

# MEAM/MSE 507

# Fundamentals of Materials

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**Week 3, Lecture 1: Bonding and hybridization**  
**Asynchronous**

# Continuing from last time: Bonding

## Primary bonds

- Ionic
- Covalent
- Metallic

## Secondary bonds

- Always present but can be masked by stronger primary bonds
- Ex: van der Waals interactions between inert (e.g., He) atoms
- Often electrostatic, but not ionic bonding

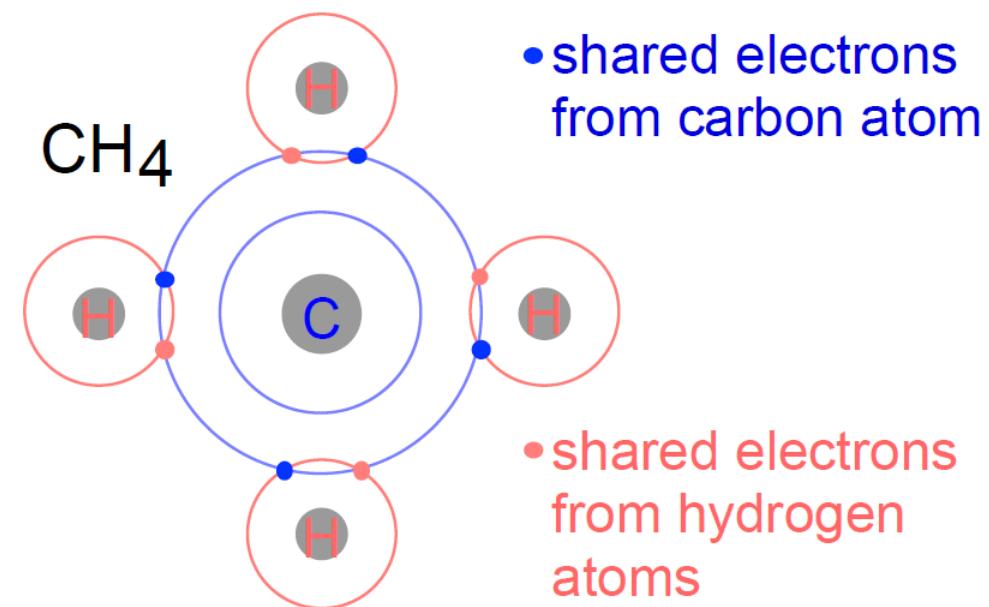
# Covalent bonding

- bonds determined by valence – s & p orbitals dominate bonding
- Example: CH<sub>4</sub>

C: has 4 valence e<sup>-</sup>,  
needs 4 more

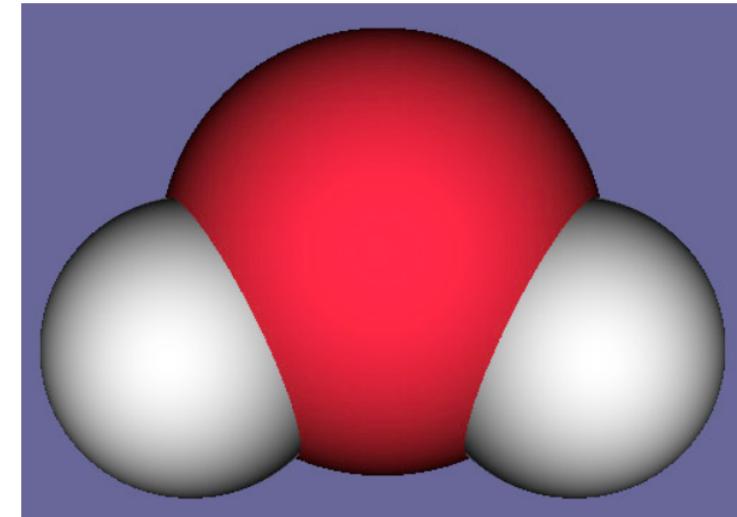
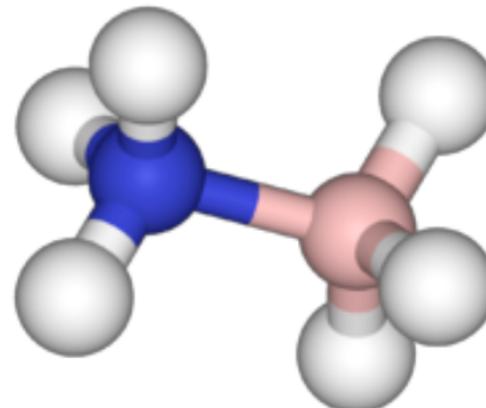
H: has 1 valence e<sup>-</sup>,  
needs 1 more

Electronegativities  
are comparable



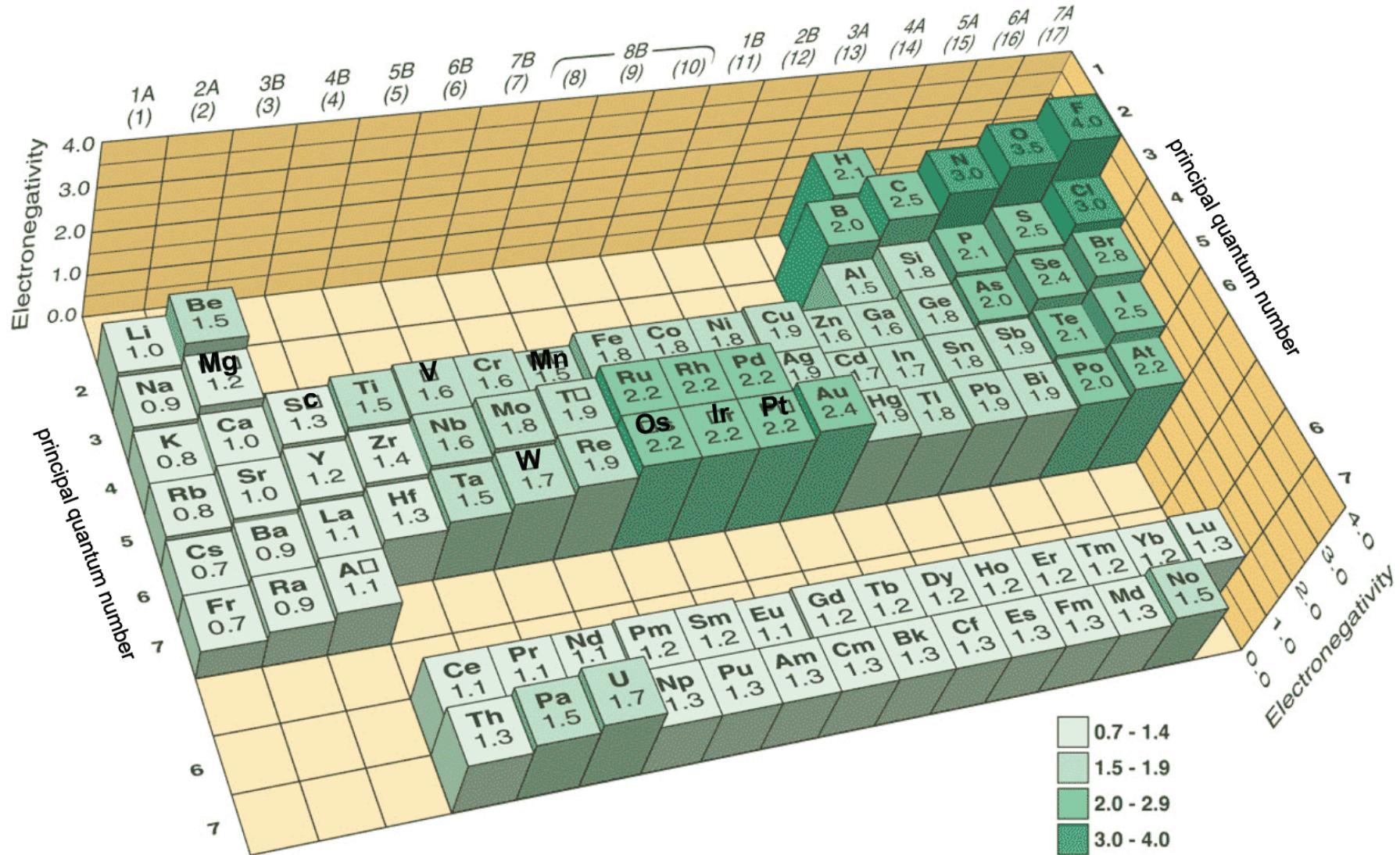
# Covalent bonding

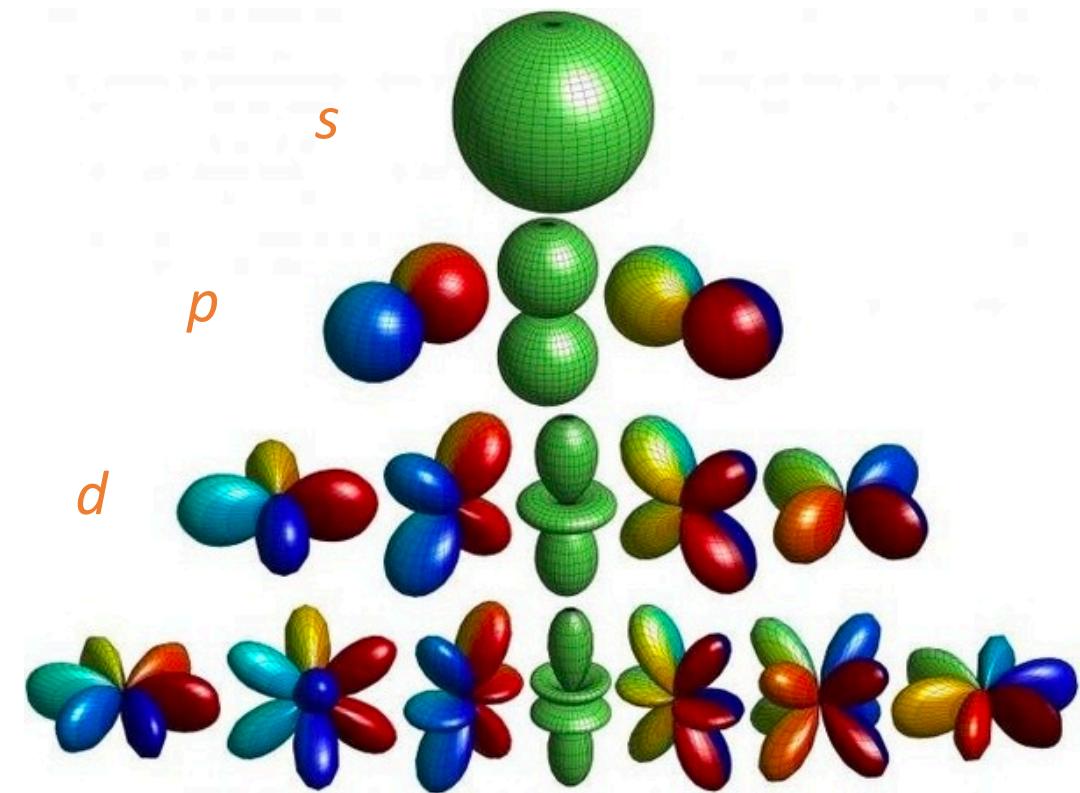
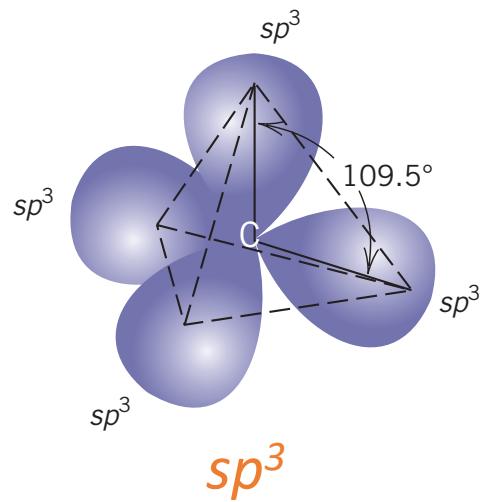
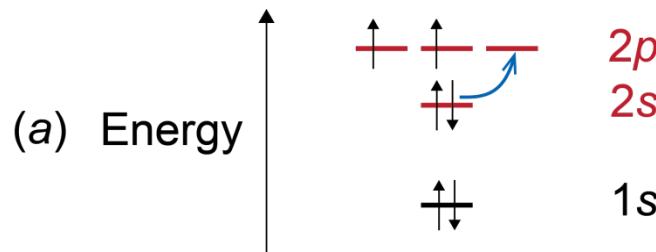
- Can be very directional – like in diamond or in ethane or in water



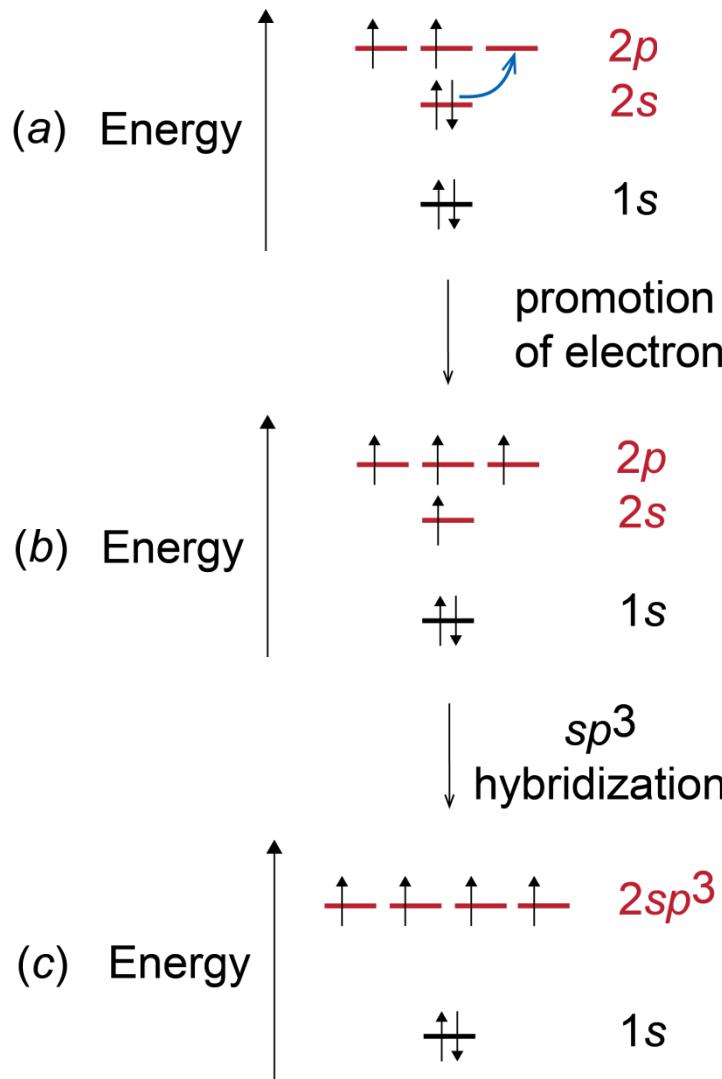
- Electrons can be equally shared H-H (non-polar bond)
- Electrons can be unequally shared H-Cl (polar bond),  
EN:  $X_{\text{H}}=2.1$ ,  $X_{\text{Cl}}=3.0$
- Bonding can be strong (diamond) but commonly weak compared to ionic bonds

# Trends in the periodic table: electronegativity



Common bond hybridization:  $sp^3$ 

# Common bond hybridization: $sp^3$



- Carbon can form  $sp^3$  hybrid orbitals

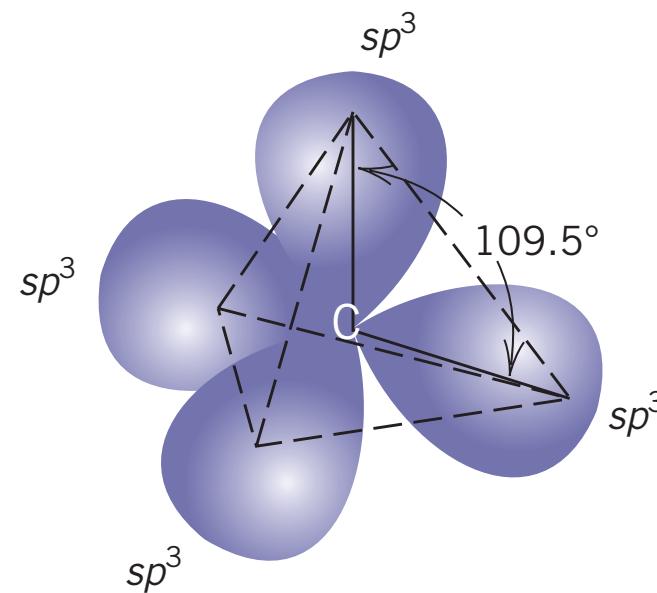


Fig. 2.13, Callister & Rethwisch 9e.

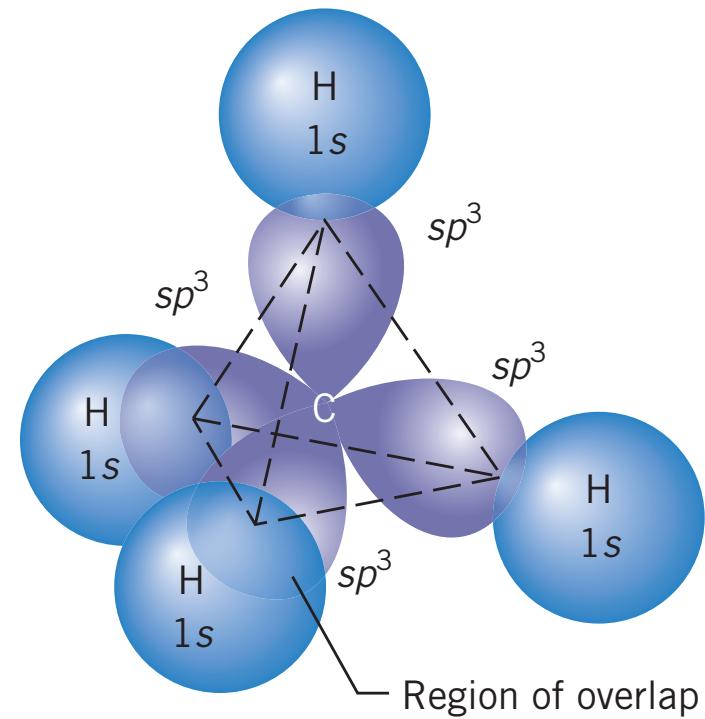
Common bond hybridization:  $sp^3$ 

- Example:  $CH_4$

C: has 4 valence  $e^-$ ,  
needs 4 more

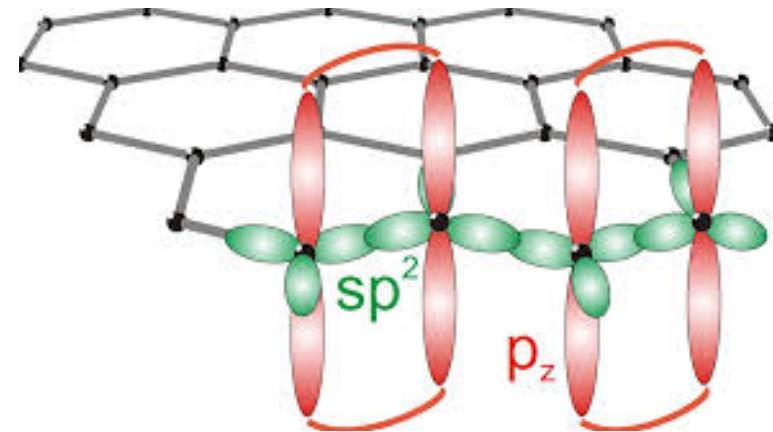
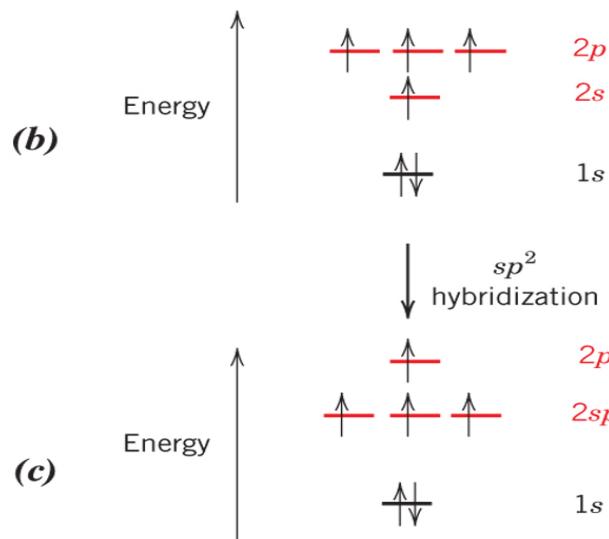
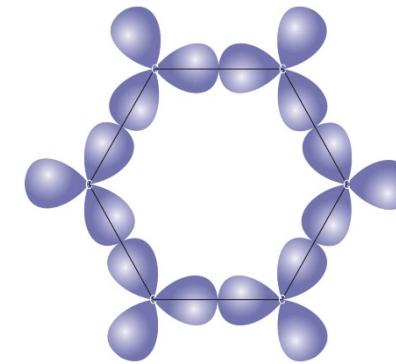
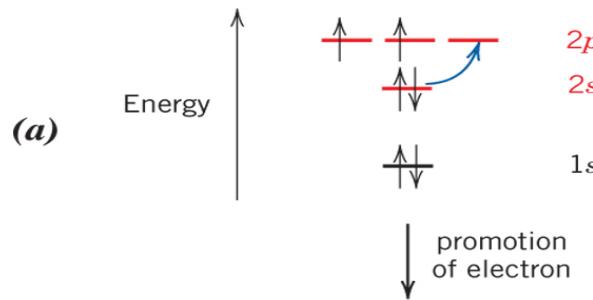
H: has 1 valence  $e^-$ ,  
needs 1 more

Electronegativities of C and H  
are comparable so electrons  
are shared in covalent bonds.



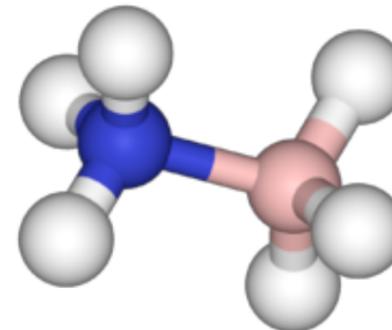
# Common bond hybridization: $sp^2$

- Example: Graphene/Carbon nanotubes



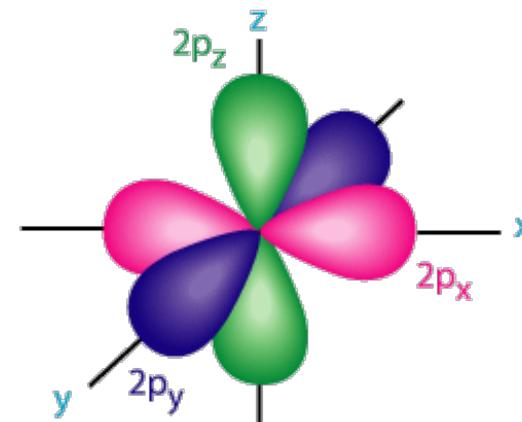
# Bond hybridization

- Number of hybrid orbitals = number of mixed orbitals  
E.g., One s orbital + Three p orbitals = Four  $sp^3$  orbitals
- Hybridization driven by energy minimization  
E.g., Ethane ( $sp^3$  comes from hydrogens interfering with one another)



E.g.,  $H_2S$  vs  $H_2O$  (S and O different sizes)

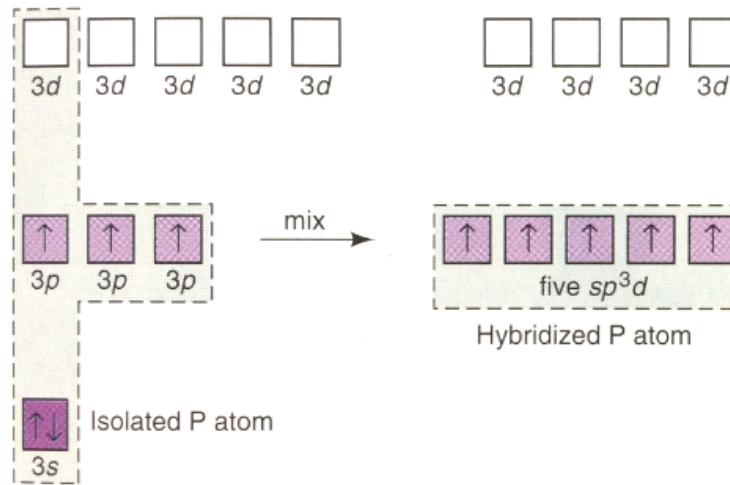
S: [Ne]3s<sup>2</sup>3p<sup>4</sup>  
O: [He]2s<sup>2</sup>2p<sup>4</sup>



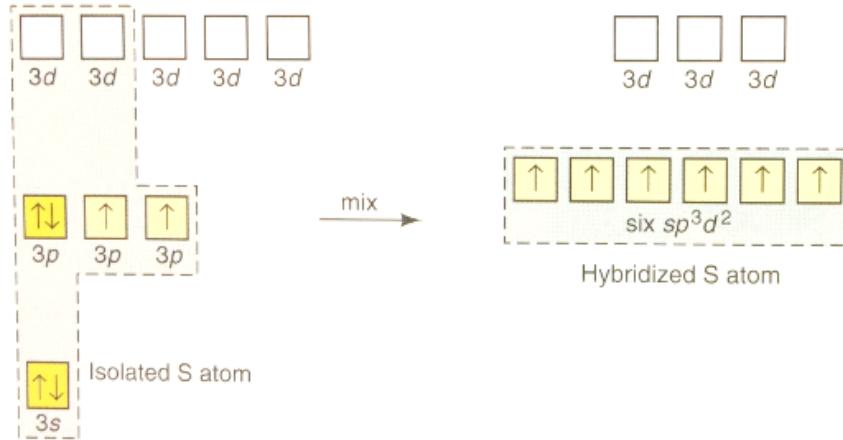
$H_2S$ : right angle  
 $H_2O$ : tetrahedral angle

# Bond hybridization with *d* orbitals

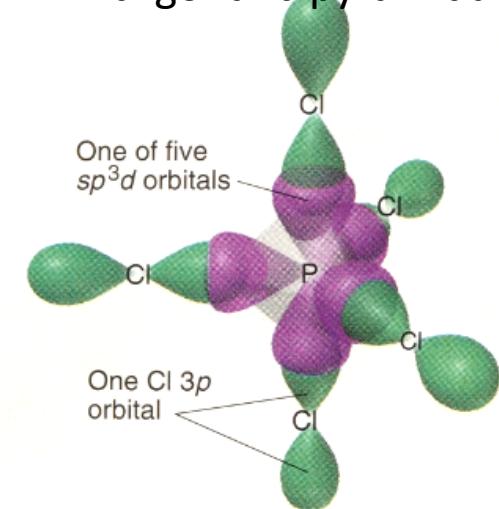
- Higher energy electron orbitals can also become involved: energy minimization leads to complicated hybridization
- $sp^3d$



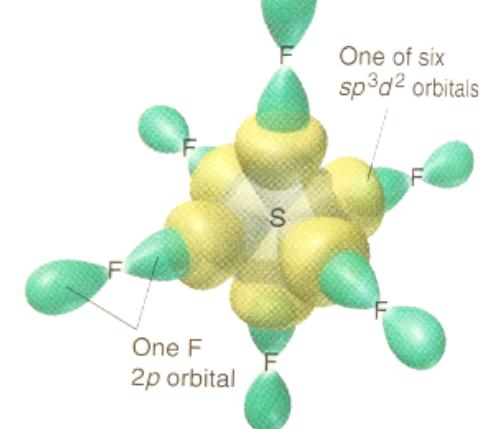
- $sp^3d^2$



trigonal bipyramidal

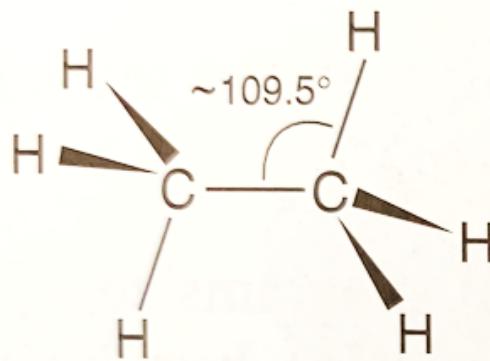


octahedral

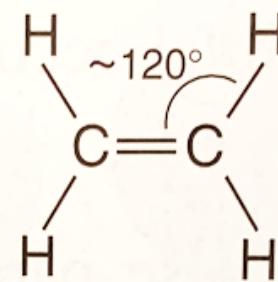


# Types of covalent bonding

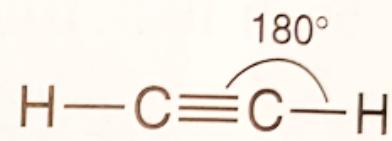
Ethane,  $C_2H_6$



Ethylene,  $C_2H_4$



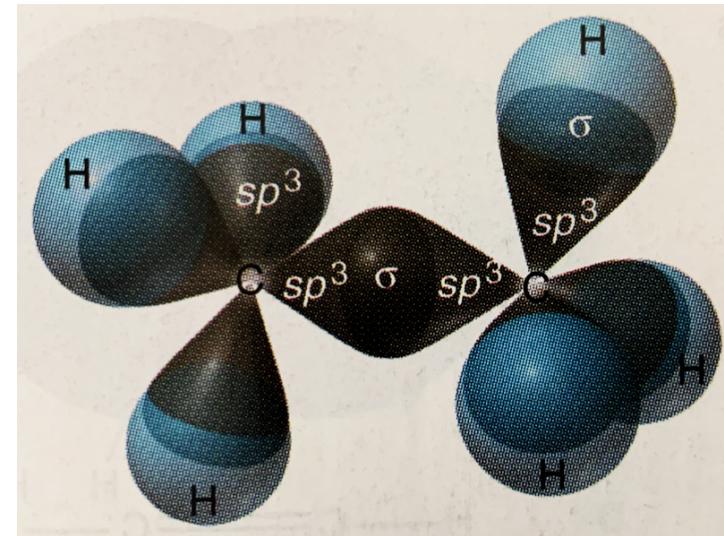
Acetylene,  $C_2H_2$



What is going on with the bonds between the carbon atoms?

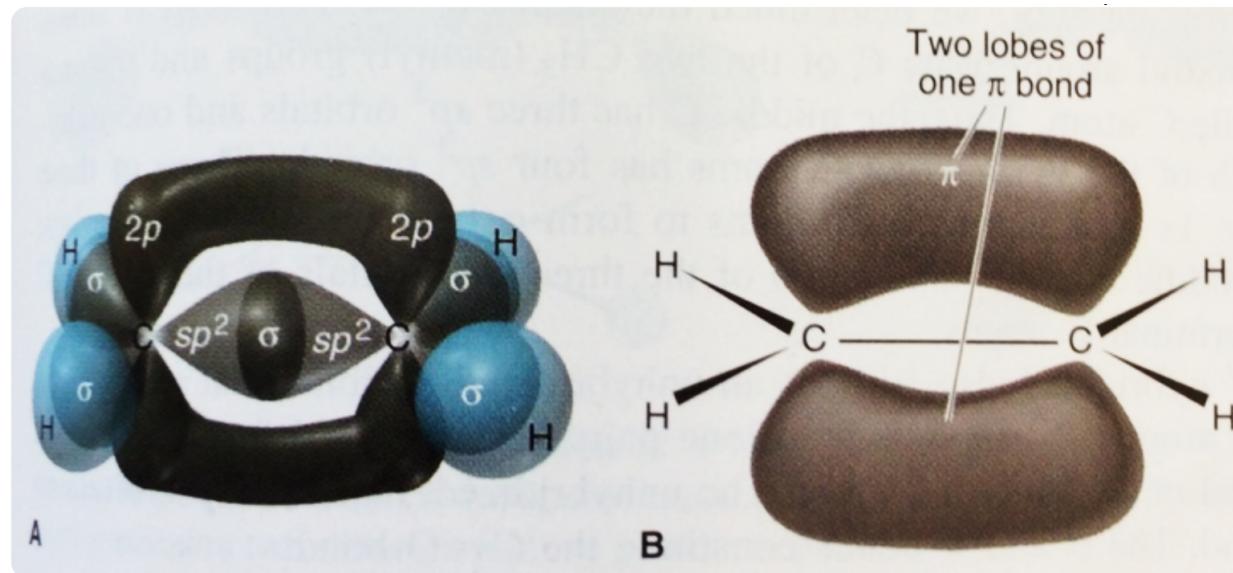
# Types of covalent bonding

- Since electrons are shared in a covalent bond, the strength of the bond depends on the degree of orbital overlap
- This is affected by both proximity and orbital shape
- In  $\sigma$  bonding the highest electron density is along the bond axis
  - All “single” covalent bonds fall into this category
  - Rotation has no effect on extent of overlap => free to rotate



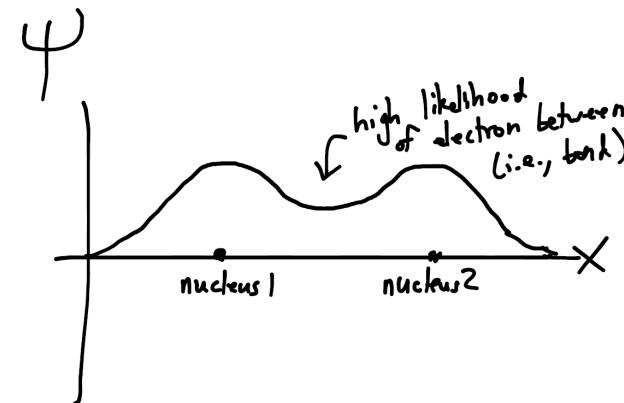
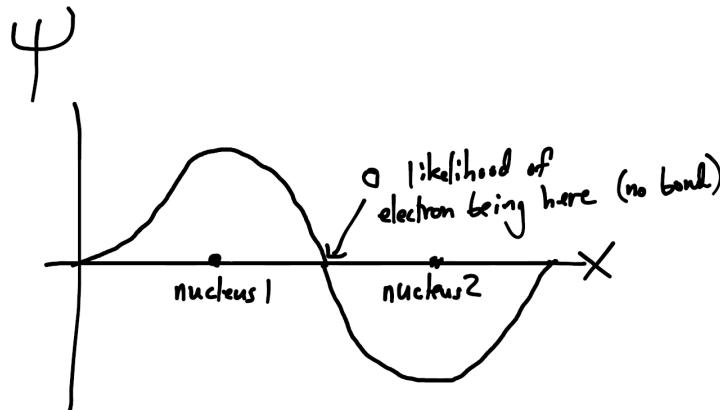
# Types of covalent bonding

- In  **$\pi$  bonding** adjacent orbitals overlap laterally
- A covalent “double” bond has one  $\sigma$  bond and one  $\pi$  bond
- A covalent “triple” bond has one  $\sigma$  and two  $\pi$  bonds
- Notice that rotation doesn’t affect  $\sigma$  bonds, but it would decrease the overlap for the  $\pi$  bonds => rotation is not allowed (this is important in polymers, and creates issues such as cis/trans configurations)



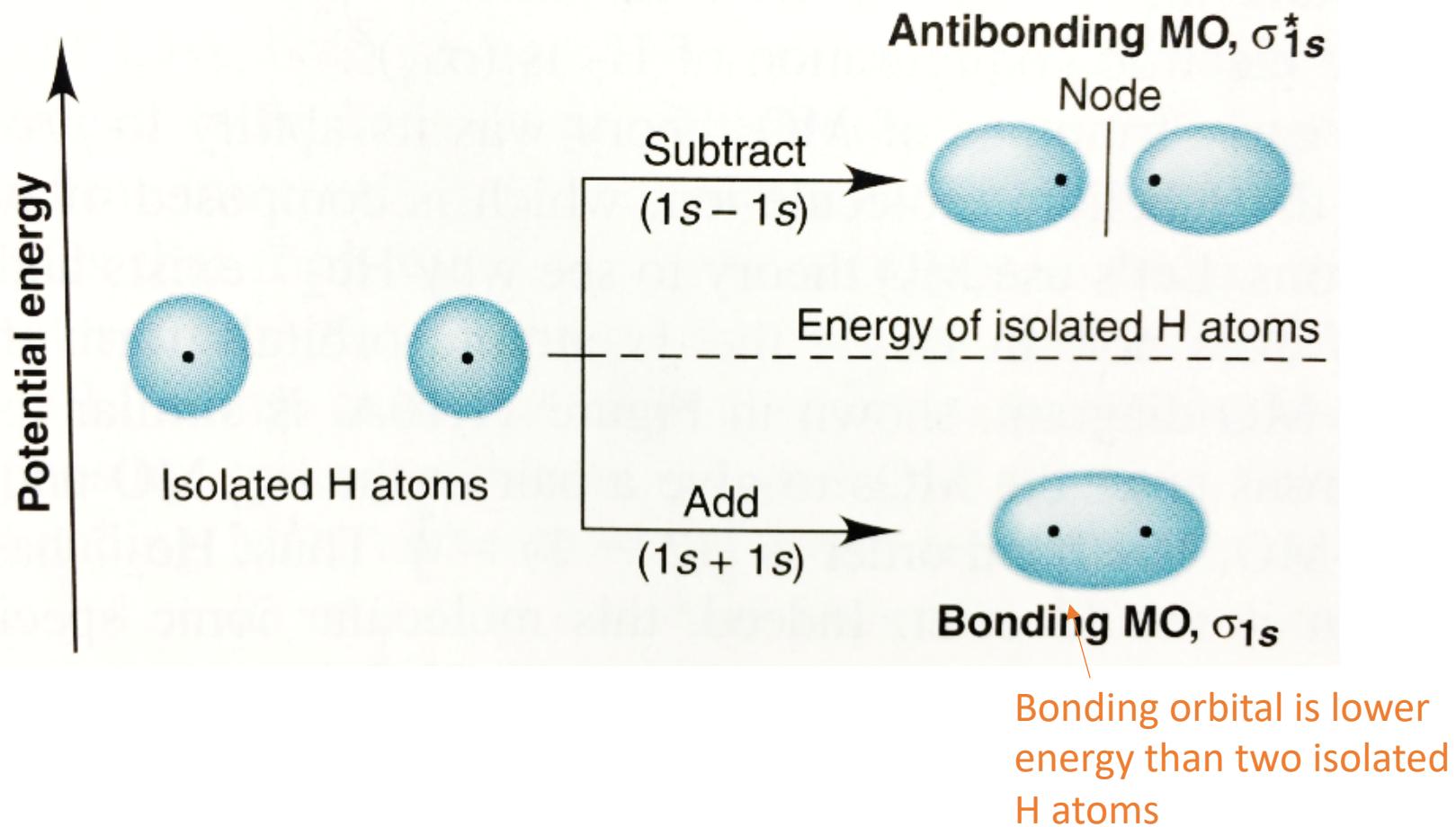
# Electron delocalization and molecular orbitals

- Treat molecule as one system with a group of nuclei and delocalized electron orbitals relevant to the whole system
- What happens when you bring two identical atoms together to bond?
  - Identical => same energy
  - Exclusion principle => problem
- Result: The two identical levels must split, with one higher energy than the original level (**antibonding orbital**) and the other lower than the original level (**bonding orbital**)
- Qualitative picture:



# Electron delocalization and molecular orbitals

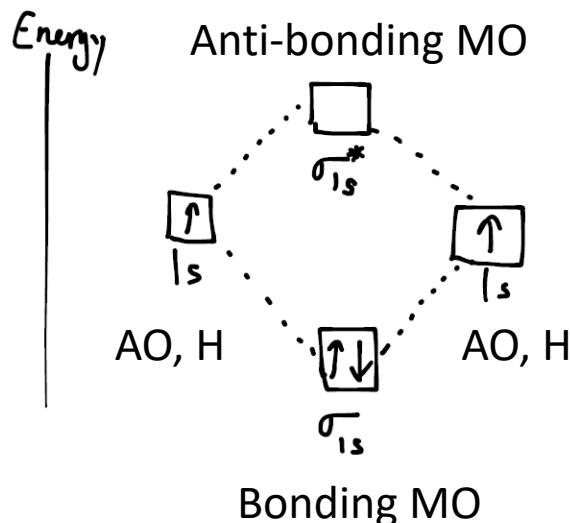
Why does  $\text{H}_2$  form but  $\text{He}_2$  not form?



**Bond Order** =  $\frac{1}{2}[(\# \text{ electrons in bonding MO}) - (\# \text{ electrons in antibonding MO})]$   
(Note: high value means strong bond)

# Electron delocalization and molecular orbitals

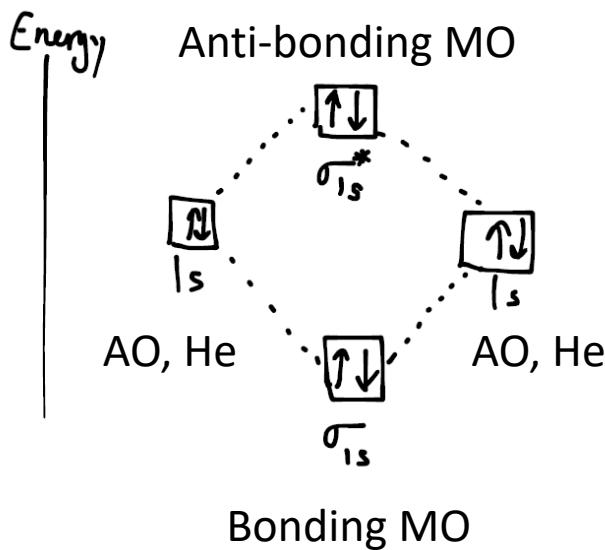
For H<sub>2</sub>:



For H<sub>2</sub>, Bond Order =  $\frac{1}{2}(2-0) = 1$

This is energetically favorable, so diatomic hydrogen readily forms

For He<sub>2</sub>:



For He<sub>2</sub>, Bond Order =  $\frac{1}{2}(2-2) = 0$

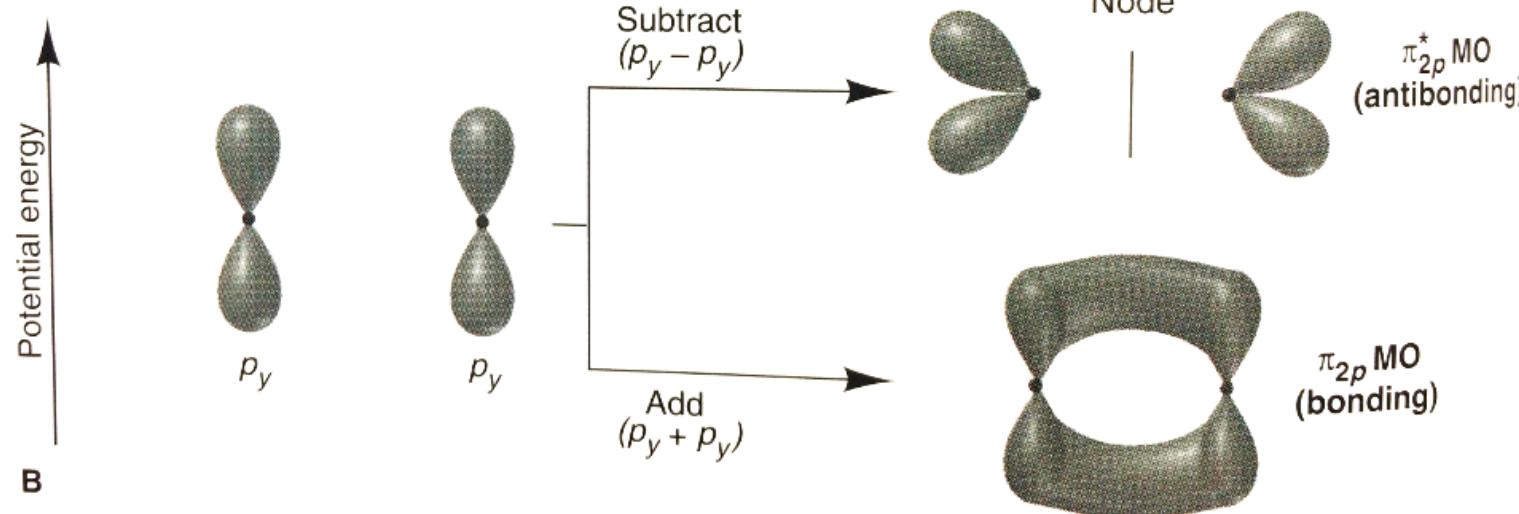
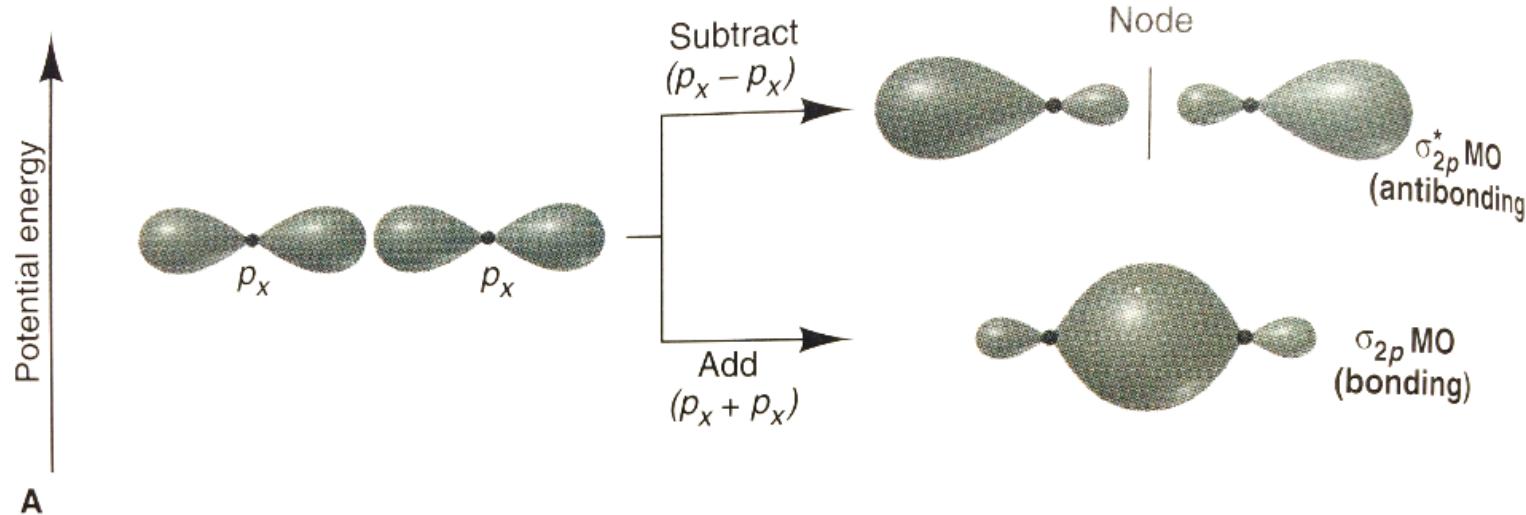
Hence diatomic helium doesn't naturally form. There is no energy benefit to form the bond.

(This approach was able to predict the existence of He<sub>2</sub><sup>+</sup>)

# Electron delocalization and molecular orbitals

$\pi$  bonding and  $\pi^*$  antibonding also occur

- Because  $\sigma$  involves more overlap,  $\sigma_{2p}$  is usually more stable than  $\pi_{2p}$  -- and  $\sigma_{2p}^*$  is usually more unstable than  $\pi_{2p}^*$  (i.e., we expect  $\sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$ )



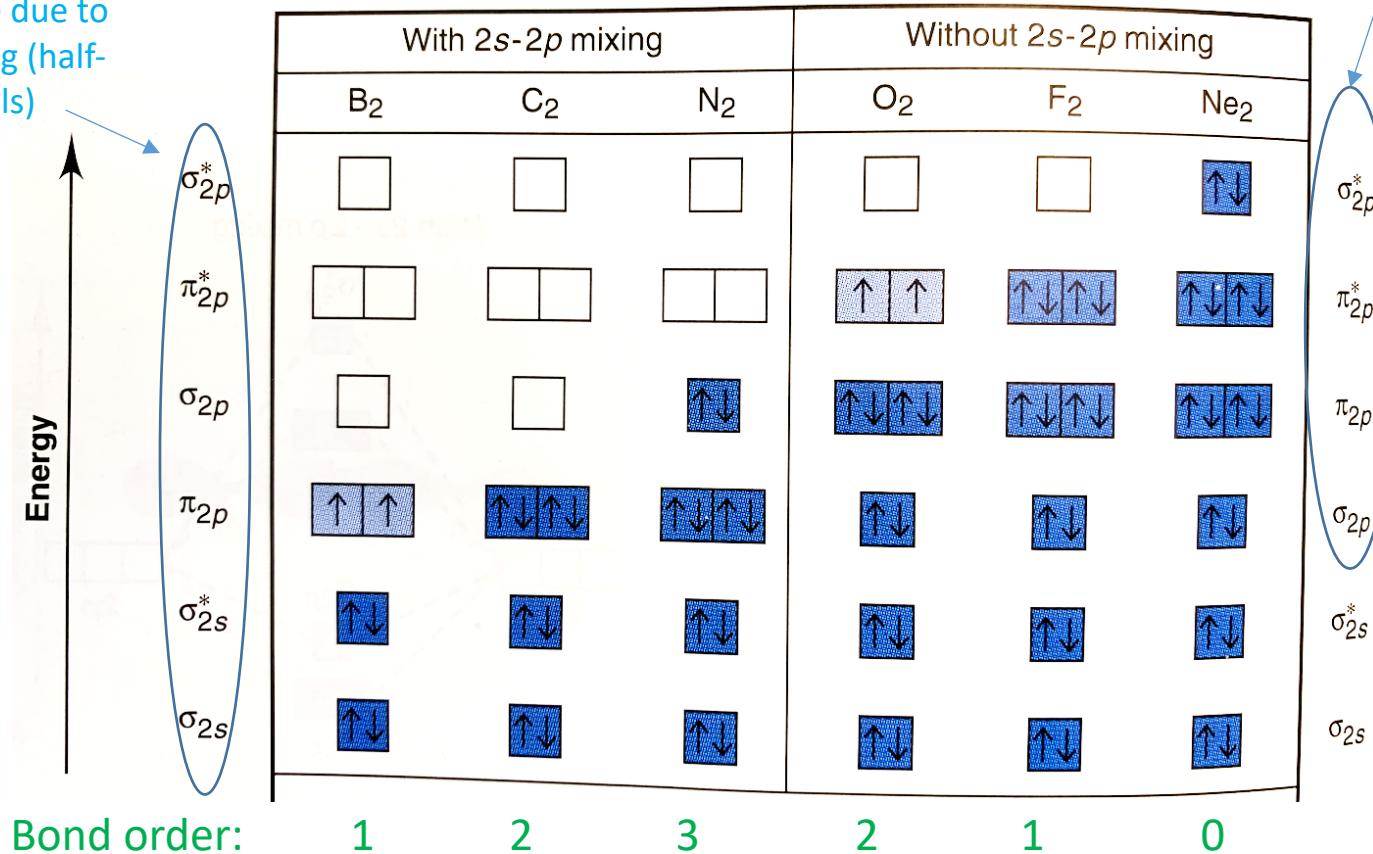
# Electron delocalization and molecular orbitals

- Mixing of energy levels can occur when 2s/2p are comparable (which can change the energy order of MOs)

Bond orders for homonuclear diatomic molecules:

O-Ne follow the expected order

B-N deviate due to 2s-2p mixing (half-filled orbitals)



(Note, this was useful for explaining paramagnetism in O<sub>2</sub>)