Quantum Mechanical Approaches to Molecular Bonding

(In principle, it is possible to construct a Schrödinger equation, , $\Psi = E\Psi$, to describe the electronic structure of a molecule.

; In practice, seeking exact solutions to the Schrödinger equation for molecules is an insurmountable mathematical problem.

L Two principal approaches have been taken to construct approximate wave functions for molecules, starting with the atomic orbitals of the atoms comprising the molecules.

1. Valence Bond (VB) theory - developed by Linus Pauling and co-workers, essentially puts the Lewis notion of electron pairs on a quantum mechanical footing, in which each shared or lone pair of electrons about an atom occupies a localized orbital.

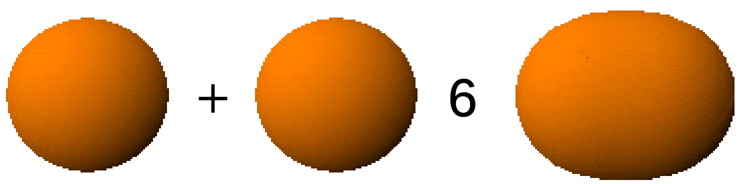
2. Molecular orbital (MO) theory, developed by Robert S. Mulliken and co-workers, constructs new orbitals that are *delocalized* (i.e., “spread out”) across the molecule.

L VB and MO theories take different mathematical approaches to constructing wave functions for the molecule, but their results are often equivalent.

Valence Bond (VB) Theory

L A chemical bond forms by sharing a pair of electrons through overlap of atomic orbitals on the bonded atoms.

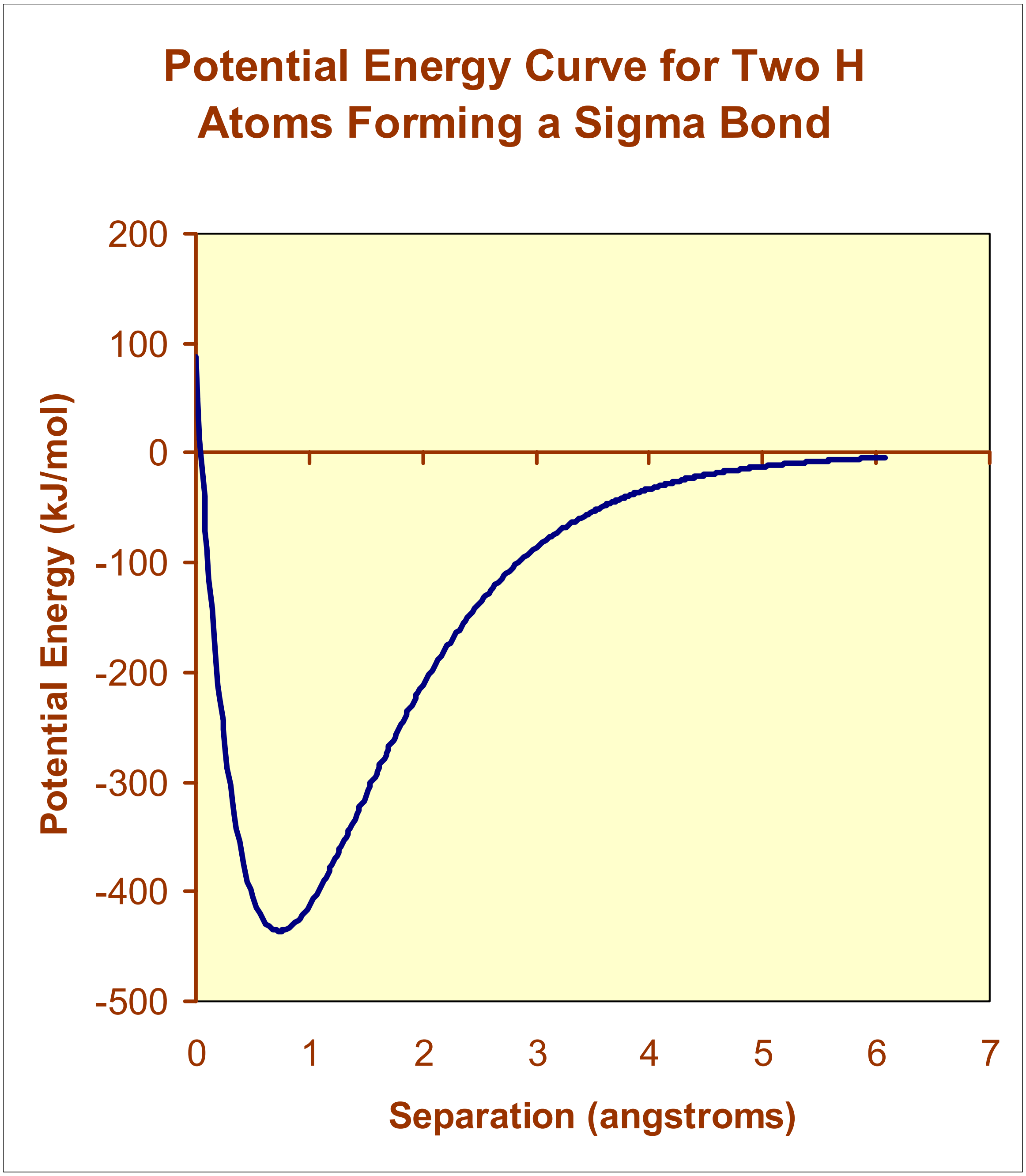
L When overlap creates an increase in electron density in the region between the two nuclei a **sigma bond** (σ bond) is formed.



Formation of sigma (σ) bond in H_2 from 1*s* orbitals

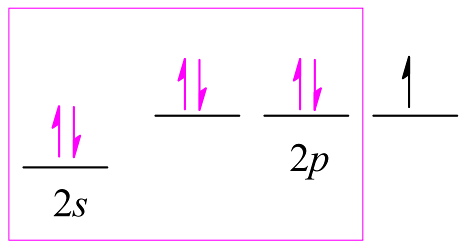
Potential Energy and Internuclear Separation

- Attraction of the electrons to two nuclei causes a lowering of the potential energy to a minimum at the normal bond distance.



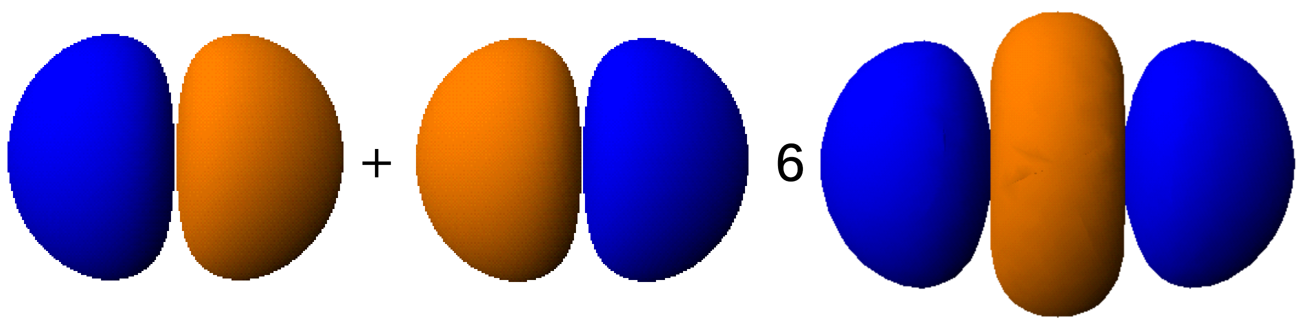
Sigma Bond Formation in F_2

Valence configuration:



Non-bonding electrons

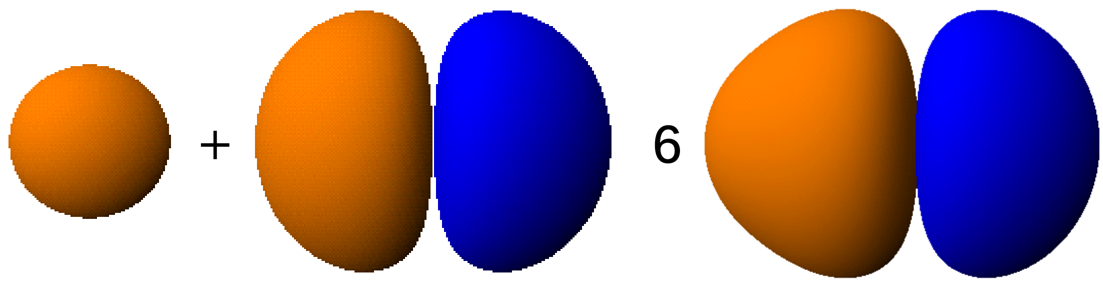
- The single bond in F_2 can be seen as a sigma bond formed by overlap of two 2*p* orbitals.



Formation of sigma (σ) bond in F_2 from 2*p*

Heteronuclear Diatomic Molecules

- In heteronuclear diatomic molecules, the overlap may involve two different types of orbitals.



Formation of sigma (σ) bond in HF from H 1*s* and F 2*p*

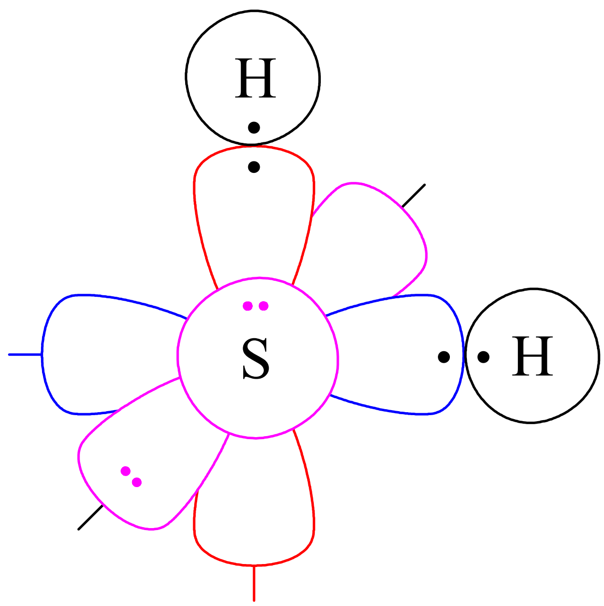
Polyatomic Molecules

Example: H_2S

H $1s^1$ ¼
$1s$

S $3s^2 3p^4$ ¼¿
$3s$

¼¿ ¼ ¼
$3p$

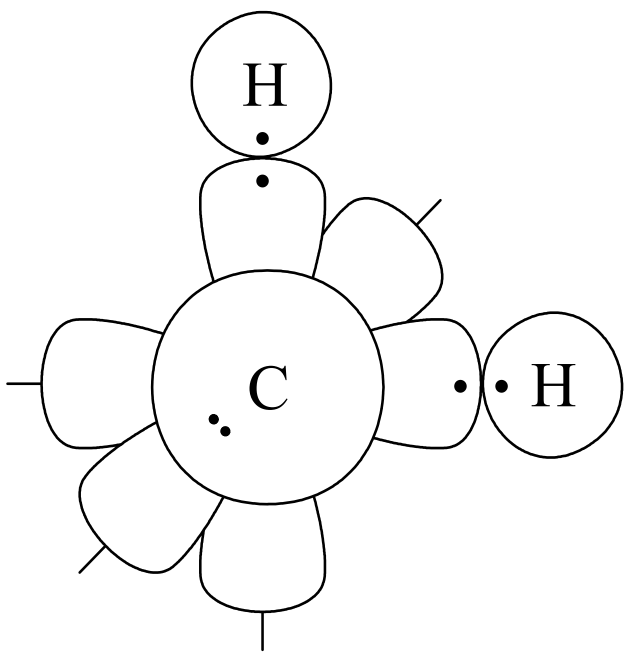


Polyatomic Molecules
The Need for Hybridization

How can we form a VB model of four equal sigma bonds around carbon, starting with its valence configuration $2s^2 2p^2$?

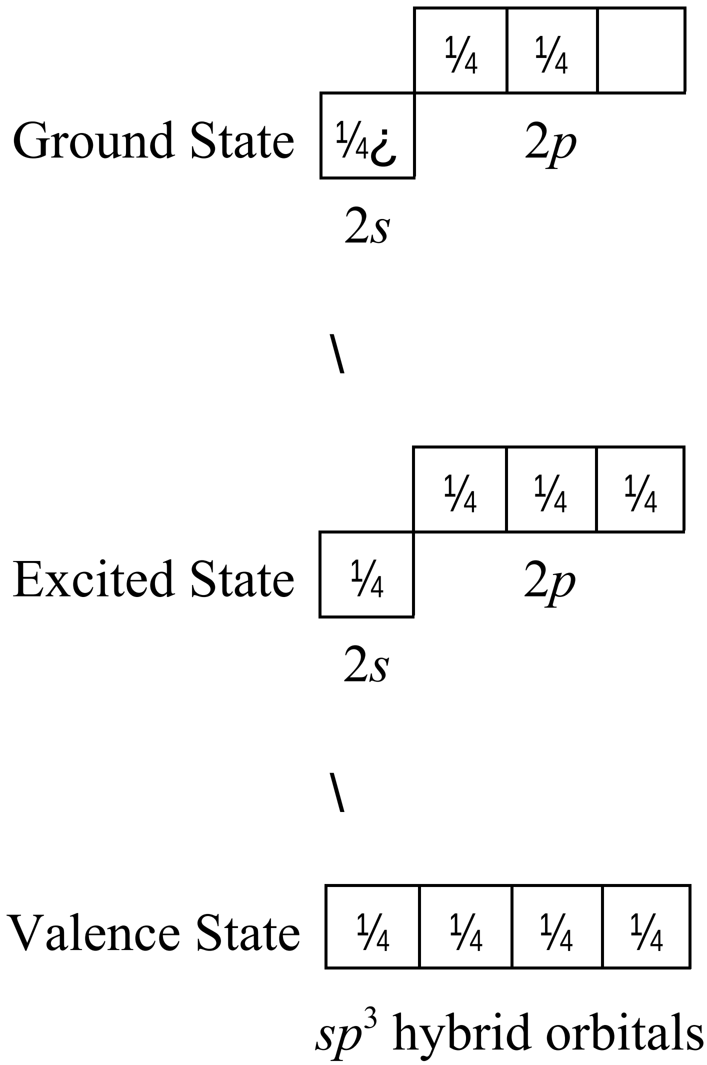
- It seems that only two bonds could be made with an angle of 90° through overlap of carbon 2*p* orbitals with hydrogen 1*s* orbitals.

C $2s^2 2p^2$ ¼¿ (2s) ¼ ¼ ___ (2*p*)

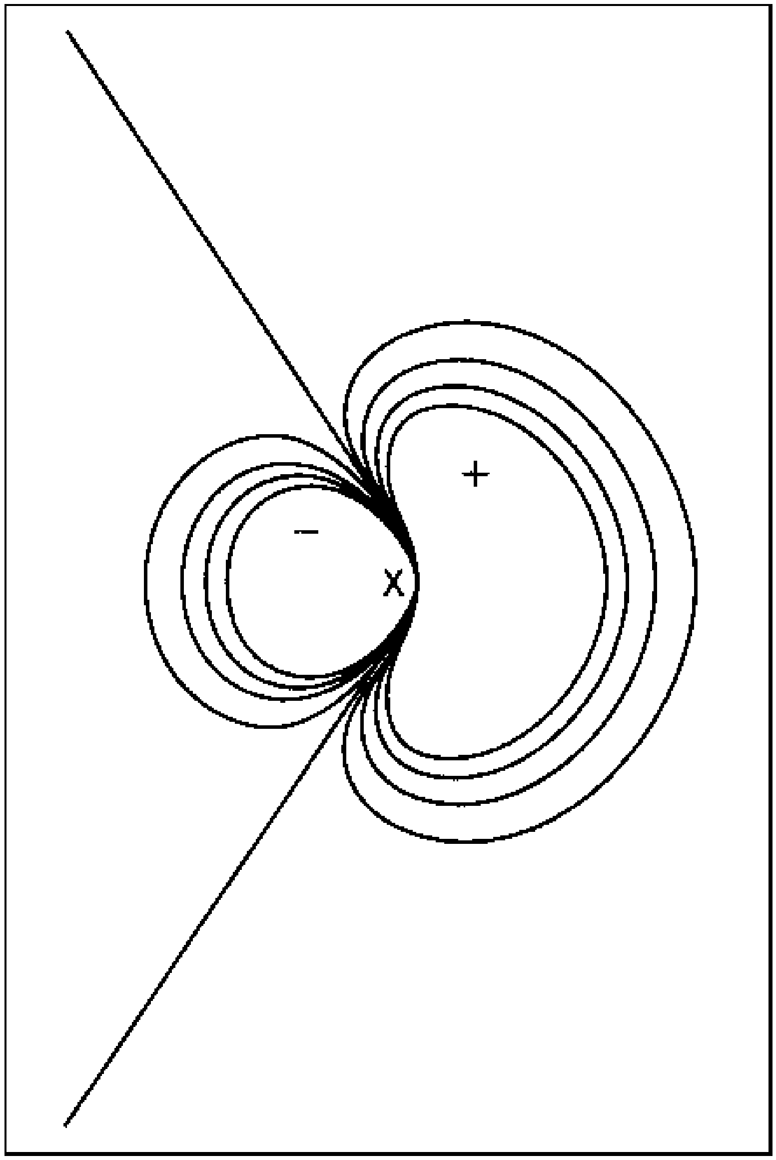


L But CH_2 does not exist as a stable molecule, and CH_4 is formed instead.

Hybrid Orbital Formation in CH_4
A Hypothetical Process



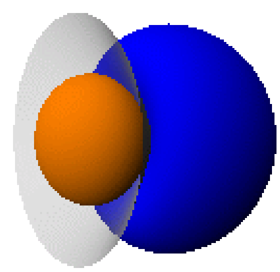
Contour Diagram of a Single sp^3 Hybrid Orbital



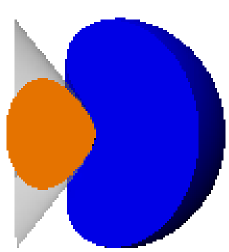
X marks the position of the nucleus

Boundary Surface Model of a Single *sp*^{3} Hybrid

Three-dimensional model (rotated 30° about a vertical axis):

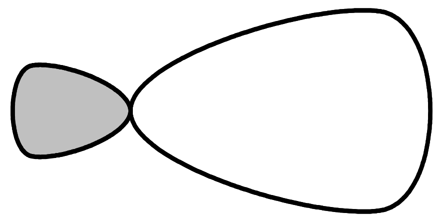


Cut-away rendering:

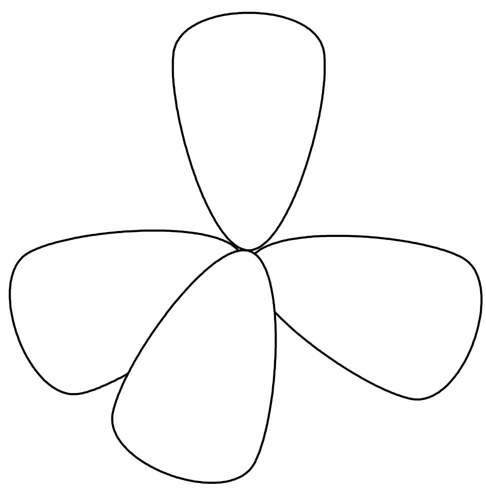


sp^3 Hybrid Orbitals - Simplified Sketches

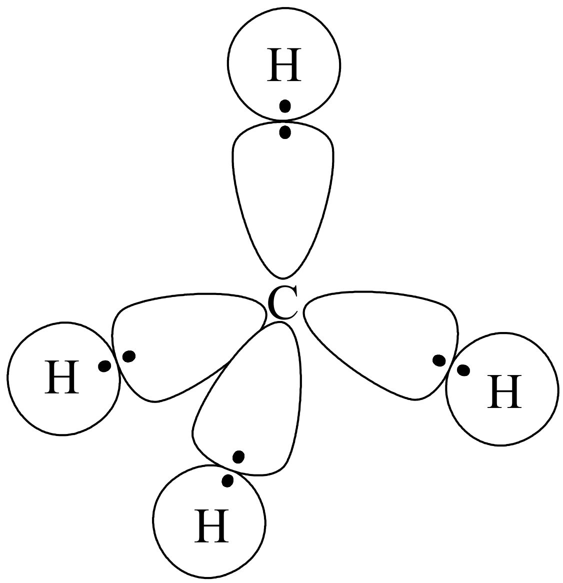
Shape of an individual *sp^3* hybrid orbital:



Set of four *sp^3* hybrid orbitals in a tetrahedral arrangement:



VB Model of CH_4 with sp^3 Hybrids on C



VB Model of NH_3 with sp^3 Hybrids on N

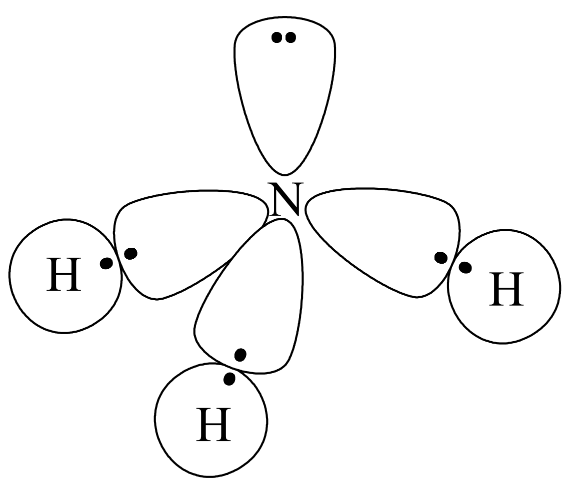
	¼	¼	¼
¼¿		2*p*	

2*s*

\

¼¿	¼	¼	¼

sp^3 hybrid orbitals



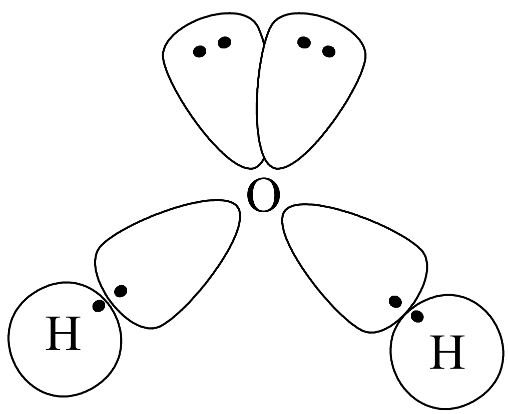
VB Model of H_2O with *sp*^{3} Hybrids on O

	¼¿	¼	¼
¼¿		2*p*	
2*s*			

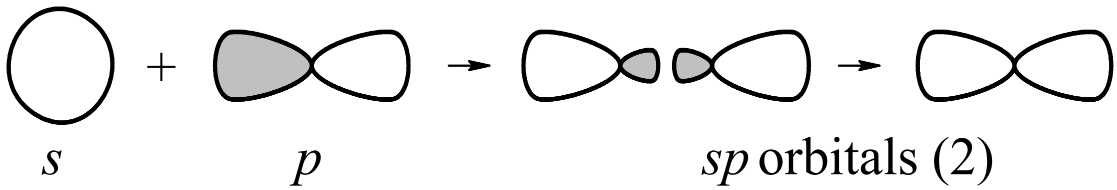
\

¼¿	¼¿	¼	¼

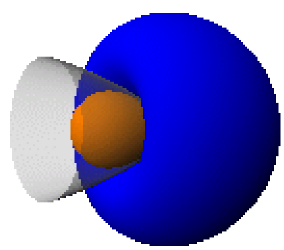
sp^3 hybrid orbitals



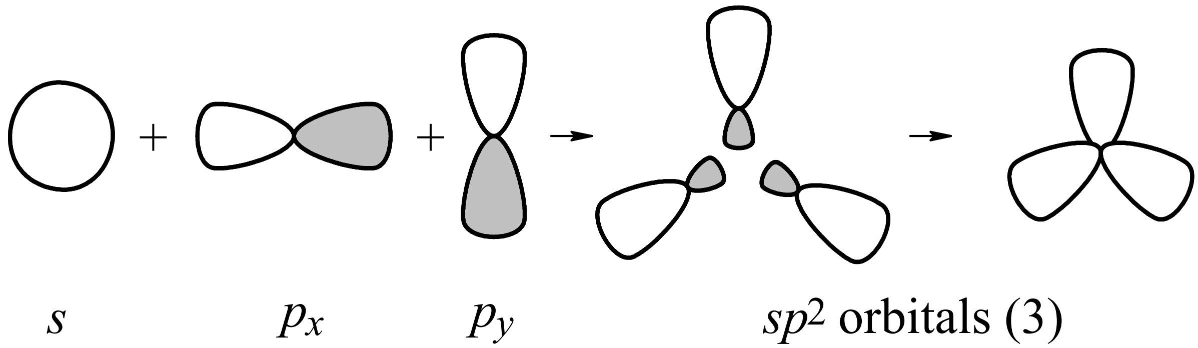
Hybrids for 2 Electron Domains



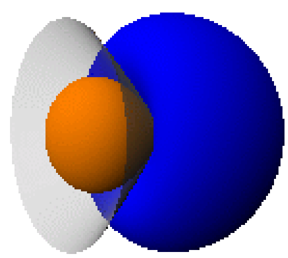
Boundary surface model of one *sp* hybrid:



Hybrids for 3 Electron Domains



Boundary surface model of one sp^2 hybrid:



Summary of Hybrid Orbital Types

Domains	Geometry	Orbitals Used	Hybrids
2	linear	s, p	sp
3	trigonal planar	s, p_x, p_y	sp^2
4	tetrahedral	s, p_x, p_y, p_z	sp^3
5	trigonal bipyramidal	s, p_x, p_y, p_z, d_{z^2}	sp^3d
6	octahedral	s, p_x, p_y, p_z,d_{z^2}, $d_{x^2-y^2}$	sp^3d^2