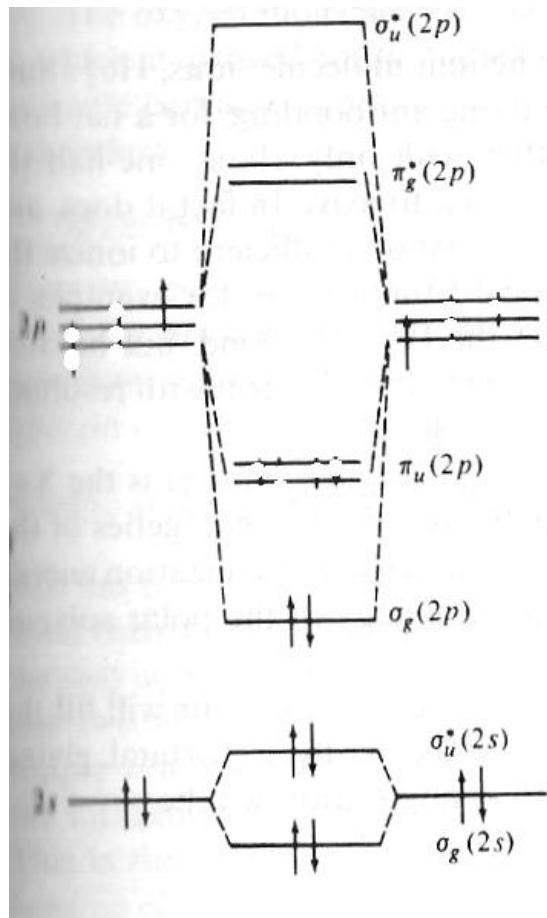
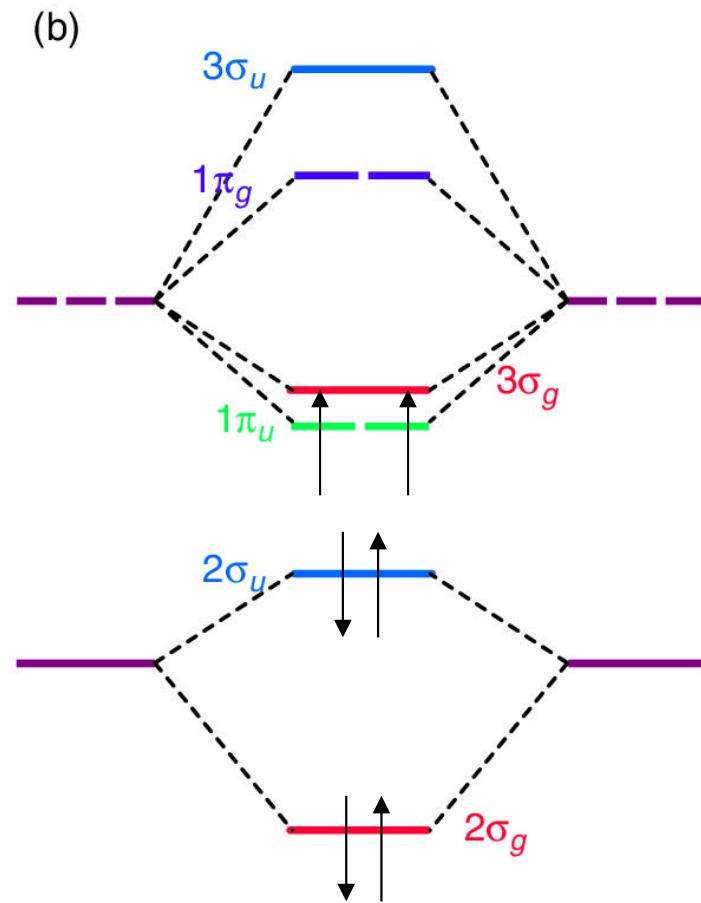


# s-p Mixing: $B_2$ magnetism confirms it!

Incorrect!

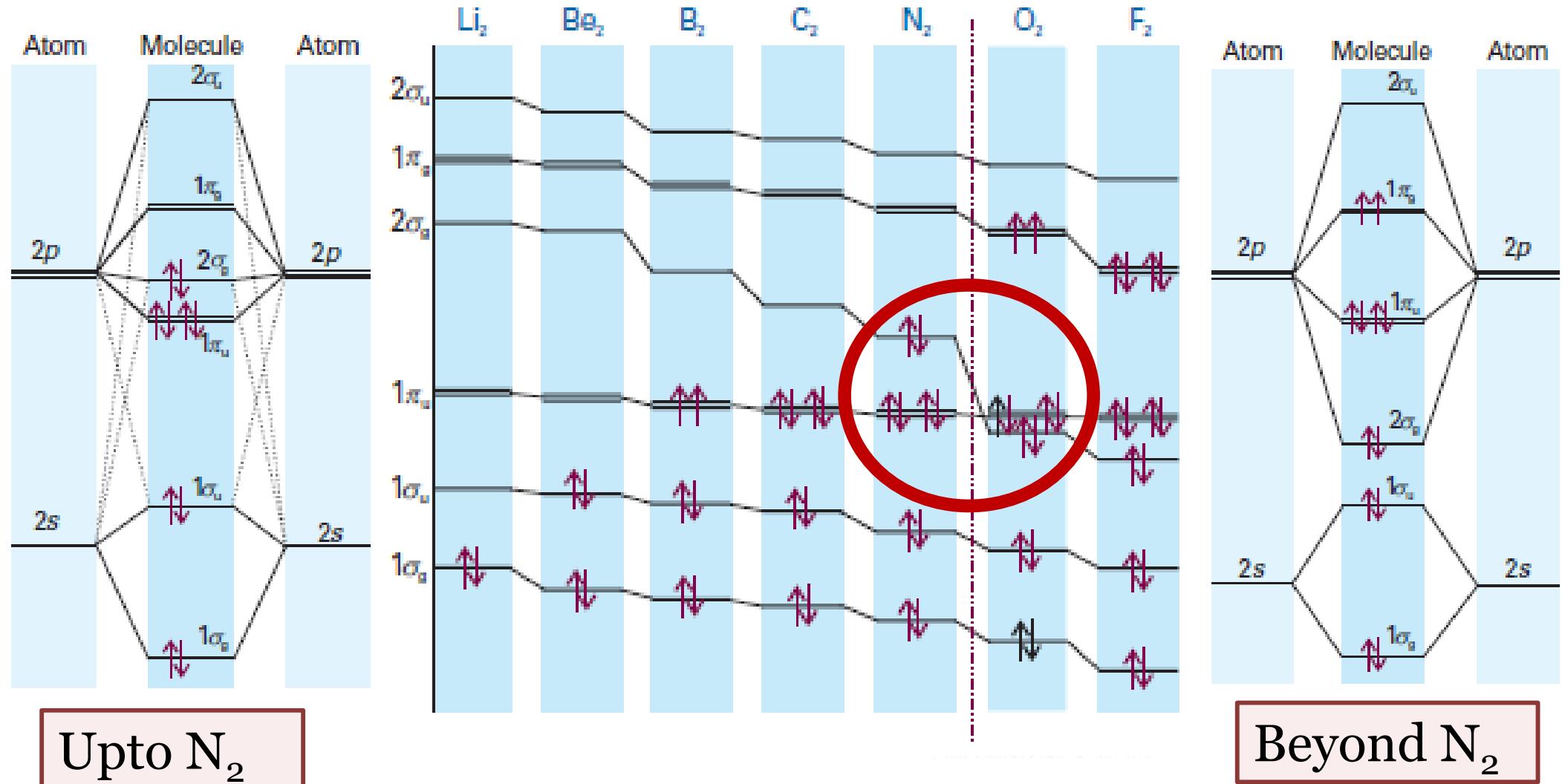


Correct!



Boron is paramagnetic. This can only happen if the two electrons with parallel spin are in the  $\pi$ -orbitals  $\rightarrow \pi$ -bonding energies lower than  $\sigma^*$ ?

# MO Energy Diagram (Homo-Diatomics)



Upto N<sub>2</sub>

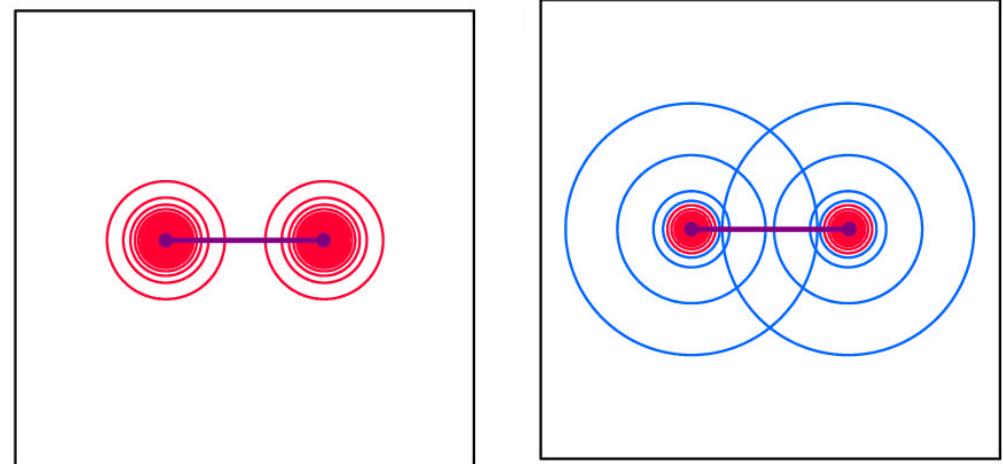
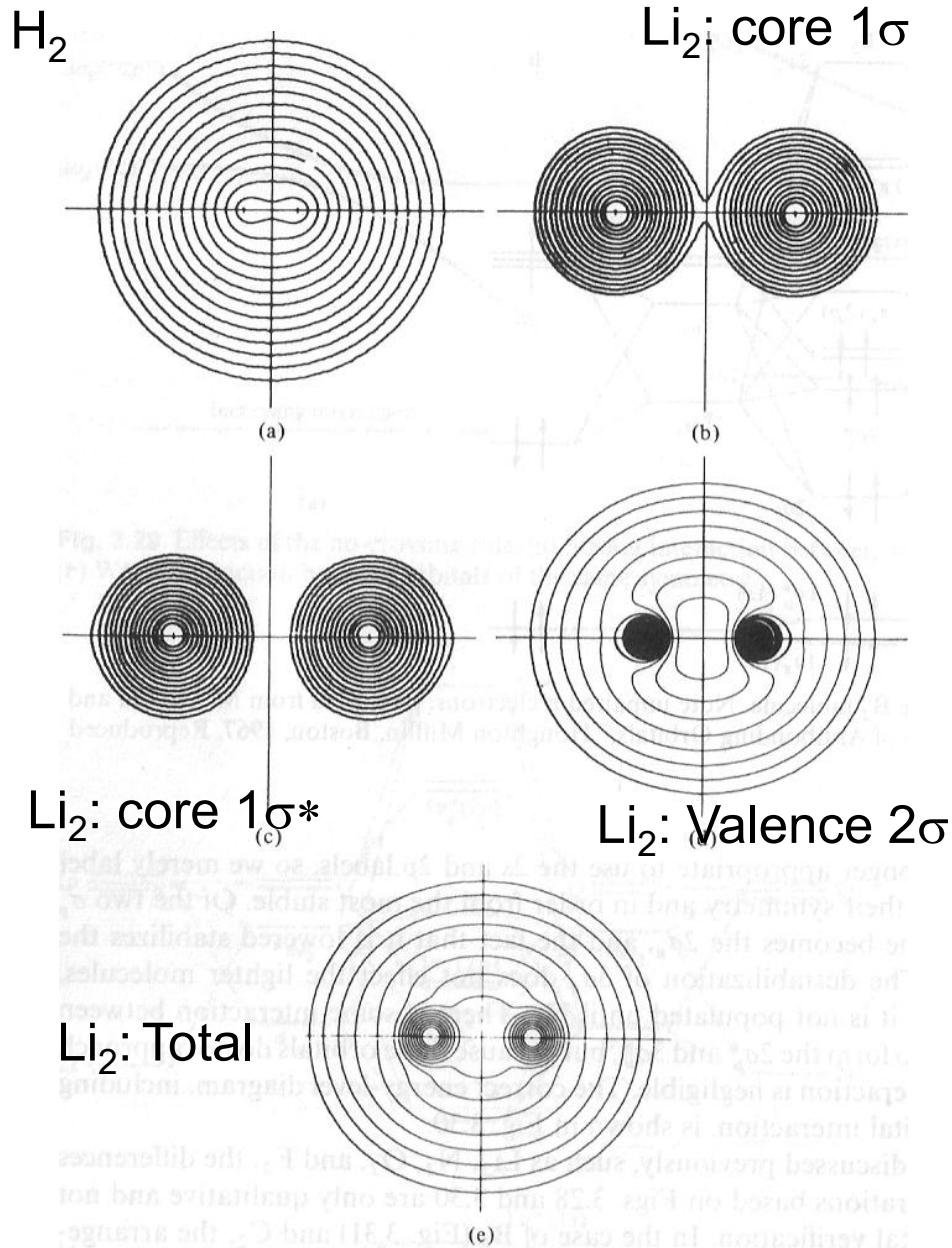
Beyond N<sub>2</sub>

Bond Order =  $0.5 \times (\text{bonding electrons} - \text{antibonding electrons})$

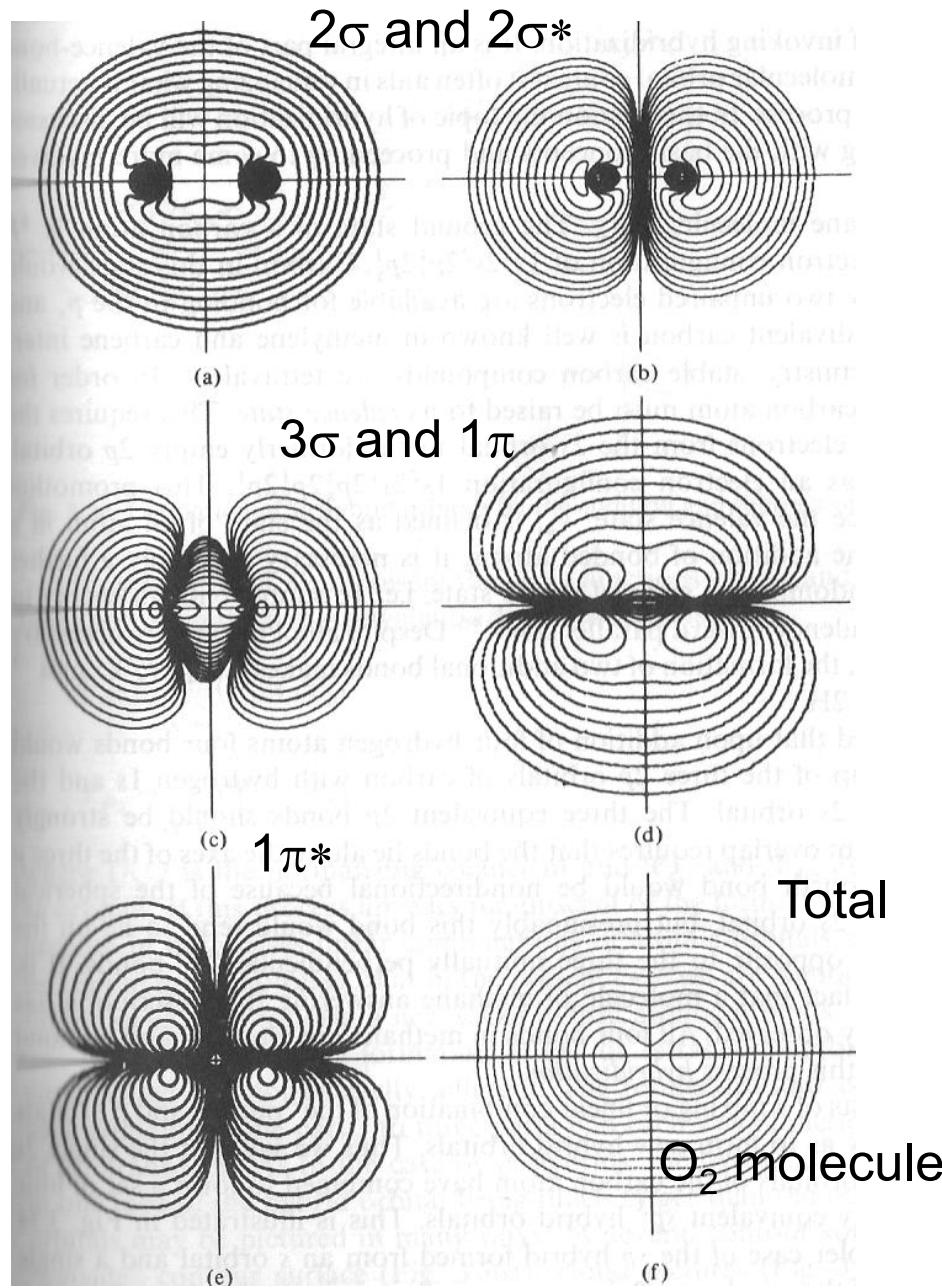
Bond order = 0 → molecular can not exist - No bond formation

Bond order higher → stronger bond, shorter bond length

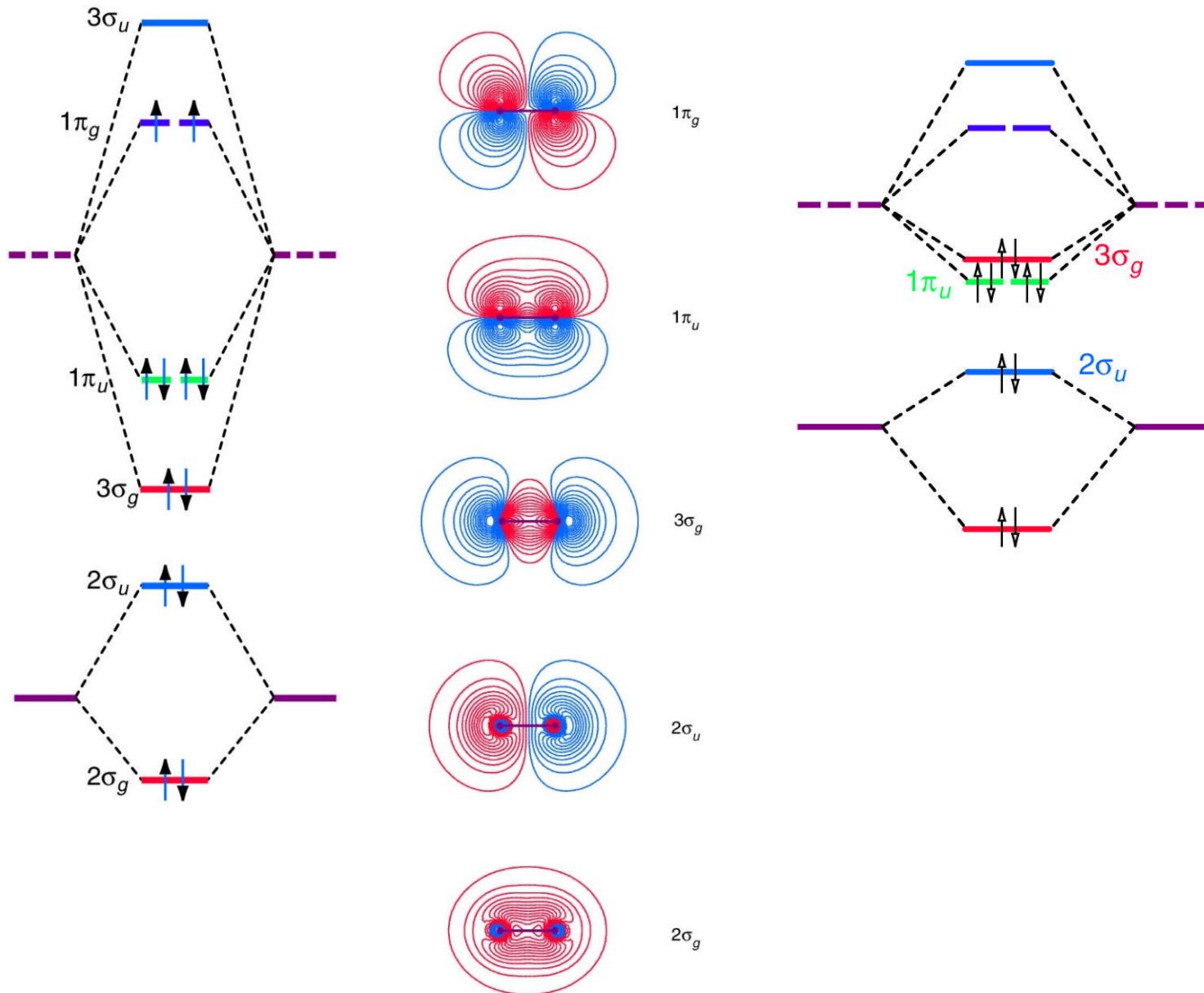
# MO Contours → electron density maps



# MO Contours → electron density maps



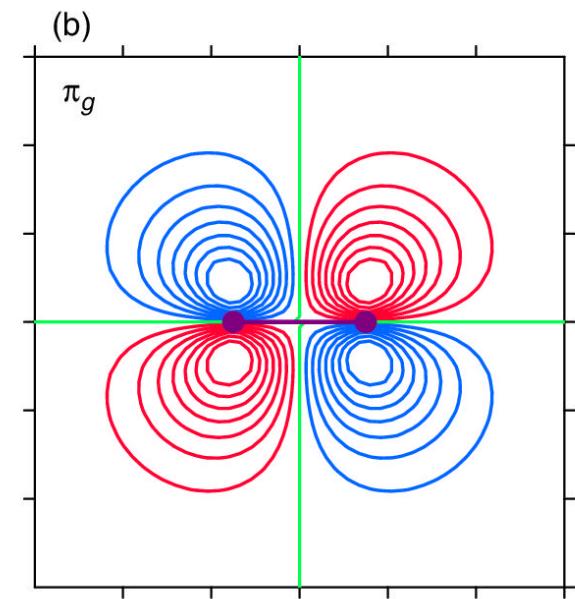
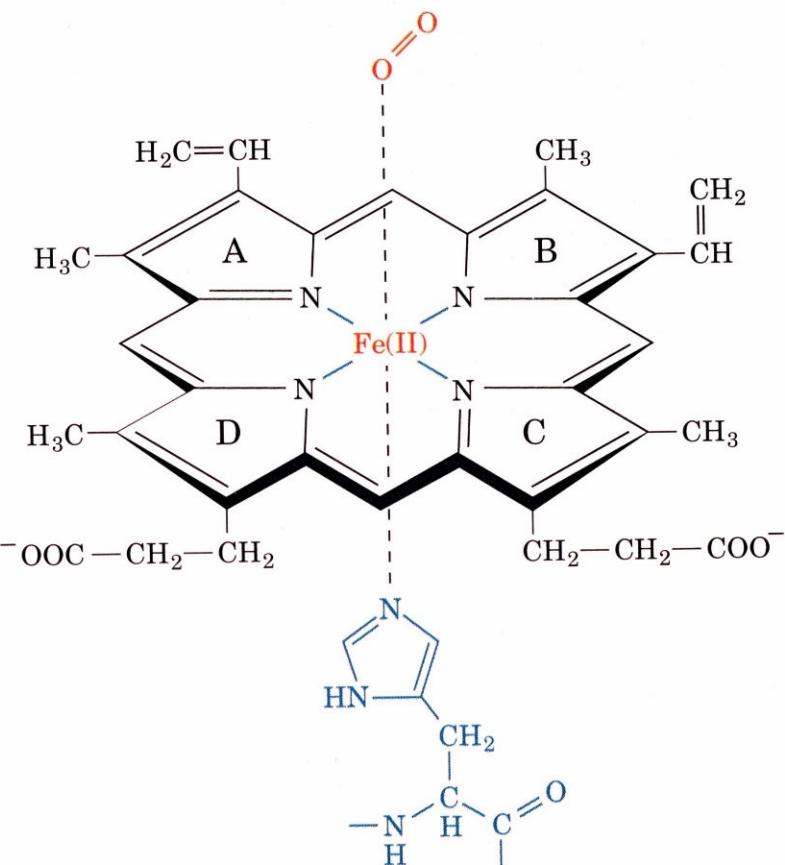
# Lessons from the MO



# $O_2$ binding to Heme group

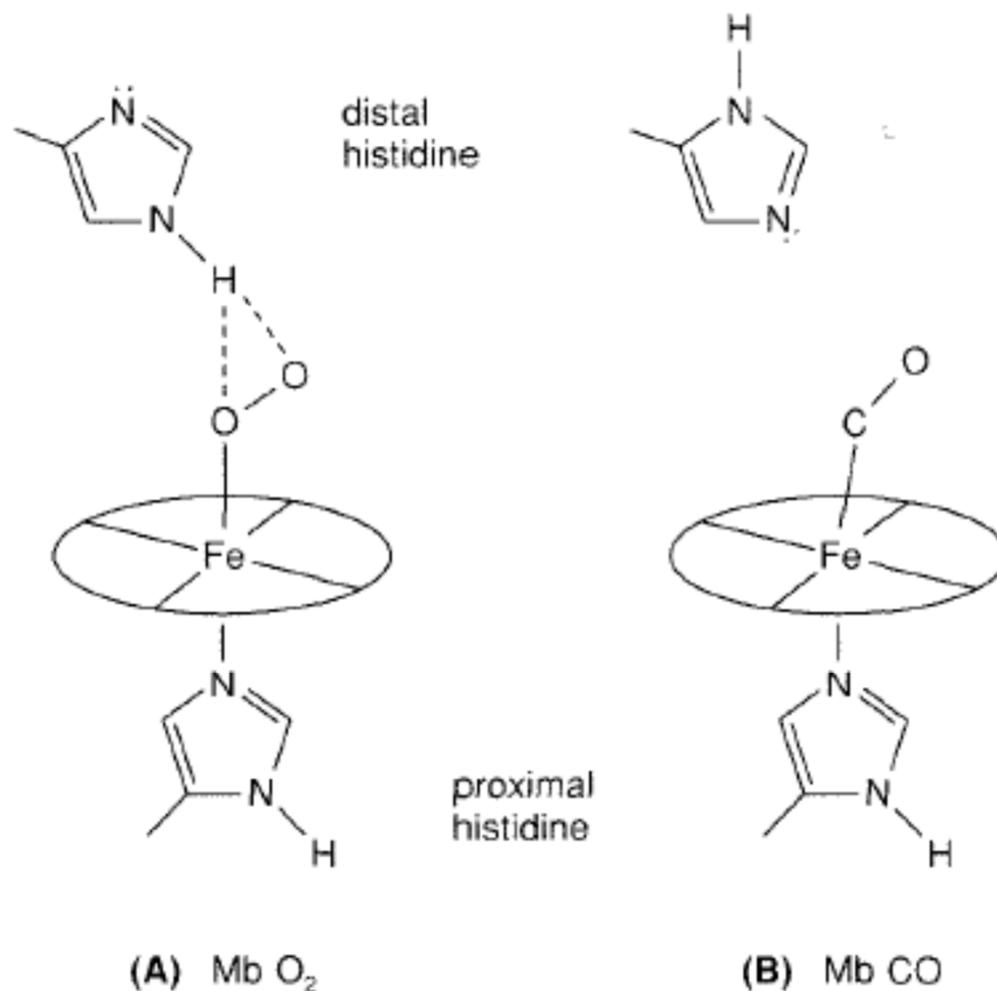
Each subunit of hemoglobin or myoglobin contains a heme.

- Binds one molecule of oxygen
- Heterocyclic porphyrin derivative
- Specifically protoporphyrin IX

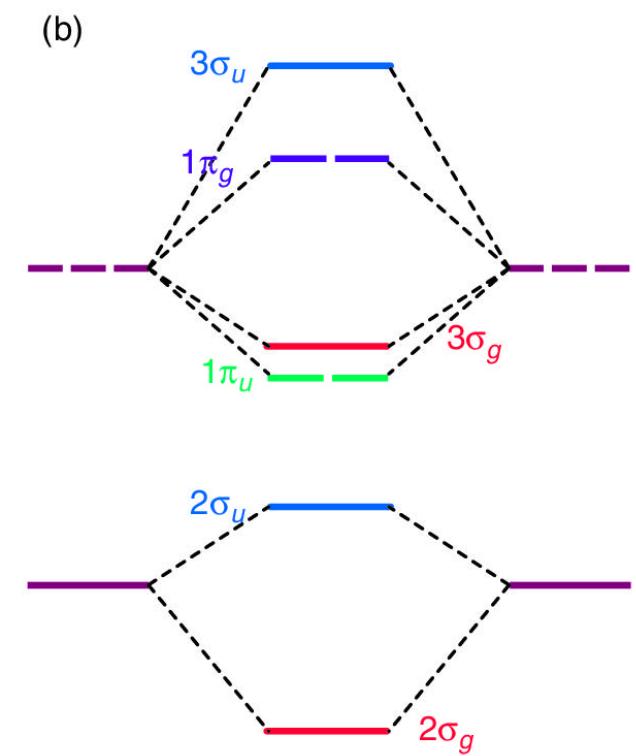
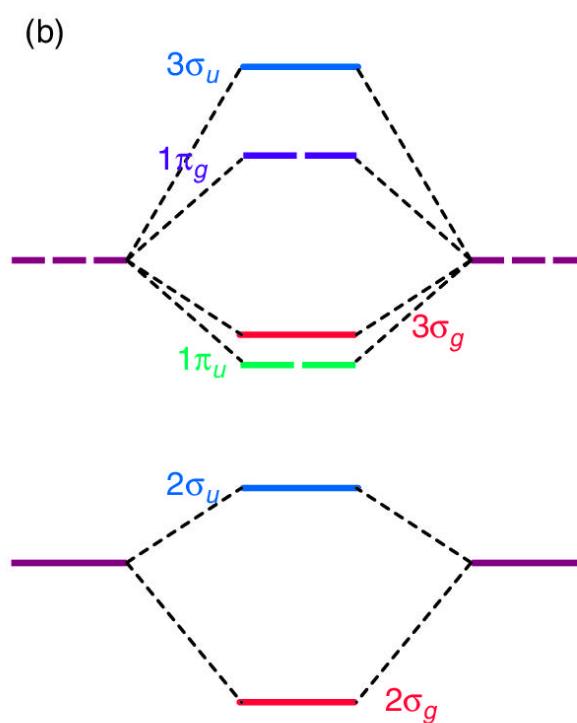
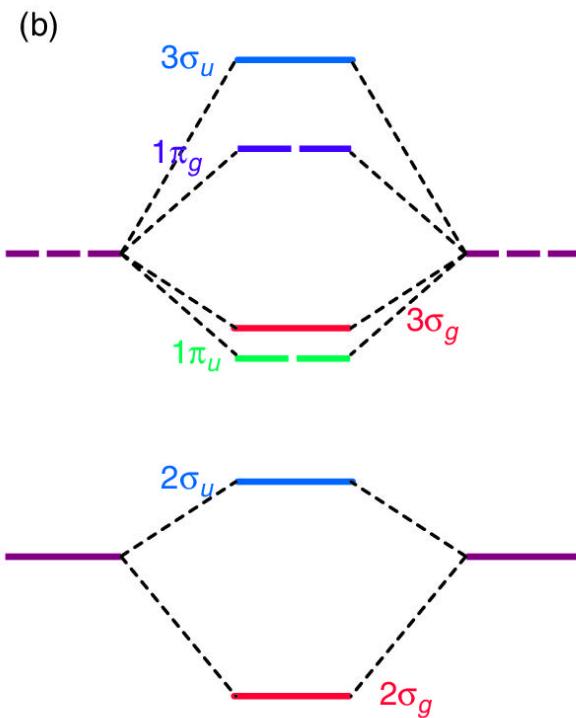


The iron must be in the Fe(II) form or reduced form. (ferrous oxidation) state.

# Binding of O<sub>2</sub> vs CO

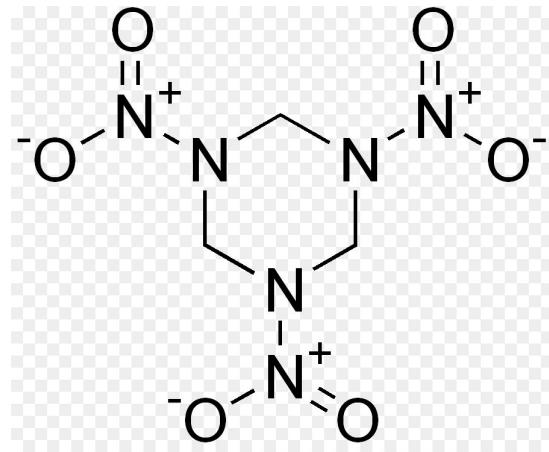


# Adding electrons to the Anti-bonding orbital in $\text{N}_2$

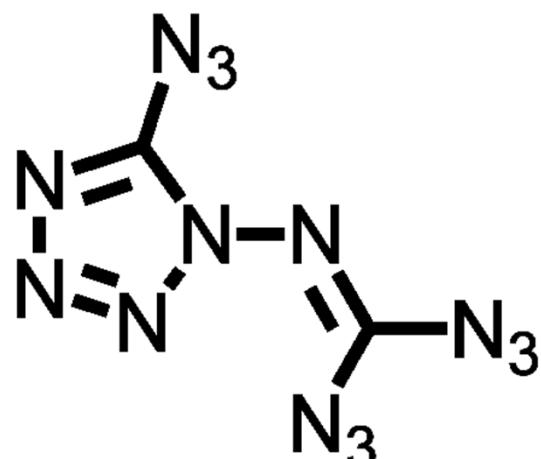


Example: Bond Dissociation energy of  $\text{N}_2$  is 945 kJ/mol;  $\text{N}=\text{N}$  is 418 kJ/mol and  $\text{N}-\text{N}$  is 167 kJ/mol

# Sodium Azide: Airbags in vehicles

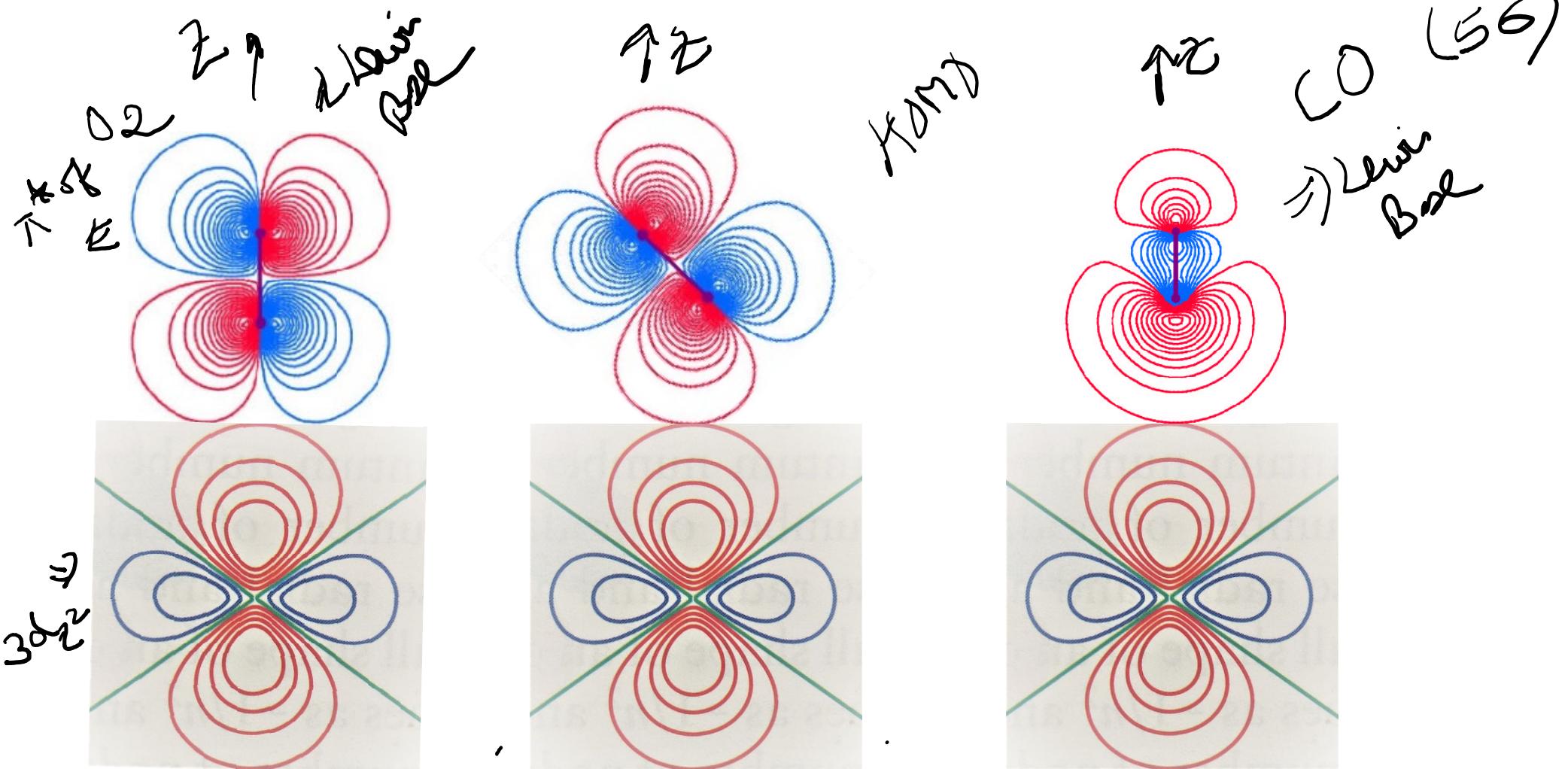


RDX



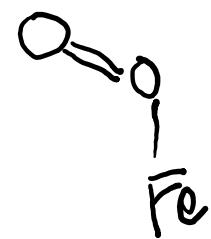
Aziroazide azide

You would never see these kinds of molecules in nature due to their incredible instability, but they were made in a German research lab by Thomas Klapötke's group as recently as 2011. Attempts to touch or handle this chemical (and some may say so much as even look at) can cause it to detonate, breaking those bonds and turning them into multiple molecules of rapidly expanding nitrogen gas.

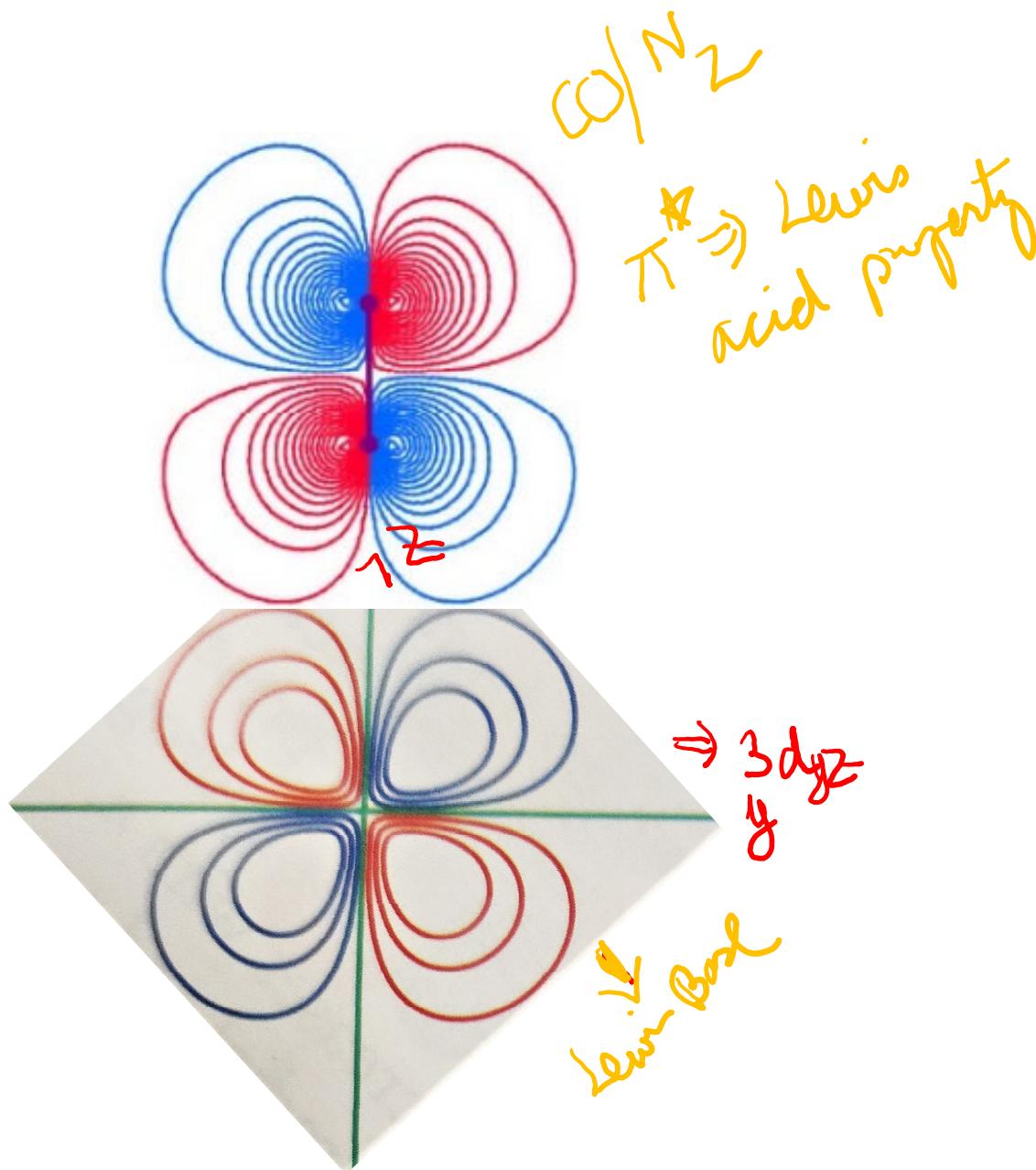
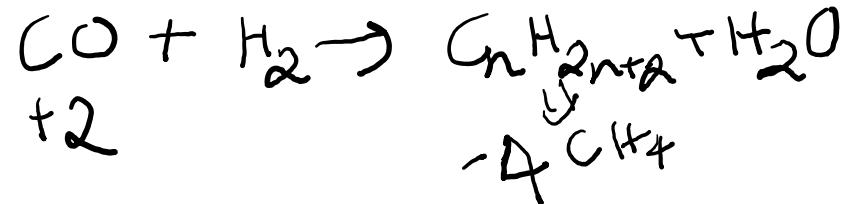


$\text{Fe} - \text{O} = \text{O}$

$\text{Loring acid}$

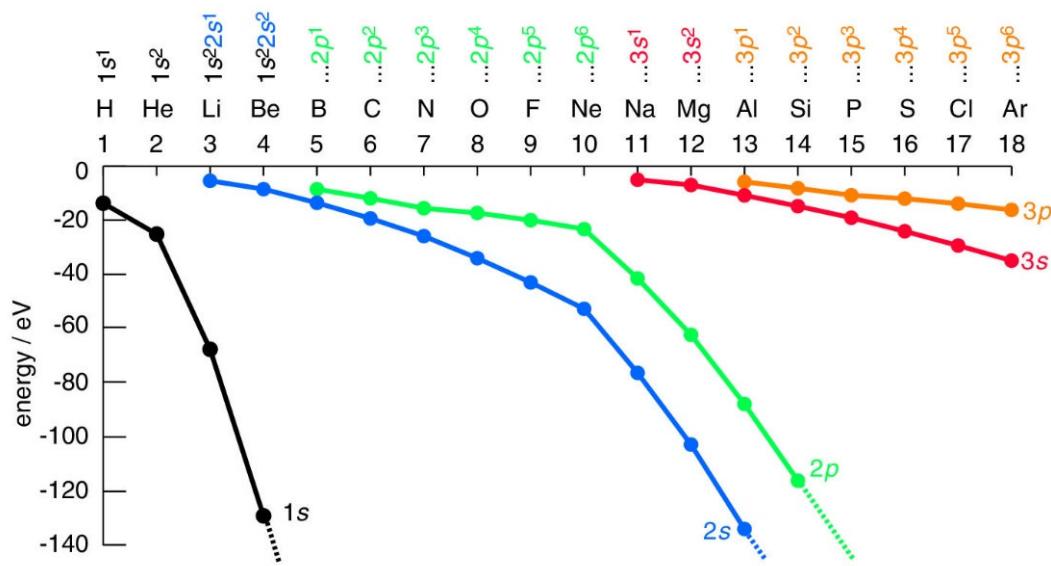


$\text{O} - \text{O} - \text{Fe}$



# Hydrides: Li-H and H-F

	Bond Length	Dipole Moment	Polarity
Li-H	160 pm	5.9 D	H is $\delta-$
F-H	91.7 pm	1.9 D	H is $\delta+$



Li (2s) = -5 eV  
 H (1s) = - 14 eV

Li (1s) >-60 eV

# Hydrides: Li-H and H-F

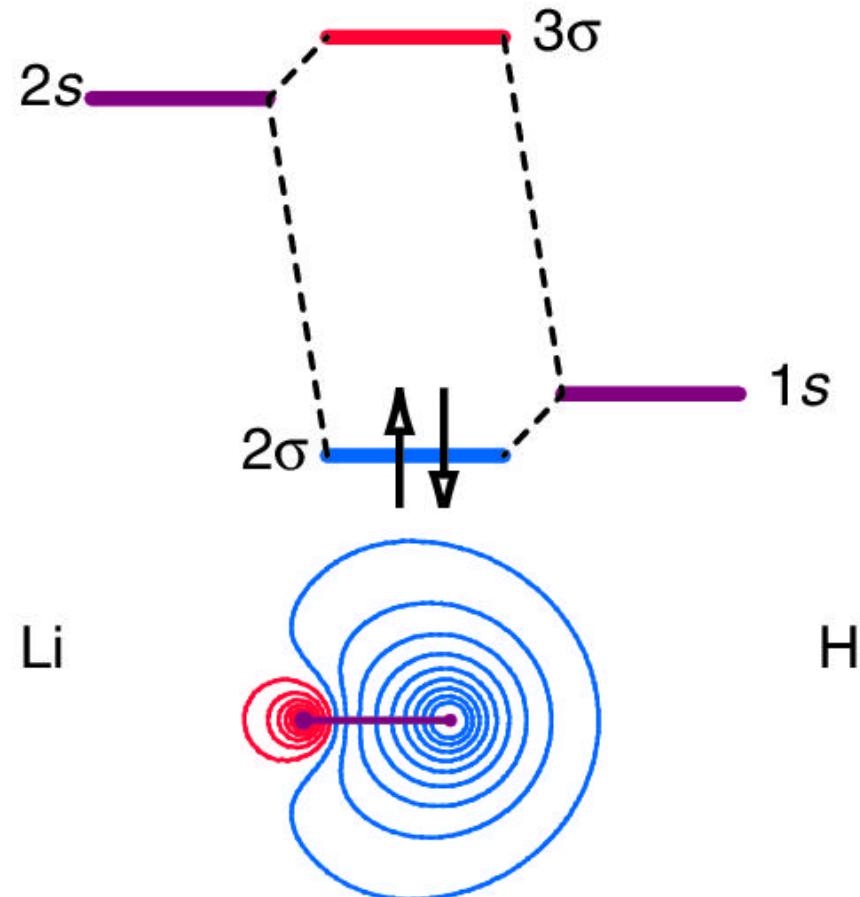
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H (1s) = - 14 eV

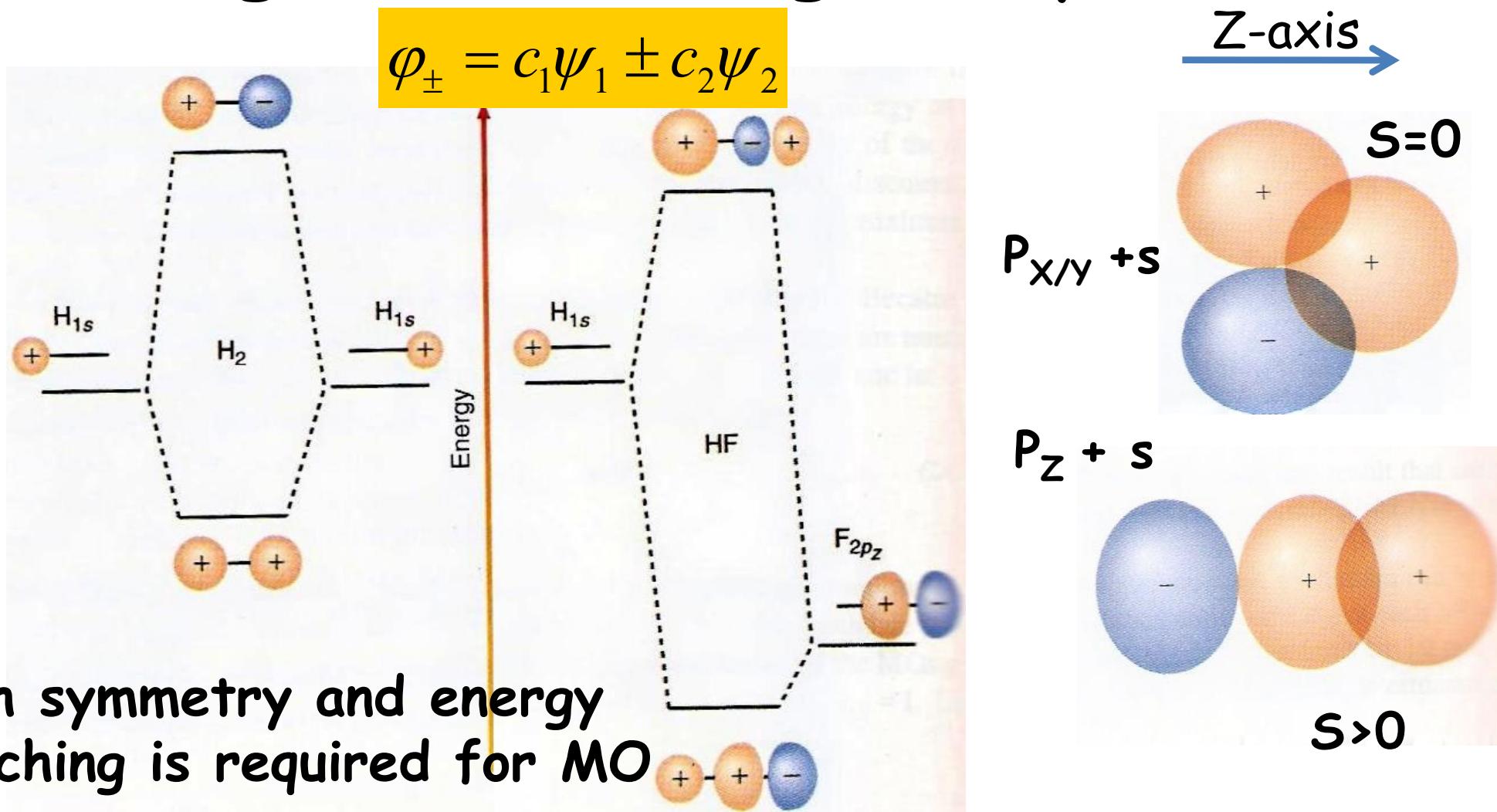
Li (1s) >-60 eV

$$\Psi_{2\sigma} = c_1 \Psi_{\text{Li}(2s)} - c_2 \Psi_{\text{H}(1s)}$$

$$\Psi_{3\sigma} = c_3 \Psi_{\text{Li}(2s)} + c_4 \Psi_{\text{H}(1s)}$$



# Matching of AO energies/symmetries



Valence electrons are most important for bonding

- Due to large difference in energy of  $1s(H)$  and  $1s(F)$ , LCAO-MO for both  $1s$  is not feasible in HF.
- Rather only  $2P_z(F)$  [NOT  $2P_{x/y}(F)$ ] and  $1s(H)$  form a  $\sigma$ -bond. <sup>70</sup>

# Hetero-nuclear Diatomics: HF

H (1s) -14 eV

F (2s) -43 eV

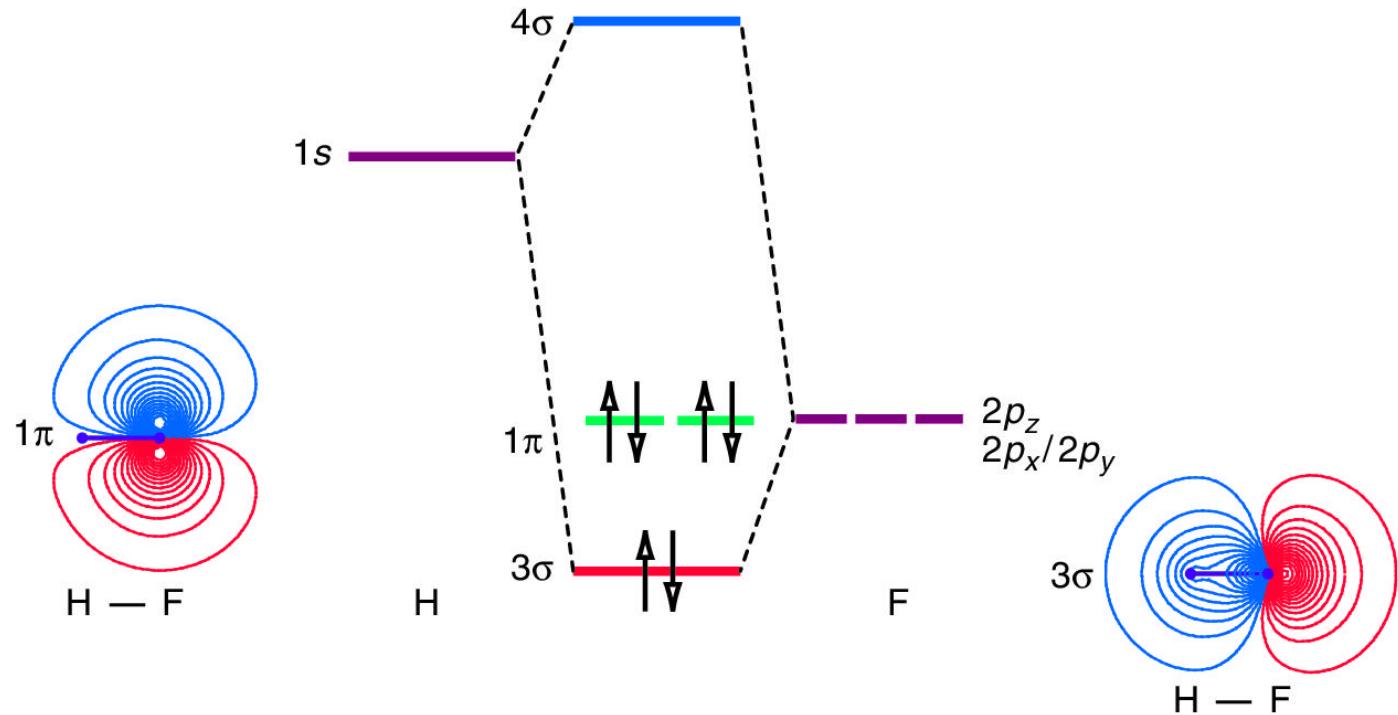
F (2p) -20 eV

# Hetero-nuclear Diatomics: HF

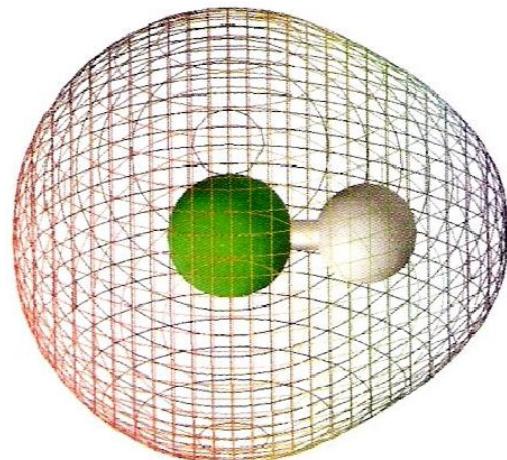
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F (2s) -43 eV

F (2p) -20 eV

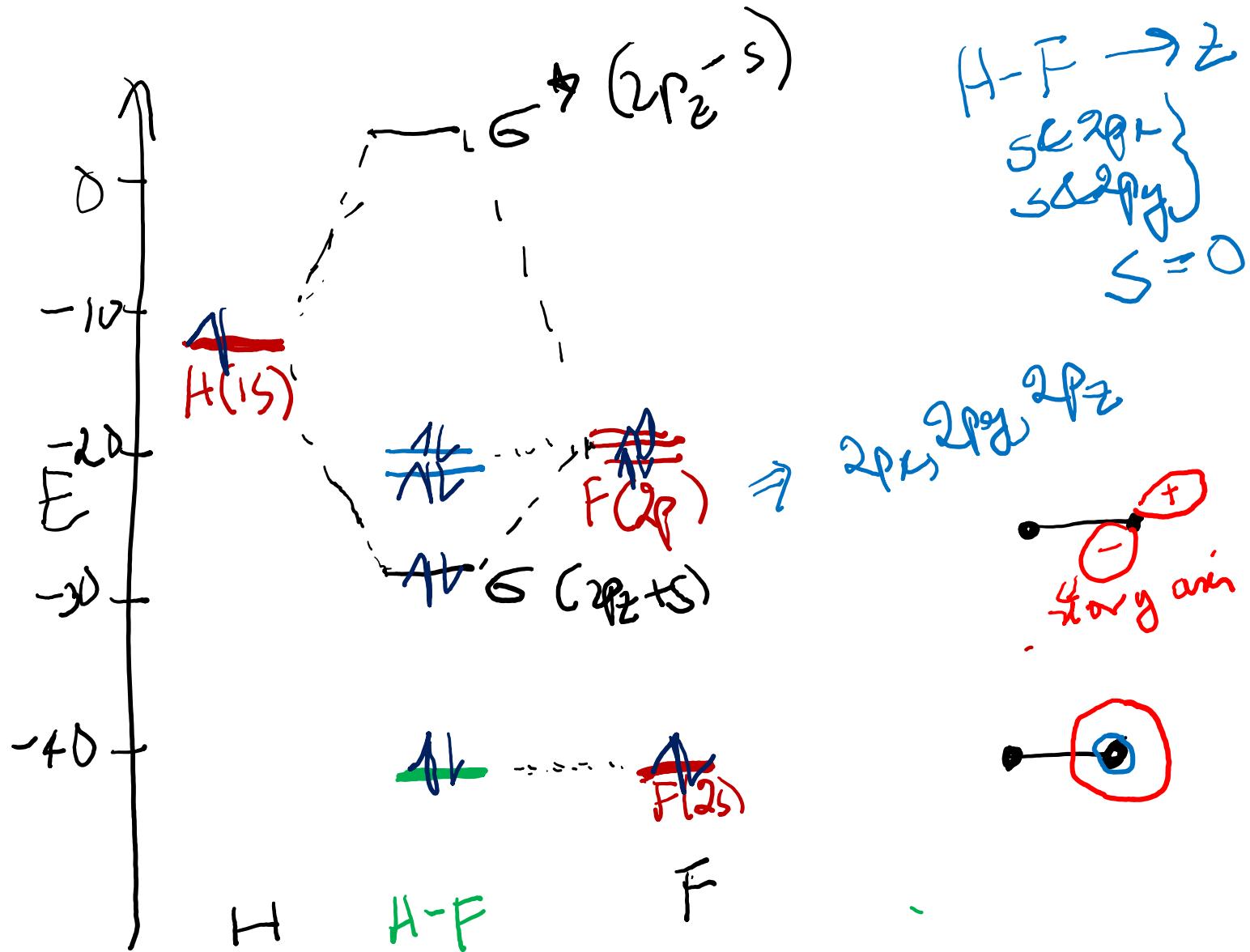


Electrostatic potentials  
can be computed which  
gives a realistic picture  
of the electron densities  
in HF: "Egg" Shaped



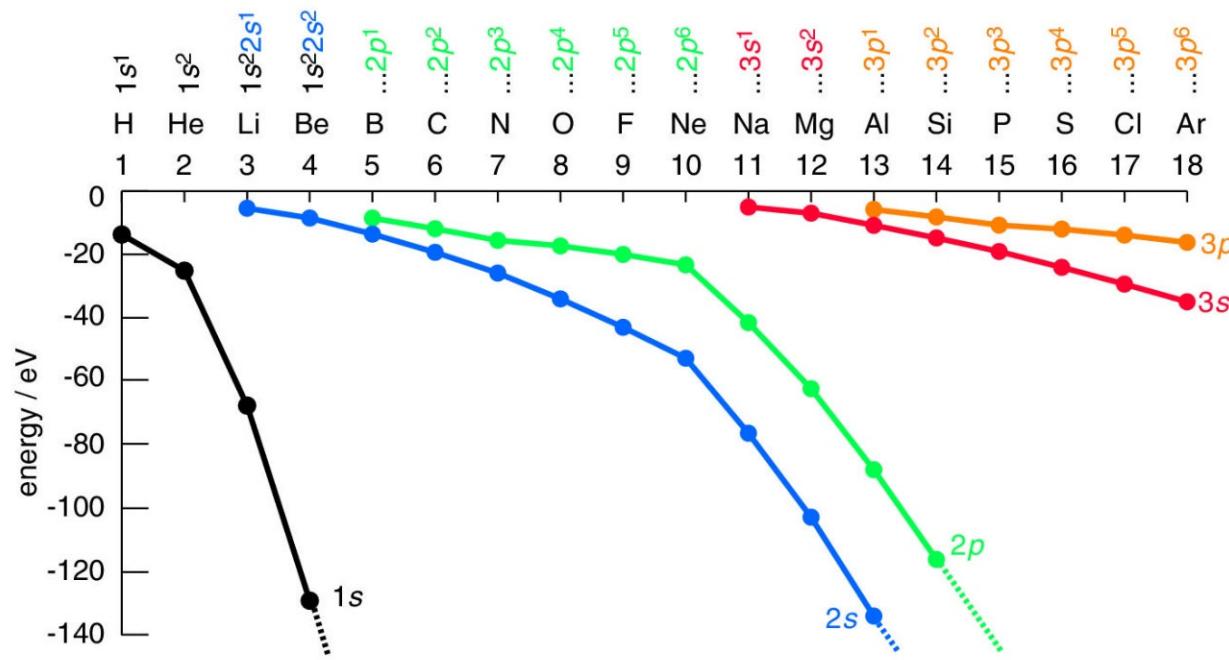
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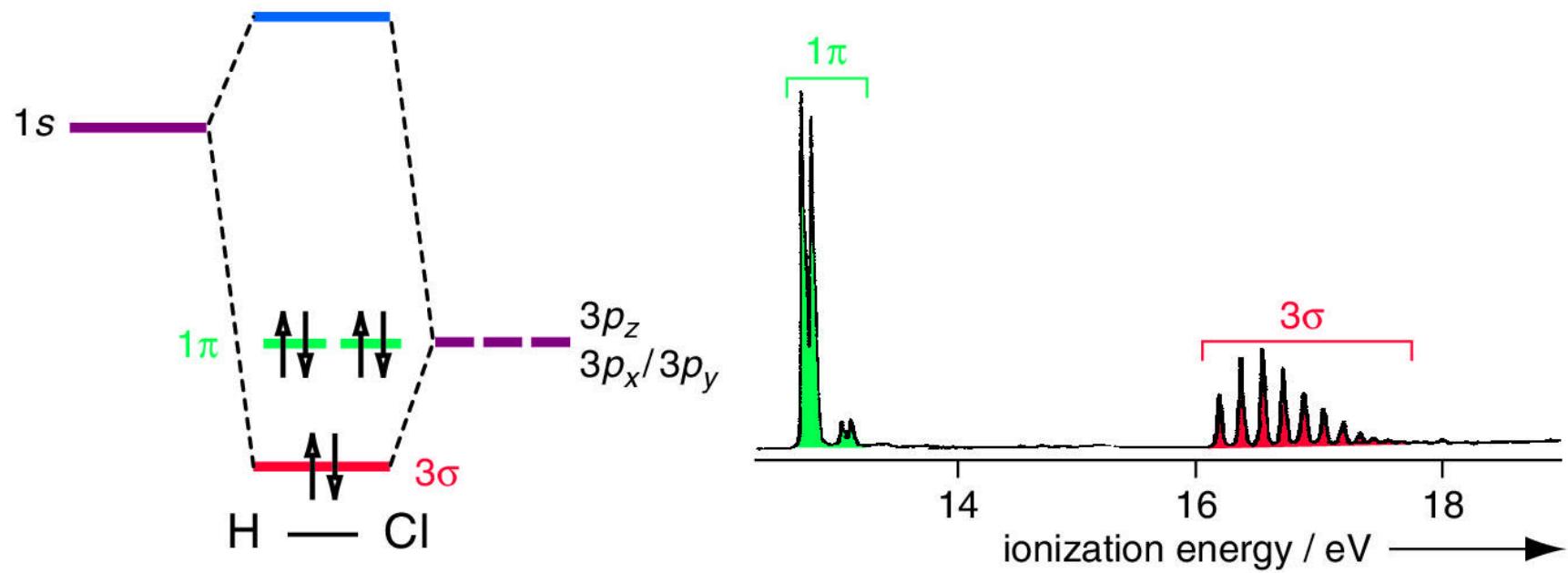
# Hetero-nuclear Diatomics: HCl

For Cl  $\rightarrow$  3p states close in energy to the 1s of H



# Hetero-nuclear Diatomics: HCl

For Cl  $\rightarrow$  3p states close in energy to the 1s of H

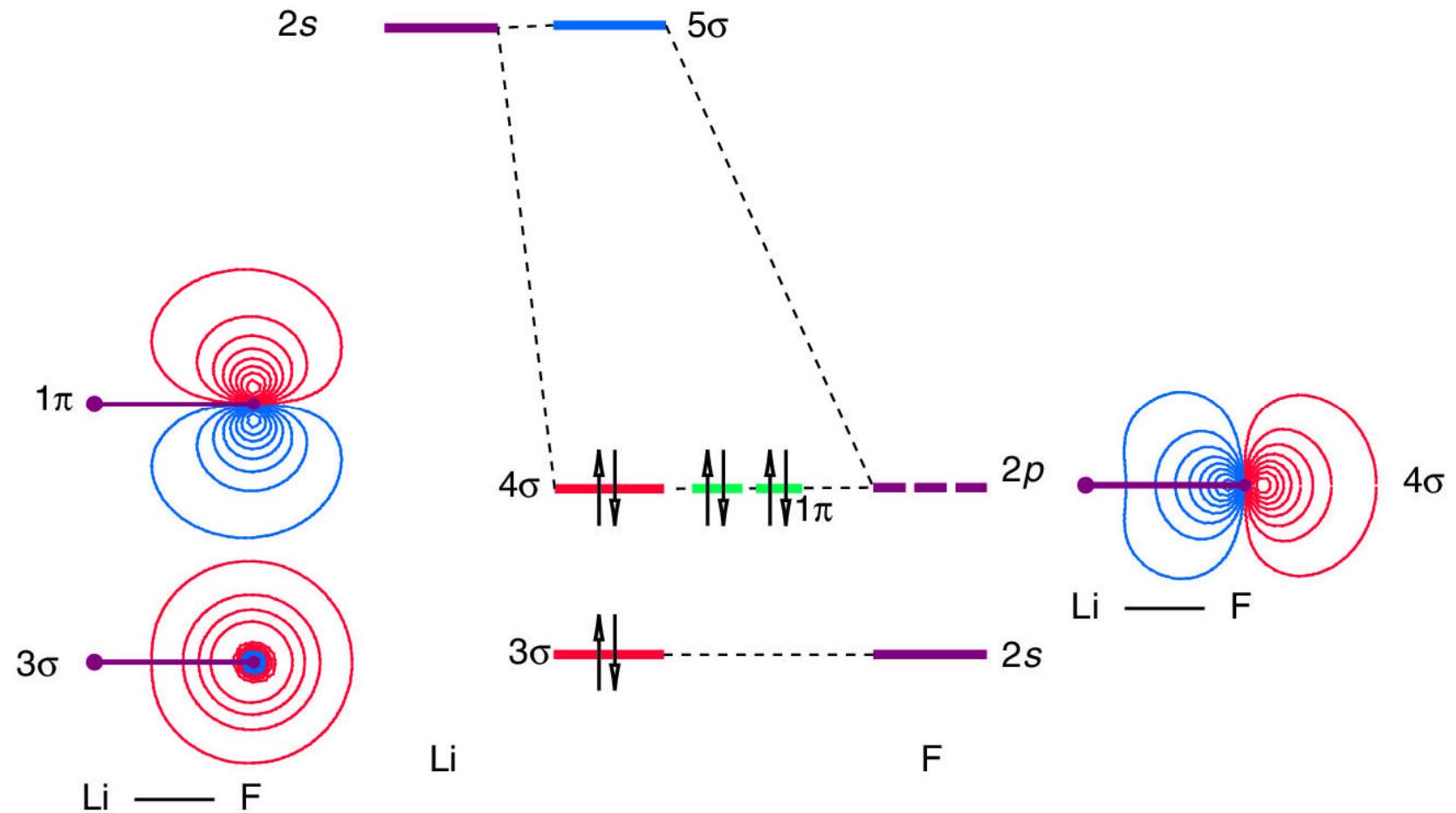


Similar to HF, expect for 2p and 3p difference.

Can not tell where absolute Energy levels will be unless Spectroscopic evidences exist, or perform QM calculations

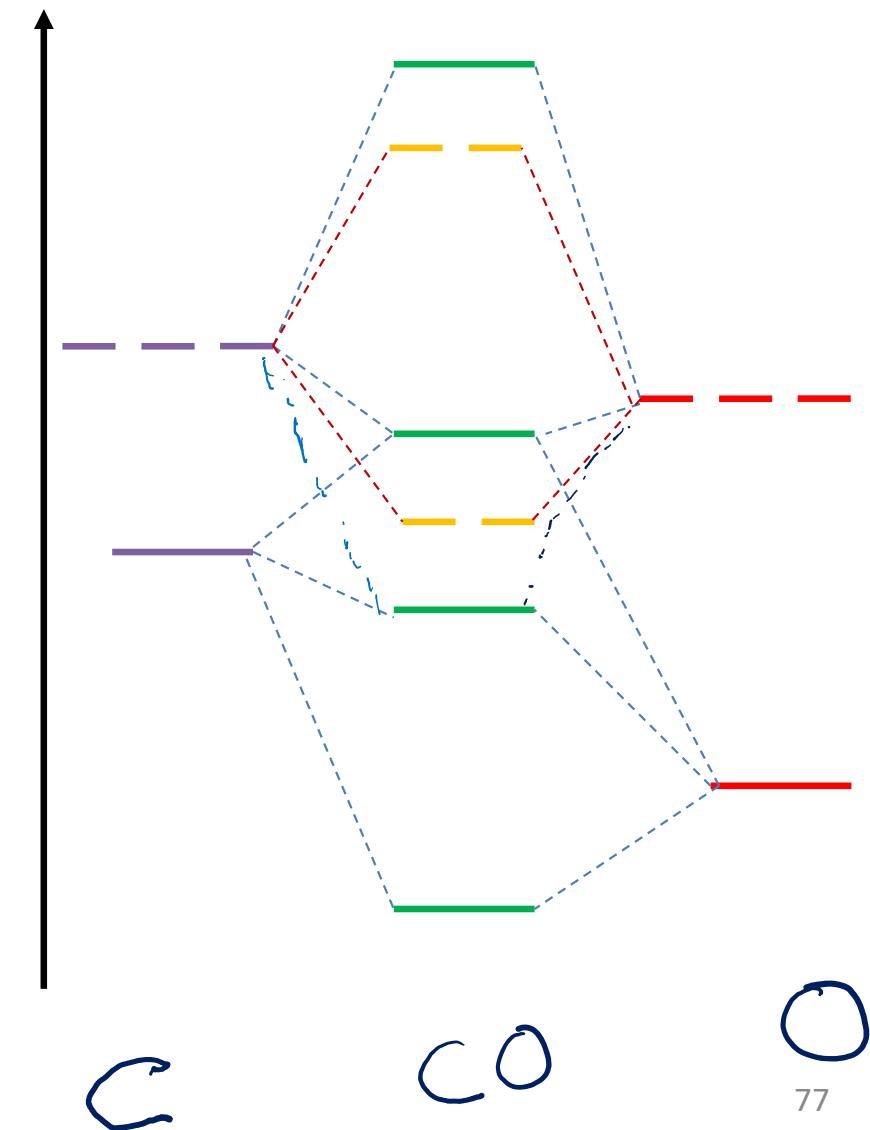
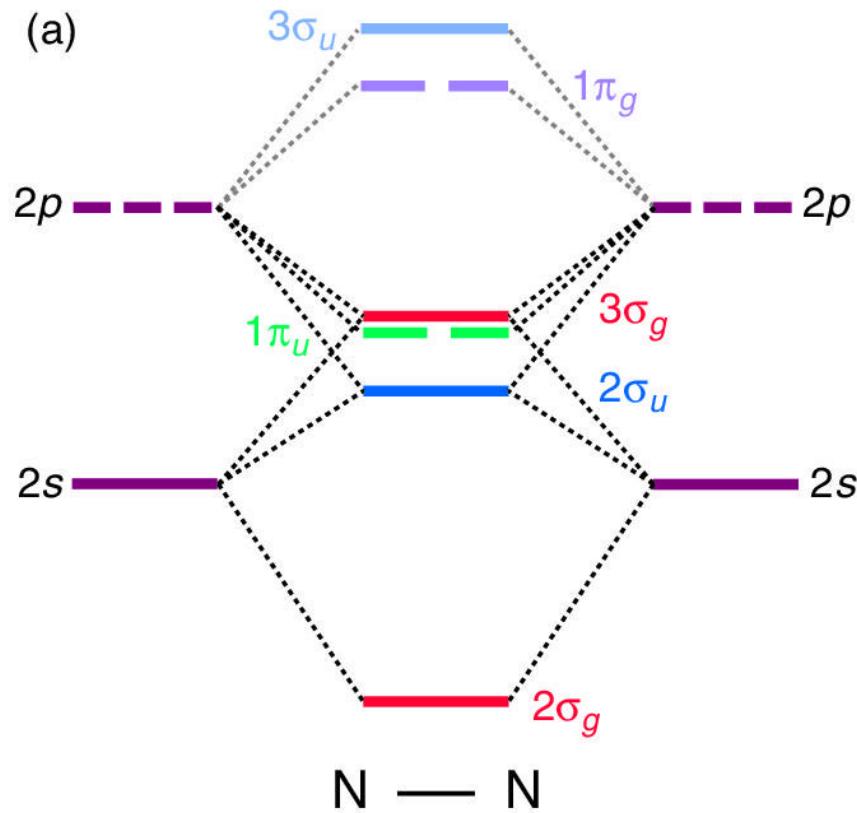
# Li-F

Li 2s (-5 eV), F (2s) -43 eV, F (2p) -20 eV



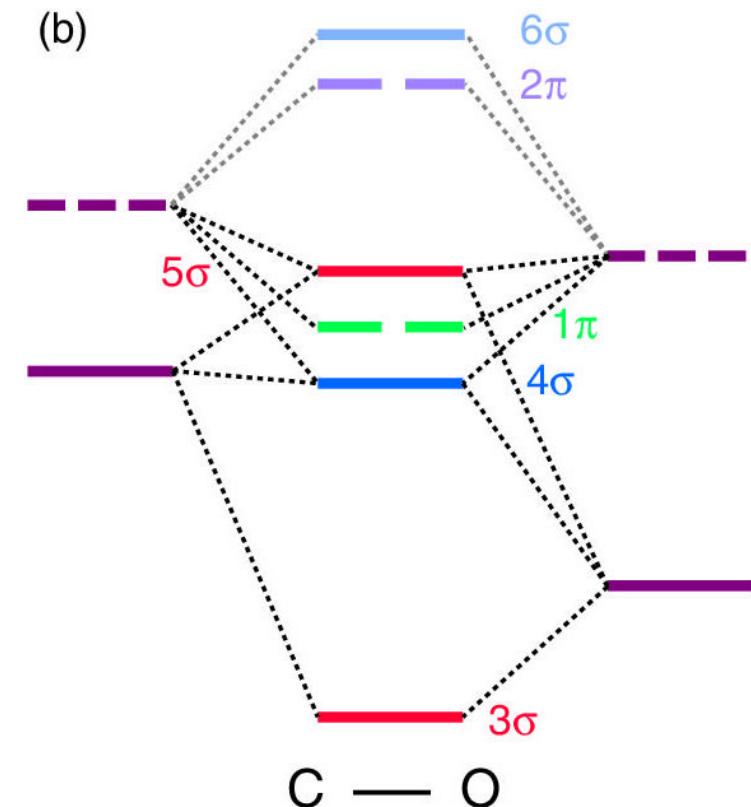
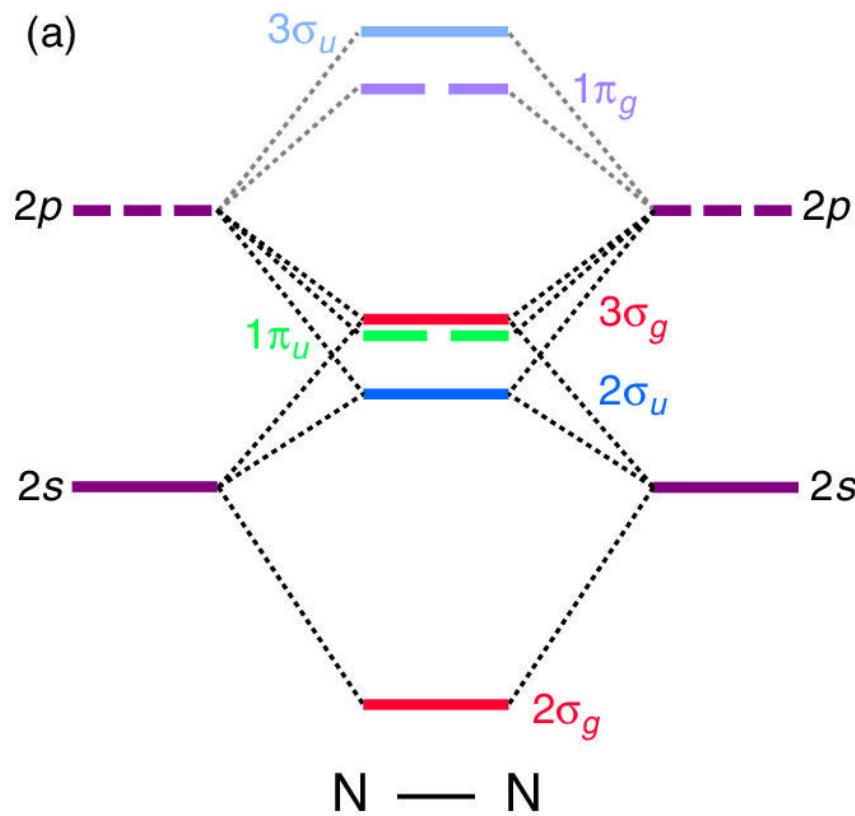
# MO energy diagram for CO

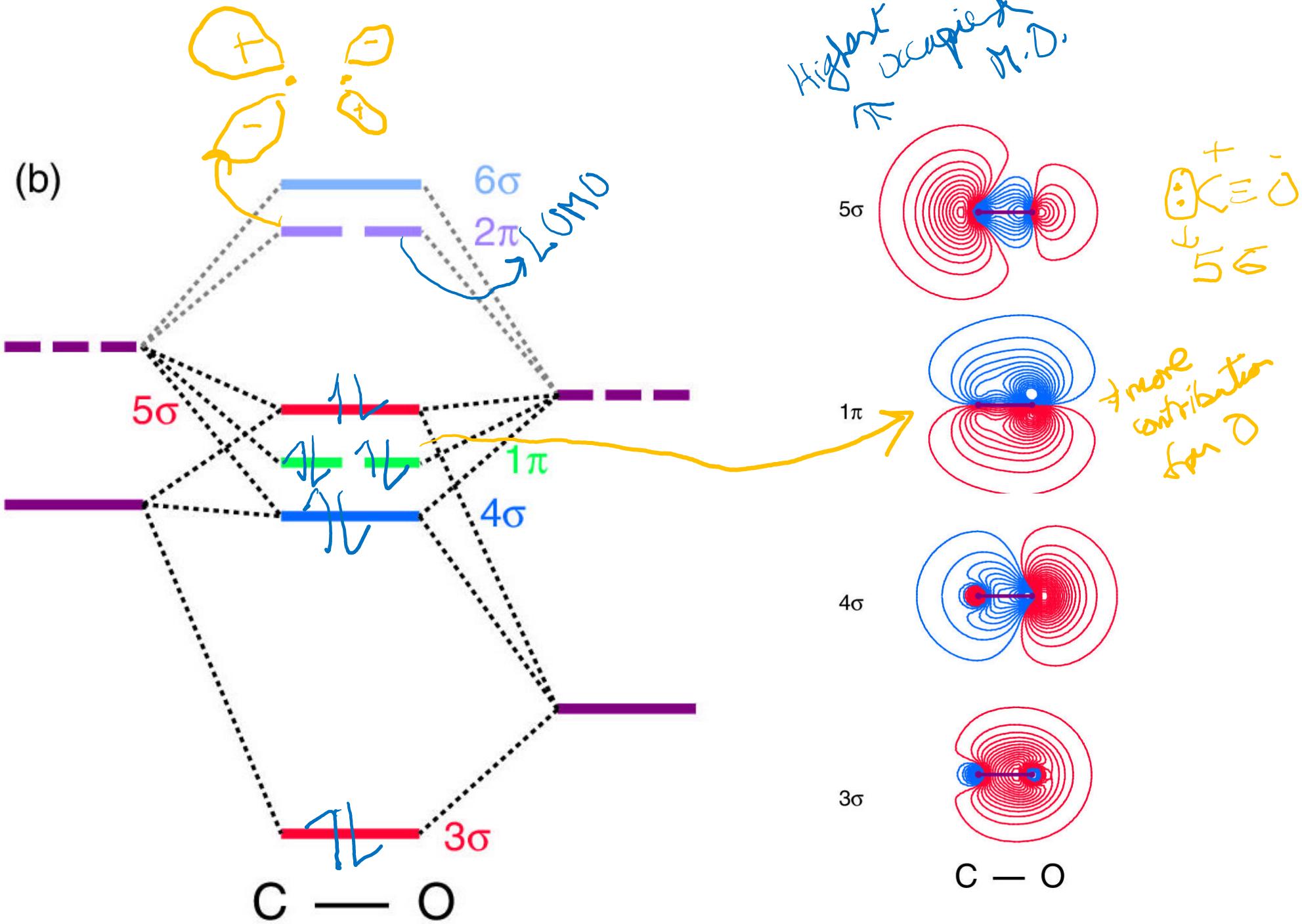
C 2s (-19 eV), 2p (-12 eV)  
O 2s (-34 eV), 2p (-17 eV)

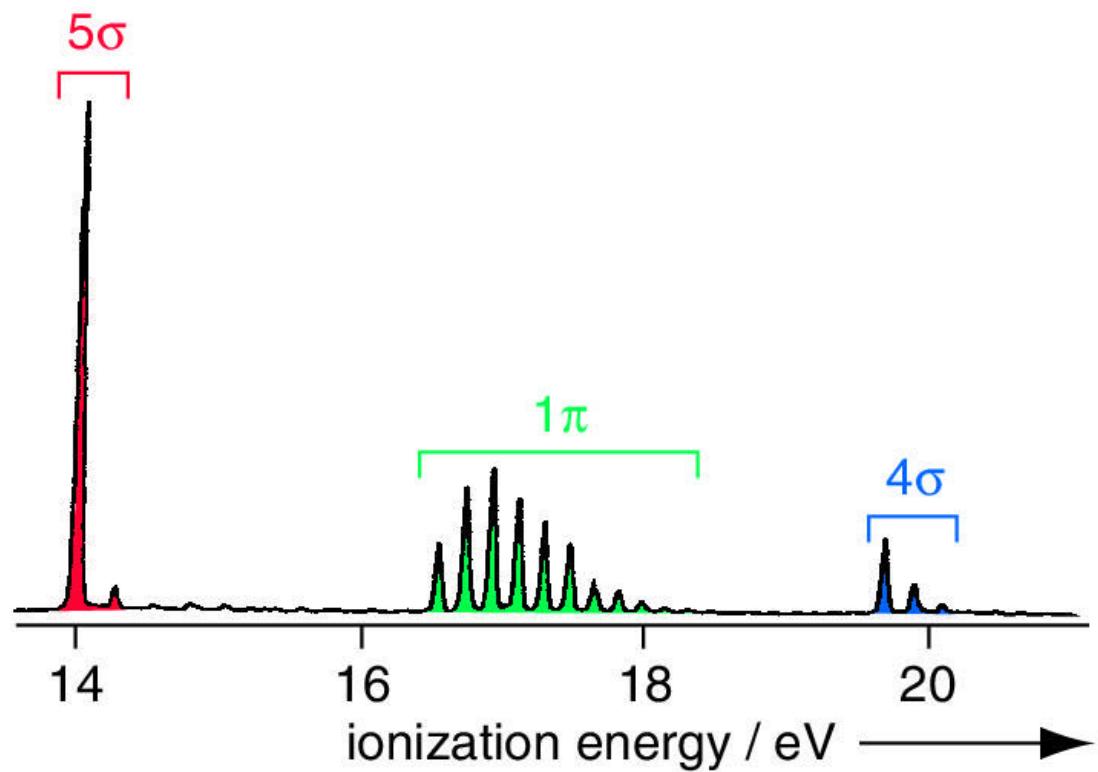
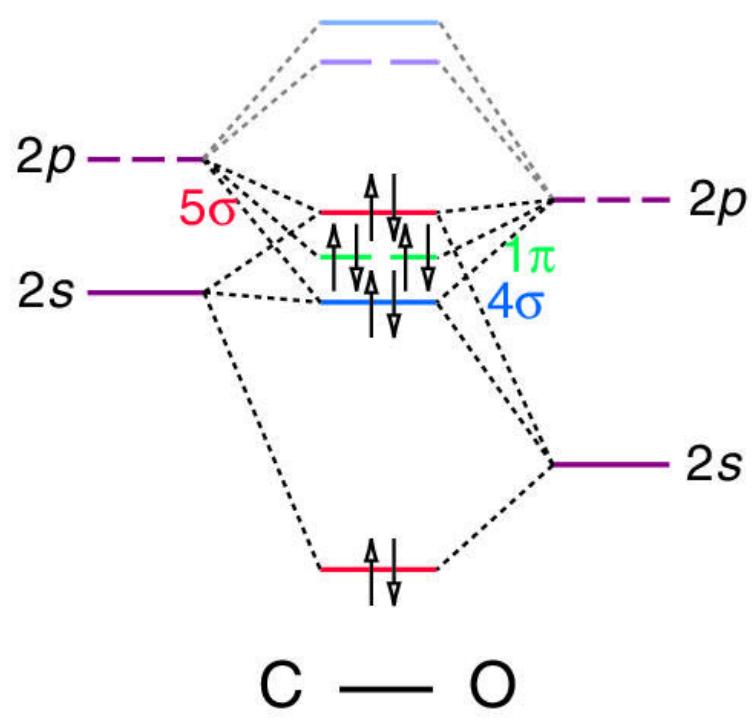


# MO energy diagram for CO

C 2s (-19 eV), 2p (-12 eV)  
O 2s (-34 eV), 2p (-17 eV)







# Fischer-Tropsch Process: Chemistry

- The Fischer-Tropsch process is a catalytic chemical reaction: syngas are converted into hydrocarbons of various molecular weights

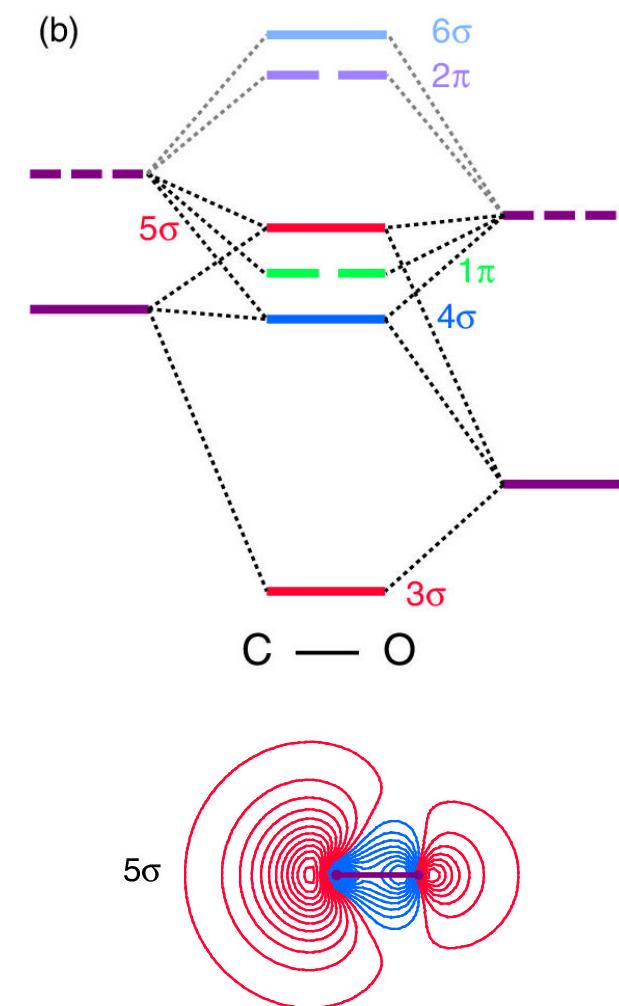


- Conditions are chosen to maximize the formation of higher molecular weight hydrocarbon liquid fuels
- $\text{H}_2$  generation from the water-gas-shift reaction is predominant

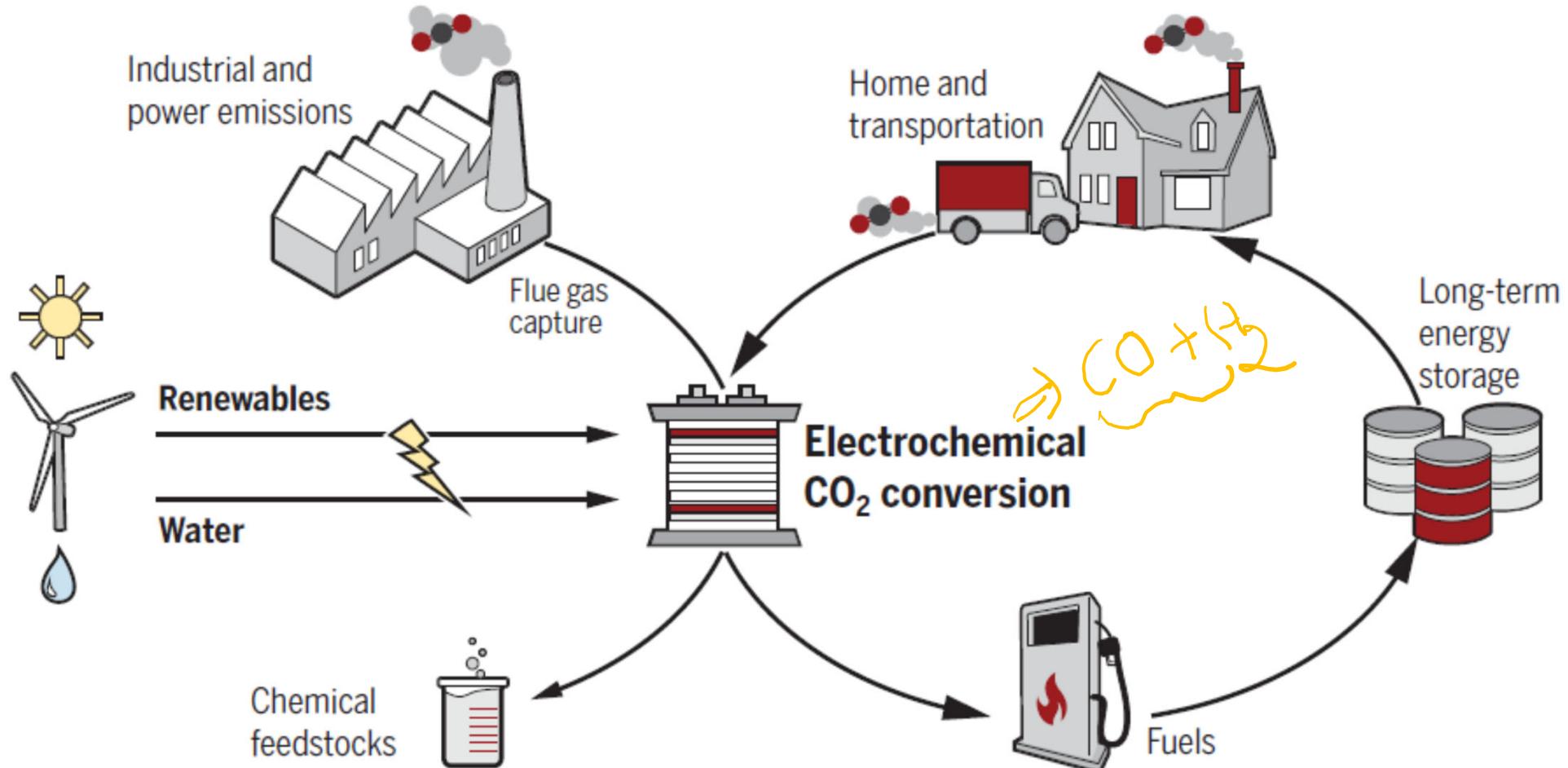


## Catalysts

Catalysts are based on transition metals of iron, cobalt, nickel and ruthenium (low valent)

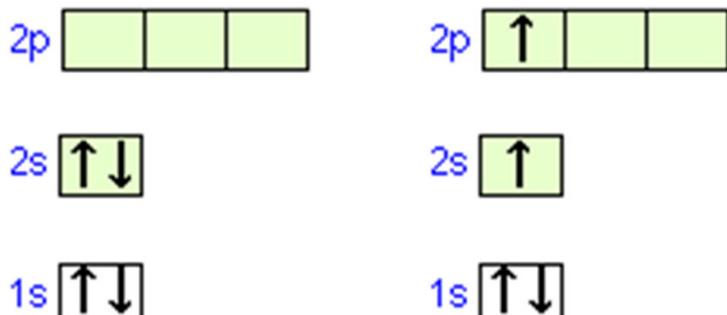


# CO<sub>2</sub> Utilization



# Sometimes it seems Atomic Orbitals alone do not work for molecules

- Bonding in a compound of divalent beryllium, such as beryllium hydride, BeH<sub>2</sub>- Be has a configuration of 1s<sup>2</sup>2s<sup>2</sup>
- The only way that we can obtain two unpaired electrons for bonding in beryllium is to promote one of the 2s electrons to the 2p level- energy required
- It is observed that Be does form reasonably stable bonds with other atoms
- Moreover, the two bonds in BeH<sub>2</sub> and similar molecules are completely equivalent; this would not be the case if the electrons in the two bonds shared Be orbitals of different types, as in the "excited state" diagram above
- These facts suggest that it is incorrect to assume that the distribution of valence electrons that are shared with other atoms can be described by atomic-type s, p, and d orbitals at all.



Be atom in ground state

Be atom in excited state

# The case for Hybrid Orbitals

- For  $\text{BeH}_2$ , we know from experimental evidence that the molecule is linear and therefore the electron density surrounding the central atom is no longer spherical, but must be concentrated along two directions  $180^\circ$  apart, and we need to construct a function  $\Psi^2$  having these geometrical properties
- There are any number of ways of doing this, but it is convenient is to use a particular set of functions  $\psi$  (which we call *hybrid orbitals*) that are constructed by combining the atomic  $s,p,d$ ,and  $f$  functions that are already familiar to us.
- You should understand that *hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals we are familiar with in such a way that the new (hybrid) orbitals possess the geometric and other properties that are reasonably consistent with what we observe in a wide range (but certainly not in all) molecules
- In other words, hybrid orbitals are abstractions that describe reality fairly well in certain classes of molecules (and fortunately, in much of the very large class of organic substances) and are therefore a useful means of organizing a large body of chemical knowledge... but they are far from infallible e.g.  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$

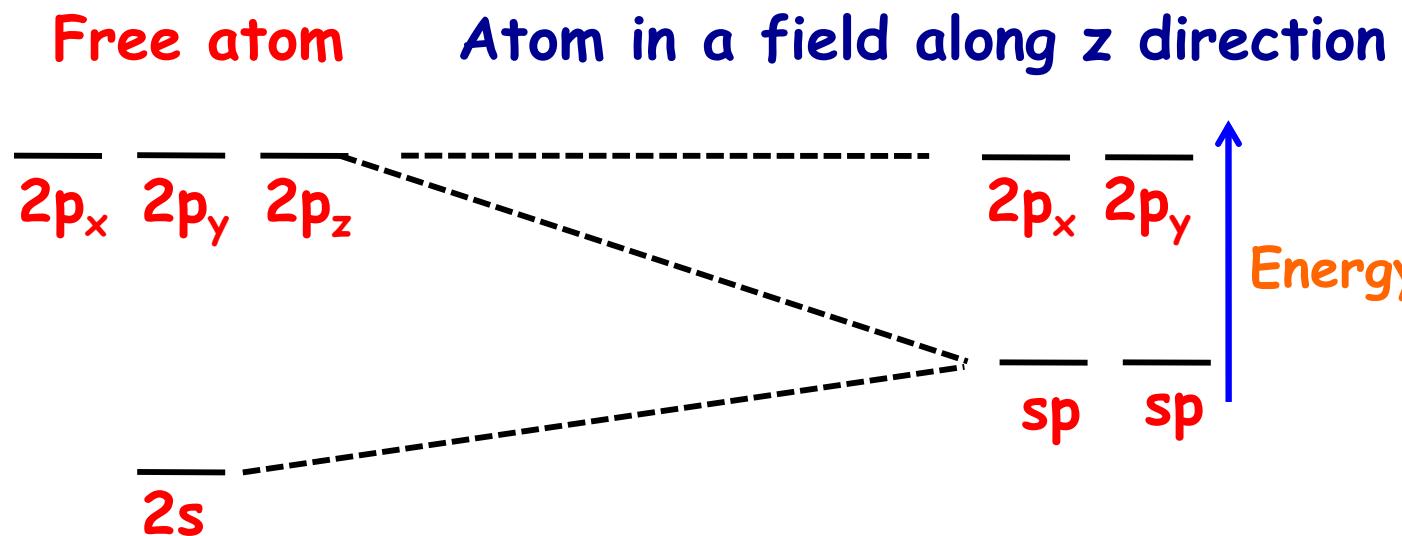
# Hybrid AOs: Linear Combination of one S and one P → lowering of energy



Linus Pauling, ~1930

## Hybrid (1e) Orbitals

- Linear combination of atomic orbital's within an atom leading to more effective bonding situation



- Hybridization is a VBT concept. Use of experimental information
- All hybrid orbitals equivalent and are orthonormal to each other

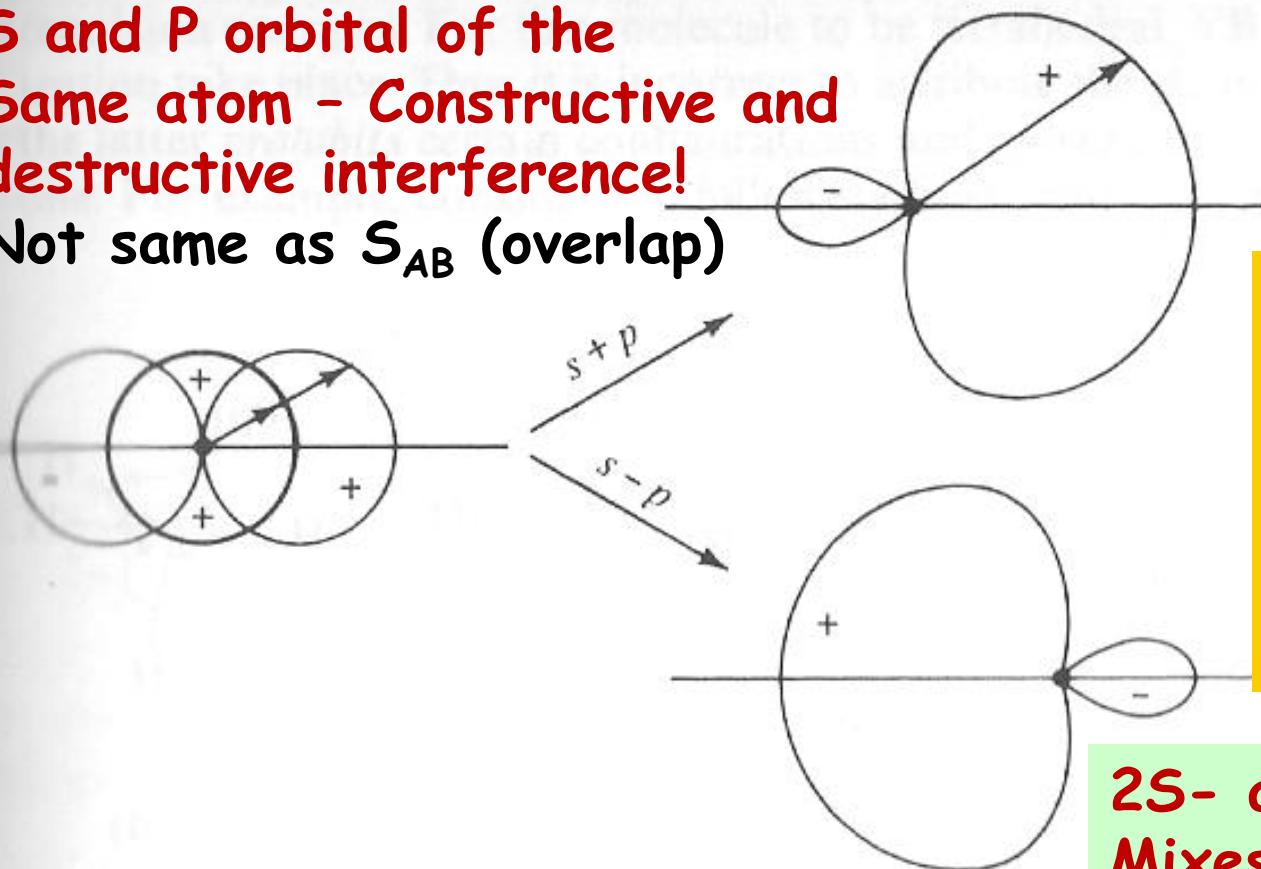
It is different from LCAO in MO's

# Linear Geometry: s&p mix: sp hybrid AOs

2 equivalent hybrid orbitals of the same energy and shape (different directions)

S and P orbital of the Same atom - Constructive and destructive interference!

Not same as  $S_{AB}$  (overlap)



$$\varphi_{h1}^{sp} = c_1 \psi_s + c_2 \psi_p$$

$$\varphi_{h2}^{sp} = c_1 \psi_s - c_2 \psi_p$$

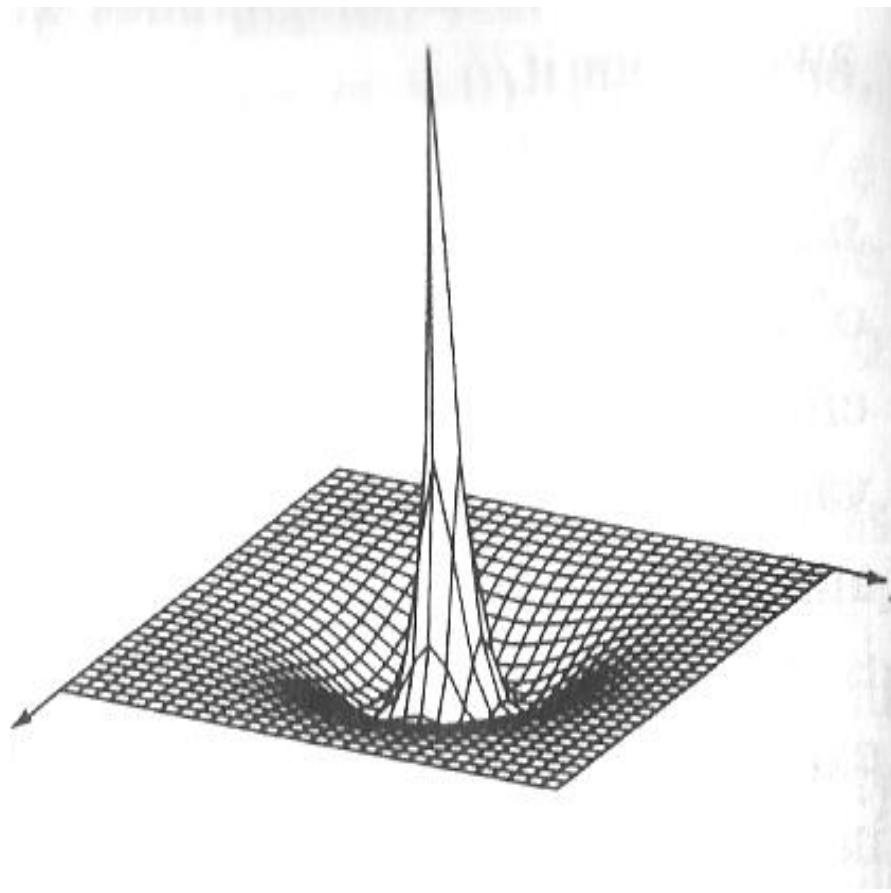
$$\varphi_{h1}^{sp} = \frac{1}{\sqrt{2}} \psi_s + \frac{1}{\sqrt{2}} \psi_p$$

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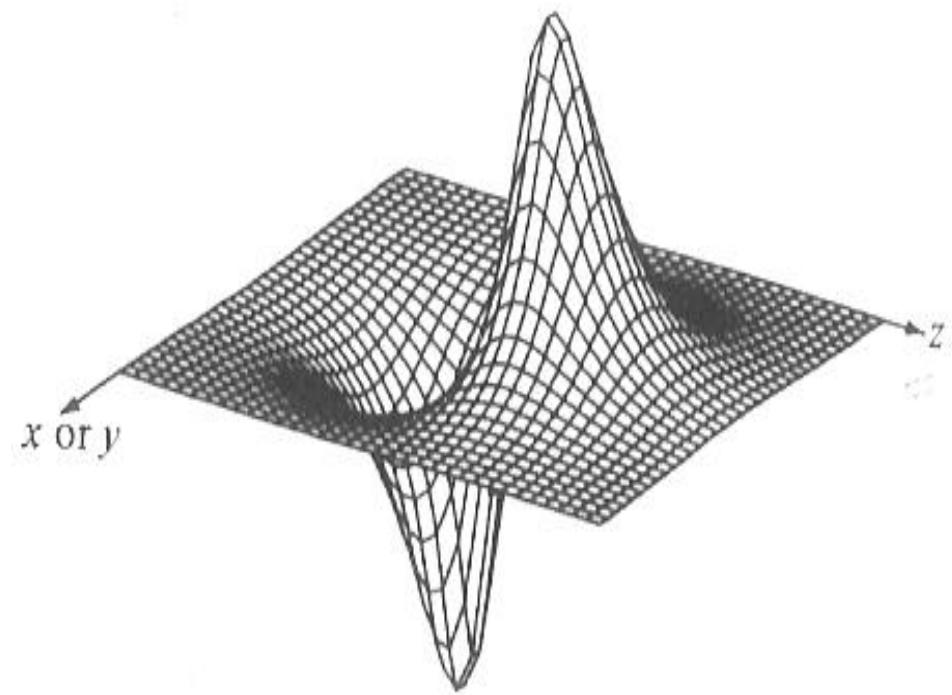
2S- and 2P- (similar energy)  
Mixes to form hybrid orbital  
which forms a MO with H (1S)

Contribution from s=0.5; contribution from p=0.5  
Have to normalize each hybridized orbital

# Recap: 2D/3D plots of 2s and 2pz WFs



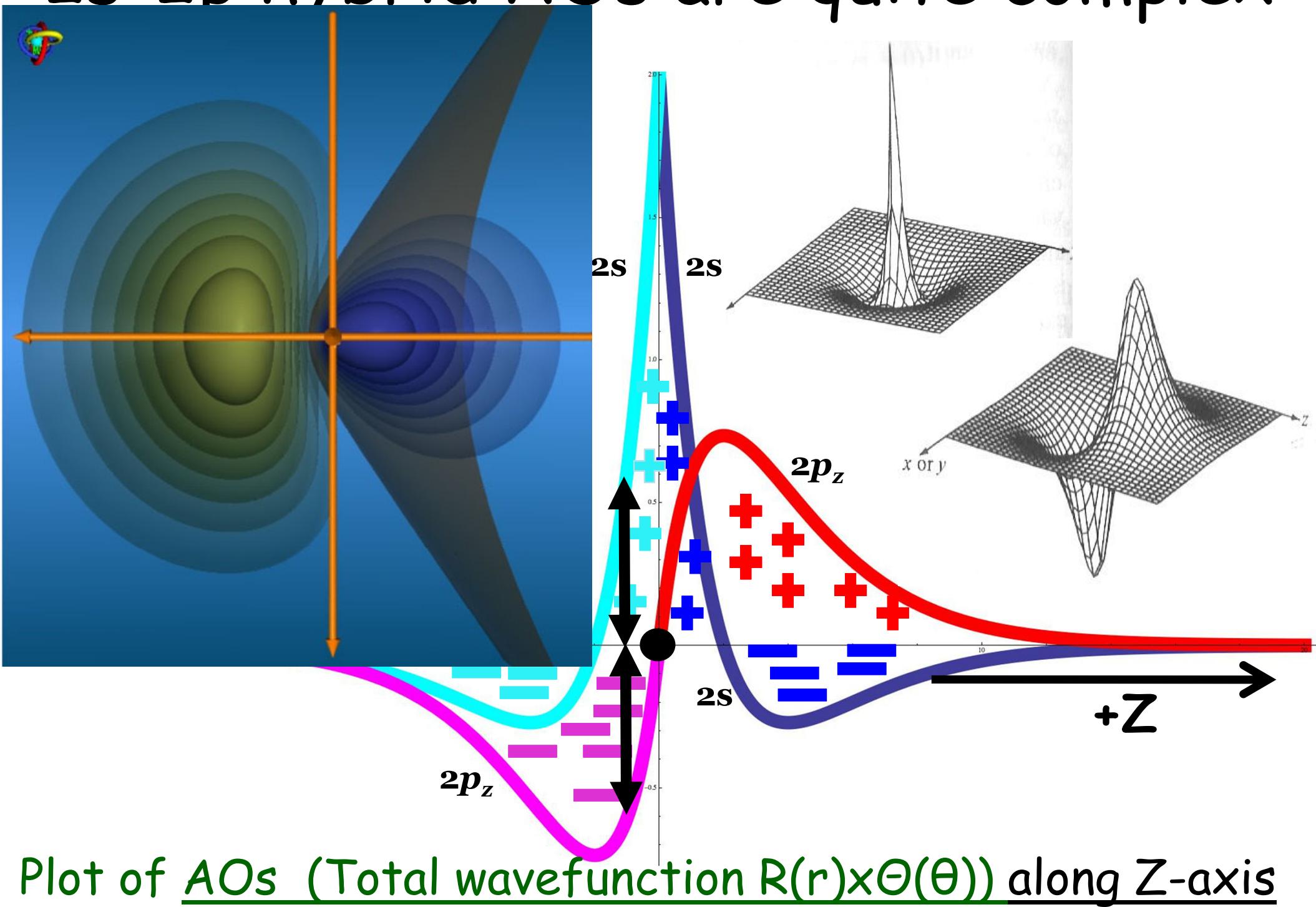
**2s**



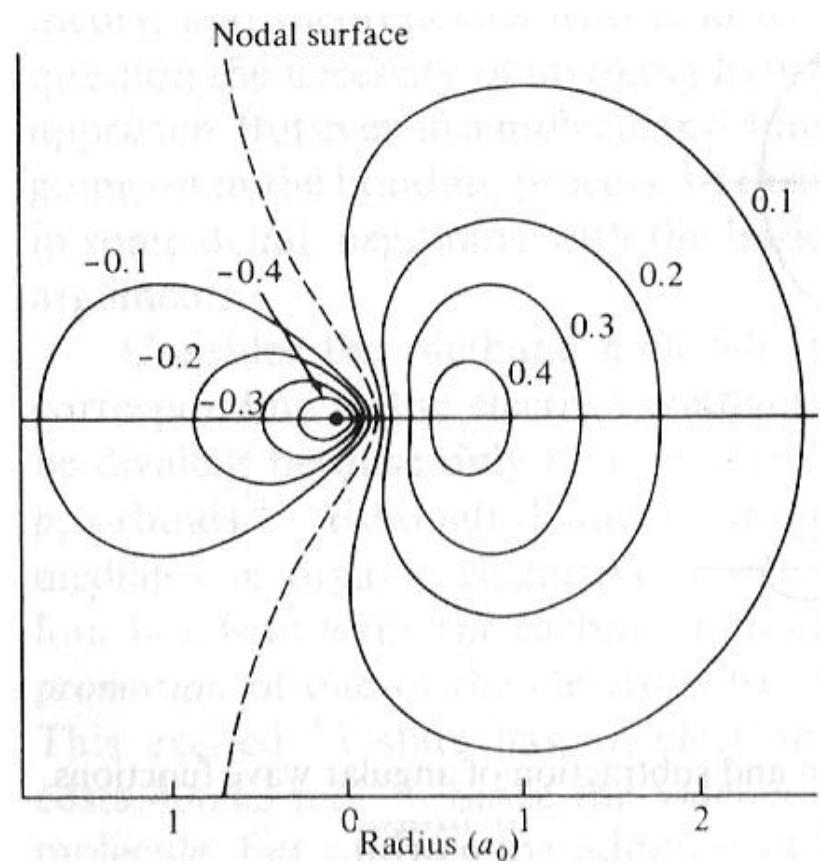
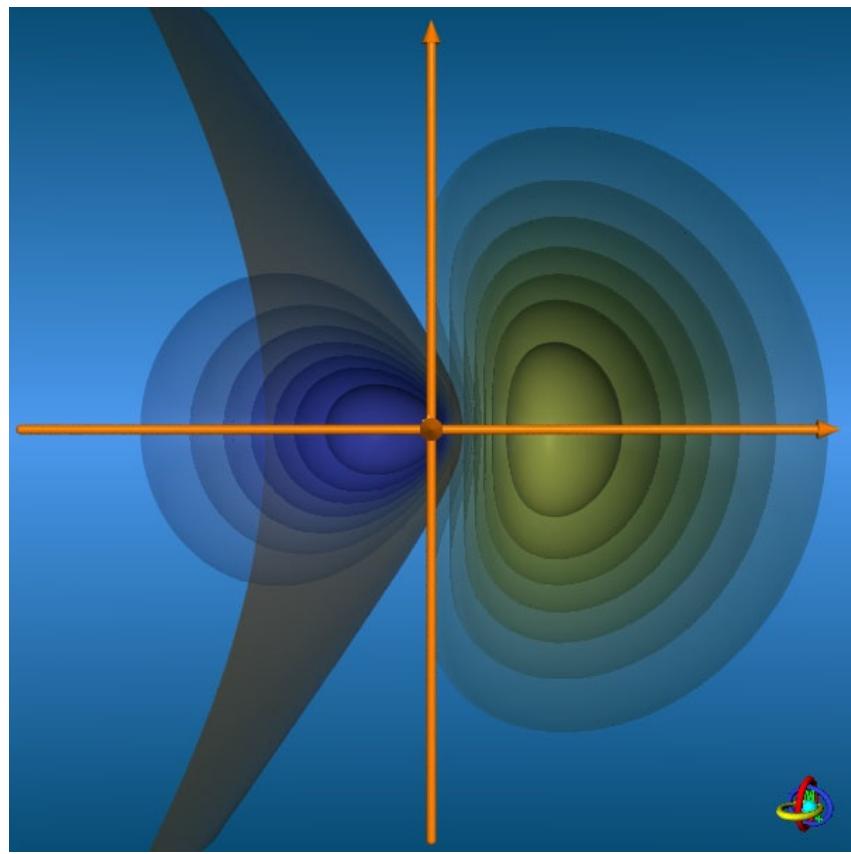
**2p<sub>z</sub>**

3D projection (plot) of AOs (Total Wavefunction  $R(r) \times \Theta(\theta)$ )

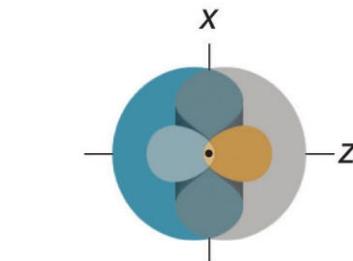
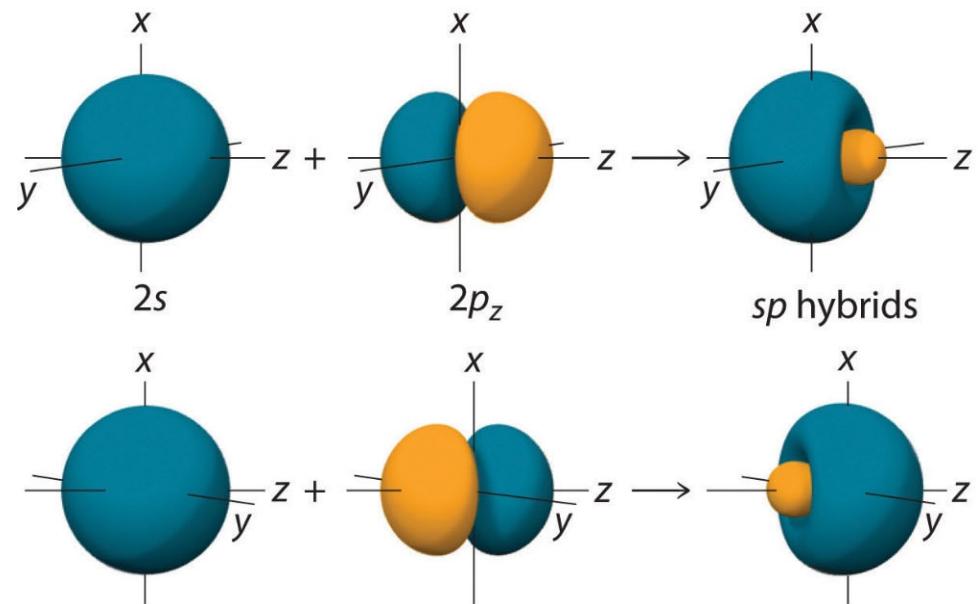
# 2s-2p hybrid AOs are quite complex



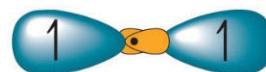
# Contours & bonding of sp-hybridization



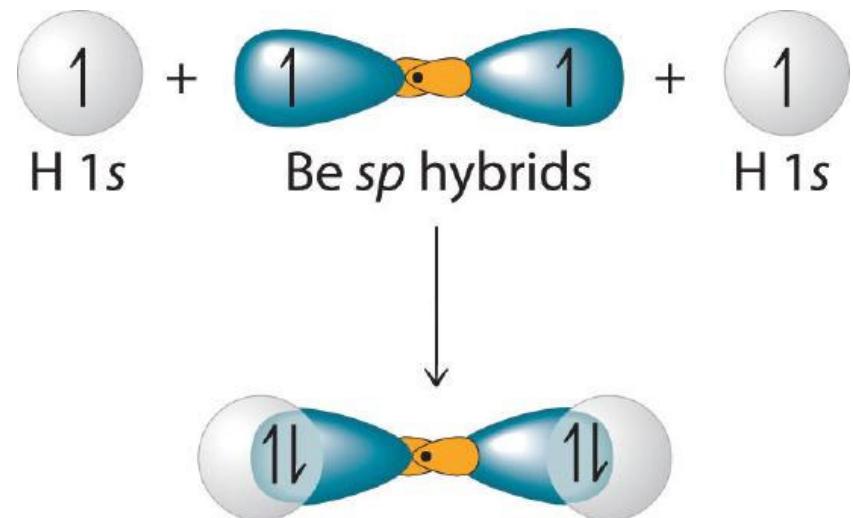
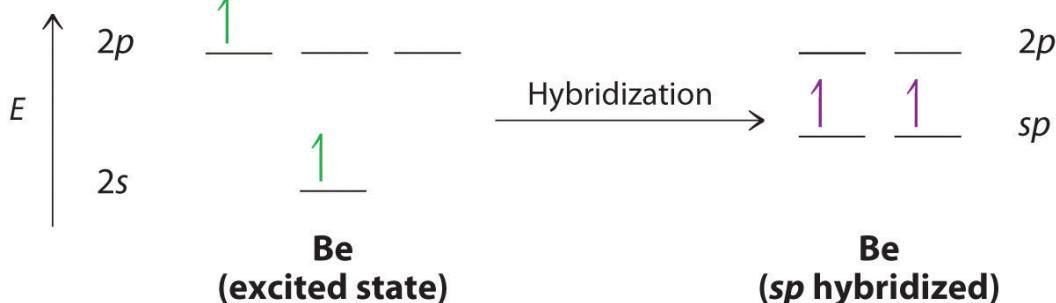
# The case of BeH<sub>2</sub>



Hybrids shown together  
in cross-section

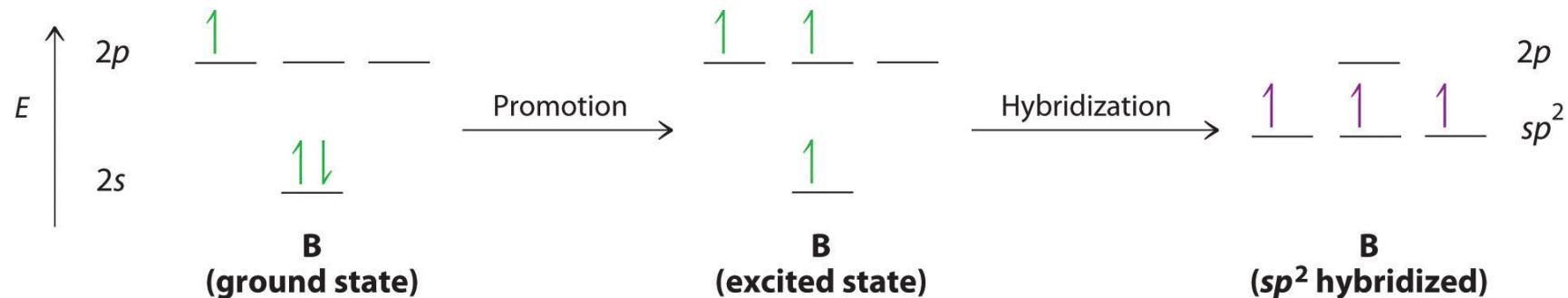
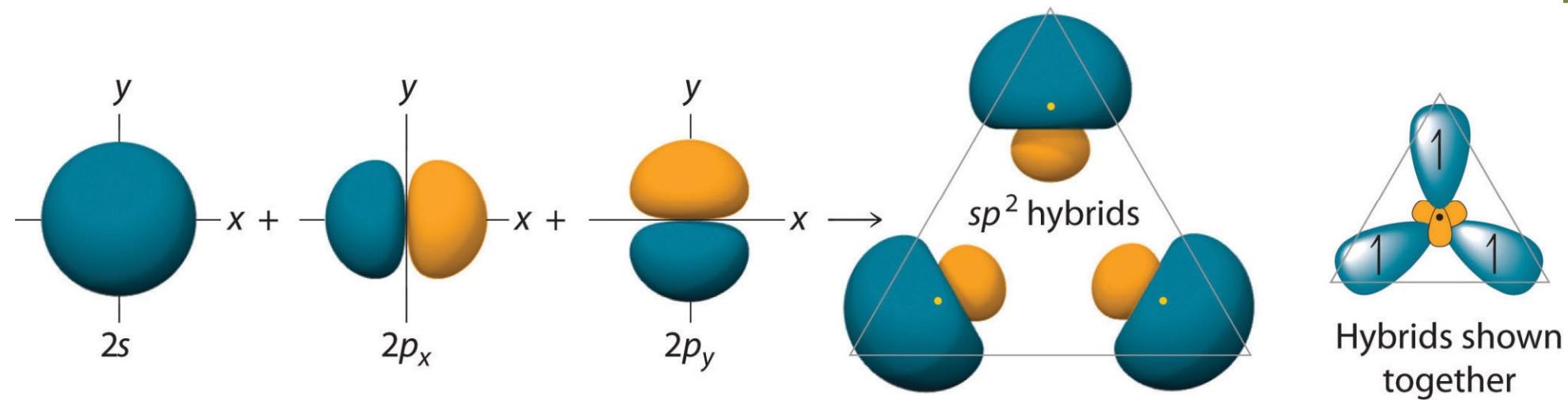


Schematic representation  
of hybrids shown together

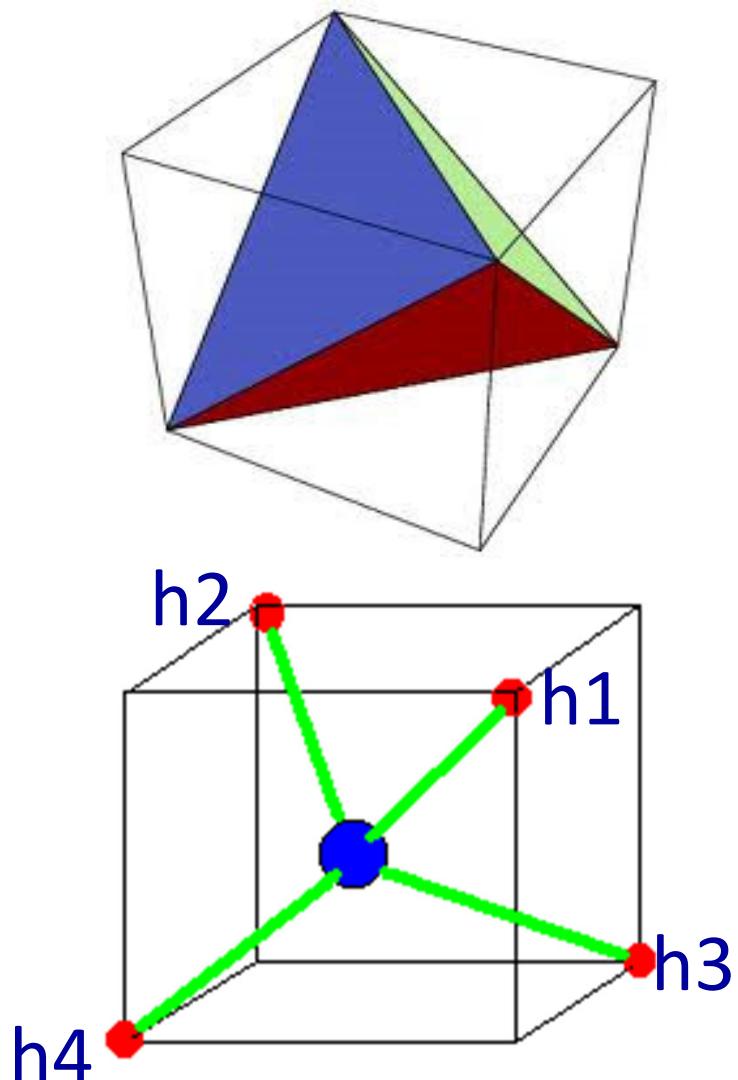


# Trigonal Geometry: Mixing s & 2-p

$p_x$  and  $p_y$  can be combined with  $s$  to get three equivalent hybrids at  $120^\circ$  to each other



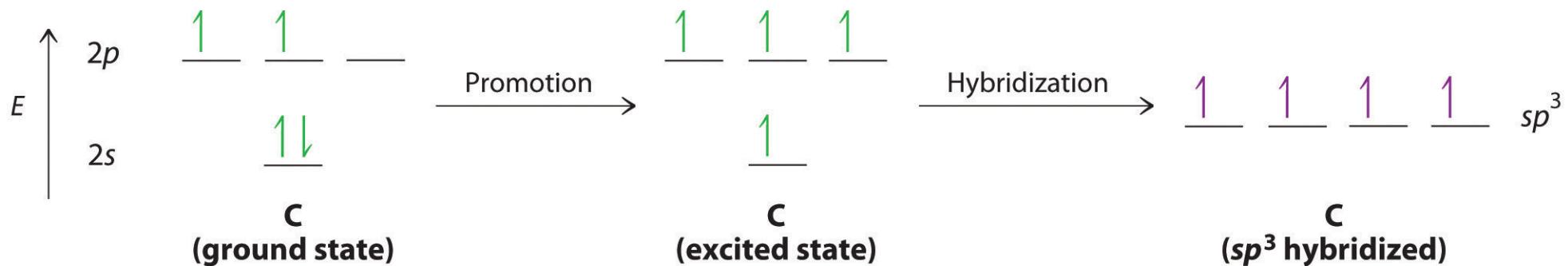
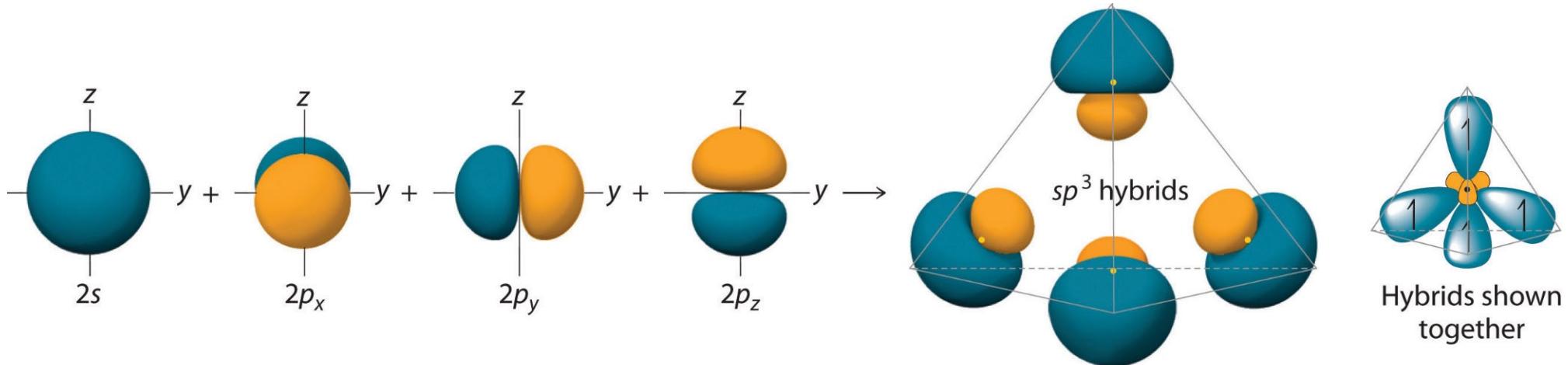
# Hybridization of s & 3-p:sp<sup>3</sup>: Tetrahedral



$$\varphi_{h1}^{sp^3} = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$
$$\varphi_{h2}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$
$$\varphi_{h3}^{sp^3} = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$
$$\varphi_{h4}^{sp^3} = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

**Contributions from s = 25%; p=75%**

# What if h<sub>1</sub> is oriented along z-axis?



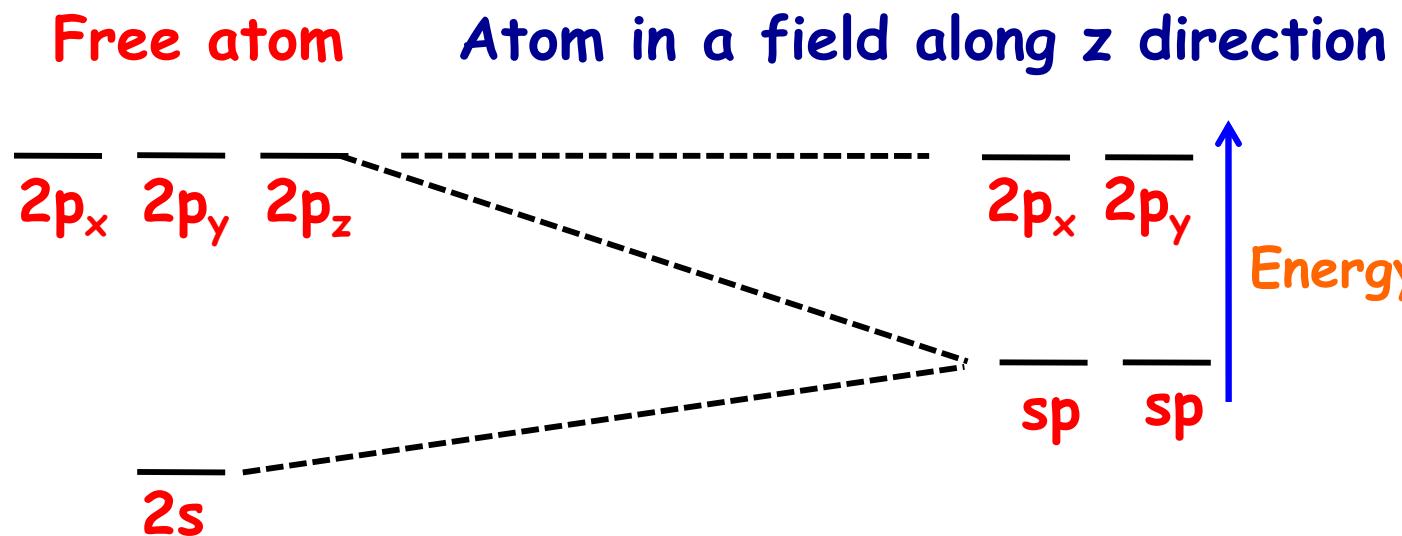
# Review: Hybrid AOs: Linear Combination of one s and one p



Linus Pauling, ~1930

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- Linear combination of atomic orbital's within an atom leading to more effective bonding situation



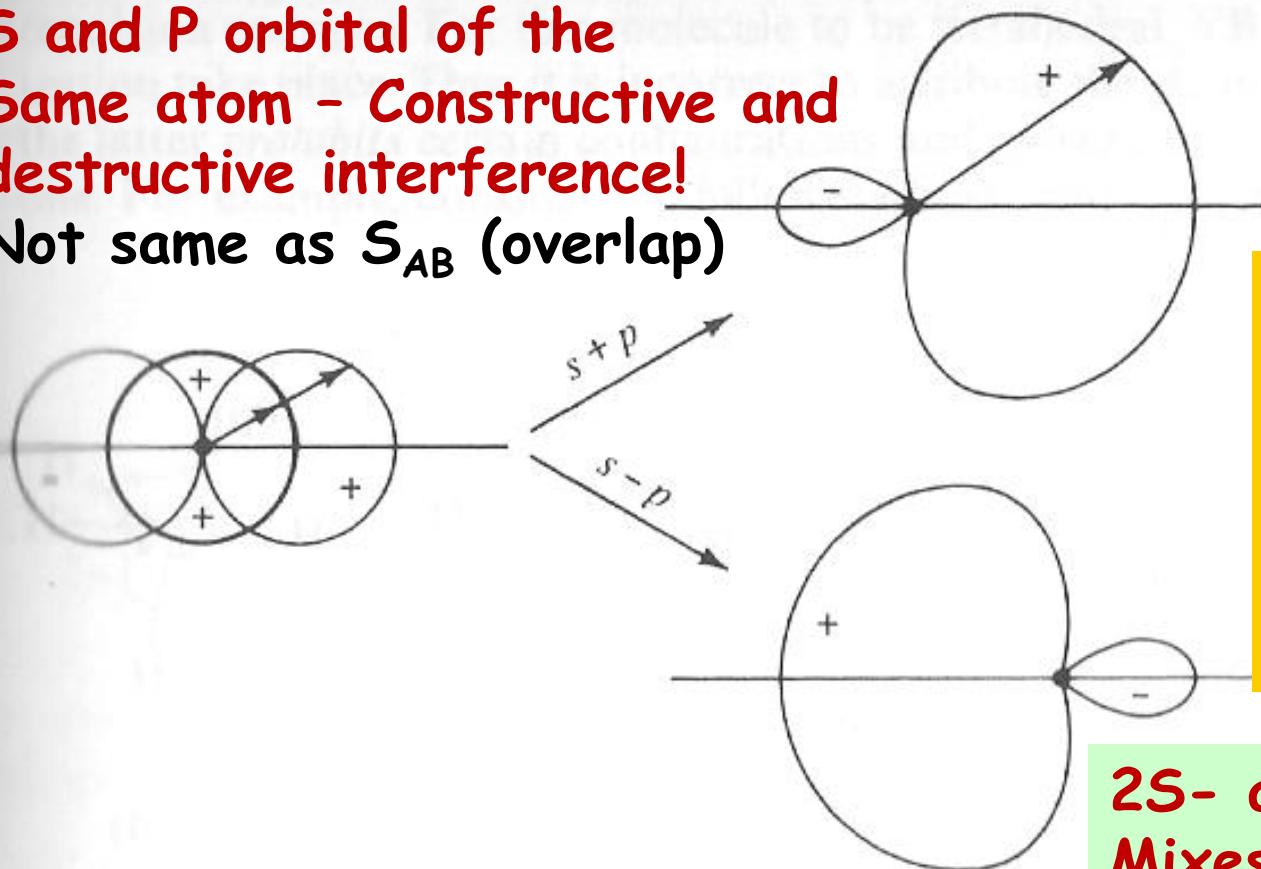
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2 equivalent hybrid orbitals of the same energy and shape (different directions)

S and P orbital of the Same atom - Constructive and destructive interference!

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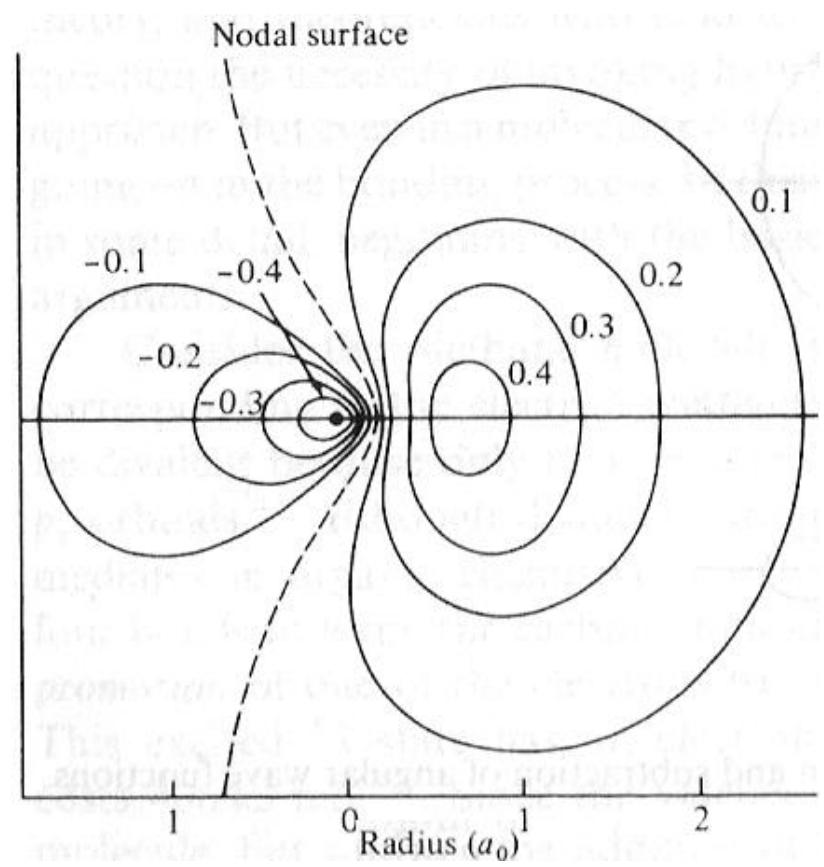
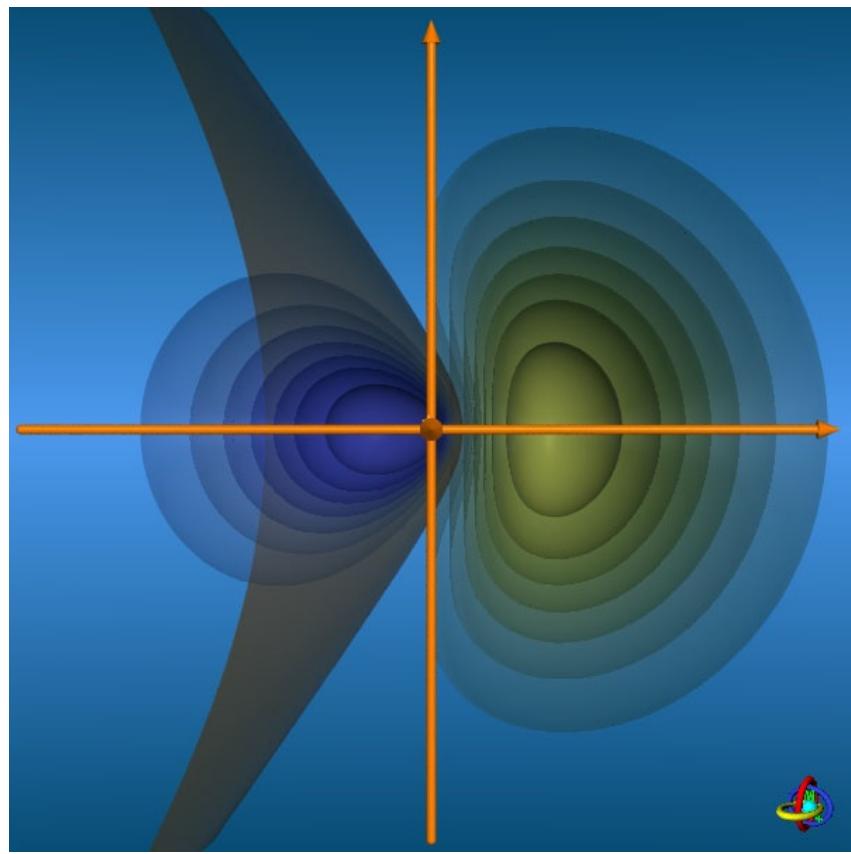
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