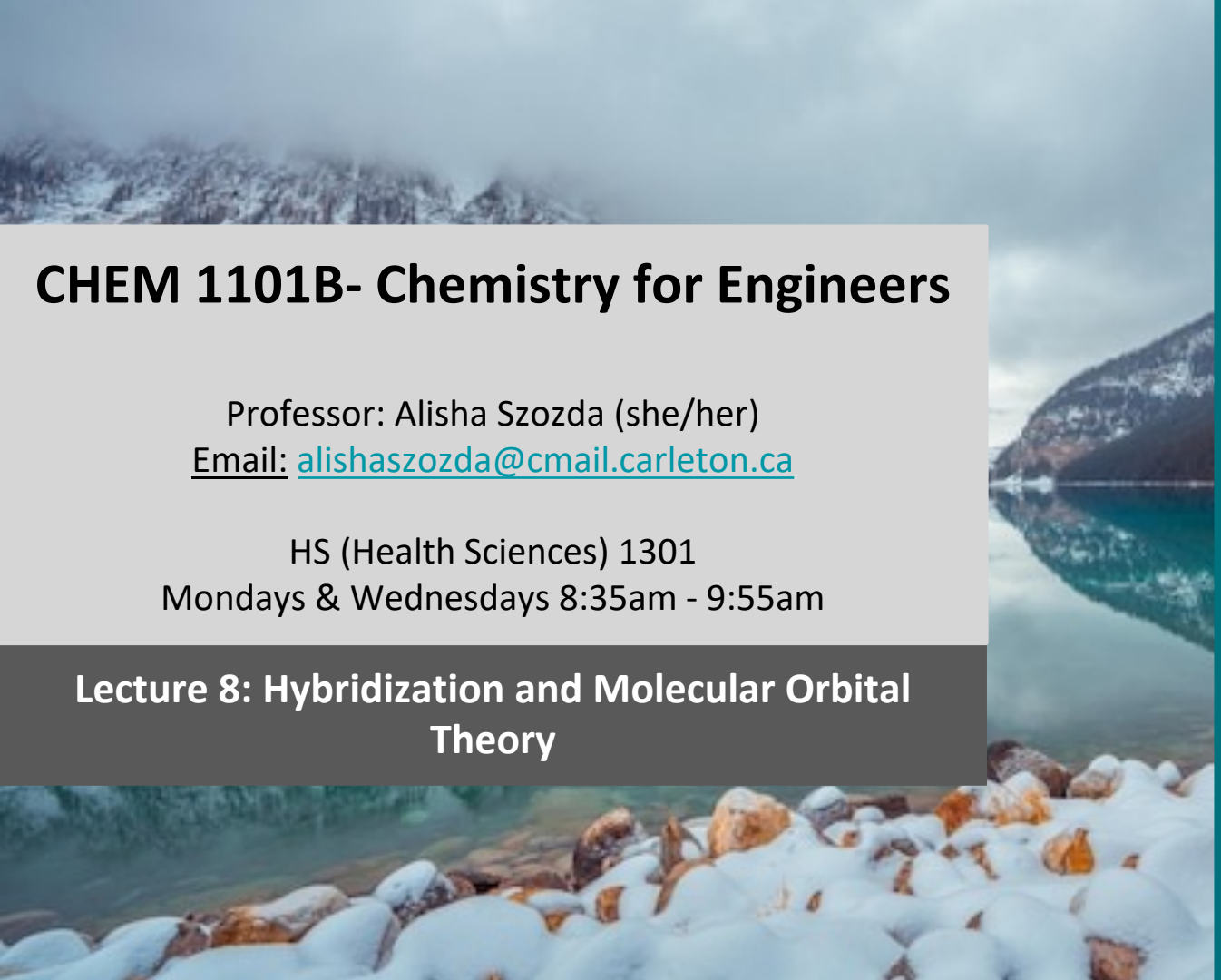


CHEM 1101B- Chemistry for Engineers

Professor: Alisha Szozda (she/her)
Email: alishaszozda@cmail.carleton.ca

HS (Health Sciences) 1301
Mondays & Wednesdays 8:35am - 9:55am

Lecture 8: Hybridization and Molecular Orbital Theory

Please feel free to introduce yourself to your neighbors– name, pronouns, a hobby, etc.

and/or

Answer the first question on Wooclap!

Learning outcome for Topic 8: The Molecule – MO Theory

LOs: (1) Use the VSEPR model to predict the shapes of molecules with steric #'s 2, 3, 4, 5, and 6.
(2) Predict bond and net dipoles

Atomic Theory

Shapes of atomic orbitals

VSEPR

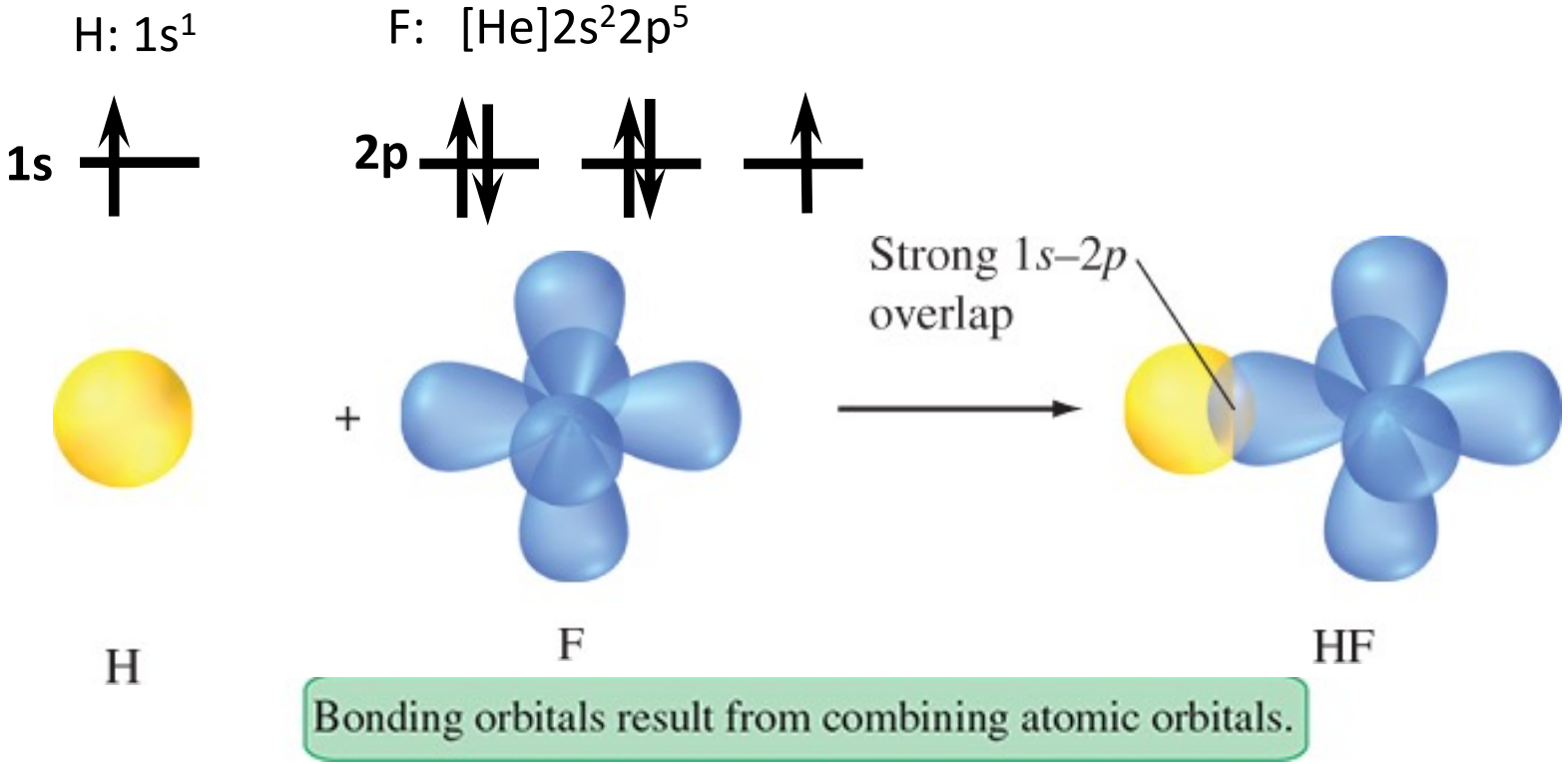
Shapes of molecules

But how are atomic orbitals combined to make bonds and give these shapes?

1. Orbital overlap model (localized overlap of atomic valence shell orbitals)
2. Hybrid orbital (Hybridization) theory (localized overlap of hybrid and atomic orbitals)
3. Molecular orbital theory (orbitals delocalized over entire molecule)

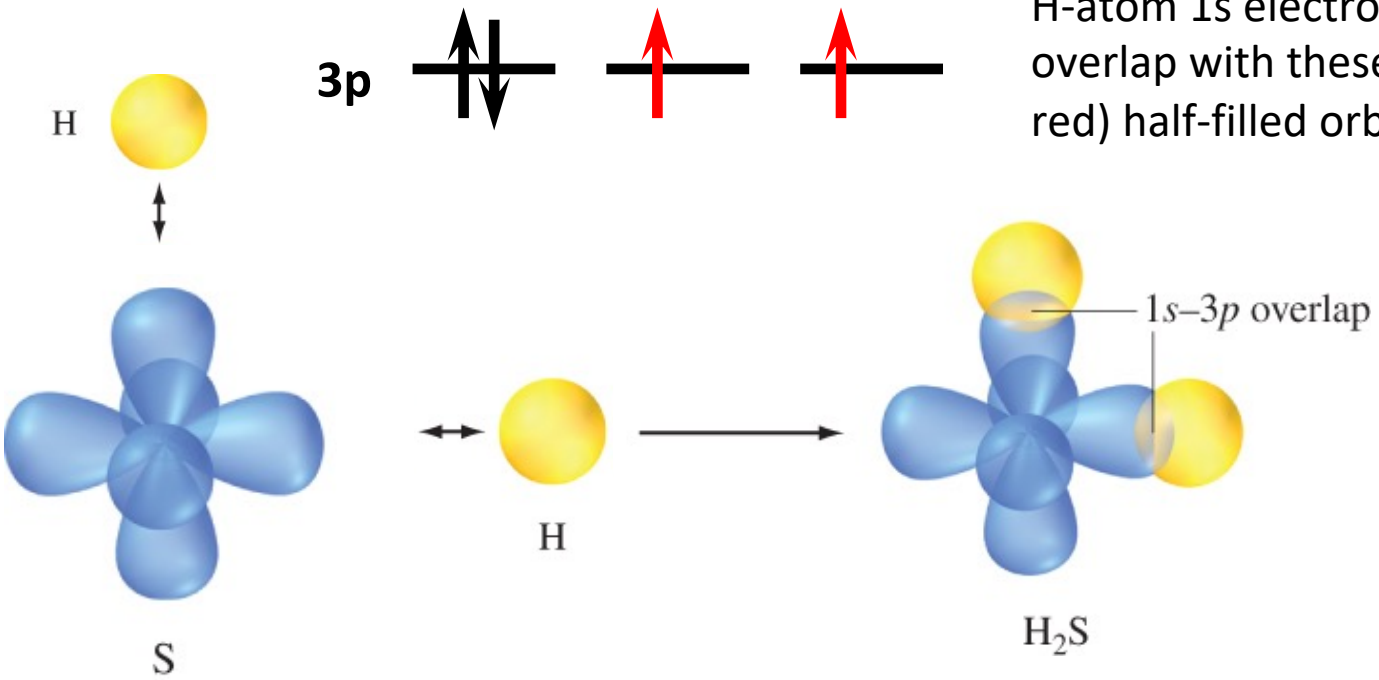
Orbital Overlap Model

Assumption: Only the valence orbitals are needed to describe bonding



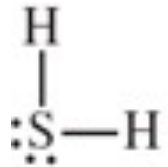
Bonding in Hydrogen Sulphide (H_2S)

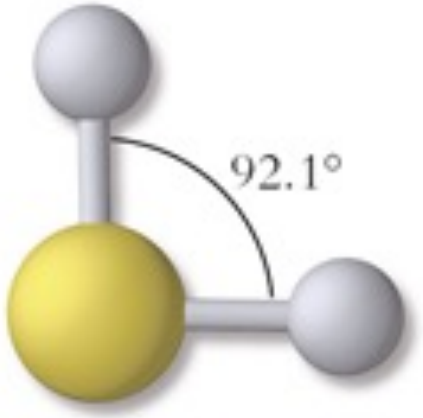
S: [Ne] $3s^2 3p^4$



H-atom 1s electrons will overlap with these (in red) half-filled orbitals

Bonding in Hydrogen Sulphide (H_2S)

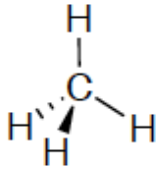




VSPER predicts **109.5**° (4 electron groups)

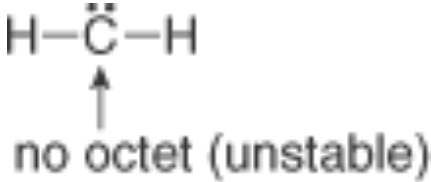
Orbital overlap model predicts **90**°, which is more consist with experimental data for H_2S (angle of **92.1**°)

Bonding in methane (CH_4): carbon

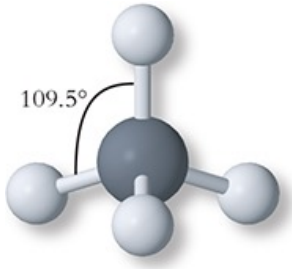


- Maximum of 2 electrons per orbital
- Based on orbital overlap model, carbon in methane should only be able to form 2 bonds:

C ($1s^2$) +
4 valence electrons

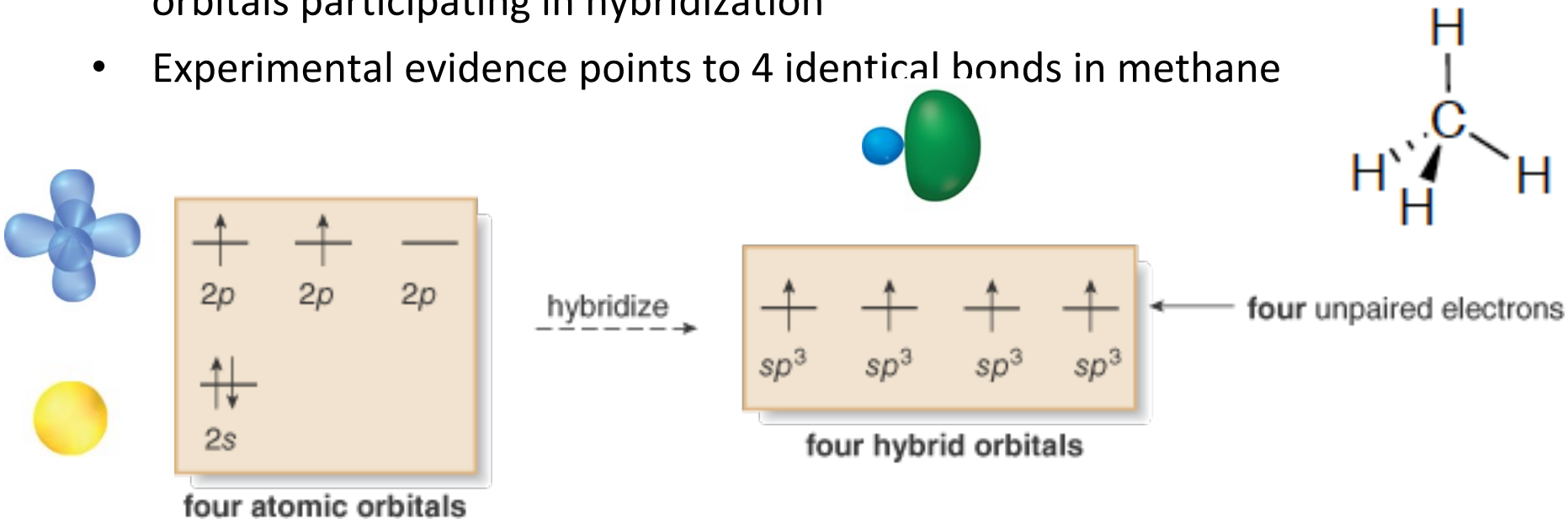


- VSPER theory tells us there are 4 C-H bonds separated at 109.5° and experiments verify these bond angles
  - Must modify the theory of bonding!

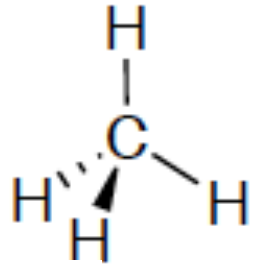


Hybridization/Hybrid Orbital Theory

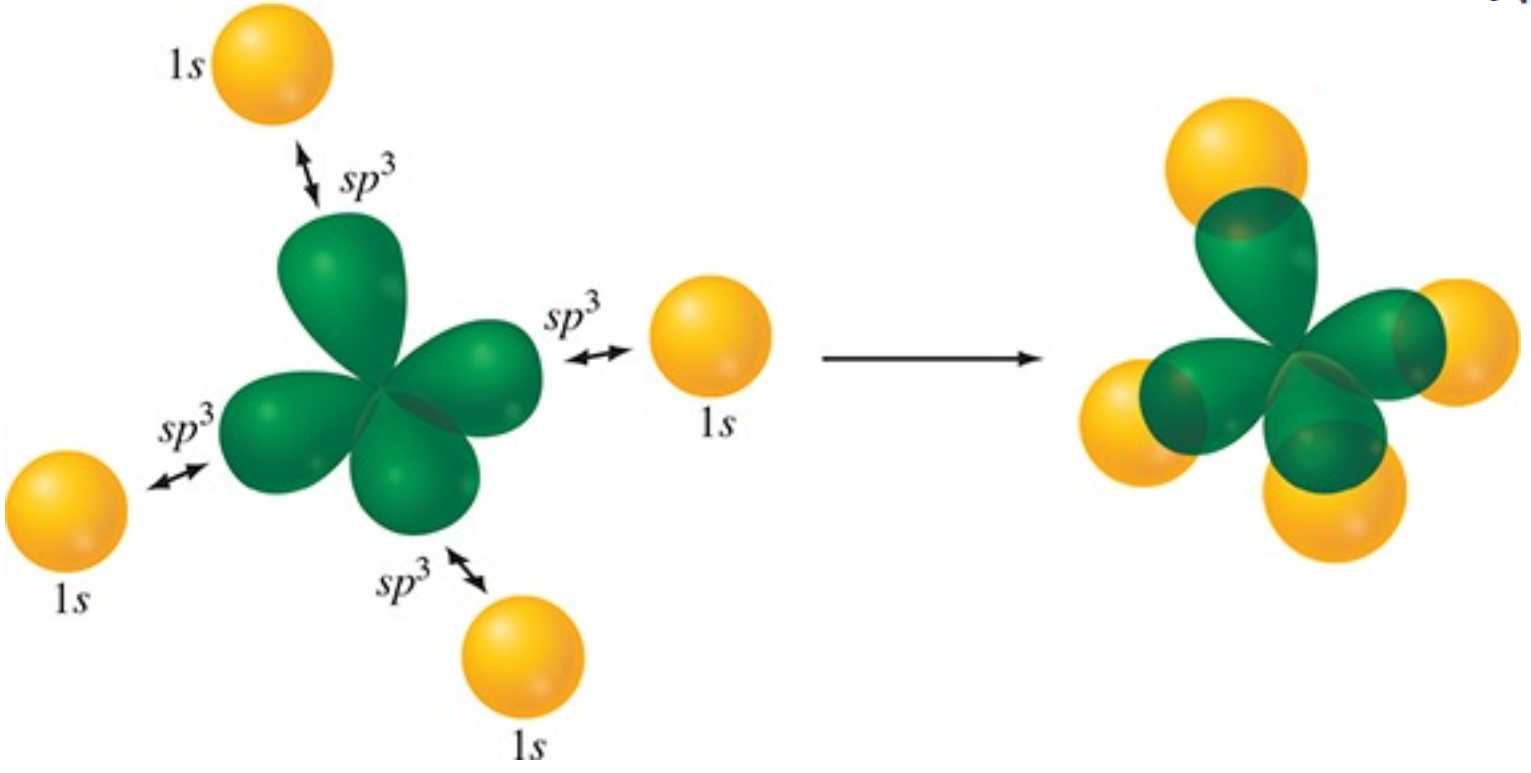
- Hybrid atomic orbitals: One “s” and 3 “p” orbitals combine in varying proportions to form hybrid orbitals (sp, sp^2, and sp^3 orbitals).
- # of hybrid orbitals generated by hybridization = # of valence atomic orbitals participating in hybridization
- Experimental evidence points to 4 identical bonds in methane



Bonding in methane (CH_4)

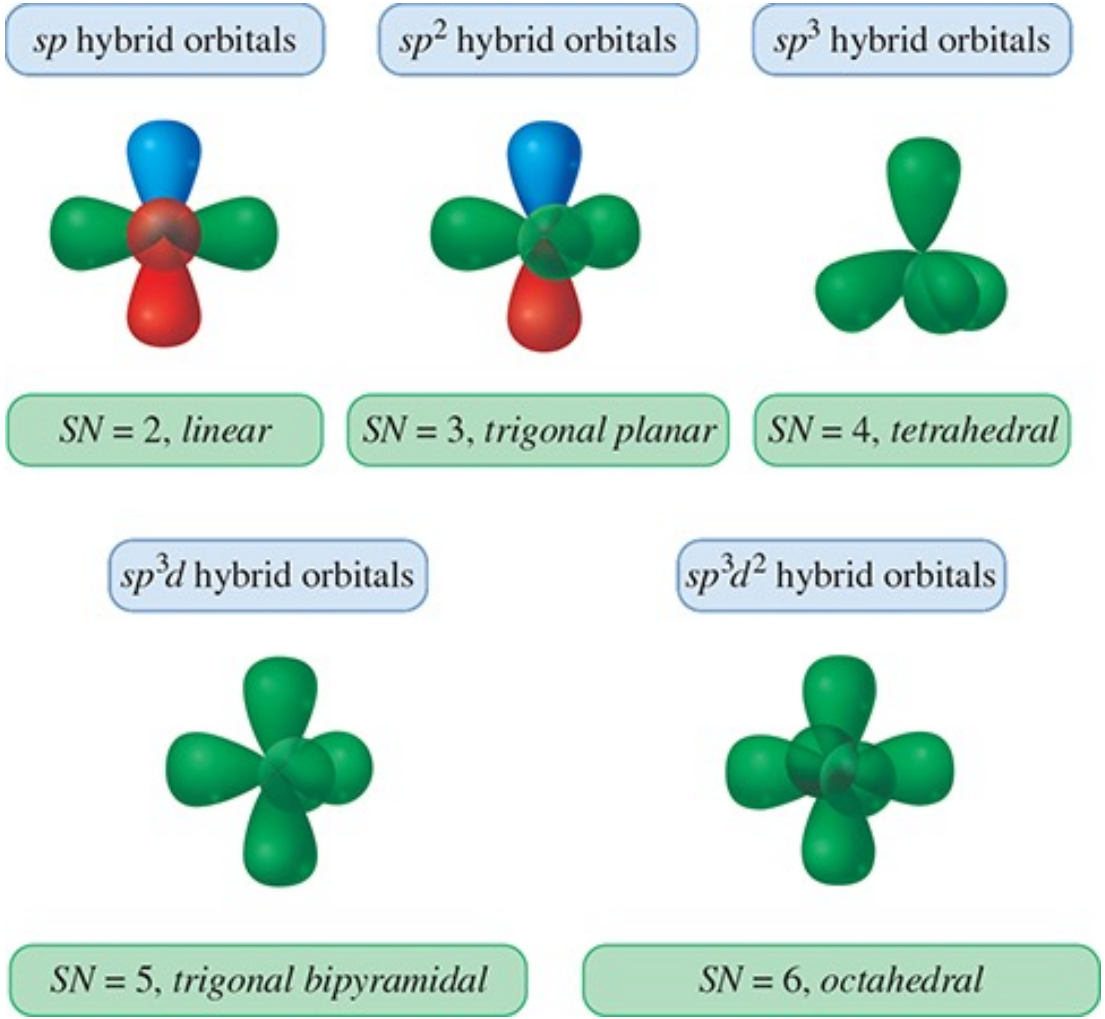


- Methane forms from orbital overlap between the hydrogen 1s orbitals and the sp^3 hybrid orbitals of the carbon atom

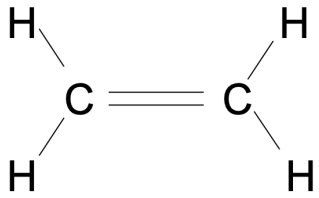


Key features of hybridization

- Steric number of an inner atom determines the number and type of hybrid orbitals
- Hybrid orbitals form localized bonds by overlap with atomic orbitals or with other hybrid orbitals
- No need to hybridize outer atom orbitals because they do not have limiting geometries

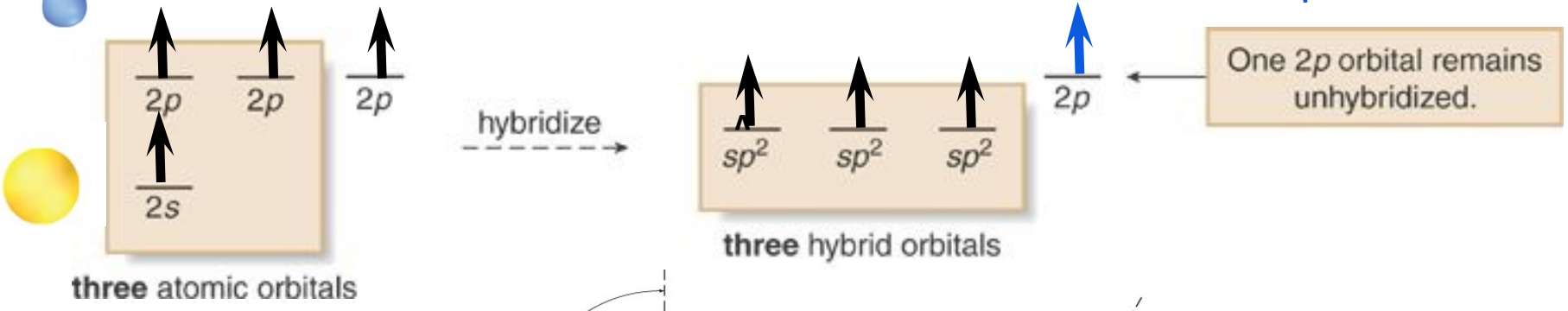


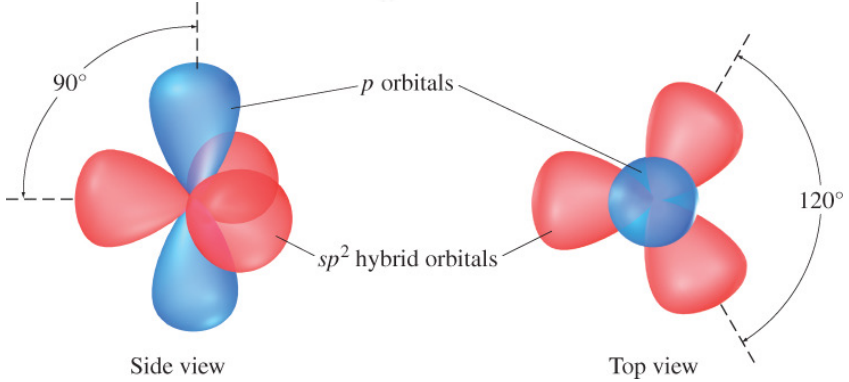
sp^2 hybrid orbitals: Bonding in Ethylene (C_2H_4)



- Experimental evidence points to 3 identical bonds in formaldehyde

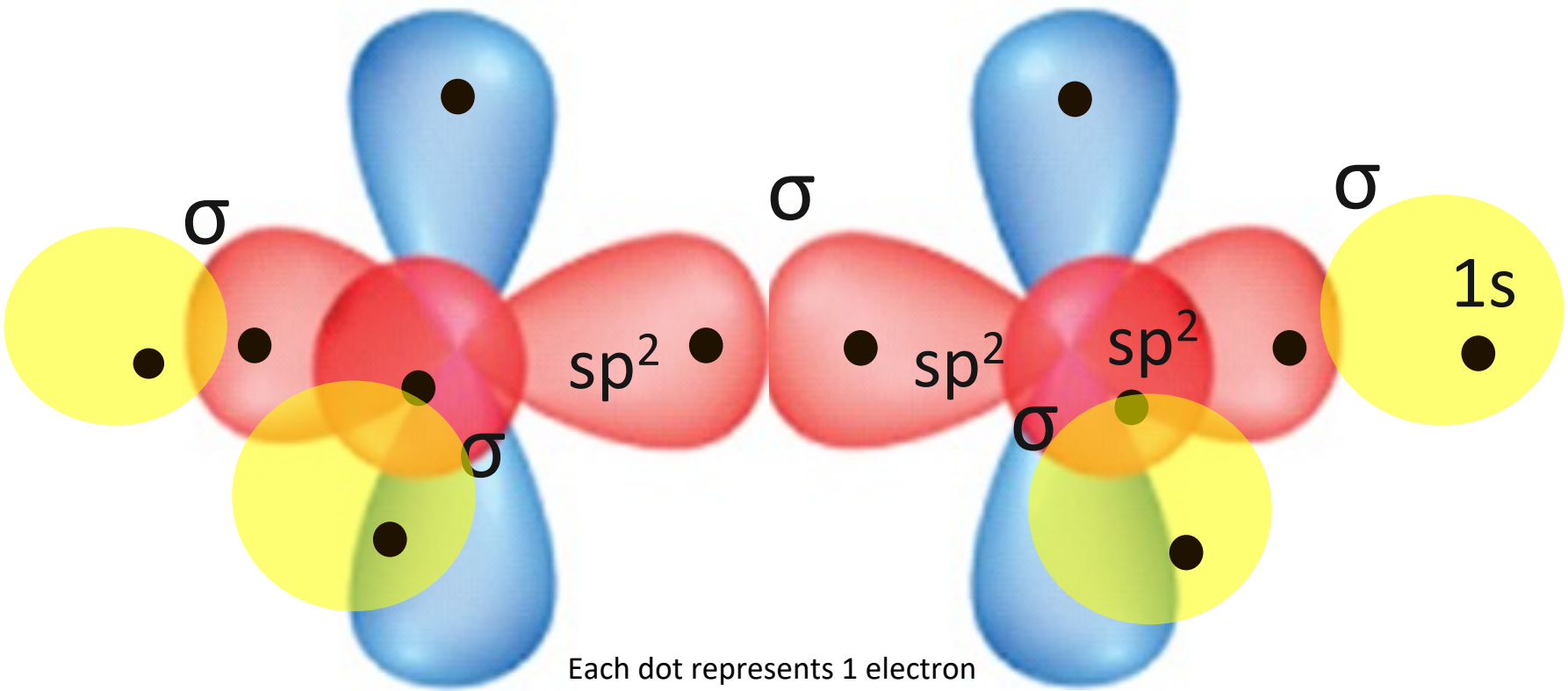
What happens to the remaining electron in the p atomic orbital?





Bonding in Ethylene (C_2H_4)

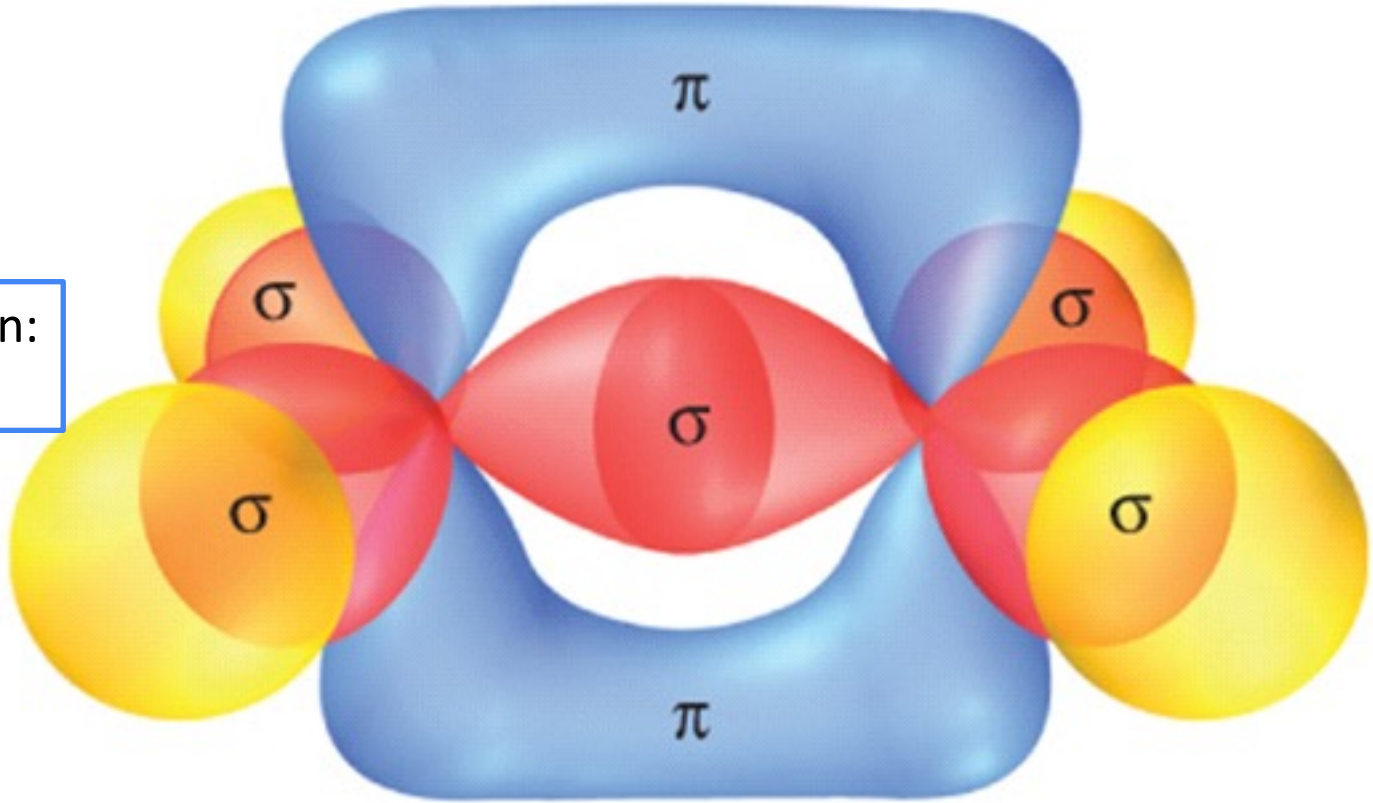
A **sigma bond (σ)** has a high electron density distributed symmetrically **along the bond axis – formed by s or sp^x hybrid orbitals**



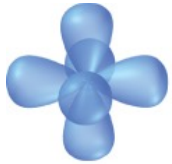
Each dot represents 1 electron

A **pi bond (π)** has a high electron density concentrated **above and below the bond axis – formed by p orbitals**

Double bonds contain:
1 **σ and 1 π** bond

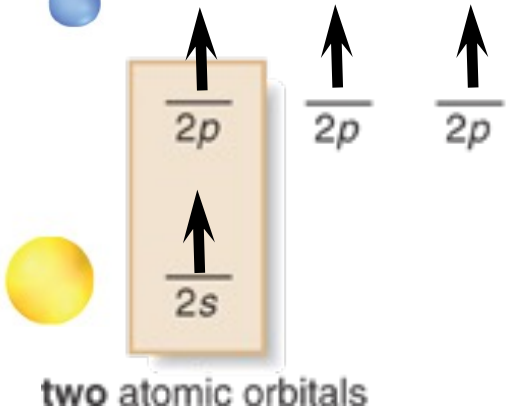


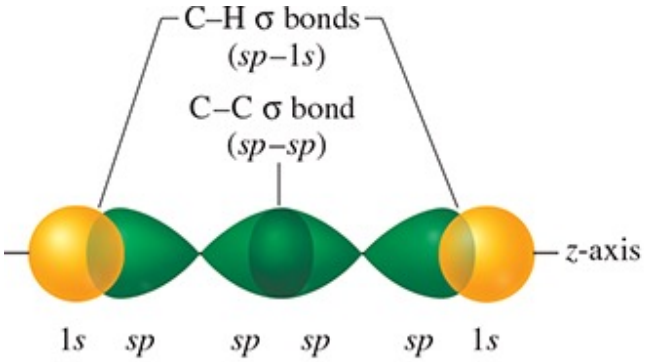
sp hybrid orbitals: Bonding in acetylene (C_2H_2)

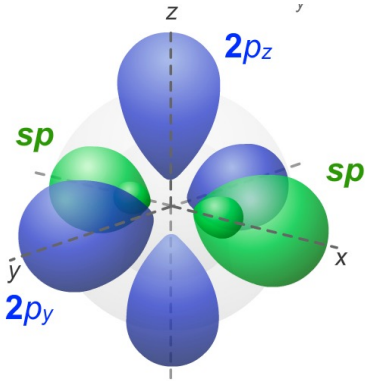


$$H-C\equiv C-H$$

Electrons in p atomic orbitals form π bonds

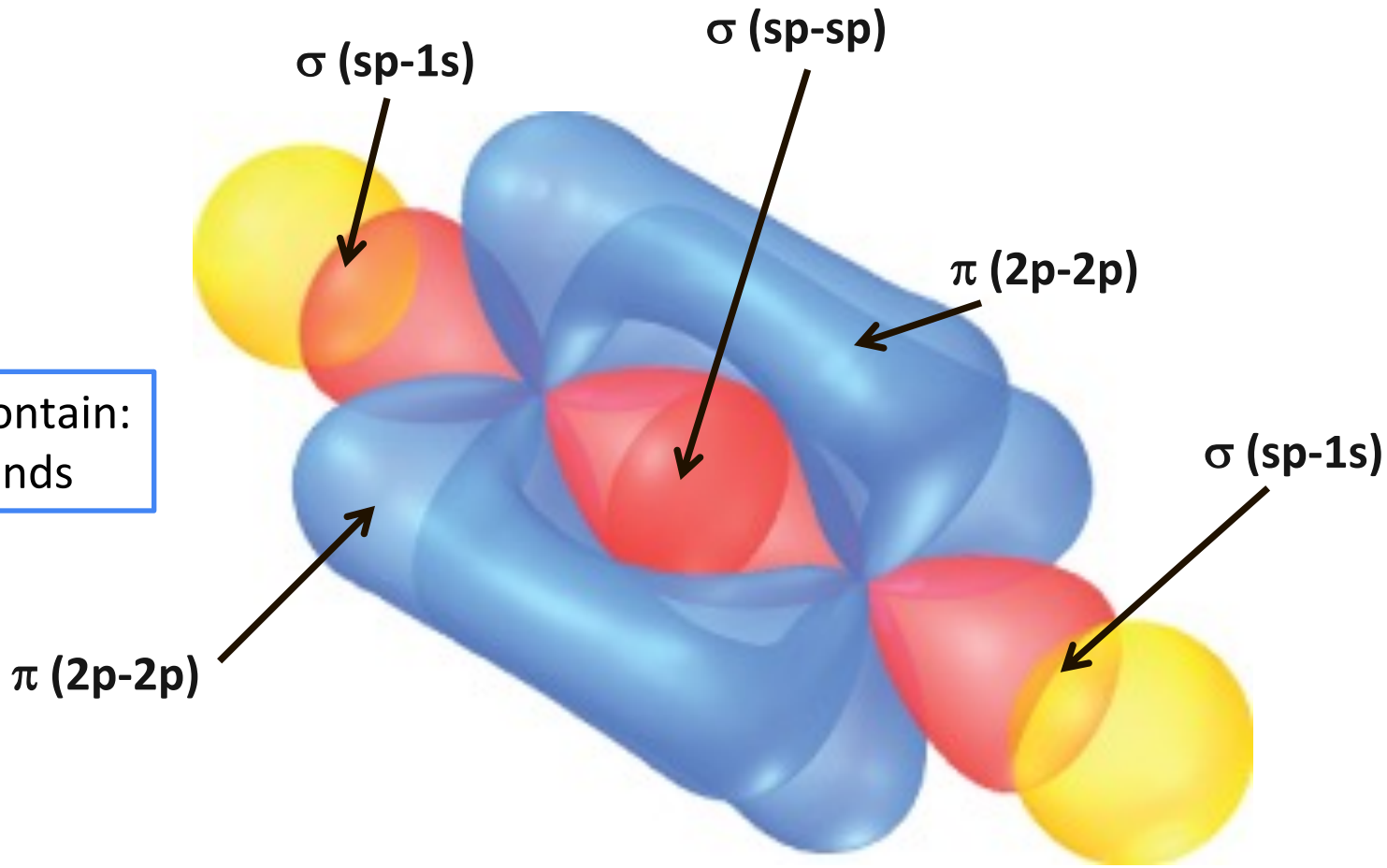




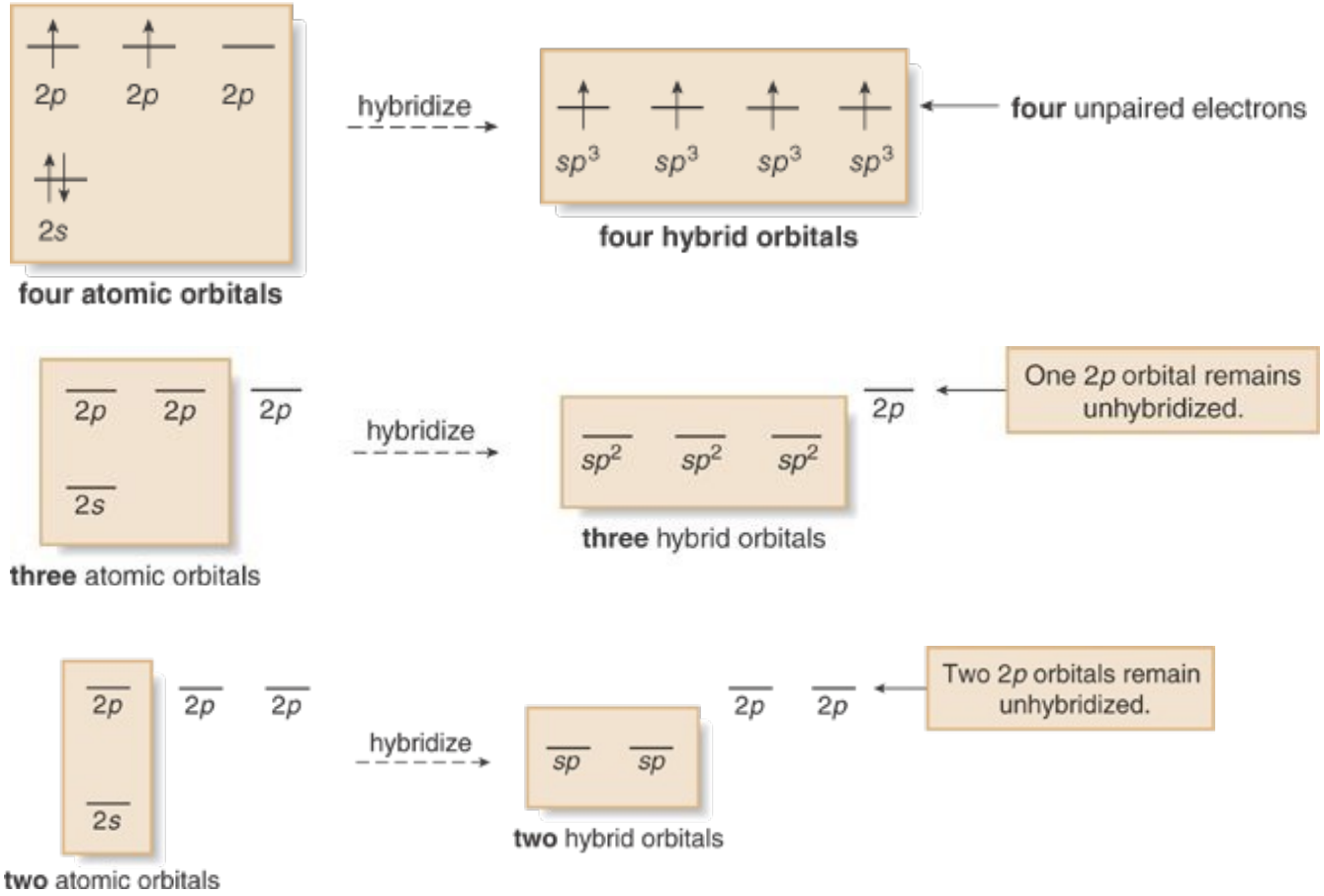


Bonding in acetylene (C_2H_2)

Triple bonds contain:
1 **σ and 2 π** bonds

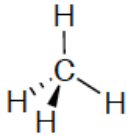
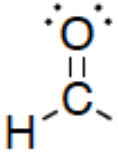


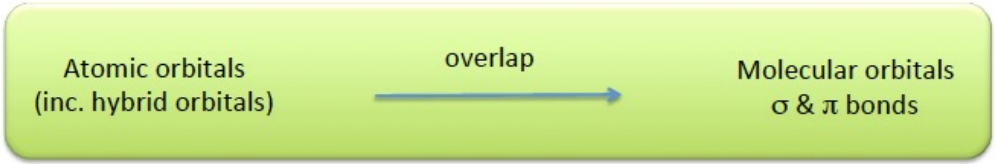
Overview: Hybridization process



Hybridization summary

Thing/group = atom or lone pair

Hybridization		Method of hybrid atomic orbital formation	The atom is bonded to ____ things*	Geometry of the atom
	**sp^3**	s + p + p + p	**4**	Tetrahedral 109.5°
	**sp^2**	s + p + p (one p orbital is left over, unhybridized	**3**	Trigonal planar 120°
H–C≡C–H	**sp**	s + p (2 p orbitals are left over, unhybridized	**2**	Linear 180°



Molecular Orbital (MO) Theory

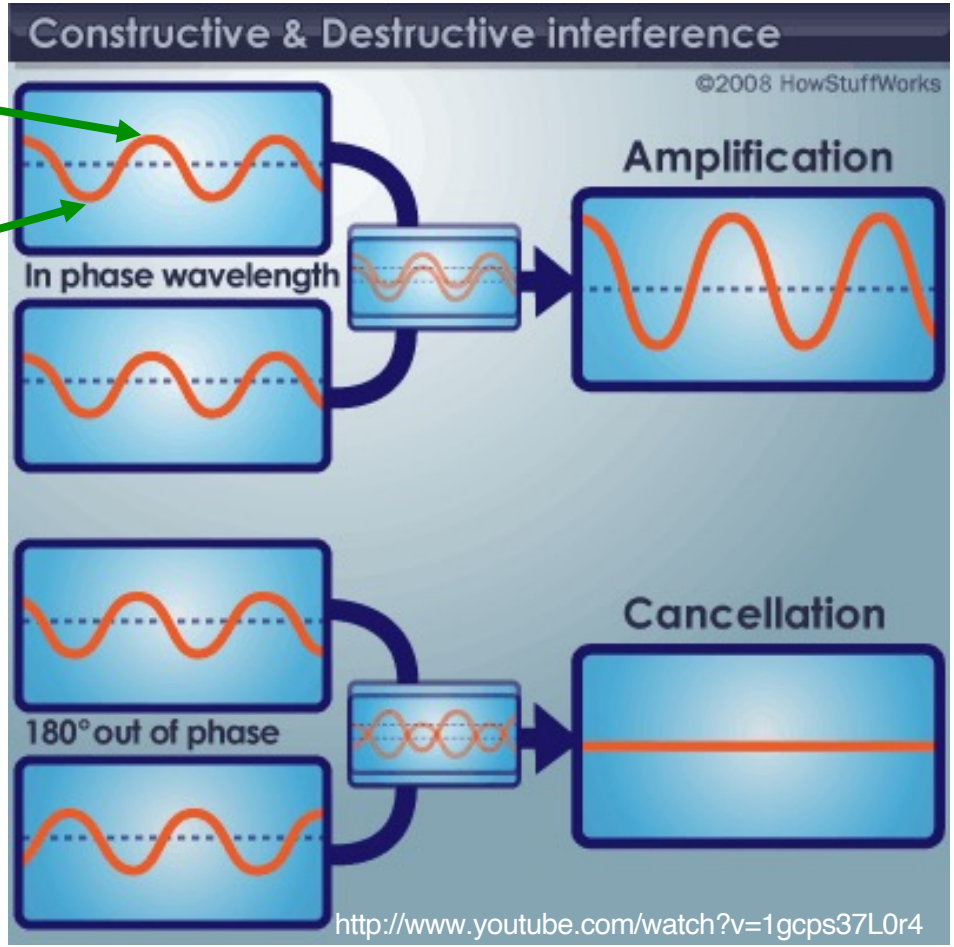
Hybrid orbitals and localized bonds provide a model of bonding that is great for rationalizing and predicting chemical structure, but localized bonds cannot predict or interpret other aspects of bonding and reactivity.

- **Molecular orbital theory involves delocalized electrons**
- **Orbital:** region in space where the probability of finding an electron in high
- Orbitals are described mathematically as wave functions
- Bonds (called bonding molecular orbitals) are formed by the overlap of atomic (or hybrid atomic) orbitals
- **Atomic** orbitals and/or hybrid atomic orbitals overlap to form **molecular** orbitals
    - Single bonds: σ, σ^*
    - To form double and triple bonds: π and π^*

Analogy: orbitals are like waves of a lake

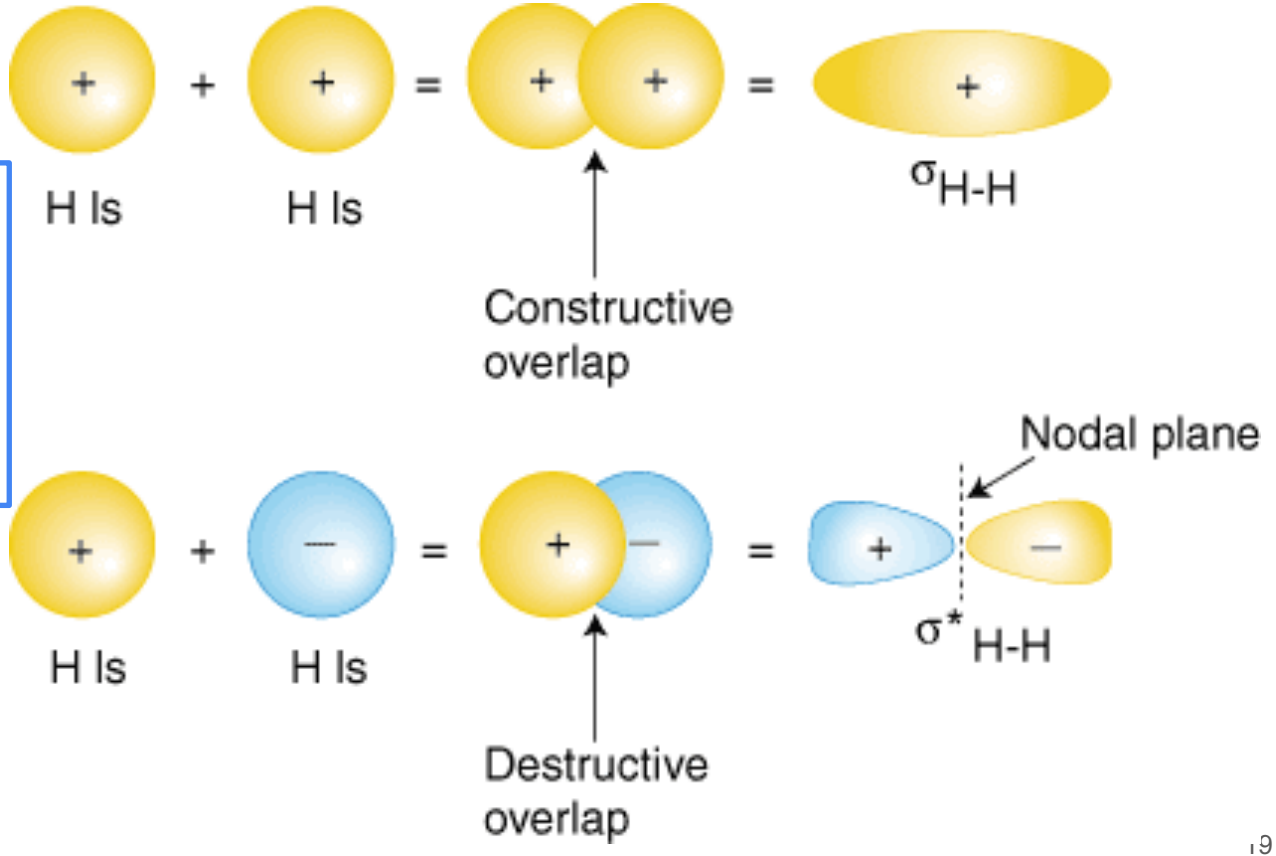
Positive phase

Negative phase

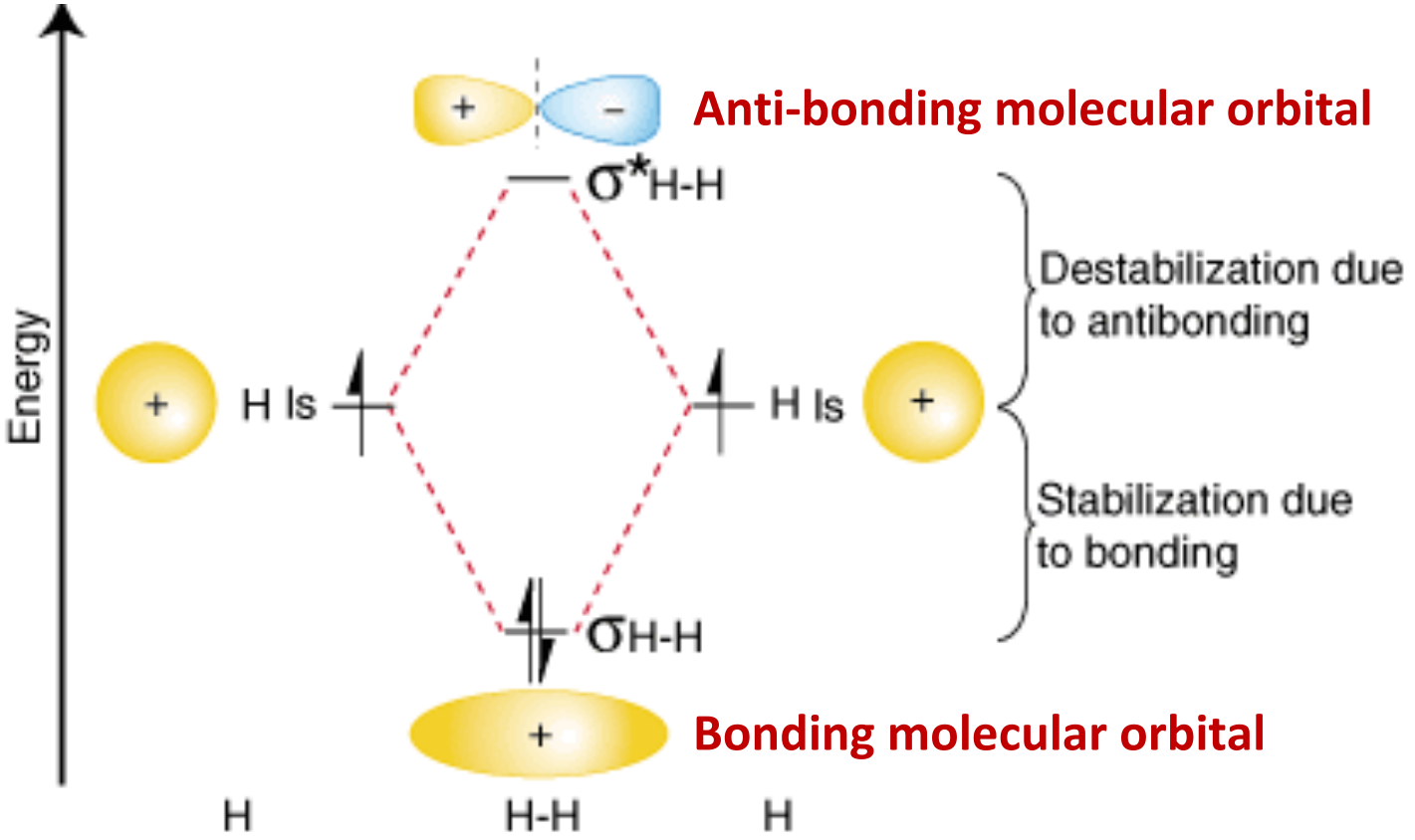


Formation of H_2

Orbitals have positive and negative phases, analogous to the top and bottom portions of a wave on a lake



Formation of H_2



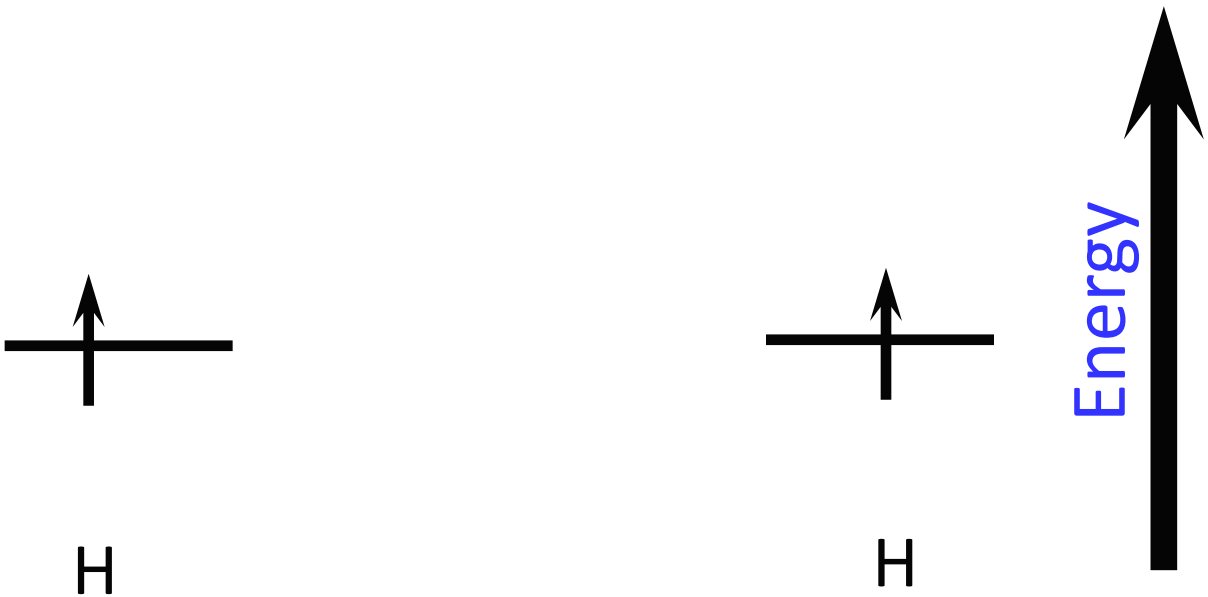
Making a MO diagram: H_2

Step 1: Start with the atomic orbitals

Step 2: Build the MO's

Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)



Step 4: Making a MO diagram: H_2

Bond Order: tells us about the stability of the molecule

If BO > 0 means molecule is stable and will exist!
If BO $\leq$ 0 means the molecule is unstable and does NOT exist!

$$BO = \frac{\text{no. of bonding electrons} - \text{no. of antibonding electrons}}{2}$$

What about H_2^{-2} ?

Draw the MO diagram for H_2^{-2}. Based on the BO, does the molecule exist?

Step 1: Start with the atomic orbitals

Step 2: Build the MO's

Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)

What about larger atoms that have p orbitals?

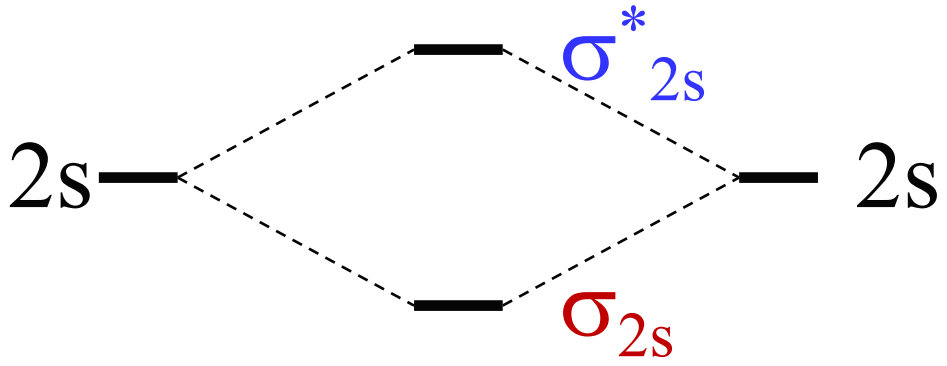
What type of MO's do p orbitals form?

Step 1: Start with the atomic orbitals

Step 2: Build the MO's

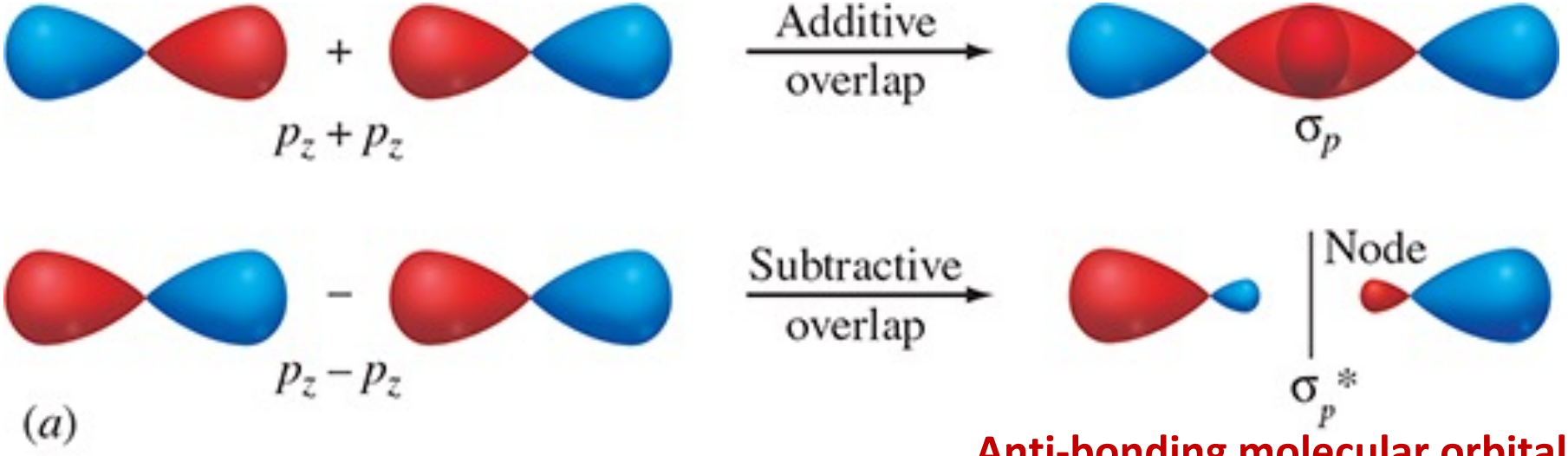
Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)



p orbitals can make σ bonds = σ and σ^* orbitals

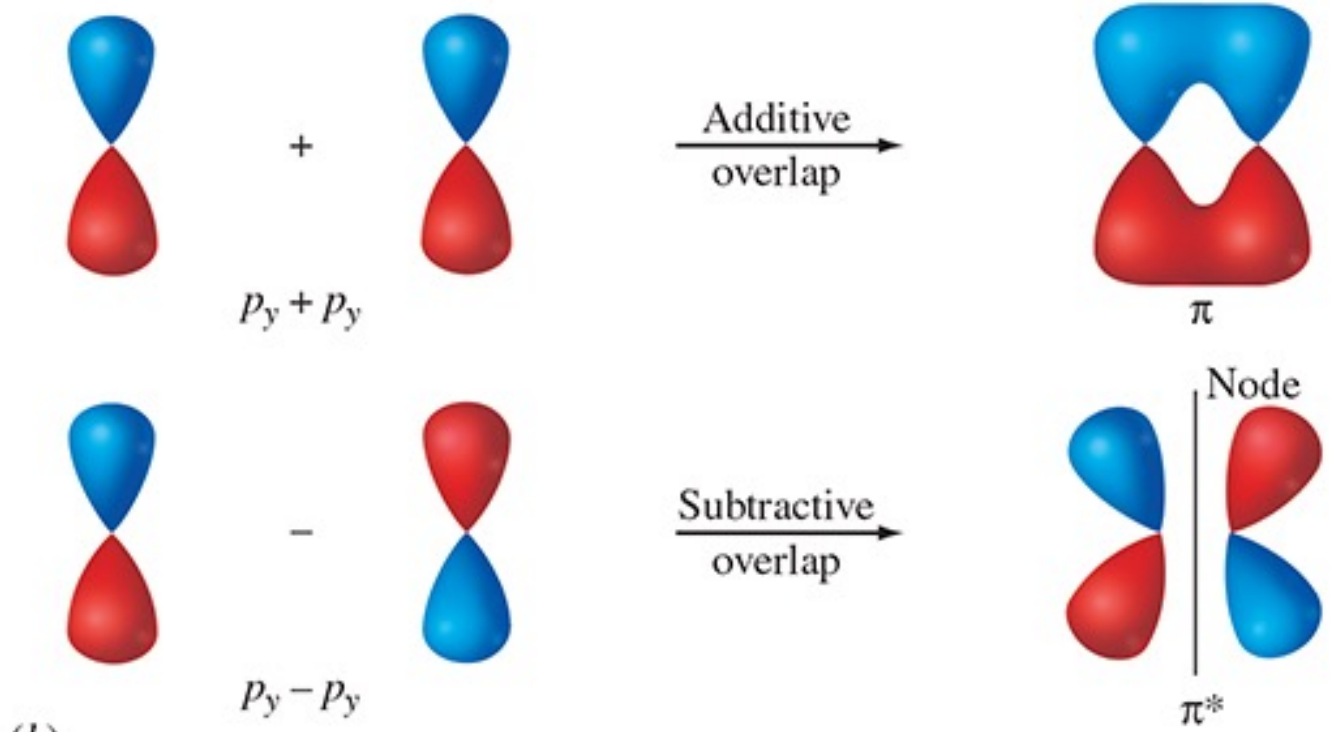
Bonding molecular orbital



Anti-bonding molecular orbital

p orbitals can make π bonds = π and π^* orbitals

Bonding molecular orbital



Anti-bonding molecular orbital

Example:
Molecular Orbital of N_2

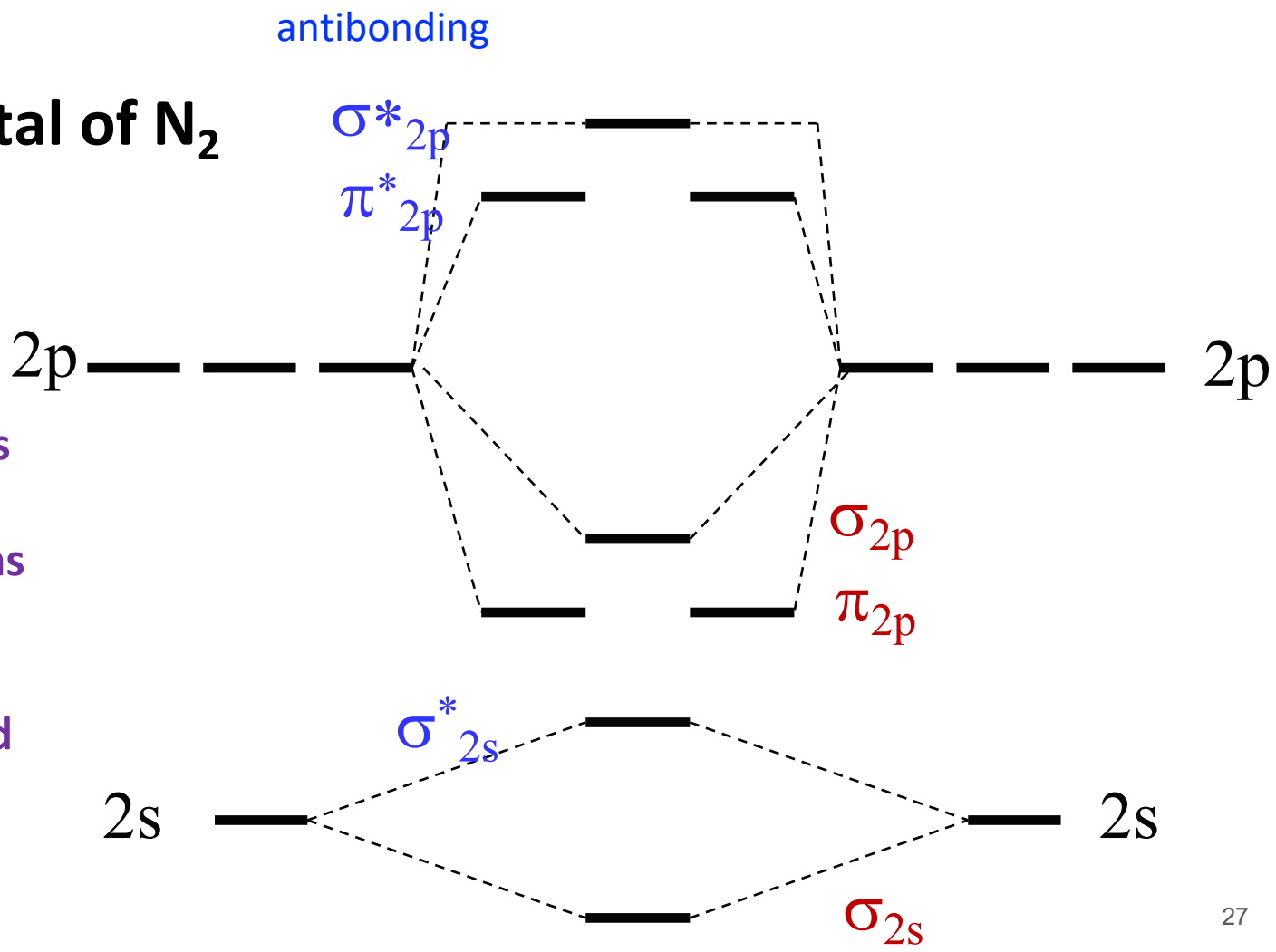
Step 1: Start with the atomic orbitals

Step 2: Build the MO's

Step 3: Move electrons into the MO's

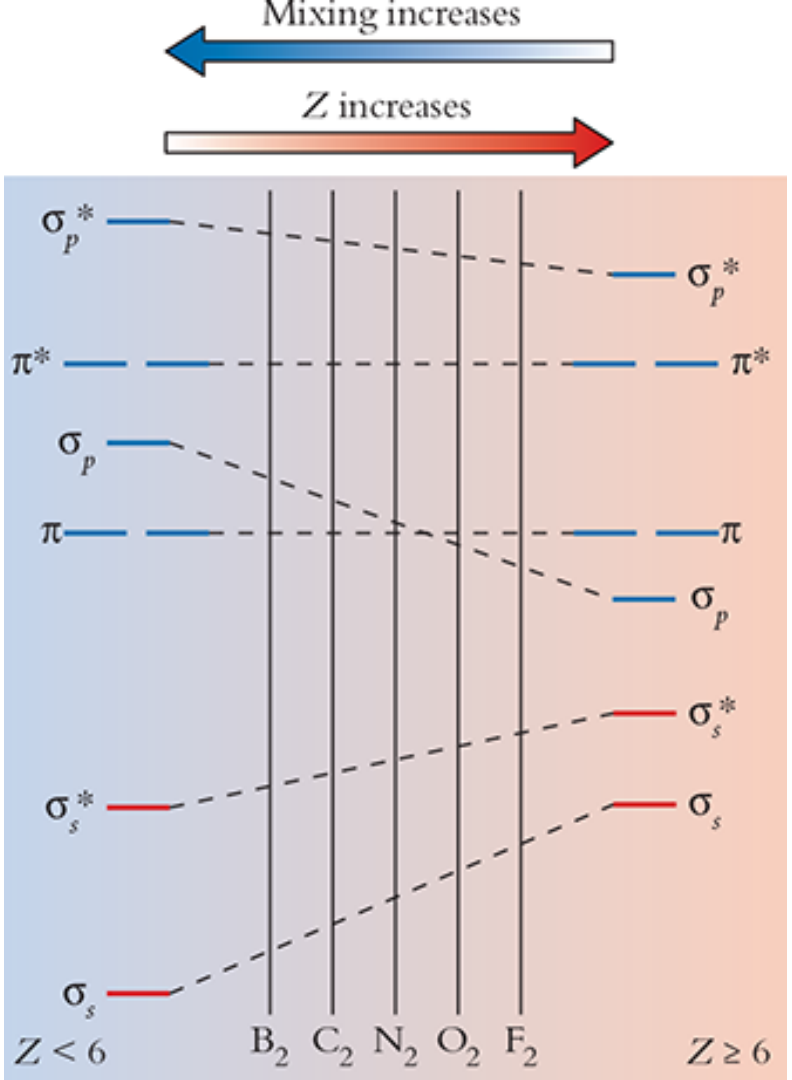
Step 4: Calculate Bond Order (BO)

What is the BO of **N_2 ?**

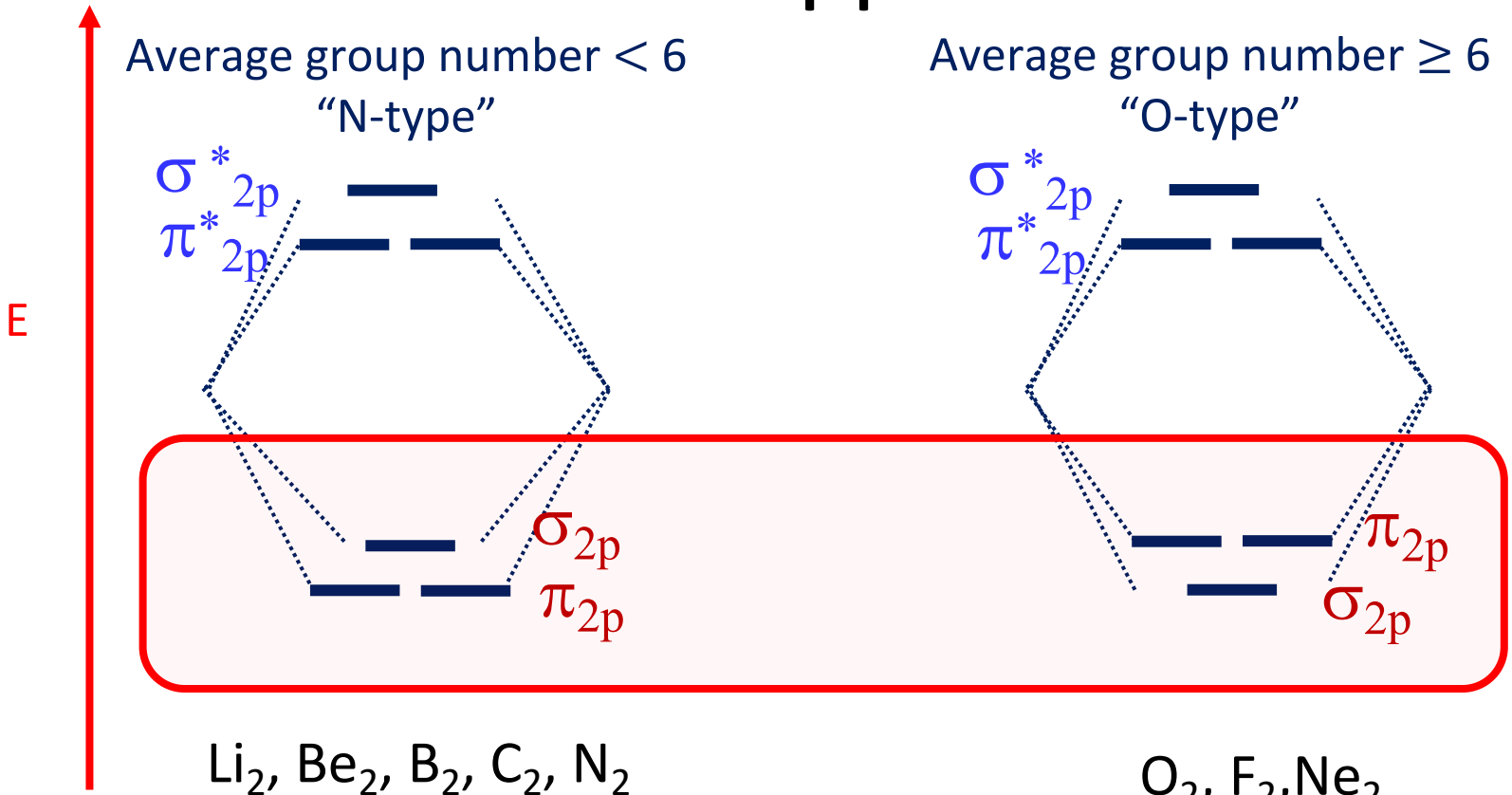


σ and π swap places!

- Diatomic molecules less than Z =6, have 2s and 2p atomic orbital closer in energy
- σ_{2s} and σ_{2p} MOs also close in energy causing them to mix
- Effect of mixing pushes σ_{2p} up in energy, to the point where π_{2p} orbitals are below σ_{2p}
- As effective nuclear charge (Z_{eff}) increases ($Z \geq 6$), less mixing of the σ 2s and 2p MOs



What do the MO diagrams look like when σ and π swap places!



Example:
Molecular Orbital of O_2

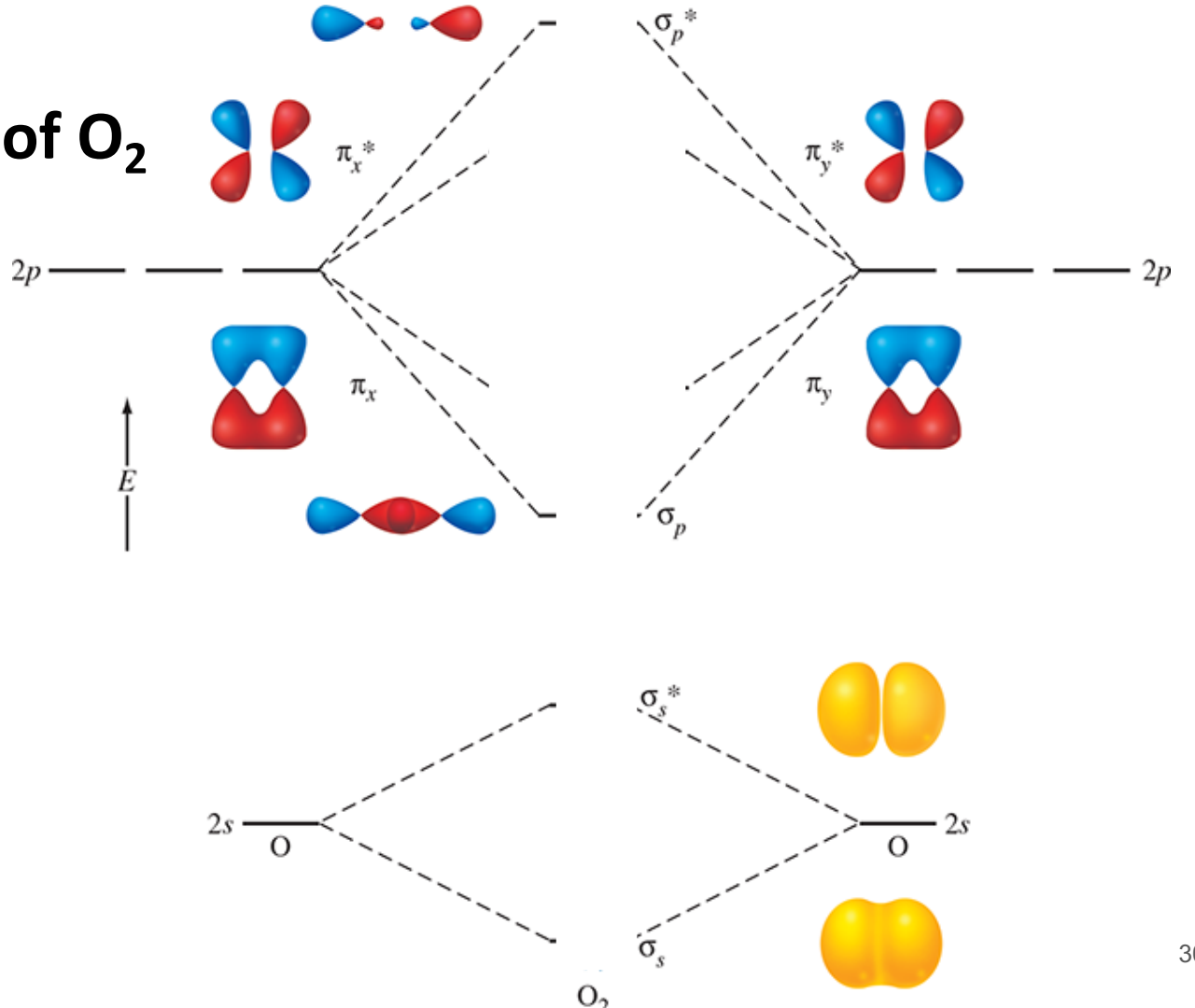
Step 1: Start with the atomic orbitals

Step 2: Build the MO's "N-type vs O-type"

Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)

What is the BO of **O_2 ?**



Example:
Build the MO of F_2

Step 1: Start with the atomic orbitals

Step 2: Build the MO's "N-type vs O-type"

Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)

What is the BO of **F_2 ?**

Example:
Build the MO of Ne_2

Step 1: Start with the atomic orbitals

Step 2: Build the MO's "N-type vs O-type"

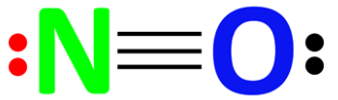
Step 3: Move electrons into the MO's

Step 4: Calculate Bond Order (BO)

What is the BO of **Ne_2 ?**

Heteronuclear Diatomic Molecules

Build the MO of NO



Individual atomic orbitals do not lie at the same energy level

N

O

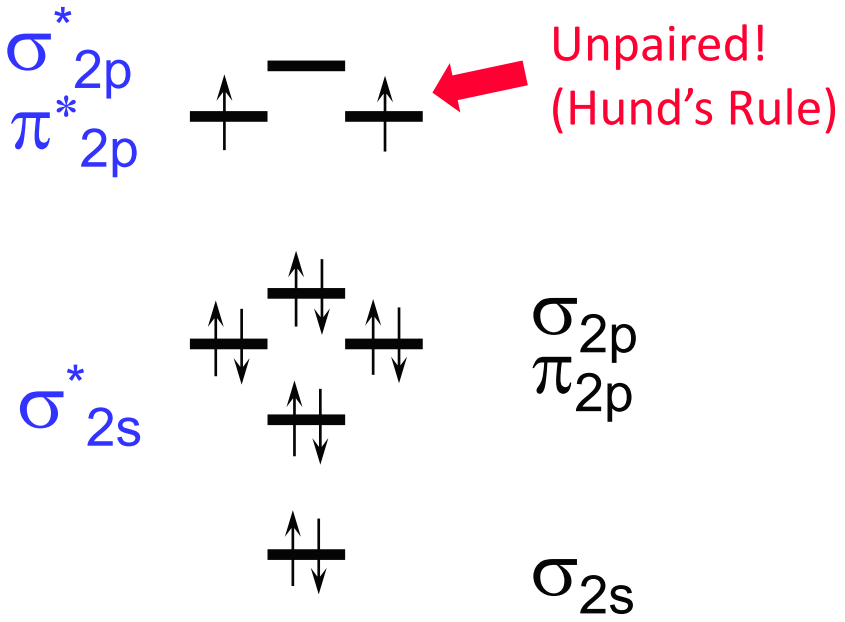
What is the BO of **NO ?**

Magnetism

Paramagnetic: unpaired electrons that are attracted to the magnetic field

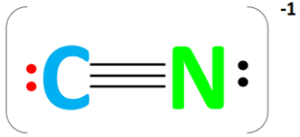
Diamagnetic: paired electrons are repelled by the magnetic field

Molecular oxygen (O_2) is paramagnetic, so it clings to the poles of a magnet



Heteronuclear Diatomic Molecules

Draw and label the MO diagram of the cyanide ion, CN^-. Give the bond order and the magnetism



Individual atomic orbitals do not lie at the same energy level

Is **CN^-** diamagnetic or paramagnetic?

C

N