

## Molecular Orbital

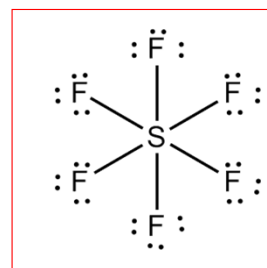
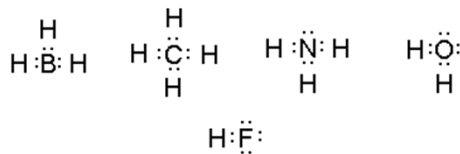
Reading: DG 2.11-14, 3.1-5, 4; MT 3.1

### Lewis Structure

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

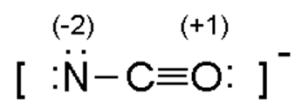
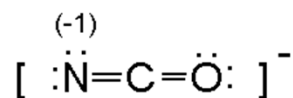
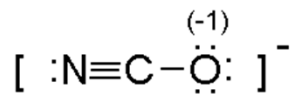


**Octet Rule: Closed shell configuration of 8 surrounding e**





## Resonance



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



## Valence Bond theory



Heitler, London (1927)



**L. Pauling (orbital hybridization)**  
Localized orbital approach

Investigating ground state molecules,  
molecular geometry  
Bond dissociation energy



Linus Pauling



## Molecular Orbital theory

**Mulliken**

**Delocalized orbital approach**

**Unoccupied orbital**

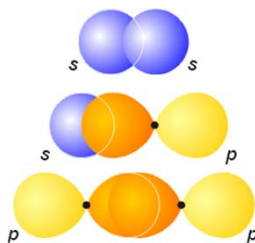
**Spectroscopic properties  
(ionization, excited states)**

## Valence Bond Theory

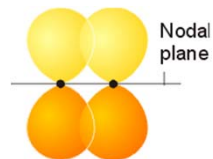
Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy *directed orbitals* localized on a particular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

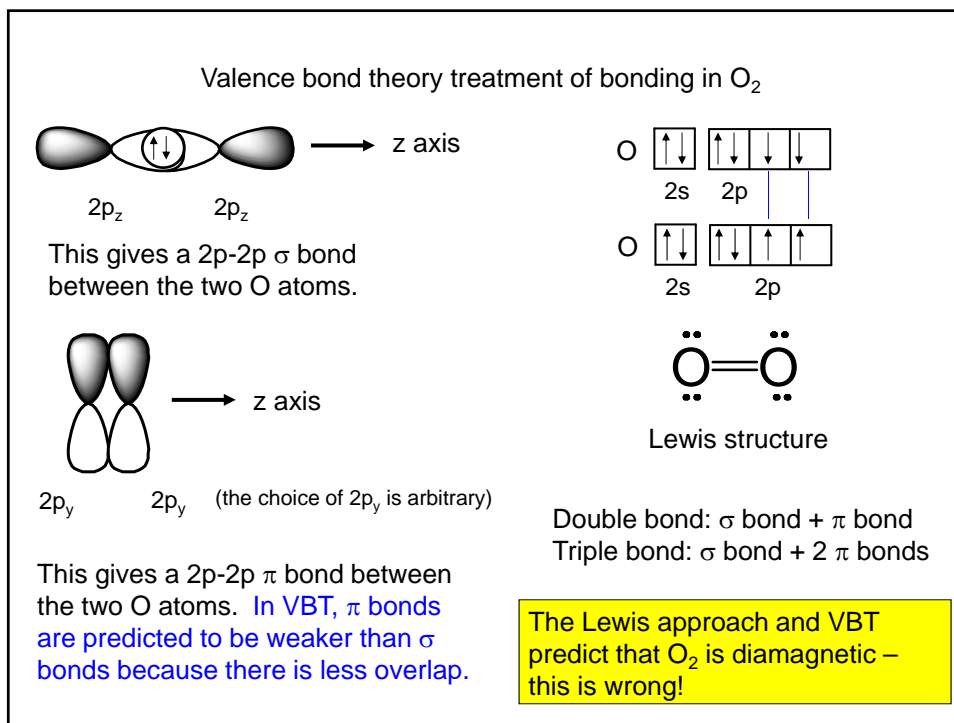
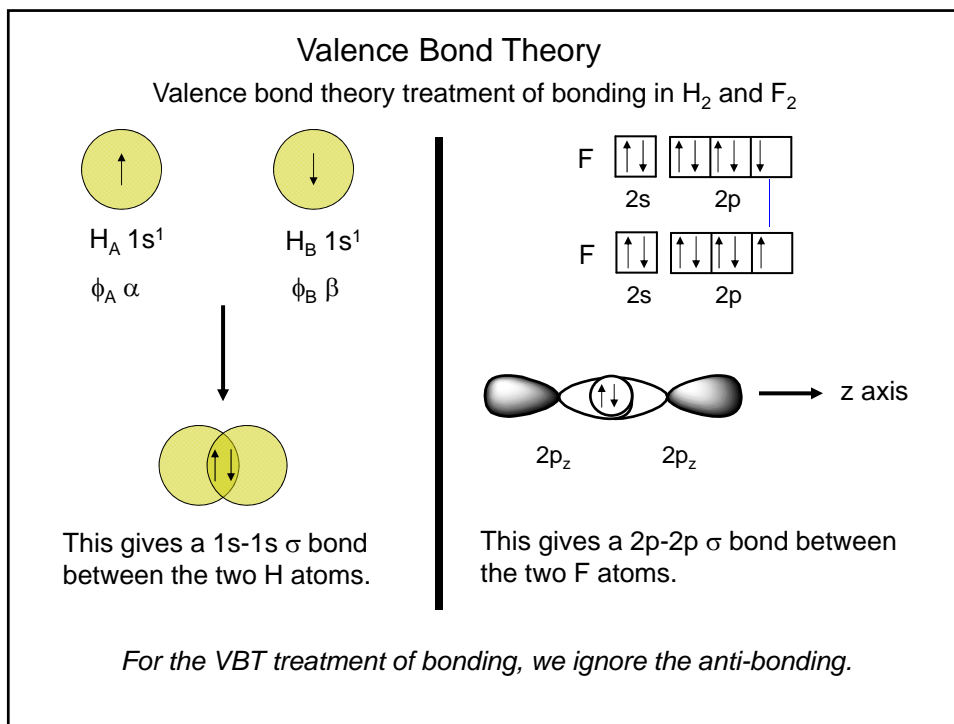
In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.

$\sigma$  bonds:  
symmetric about  
the internuclear  
axis



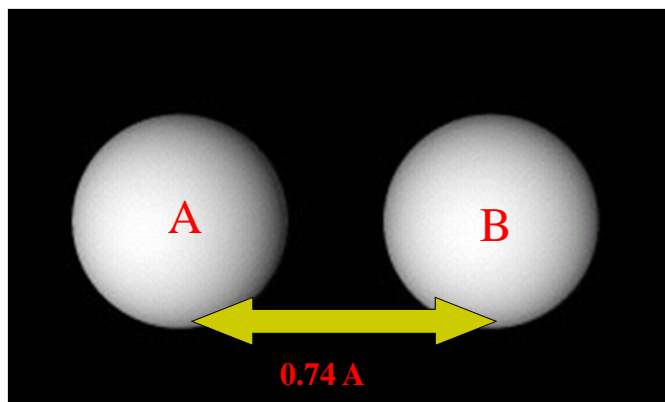
$\pi$  bonds: have  
a node on the  
inter-nuclear axis  
and the sign of  
the lobes  
changes across  
the axis.







## Valence Bond theory

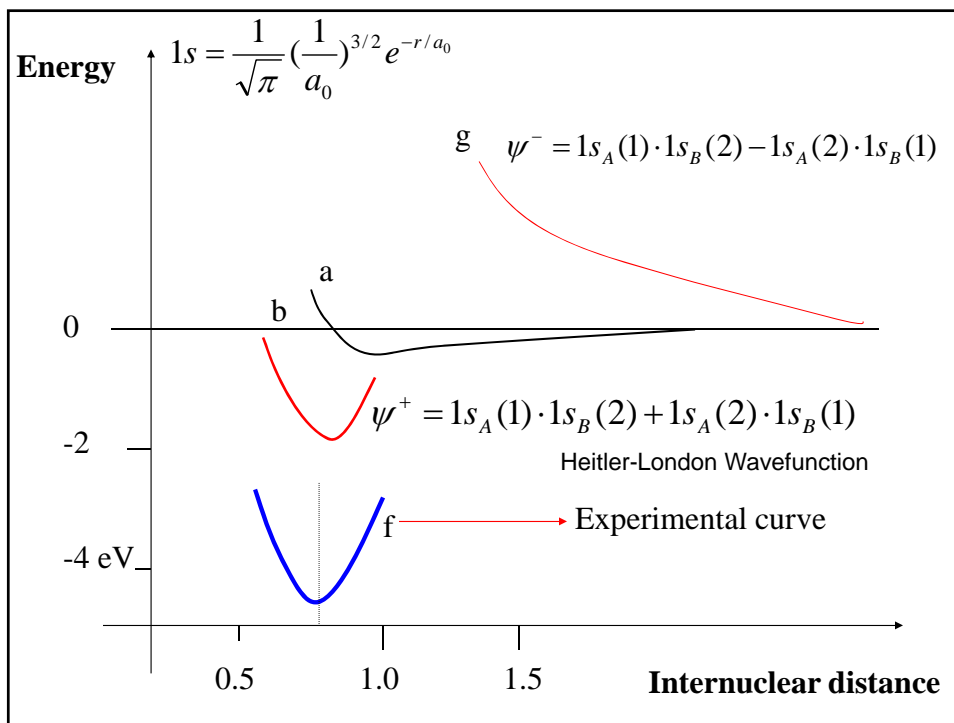
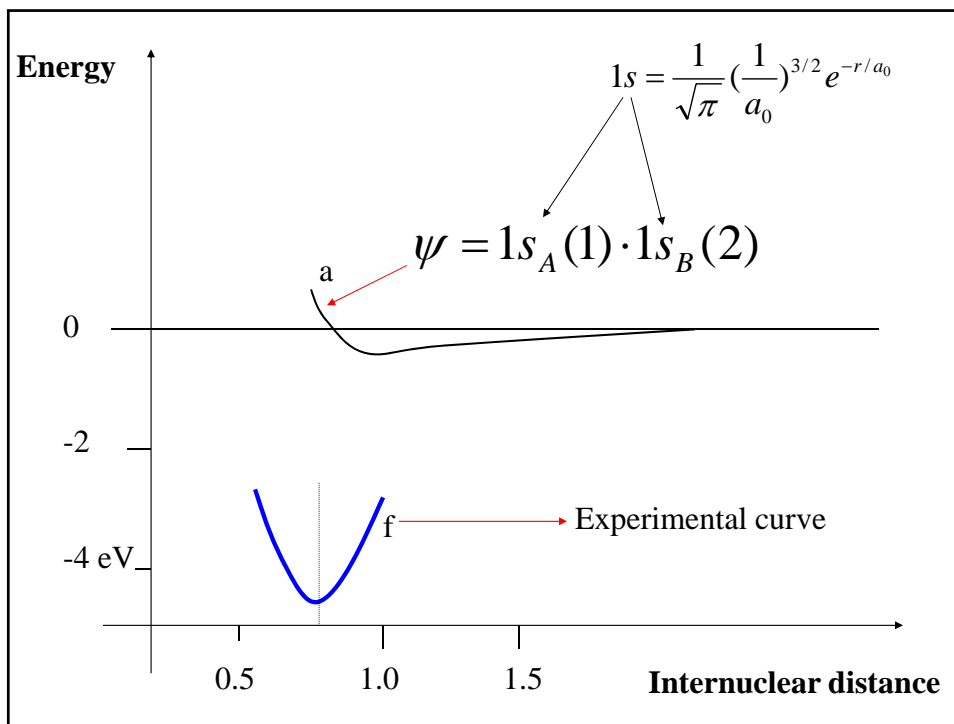


Bond dissociation energy: 103 kcal/mol



## Our Goal

Use atomic orbitals to compose a wavefunction  
that accurately describe these observations.





### Variation Principle:

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

$$\langle H \rangle = \frac{\int \Psi^*(x) H \Psi(x) dx}{\int \Psi^*(x) \Psi(x)}$$



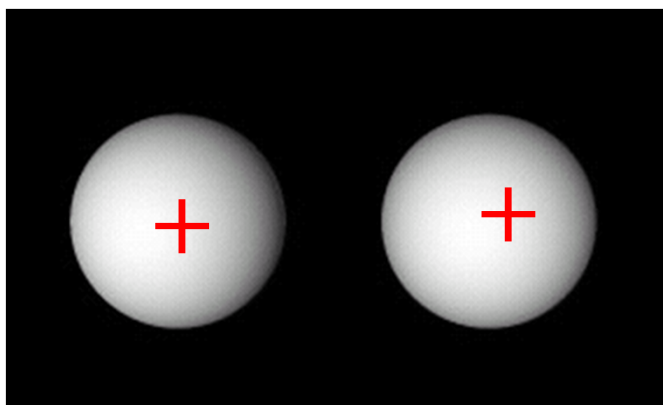
### Variation Principle:

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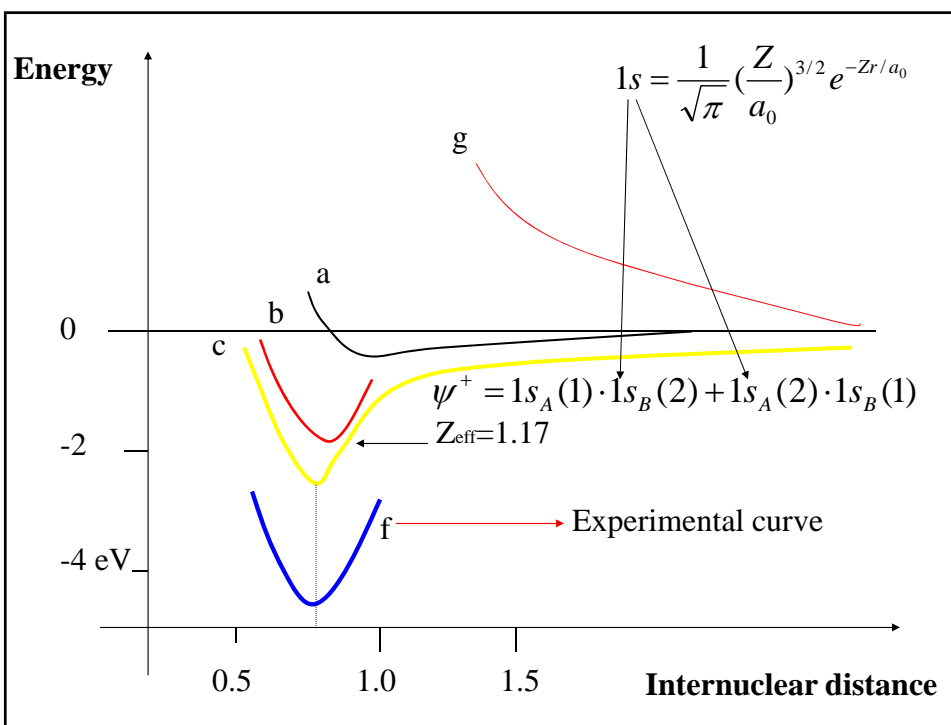
Can always minimize  $E_{\psi(x)}$



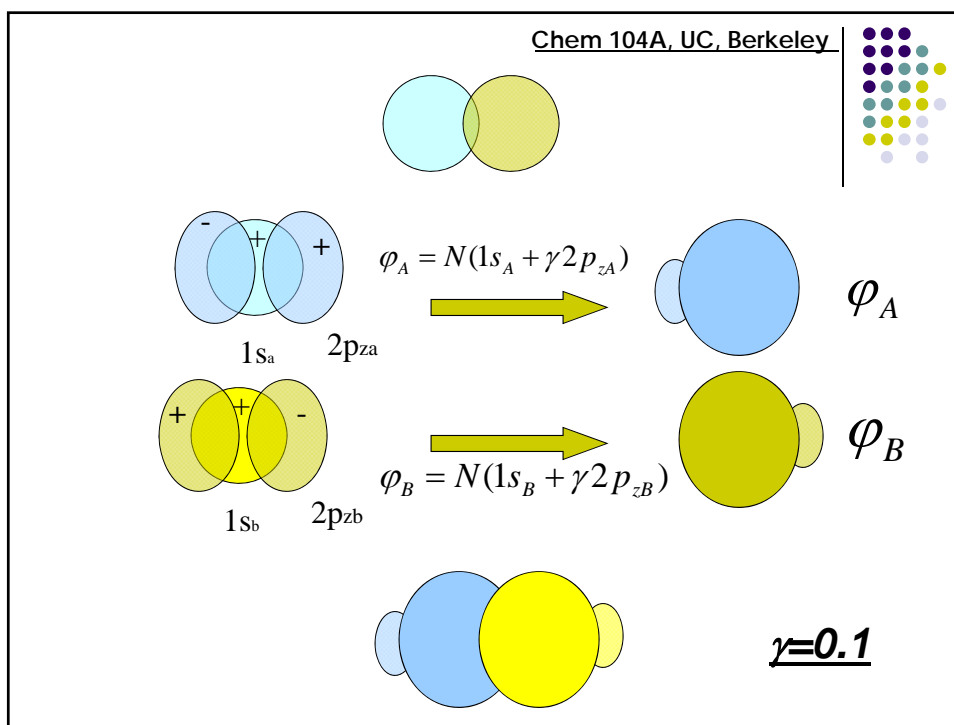
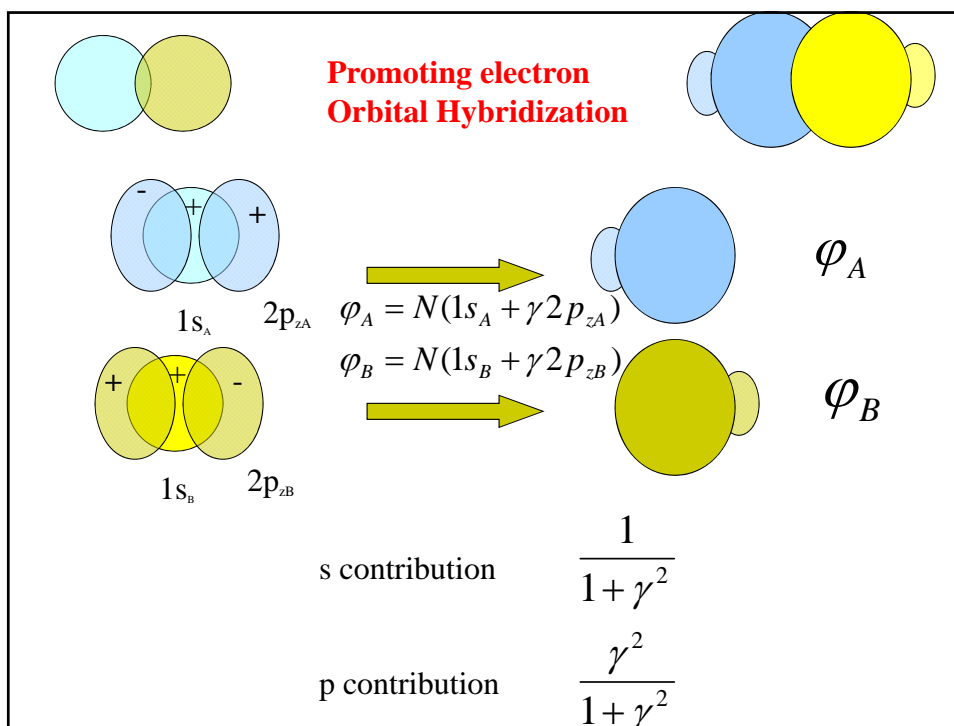
$$1s = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

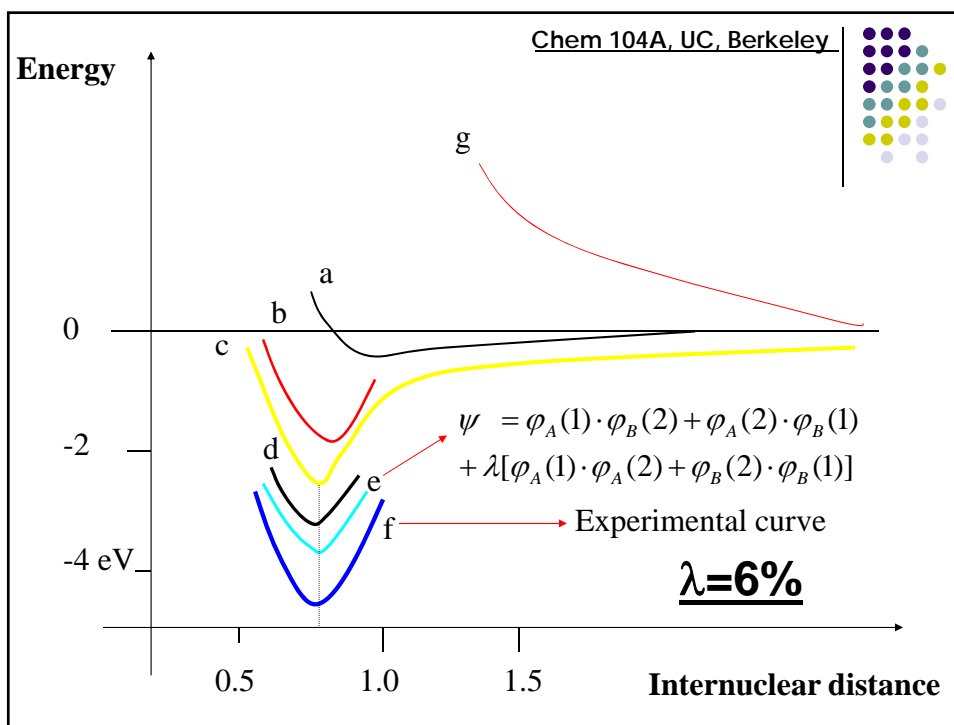
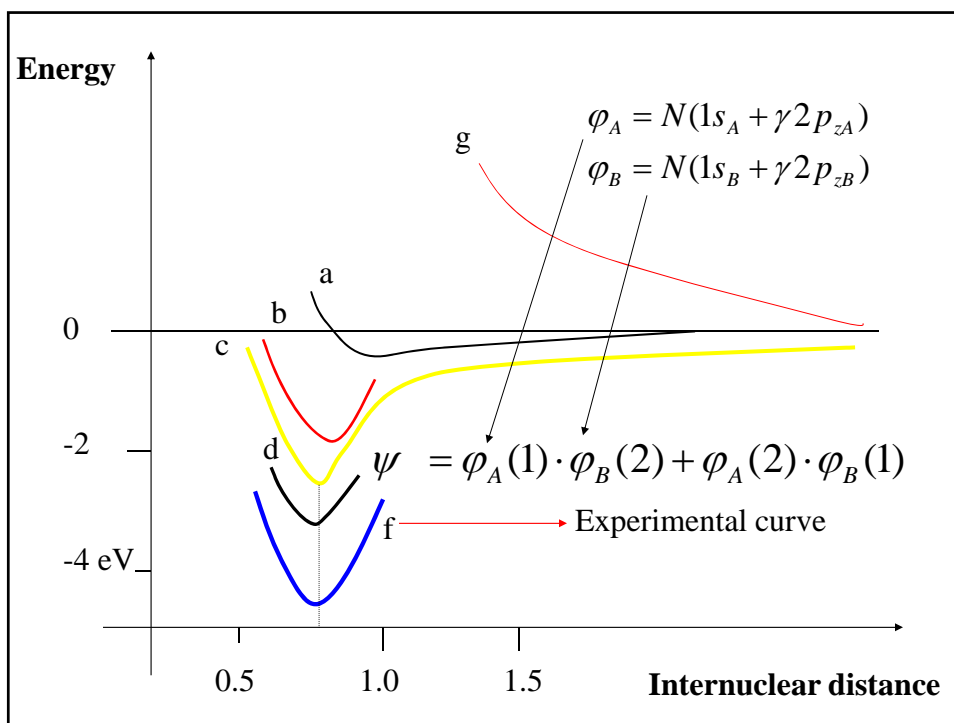


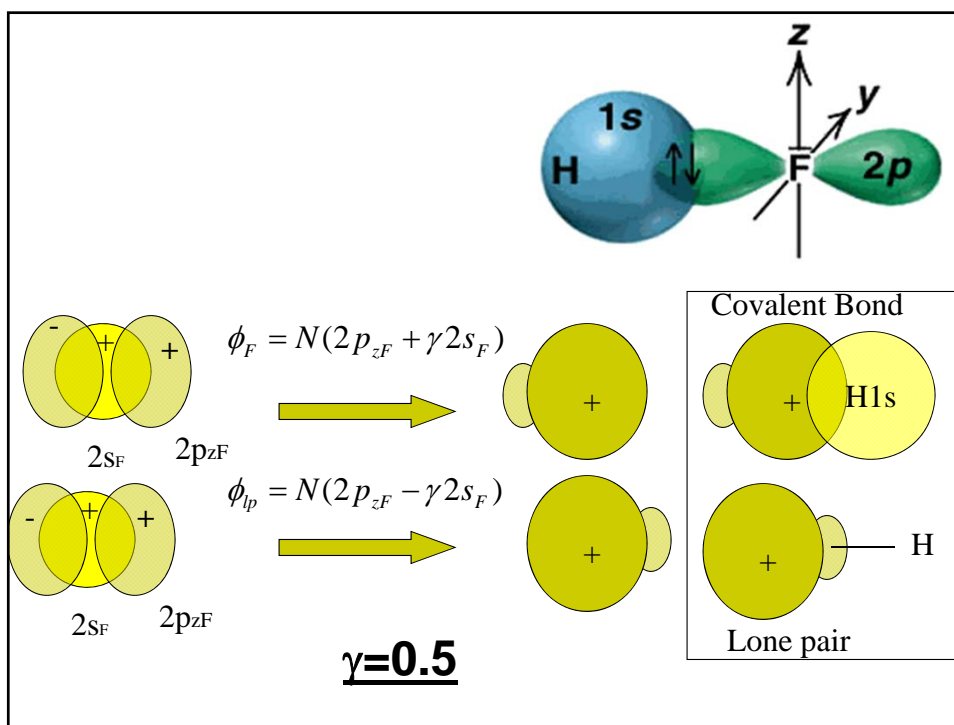
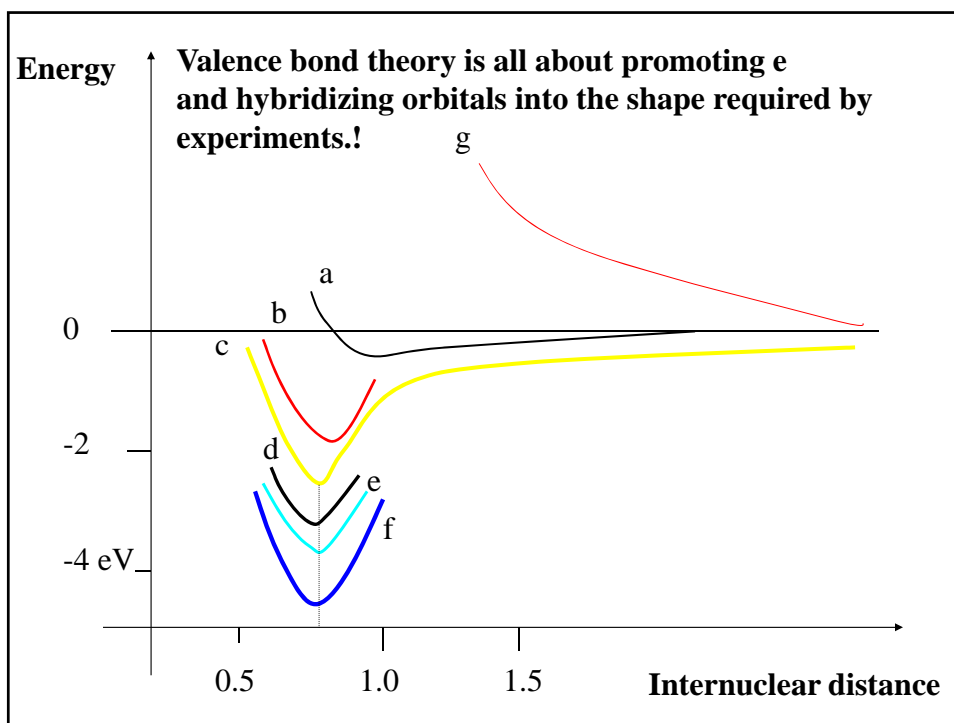
$$1s = \psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$





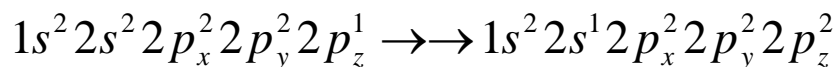








promotion



$$\Delta E = 500 \text{ kcal/mol}$$

$$1 \text{ eV} = 96.4 \text{ kJ/mol} = 23.1 \text{ kcal/mol}$$

**Benefit of hybridization**

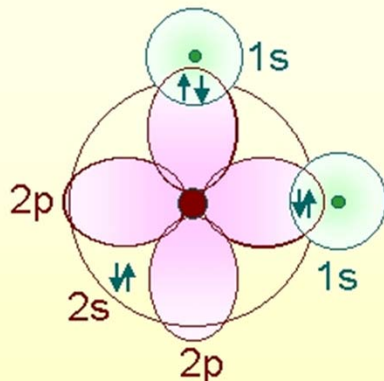
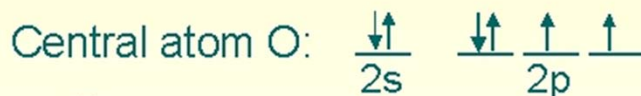
1. Increase in e density between nuclei, enhanced bonding
2. Decrease in e-e repulsion by formation of a lone-pair orbital, LP Orbital more directed away from BP than the Original s LP

**Ionic Contribution: 50%**

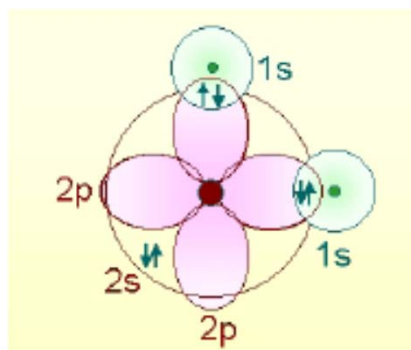
$$\psi = 1s_H(1)\phi_F(2) + 1s_H(2)\phi_F(1) + \lambda\phi_F(2)\phi_F(1)$$

## Valence Bond Theory and Molecular Geometry

Consider the H<sub>2</sub>O molecule:

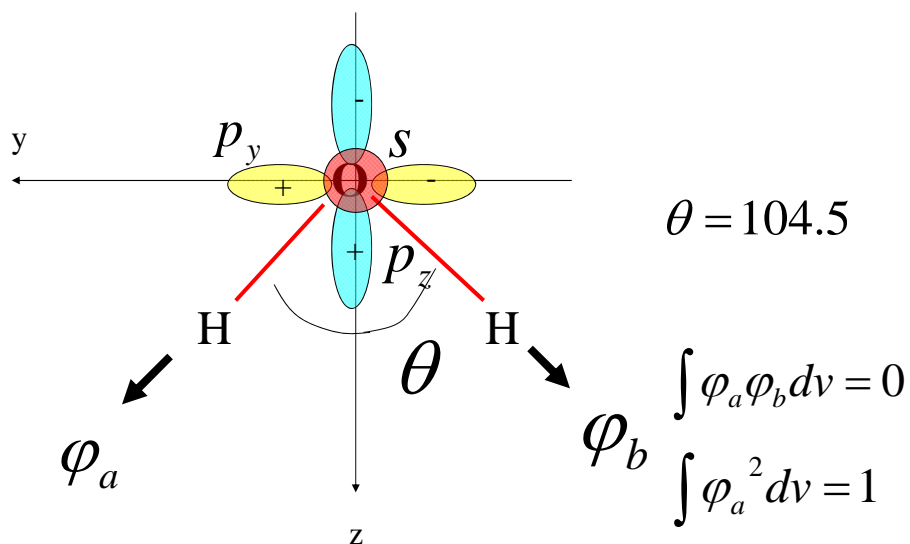


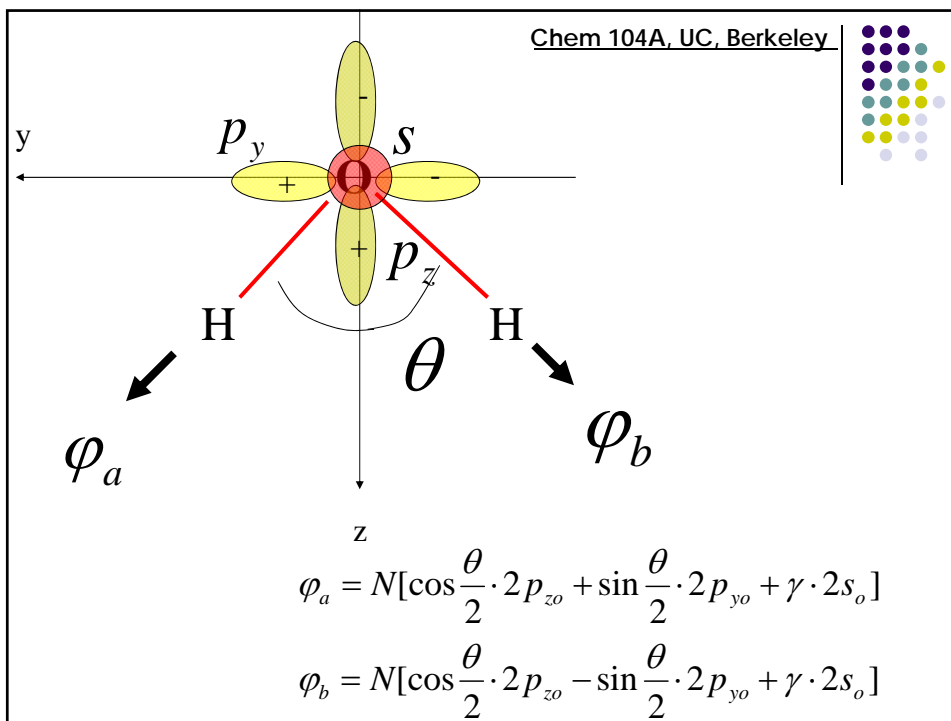
Orbital overlap suggests that the bond angle is 90°.



$$\psi = [1s_{Ha}(1)2p_{yo}(2) + 1s_{Ha}(2)2p_{yo}(1)] \cdot [1s_{Hb}(3)2p_{zo}(4) + 1s_{Hb}(4)2p_{zo}(3)]$$

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





### 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.:

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

where  $n \neq m$  and  $\delta\tau$  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.:

$$\int \Psi_n \Psi_n \delta\tau = 1$$

**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".

$$\varphi_a = N[\cos\frac{\theta}{2} \cdot 2p_{z_o} + \sin\frac{\theta}{2} \cdot 2p_{y_o} + \gamma \cdot 2s_o]$$

$$\varphi_b = N[\cos\frac{\theta}{2} \cdot 2p_{z_o} - \sin\frac{\theta}{2} \cdot 2p_{y_o} + \gamma \cdot 2s_o]$$

Chem 104A, UC, Berkeley



$$\theta = 104.5 \quad \int \varphi_a \varphi_b dV = 0 \quad \text{Orthogonality}$$

$$\int \varphi_a^2 dV = 1 \quad \text{Normalization}$$

$$\gamma = 0.5$$

$$N = 1/\sqrt{1.25}$$

$$\varphi_a = 0.55 \cdot 2p_{z_o} + 0.71 \cdot 2p_{y_o} + 0.452 \cdot 2s_o$$

$$\varphi_b = 0.55 \cdot 2p_{z_o} - 0.712 \cdot 2p_{y_o} + 0.452 \cdot 2s_o$$

$$\psi = [1s_{Ha}(1)2p_{y_o}(2) + 1s_{Ha}(2)2p_{y_o}(1)] \cdot [1s_{Hb}(3)2p_{z_o}(4) + 1s_{Hb}(4)2p_{z_o}(3)]$$

**New Wavefunction:**

$$\psi = [1s_{Ha}(1)\varphi_a(2) + 1s_{Ha}(2)\varphi_a(1)] \cdot [1s_{Hb}(3)\varphi_b(4) + 1s_{Hb}(4)\varphi_b(3)]$$

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**Unit Orbital Contribution:**

**The contribution of any atomic orbital to all hybrid Orbitals must add up to 1.0.**

Orbital contribution

$$\varphi_a = 0.55 \cdot 2p_{z_o} + 0.71 \cdot 2p_{y_o} + 0.452 \cdot 2s_o$$

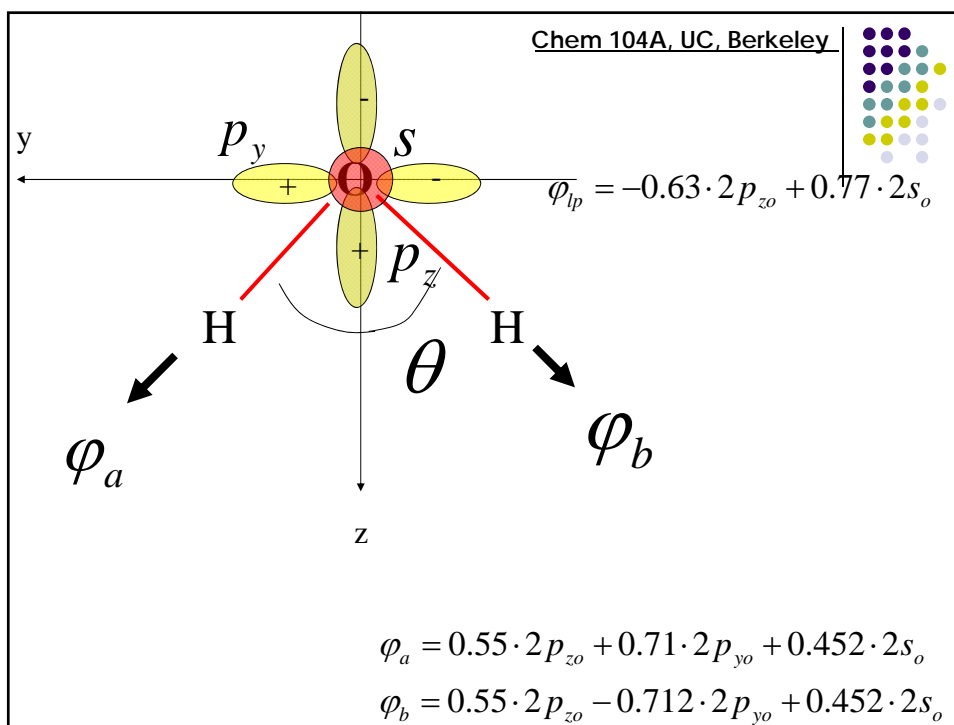
$$\varphi_b = 0.55 \cdot 2p_{z_o} - 0.712 \cdot 2p_{y_o} + 0.452 \cdot 2s_o$$

	$\varphi_a$	$\varphi_b$	
$2p_{z_o}$ <small><math>0.55^2 = 30\%</math></small>	30%	30%	60%
$2p_{y_o}$ <small><math>0.71^2 = 50\%</math></small>	50%	50%	100%
$2s_o$ <small><math>0.452^2 = 20\%</math></small>	20%	20%	40%

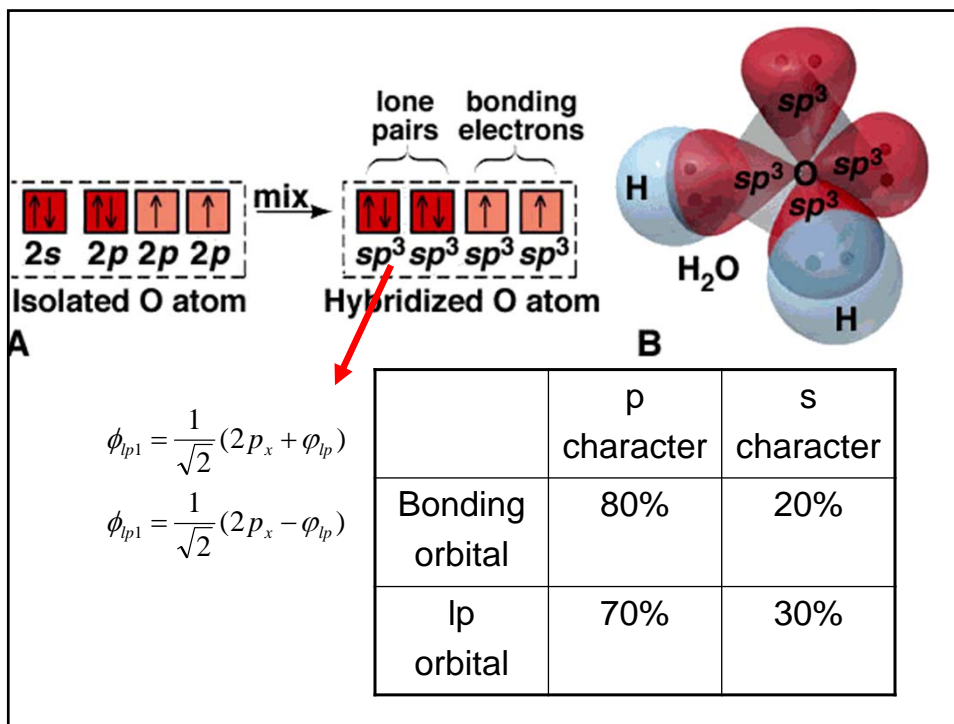
**Bonding: Average 80% p character, 20% s character**

What's left? 40% p +60% s

$$\varphi_{lp} = -0.63 \cdot 2p_{z_o} + 0.77 \cdot 2s_o$$



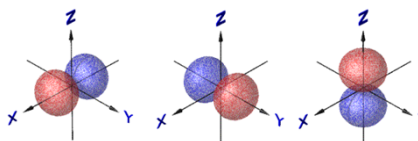
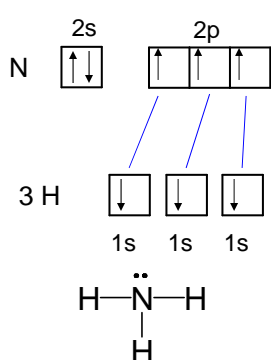




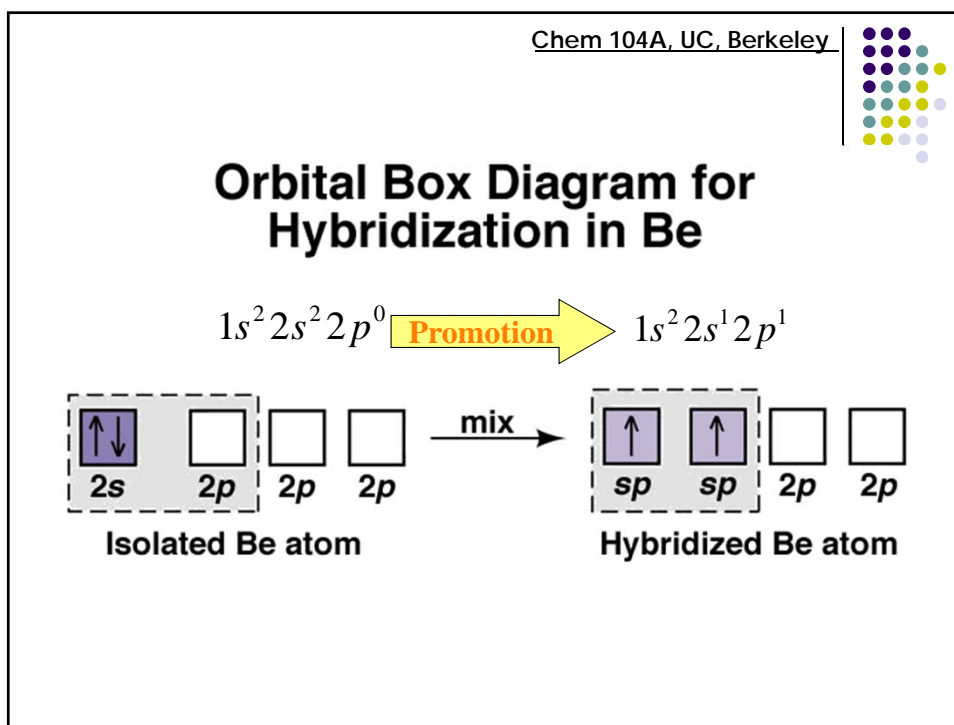
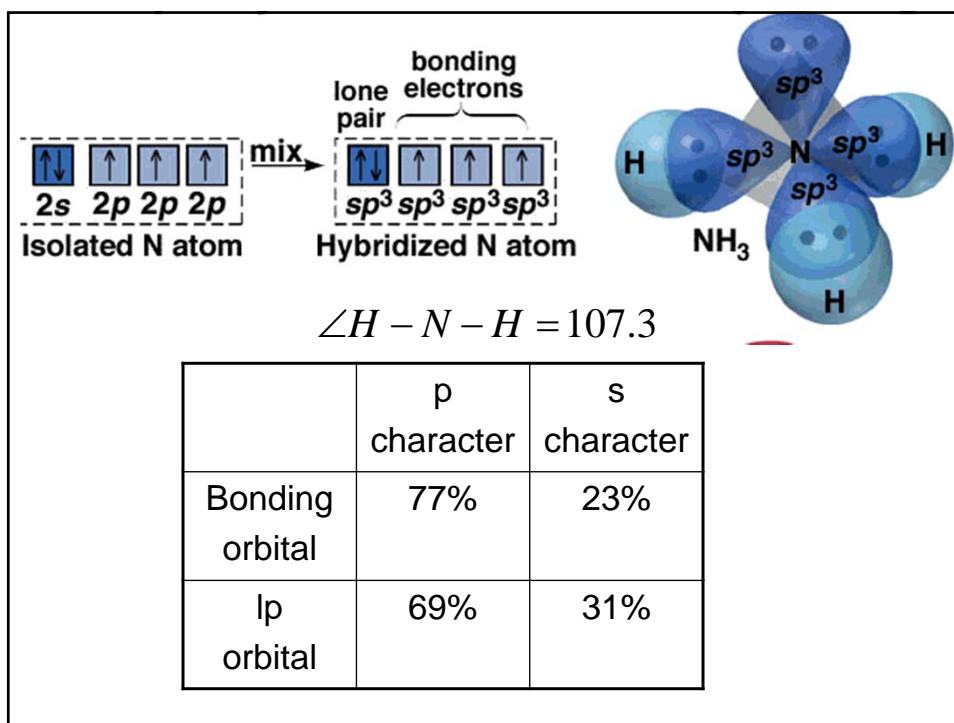
### Directionality

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.

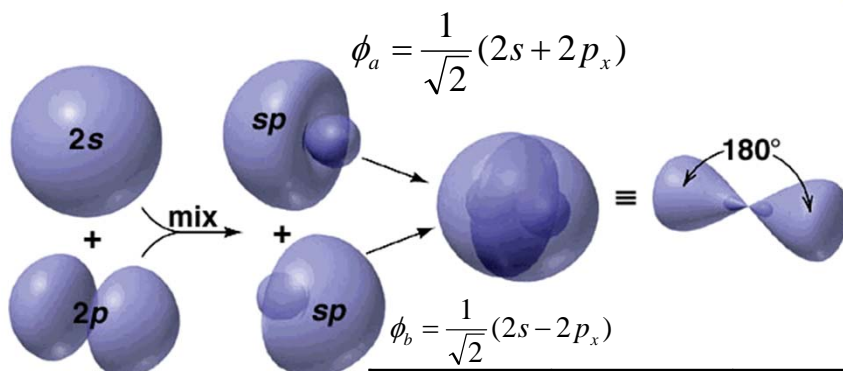
Examine the predicted bonding in ammonia using “pure” atomic orbitals:



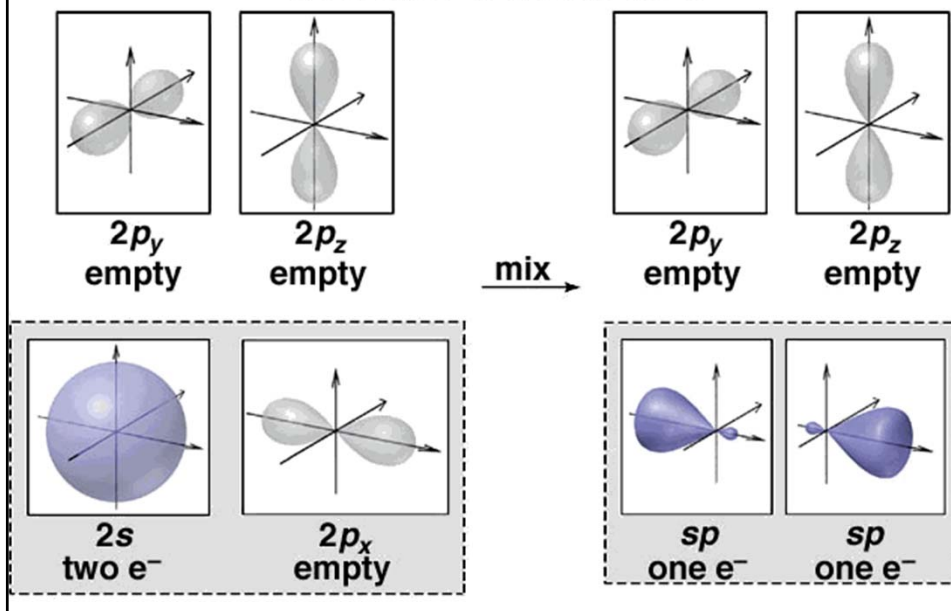
The 2p orbitals on N are oriented along the X, Y, and Z axes so we would predict that the angles between the 2p-1s  $\sigma$  bonds in  $\text{NH}_3$  would be  $90^\circ$ . We know that this is not the case.



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

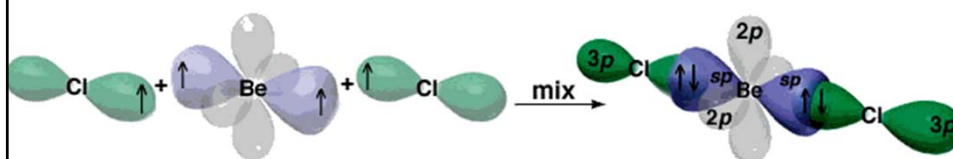


## Orbital Box Diagram with Orbital Contours





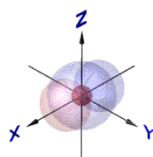
## The $sp$ Hybrid Orbitals in Gaseous $\text{BeCl}_2$



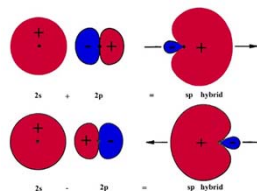
### Hybridization

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



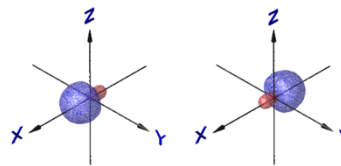
A 2s orbital superimposed on a  $2p_x$  orbital



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

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

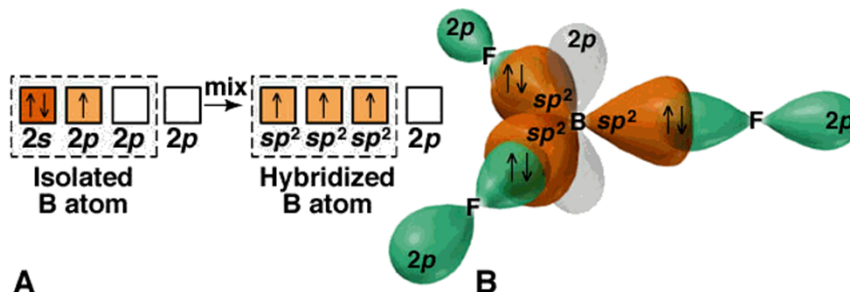
The  $1/\sqrt{2}$  are normalization coefficients.



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

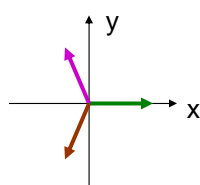
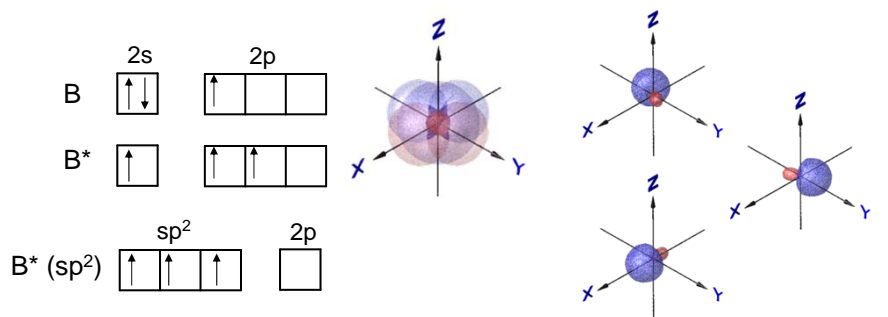


## The $sp^2$ Hybrid Orbitals in $BF_3$



	p character	s character
Bonding orbital	67%	33%

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



This gives three  $sp^2$  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.

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

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

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

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.

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

So this hybrid is normal

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

So this hybrid is normal

$$\Psi_3 = \frac{1}{\sqrt{3}}\phi_s + \frac{2}{\sqrt{6}}\phi_{p_x} \quad \leftarrow \quad 1/3 + 4/6 = 1$$

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<sub>x</sub> orbital has been used

$$1/2 + 1/2 = 1$$

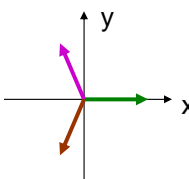
So the entire p<sub>y</sub> orbital has been used

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

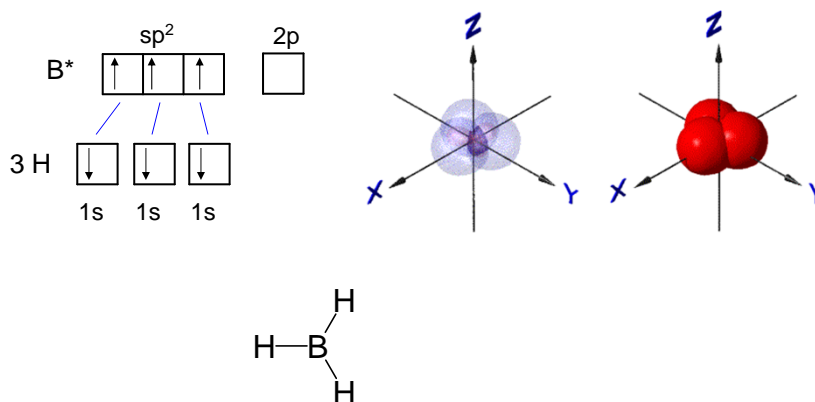
$\Psi_1$ : -x, +y

$\Psi_2$ : -x, -y

$\Psi_3$ : +x, 0y

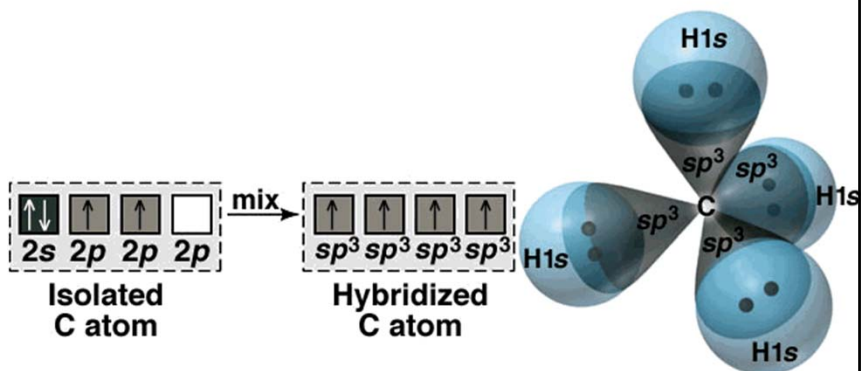


Valence bond theory treatment of a trigonal planar molecule: the bonding in BH<sub>3</sub>



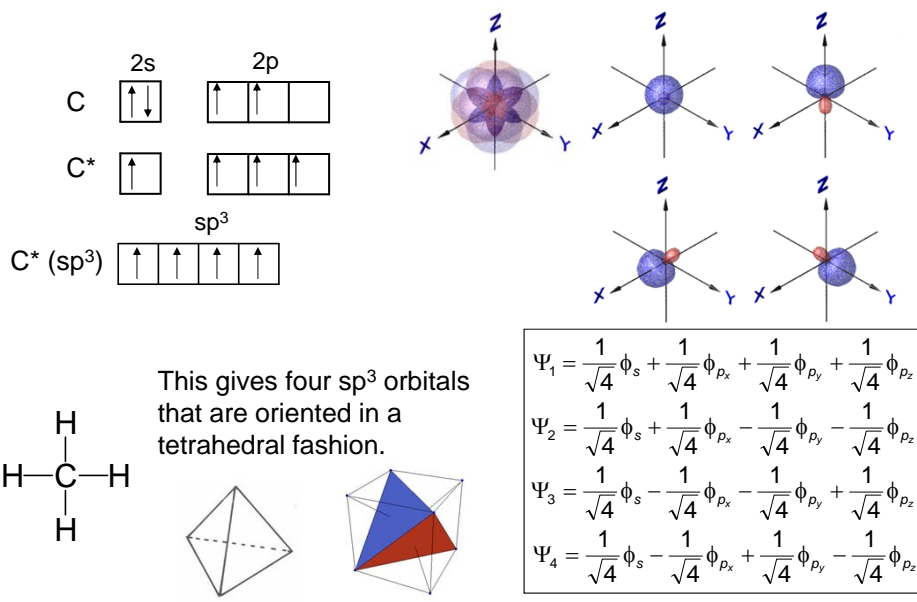
The overlap of the sp<sup>2</sup> hybrid orbitals on B with the 1s orbitals on the H atoms gives three B-H (sp<sup>2</sup>)-1s  $\sigma$  bonds oriented 120° from each other. This agrees with the VSEPR theory prediction.

## The $sp^3$ Hybrid Orbitals in $CH_4$



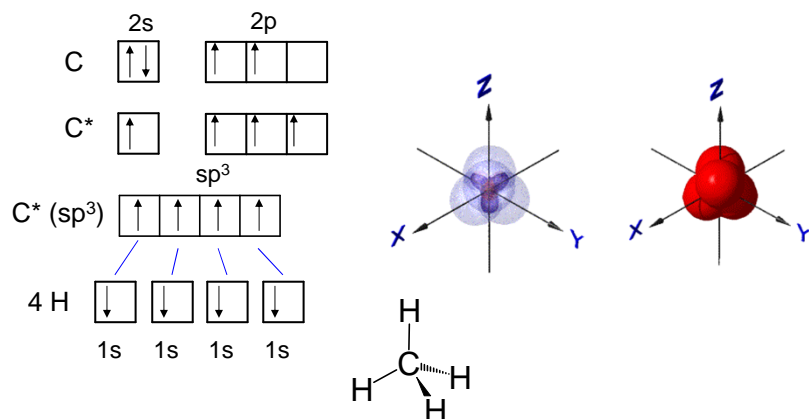
	p character	s character
Bonding orbital	75%	25%

Valence bond theory treatment of a tetrahedral molecule: the bonding in  $CH_4$

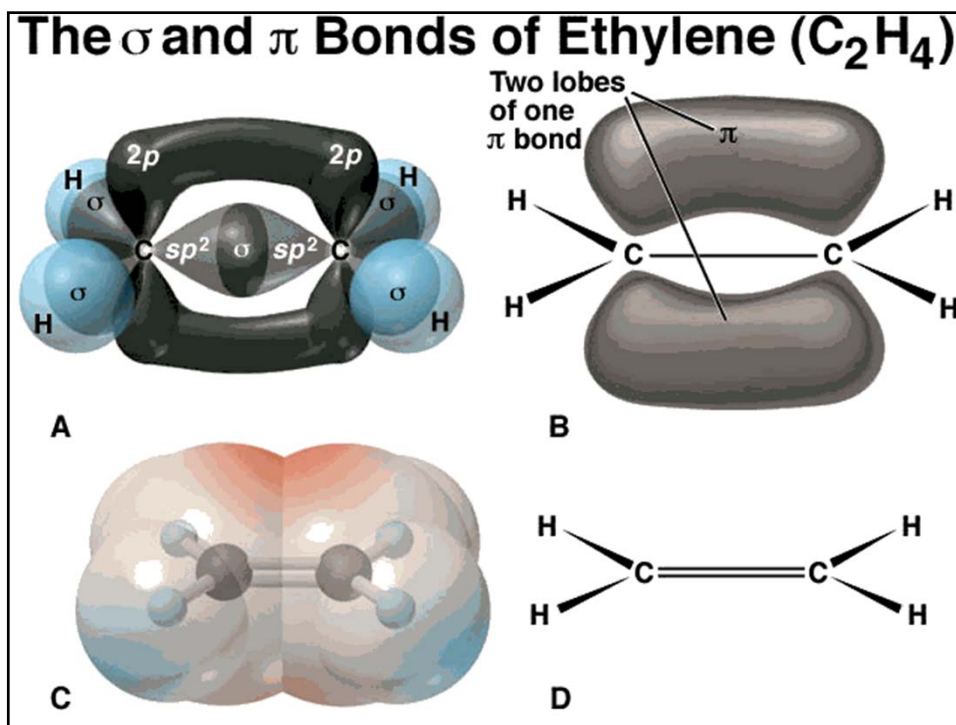
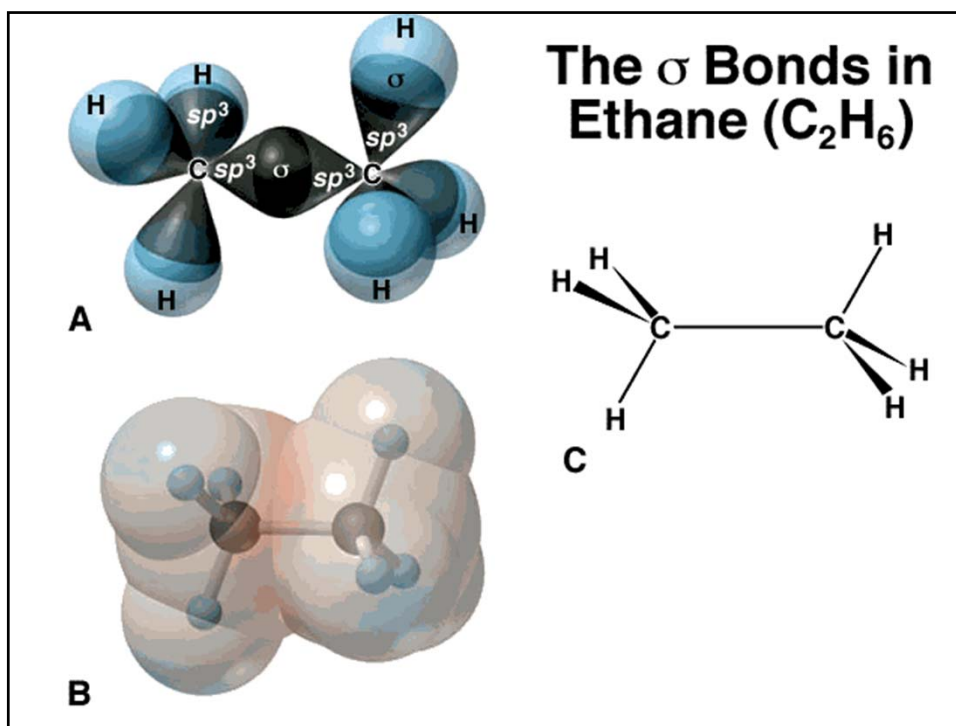




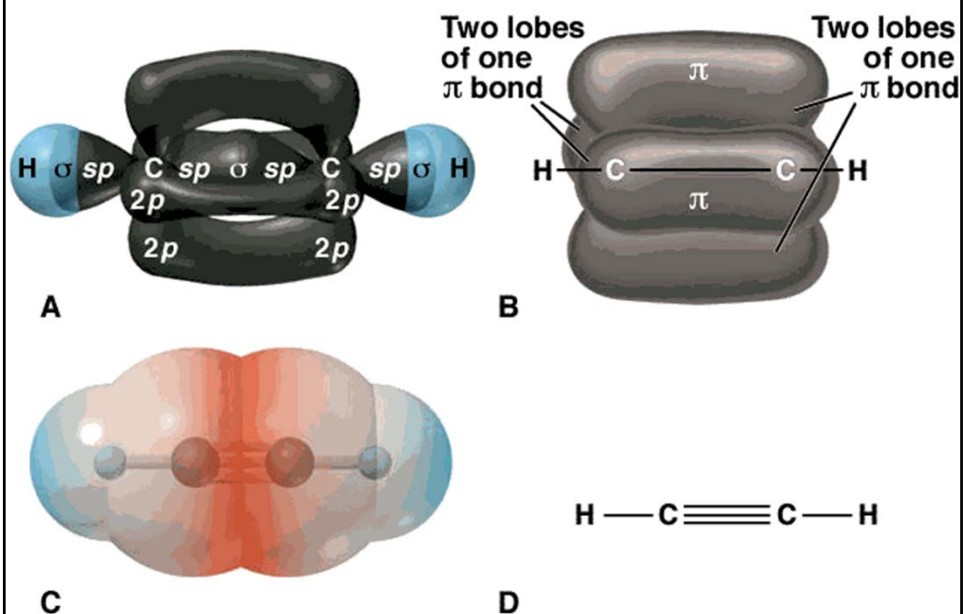
Valence bond theory treatment of a tetrahedral molecule: the bonding in CH<sub>4</sub>



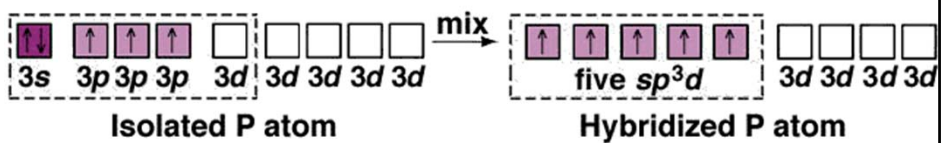
The overlap of the sp<sup>3</sup> hybrid orbitals on C with the 1s orbitals on the H atoms gives four C-H (sp<sup>3</sup>)-1s σ bonds oriented 109.47° from each other. This provides the tetrahedral geometry predicted by VSEPR theory.



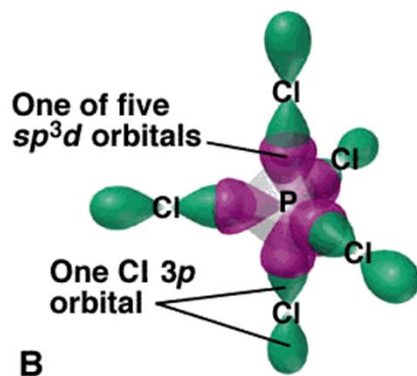
## The $\sigma$ and $\pi$ Bonds of Acetylene ( $C_2H_2$ )



## The $sp^3d$ Hybrid Orbitals in $PCl_5$



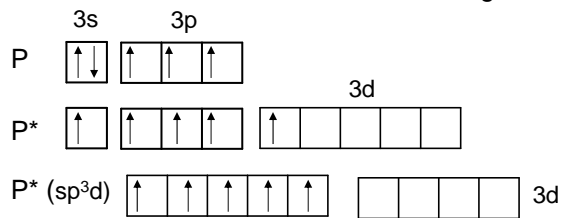
A



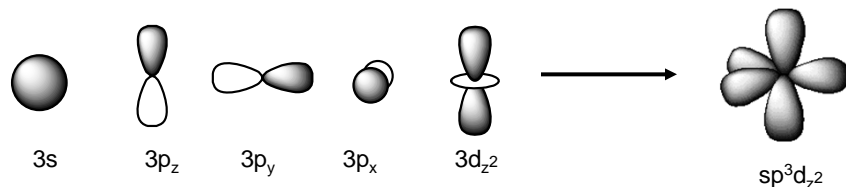
B

**Trigonal bipyramidal**

Valence bond theory treatment of a trigonal bipyramidal molecule:  
the bonding in PF<sub>5</sub>



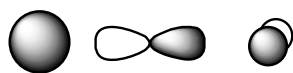
PF<sub>5</sub> has a VSEPR theory AX<sub>5</sub> geometry so we need hybrid orbitals suitable for bonds to 5 atoms. ns and np combinations can only provide four, so we need to use nd orbitals (**if they are available**).



The appropriate mixture to form a trigonal bipyramidal arrangement of hybrids involves all the ns and np orbitals as well as the nd<sub>z<sup>2</sup></sub> orbital.

Valence bond theory treatment of a trigonal bipyramidal molecule

The orbitals are treated in two different sets.

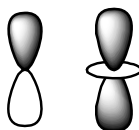


$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_s + \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y}$$

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

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

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



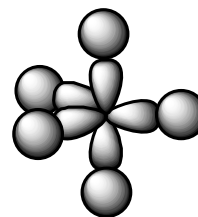
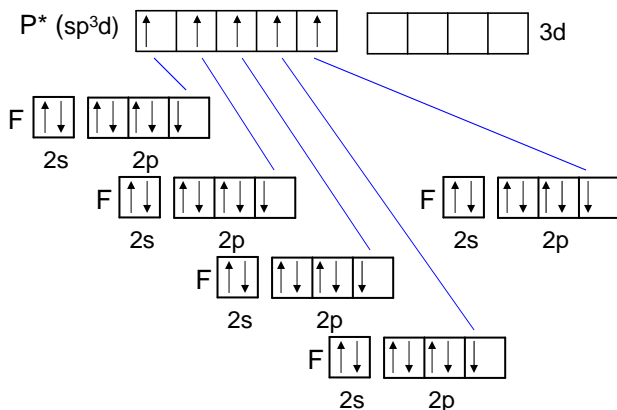
$$\Psi_4 = \frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}$$

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

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

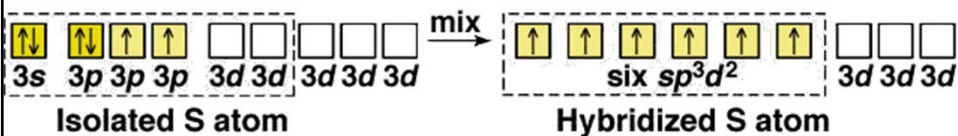
Remember that d orbitals are more *diffuse* than s or p orbitals so VBT predicts that the bonds **formed by hybrids involving d orbitals will be longer than those formed by s and p hybrids.**

Valence bond theory treatment of a trigonal bipyramidal molecule:  
the bonding in PF<sub>5</sub>

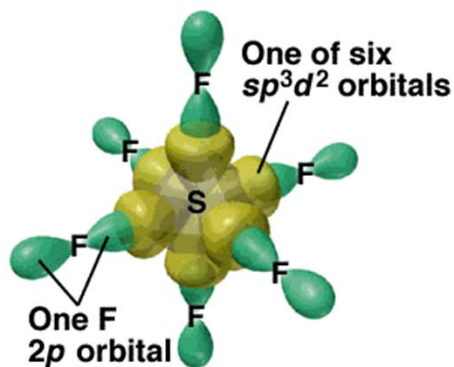


The overlap of the  $sp^3d$  hybrid orbitals on P with the 2p orbitals on the F atoms gives five P-F ( $sp^3d$ )-2p  $\sigma$  bonds in two sets: the two *axial* bonds along the z-axis ( $180^\circ$  from each other) and three *equatorial* bonds in the xy plane ( $120^\circ$  from each other and  $90^\circ$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

### The $sp^3d^2$ Hybrid Orbitals in SF<sub>6</sub>



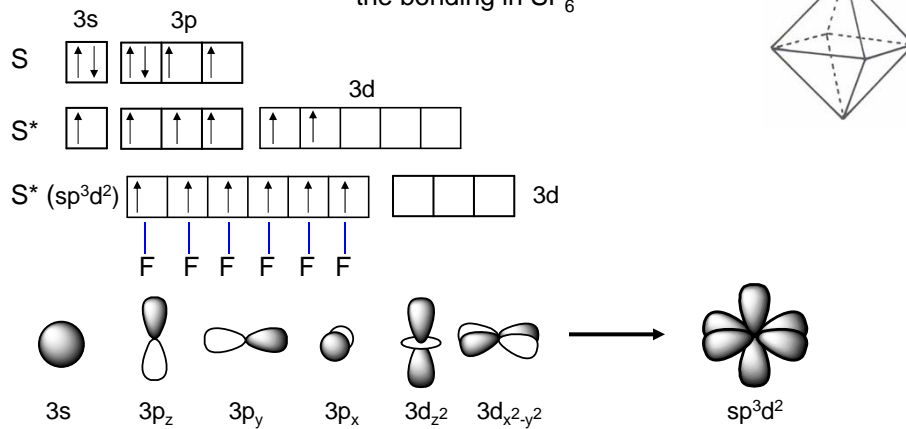
A



B

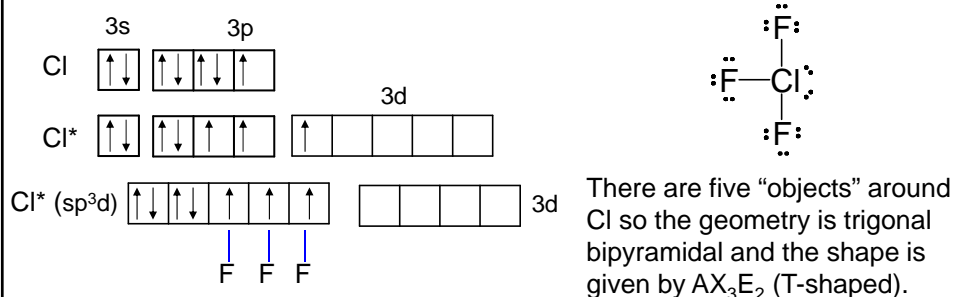
**octahedral**

Valence bond theory treatment of an octahedral molecule:  
the bonding in SF<sub>6</sub>



The overlap of the sp<sup>3</sup>d<sup>2</sup> hybrid orbitals on S with the 2p orbitals on the F atoms gives six S-F (sp<sup>3</sup>d<sup>2</sup>)-2p σ bonds 90° from each other **that are equivalent**. You can figure out the normalization coefficients.

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



The overlap of the  $sp^3d$  hybrid orbitals on Cl with the  $2p$  orbitals on the F atoms gives three P-F ( $sp^3d$ )- $2p$   $\sigma$  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.

Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2<sup>nd</sup> Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

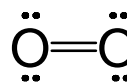
**Table 11.1** Composition and Orientation of Hybrid Orbitals

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



**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