Chem 241

Lecture 5

Homework

Start reading Chapter 4

Chapter 2

- Exercises: 1, 3, 6-9, 14 – 17, 19, 23
- Problems: 2.1, 2.4

Recap

- VSEPR
- Valance Bond Theory

MOT

Molecular orbitals are similar to atomic orbitals except spread over the entire molecule. As such, they are molecular features.

Approximations:

Orbital approximation: The product of the many electron wavefunction for the molecule can be written as the product of one electron wavefunctions:

$$\Psi = \psi(1)\psi(2)...\psi(\mathrm{N})$$

LCAO: To the extent that MOs look like combinations of atomic orbitals, we can approximate them as linear combinations of atomic orbitals.

MOT

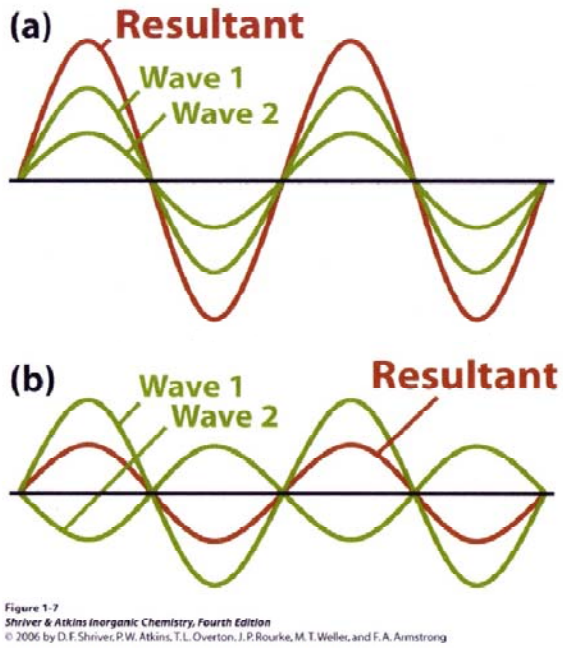


Figure 1-7
Shriver & Atkins Inorganic Chemistry, Fourth Edition

$$\Psi_{bonding} = \Psi_A + \Psi_B$$

$$\Psi_{antibonding} = \Psi_A - \Psi_B$$

MOT

$\psi_{bond} = \psi_A + \psi_B$

$\psi_{anti} = \psi_A - \psi_B$

<u>One electron</u>

$\psi = \psi_{bond(1)} = \psi_A + \psi_B$

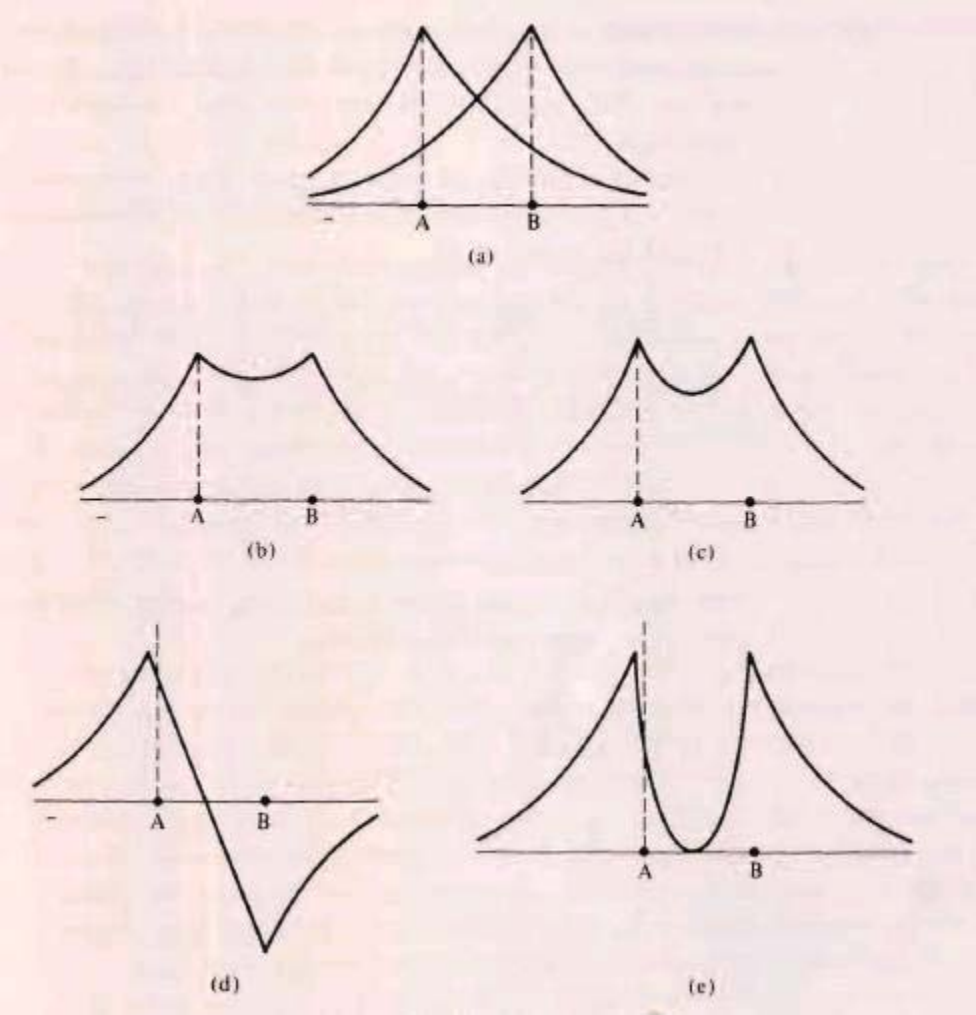
$\psi = \psi_{anti(1)} = \psi_A - \psi_B$

<u>Two electrons</u>

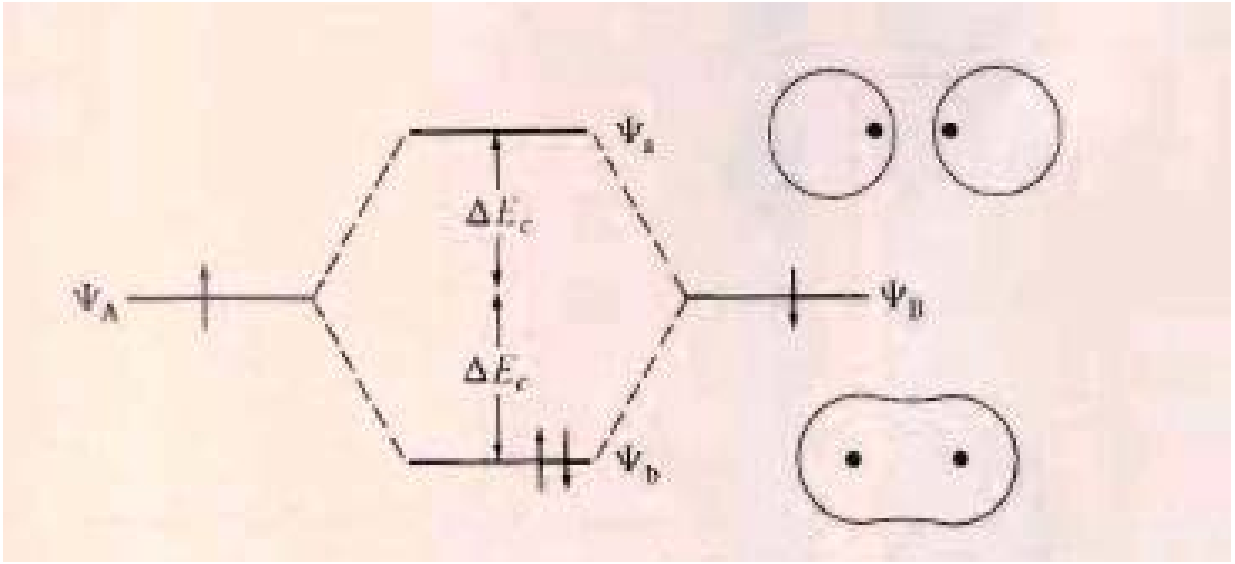
$\psi = \psi_{bond(1)}\,\psi_{bond(2)} = [\psi_{A(1)} + \psi_{B(1)}]\,[\psi_{A(2)} + \psi_{B(2)}]$

$\psi = \psi_{anti(1)}\,\psi_{anti(2)} = [\psi_{A(1)} - \psi_{B(1)}]\,[\psi_{A(2)} - \psi_{B(2)}]$

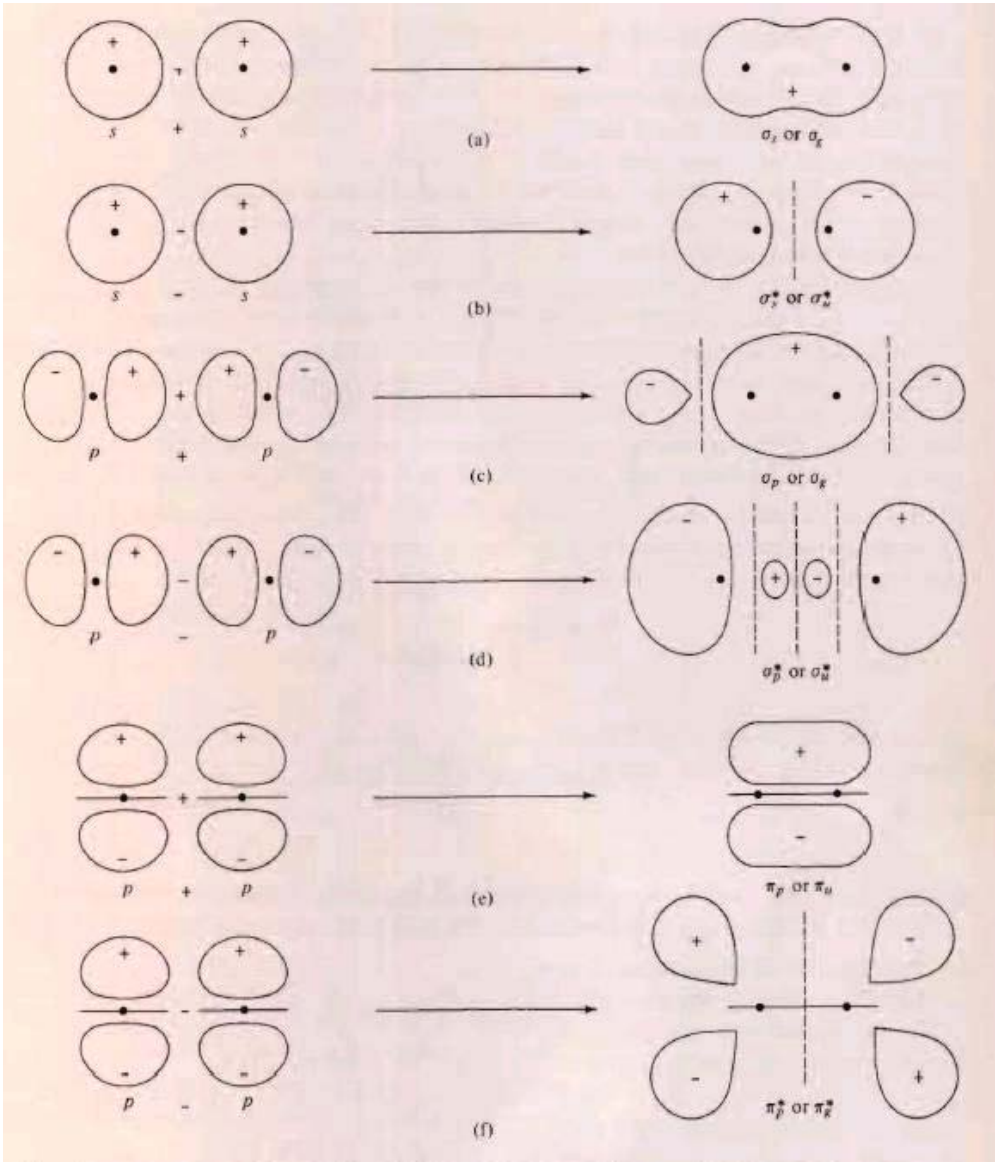
MOT

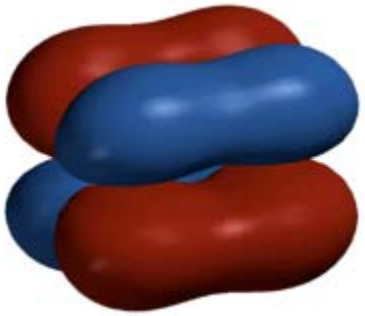


MO Diagram



LCAOs


s + s
(a)
σ_s or σ_g
s − s
(b)
σ_s^* or σ_u^*
p + p
(c)
σ_p or σ_g
p − p
(d)
σ_p^* or σ_u^*
p + p
(e)
π_p or π_u
p − p
(f)
π_p^* or π_g^*



MO diagram

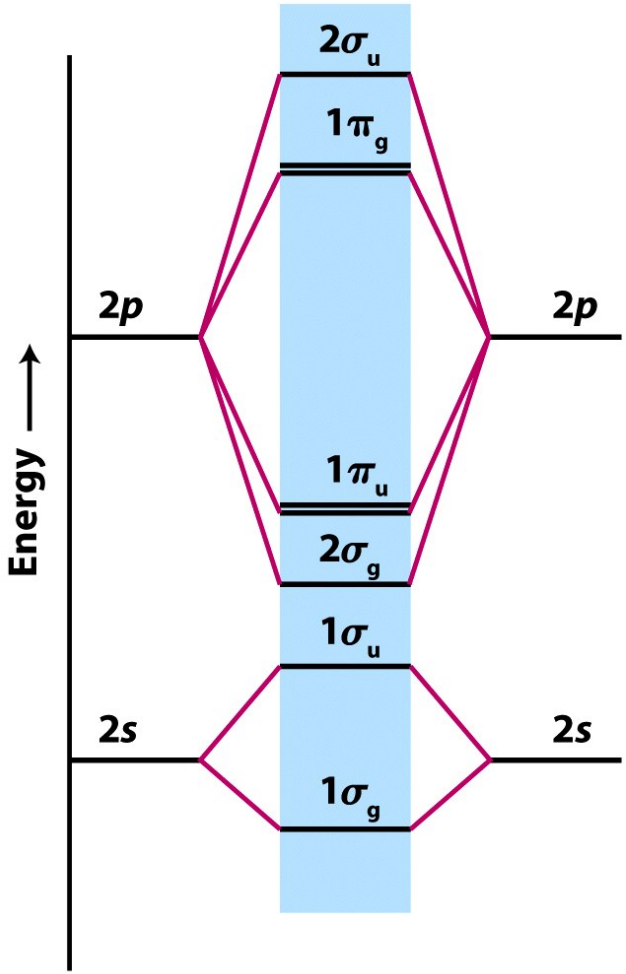


Figure 2-14
Shriver & Atkins Inorganic Chemistry, Fourth Edition

MOT-Homonuclear Diatomics

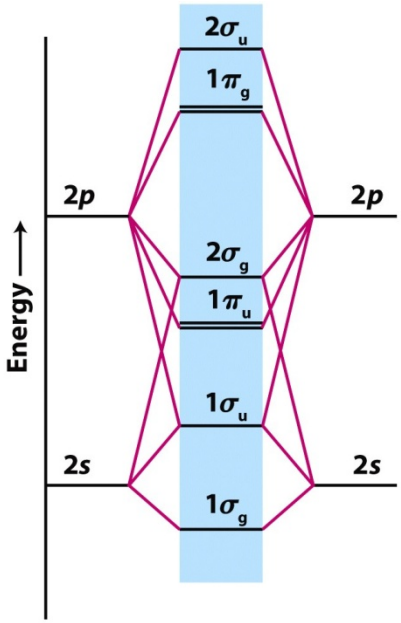


Figure 2-18
Shriver & Atkins Inorganic Chemistry, Fourth Edition

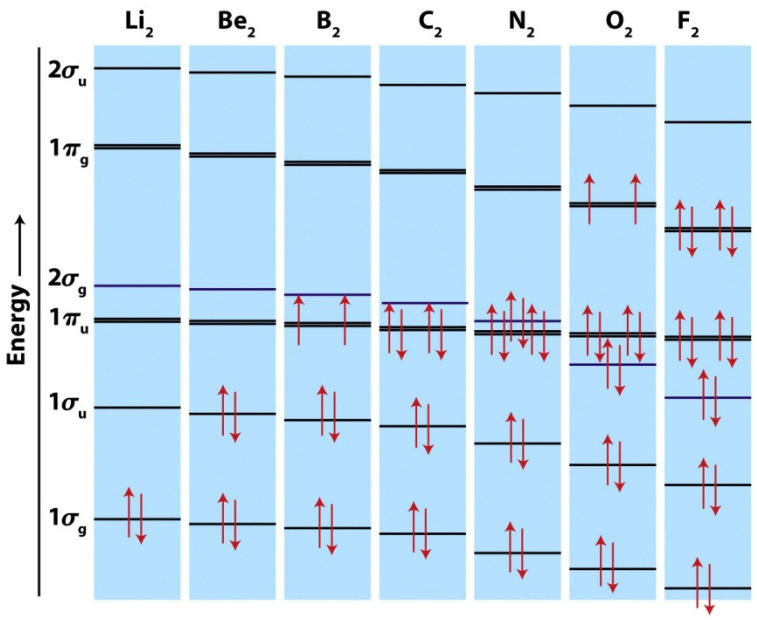


Figure 2-17
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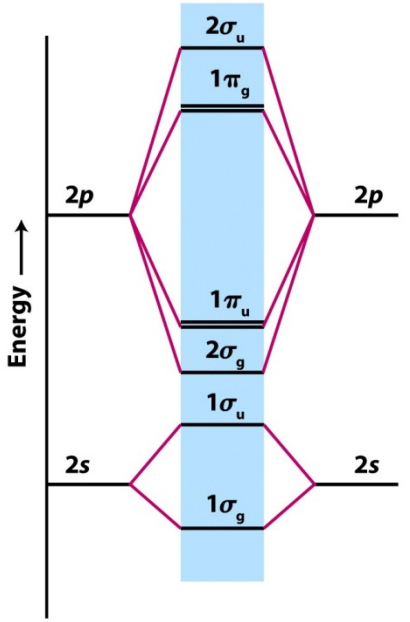
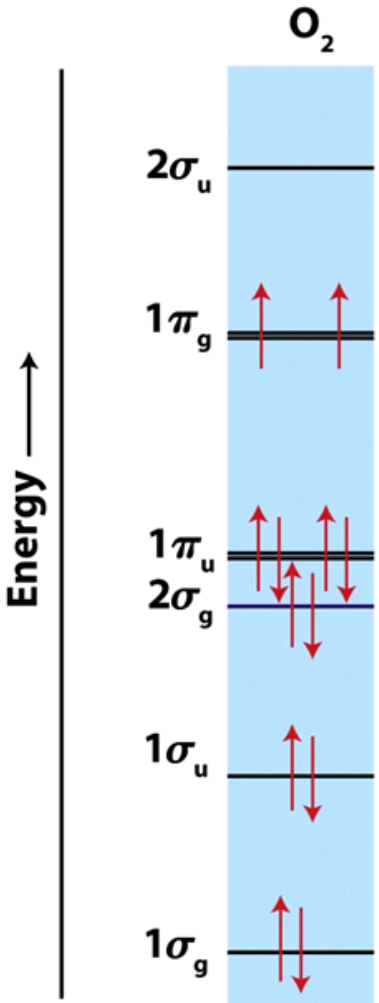


Figure 2-14
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Electron filling is done just like for atomic orbitals
Paramagnetism is a property associated with unpaired e-

MOT-Homonuclear Diatomics



Valence electron configuration

$$O_2 = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$$

Can be done for ions as well

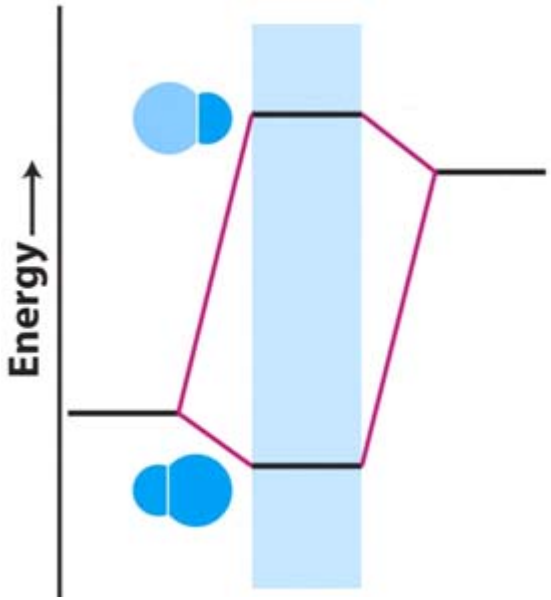
HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital
SOMO = Singly Occupied Molecular Orbital
SLUMO

MOT-Heteronuclear Diatomics

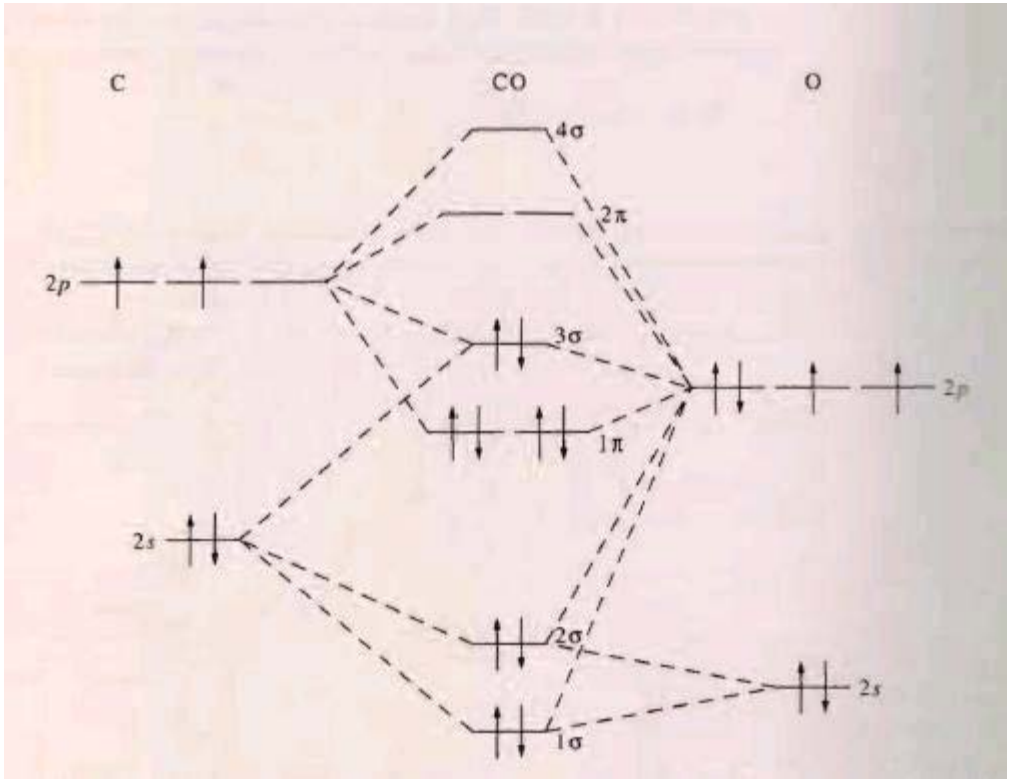
- Differences from Homonuclear case:
  - for $\psi_{bond(1)} = \psi_A + \psi_B$, ψ_A does not = ψ_B
  - Electrons will be drawn to the more electronegative element . Thus bonding orbitals will have more of that element character and antibonding orbitals will have more AO character from the more electropositive element.
  - As a result of having more A character,

The molecular orbital will be closer in

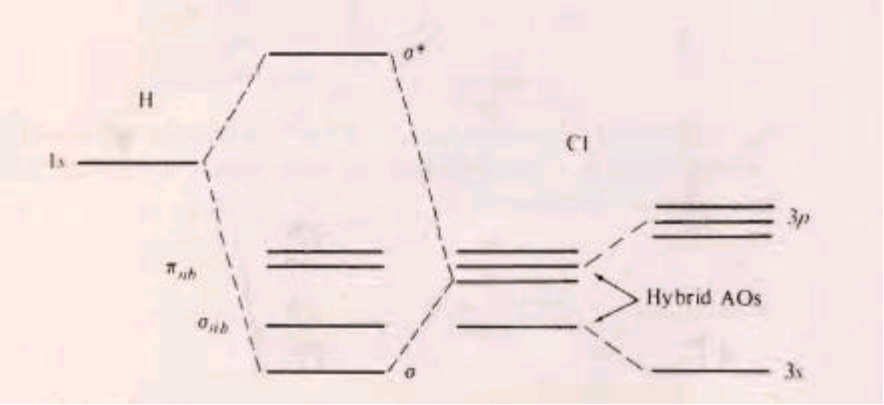
Energy to the AO of A.



Consider CO



Consider HCl



MOT-predicting bond order, bond length and bond strength

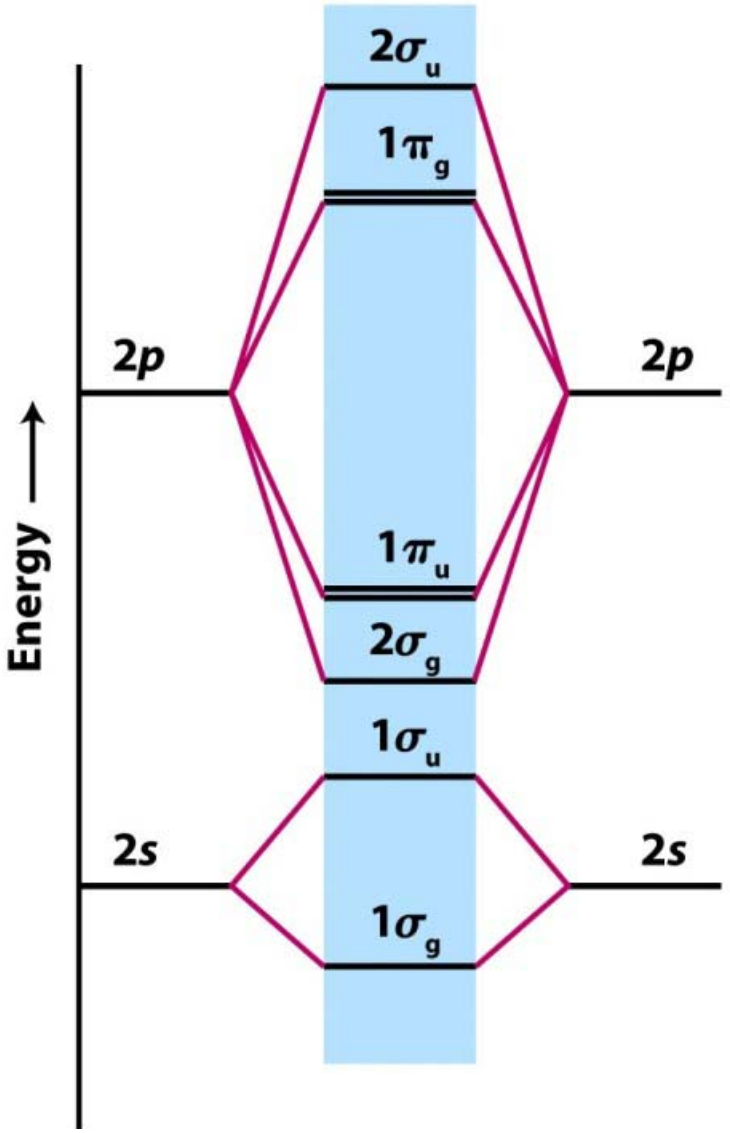
- Consider O_2, O_2^-, O_2^{2-}, O_2^+
- Bond Order b= ½(bond – anti)

$\nu_{o\text{-}o}$ = 1555 cm^{-1}

1108 cm^{-1} ($K[O_2^-]$)

760 cm^{-1} ($Na_2[O_2^{2-}]$)

1858 cm^{-1} ($[O_2^+]AsF_6$



MOT of polyatomic molecules

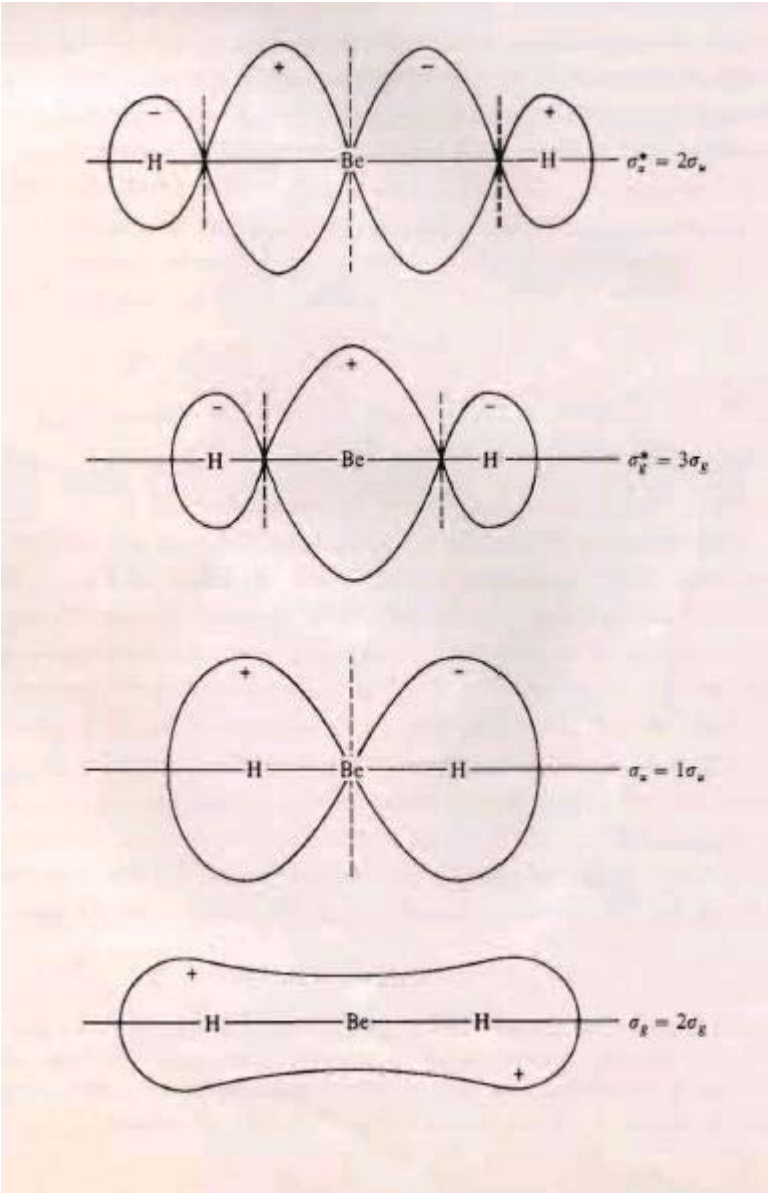
- General rules:
- 1. Molecular orbitals are formed from linear combinations of atomic orbitals with the same symmetry

- 2. The greater the number of nodes in a molecular orbital, the more antibonding and higher in energy it is.

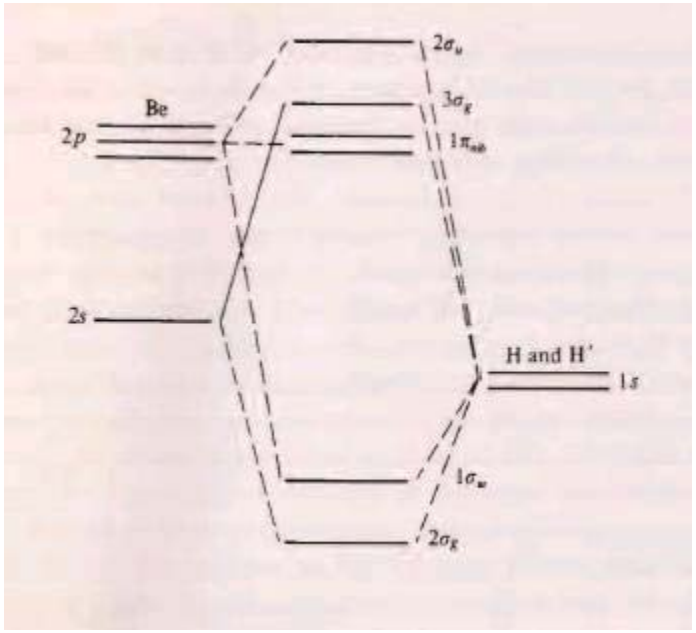
- 3. Interactions between atoms that are not nearest neighbors are weak (bonding or anti-bonding).

- 4. Orbitals constructed from lower energy AOs lie lower in energy.

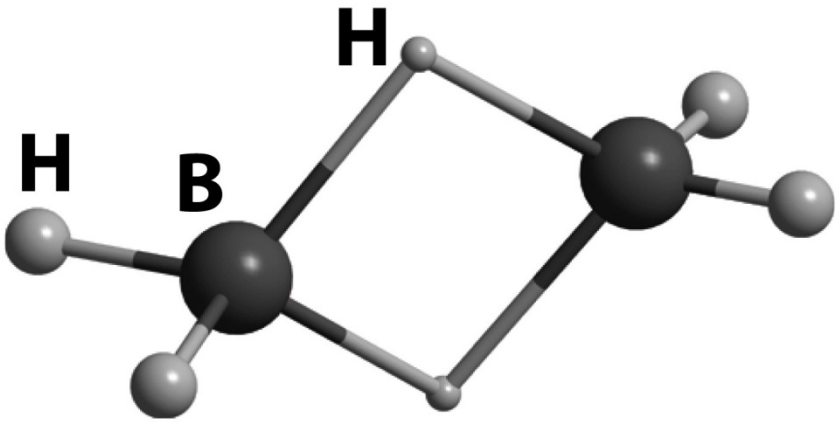
BeH_2


H
Be
H
$\sigma_u^* = 2\sigma_u$
H
Be
H
$\sigma_g^* = 3\sigma_g$
H
Be
H
$\sigma_u = 1\sigma_u$
H
Be
H
$\sigma_g = 2\sigma_g$

BeH_2



Diborane



27 Diborane, B_2H_6

Structure 2-27
Shriver & Atkins Inorganic Chemistry, Fourth Edition

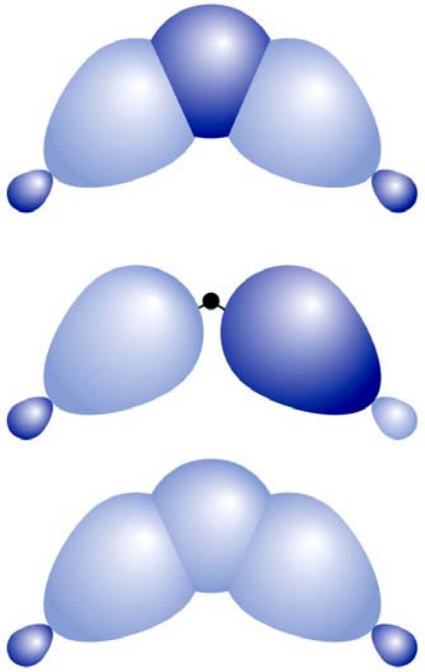


Figure 2-32
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Please look in your book about NH_3, Hypervalence

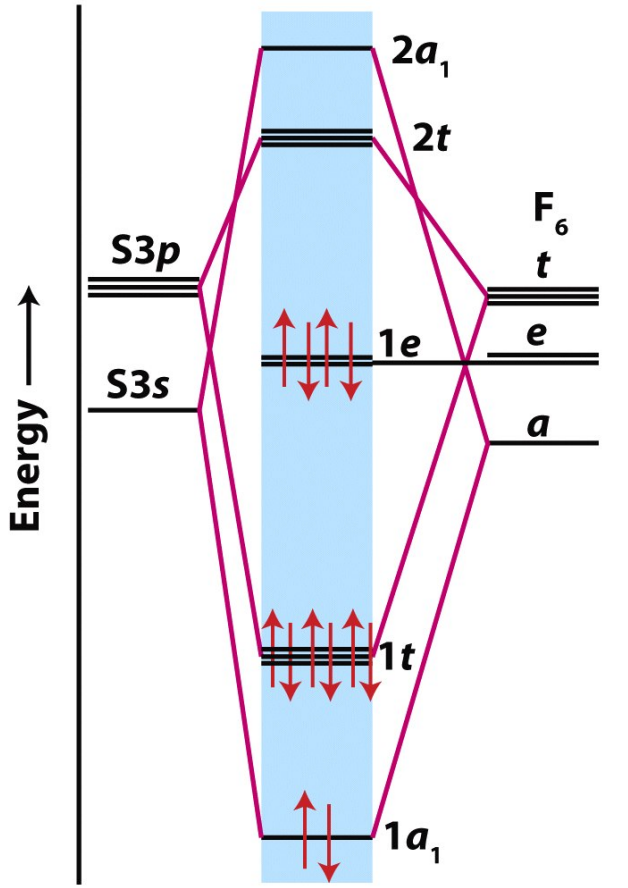


Figure 2-31
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