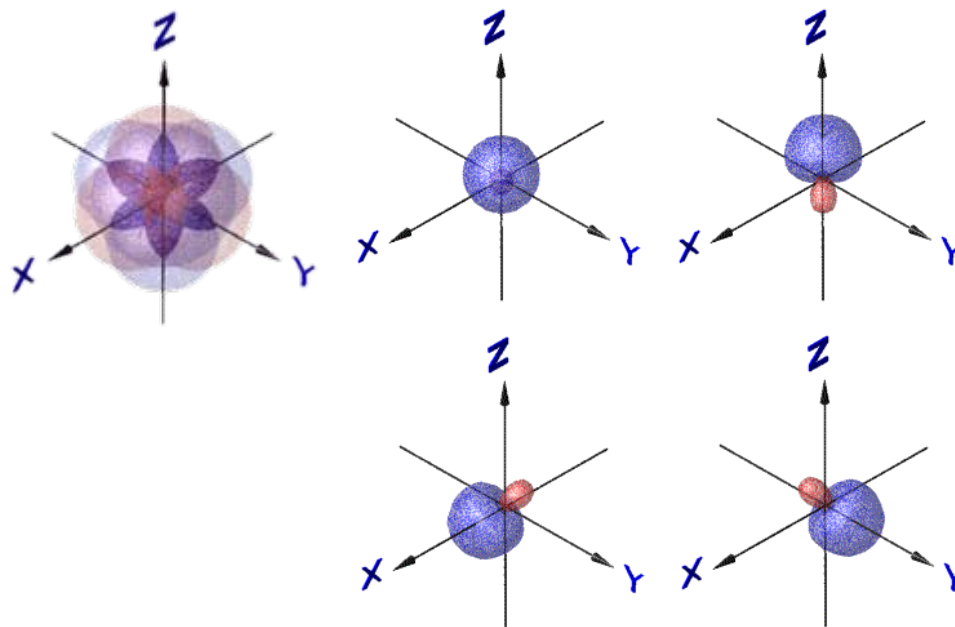
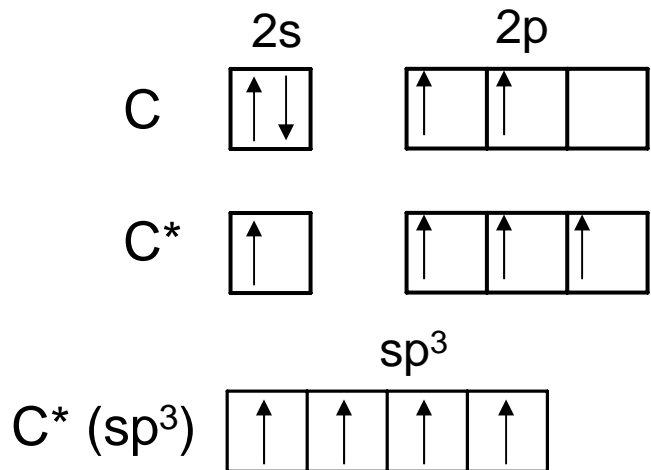


Valence bond theory treatment of a trigonal planar molecule: the bonding in BH_3

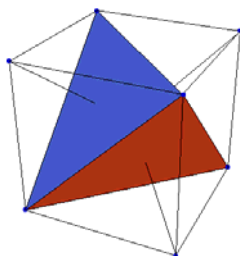
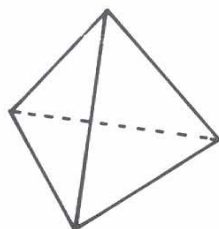
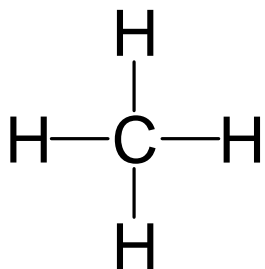


The overlap of the sp^2 hybrid orbitals on B with the $1s$ orbitals on the H atoms gives three B-H (sp^2)- $1s$ σ bonds oriented 120° from each other. This agrees with the VSEPR theory prediction.

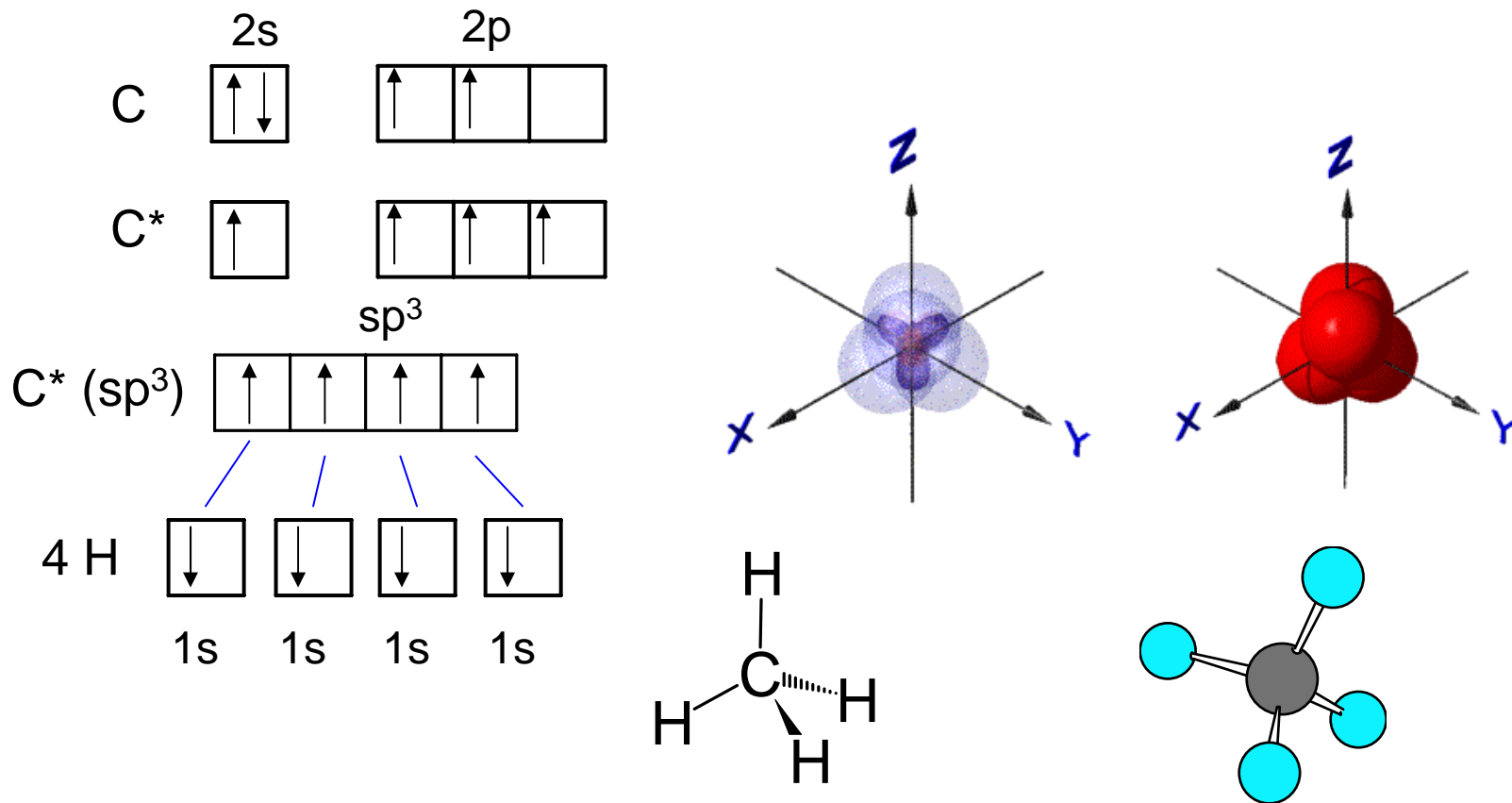
Valence bond theory treatment of a tetrahedral molecule: the bonding in CH₄



This gives four sp³ orbitals that are oriented in a tetrahedral fashion.

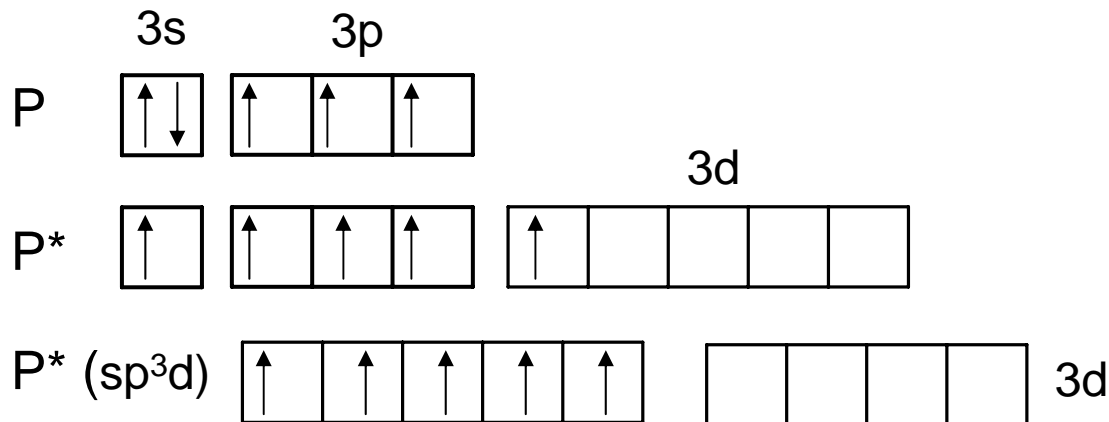


$$\begin{aligned}
 \Psi_1 &= \frac{1}{\sqrt{4}} \phi_s + \frac{1}{\sqrt{4}} \phi_{p_x} + \frac{1}{\sqrt{4}} \phi_{p_y} + \frac{1}{\sqrt{4}} \phi_{p_z} \\
 \Psi_2 &= \frac{1}{\sqrt{4}} \phi_s + \frac{1}{\sqrt{4}} \phi_{p_x} - \frac{1}{\sqrt{4}} \phi_{p_y} - \frac{1}{\sqrt{4}} \phi_{p_z} \\
 \Psi_3 &= \frac{1}{\sqrt{4}} \phi_s - \frac{1}{\sqrt{4}} \phi_{p_x} - \frac{1}{\sqrt{4}} \phi_{p_y} + \frac{1}{\sqrt{4}} \phi_{p_z} \\
 \Psi_4 &= \frac{1}{\sqrt{4}} \phi_s - \frac{1}{\sqrt{4}} \phi_{p_x} + \frac{1}{\sqrt{4}} \phi_{p_y} - \frac{1}{\sqrt{4}} \phi_{p_z}
 \end{aligned}$$

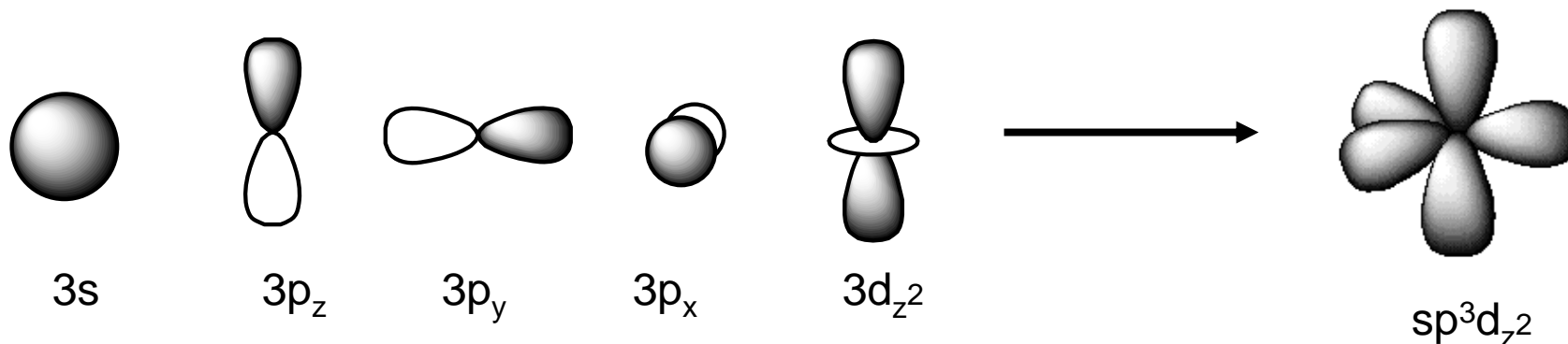
Valence bond theory treatment of a tetrahedral molecule: the bonding in CH₄


The overlap of the sp³ hybrid orbitals on C with the 1s orbitals on the H atoms gives four C-H (sp³)-1s σ bonds oriented 109.47° from each other. This provides the tetrahedral geometry predicted by VSEPR theory.

Valence bond theory treatment of a trigonal bipyramidal molecule:
the bonding in PF_5



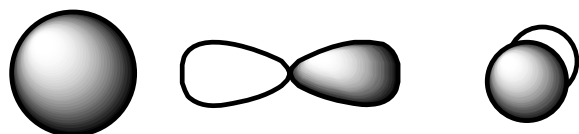
PF_5 has an VSEPR theory AX_5 geometry so we need hybrid orbitals suitable for bonds to 5 atoms. s and p combinations can only provide four, so we need to use d orbitals (**if they are available**).



The appropriate mixture to form a trigonal bipyramidal arrangement of hybrids involves all the s and p orbitals as well as the d_{z^2} orbital.

Valence bond theory treatment of a trigonal bipyramidal molecule

The orbitals are treated in two different sets.

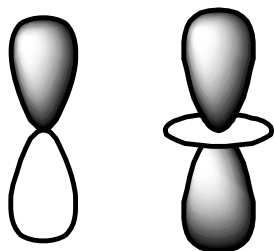


$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_s + \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y}$$

$$\Psi_2 = \frac{1}{\sqrt{3}}\phi_s + \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y}$$

$$\Psi_3 = \frac{1}{\sqrt{3}}\phi_s - \frac{2}{\sqrt{6}}\phi_{p_x}$$

These coefficients are exactly the same as the result for the trigonal planar molecules because they are derived from the same orbitals (sp^2)



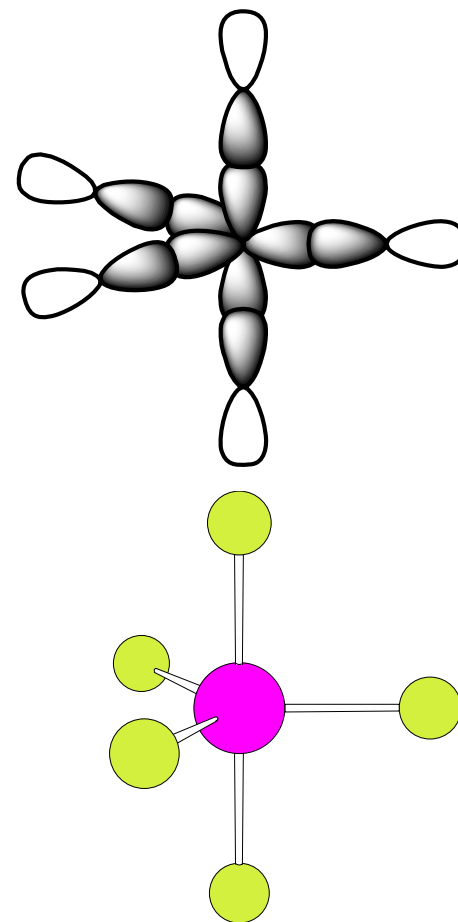
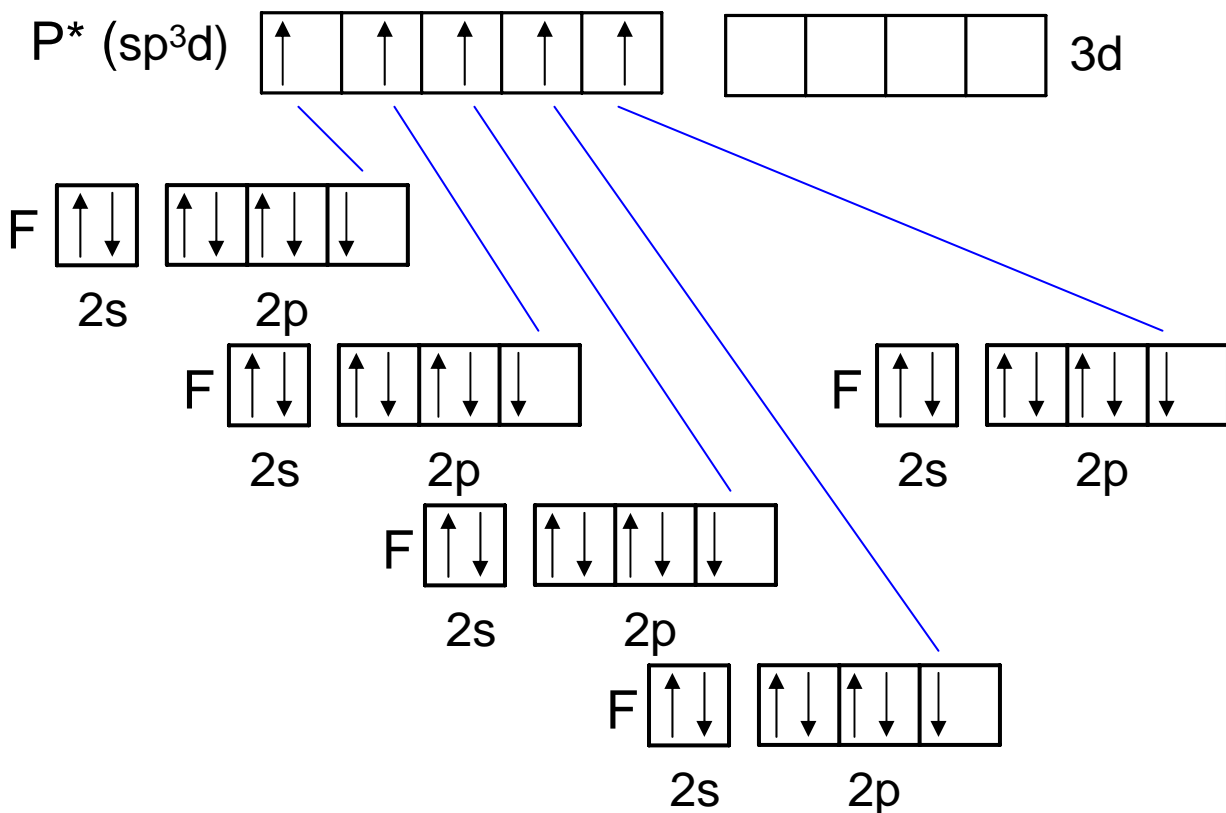
$$\Psi_4 = \frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}$$

$$\Psi_5 = -\frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}$$

These coefficients are similar to those for the sp hybrids because they are formed from a combination of two orbitals (pd).

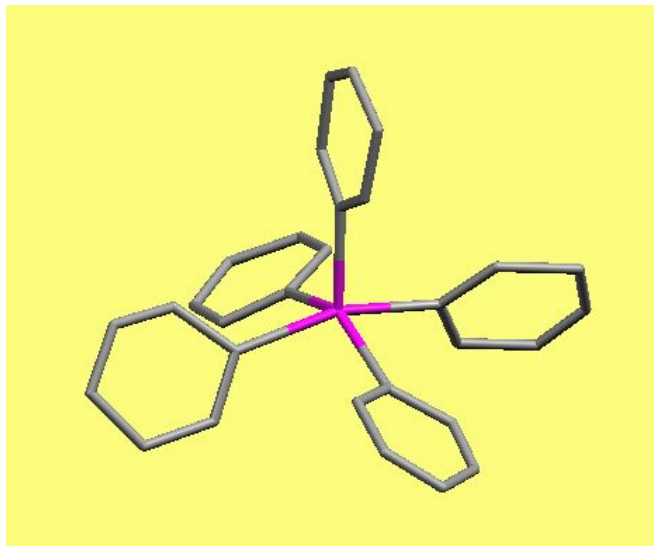
Remember that d orbitals are more *diffuse* than s or p orbitals so VBT predicts that the bonds formed by hybrids involving d orbitals will be longer than those formed by s and p hybrids.

Valence bond theory treatment of a trigonal bipyramidal molecule:
the bonding in PF_5

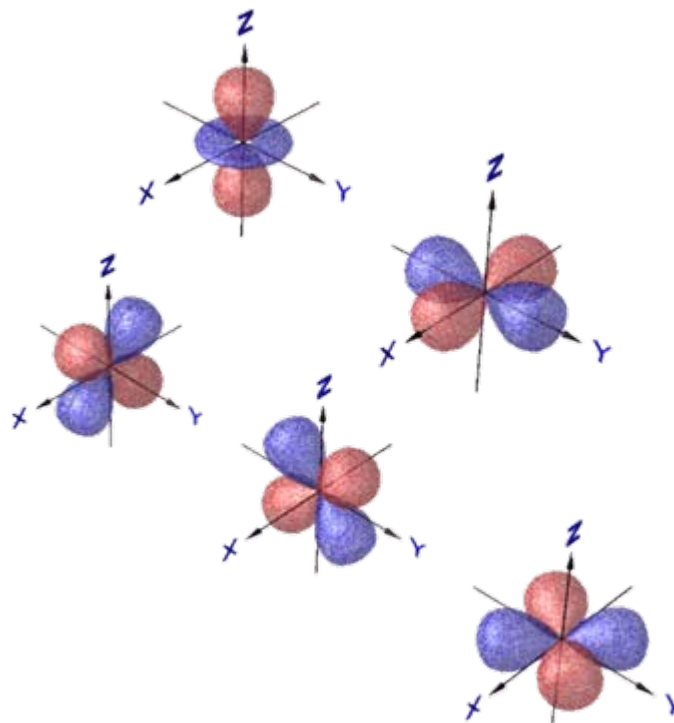


The overlap of the sp^3d hybrid orbitals on P with the 2p orbitals on the F atoms gives five P-F (sp^3d)-2p σ bonds in two sets: the two *axial* bonds along the z-axis (180° from each other) and three *equatorial* bonds in the xy plane (120° from each other and 90° from each axial bond). **This means that the 5 bonds are not equivalent!**

The square pyramidal AX_5 geometry requires mixing with a different d orbital than in the trigonal bipyramidal case.



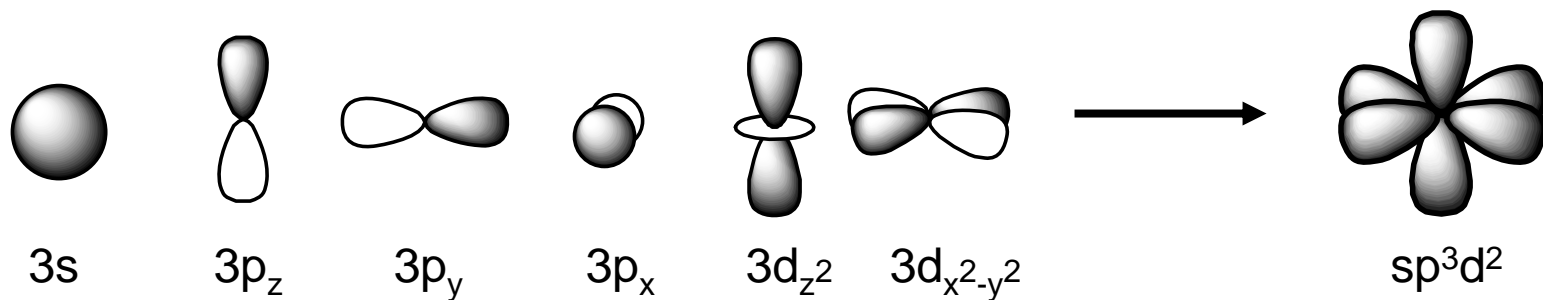
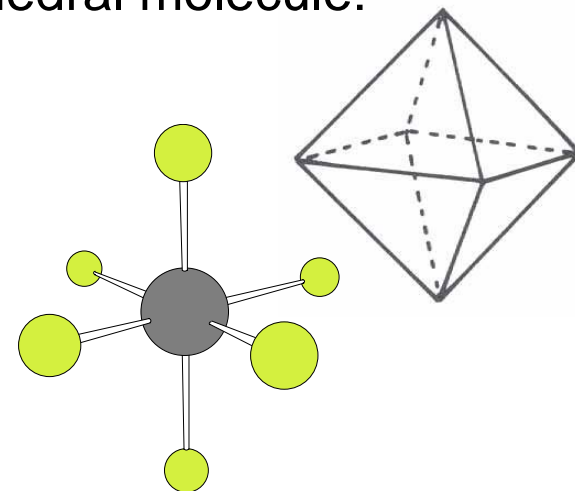
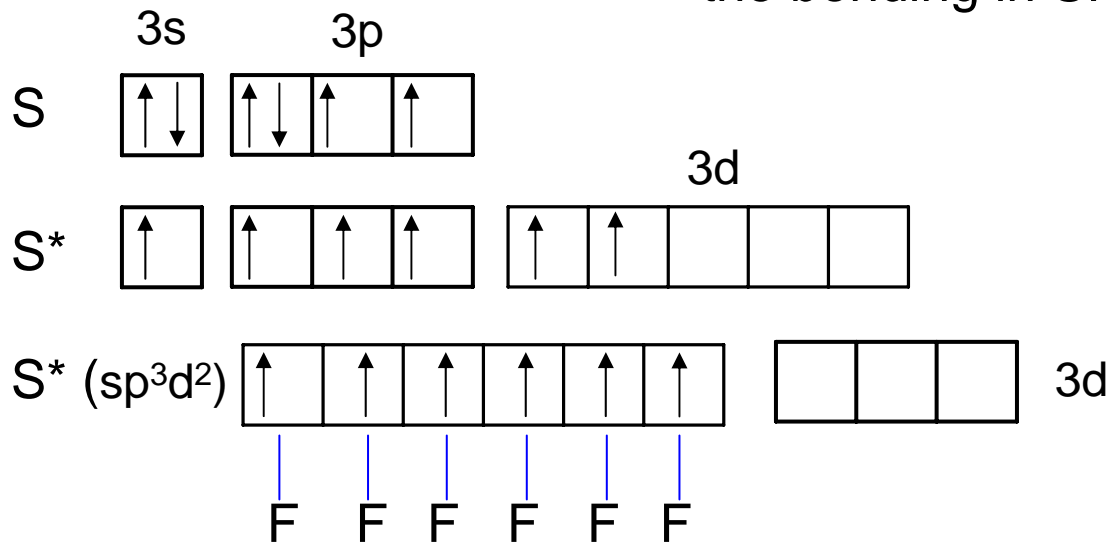
$Sb(C_6H_5)_5$



d orbitals

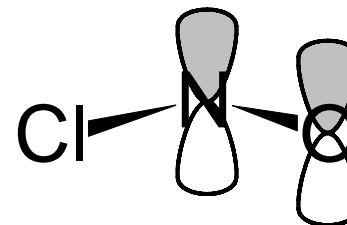
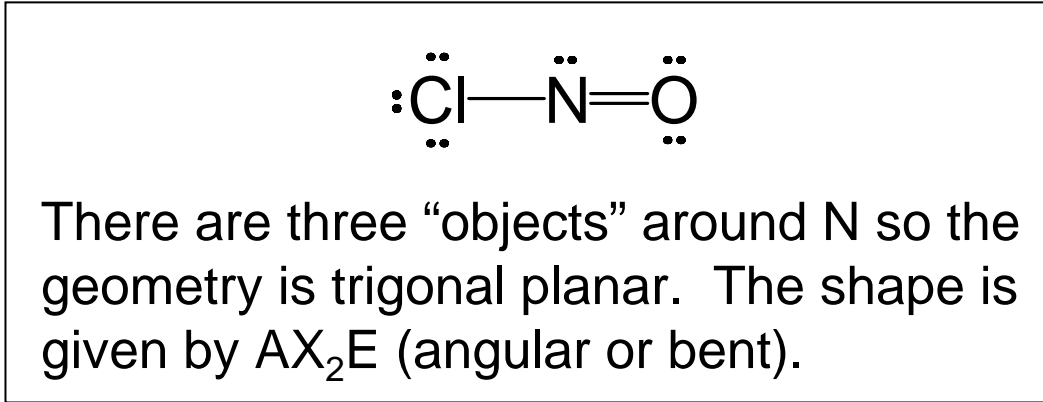
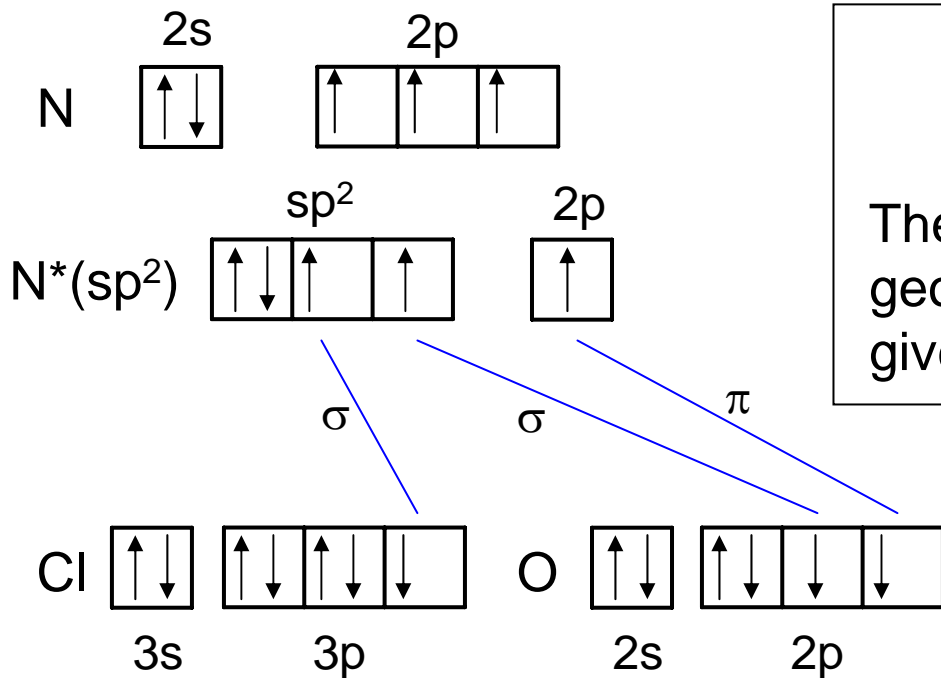
You should consider what orbital(s) would be useful for such a geometry and we will see a way to figure it out unambiguously when we examine the symmetry of molecules.

Valence bond theory treatment of an octahedral molecule:
the bonding in SF₆



The overlap of the sp³d² hybrid orbitals on S with the 2p orbitals on the F atoms gives six S-F (sp³d²)-2p σ bonds 90° from each other **that are equivalent**. You can figure out the normalization coefficients.

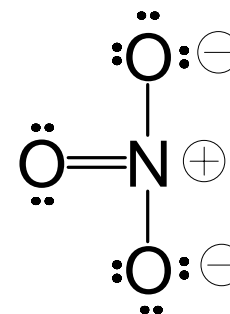
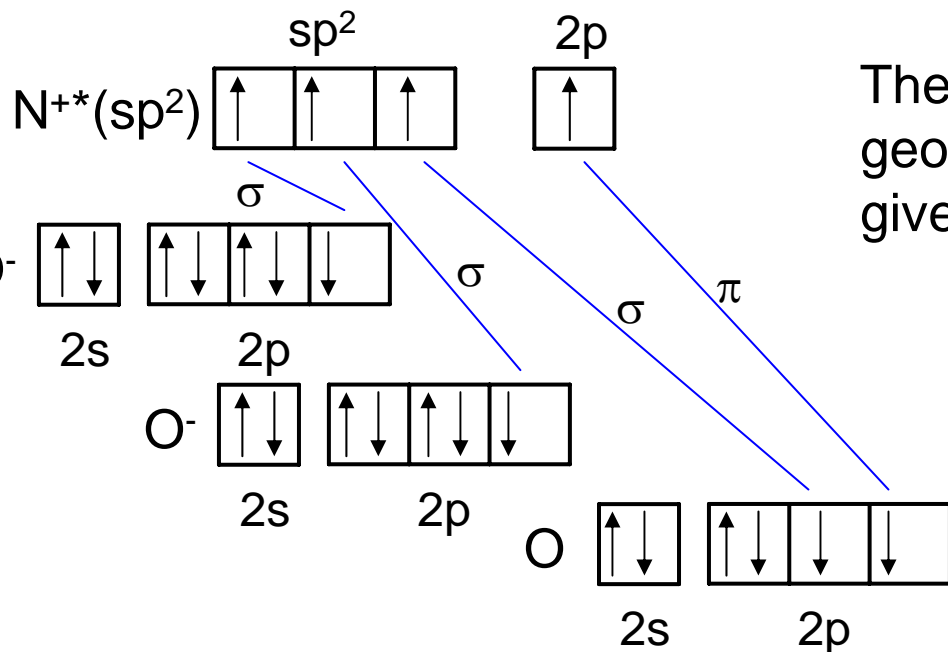
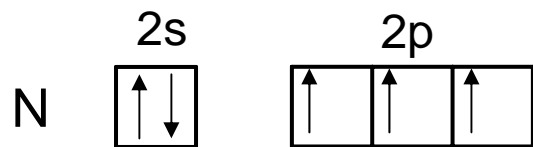
Valence bond theory treatment of π -bonding: the bonding in ClNO



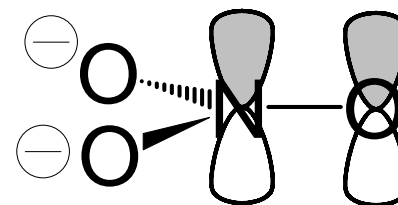
A drawing of the VBT π bond in ClNO.

The overlap of the sp^2 hybrid orbitals on N with the 3p orbital on Cl and the 2p orbital on O give the two σ bonds and it is the overlap of the “left over” p orbital on N with the appropriate orbital on O that forms the (2p-2p) π bond between the two atoms.

Valence bond theory treatment of π -bonding: the bonding in the nitrate anion



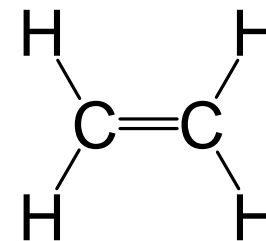
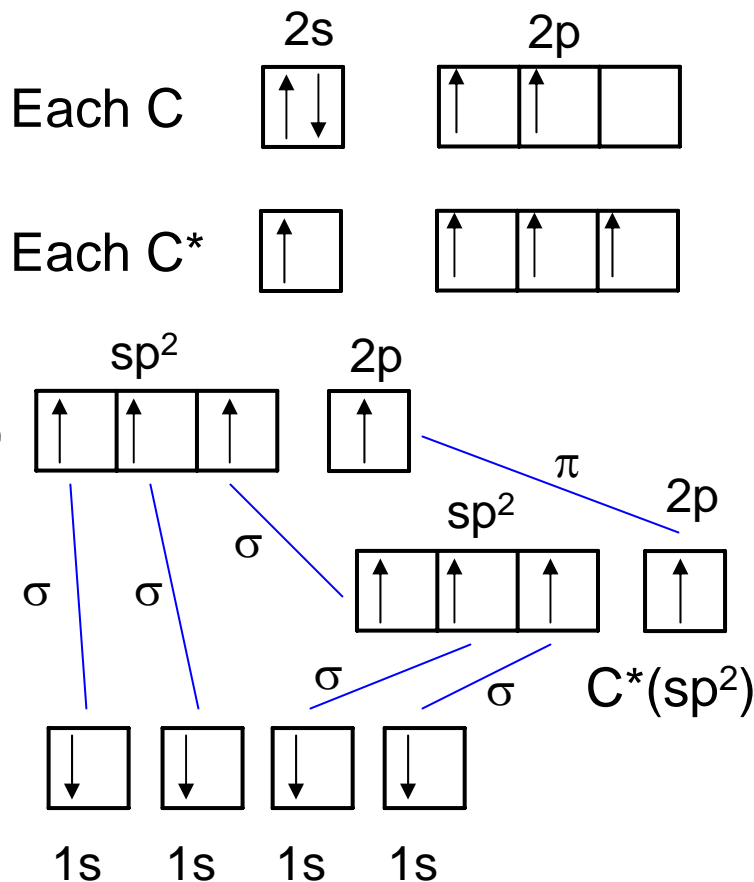
There are three “objects” around N so the geometry is trigonal planar. The shape is given by AX₃ (trigonal planar).



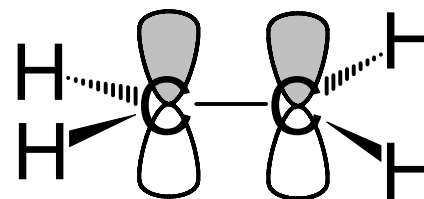
VBT gives only one of the canonical structures at a time.

The overlap of the sp² hybrid orbitals on N with the the 2p orbitals on the O give the three (sp²-2p) σ bonds and it is the overlap of the “left over” p orbital on N with the appropriate orbital on the uncharged O atom that forms the (2p-2p) π bond.

Valence bond theory treatment of π -bonding: the bonding in ethene

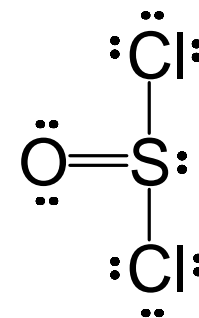
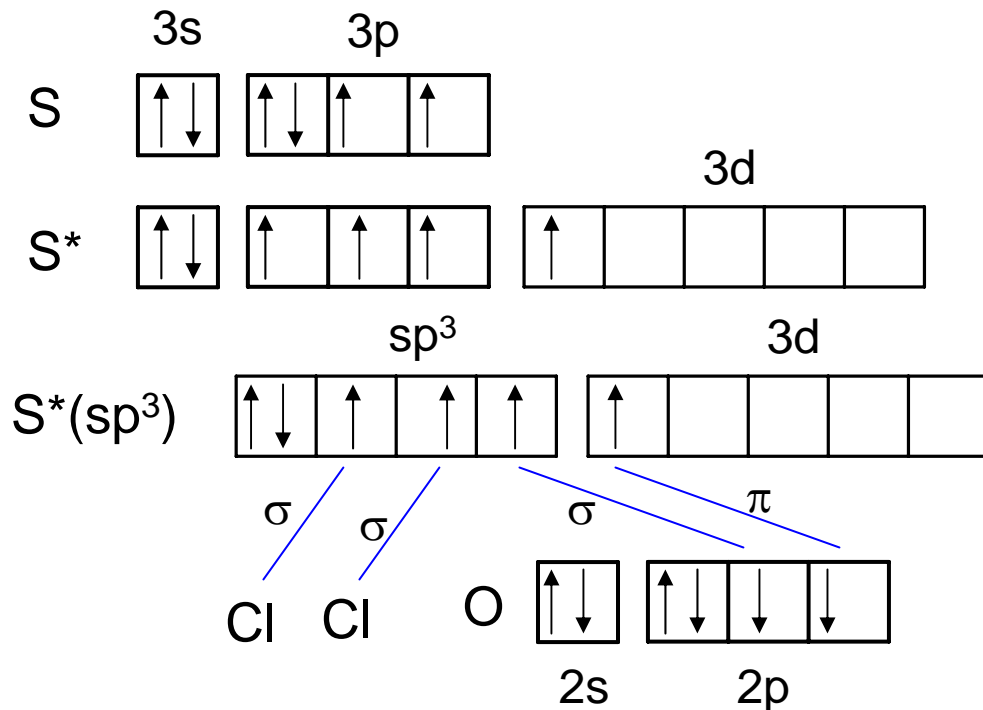


There are three “objects” around each C so the geometry is trigonal planar at each carbon. The shape is given by AX_3 for each carbon.

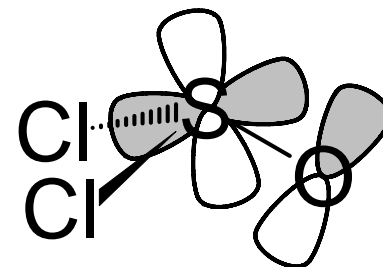


The overlap of the sp^2 hybrid orbitals on C with the the $1s$ orbitals on each H give the four terminal (sp^2 - $1s$) σ bonds. The double bond between the C atoms is formed by a (sp^2 - sp^2) σ bond and the ($2p$ - $2p$) π bond.

Valence bond theory treatment of π -bonding: the bonding in SOCl_2

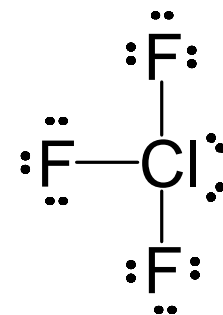
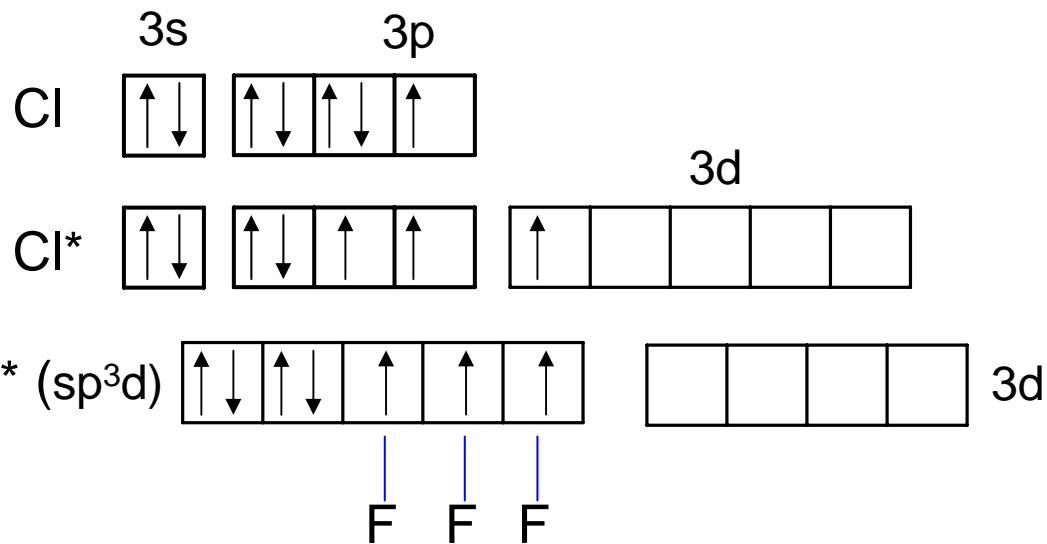


There are four “objects” around S so the geometry is **tetrahedral** and the shape is given by AX₃E (pyramidal).



The overlap of the sp³ hybrid orbitals on S with the 3p orbitals on Cl and the 2p orbital on O give the three σ bonds and, because the lone pair is located in the final sp³ hybrid, it is the overlap of the “left over” d orbital on S with an appropriate p orbital on O that forms the (3d-2p) π bond in the molecule.

Valence bond theory treatment of bonding: a hypervalent molecule, ClF_3



There are five “objects” around Cl so the geometry is trigonal bipyramidal and the shape is given by AX_3E_2 (T-shaped).
 Consider this: Why are such molecules T-shaped instead of pyramidal or planar?

The overlap of the sp^3d hybrid orbitals on Cl with the 2p orbitals on the F atoms gives three P-F (sp^3d)-2p σ bonds in two sets: the two *axial* bonds along the z-axis (less than 180° from each other because of the repulsion from the lone pairs) and the one *equatorial* bond halfway between the other Cl bonds. Again, the bond lengths will not be the same because there is more d contribution to the axial hybrid orbitals.

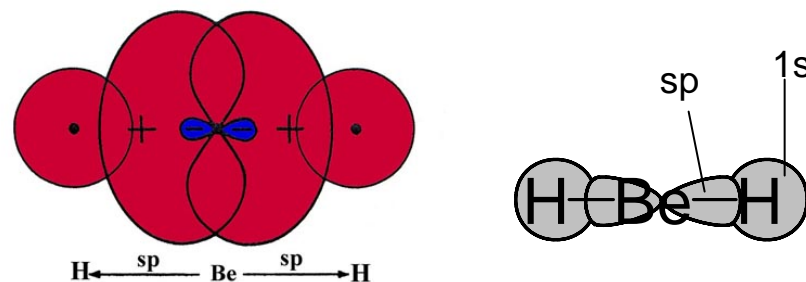
Chem 59-250 Summary of Valence Bond Theory

1. Write an acceptable Lewis structure for the molecule.
2. Determine the number of VSEPR objects around all central atoms and determine the geometry around the atom.
3. Construct hybrid orbitals suitable for the predicted bonding.
4. Link orbitals together to make bonds.
5. Describe the bonding. Include the names of the orbitals involved in each bond. Draw pictures of the bonds formed by the overlap of these orbitals.



Two objects around Be, so AX_2 (linear)

Two orbitals pointing 180° from each other needed, so use two sp hybrids



Two (sp-1s) Be-H σ bonds.