

## Molecular Orbital

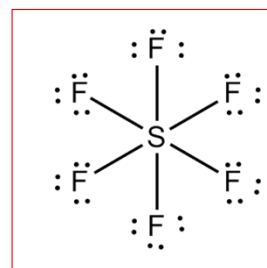
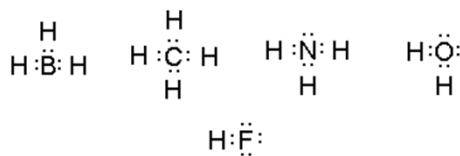
Reading: DG 2.11-14, 3.1-5, 4; MT 3.1

### Lewis Structure

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

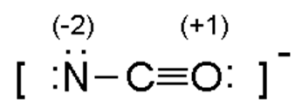
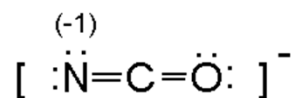
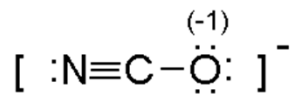


**Octet Rule: Closed shell configuration of 8 surrounding e**





## 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**

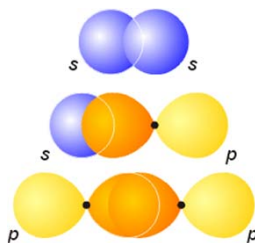
**Spectroscopic properties  
(ionization, excited states)**

## Valence Bond Theory

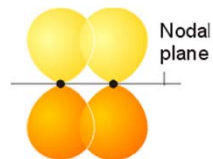
Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules. VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms. VBT asserts that electron pairs occupy *directed orbitals* localized on a particular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

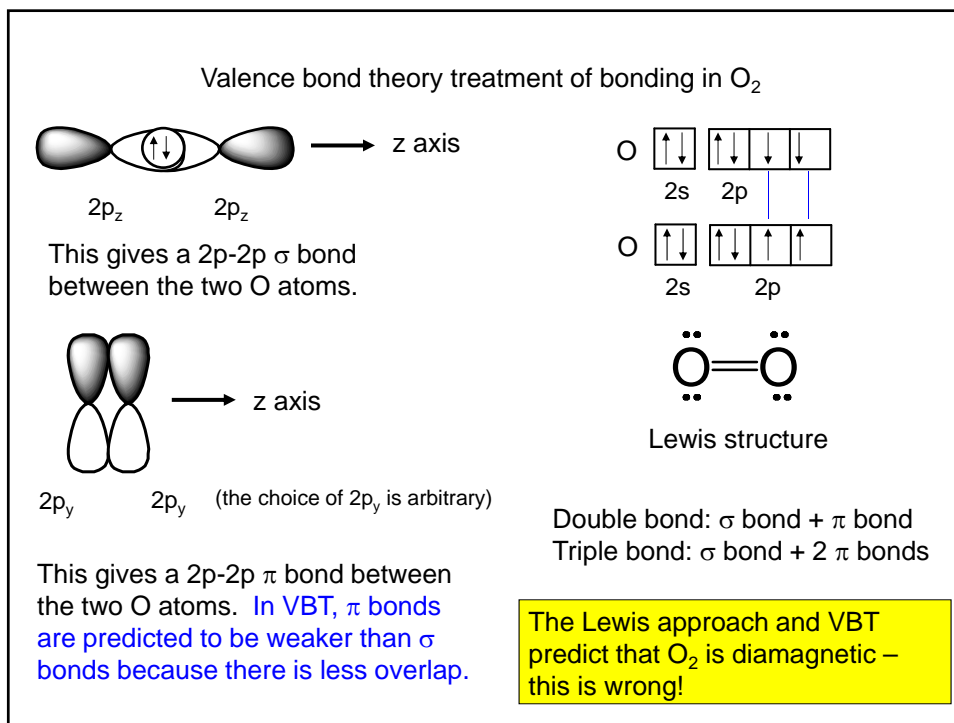
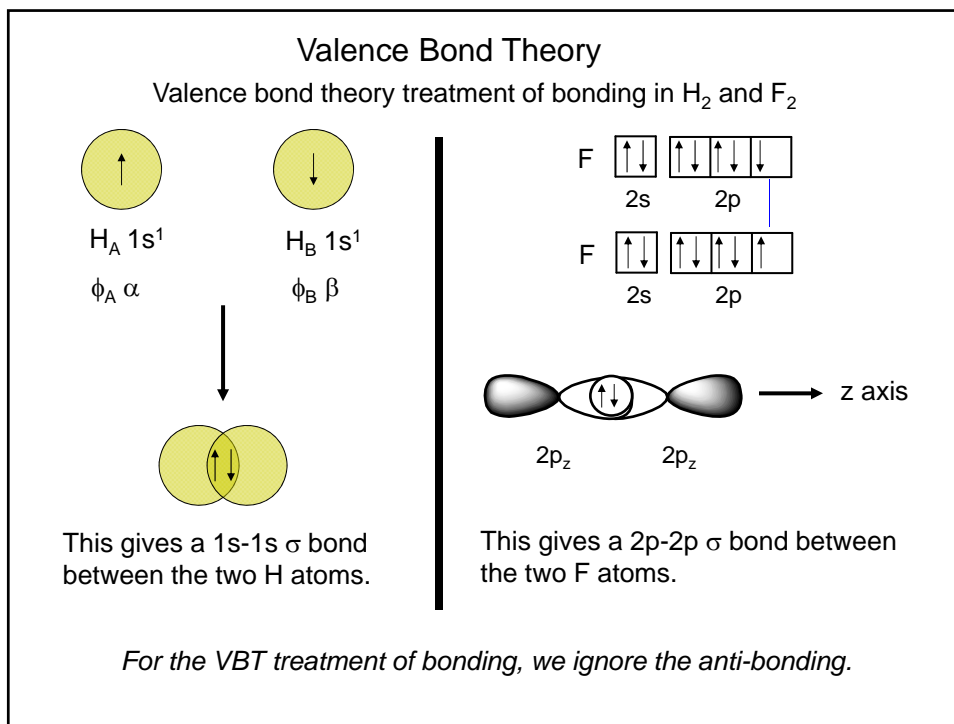
In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.

$\sigma$  bonds:  
symmetric about  
the internuclear  
axis



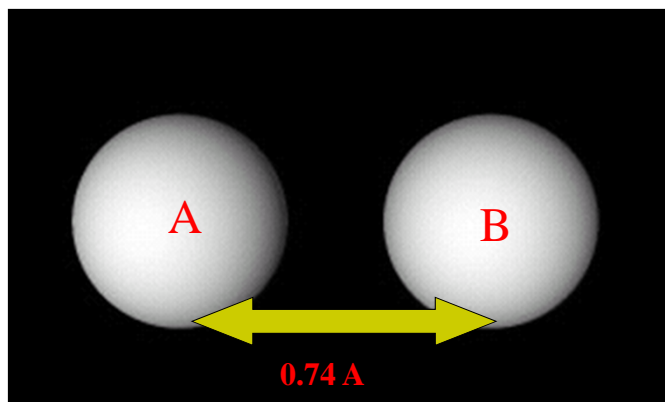
$\pi$  bonds: have  
a node on the  
inter-nuclear axis  
and the sign of  
the lobes  
changes across  
the axis.







## Valence Bond theory

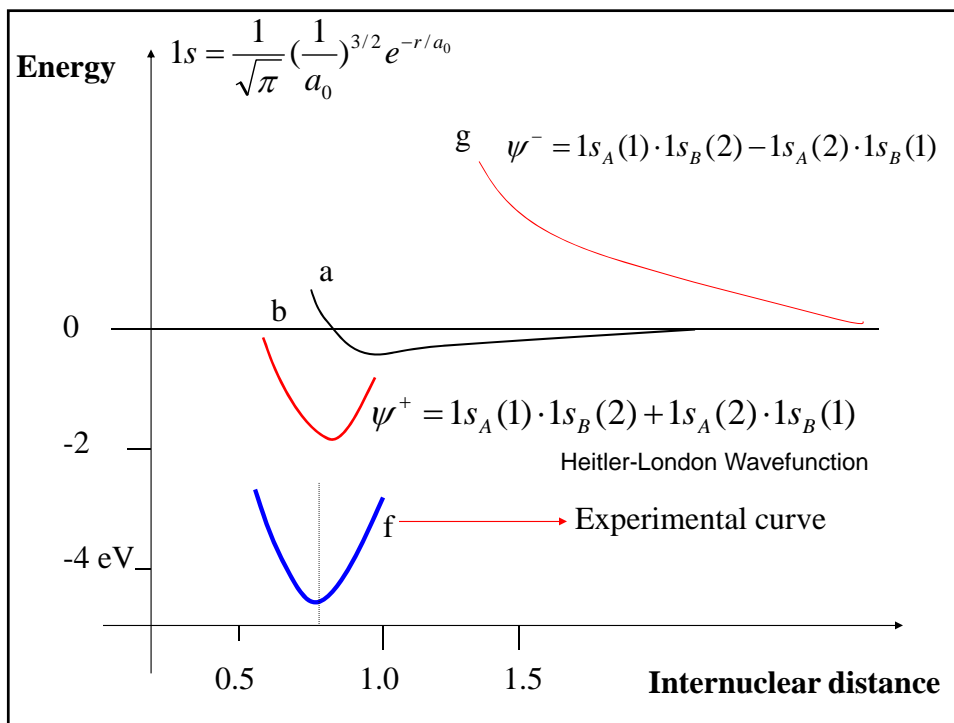
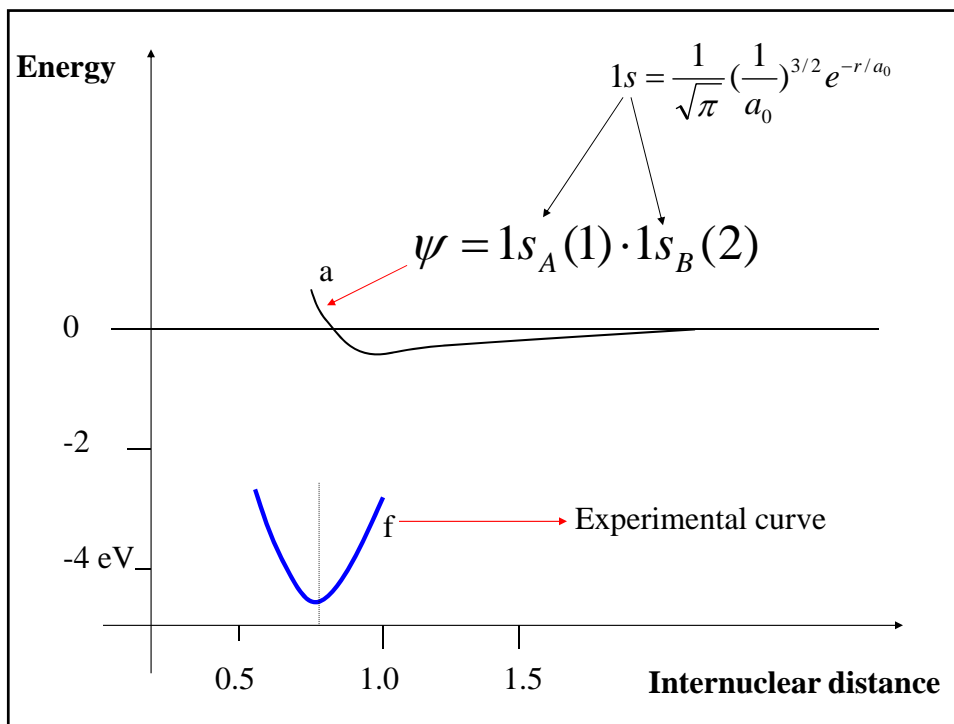


Bond dissociation energy: 103 kcal/mol



## 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.

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



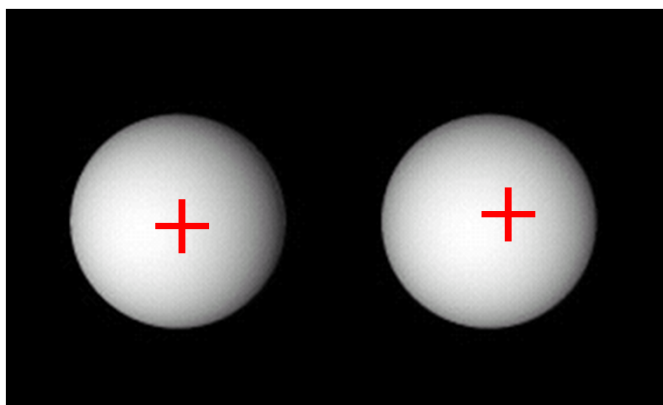
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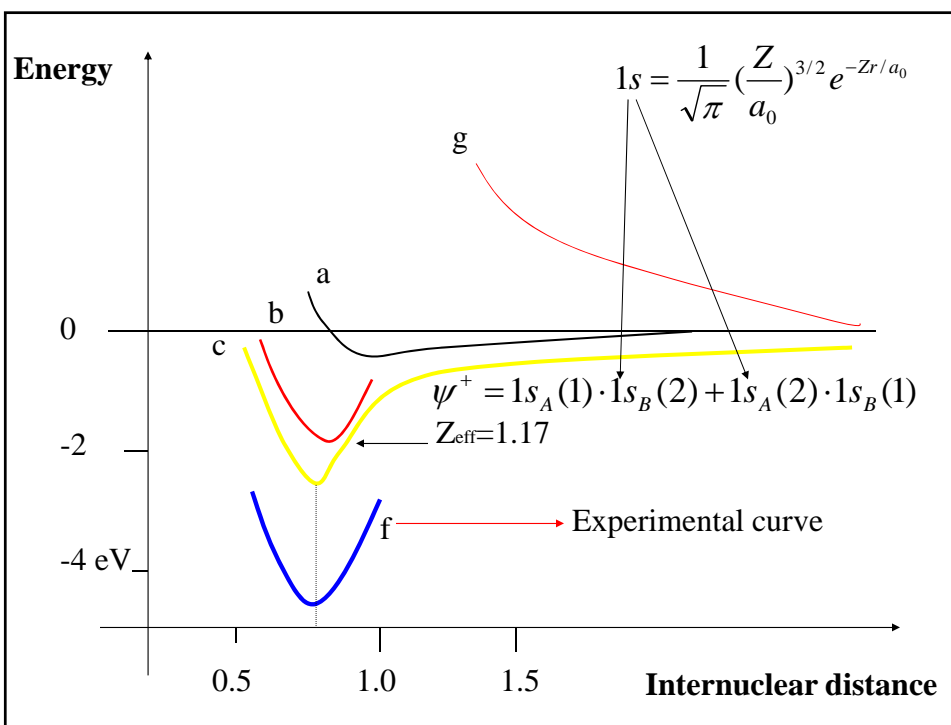
Can always minimize  $E_{\psi(x)}$



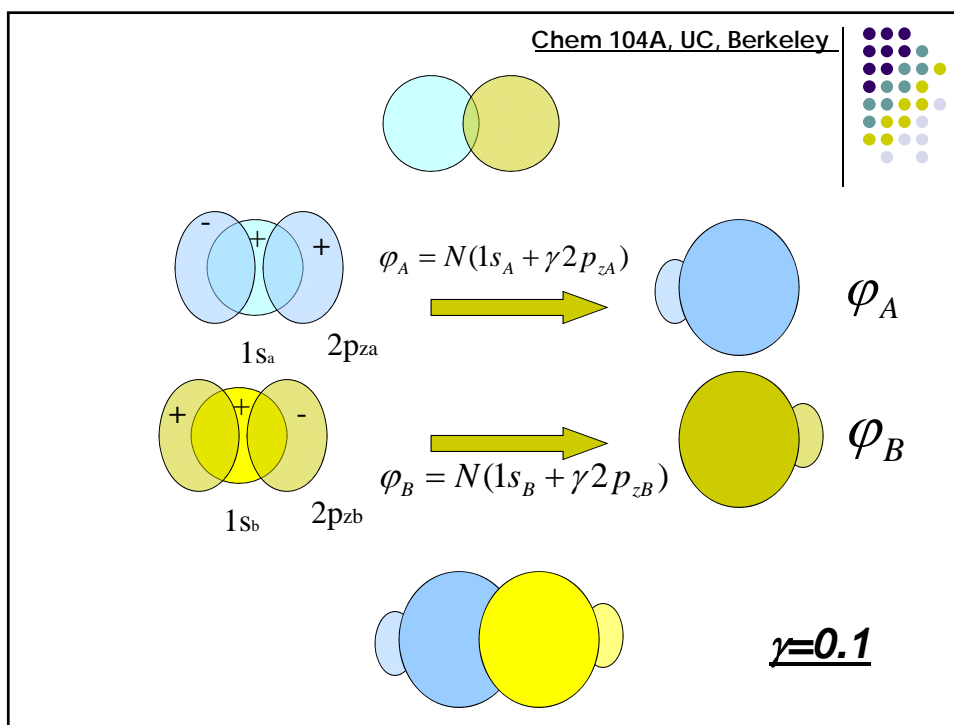
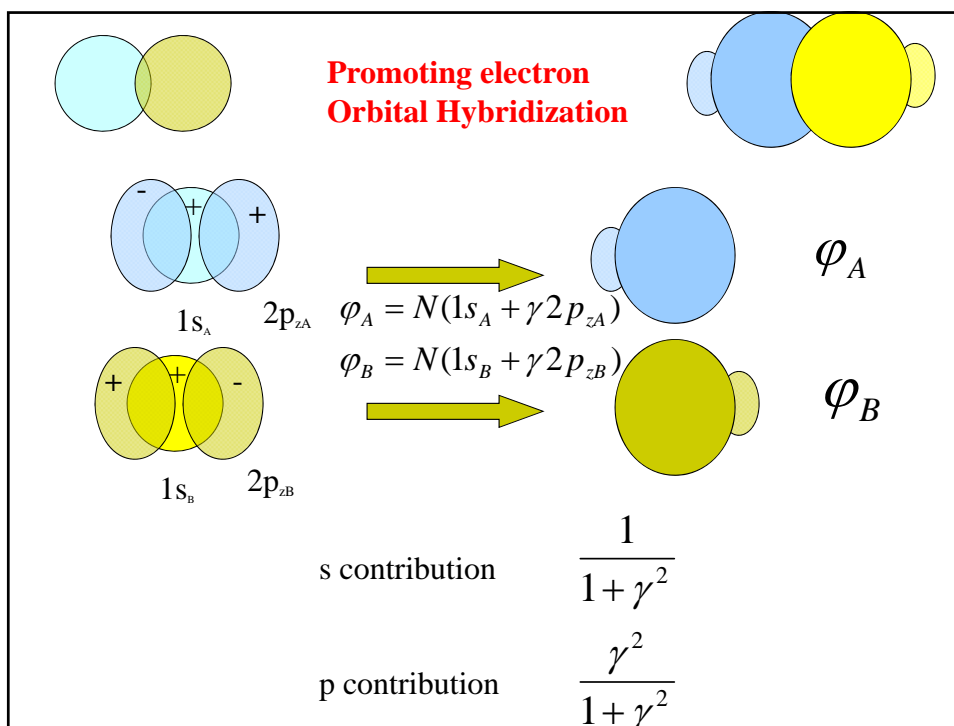
$$1s = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

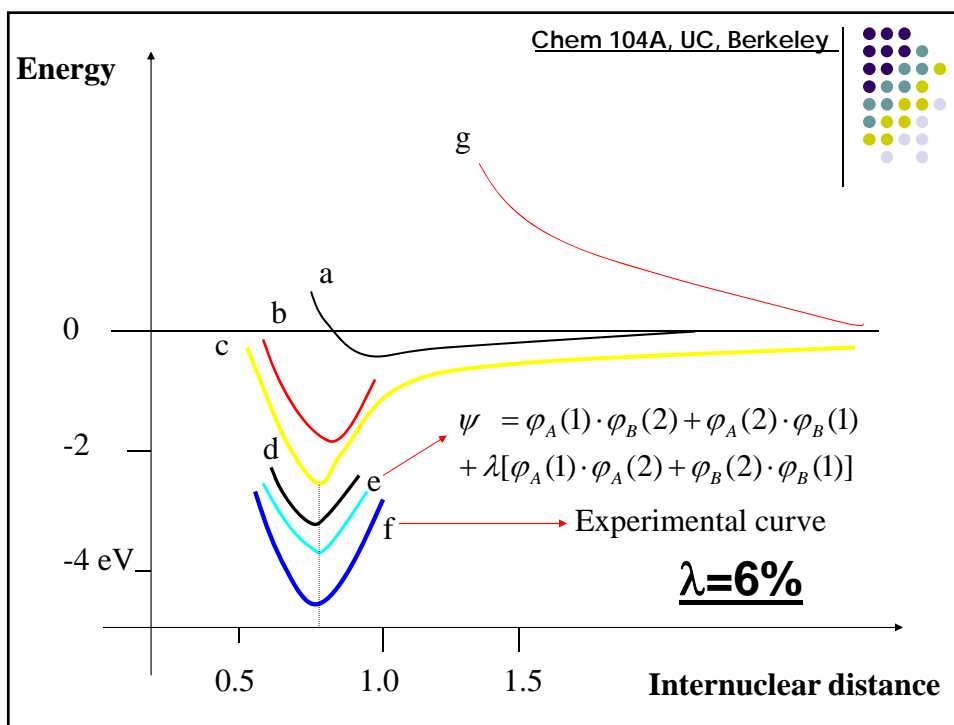
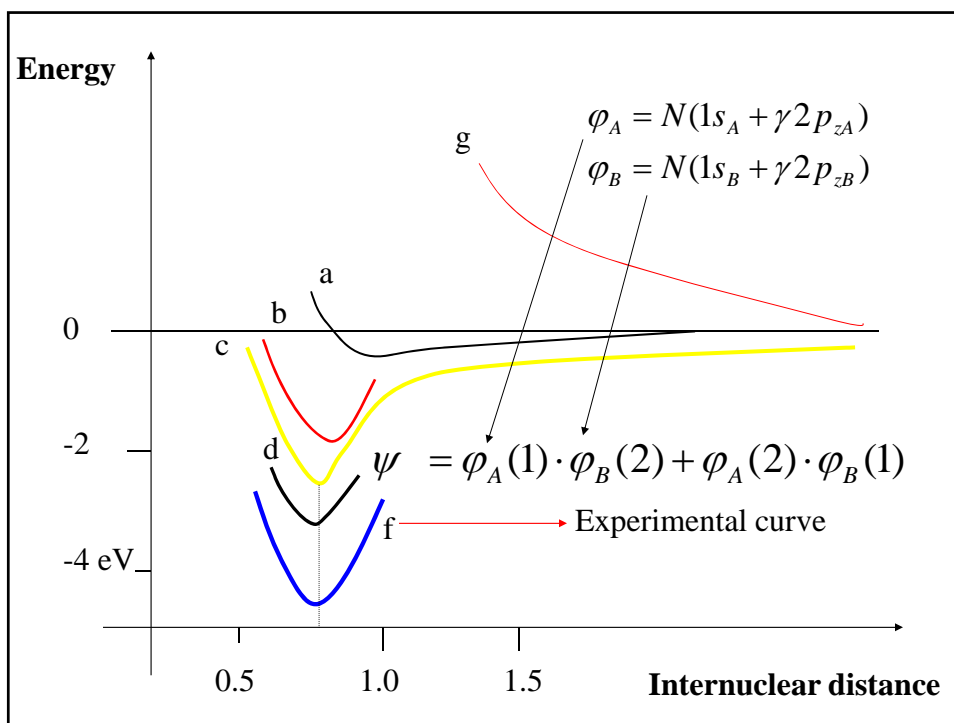


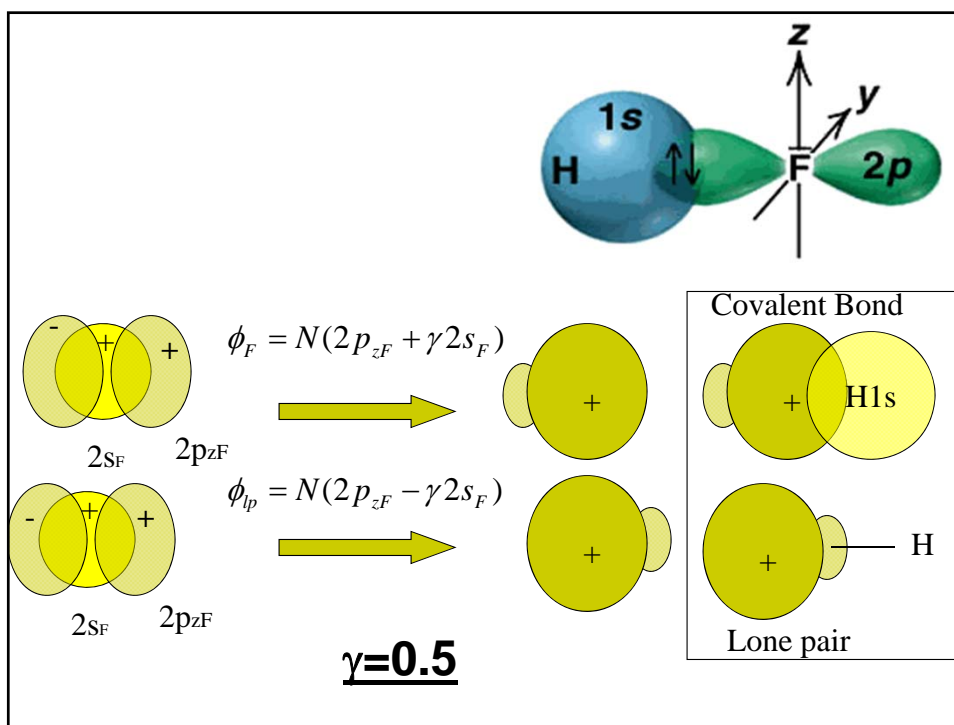
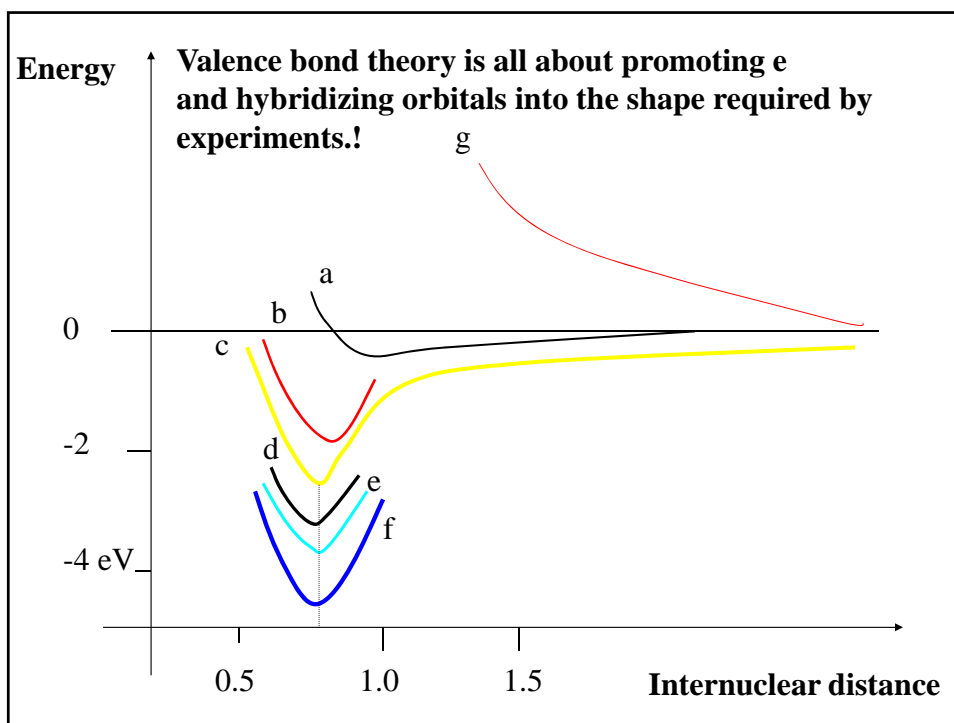
$$1s = \psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$





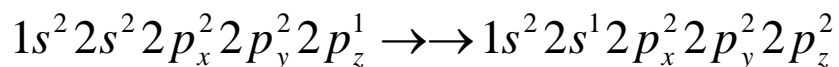








promotion



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

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

**Benefit of hybridization**

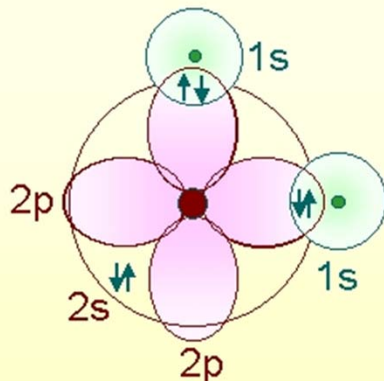
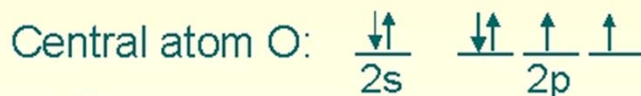
1. Increase in e density between nuclei, enhanced bonding
2. Decrease in e-e repulsion by formation of a lone-pair orbital, LP Orbital more directed away from BP than the Original s LP

**Ionic Contribution: 50%**

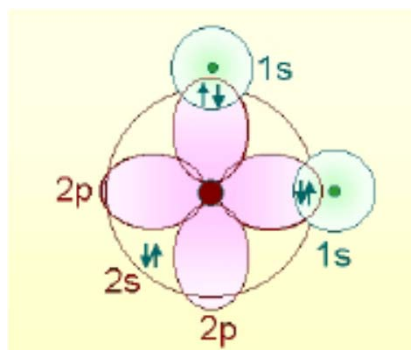
$$\psi = 1s_H(1)\phi_F(2) + 1s_H(2)\phi_F(1) + \lambda\phi_F(2)\phi_F(1)$$

## Valence Bond Theory and Molecular Geometry

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

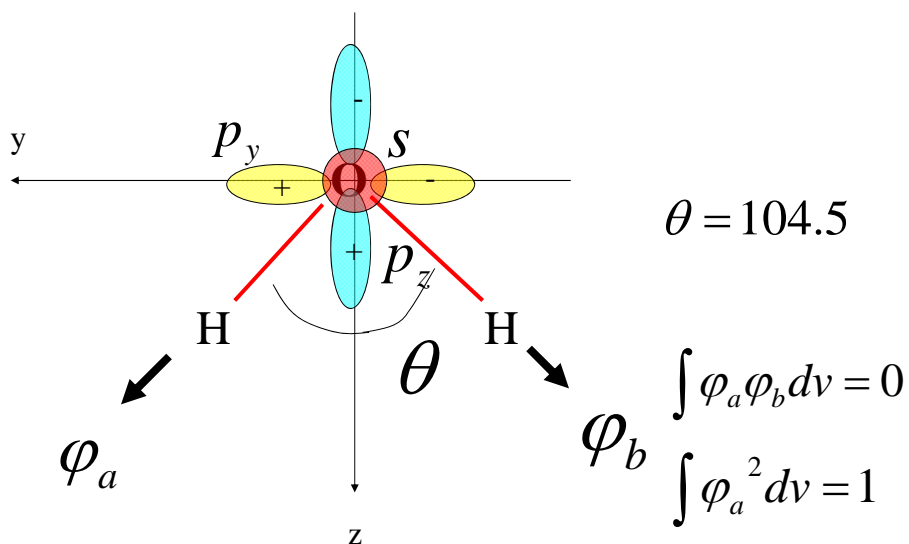


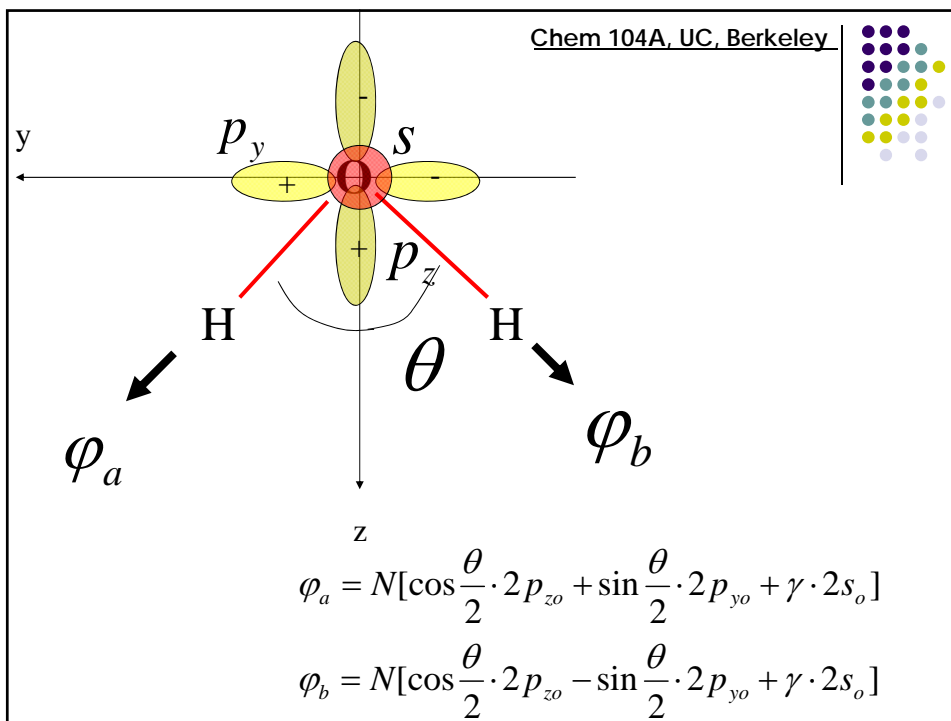
Orbital overlap suggests that the bond angle is 90°.



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

**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".

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

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

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

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

$$\gamma = 0.5$$

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

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

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

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

**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

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

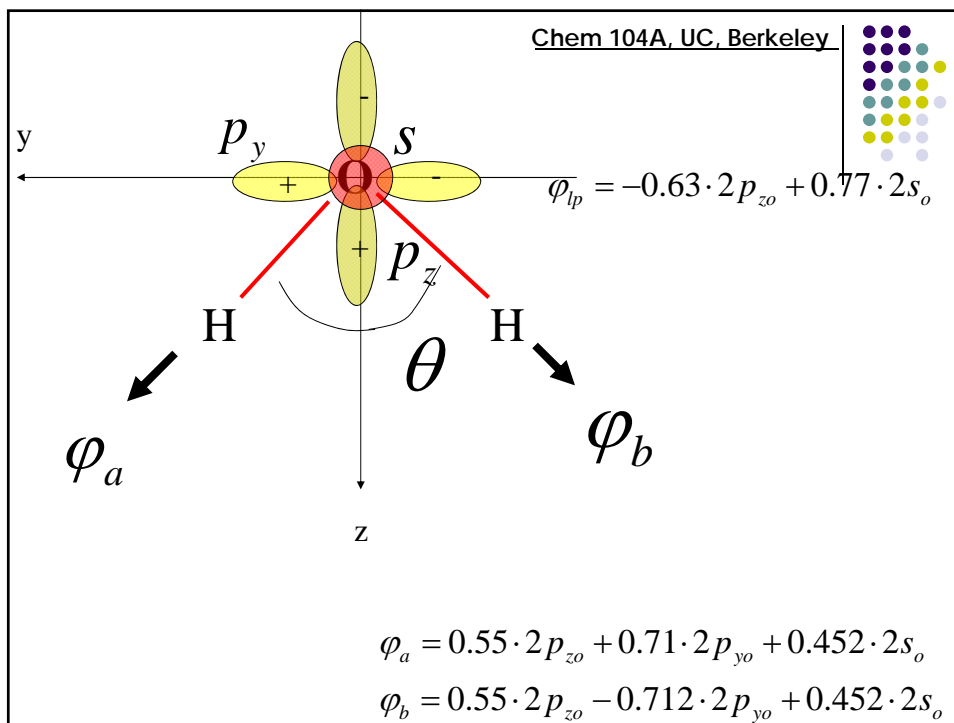
$$\varphi_b = 0.55 \cdot 2p_{z_o} - 0.712 \cdot 2p_{y_o} + 0.452 \cdot 2s_o$$

	$\varphi_a$	$\varphi_b$	
$2p_{z_o}$ <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%

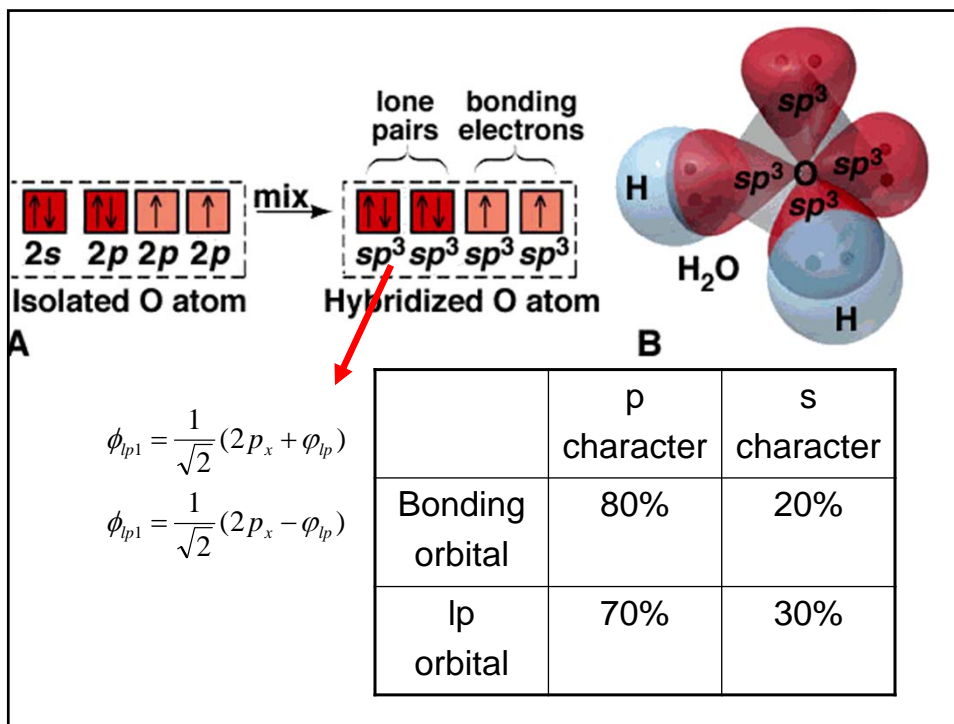
**Bonding: Average 80% p character, 20% s character**

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

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



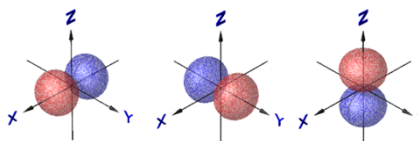
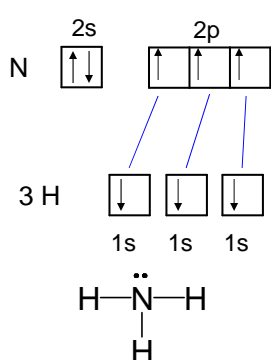




### Directionality

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  $NH_3$  would be  $90^\circ$ . We know that this is not the case.