

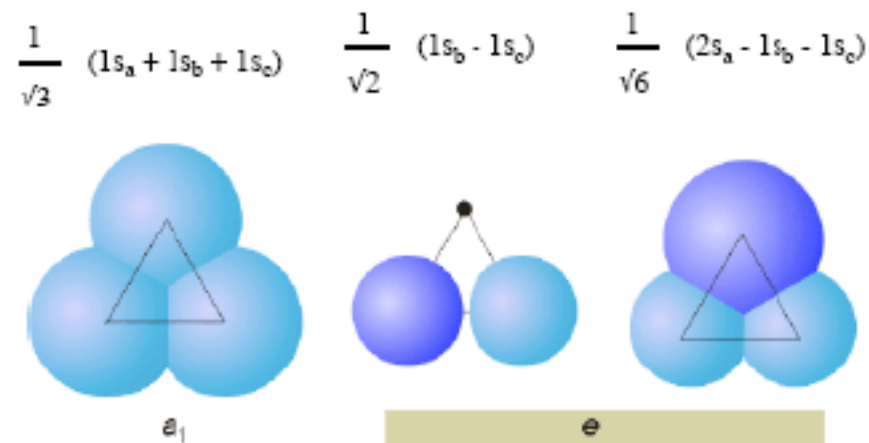
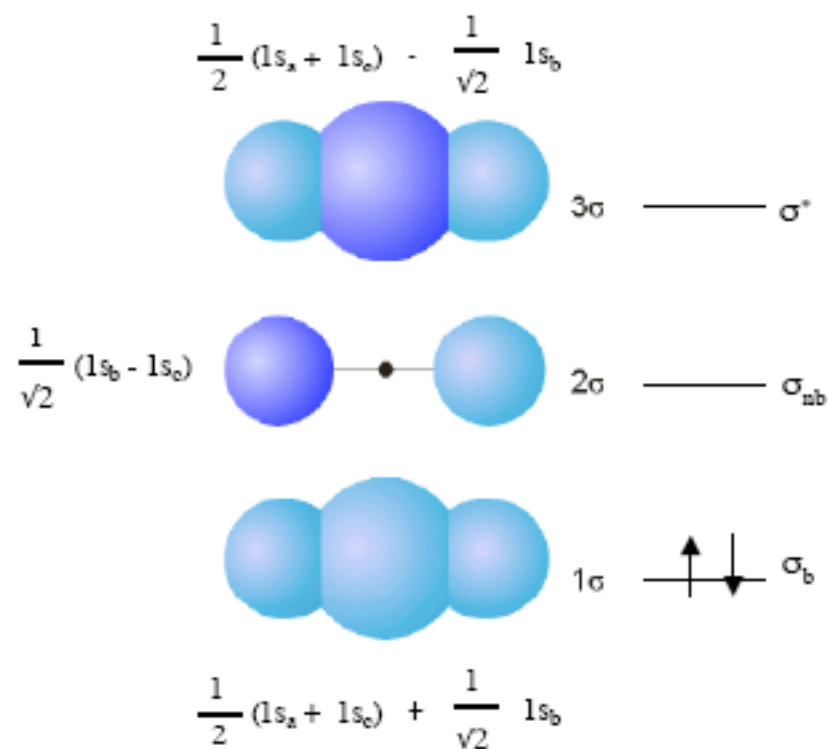
# Taking MO Theory Past the Diatomics

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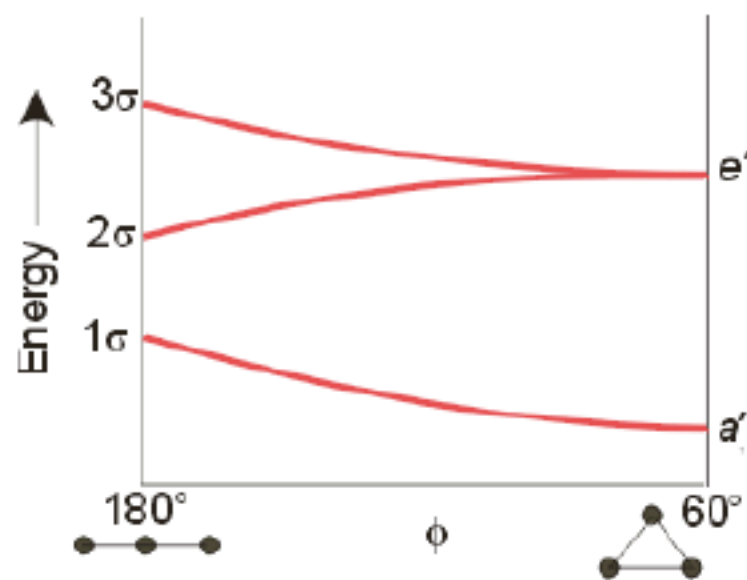
- Molecular orbital theory is valid for all molecules. Thus far, we've focused on the diatomics because it's only convenient to manually derive complete MO diagrams for molecules that are either very small or highly symmetric.
- It was easier for us to predict MOs for symmetric molecules (like  $O_2$ ) than asymmetric molecules (like CO). For this reason, our studies of larger molecules will be confined to highly symmetric ones – like  $BeH_2$ ,  $CO_2$  and  $C_6H_6$ . Computers are used to predict MOs for less symmetric molecules ("computational chemistry").
- The principles used to predict MOs and MO diagrams for the diatomics are the same as those used for larger molecules.
  - Continue to look for valence atomic orbitals with:
    - COMPATIBLE SYMMETRY ( $\sigma$  vs.  $\pi$ )
    - COMPATIBLE ENERGY (as close as possible; no farther apart than  $\sim 1$  Ry)
  - Make sure you make the same number of MOs as you had AOs!
  - Keep electron distribution in MOs symmetric if molecule is symmetric.

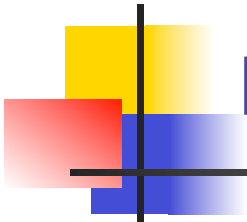
# Polynuclear molecules

## Simplest Example: $\text{H}_3^+$



Walsh diagram

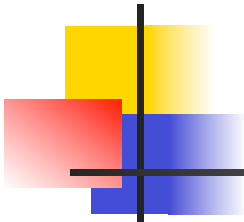




## Molecular Orbitals for BeH<sub>2</sub>

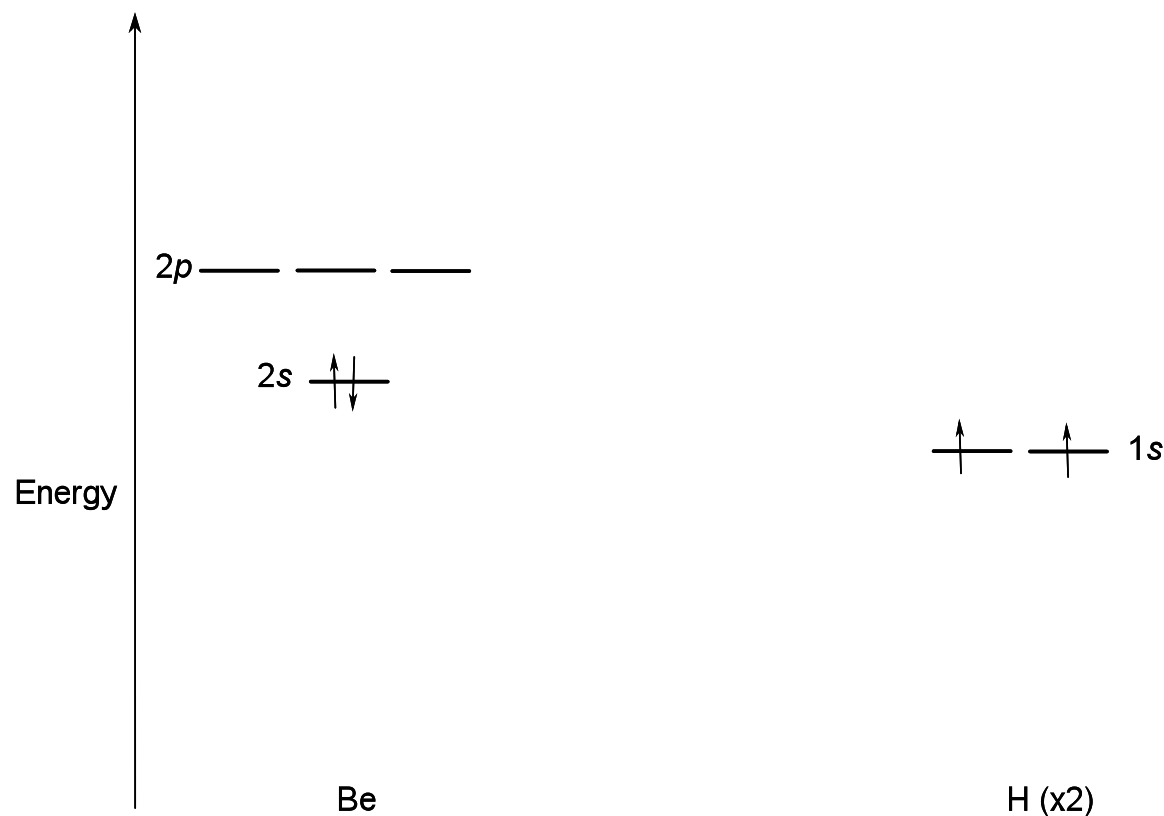
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- BeH<sub>2</sub> is the simplest triatomic molecule. In the gas phase, it is linear (as we'd expect from the Lewis structure)
- The relative energies for the atomic orbitals of Be and H are:
  - $1s(\text{Be}) = -9.38 \text{ Ry}$
  - $2s(\text{Be}) = -0.61 \text{ Ry}$
  - $2p(\text{Be}) = +0.14 \text{ Ry}$
  - $1s(\text{H}) = -0.99 \text{ Ry}$

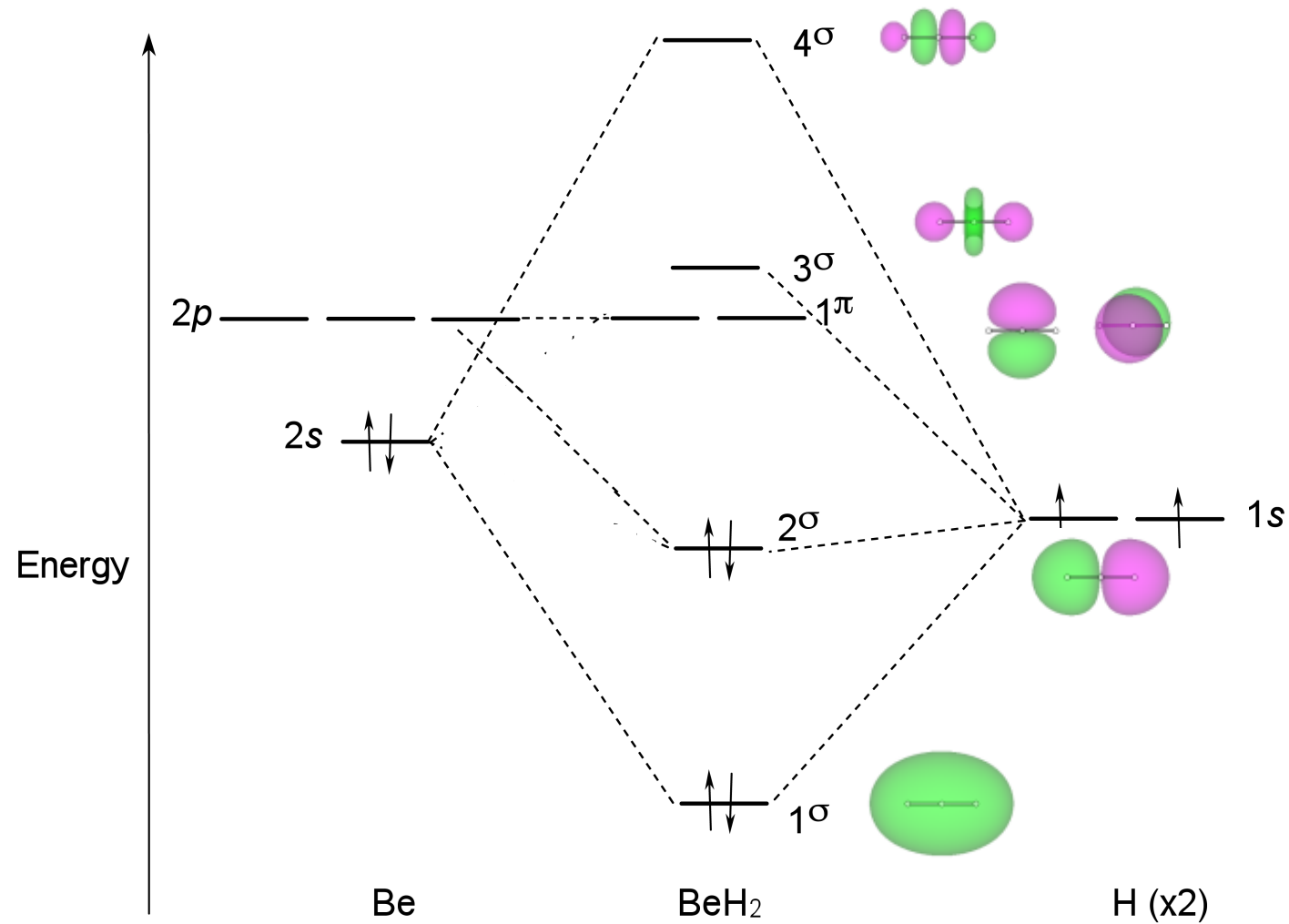


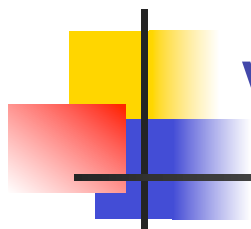
## Molecular Orbitals for BeH<sub>2</sub>

- As in the MO diagrams for diatomics, the MOs are tracked in the middle of the diagram with the AOs at the sides. Equivalent atoms (such as the Hs in BeH<sub>2</sub>) are grouped at one side, making sure to include all their valence AOs (one 1s AO for each H):



# MO Diagram for BeH<sub>2</sub>



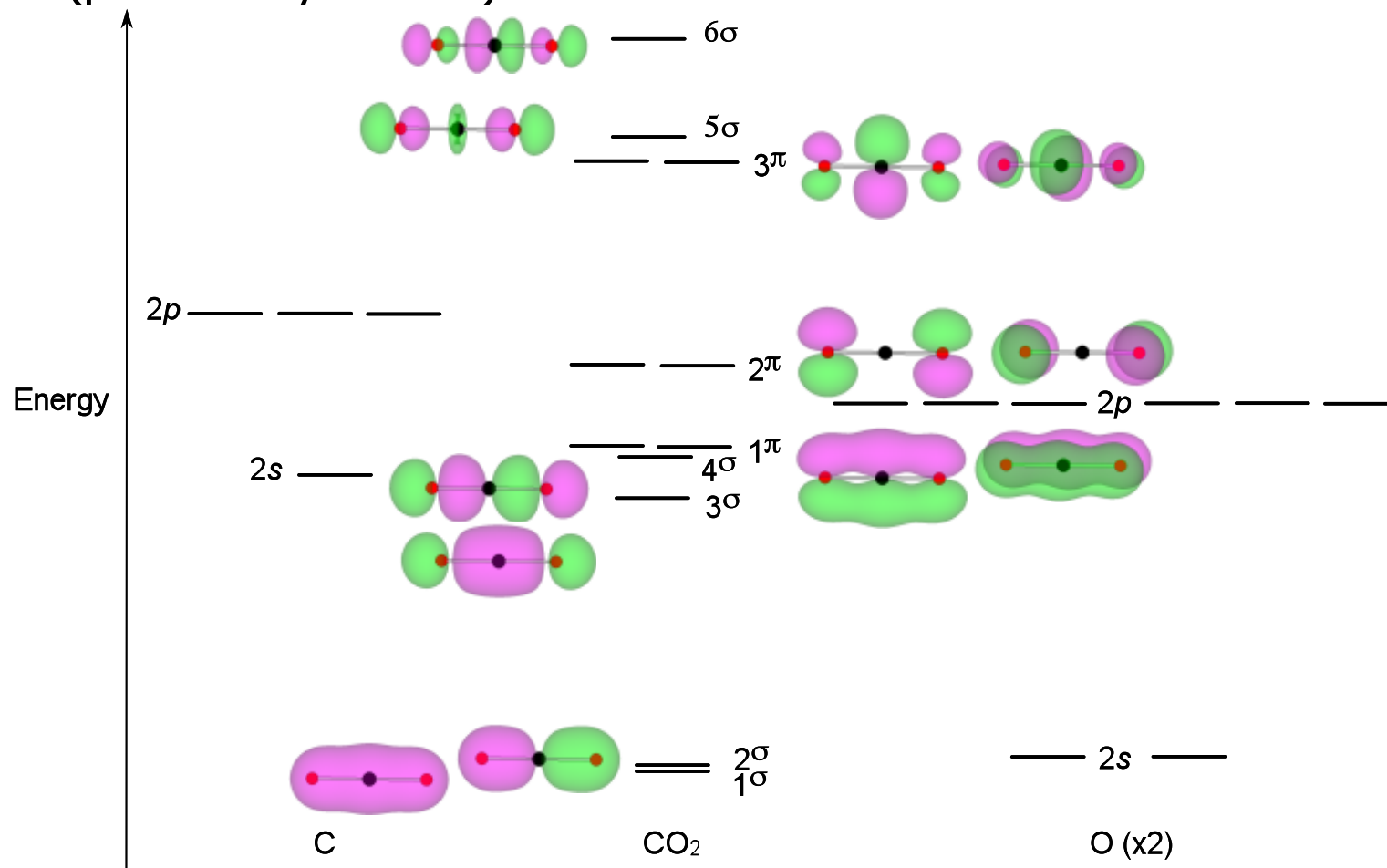


## Valence Molecular Orbitals for CO<sub>2</sub>

- CO<sub>2</sub> may not appear much more complicated than BeH<sub>2</sub> – both of them being linear triatomic molecules – but it has rather more valence orbitals to consider. As usual, we will split them into  $\sigma$ -symmetric AOs and  $\pi$ -symmetric AOs
- The six  $\pi$ -symmetric AOs can be subdivided into two sets: the  $2p_x$  AOs and the  $2p_y$  AOs. Each of those sets can be combined to make three MOs. We use symmetry and nodes to predict the shapes of these MOs and their relative energies
- The six  $\sigma$ -symmetric AOs must be treated as a group. They are combined to make six  $\sigma$ -symmetric MOs. Again, we use symmetry and nodes to predict the shapes of these MOs and their relative energies

# Valence MO Diagram for CO<sub>2</sub>

- A computer helps us find the relative energies of the MOs (particularly  $\sigma$  vs.  $\pi$ ):



# Walsh Diagrams

$AH_2$

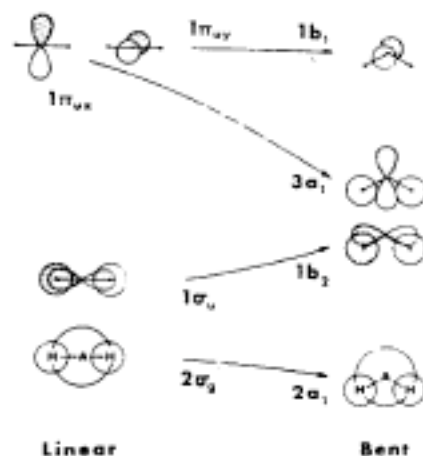


Figure 1. Qualitative MO correlation diagram for linear and bent  $AH_2$  molecules. Changes in geometry which increase in-phase overlaps between AO's lower the MO energy.

$AH_3$

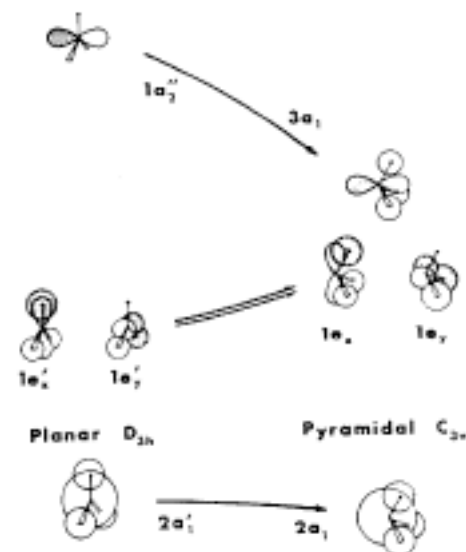


Figure 2. Qualitative MO correlation diagram for an  $AH_3$  molecule in planar and pyramidal shapes.

from Gimarc, B. J. *Acc. Chem. Research* 1974, 7, 384.

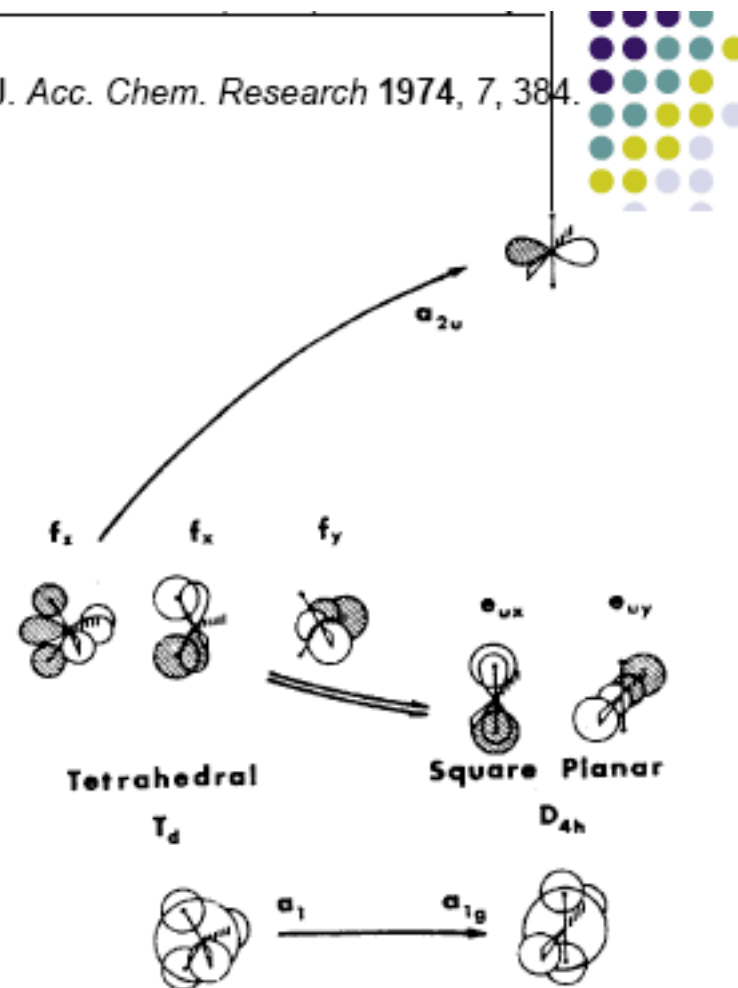
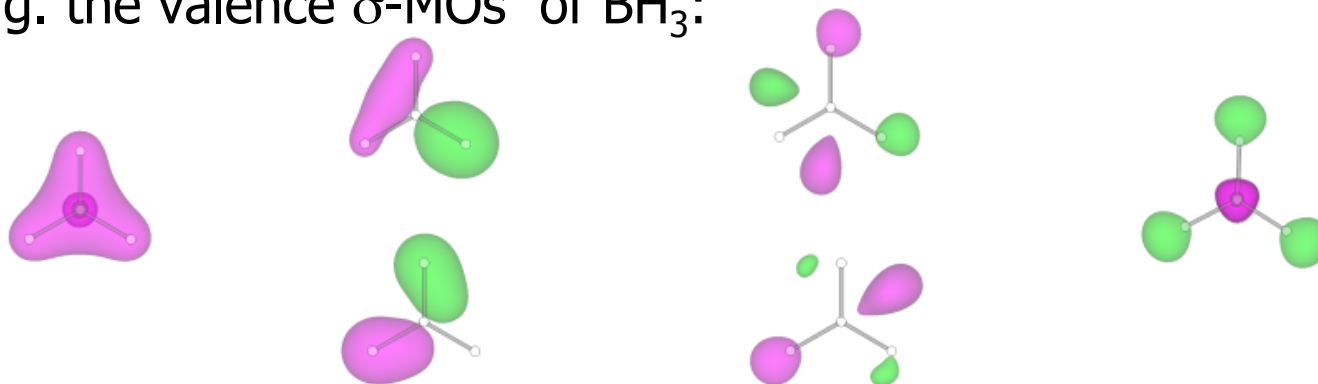


Figure 3. Molecular orbital pictures for  $AH_4$  in tetrahedral and square-planar geometry.

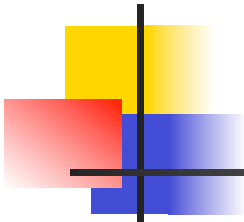
$AH_4$

# MO Theory and Delocalized $\pi$ Electrons

- Once we move beyond the linear triatomics, the  $\sigma$ -MOs quickly become relatively complicated and difficult to predict.  
e.g. the valence  $\sigma$ -MOs of  $\text{BH}_3$ :



- The  $\pi$ -MOs, on the other hand, are still relatively straightforward to predict. When we can draw multiple resonance structures for a molecule, we are often interested in the electrons that “move” between resonance structures. MO theory treats these electrons as being in **delocalized**  $\pi$ -MOs. Since  $\sigma$ -MOs and  $\pi$ -MOs are always treated separately (a phenomenon called **sigma-pi separation**), we often ignore the  $\sigma$ -MOs and discuss just the  $\pi$ -MOs for large molecules with multiple resonance structures. This is similar to our practice of ignoring core MOs and discussing bonding using only the valence MOs.



# MO Theory and Delocalized $\pi$ Electrons

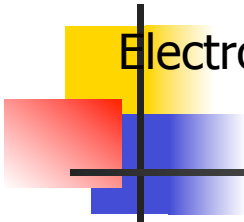
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- Important points to remember:
  - We are approximating that, for every bond (single, double or triple), there are two electrons in  $\sigma$  bonding MOs. This does not mean that there is a  $\sigma$ -MO focussed on the bonding region. It may, for example, mean that there are three bonding  $\sigma$ -MOs holding together three different bonds (*as shown for  $BH_3$  on the previous page – the three leftmost MOs are  $\sigma$ -bonding MOs, each containing 2 electrons*)
  - When discussing bond order, only  $\pi$  bond order can be determined from a  $\pi$ -MO diagram. Total bond order will typically be 1 greater.

$$\text{Total bond order} = \pi \text{ bond order} + \sigma \text{ bond order}$$

- Recall that:
  - A  $\pi$  orbital with lower energy than  $p$  orbitals is net bonding.
  - A  $\pi$  orbital with the same energy as  $p$  orbitals is net nonbonding.
  - A  $\pi$  orbital with higher energy than  $p$  orbitals is net antibonding.

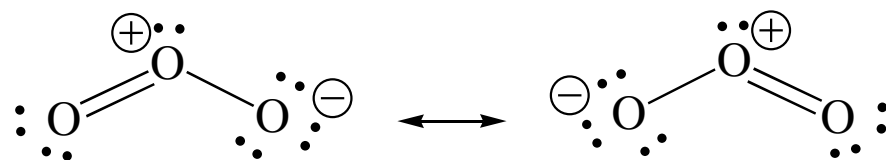
Looking at the nodes tells us which atoms are pulled together and which atoms are pulled apart by electrons in a particular MO.



## Electron delocalization (Resonance) and the FMOs of molecules with multiple bonds.

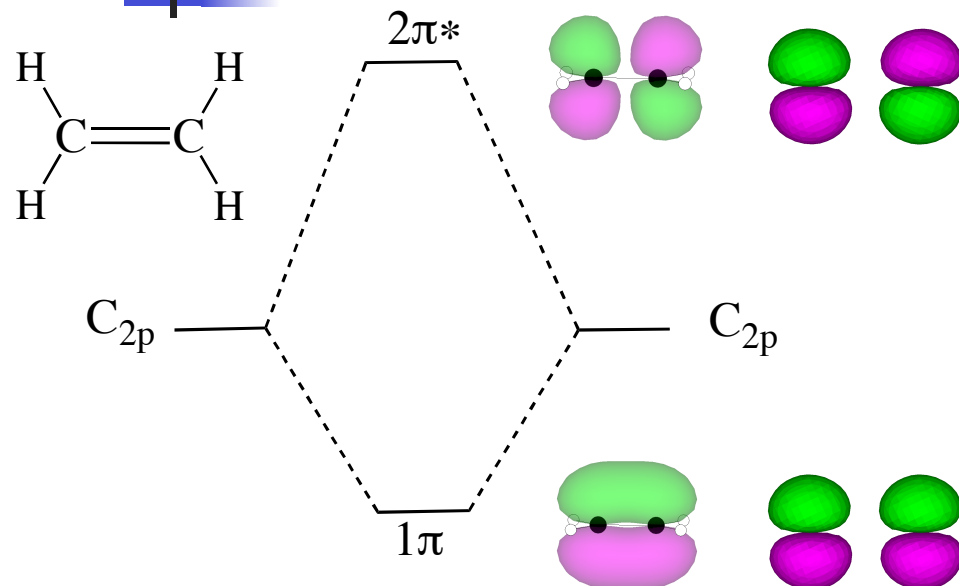
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In resonance structures, the only electrons that move are:

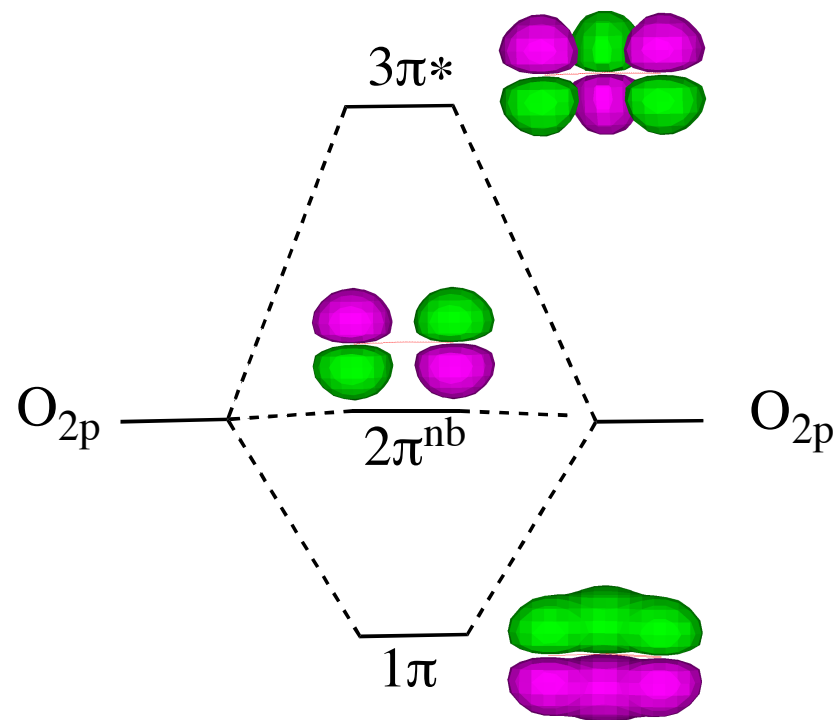
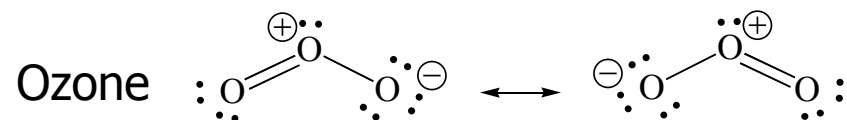


- Delocalized electrons are always found in  $\pi$  orbitals. Whenever a lone pair is found on an atom adjacent to a multiple bond, it is delocalized in the pi system.
  - At the same time, because the  $\pi$  orbitals are usually found at higher energy than the  $\sigma$  orbitals, the HOMO and LUMO of molecules with multiple bonds are usually  $\pi$  orbitals.
- As a result of this, we often look only at the  $\pi$  orbitals and construct  $\pi$  MO diagrams.

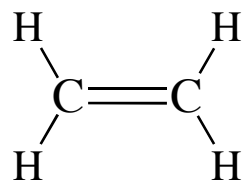
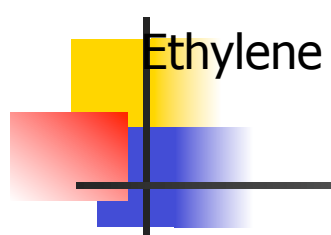
# The $\pi$ -MO diagram of Ethylene



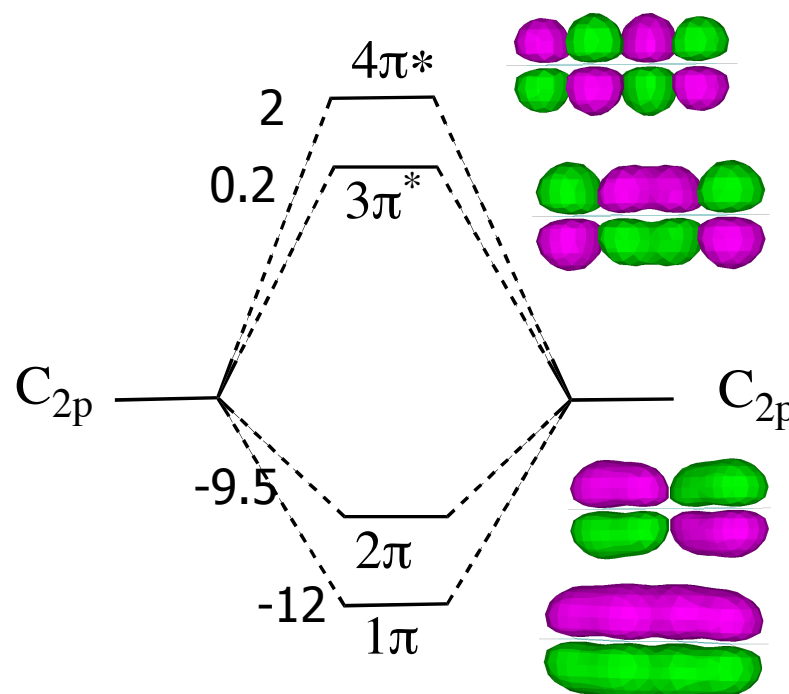
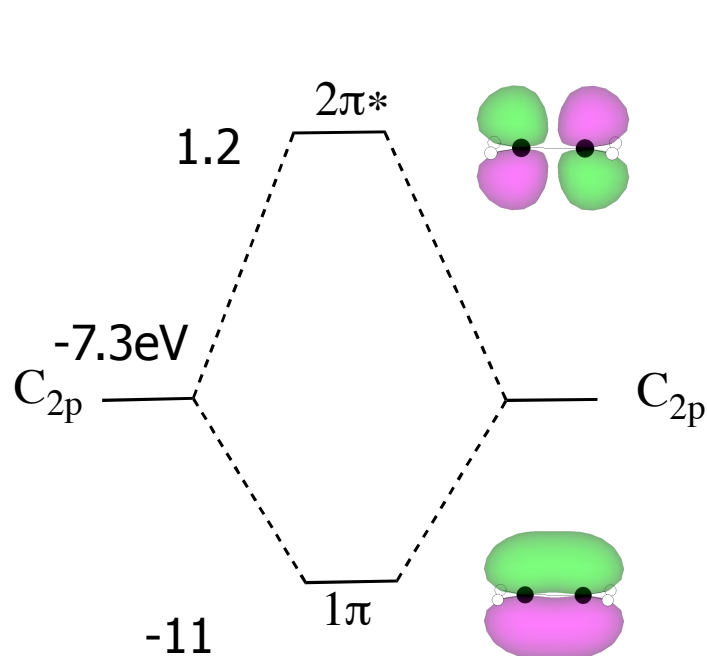
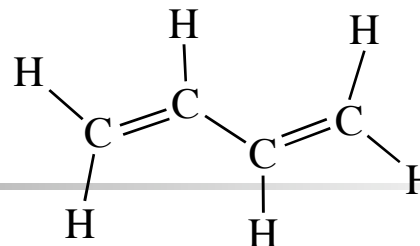
Nodes...  
 Pi-bond order...  
 Total bond order  
 When Ethylene reacts...



Nodes...  
 Pi-bond order...  
 Total bond order  
 Lewis BO  
 Formal Charge:  
 Lone pairs.



Butadiene



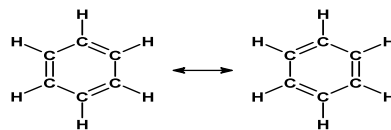
Nodes...

The importance of the HOMO/LUMO gap.

Note that this is not two isolated double bonds but a single  $\pi$ -system spread out over four carbons.

# Resonance and MO Theory: Benzene ( $C_6H_6$ )

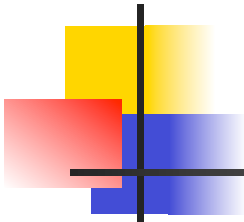
- The classic example of delocalized  $\pi$  electrons and MO theory is benzene. The Lewis structure of benzene is:



- If we assign molecular geometries to each carbon atom, we see that benzene is a planar molecule:

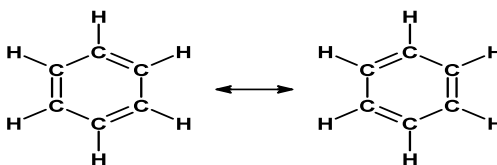


- As usual, we divide the valence atomic orbitals into  $\sigma$ -symmetric and  $\pi$ -symmetric. Since  $\pi$ -symmetric orbitals are perpendicular to the plane/line of the molecule, only one set of  $2p$  orbitals is  $\pi$ -symmetric in benzene (usually designated  $2p_z$ ).

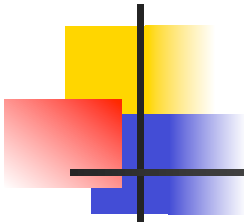


# Resonance and MO Theory: Benzene ( $C_6H_6$ )

- This gives us 6  $\sigma$ -MOs and 6  $\pi$ -MOs.
- To divide the electrons between these MOs, we recall that:
  - There are 2 electrons in  $\sigma$ -MOs for every bonded pair of electrons in the molecule. We also count 2 electrons for every lone pair of electrons that doesn't move \* between resonance structures. Benzene contains 6 C-C bonds, 6 C-H bonds and no lone pairs, so it has 24 electrons in its  $\sigma$ -MOs.
  - Any electrons which move between resonance structures are in  $\pi$ -MOs. In benzene, 6 electrons are in different places in the two resonance structures, so benzene has 6 electrons in its  $\pi$ -MOs.

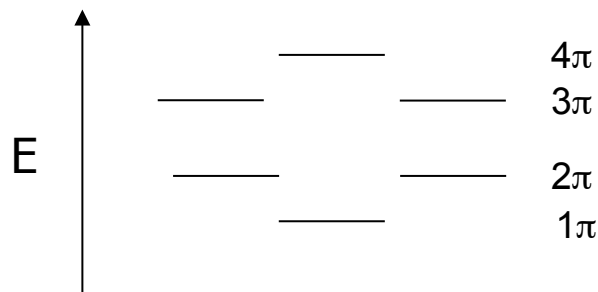
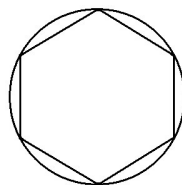
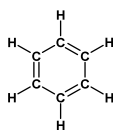


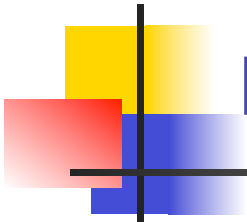
\* There are rare cases where lone pairs that remain in place for all reasonable resonance structures are, in fact, in  $\pi$ -MOs.



# Resonance and MO Theory: Benzene ( $C_6H_6$ )

- So, we know that benzene has 6  $\pi$ -MOs containing 6 electrons. We also know that these  $\pi$ -MOs were made by combining six  $2p_z$  orbitals on the six carbon atoms.
- Cyclic molecules tend to have degenerate  $\pi$  energy levels.
  - A “quick and dirty” trick to predict the relative energy levels for this kind of molecule is to draw a circle. Inside the circle, draw a polygon the same shape as your molecule. Make sure the tip of the polygon is at the bottom of the circle. The corners of the polygon are at the same height as the relative energy levels. If you draw a horizontal line across the middle of the circle (representing the energy of the  $p$  atomic orbitals), all orbitals below it are net bonding and all orbitals above it are net antibonding. This method is a huge oversimplification but it works.



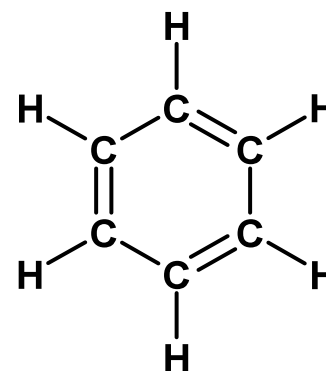
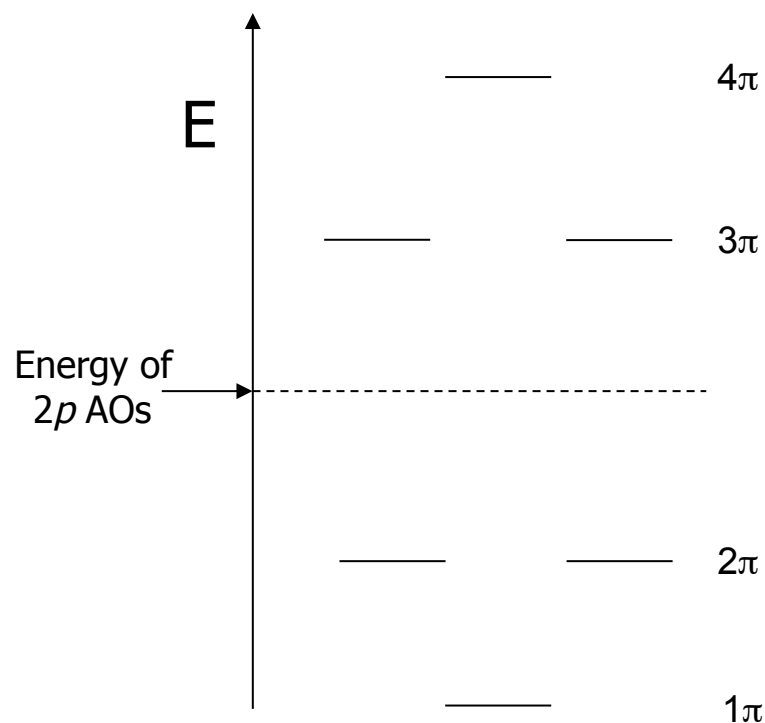


## Resonance and MO Theory: Benzene ( $C_6H_6$ )

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- We've worked out the energy levels, but what do the MOs look like? To answer that, we go back to our old standby method – symmetry and nodes!
  - The lowest energy  $\pi$ -MO ( $1\pi$ ) has one nodal plane – the one cutting through the plane of the molecule. It has no nodes perpendicular to the plane of the molecule.
  - Every time you go up to the next energy level, add a node perpendicular to the plane of the molecule, keeping them as evenly spaced as possible. If there are two degenerate  $\pi$ -MOs, keep their nodes as askew as possible (perpendicular if possible, at a  $45^\circ$  angle as next choice, etc.)
  - The highest energy  $\pi$ -MO should be “as antibonding as possible” – i.e. nodes between every pair of neighbouring atoms
- Once you've determined the energy levels and the shapes of the  $\pi$ -MOs, the last step is to fill in the electrons. Recall that we have 6  $\pi$  electrons to add to the  $\pi$ -MO diagram.

# Resonance and MO Theory: Benzene ( $C_6H_6$ )

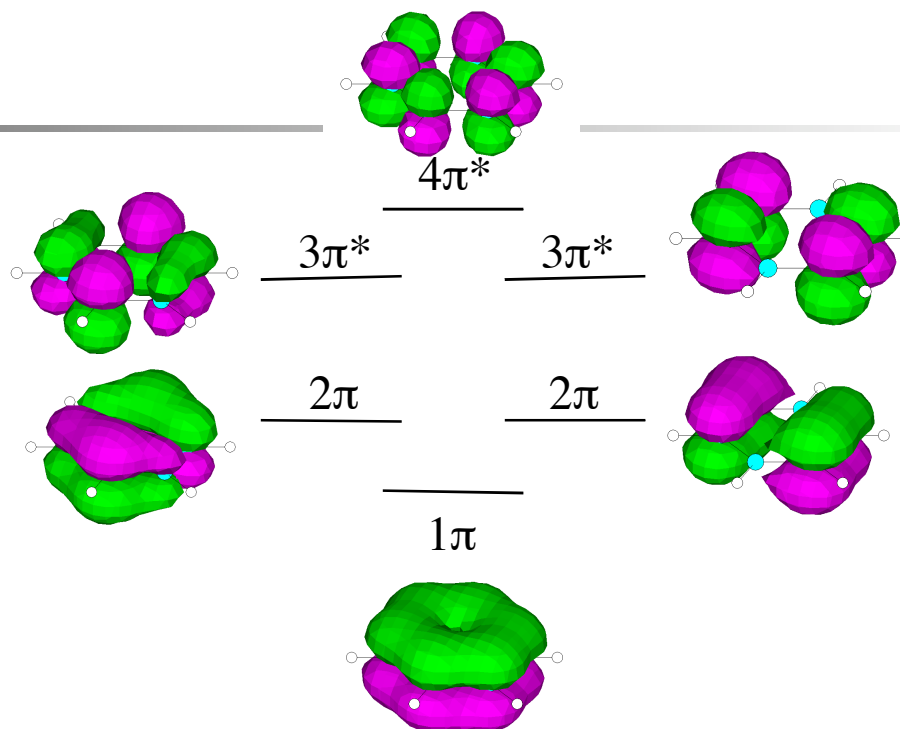


- This MO diagram confirms that benzene can't be considered to have "three double bonds and three single bonds". It really does have six bonds with bond order 1.5. *This has been proven experimentally: all six C-C bonds in benzene are 140 pm (whereas pure C-C bonds are 154 pm and pure C=C bonds are 134 pm).*

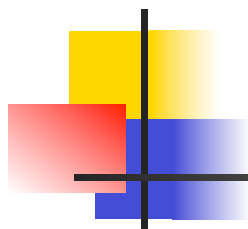
## The $\pi$ -MOs of Benzene

How many  $\pi$ -electrons?

Nodes...



Benzene can't be considered to have "three double bonds and three single bonds". It has three bonds with bond order \_\_\_\_\_.  
*Accordingly, all six C-C bonds in benzene are 140 pm (whereas pure C-C bonds are 154 pm and pure C=C bonds are 134 pm).*



## **VSEPR** *Valence Shell Electron Pair Repulsion*

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- Allows the prediction of molecular geometry
  - Sidgwick + Powell 1940
  - Gillespie + Nyholm 1957
  - Count up the number of steric contribution around the central atom. **Steric number (SN) = # of attached atom + # of lone pairs**
- Rule 1:** Assume that electron pairs around central atom repel each other, the most stable geometry corresponds to that obtained by **maximizing** the distance between SN points on the surface of a sphere, **minimizing** electron pair repulsion.

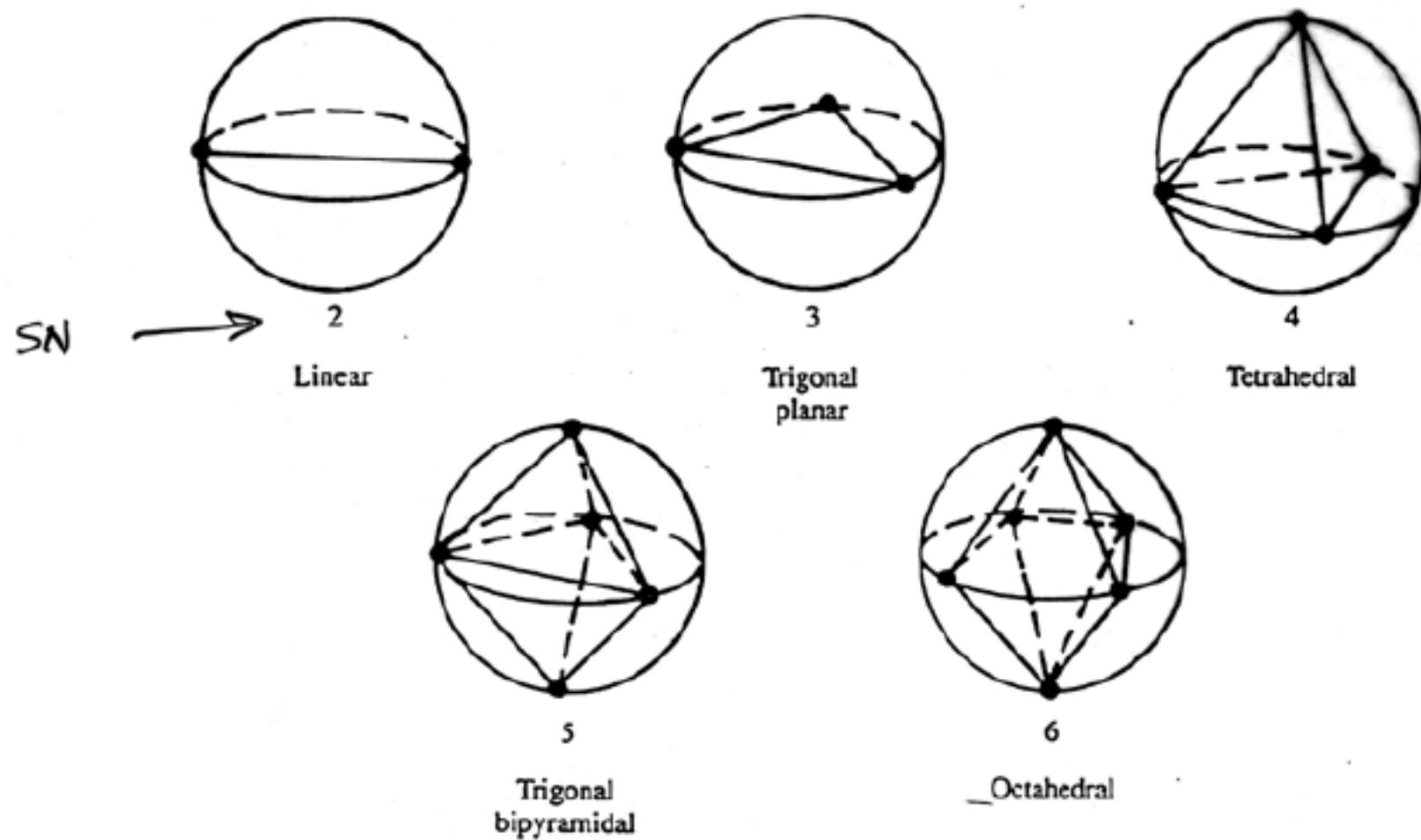
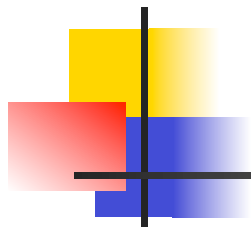


Figure 2-8 The arrangement of electron pairs on the surface of a sphere so that the distance between electron pairs is maximized.

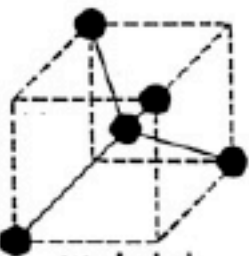
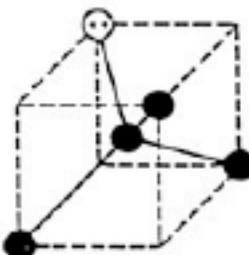


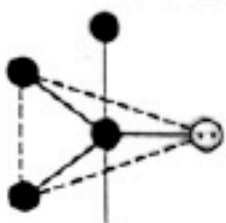
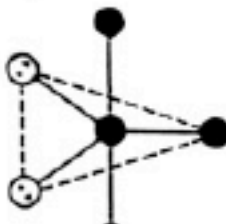
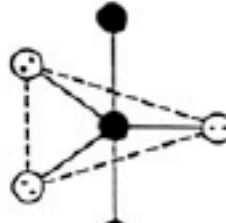
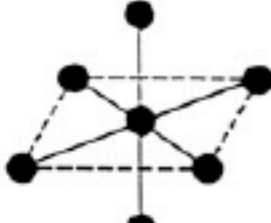
## **VSEPR**

### ***Valence Shell Electron Pair Repulsion***

**Rule 2:** Lone pair electrons are held in closer to the nucleus. Most prohibitive repulsion is lp-lp, followed by lp-bp, then bp-bp...*lps* will spread out as much as possible.

**Rule 3:** *lps* occupy more space than bond pairs, ....large angle between *lps* than *bps*.

| SN | Number of lone pairs | Molecular shape                                                                                             | Example                                               |
|----|----------------------|-------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|
| 2  | 0                    | <br>linear                 | $\text{BeH}_2$ , $\text{CO}_2$                        |
| 3  | 0                    | <br>trigonal planar        | $\text{SO}_3$ , $\text{BF}_3$                         |
| 3  | 1                    | <br>angular                | $\text{SO}_2$ , $\text{O}_3$                          |
| 4  | 0                    | <br>tetrahedral           | $\text{CH}_4$ , $\text{CF}_4$ ,<br>$\text{SO}_4^{2-}$ |
| 4  | 1                    | <br>trigonal bipyramidal | $\text{NH}_3$ , $\text{PF}_5$ ,<br>$\text{AsCl}_5$    |

| SN | Number of lone pairs | Molecular shape                                                                                         | Example                                                  |
|----|----------------------|---------------------------------------------------------------------------------------------------------|----------------------------------------------------------|
| 5  | 1                    | <br>square pyramidal | $\text{SF}_4$                                            |
| 5  | 2                    | <br>T-shaped         | $\text{ClF}_3$                                           |
| 5  | 3                    | <br>linear          | $\text{XeF}_2$ , $\text{I}_3^-$ ,<br>$\text{IF}_2^-$     |
| 6  | 0                    | <br>octahedral     | $\text{SF}_6$ , $\text{PF}_6^-$ ,<br>$\text{SiF}_6^{2-}$ |

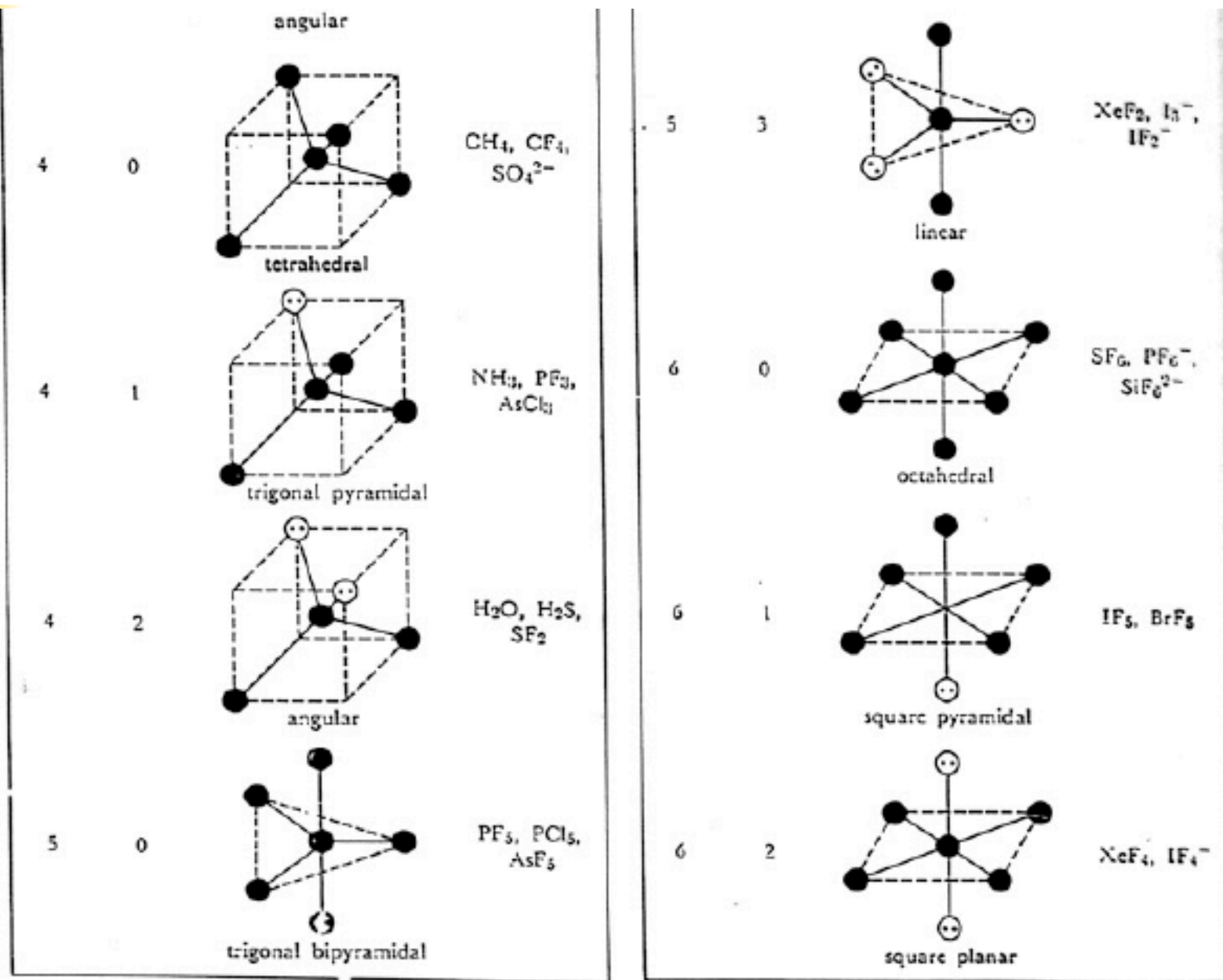


Figure 2-9 Molecular shapes predicted by the VSEPR method.



**SN=5**

**Rule 1: Structure based on trigonal bipyramid.**

**Rule 2: LPs are on equatorial positions.**

**Rule 3. axial F atoms bend away from LPs.**



**XeF<sub>6</sub> 14 e SN=7**

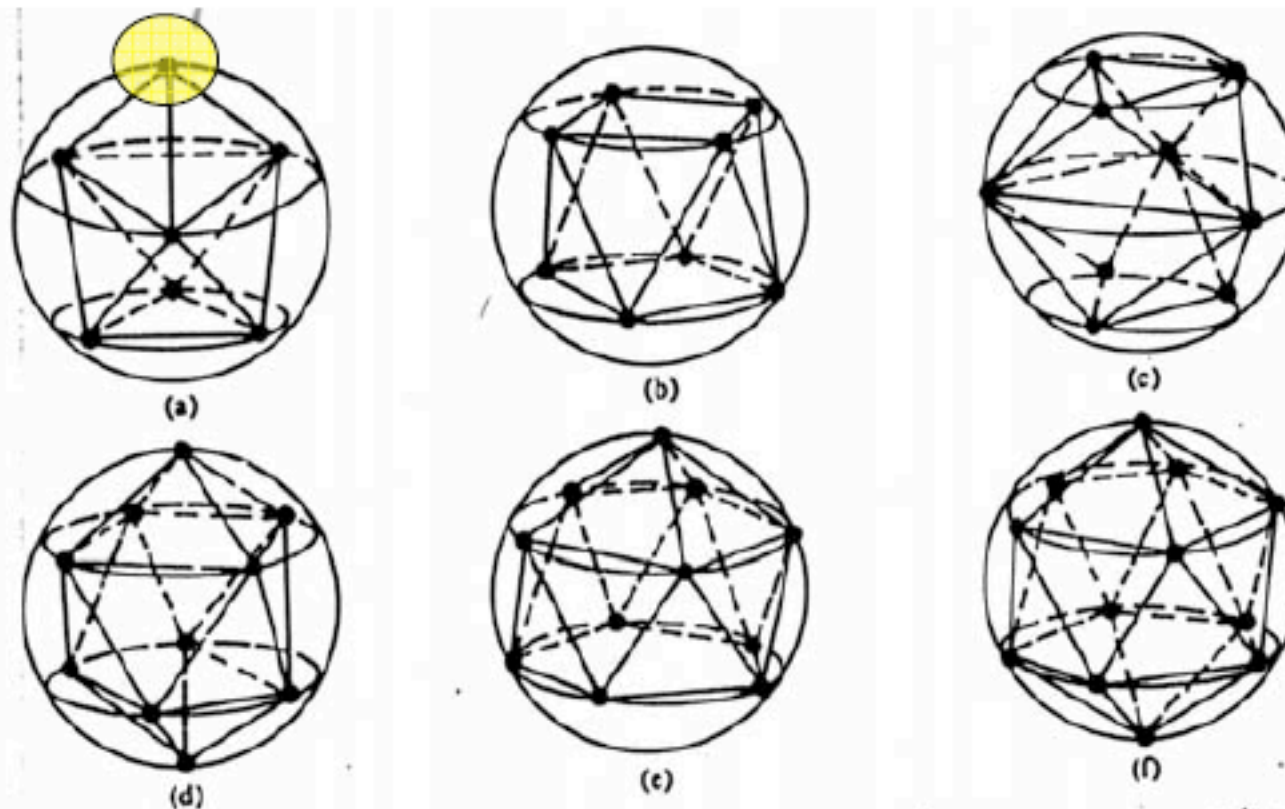
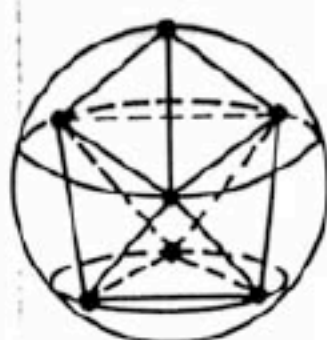
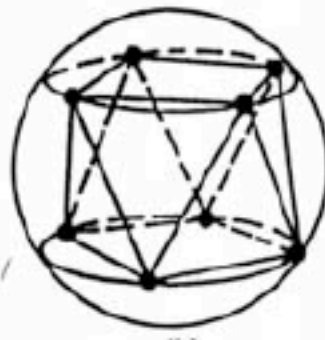


Figure 2-10 Arrangements of 7 through 12 electron pairs on a sphere to maximize distance between pairs. (a) 7 pairs: monocapped octahedron; (b) 8 pairs: square antiprism; (c) 9 pairs: tricapped trigonal prism; (d) 10 pairs: bicapped square antiprism; (e) 11 pairs: monocapped pentagonal antiprism; (f) 12 pairs: icosahedron.

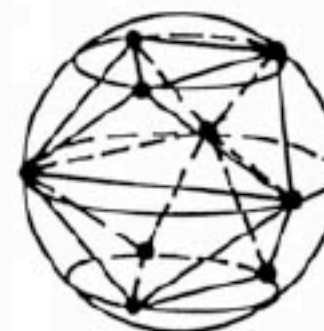
**IF<sub>7</sub> 14 e SN=7 Pentagonal bipyramidal**



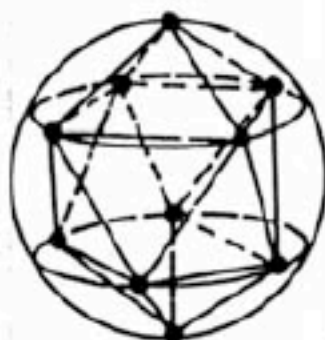
(a)



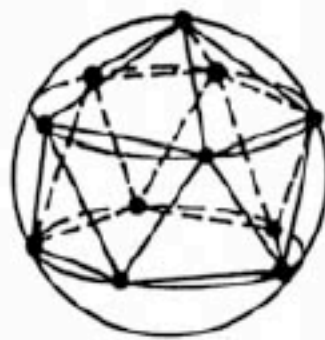
(b)



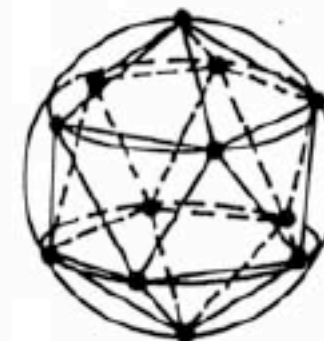
(c)



(d)



(e)



(f)

Figure 2-10 Arrangements of 7 through 12 electron pairs on a sphere to maximize distance between pairs. (a) 7 pairs: monocapped octahedron; (b) 8 pairs: square antiprism; (c) 9 pairs: tricapped trigonal prism; (d) 10 pairs: bicapped square antiprism; (e) 11 pairs: monocapped pentagonal antiprism; (f) 12 pairs: icosahedron.

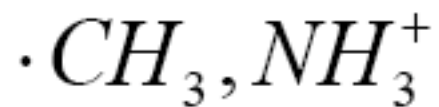


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**Some failure of VSEPR:**

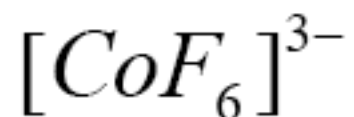


**Does not predict geometries of molecules with unpaired electron  
(USE MO instead)**



*Trigonal planar*

**Does not predict geometries of transition metal complexes**



**18 e, SN=9???**

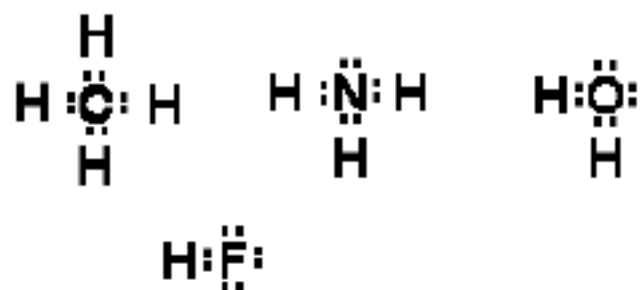


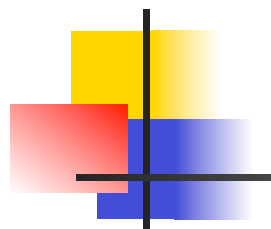
## Lewis Structure

G. N. Lewis (UC, Berkeley, 1915)

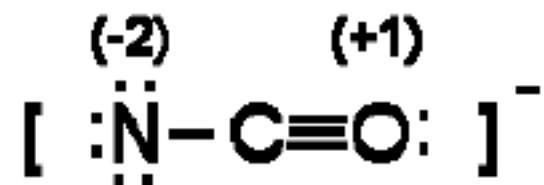
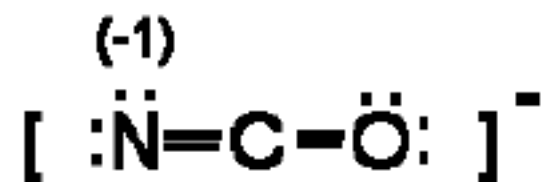
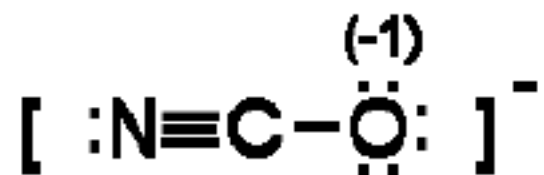


**Octet Rule: Closed shell configuration of 8 surrounding e**

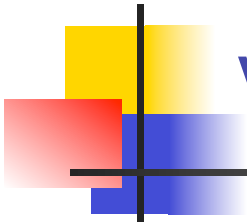




## Resonance



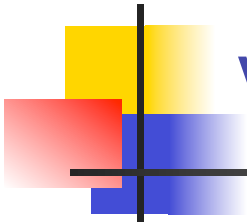
The best structure has the fewest formal charges and has the negative charge on the highest electronegativity atom.



# Valence Bond Theory vs. MO Theory

---

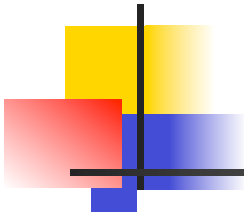
- There are two major models for bonding theory:
  - **molecular orbital theory** – in which atomic orbitals are combined to make molecular orbitals in which electrons reside. From a computational perspective, MO calculations are much simpler than the alternative, and there are several very good software packages that allow just about anyone to build models and use MO theory to predict their properties. Even organic chemists. ☺
  - The alternative is **valence bond theory**. In valence bond theory, the orbitals on each atom are first “hybridized” so that they can then be combined to make localized bonds. This is more computationally difficult than molecular orbital theory – particularly for larger molecules. I don’t know of any software packages that will let the “lay chemist” do valence bond calculations.
- While some chemists like to mix VB theory into their MO theory (or MO theory into their VB theory), it’s not good practice.



# Valence Bond Theory vs. MO Theory

---

- VB Theory begins with two steps:
  - hybridization (*where necessary to get atomic orbitals that "point at each other"*)
  - combination of hybrid orbitals to make bonds with electron density localized between the two bonding atoms
- Key differences between MO and VB theory:
  - MO theory has electrons distributed over molecule
  - VB theory localizes an electron pair between two atoms
  - MO theory combines AOs on DIFFERENT atoms to make MOs (*LCAO*)
  - VB theory combines AOs on the SAME atom to make hybridized atomic orbitals (*hybridization*)
  - In MO theory, the symmetry (or antisymmetry) must be retained in each orbital.
  - In VB theory, all orbitals must be looked at at once to see retention of the molecule's symmetry.



## Valence Bond theory

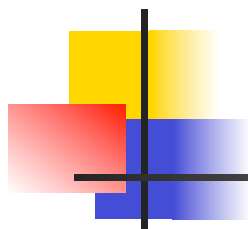


Heitler, London (1927)  
L. Pauling (orbital hybridization)  
Localized orbital approach



Investigating ground state molecules, molecular geometry  
Bond dissociation energy





## **Molecular Orbital theory**



**Mulliken**

**Delocalized orbital approach**

**Unoccupied orbital**

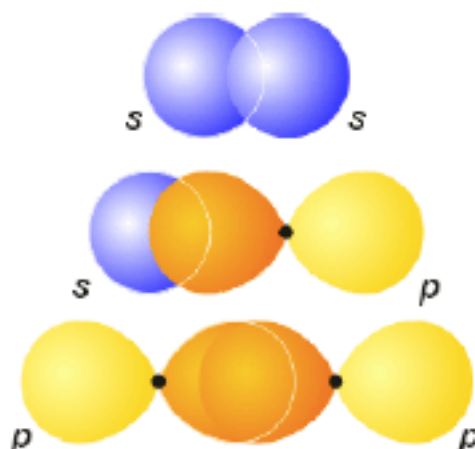
**Spectroscopic properties  
(ionization, excited states)**

# Valence Bond Theory

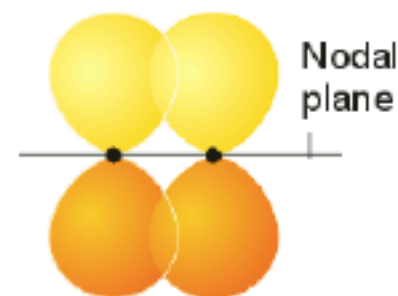
Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy *directed orbitals* localized on a particular atom. The directionality of the orbitals is determined by the geometry around the atom which is obtained from the predictions of VSEPR theory.

In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.

**$\sigma$  bonds:**  
symmetric about  
the internuclear  
axis

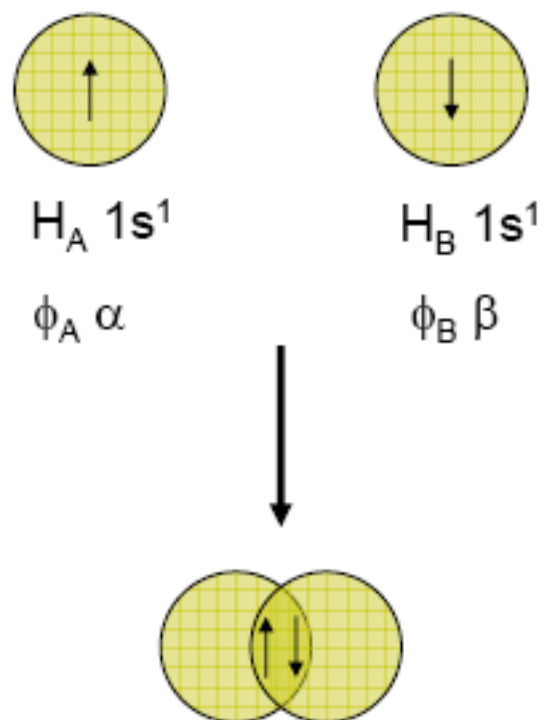


**$\pi$  bonds:** have  
a node on the  
inter-nuclear axis  
and the sign of  
the lobes  
changes across  
the axis.

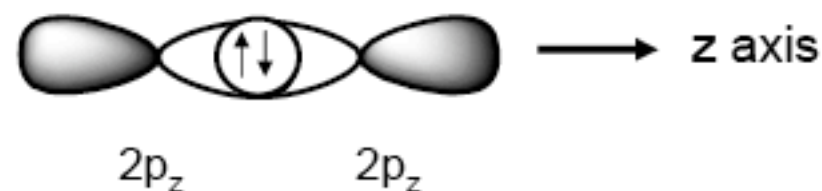
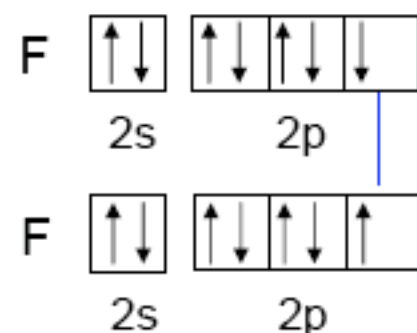


# Valence Bond Theory

Valence bond theory treatment of bonding in  $H_2$  and  $F_2$



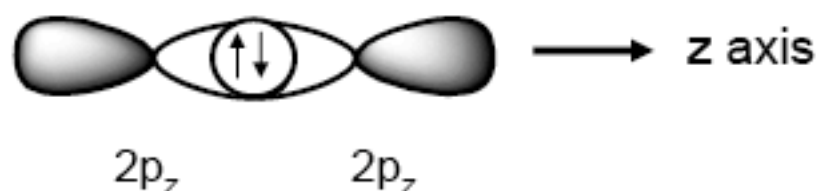
This gives a  $1s-1s$   $\sigma$  bond between the two H atoms.



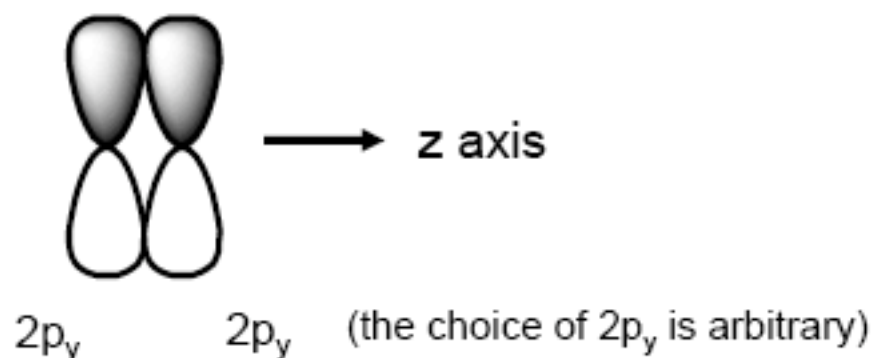
This gives a  $2p-2p$   $\sigma$  bond between the two F atoms.

*For the VBT treatment of bonding, we ignore the anti-bonding.*

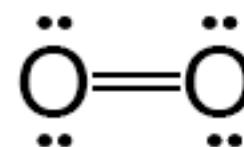
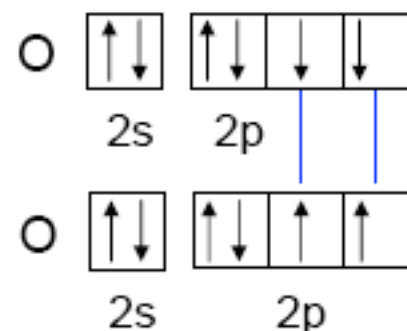
## Valence bond theory treatment of bonding in O<sub>2</sub>



This gives a 2p-2p  $\sigma$  bond between the two O atoms.



This gives a 2p-2p  $\pi$  bond between the two O atoms. In VBT,  $\pi$  bonds are predicted to be weaker than  $\sigma$  bonds because there is less overlap.

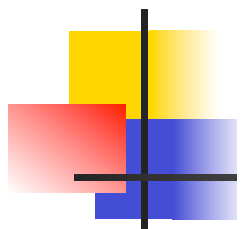


Lewis structure

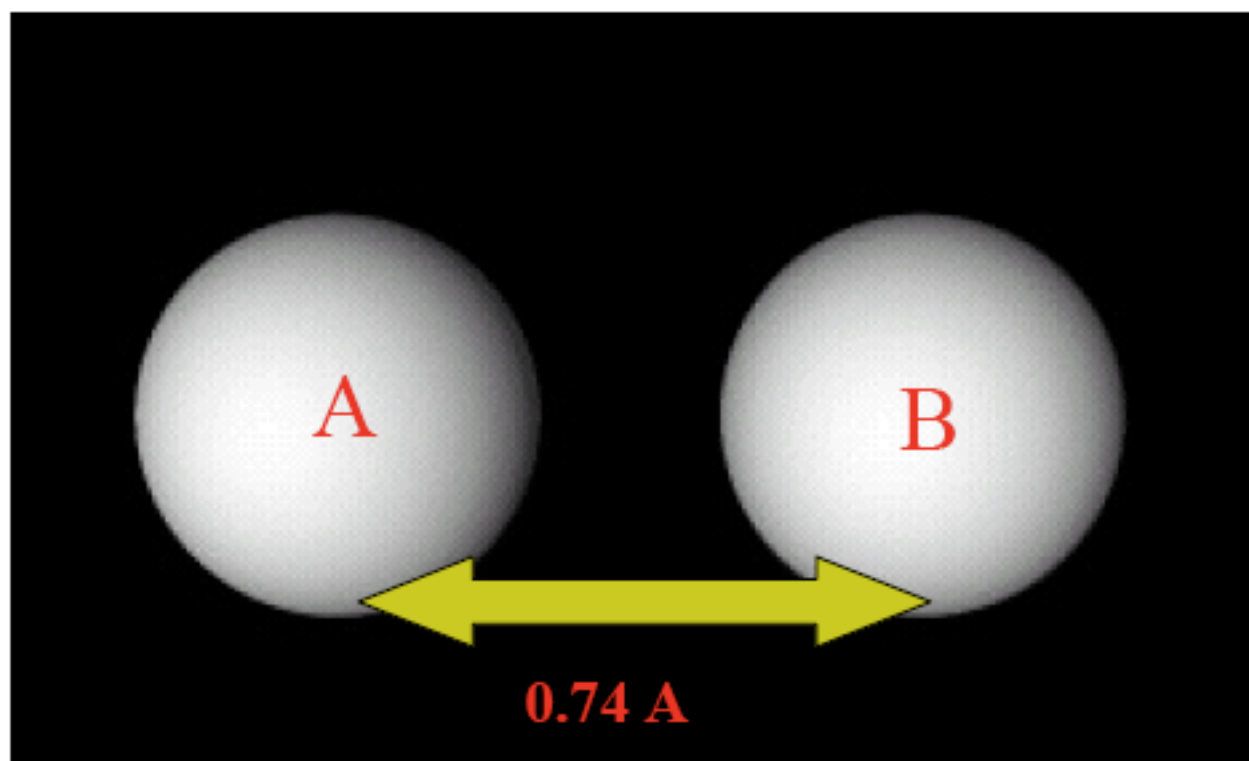
Double bond:  $\sigma$  bond +  $\pi$  bond

Triple bond:  $\sigma$  bond + 2  $\pi$  bonds

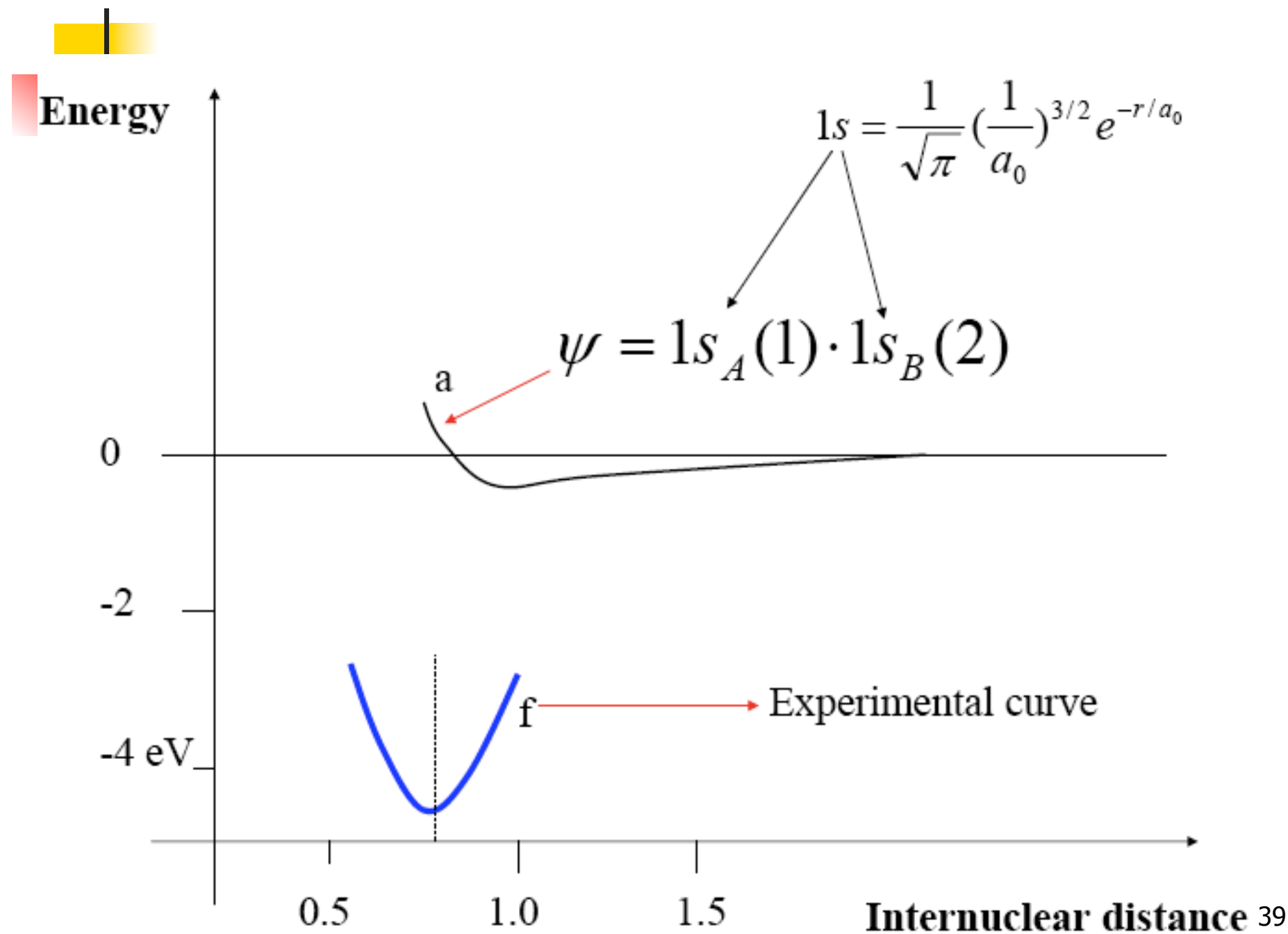
The Lewis approach and VBT predict that O<sub>2</sub> is diamagnetic – this is wrong!

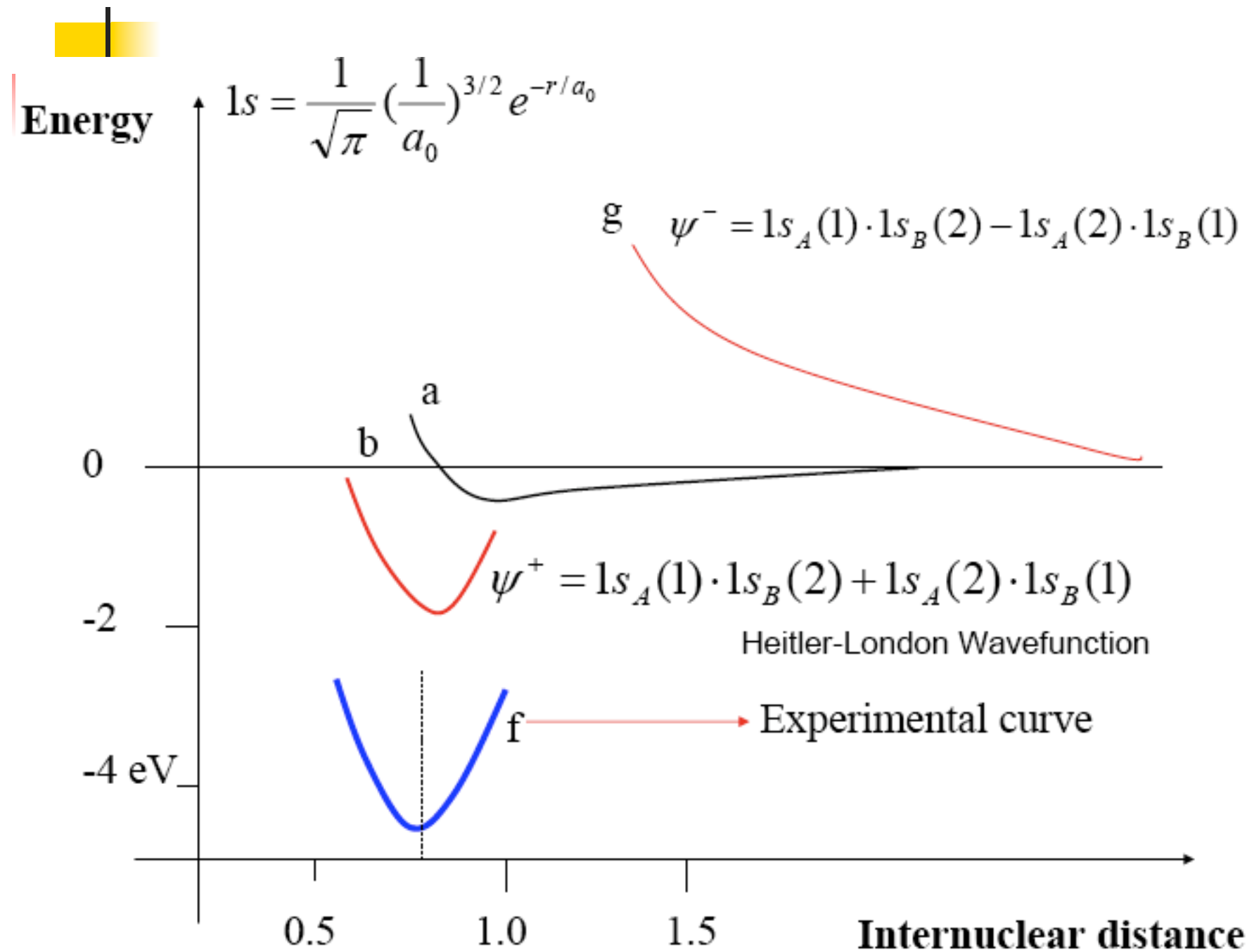


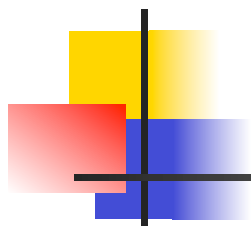
## Valence Bond theory



Bond dissociation energy: 103 kcal/mol



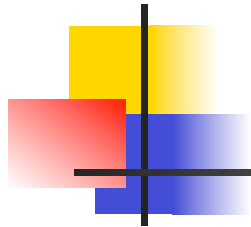




## Variation Principle:

If an arbitrary wavefunction is used to calculate the energy, then the value obtained is **never less** than the true value.

$$\langle \underline{H} \rangle = \frac{\int \Psi^*(\mathbf{x}) \underline{H} \Psi(\mathbf{x}) d\mathbf{x}}{\int \Psi^*(\mathbf{x}) \Psi(\mathbf{x}) d\mathbf{x}} = \frac{\langle \Psi | \underline{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$



## Variation Principle:

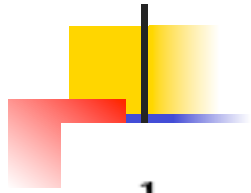


If an arbitrary wavefunction is used to calculate the energy, then the value obtained is **never less** than the true value.

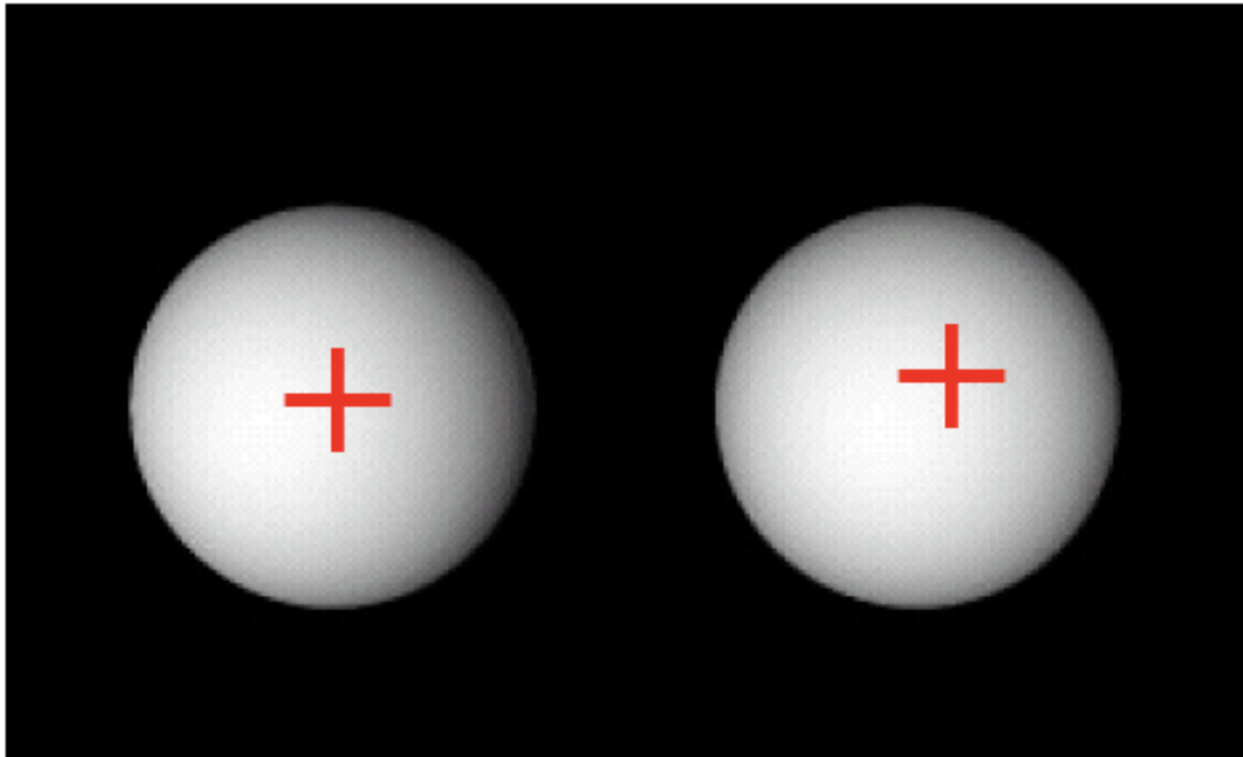
Can always minimize  $E_{\psi(x)}$



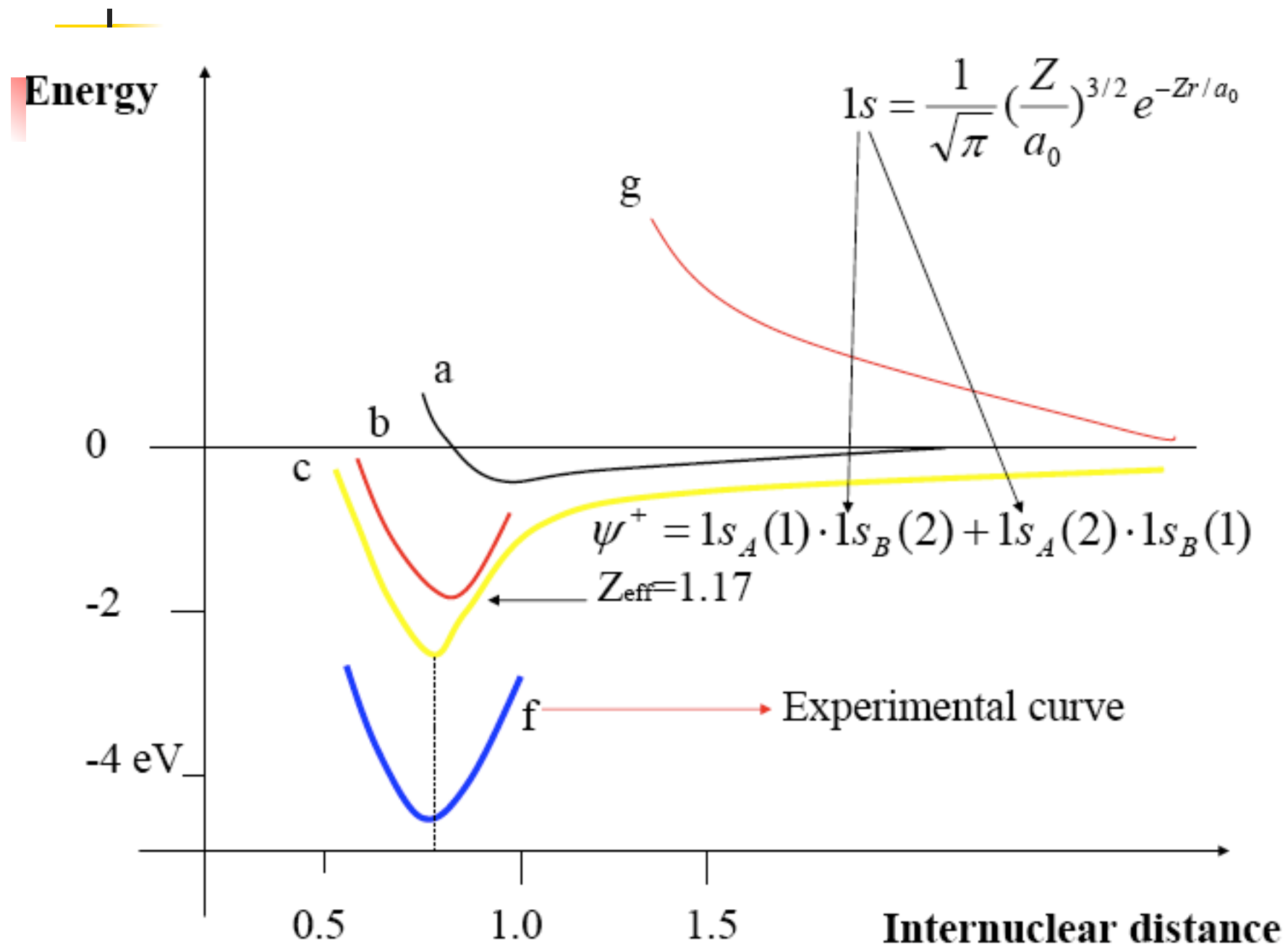
$\psi(x)$

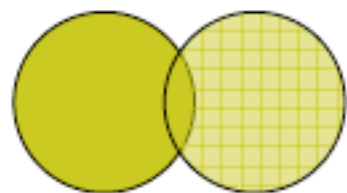


$$1s = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

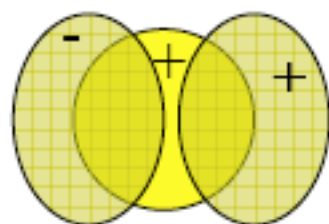
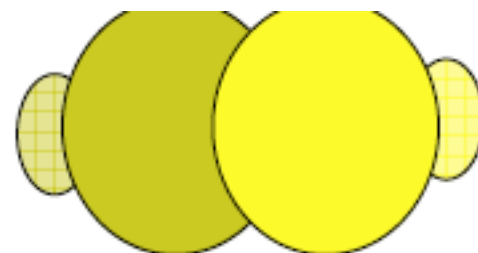


$$1s = \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$



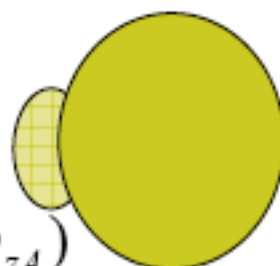


## Promoting electron Orbital Hybridization



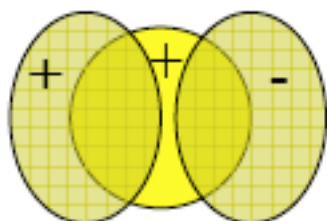
$1s_a$

$2p_{za}$



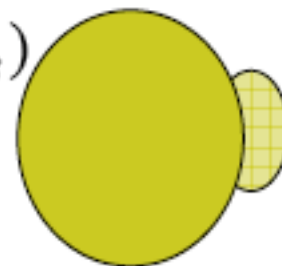
$\varphi_A$

$$\varphi_A = N(1s_A + \gamma 2p_{zA})$$



$1s_b$

$2p_{zb}$



$\varphi_B$

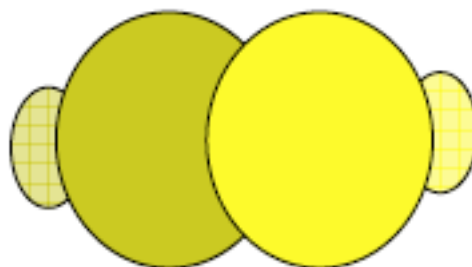
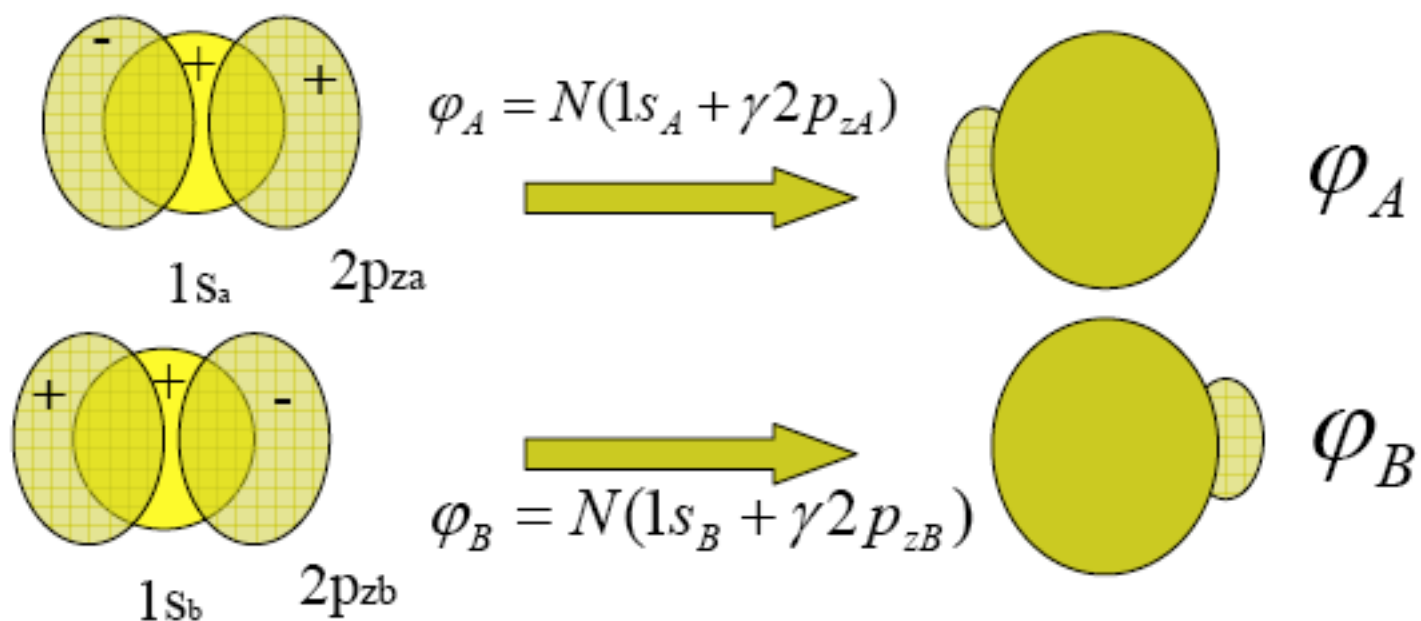
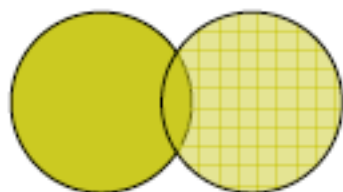
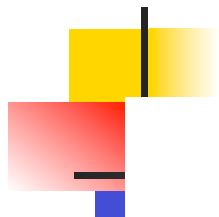
$$\varphi_B = N(1s_B + \gamma 2p_{zB})$$

s contribution

$$\frac{1}{1+r^2}$$

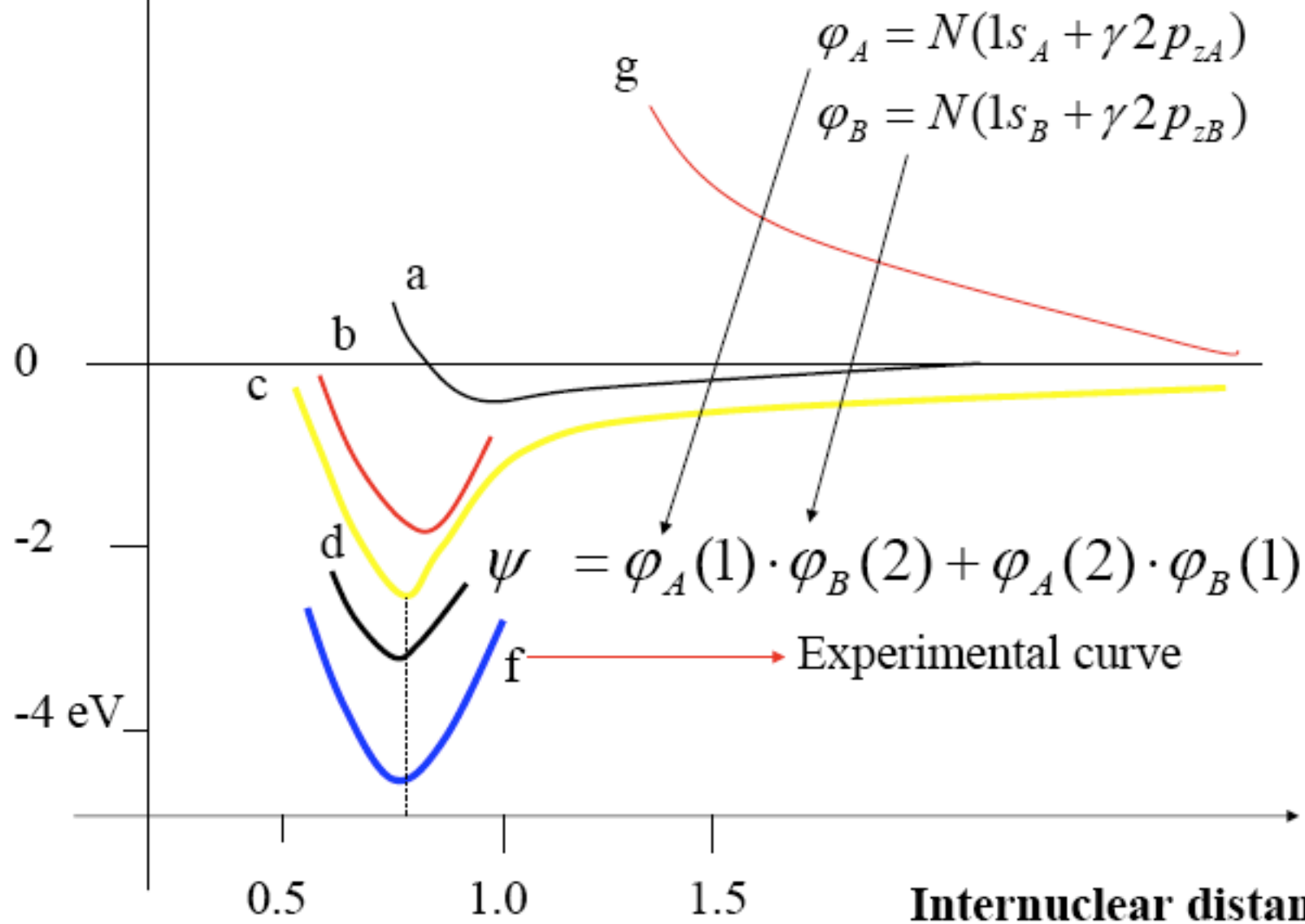
p contribution

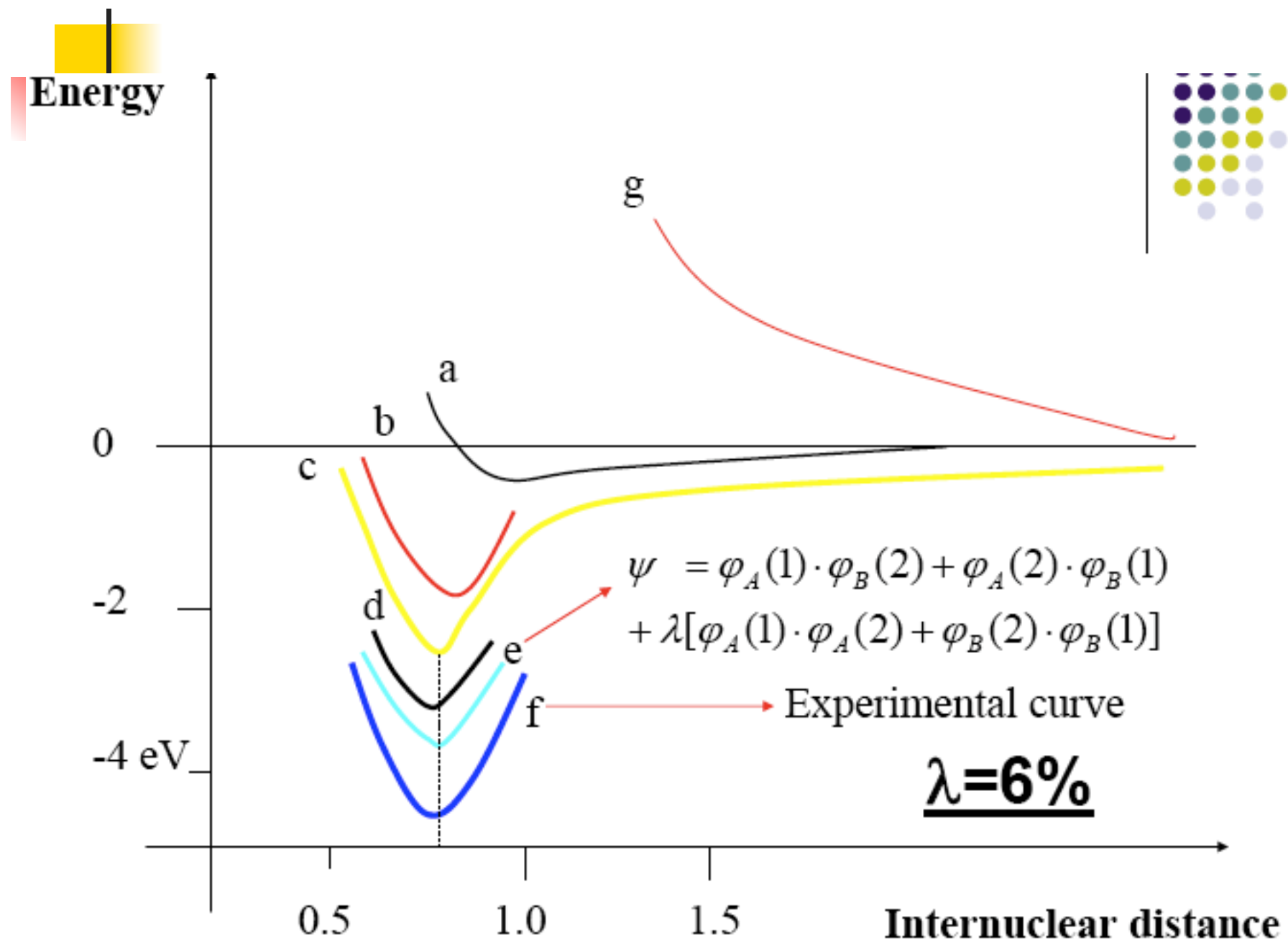
$$\frac{r^2}{1+r^2}$$



**$\gamma=0.1$**

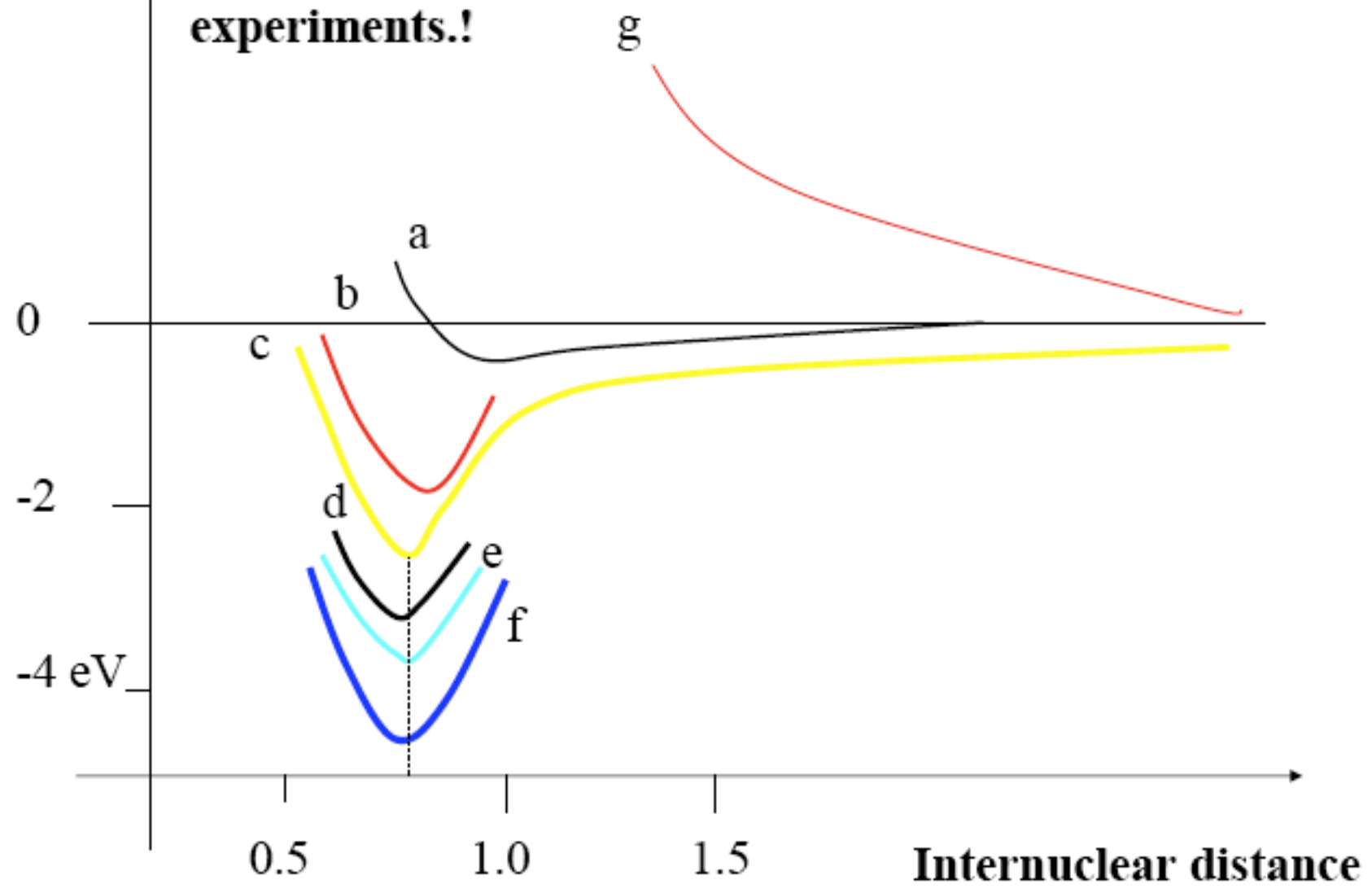
Energy







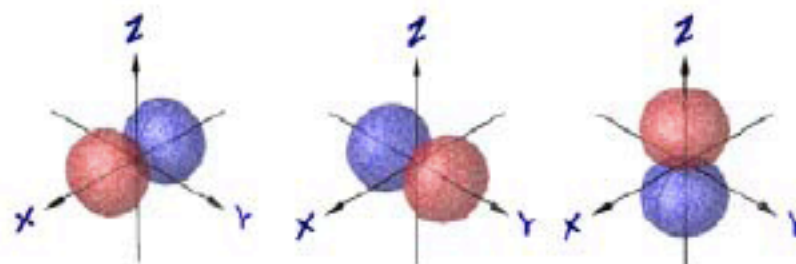
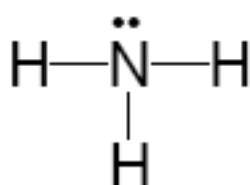
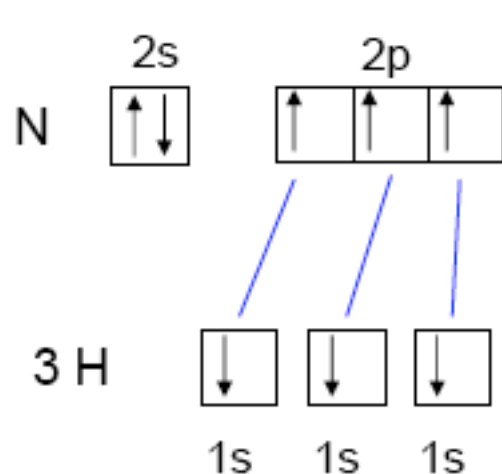
**Valence bond theory is all about promoting e and hybridizing orbitals into the shape required by experiments.!**



## Directionality

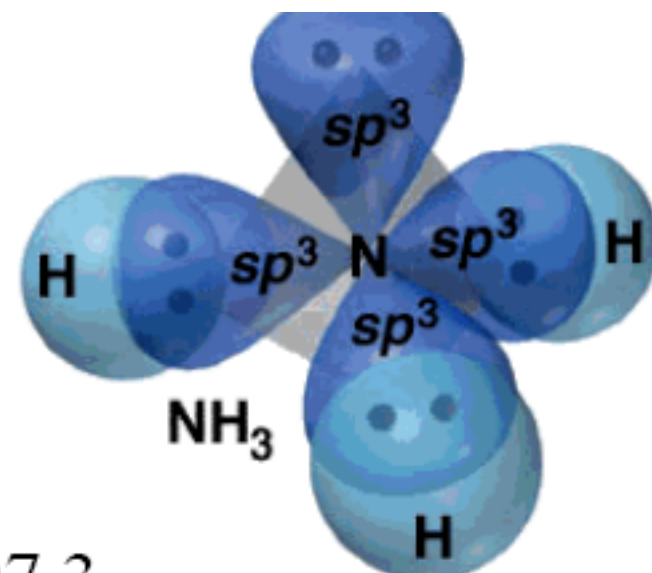
The bonding in diatomic molecules is adequately described by combinations of “pure” atomic orbitals on each atom. The only direction that exists in such molecules is the inter-nuclear axis and the geometry of each atom is undefined in terms of VSEPR theory (both atoms are terminal). This is not the case with polyatomic molecules and the orientation of orbitals is important for an accurate description of the bonding and the molecular geometry.

Examine the predicted bonding in ammonia using “pure” atomic orbitals:



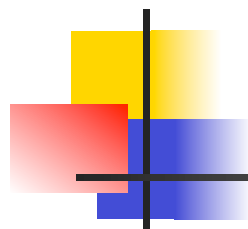
The  $2p$  orbitals on N are oriented along the X, Y, and Z axes so we would predict that the angles between the  $2p$ - $1s$   $\sigma$  bonds in  $\text{NH}_3$  would be  $90^\circ$ . We know that this is not the case.



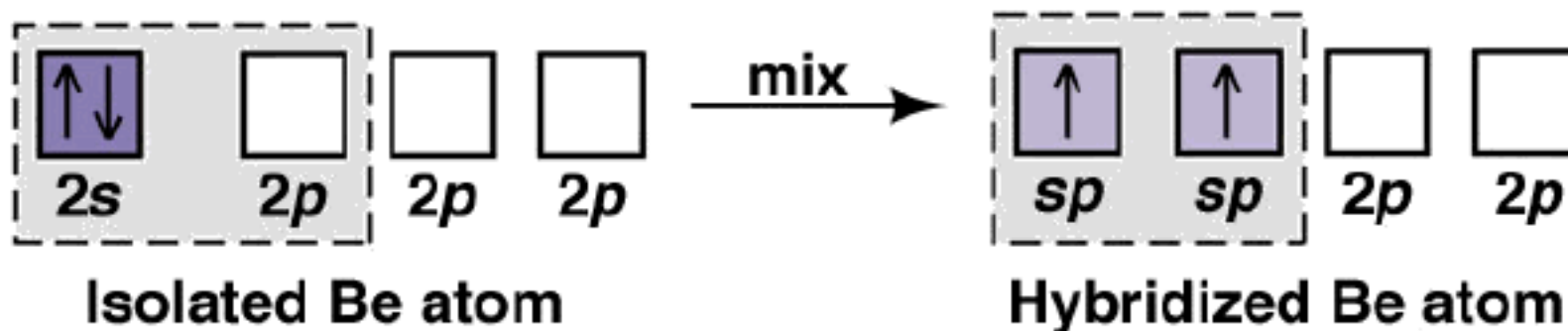


$$\angle H - N - H = 107.3$$

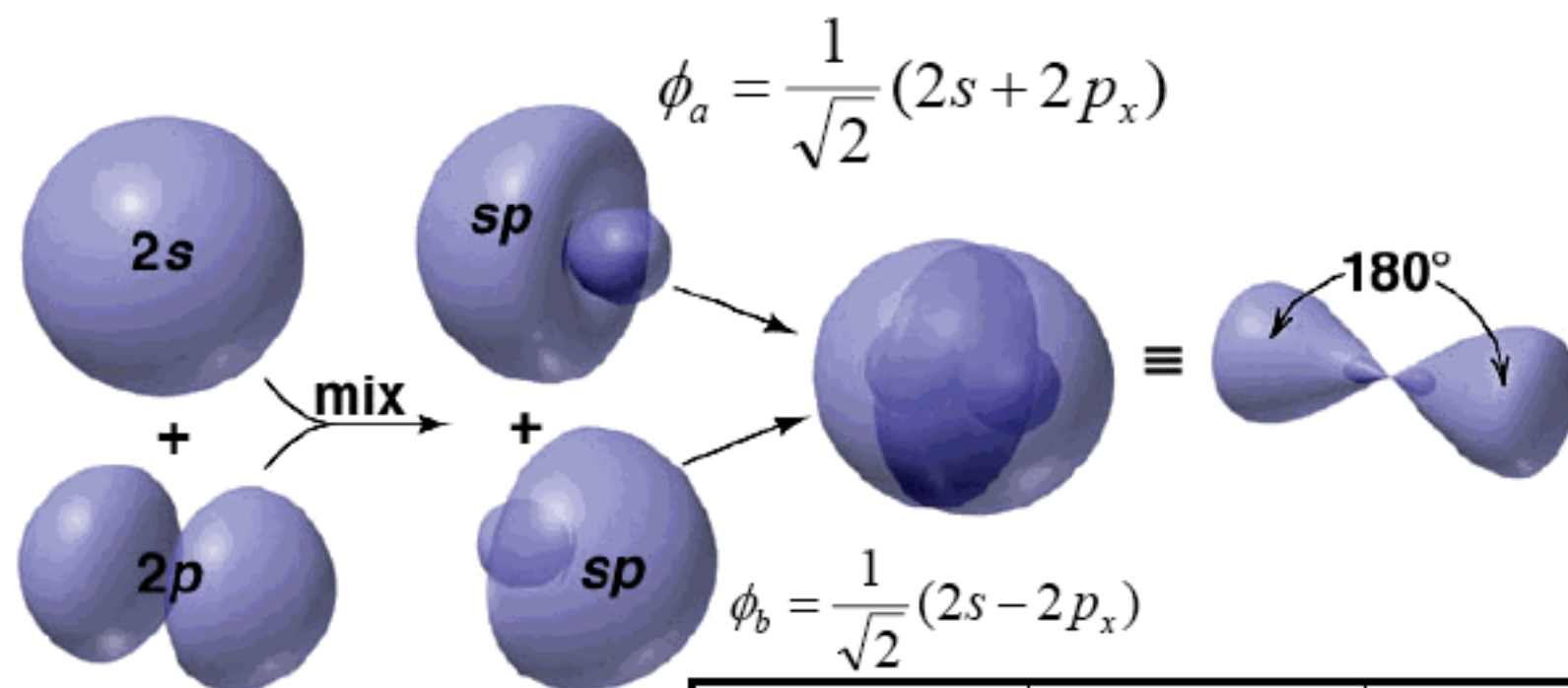
|                    | p<br>character | s<br>character |
|--------------------|----------------|----------------|
| Bonding<br>orbital | 77%            | 23%            |
| lp<br>orbital      | 69%            | 31%            |



## Orbital Box Diagram for Hybridization in Be

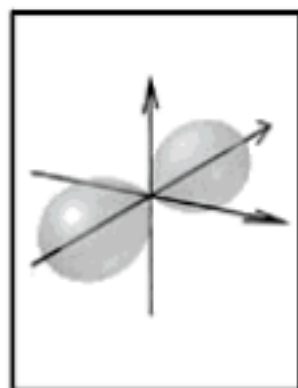


# The $sp$ Hybrid Orbitals in Gaseous $\text{BeCl}_2$

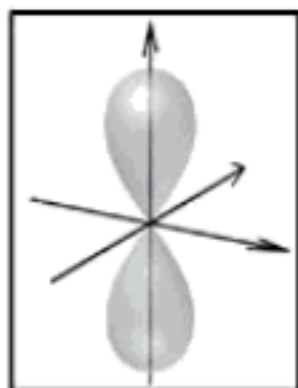


|                    | p<br>character | s<br>character |
|--------------------|----------------|----------------|
| Bonding<br>orbital | 50%            | 50%            |

# Orbital Box Diagram with Orbital Contours

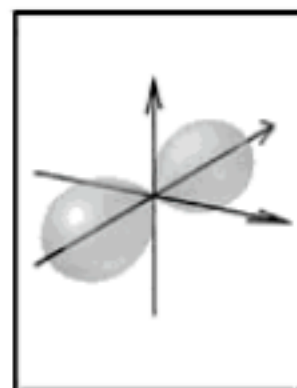


$2p_y$   
empty

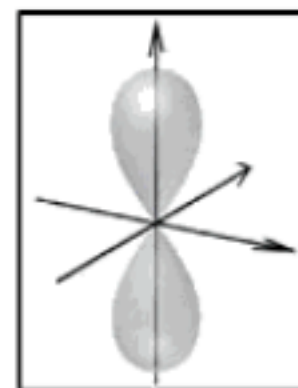


$2p_z$   
empty

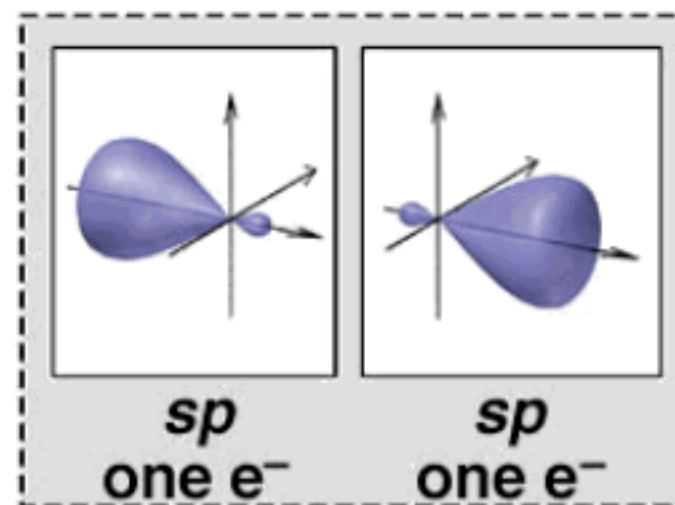
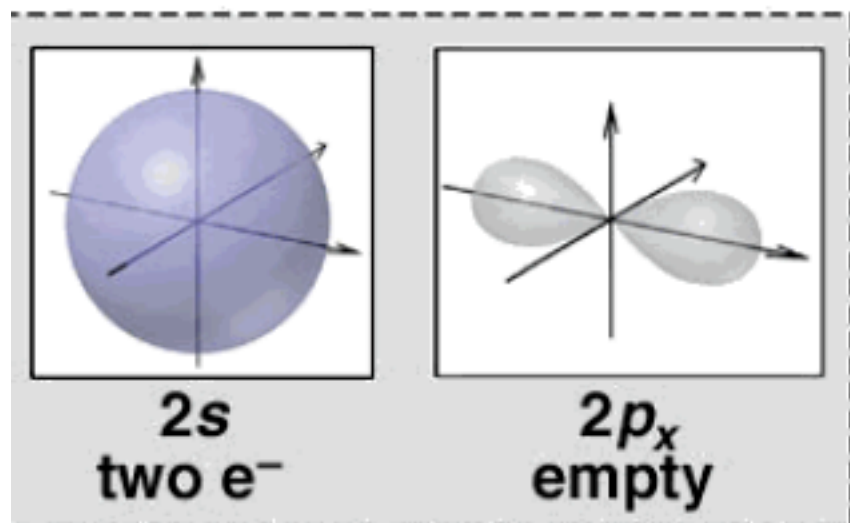
$\xrightarrow{\text{mix}}$



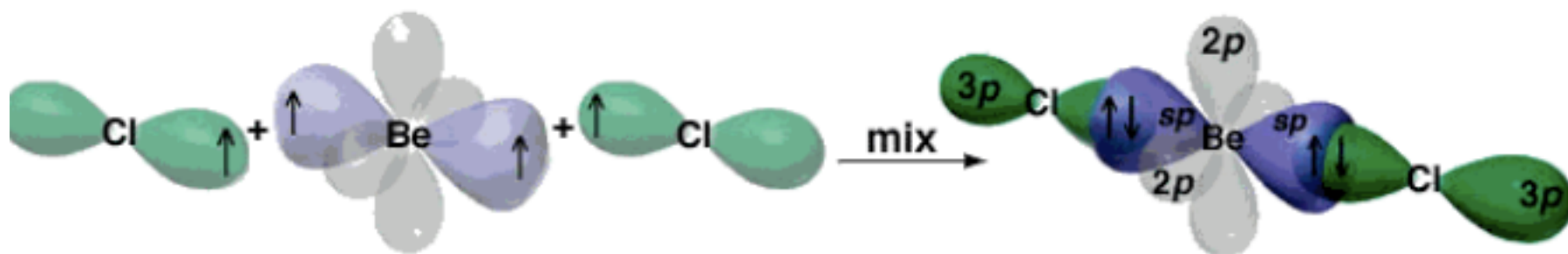
$2p_y$   
empty



$2p_z$   
empty



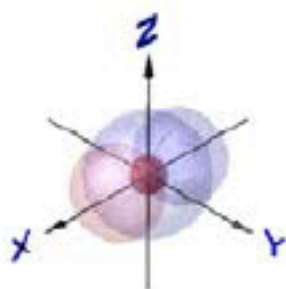
# The $sp$ Hybrid Orbitals in Gaseous $\text{BeCl}_2$



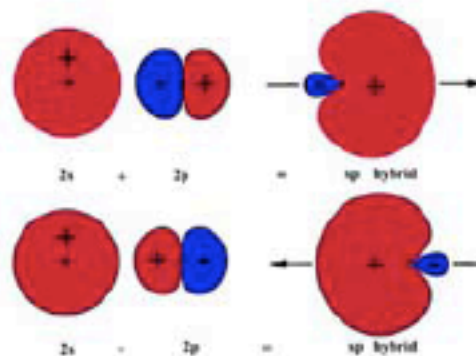
# Hybridization

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.

## Linear sp hybrid orbitals



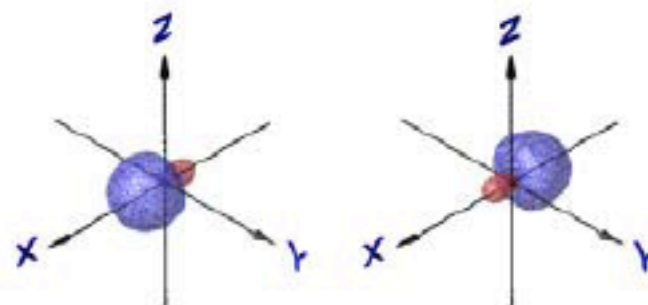
A 2s orbital superimposed on a 2p<sub>x</sub> orbital



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

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

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



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



## 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 ( $\phi$ ) we use can be considered to be both orthogonal and normal or “orthonormal”.

Example of the orthogonality of  $\Psi_1$  and  $\Psi_2$

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

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

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

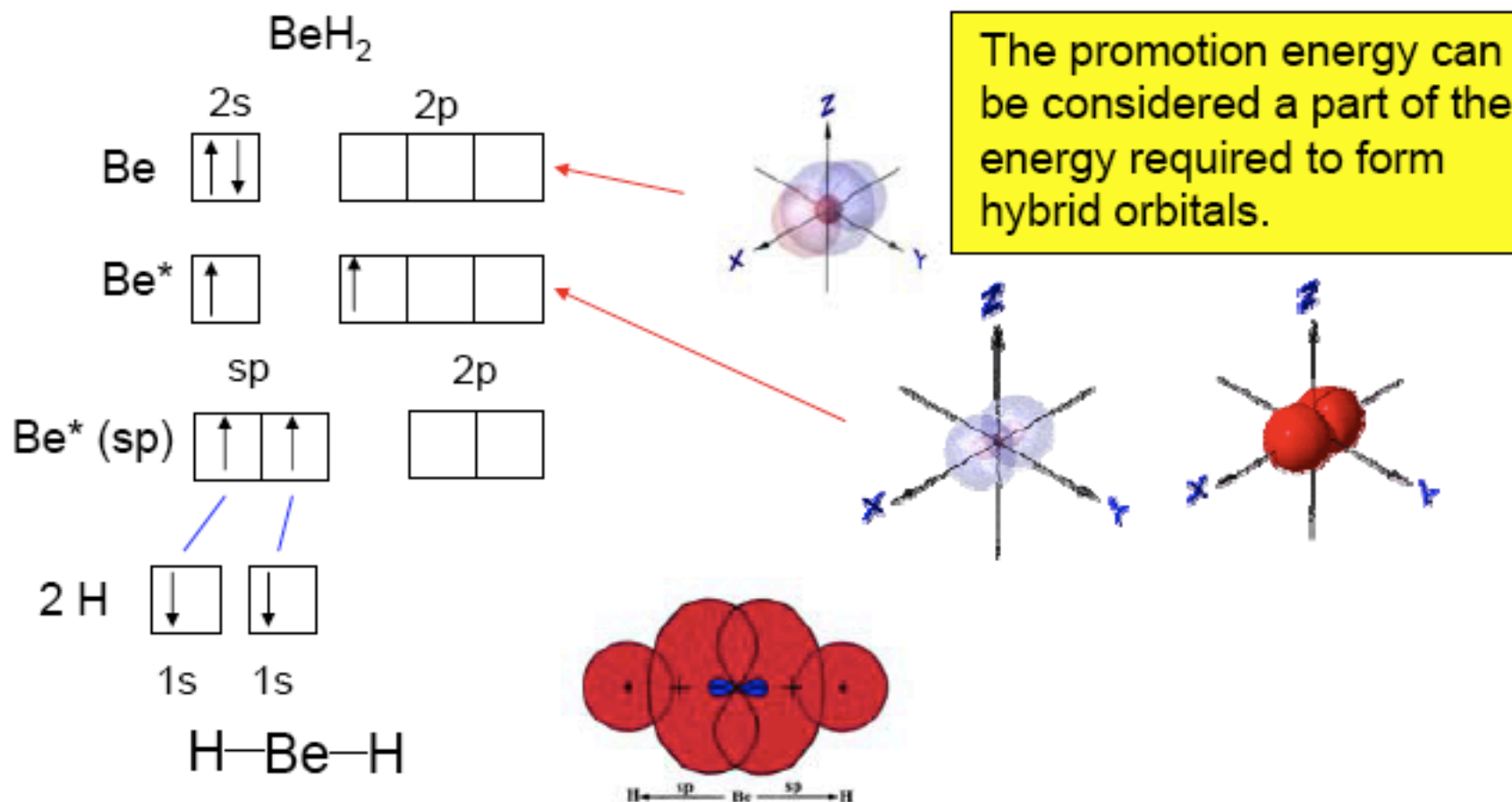
$$\int \Psi_1 \Psi_2 d\tau = \frac{1}{2}(1) - \frac{1}{2}(0) + \frac{1}{2}(0) - \frac{1}{2}(1)$$

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

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

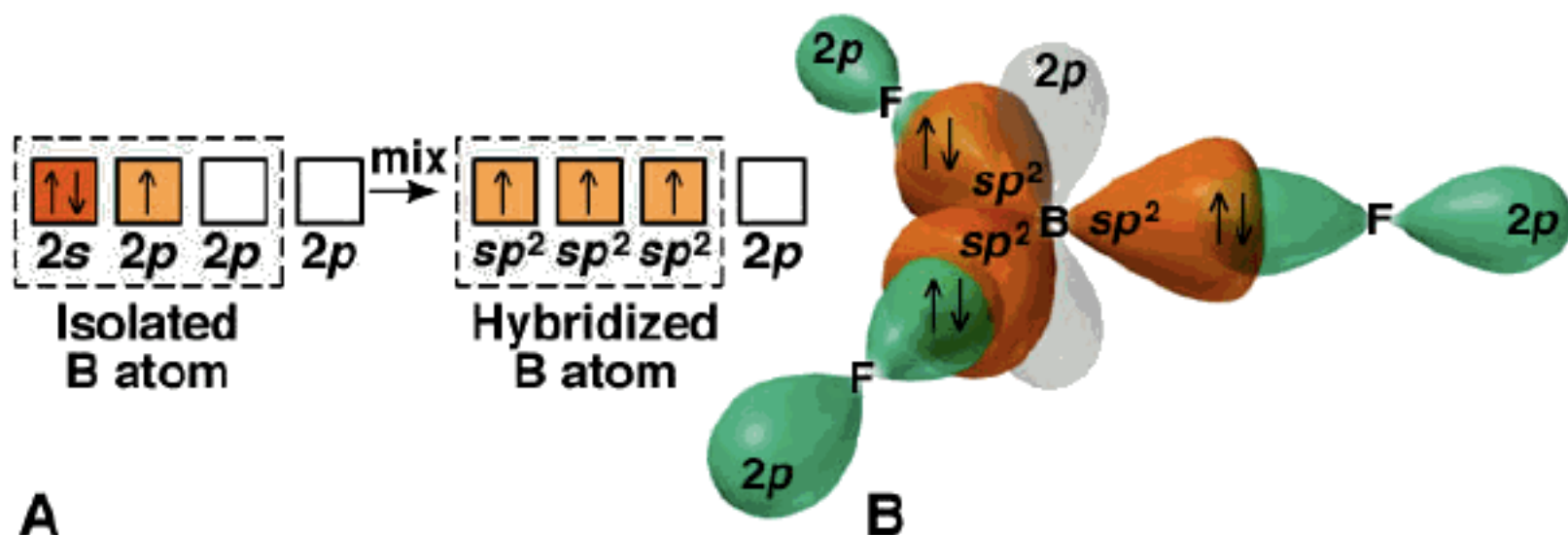
# Hybridization

Valence bond theory treatment of a linear molecule: the bonding in  $\text{BeH}_2$



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

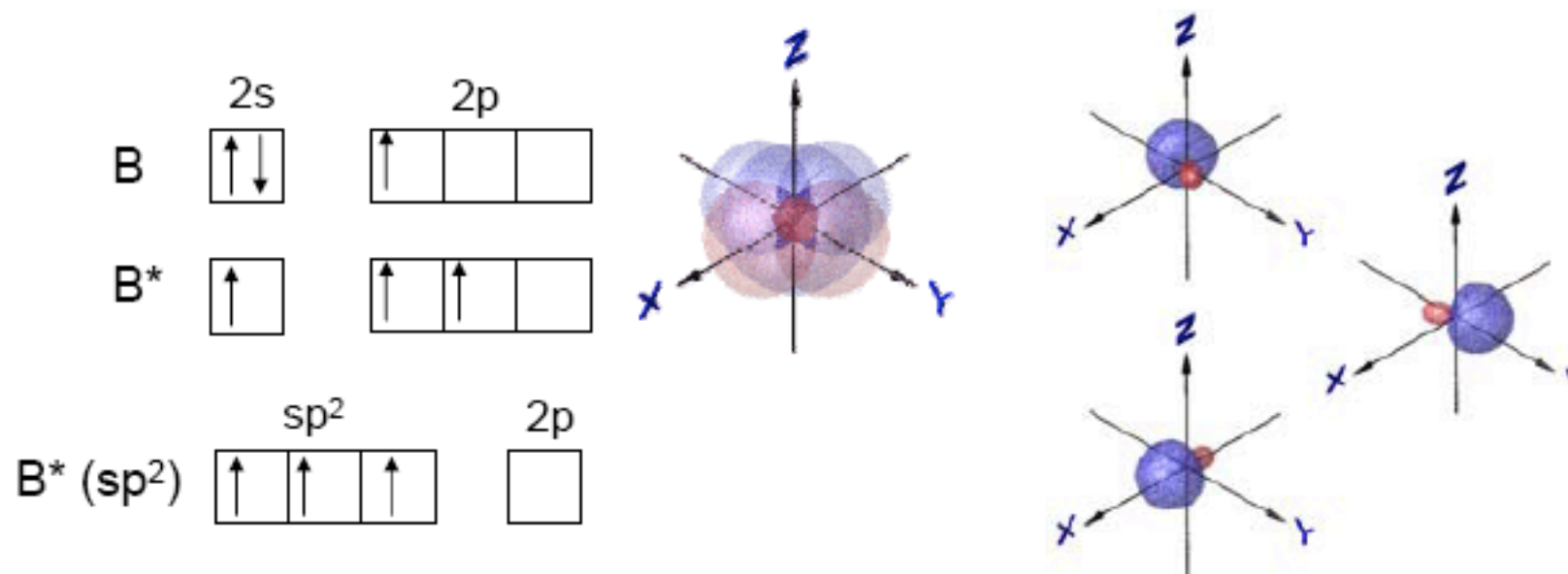
# The $sp^2$ Hybrid Orbitals in $\text{BF}_3$



|                    | p<br>character | s<br>character |
|--------------------|----------------|----------------|
| Bonding<br>orbital | 67%            | 33%            |



## Valence bond theory treatment of a trigonal planar molecule: the bonding in $\text{BH}_3$



This gives three  $\text{sp}^2$  orbitals that are oriented  $120^\circ$  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.

$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y} \quad \leftarrow \begin{array}{l} 1/3 + 1/6 + 1/2 = 1 \\ \text{So this hybrid is normal} \end{array}$$

$$\Psi_2 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y} \quad \leftarrow \begin{array}{l} 1/3 + 1/6 + 1/2 = 1 \\ \text{So this hybrid is normal} \end{array}$$

$$\Psi_3 = \frac{1}{\sqrt{3}}\phi_s + \frac{2}{\sqrt{6}}\phi_{p_x} \quad \leftarrow \begin{array}{l} 1/3 + 4/6 = 1 \\ \text{So this hybrid is normal} \end{array}$$

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

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

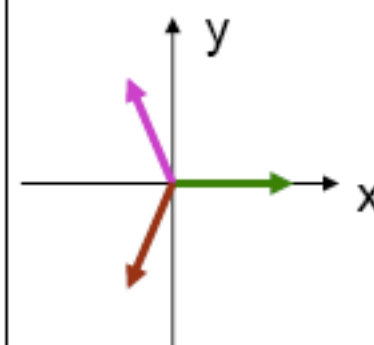
$1/2 + 1/2 = 1$   
So the entire  $p_y$  orbital  
has been used

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

$\Psi_1$ : -x, +y

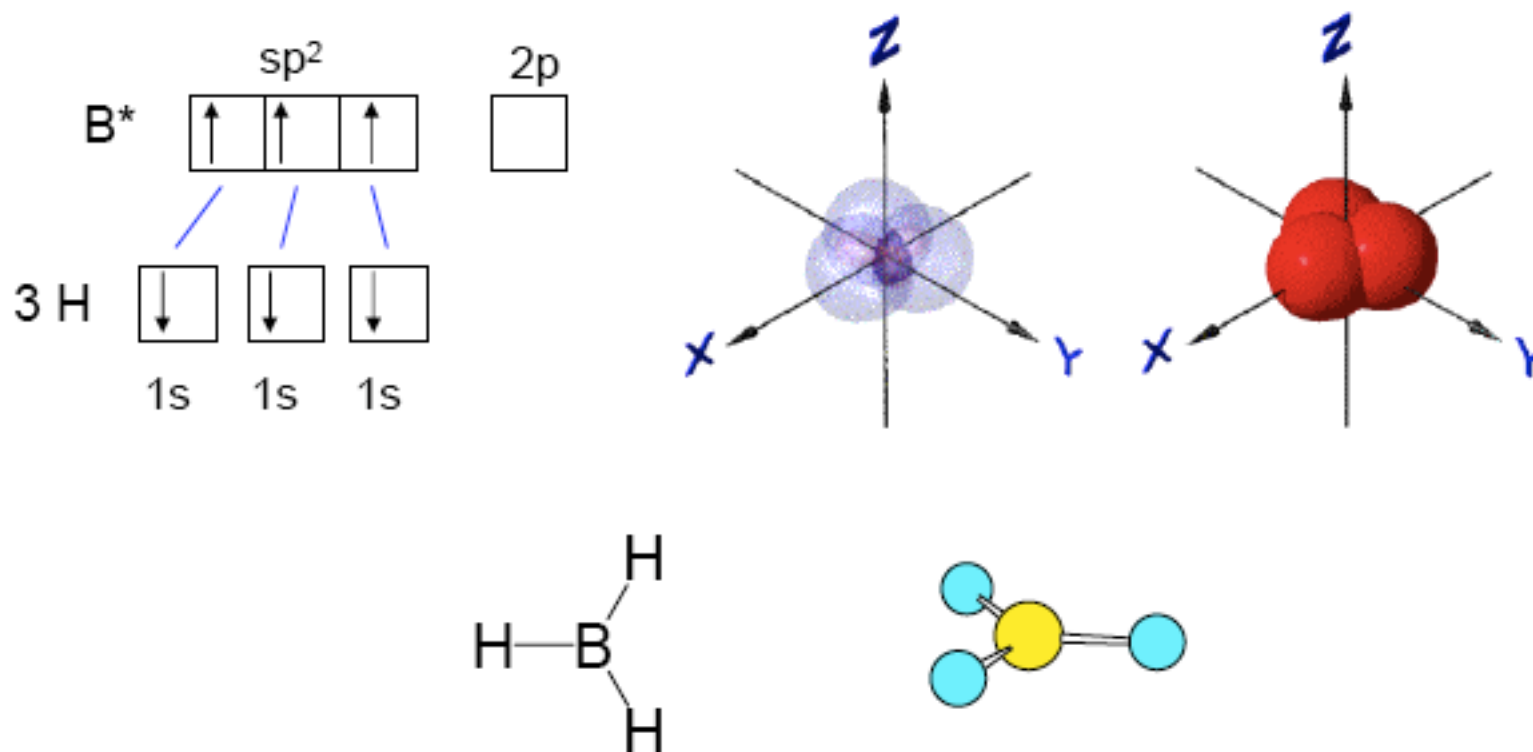
$\Psi_2$ : -x, -y

$\Psi_3$ : +x, 0y



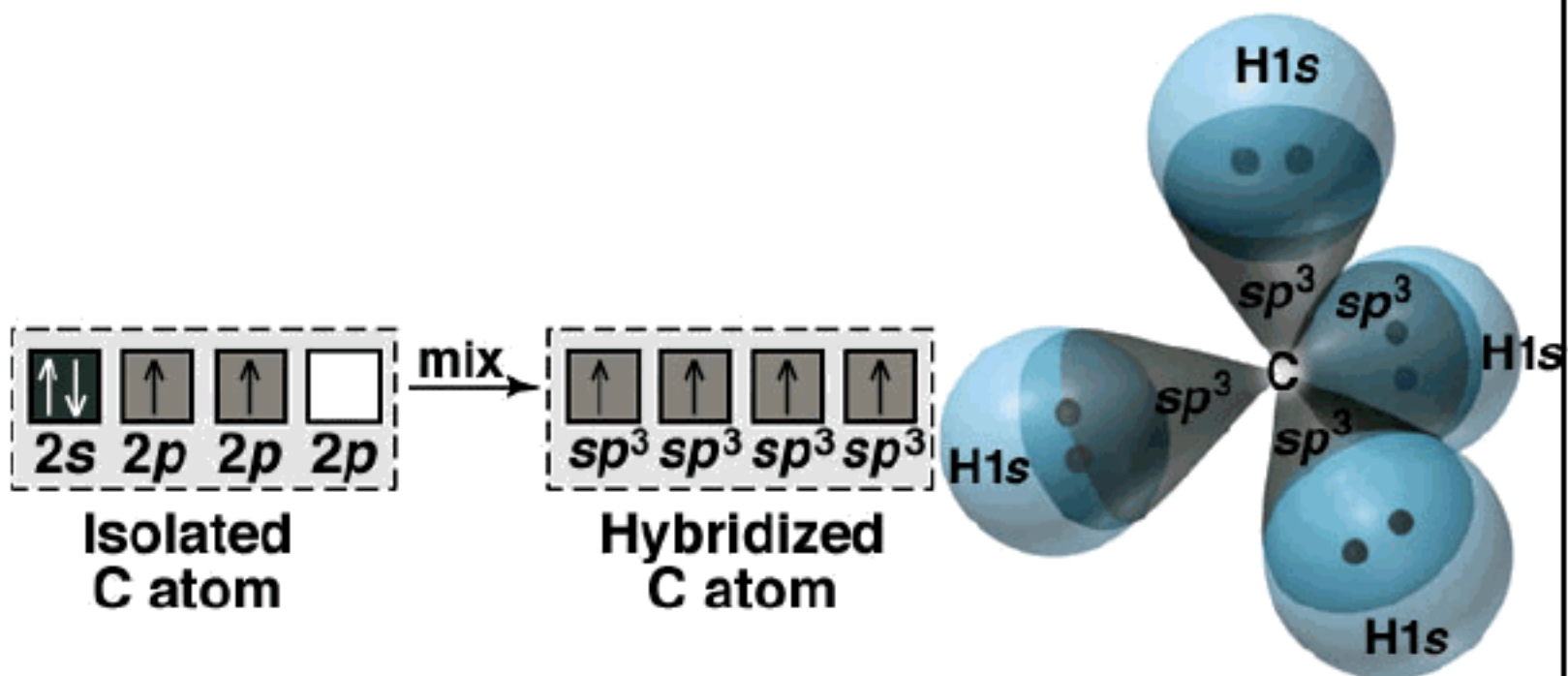


## Valence bond theory treatment of a trigonal planar molecule: the bonding in $\text{BH}_3$



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

# The $sp^3$ Hybrid Orbitals in $\text{CH}_4$

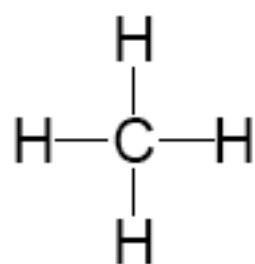
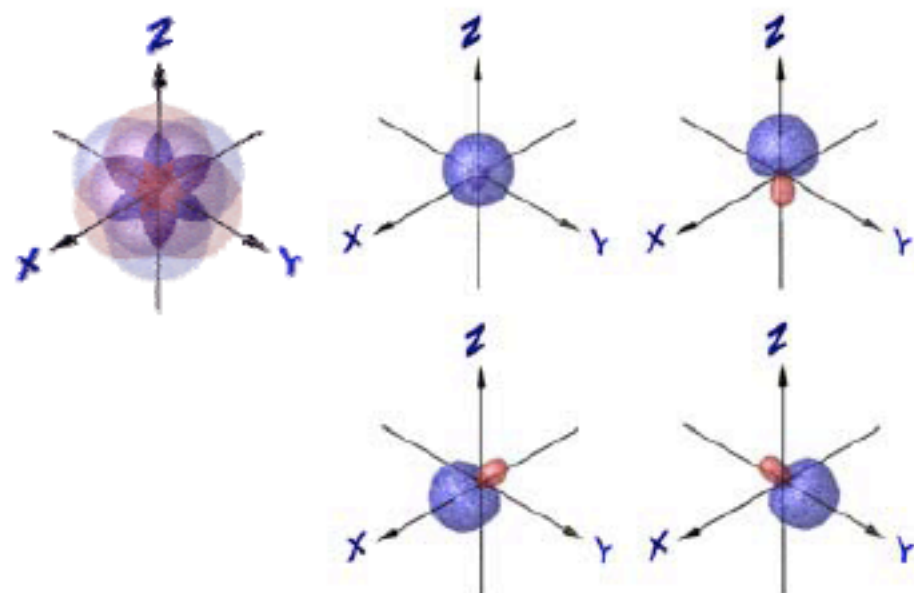
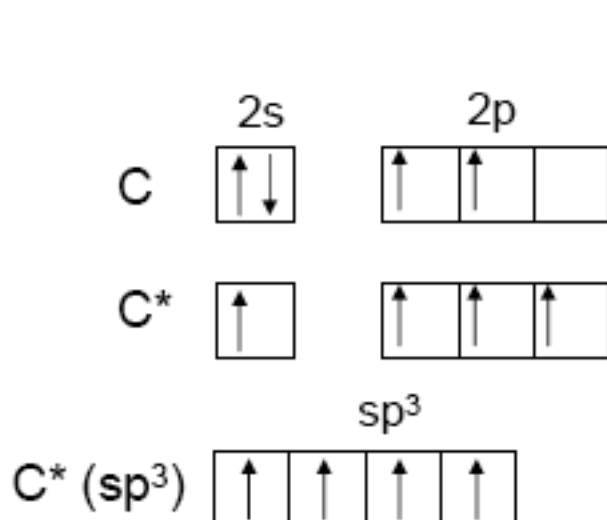


**A**

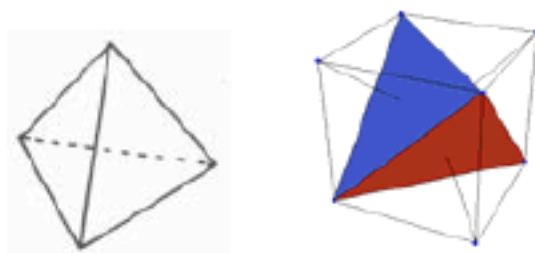
|                    | p<br>character | s<br>character |
|--------------------|----------------|----------------|
| Bonding<br>orbital | 75%            | 25%            |

**B**

# Valence bond theory treatment of a tetrahedral molecule: the bonding in CH<sub>4</sub>



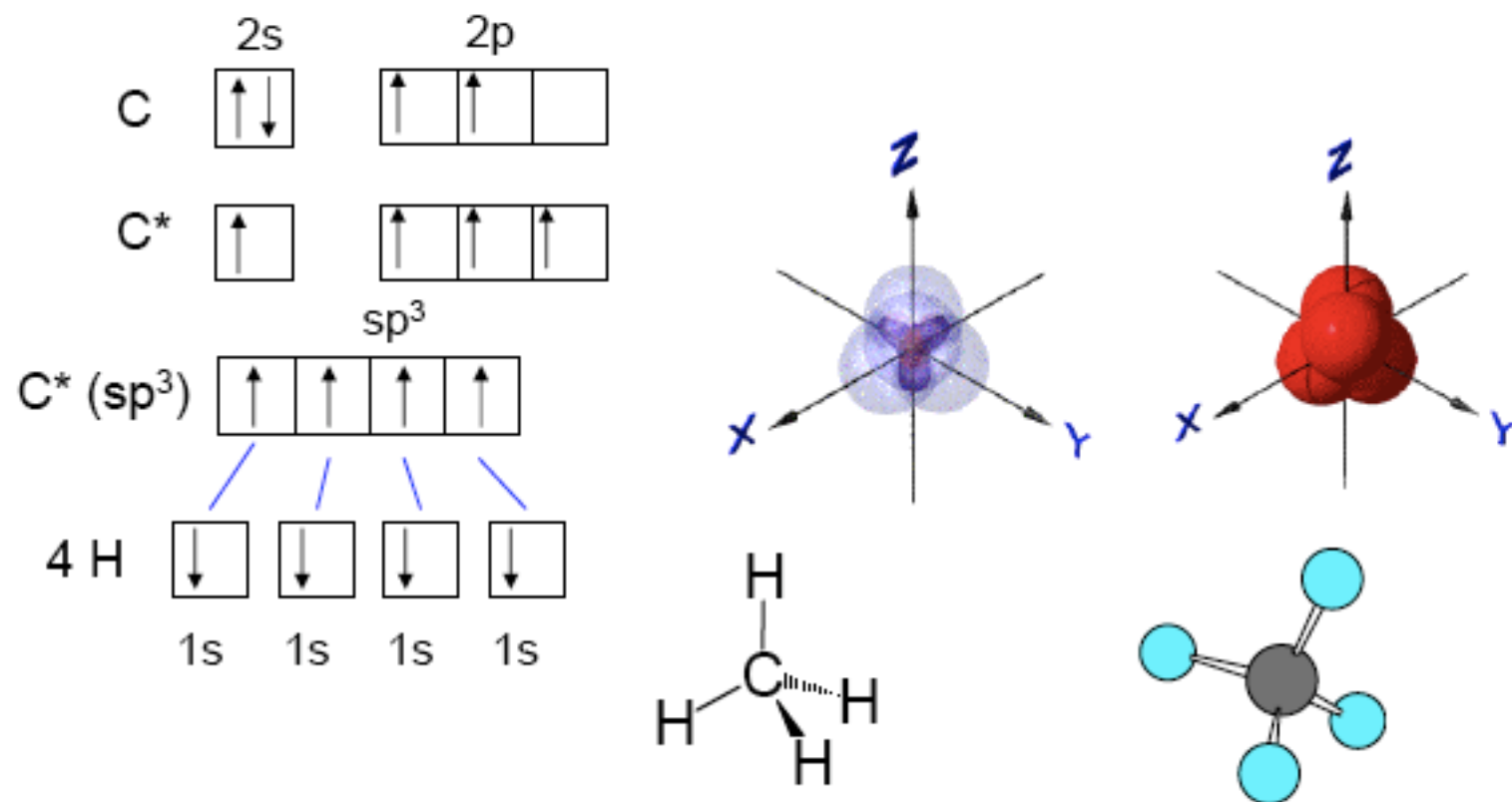
This gives four sp<sup>3</sup> orbitals that are oriented in a tetrahedral fashion.



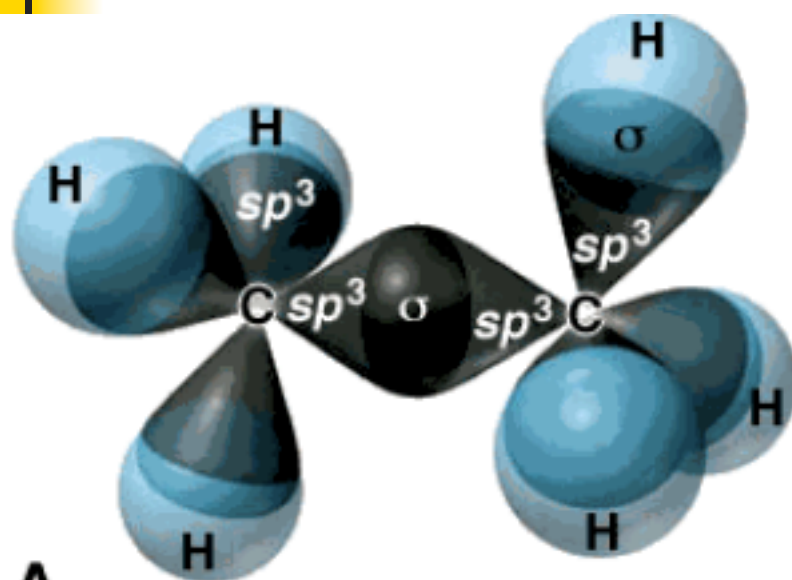
$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{4}}\phi_s + \frac{1}{\sqrt{4}}\phi_{p_x} + \frac{1}{\sqrt{4}}\phi_{p_y} + \frac{1}{\sqrt{4}}\phi_{p_z} \\ \Psi_2 &= \frac{1}{\sqrt{4}}\phi_s + \frac{1}{\sqrt{4}}\phi_{p_x} - \frac{1}{\sqrt{4}}\phi_{p_y} - \frac{1}{\sqrt{4}}\phi_{p_z} \\ \Psi_3 &= \frac{1}{\sqrt{4}}\phi_s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



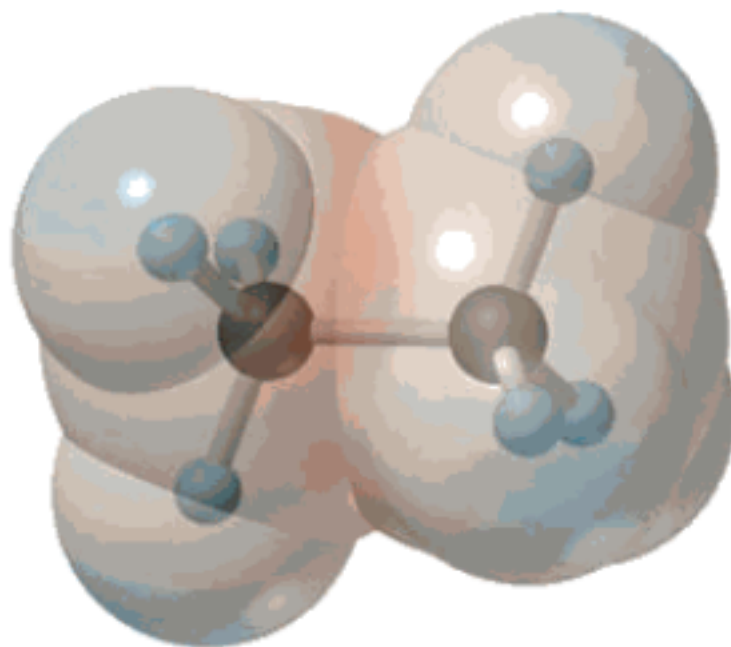
## Valence bond theory treatment of a tetrahedral molecule: the bonding in $\text{CH}_4$



The overlap of the  $\text{sp}^3$  hybrid orbitals on C with the  $1s$  orbitals on the H atoms gives four  $\text{C-H}$  ( $\text{sp}^3$ )- $1s$   $\sigma$  bonds oriented  $109.47^\circ$  from each other. This provides the tetrahedral geometry predicted by VSEPR theory.

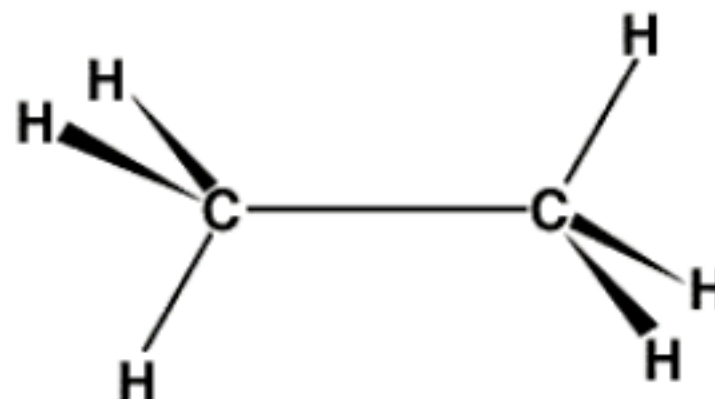


A



B

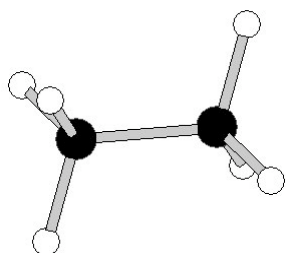
## The $\sigma$ Bonds in Ethane ( $\text{C}_2\text{H}_6$ )



C

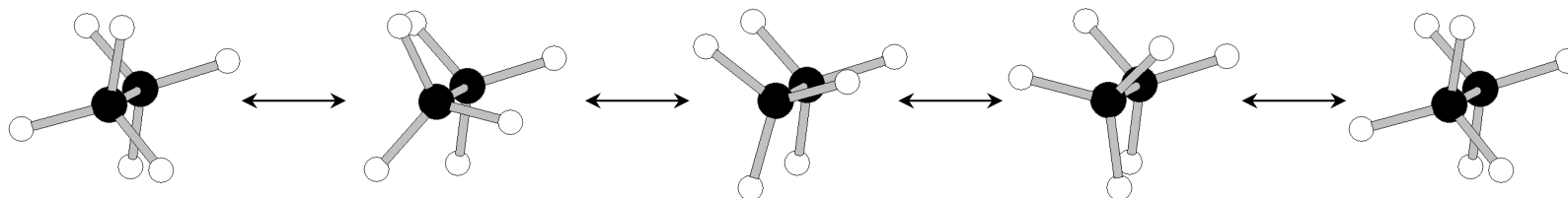
# VB Theory for Larger Molecules: Ethane

- The bonding in ethane can be explained using  $sp^3$  hybridization of each carbon atom and  $1s$  orbitals on each hydrogen.

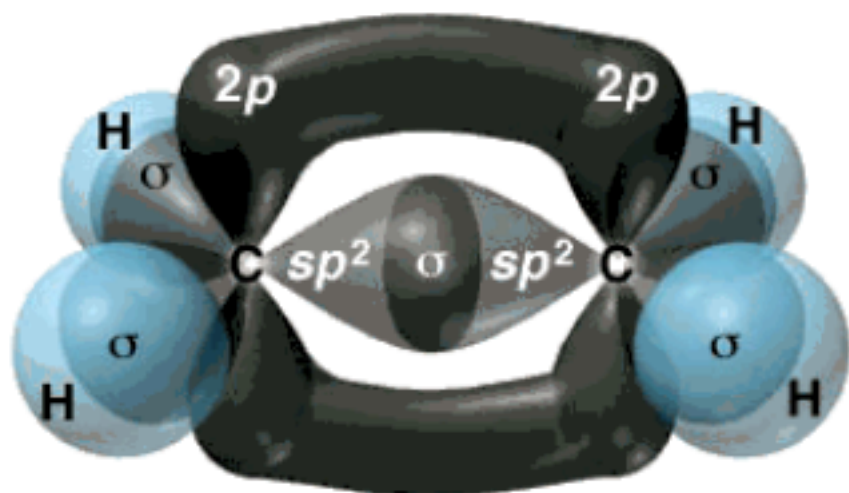


- Each C-H  $\sigma$  bond is due to combination of an  $sp^3$  orbital from C and an  $s$  orbital from H.
- The C-C  $\sigma$  bond is due to combination of  $sp^3$  orbitals from each C.

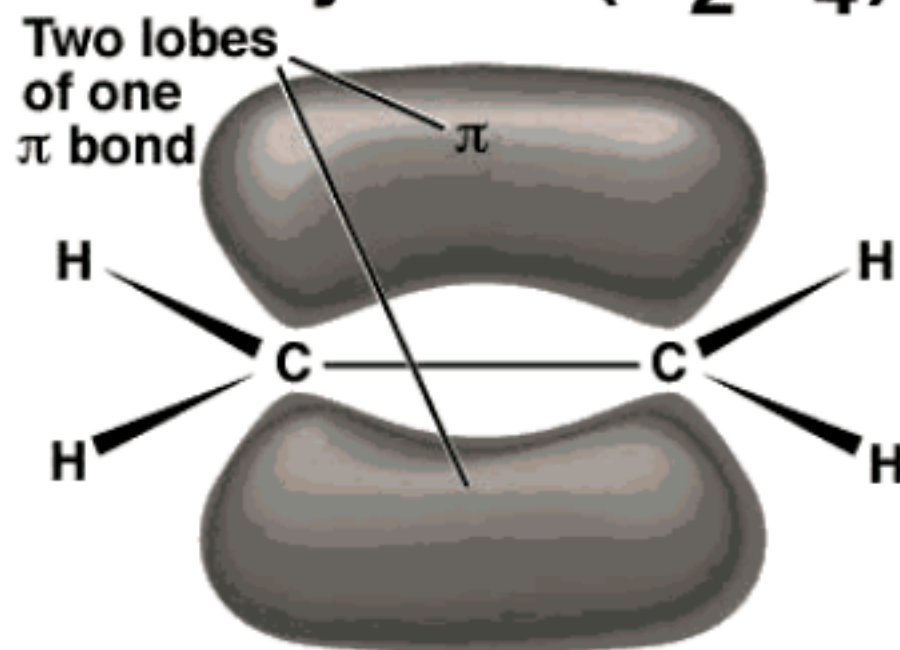
- Because the C-C bond is a  $\sigma$  bond, it can be rotated freely without breaking. Ethane is therefore not limited to one conformation. It can rotate freely between them:



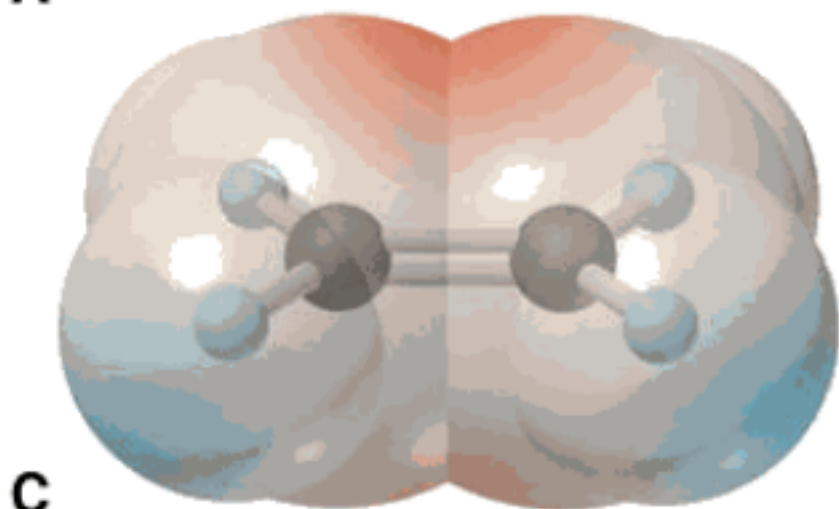
# The $\sigma$ and $\pi$ Bonds of Ethylene ( $\text{C}_2\text{H}_4$ )



A



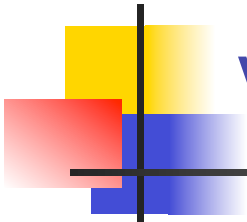
B



C



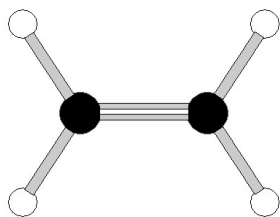
D



## VB Theory for Larger Molecules: Ethylene

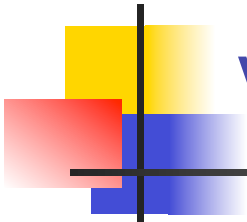
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- The bonding in ethylene can be explained using  $sp^2$  hybridization of each carbon atom and  $1s$  orbitals on each hydrogen.



- Each C–H  $\sigma$  bond is due to combination of an  $sp^2$  orbital from C and an  $s$  orbital from H.
- The C–C  $\sigma$  bond is due to combination of  $sp^2$  orbitals from each C.
- The C–C  $\pi$  bond is due to combination of  $p$  orbitals from each C.

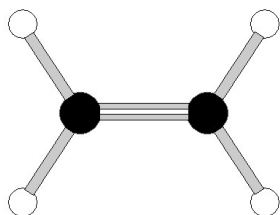




# VB Theory for Larger Molecules: Ethylene

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- Why is ethylene flat?



- The only way that the  $\pi$  bond can form is if the two  $p$  orbitals are lined up (same symmetry):

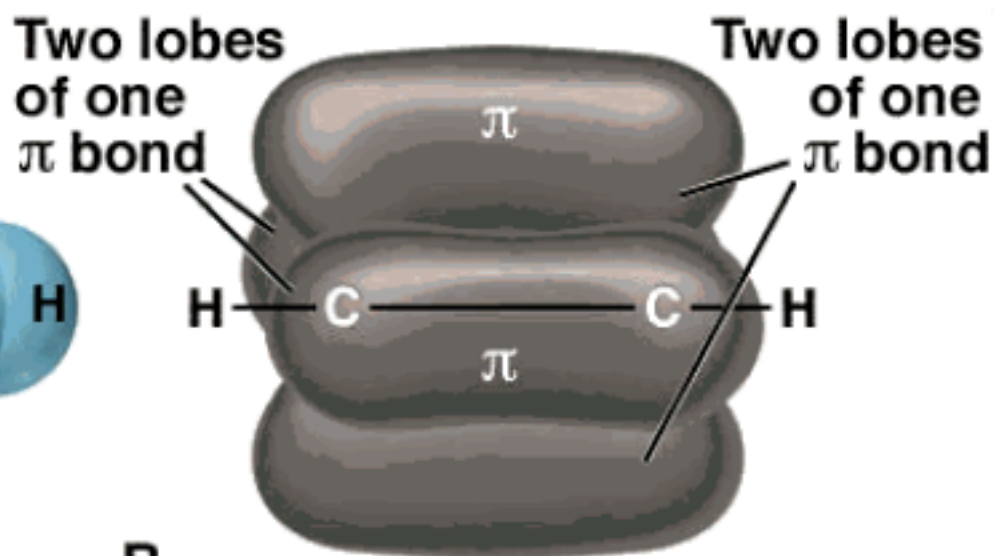


- If we rotate the C-C bond by  $90^\circ$ , the C-H  $\sigma$  bonds are farther apart, but the  $p$  orbitals are **orthogonal** and therefore do not overlap at all. Thus, there is no  $\pi$  bond:
- Since ethylene would be much less stable without the  $\pi$  bond, the  $\text{CH}_2$  fragments are forced to be **coplanar**, making the molecule flat. In other words, rotating around the C=C bond would require **BREAKING** the  $\pi$  bond – which requires a fair amount of energy. As such,  $\pi$  bonds always make a molecule more rigid.

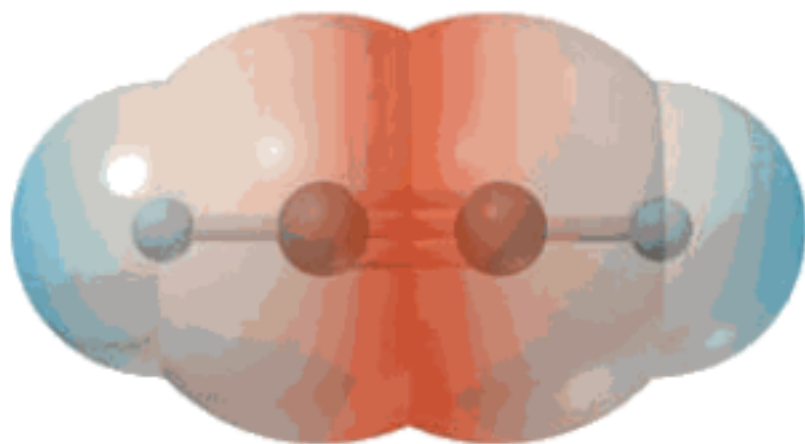
# The $\sigma$ and $\pi$ Bonds of Acetylene ( $\text{C}_2\text{H}_2$ )



A



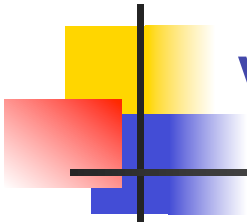
B



C



D



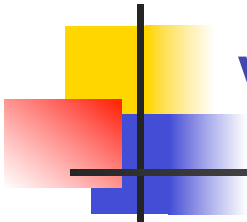
## VB Theory for Larger Molecules: acetylene

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- The Lewis structure for acetylene ( $\text{C}_2\text{H}_2$ ) is:

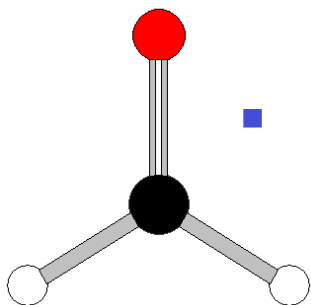


- According to VSEPR theory, each carbon atom is **linear** and therefore ***sp*** hybridized:
  - Each C–H  $\sigma$  bond is due to combination of an *sp* orbital from C and a 1s orbital from H.
  - The C–C  $\sigma$  bond is due to combination of *sp* orbitals from each C.
  - The C–C  $\pi$  bonds are due to combination of 2*p* orbitals from each C.

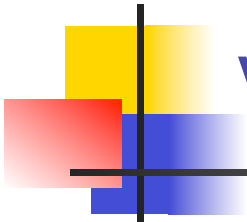


# VB Theory for Larger Molecules: Formaldehyde

- The Lewis structure for formaldehyde ( $\text{CH}_2\text{O}$ ) is:



- According to VSEPR theory, the carbon atom is **trigonal planar** and therefore  **$sp^2$**  hybridized:
  - Each C–H  $\sigma$  bond is due to combination of an  $sp^2$  orbital from C and a  $1s$  orbital from H.
  - The C–O  $\sigma$  bond is due to combination of an  $sp^2$  orbital from C and a  $2p$  orbital from O. (*You could hybridize O too, but it's unnecessary.*)
  - The C–O  $\pi$  bond is due to combination of  $2p$  orbitals from C and O.
  - The lone pairs on O are its two remaining AOs ( $2s$  and a  $2p$ ).



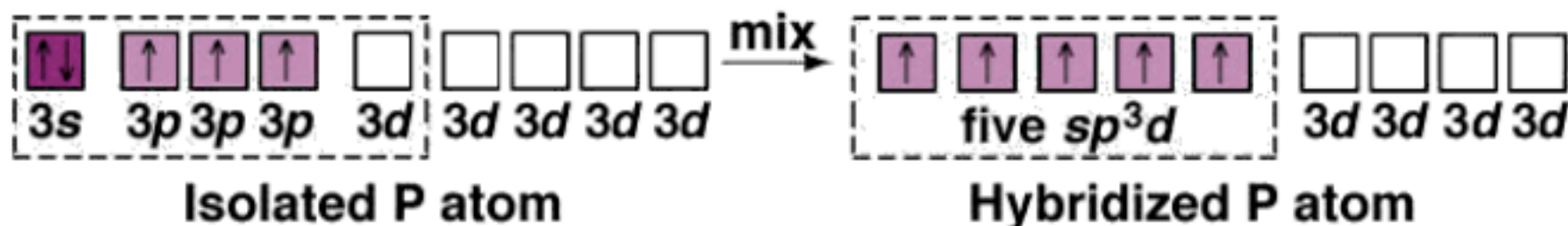
## VB Theory for Larger Molecules: HCN

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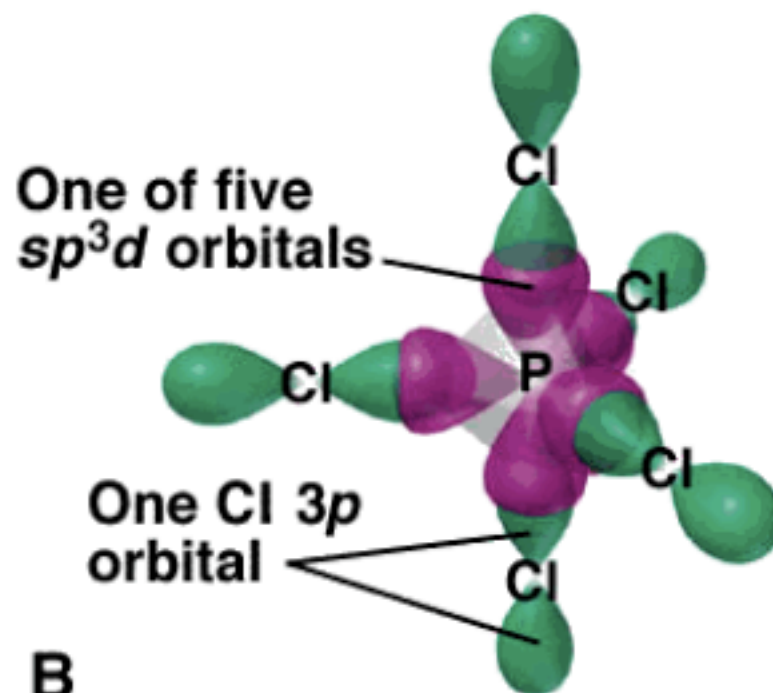


- The Lewis structure for hydrogen cyanide (HCN) is:
- According to VSEPR theory, the carbon atom is **linear** and therefore ***sp*** hybridized:
  - The C–H  $\sigma$  bond is due to combination of an *sp* orbital from C and a 1s orbital from H.
  - The C–N  $\sigma$  bond is due to combination of an *sp* orbital from C and a 2*p* orbital from N. (*You could hybridize N too, but it's unnecessary.*)
  - The C–N  $\pi$  bonds are due to combination of 2*p* orbitals from C and N.
  - The lone pair on N is its remaining atomic orbital (2*s*).

# The $sp^3d$ Hybrid Orbitals in $\text{PCl}_5$



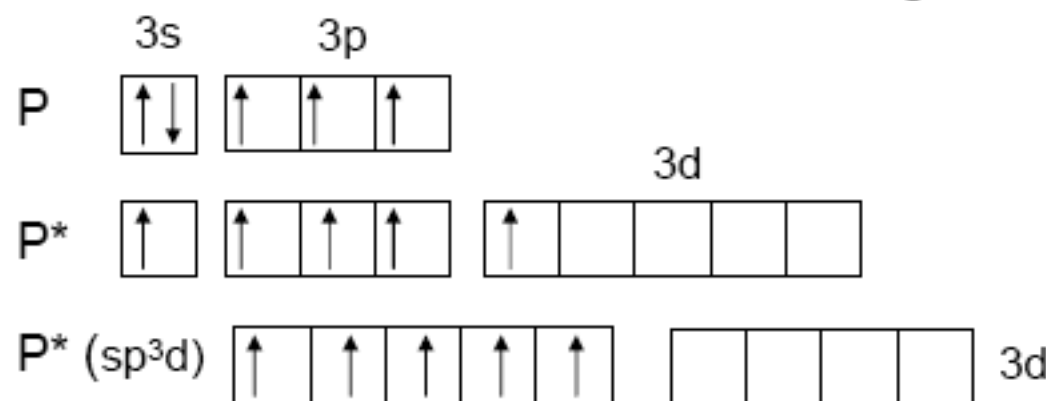
A



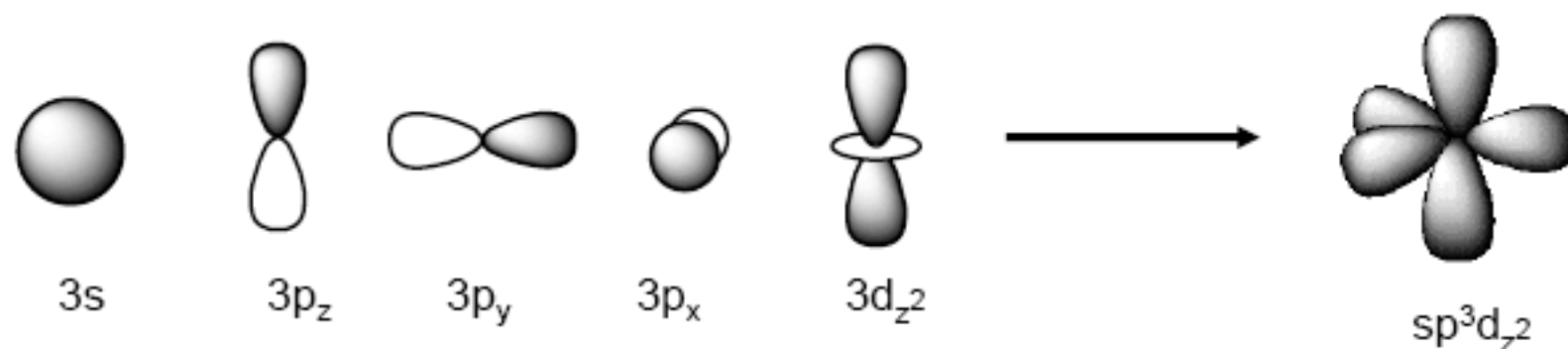
B

**Trigonal bipyramidal**

Valence bond theory treatment of a trigonal bipyramidal molecule:  
the bonding in  $\text{PF}_5$



$\text{PF}_5$  has a VSEPR theory  $\text{AX}_5$  geometry so we need hybrid orbitals suitable for bonds to 5 atoms. ns and np combinations can only provide four, so we need to use nd orbitals (if they are available).



The appropriate mixture to form a trigonal bipyramidal arrangement of hybrids involves all the ns and np orbitals as well as the  $\text{nd}_{z^2}$  orbital.

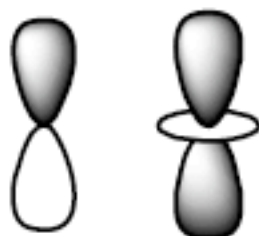
## Valence bond theory treatment of a trigonal bipyramidal molecule

The orbitals are treated in two different sets.



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

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

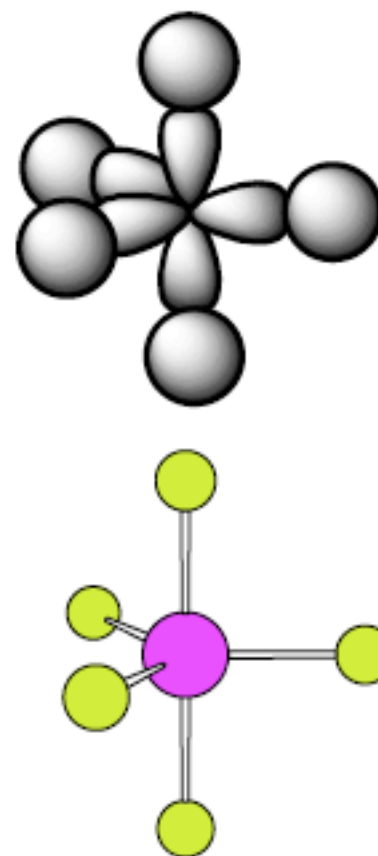
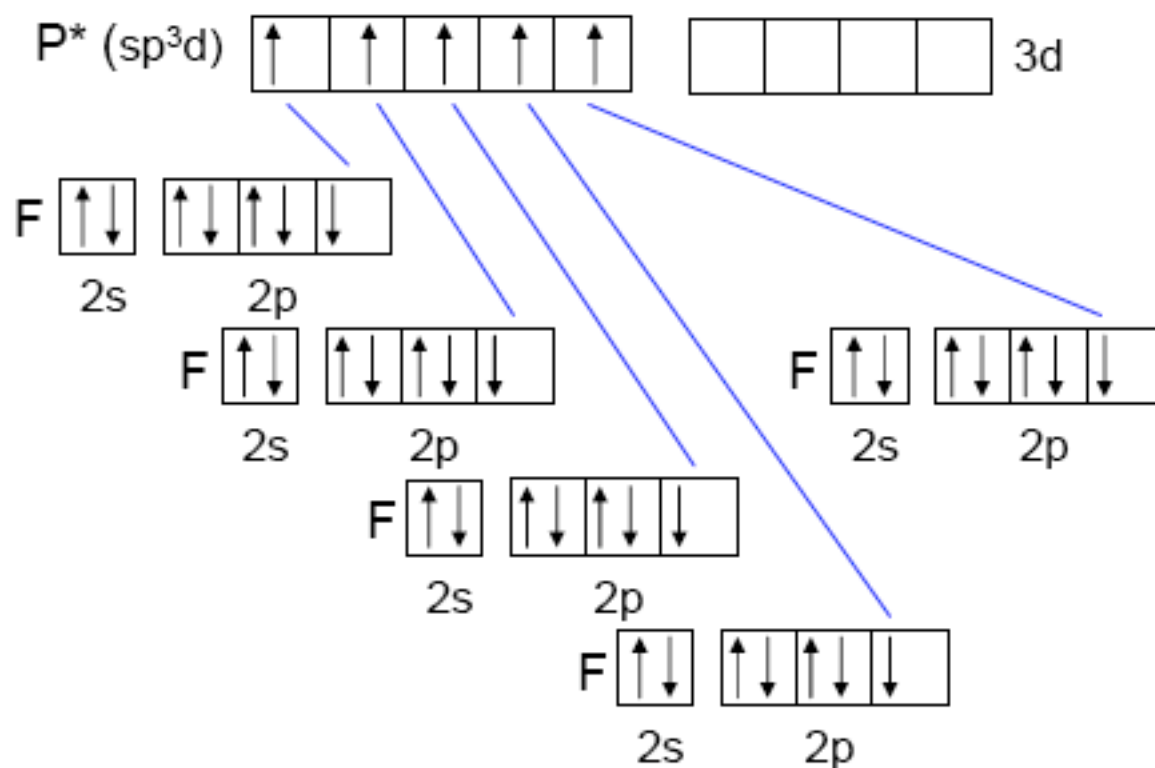


$$\begin{aligned}\Psi_4 &= \frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}} \\ \Psi_5 &= -\frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}\end{aligned}$$

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

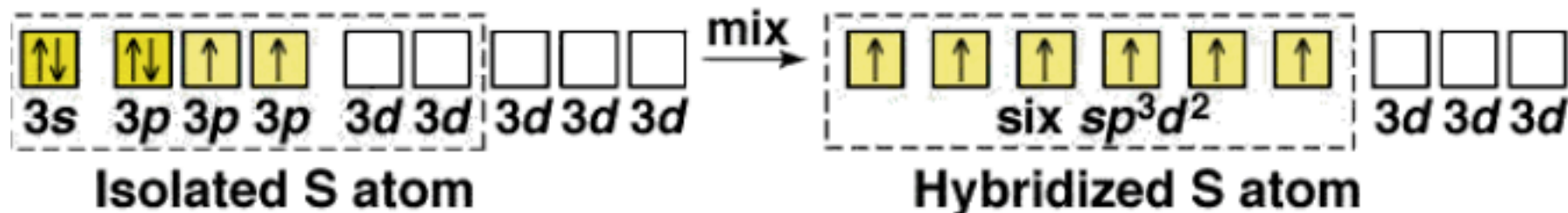
Remember that  $d$  orbitals are more *diffuse* than  $s$  or  $p$  orbitals so VBT predicts that the bonds formed by hybrids involving  $d$  orbitals will be longer than those formed by  $s$  and  $p$  hybrids.

Valence bond theory treatment of a trigonal bipyramidal molecule:  
the bonding in  $\text{PF}_5$

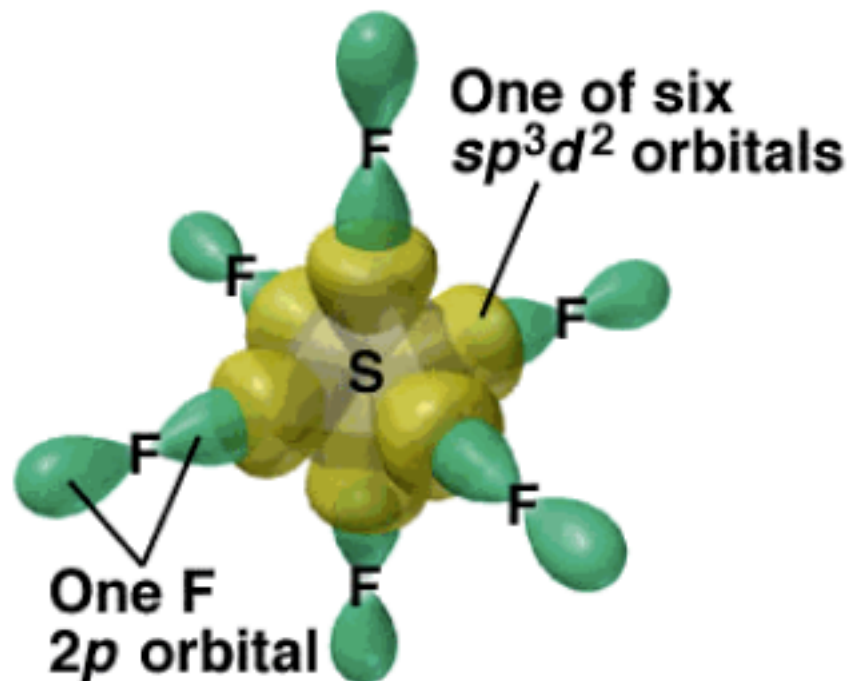


The overlap of the  $\text{sp}^3\text{d}$  hybrid orbitals on P with the  $2p$  orbitals on the F atoms gives five  $\text{P-F}$  ( $\text{sp}^3\text{d}$ )- $2p$   $\sigma$  bonds in two sets: the two *axial* bonds along the  $z$ -axis ( $180^\circ$  from each other) and three *equatorial* bonds in the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

# The $sp^3d^2$ Hybrid Orbitals in $\text{SF}_6$



A

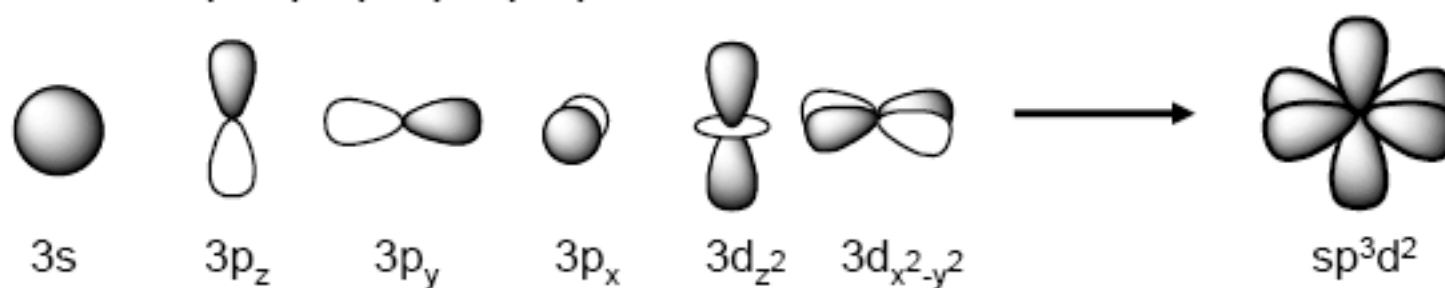
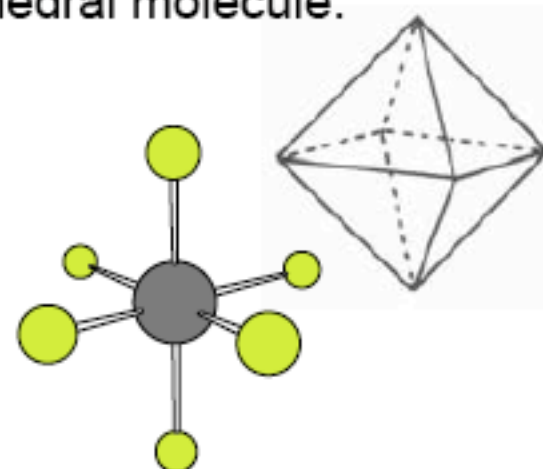
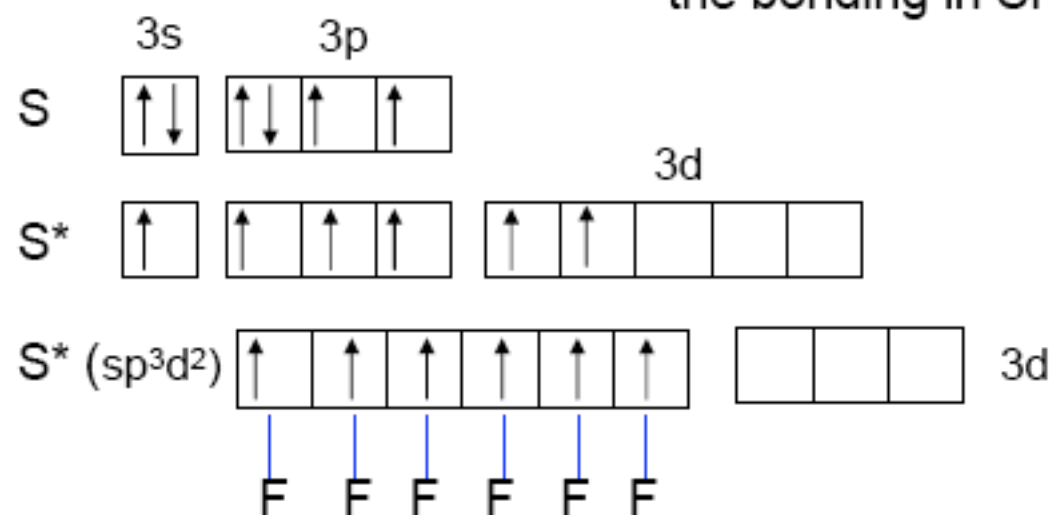


B

octahedral

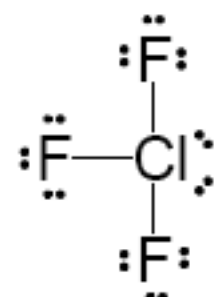
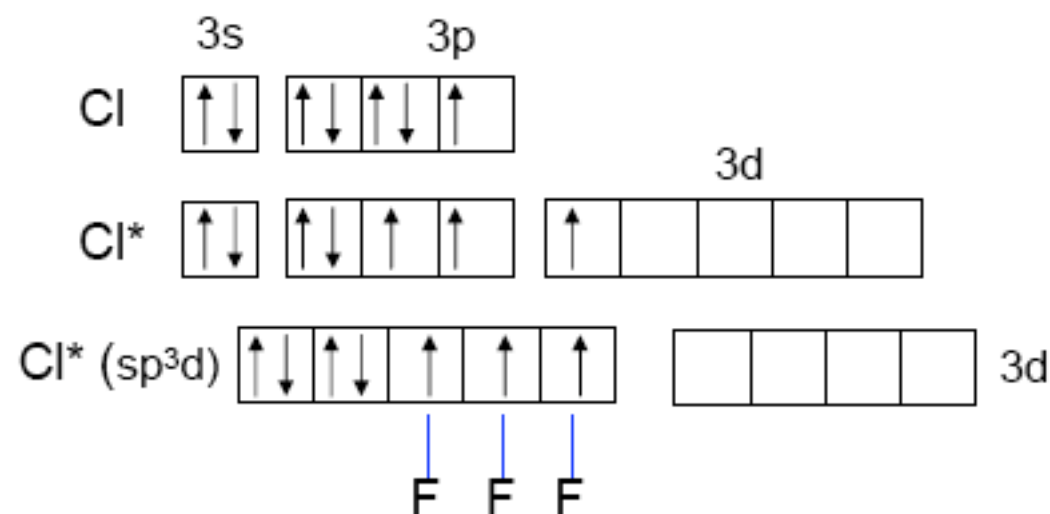


# Valence bond theory treatment of an octahedral molecule: the bonding in $\text{SF}_6$



The overlap of the  $\text{sp}^3\text{d}^2$  hybrid orbitals on S with the 2p orbitals on the F atoms gives six S-F ( $\text{sp}^3\text{d}^2$ )-2p  $\sigma$  bonds  $90^\circ$  from each other that are **equivalent**. *You can figure out the normalization coefficients.*

Valence bond theory treatment of bonding: a hypervalent molecule,  $\text{ClF}_3$

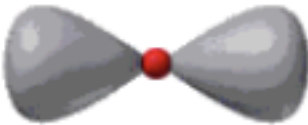
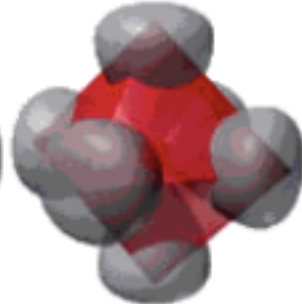


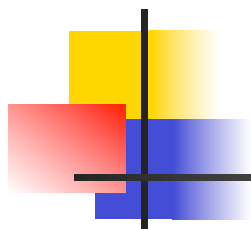
There are five “objects” around Cl so the geometry is trigonal bipyramidal and the shape is given by  $\text{AX}_3\text{E}_2$  (T-shaped).

The overlap of the  $\text{sp}^3\text{d}$  hybrid orbitals on Cl with the 2p orbitals on the F atoms gives three  $\text{Cl-F}$  ( $\text{sp}^3\text{d}$ )-2p  $\sigma$  bonds in two sets: the two *axial* bonds along the z-axis (**less than  $180^\circ$  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.



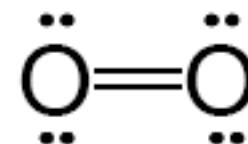
**Table 11.1** Composition and Orientation of Hybrid Orbitals

|                                 | Linear                                                                              | Trigonal Planar                                                                      | Tetrahedral                                                                           | Trigonal Bipyramidal                                                                  | Octahedral                                                                            |
|---------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Atomic orbitals mixed           | one $s$<br>one $p$                                                                  | one $s$<br>two $p$                                                                   | one $s$<br>three $p$                                                                  | one $s$<br>three $p$<br>one $d$                                                       | one $s$<br>three $p$<br>two $d$                                                       |
| Hybrid orbitals formed          | two $sp$                                                                            | three $sp^2$                                                                         | four $sp^3$                                                                           | five $sp^3d$                                                                          | six $sp^3d^2$                                                                         |
| Unhybridized orbitals remaining | two $p$                                                                             | one $p$                                                                              | none                                                                                  | four $d$                                                                              | three $d$                                                                             |
| Orientation                     |  |  |  |  |  |



**VBT does not adequately explain:**

**1. Excited state properties**



**2. Paramagnetism of oxygen:  
presence of unpaired electrons**

Lewis structure

**3. Bond in hypervalent molecules,  
energy cost too high**



## **VB**

**Localized picture**

**Orbital hybridization, electron promotion, using d orbital**

**Ground state, molecular geometry**

**No excited state information**

**Can not explain oxygen paramagnetism**

## **MO**

**Delocalized picture**

**Without using high energy d orbitals**

**Both occupied and empty orbital**

**Excited state information, allow spectroscopic study:**

**example: PES**

**Explain unpaired electron in oxygen and others.**

**Molecular geometry**

**Orbital character: CH<sub>4</sub>**

**Exact bond order: PF<sub>5</sub>**

**Chemical reaction: LUMO, HOMO, frontier orbital**