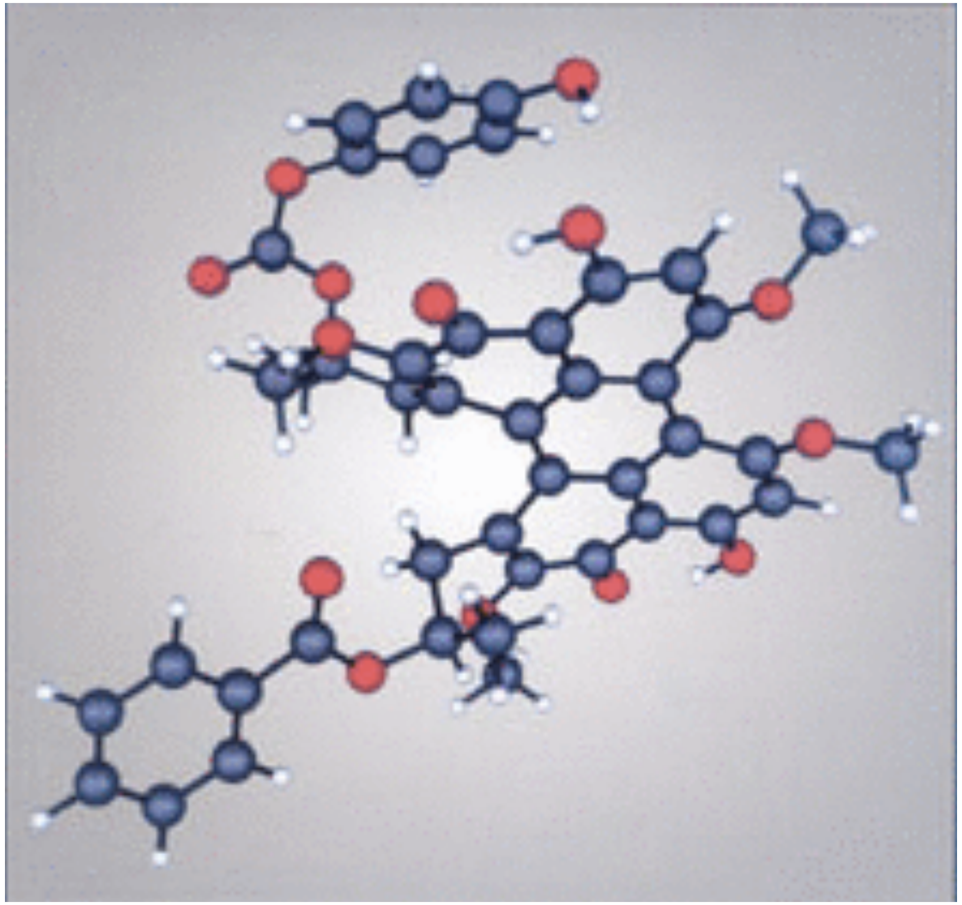
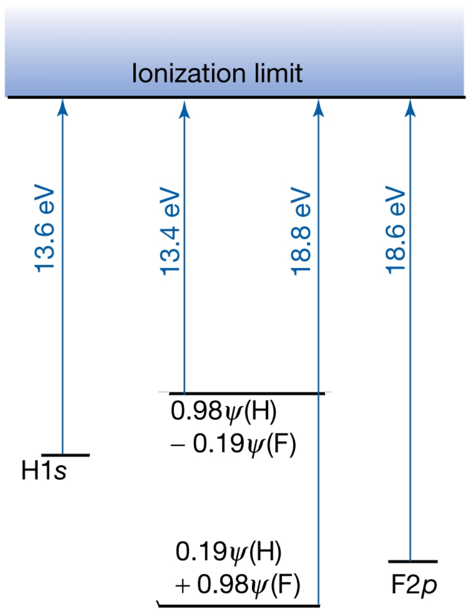
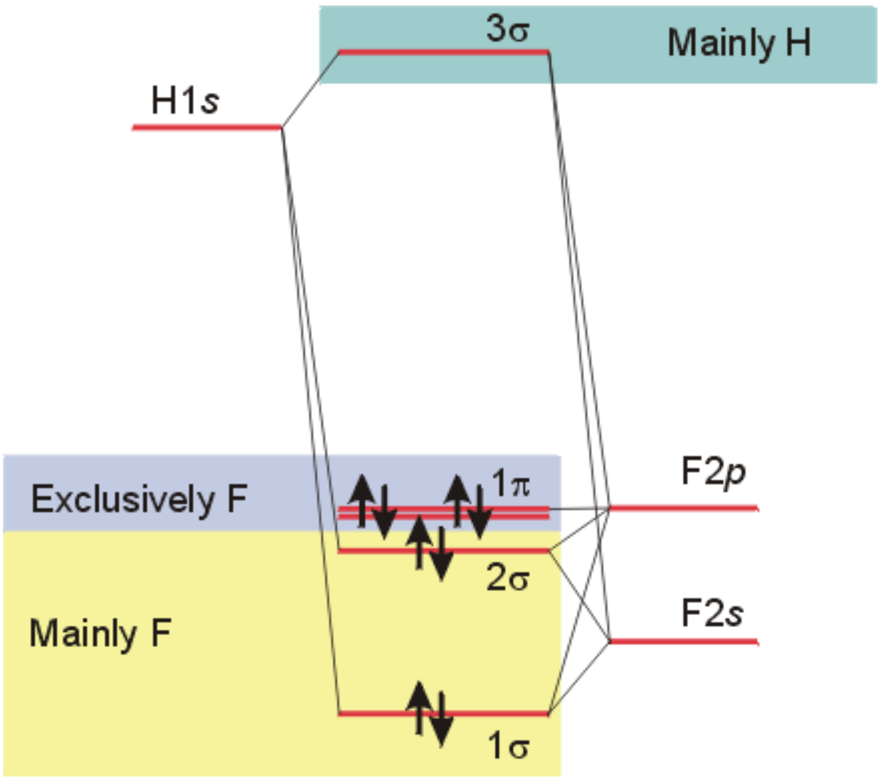
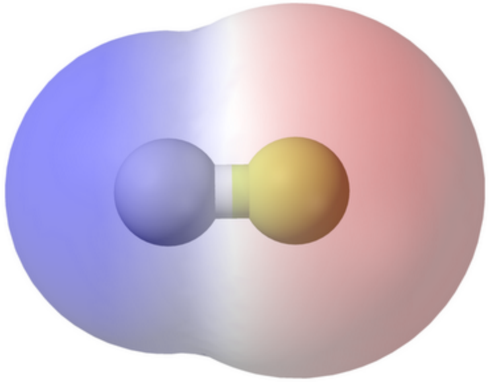
# Beyond Homonuclear Diatomic molecules



# Heteronuclear Diatomics: HF



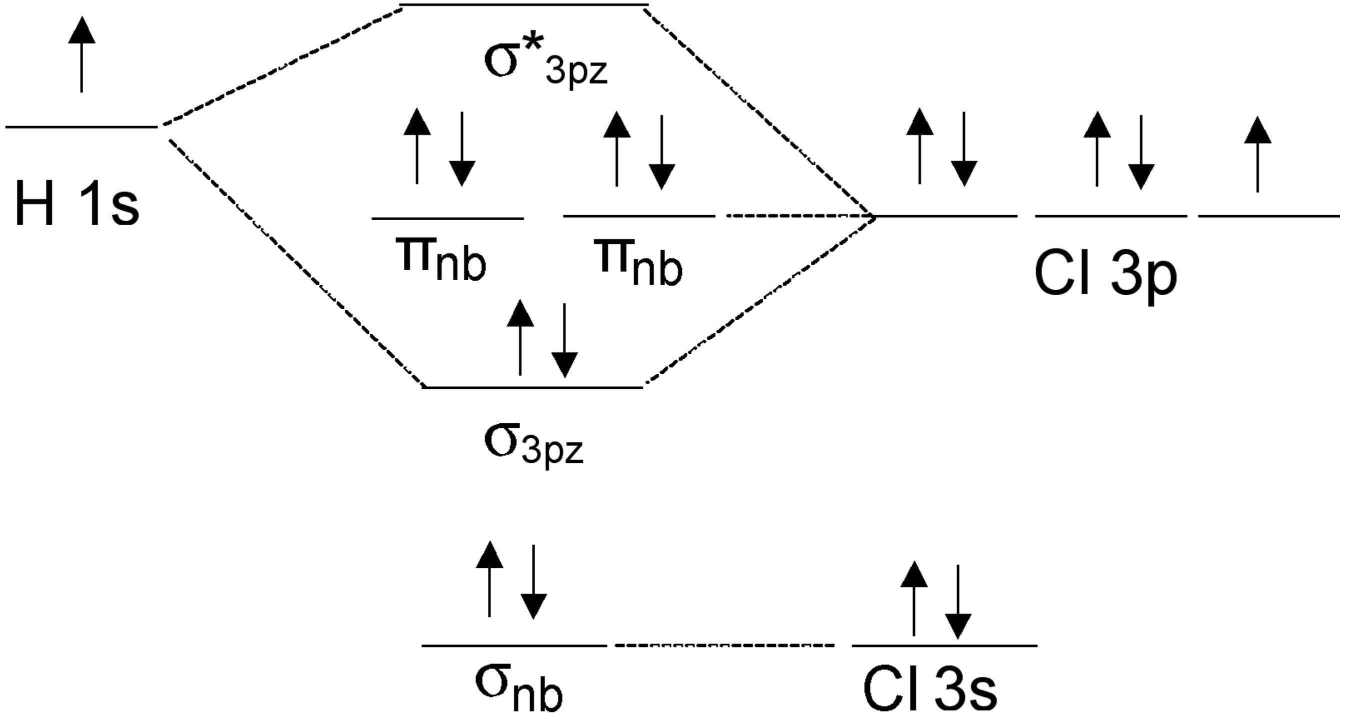
Higher electronegativity of F: Lopsided electron distribution

Bonding and antibonding MOs: *s* as well as *p*

Unequal contribution from the two atoms

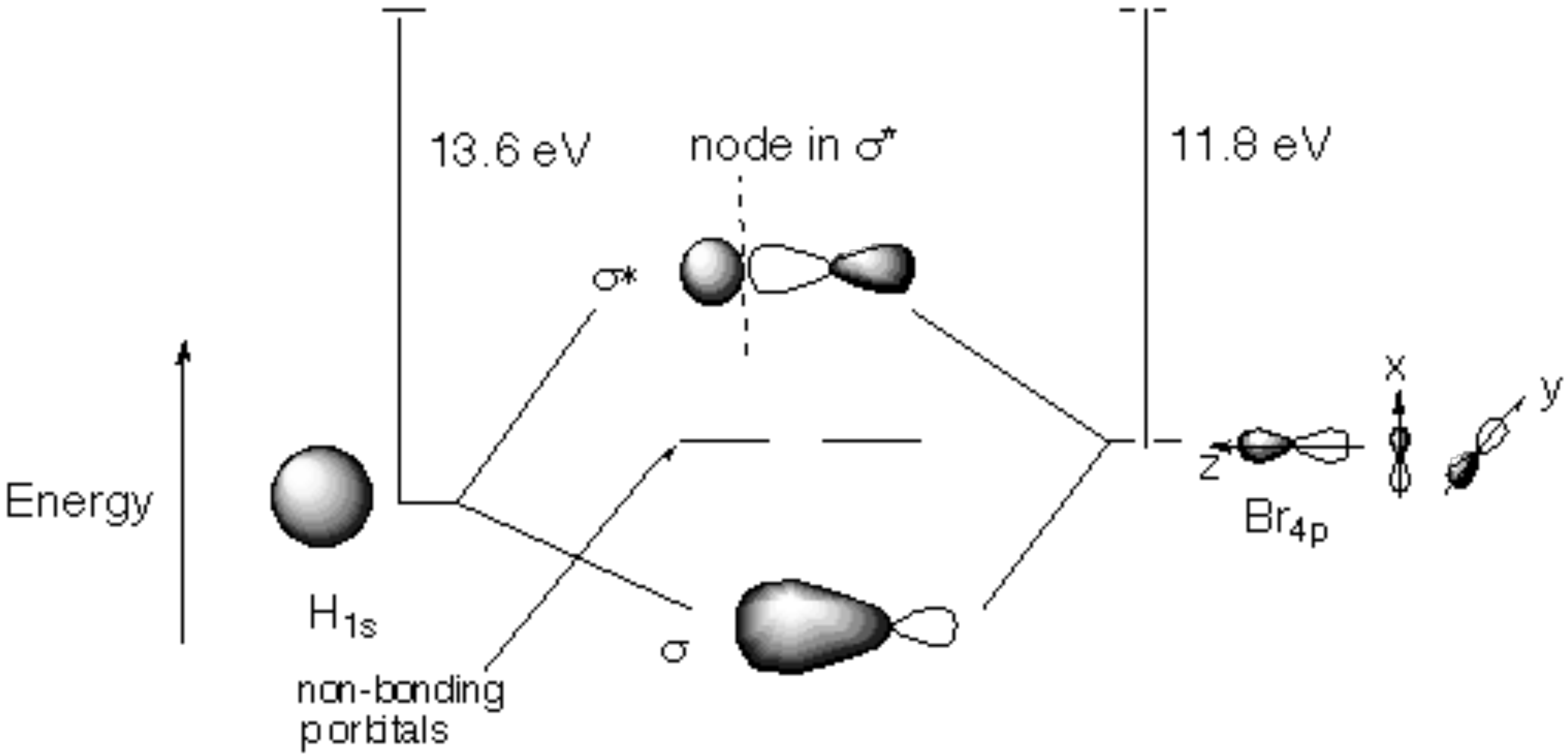
# Heteronuclear Diatomics: HCl

For Cl ***3p*** states close in energy to the ***1s*** of H



# Heteronuclear Diatomics: HBr

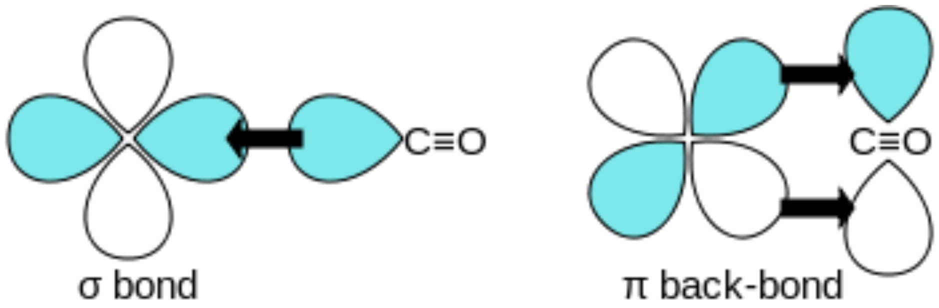
For Br ***4p*** states close (higher) in energy to the ***1s*** of H

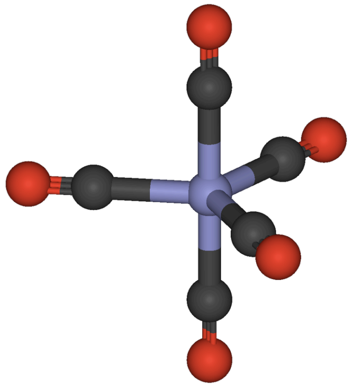


## Carbonyl complexes

**Carbon atom:**

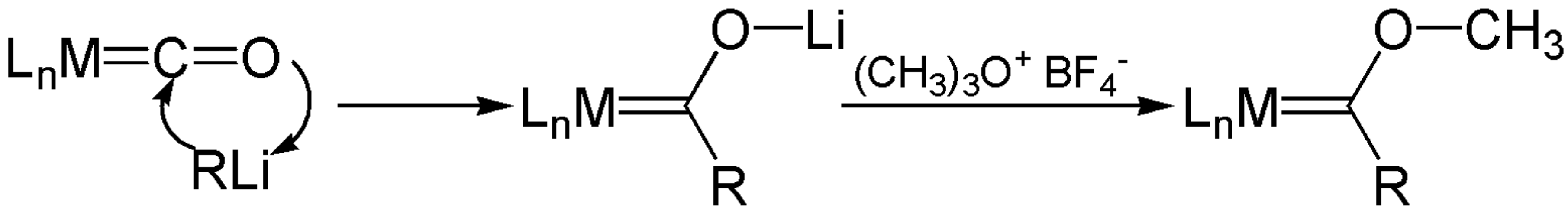
$\sigma$-donor = dative bond , $\pi$-acceptor = back bonding



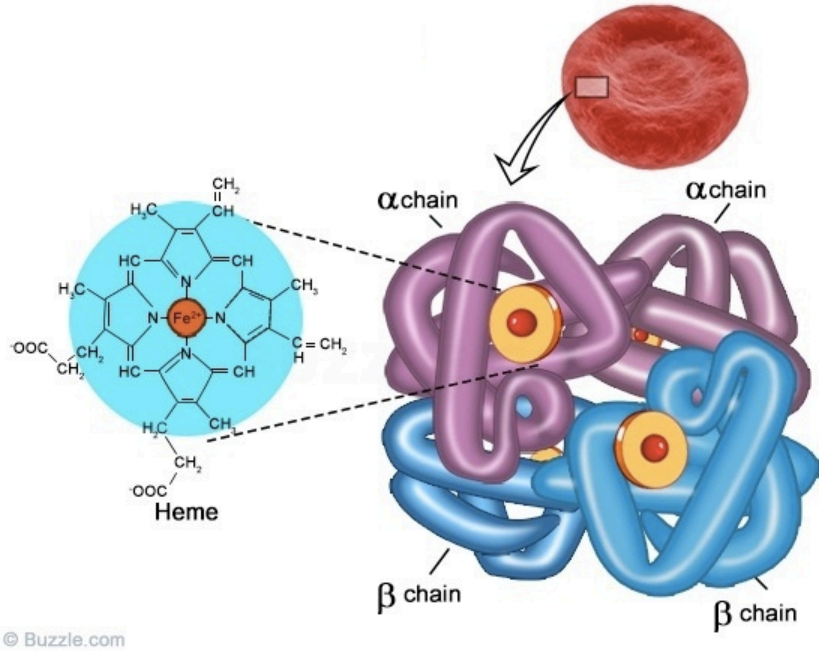
*Synergistic effect*

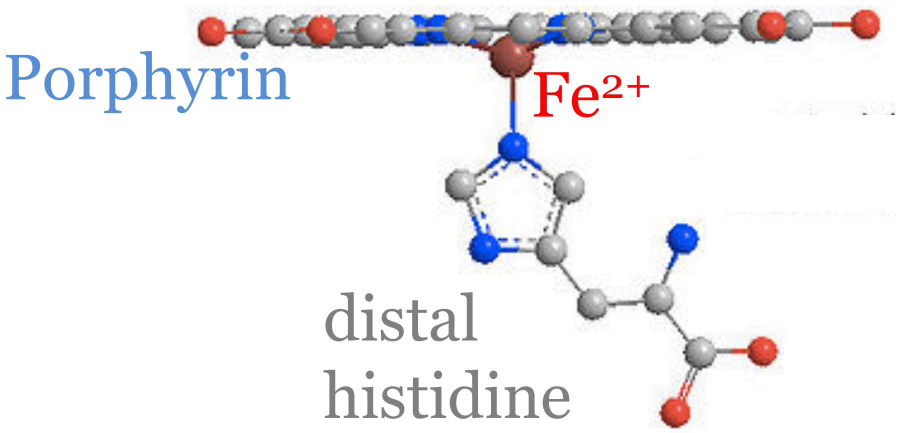
**Applications in Organometallic Chemistry**

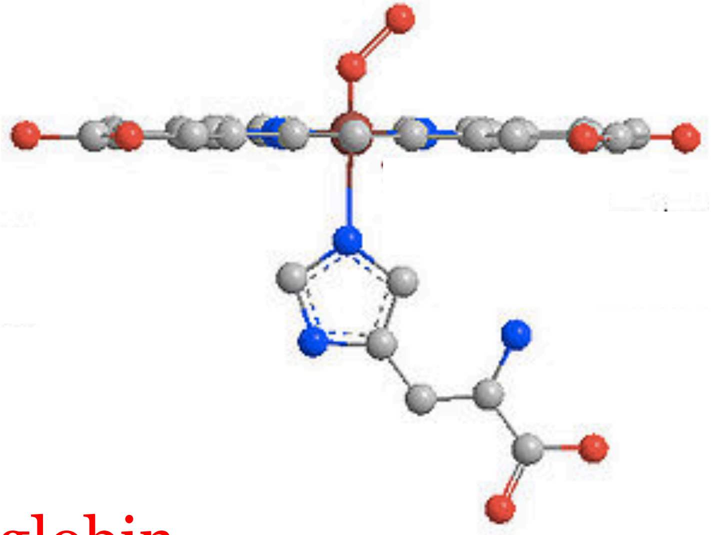


# Why is CO a poisonous gas?

**Hemoglobin (Hb):** Transports $O_2$ and $CO_2$ in blood



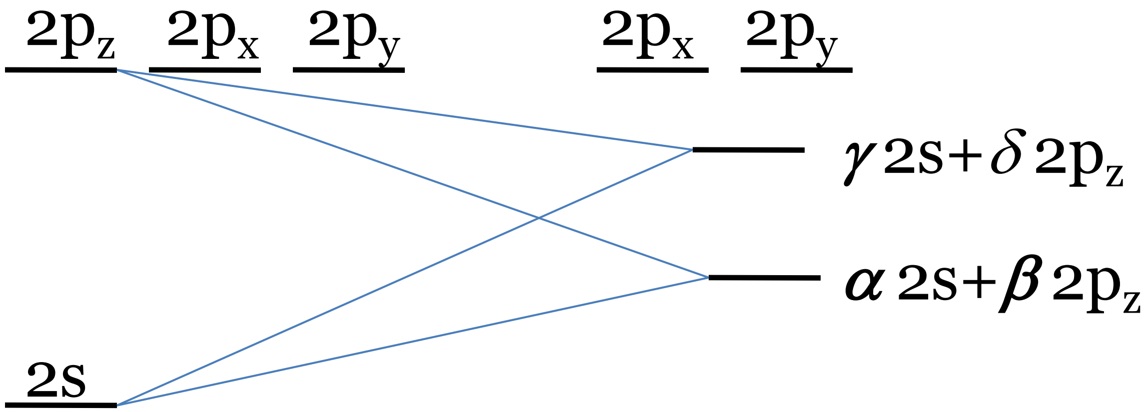
**$O_2$-Hb, $CO_2$-Hb:** Reversible

**CO-Hb:** Almost ireversible, half life of several hours

https://en.wikipedia.org/wiki/Hemoglobin

# Hybridization

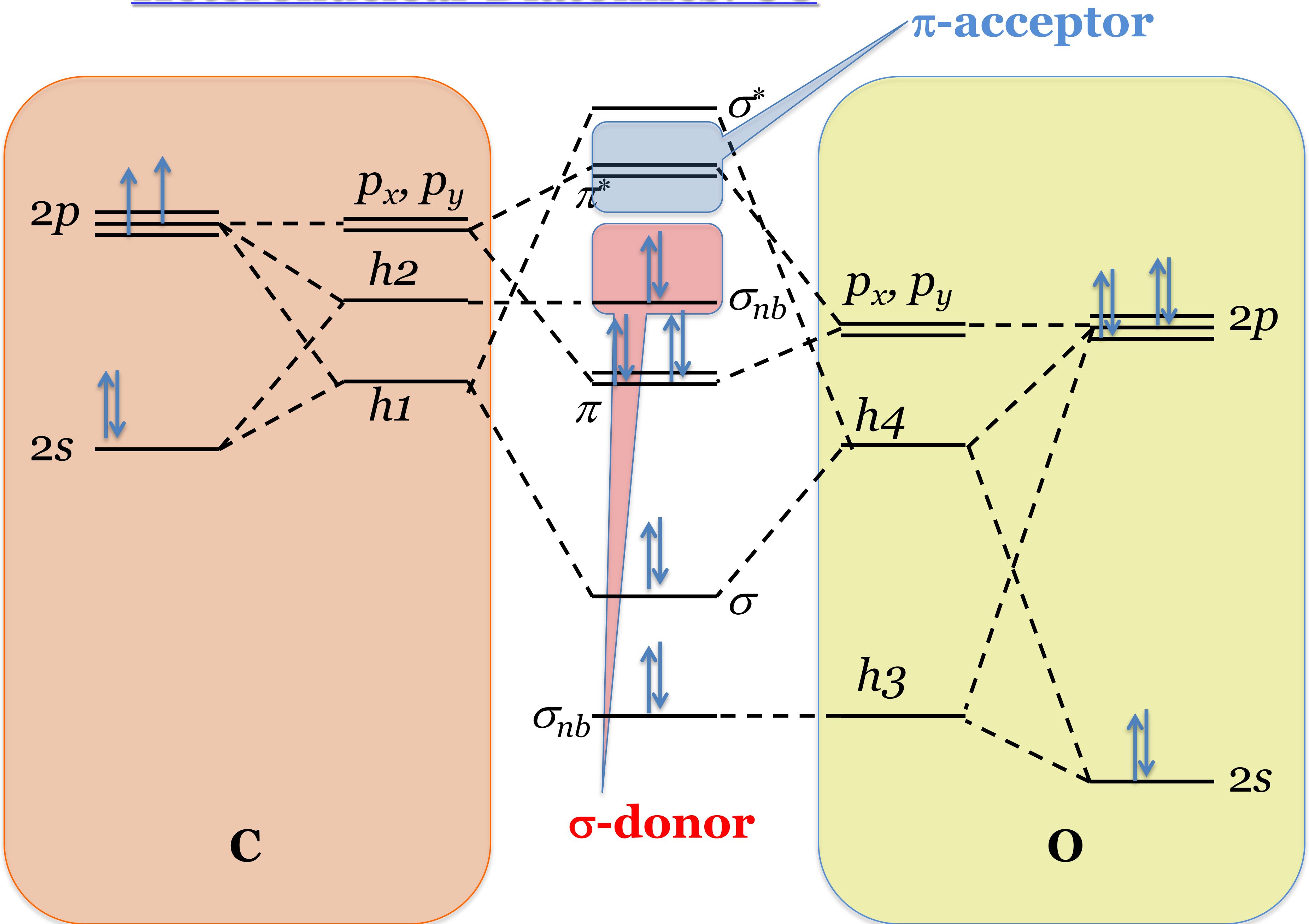
Linear combination of atomic orbitals **within an atom** leading to more effective bonding




- The ***coefficients*** $\alpha$, $\beta$, $\gamma$ and $\delta$ depend on ***field strength***
- ***Square*** of a coefficient = ***contribution*** of that AO in the hybrid orbital
- ***Equivalent*** hybrid orbitals (same *s*-contribution, same *p*-contribution in each hybrid orbital) have *same energies*
- Hybrid orbitals are ***ortho-normal*** to each other

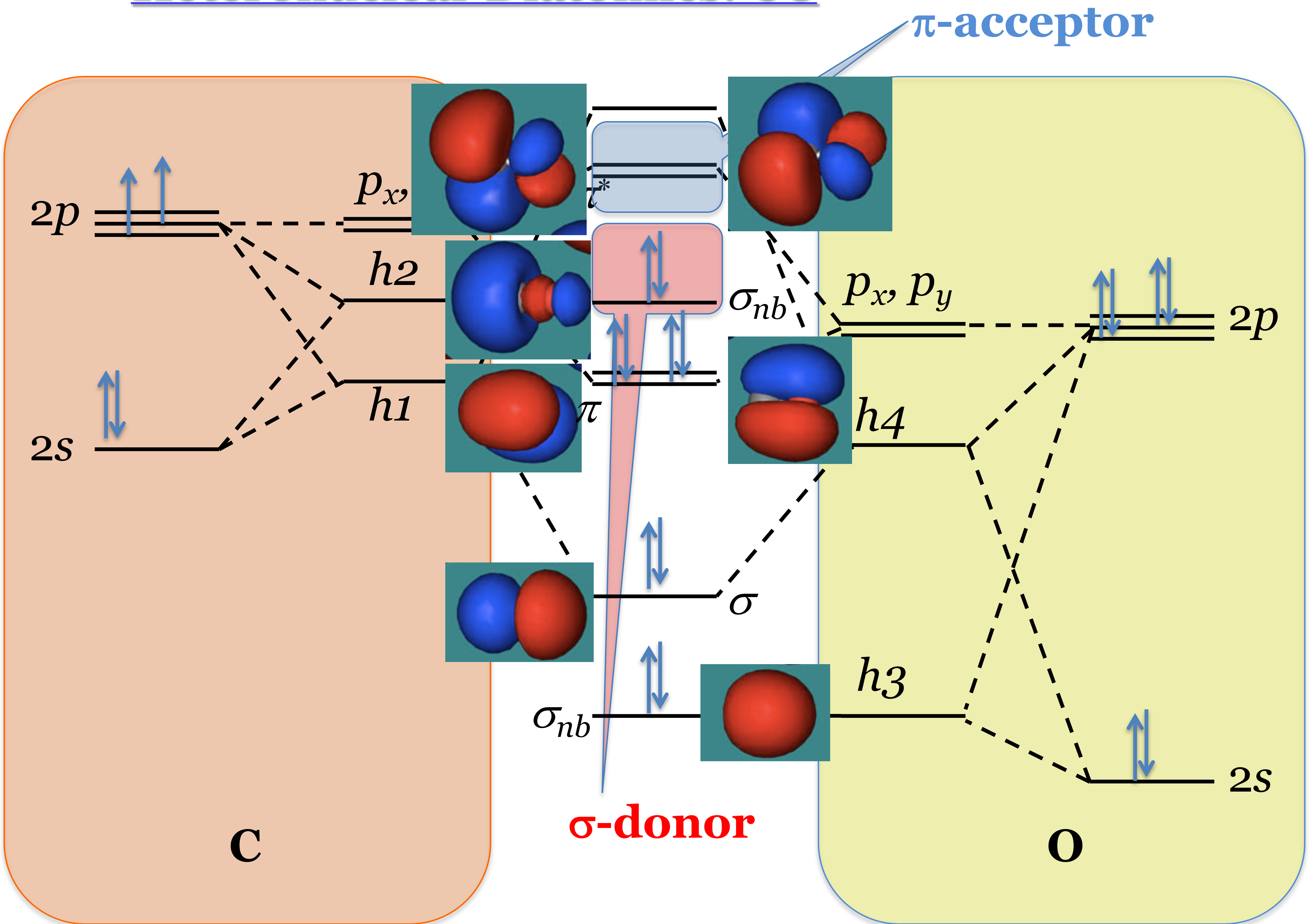
Hybridization origintes in VBT and relies on experimental results

# Heteronuclear Diatomics: CO

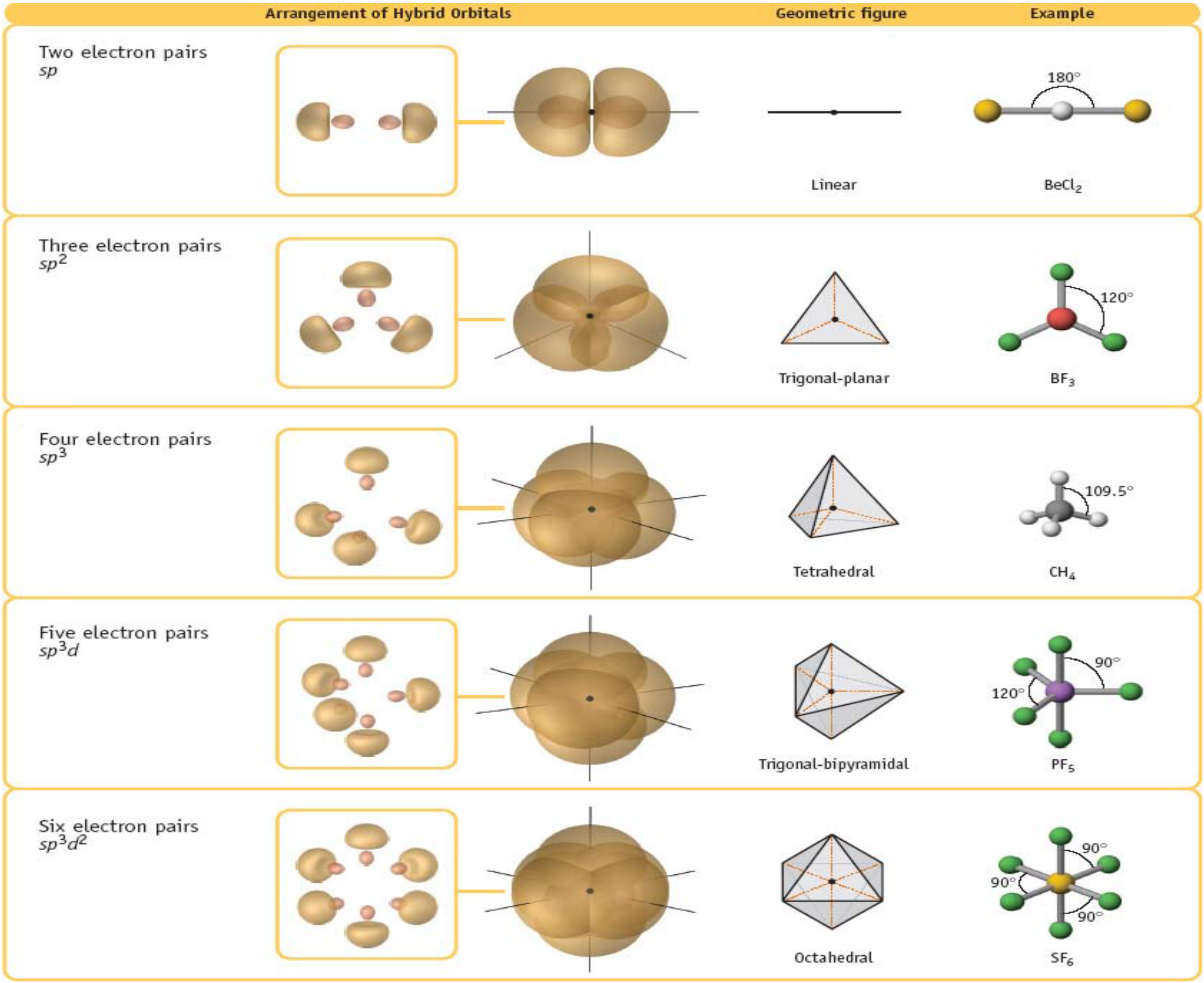


http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

# Heteronuclear Diatomics: CO

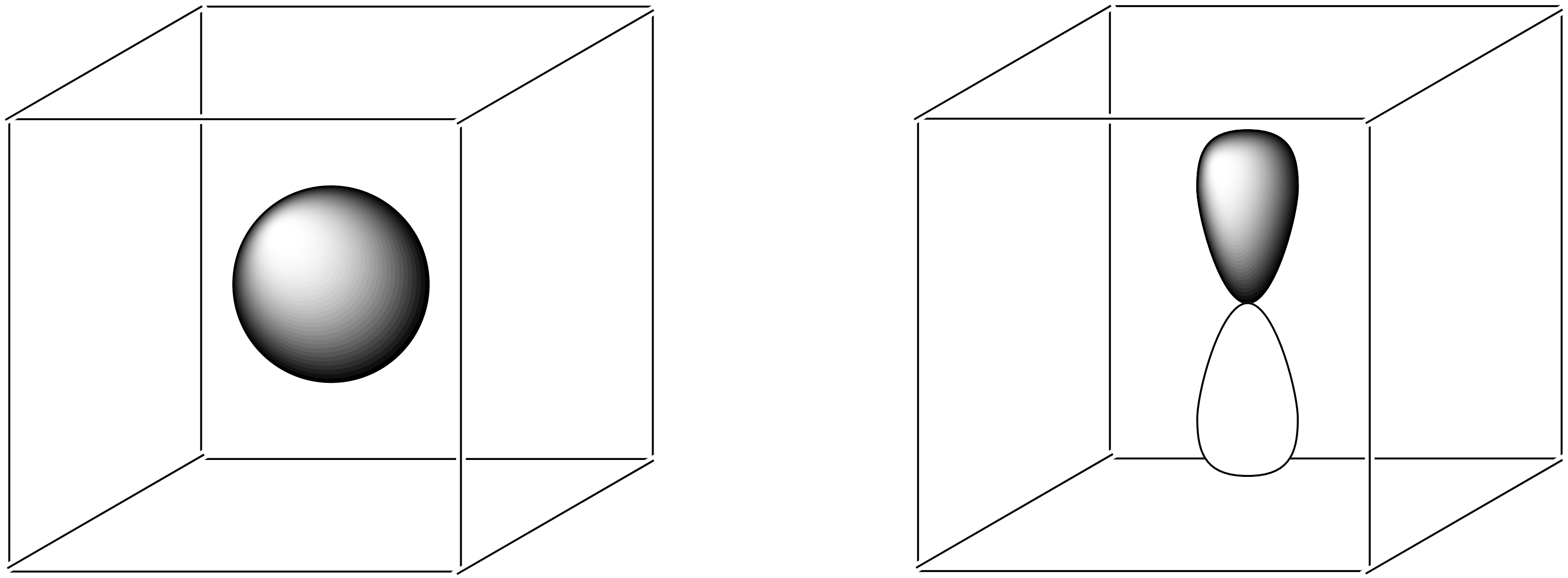


# Polyatomic molecules: Geometry



# Methane: Delocalized MOT picture

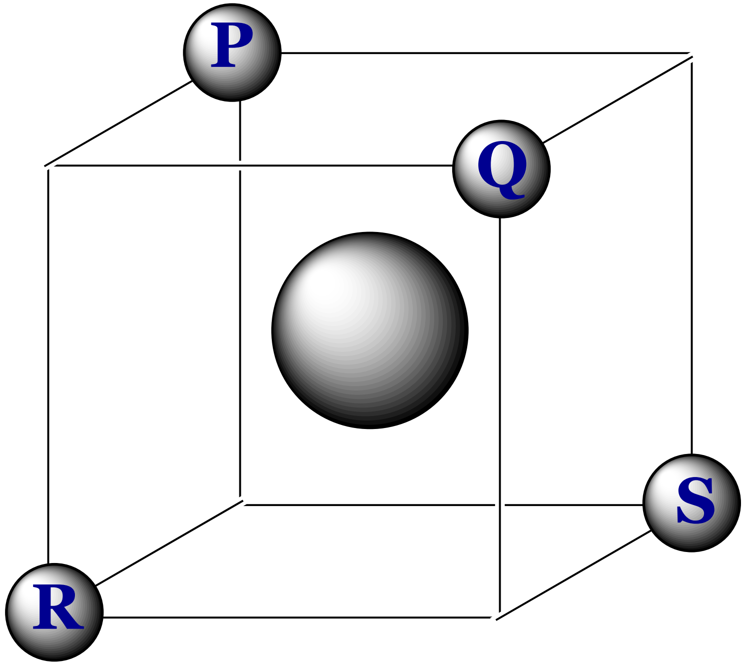
AOs with proper symmetry can only be combined



Central Carbon atom: 2*s* and 2*p* orbitals

# Methane: Delocalized MOT picture

2*s* orbital



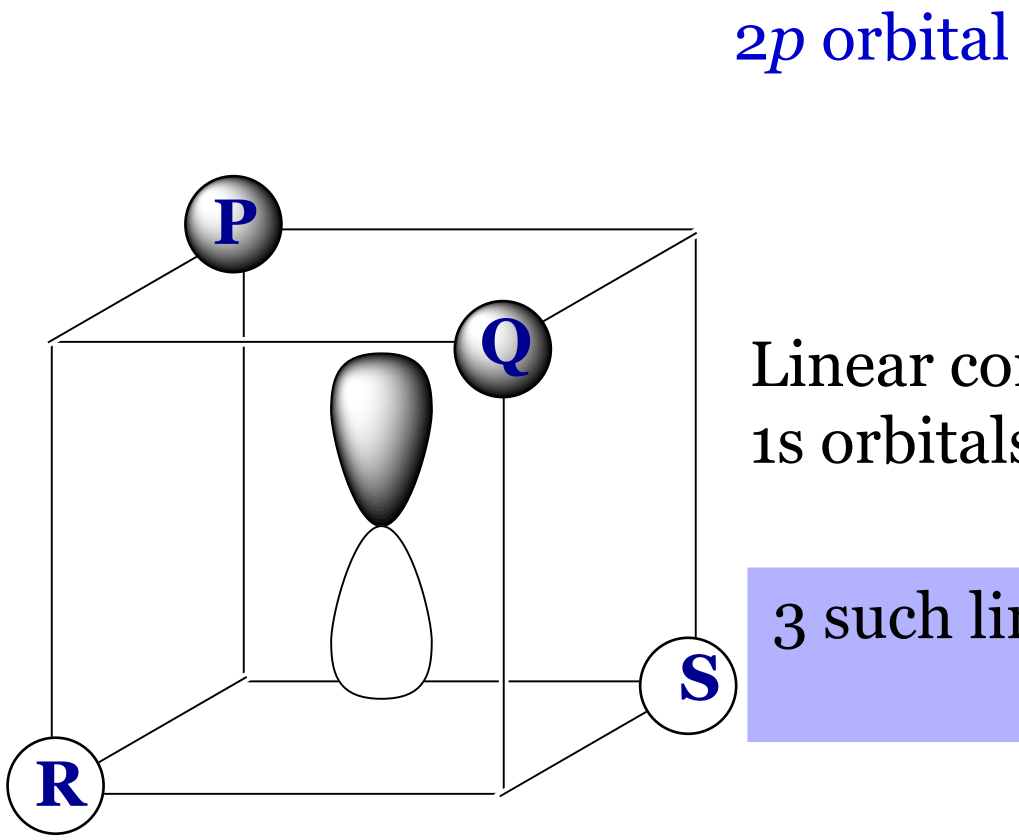

Linear combination of hydrogen 1s orbitals with matching symmetry:

Symmetry Adapted Linear Combinations (SALCs)

$$\psi_{H,s} = \psi_{1s}(P) + \psi_{1s}(Q) + \psi_{1s}(R) + \psi_{1s}(S)$$

$$\psi_{MO,s} = c_1\psi_{2s}(C) \pm c_2\left(\psi_{1s}(P) + \psi_{1s}(Q) + \psi_{1s}(R) + \psi_{1s}(S)\right)$$

# Methane: Delocalized MOT picture




Linear combination of hydrogen 1s orbitals with matching symmetry:

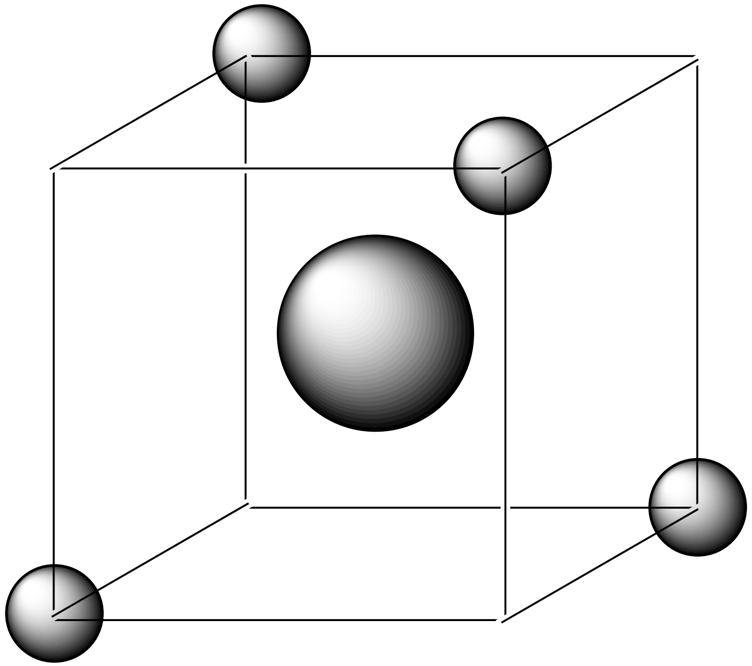
3 such linear combinations:
$x, y, z$

$$\psi_{H,p} = \psi_{1s}(P) + \psi_{1s}(Q) - \psi_{1s}(R) - \psi_{1s}(S)$$

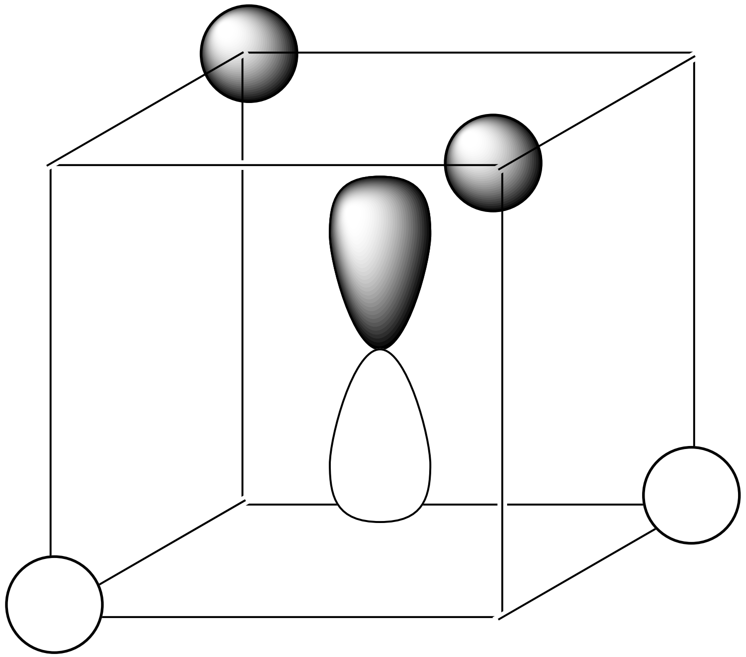
$$\psi_{MO,p} = c_3\psi_{2p}(C) \pm c_4\left(\psi_{1s}(P) + \psi_{1s}(Q) - \psi_{1s}(R) - \psi_{1s}(S)\right)$$

# Methane: Delocalized MOT picture

Two kinds of Molecular Orbitals



1 MO, no node

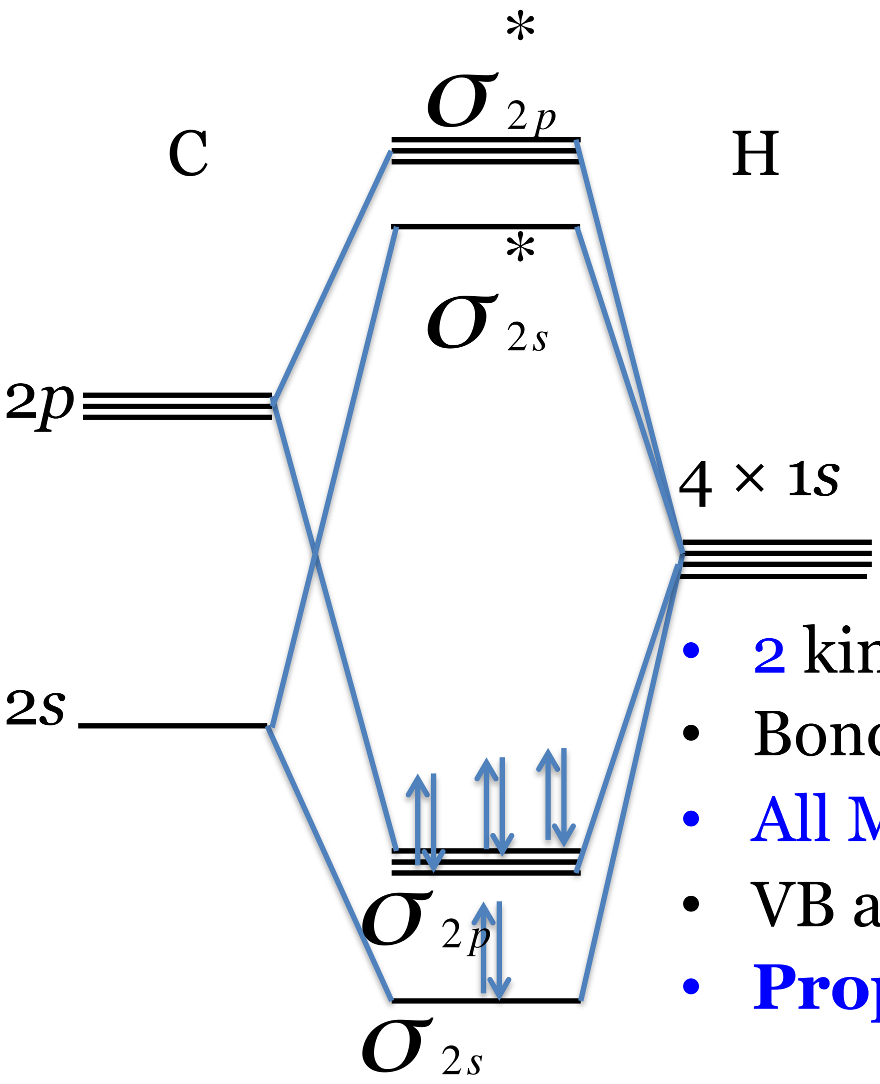


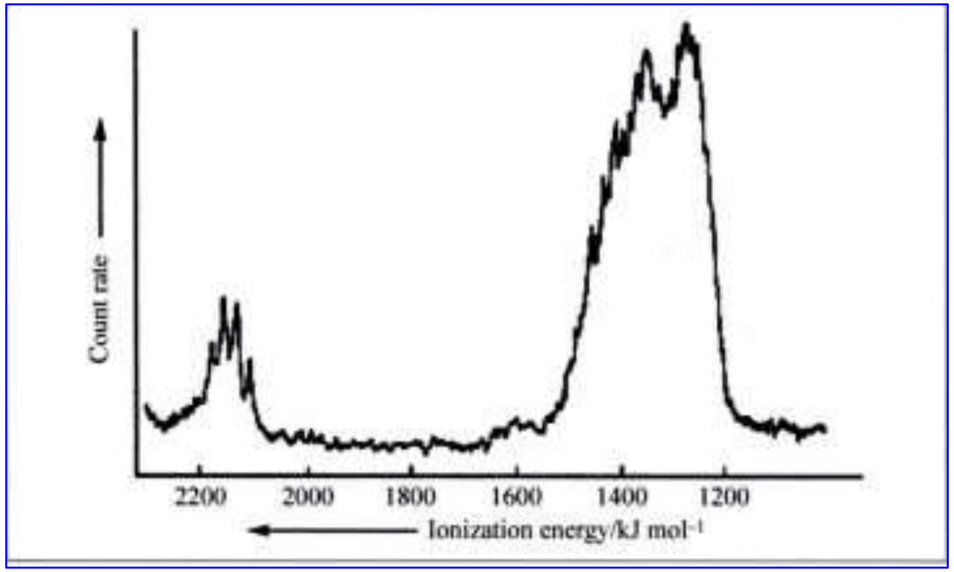
3 MOs, one node in each

- Same energy?

- Experimental evidence?

# Methane: Energy Diagram and Photoelectron spectrum




- 2 kinds of MOs: 2 energy levels
- Bond lengths: equal
- All MOs contribute equally to each bond
- VB and MO pictures correlated
- **Properties** depend on the **experiment**

http://bilbo.chm.uri.edu/CHM401/fall2008exam1-4.html