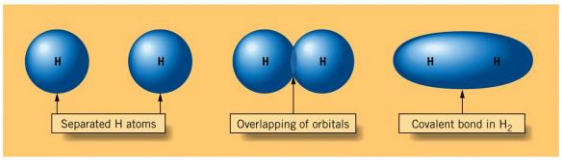
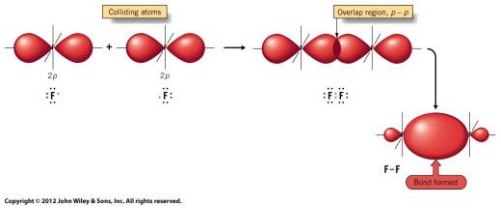
Valence Bond Theory – H_2

- H_2 bonds form because **1*s*** atomic valence orbital from each H atom overlaps



Valence Bond Theory – F_2

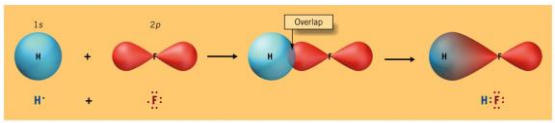


- F_2 bonds form because **2*p*** valence orbitals overlap

Valence Bond Theory – HF

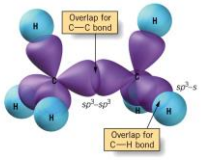
- HF involves overlaps between **1*s*** orbital on H and **2*p*** orbital of F

1*s* 2*p*

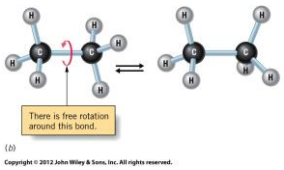


Conformations

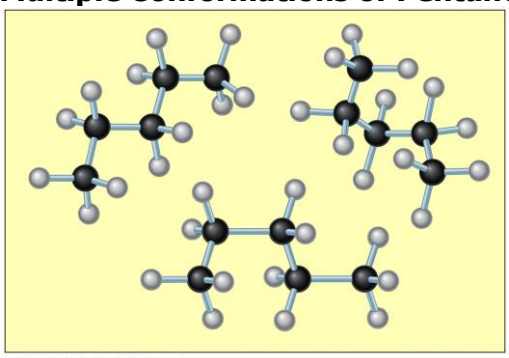
- C—C single bond has free rotation around the C—C bond



- **Conformations**
  - Different relative orientations on molecule upon rotation



Multiple Conformations of Pentane



Double and Triple Bonds

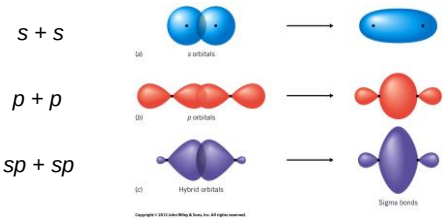
- So where do extra electron pairs in multiple bonds go?
  - Not in hybrid orbitals
  - Remember VSEPR, multiple bonds have no effect on geometry

Two types of bond result from orbital overlap

- Sigma (σ) bond
  - Accounts for first bond
- Pi (π) bond
  - Accounts for second and third bonds

Sigma (σ) Bonds

- Head on overlap of orbitals
- Electron density concentrated most heavily between nuclei of two atoms
- Lie along imaginary line joining their nuclei



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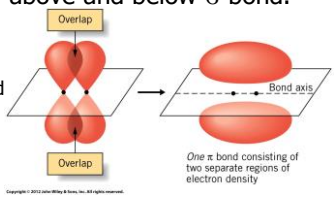
Pi (π) Bonds

- Sideways overlap of unhybridized *p* orbitals
- Electron density divided into two regions
  - Lie on opposite sides of imaginary line connecting two atoms
- Electron density above and below σ bond.
- Can never occur alone
  - Must have **σ** bond
- **π** bonds allow atoms to form double and triple bonds



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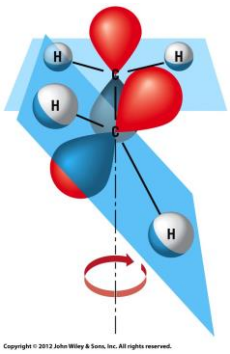
Properties of π-Bonds

- Can't rotate about double bond
- π bond must first be broken before rotation can occur



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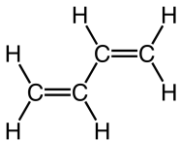
Your Turn!

How many σ and π bonds are there in $CH_2CHCHCH_2$



9, 2

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Molecular Orbital (MO) Theory

1. Molecular orbitals are associated with entire molecule as opposed to one atom
2. Allows us to accurately predict magnetic properties and bonds of molecules
3. Energies of molecular orbitals determined by combining electron waves of atomic orbitals

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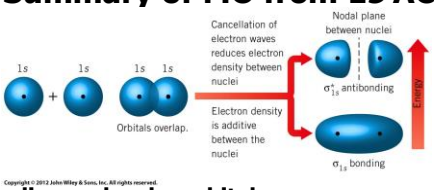
Summary of MO from 1*s* AO



- **Bonding molecular orbital** σ
  - Electron density builds up between nuclei
  - Electrons in bonding MOs tend to stabilize molecule
- **Antibonding molecular orbital** σ*
  - Cancellation of electron waves reduces electron density between nuclei
  - Electrons in antibonding MOs tend to destabilize molecule

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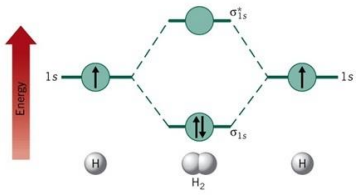
MO Energy diagram for H_2



- H_2 is very stable molecule

Rules for Filling MO Energy Diagrams

1. Electrons fill lowest-energy orbitals that are available
   - **Aufbau principle applies**
2. No more than two electrons, with spin paired, can occupy any orbital
   - **Pauli exclusion principle applies**
3. Electrons spread out as much as possible, with spins unpaired, over orbitals of same energy
   - **Hund's rule applies**

Bond Order

- Measure of number of electron pairs shared between two atoms

$$\text{Bond order} = \frac{(\text{number of bonding } e^-) - (\text{number of antibonding } e^-)}{2 \text{ electrons/bond}}$$

- As **bond order increases**, **bond length decreases**, and **bond energy increases**

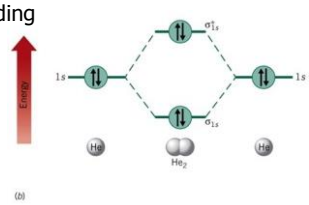
- H_2 bond order = 1
- A bond order of 1 corresponds to a single bond

MO Energy Diagram for He_2

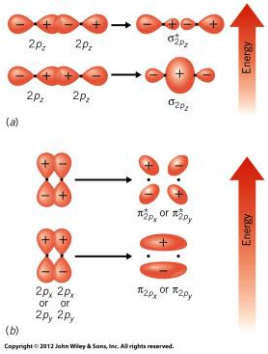
- Four electrons, so both σ and σ* molecular orbitals are filled
- Bond order

$$\text{Bond order} = \frac{2 - 2}{2} = 0$$

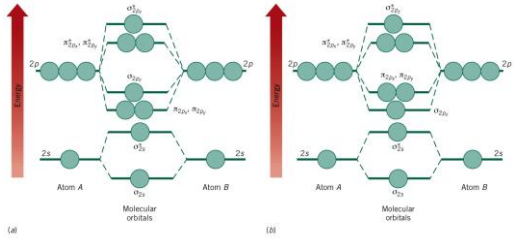
- There is no net bonding
- He_2 **does not form**



MO from 2*p* Orbital



MO Energy Diagrams for 2nd Row of Periodic Table



$Li_2 \rightarrow N_2$
π_{2p} *Lower* in energy than σ_{2p}

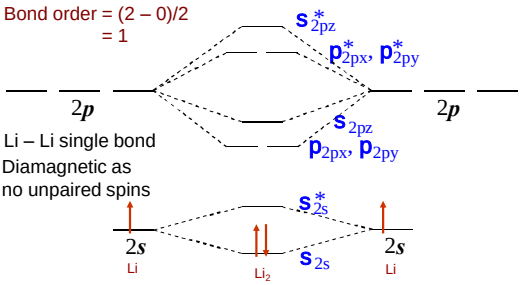
O_2, F_2 and Higher σ_{2p} *Lower* in energy than π_{2p}

MO Energy Diagram for Li_2

π_{2p} *Lower* in Energy than σ_{2p}

Li electron configuration = $[He]2s^1$ 1 ve

Bond order = (2 – 0)/2
= 1



Li – Li single bond
Diamagnetic as
no unpaired spins

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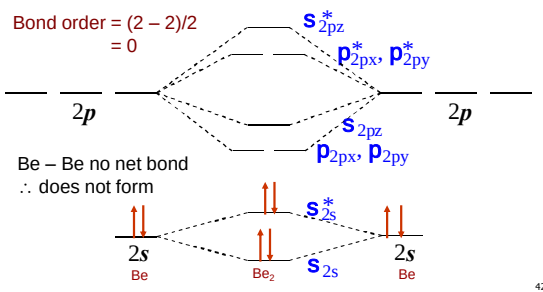
MO Energy Diagram for Be_2

π_{2p} *Lower* in Energy than σ_{2p}

Be electron configuration = $[He]2s^2$ 2 ve

Bond order = (2 – 2)/2
= 0



Be – Be no net bond
∴ does not form

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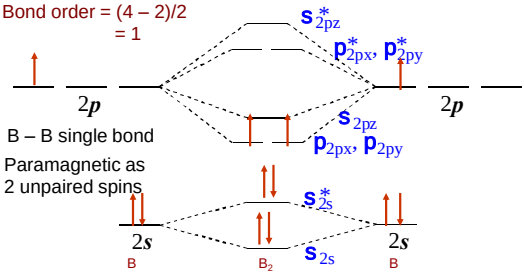
MO Energy Diagram for B_2

π_{2p} *Lower* in Energy than σ_{2p}

B electron configuration = $[He]2s^22p^1$ 3 ve

Bond order = (4 – 2)/2
= 1



B – B single bond
Paramagnetic as
2 unpaired spins

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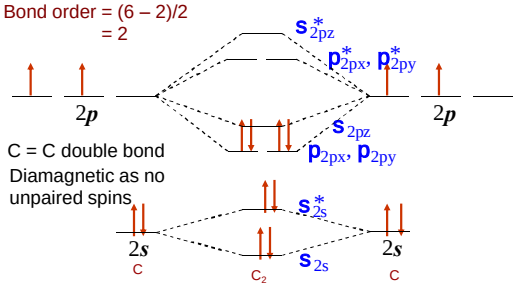
MO Energy Diagram for C_2

π_{2p} *Lower* in Energy than σ_{2p}

C electron configuration = $[He]2s^22p^2$ 4 ve

Bond order = (6 – 2)/2
= 2



C = C double bond
Diamagnetic as no
unpaired spins

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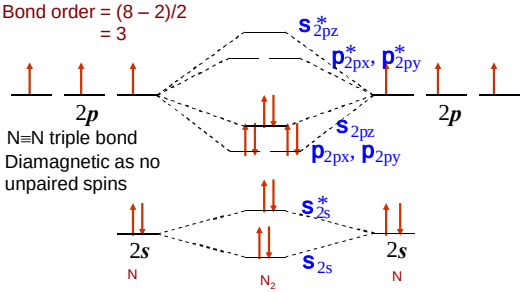
MO Energy Diagram for N_2

π_{2p} *Lower* in Energy than σ_{2p}

N electron configuration = $[He]2s^22p^3$ 5 ve

Bond order = (8 – 2)/2
= 3



N≡N triple bond
Diamagnetic as no
unpaired spins

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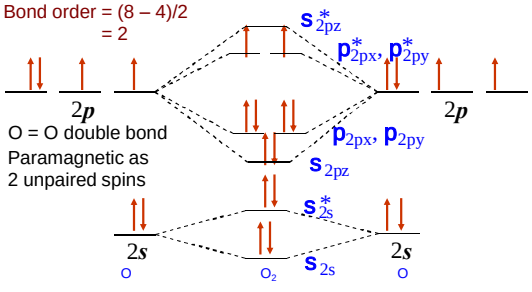
MO Energy Diagram for O_2

σ_{2p} *Lower* in Energy than π_{2p}

O electron configuration = $[He]2s^22p^4$ 6 ve

Bond order = (8 – 4)/2
= 2



O = O double bond
Paramagnetic as
2 unpaired spins

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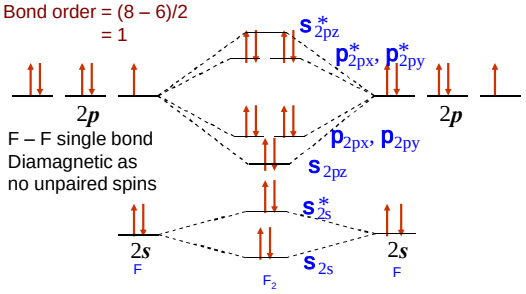
MO Energy Diagram for F_2

σ_{2p} *Lower* in Energy than π_{2p}

F electron configuration = [He]$2s^2 2p^5$ 7 ve

Bond order = (8 – 6)/2
= 1



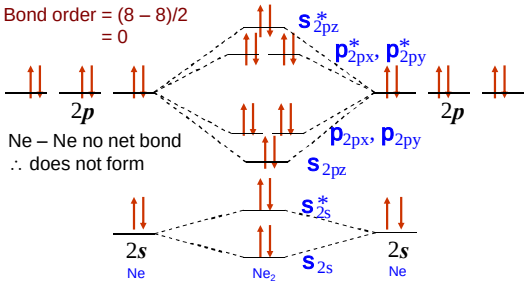
F – F single bond
Diamagnetic as
no unpaired spins

MO Energy Diagram for Ne_2

σ_{2p} *Lower* in Energy than π_{2p}

Ne electron configuration = [He]$2s^2 2p^6$ 8 ve

Bond order = (8 – 8)/2
= 0



Ne – Ne no net bond
∴ does not form