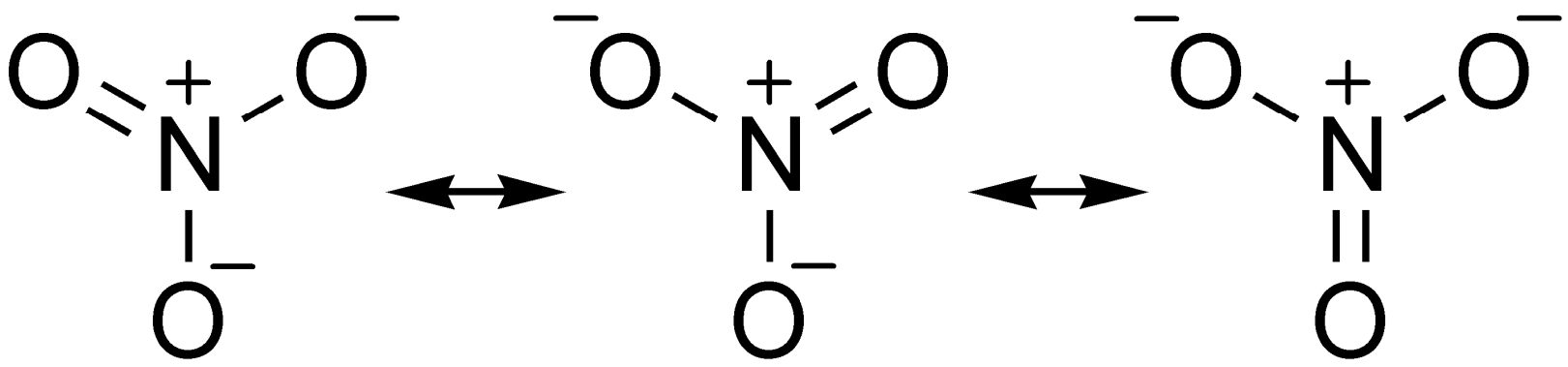
Chem 241

Lecture 4

Recap

- Finished off trends
- Lewis structure – formal charges
- Resonance states
- Nature of bonding
- Oxidation State
- f = V – L - 1/2P

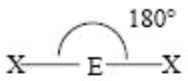
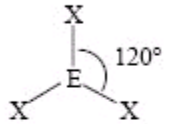
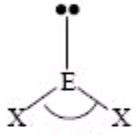
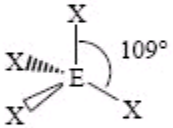
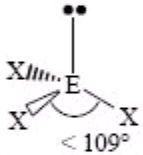
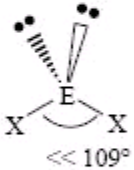
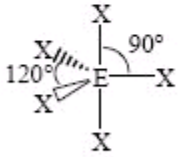
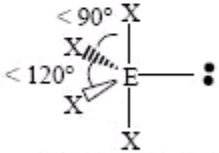
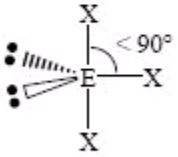
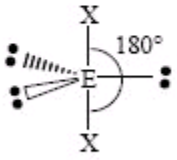
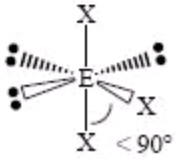
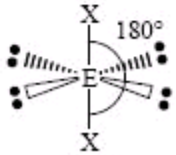


VSEPR (valence shell electron pair repulsion)

Number of electron regions	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

- Basic Tenents
  - 1. Regions of high electron density (bp(s) + lp(s)) take up positions as far apart as possible.
  - 2. Molecular shape is determined by the resulting atomic positions
  - 3. lone pairs take up more space than bond pairs

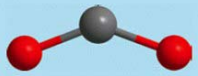
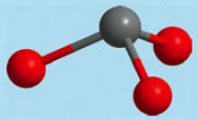
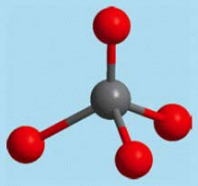
VSEPR

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

VSEPR

- Consider SO_3^{2-}

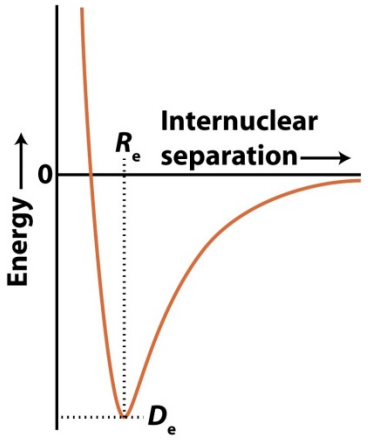
Table 2.7 The description of molecular shapes

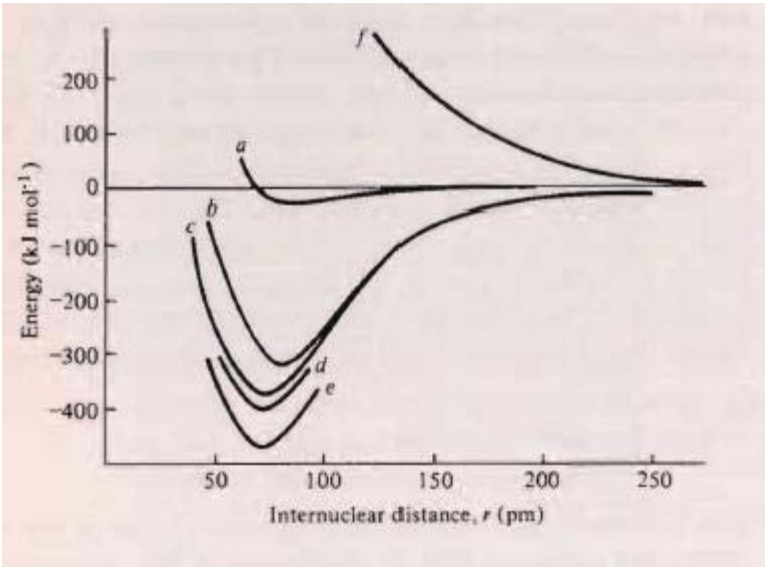
Linear		HCN, CO_2
Angular		H_2O, O_3, NO_2^-
Trigonal planar		BF_3, SO_3, NO_3^-, CO_3^{2-}
Trigonal pyramidal		NH_3, SO_3^{2-}
Tetrahedral		CH_4, SO_4^{2-}

Valence Bond Theory

Spin pairing of electrons in overlapping atomic orbitals

Consider H_2, $1s^1$





Valence Bond Theory

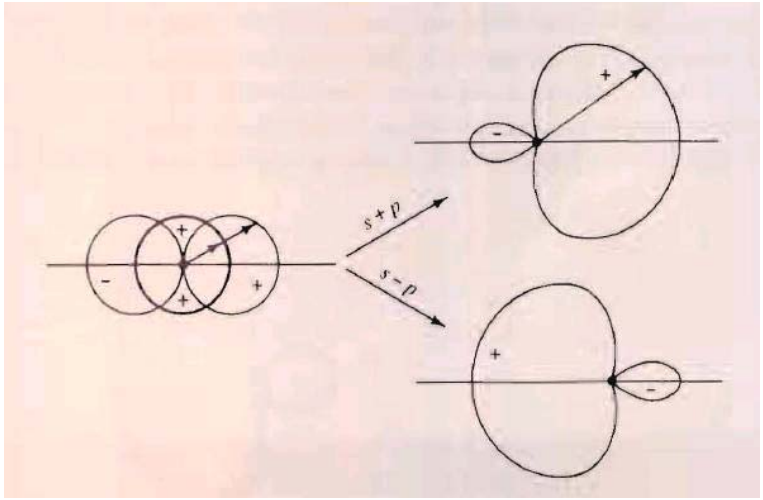
Spin pairing of electrons in overlapping atomic orbitals.

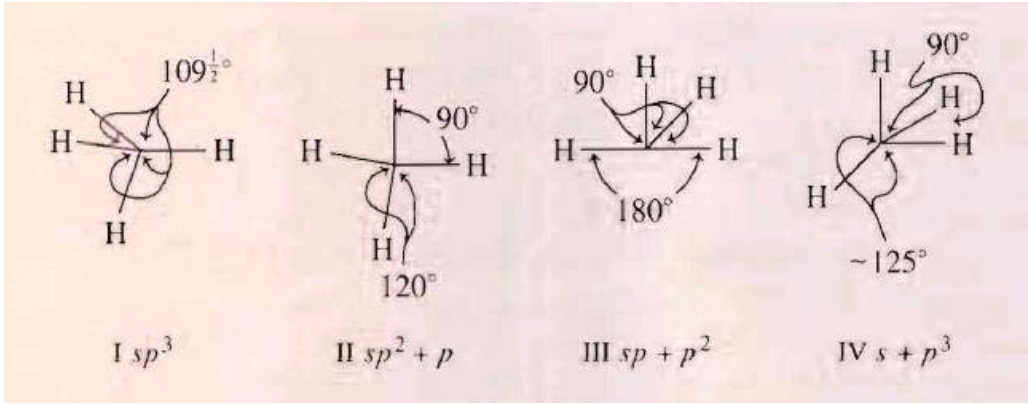
Consider N_2, $2s^2sp_x^{\,1}2p_y^{\,1}2p_z^{\,1}$

Consider H_2O, $O=2s^2sp_x^{\,2}2p_y^{\,1}2p_z^{\,1}$

Promotion & Hybridization

C $2s^2sp_x^{1}2p_y^{1}$





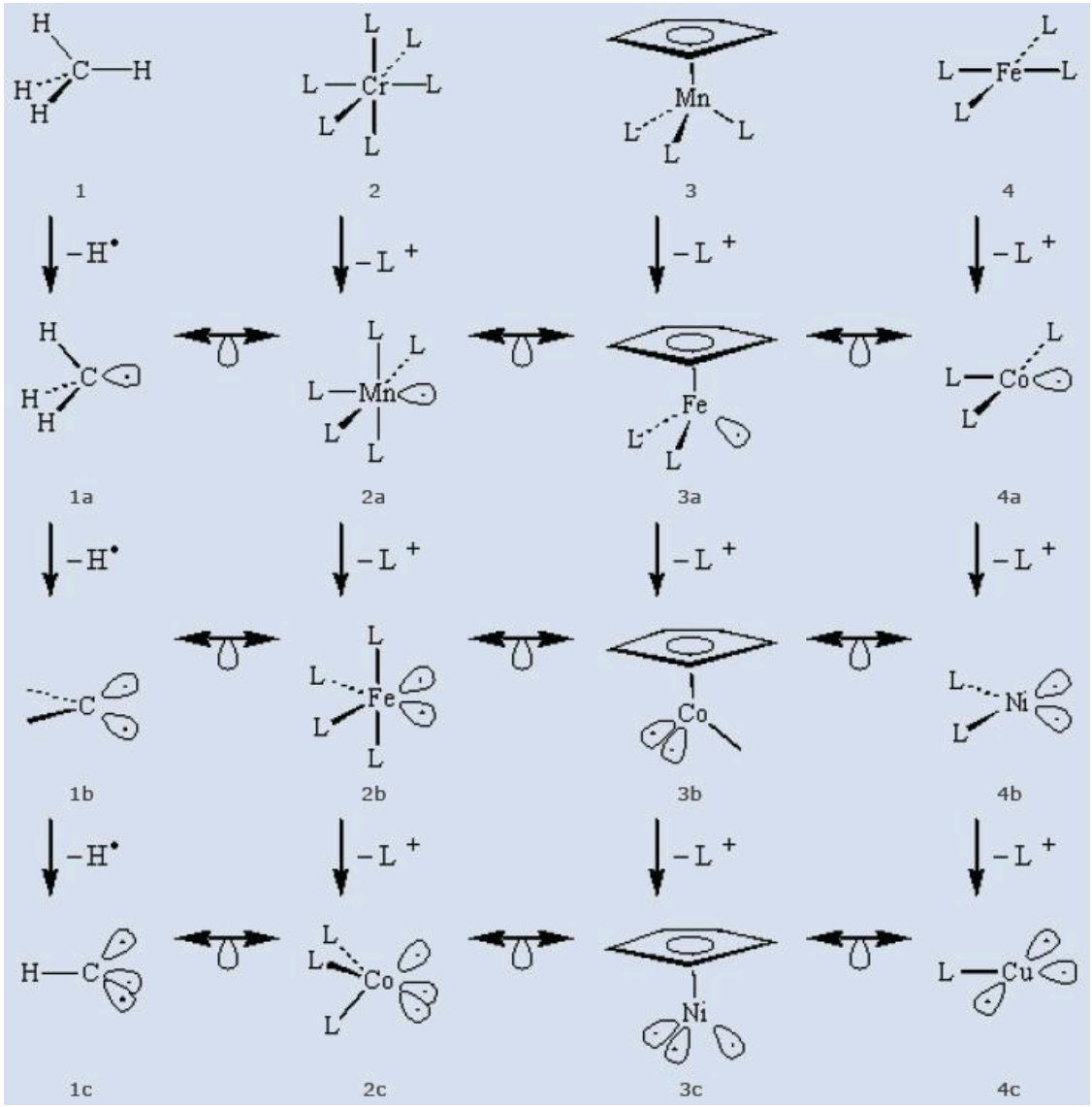
Hybridization

Table 2.8 Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, pd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

Table 2-8
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Isolobal and overlap



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:

$$\Psi = \psi(1)\psi(2)...\psi(N)$$

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

MOT

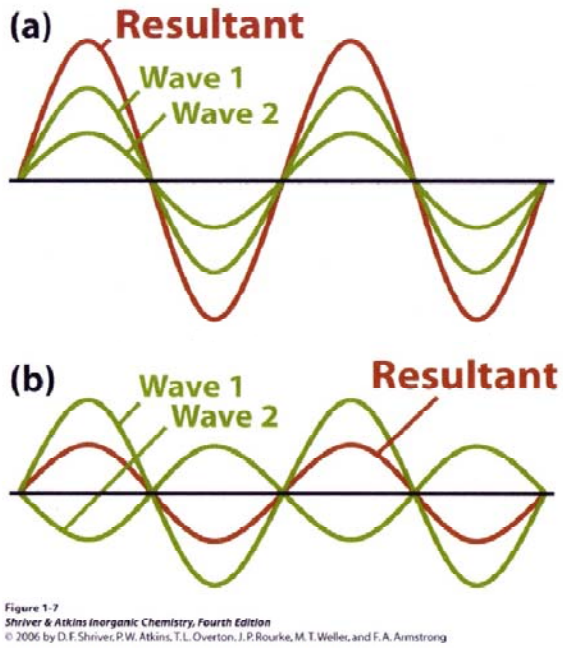


Figure 1-7
Shriver & Atkins Inorganic Chemistry, Fourth Edition

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

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

MOT

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

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

<u>One electron</u>

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

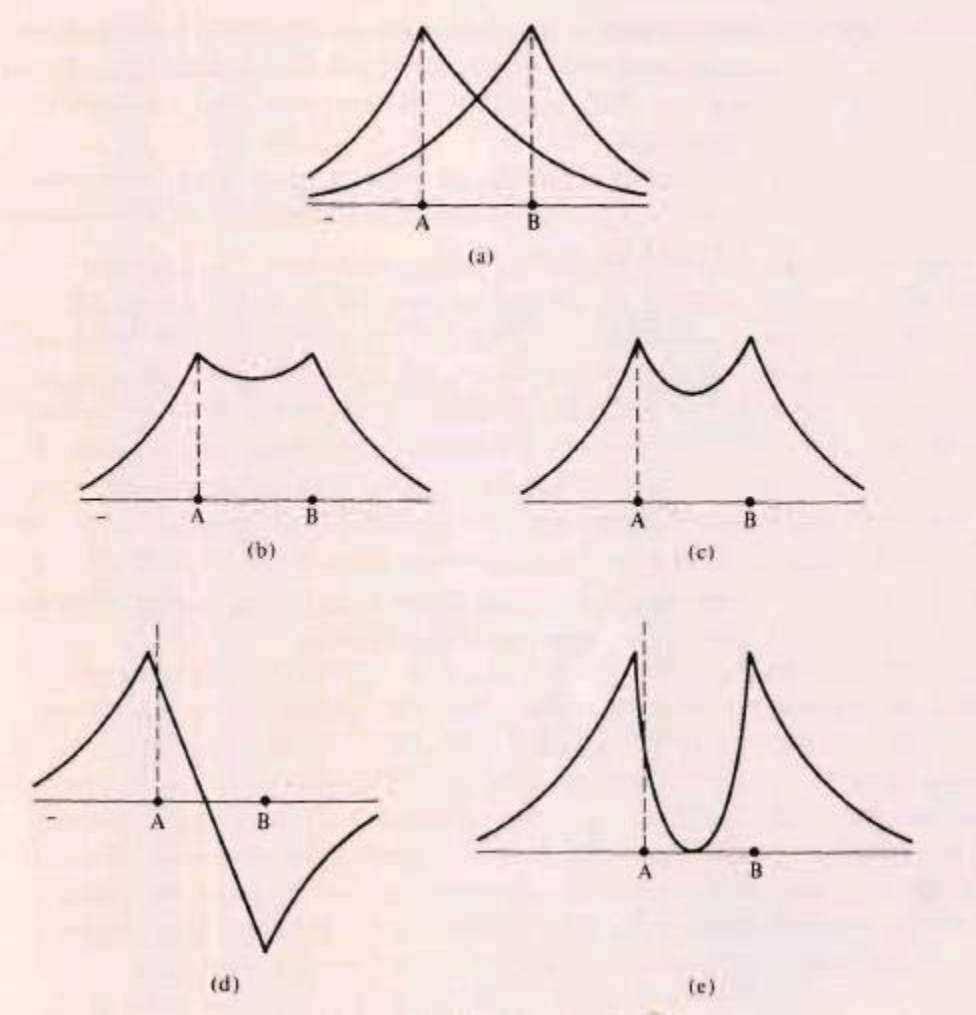
$\psi_m = \psi_{anti(1)} = \psi_A - \psi_B$

<u>Two electrons</u>

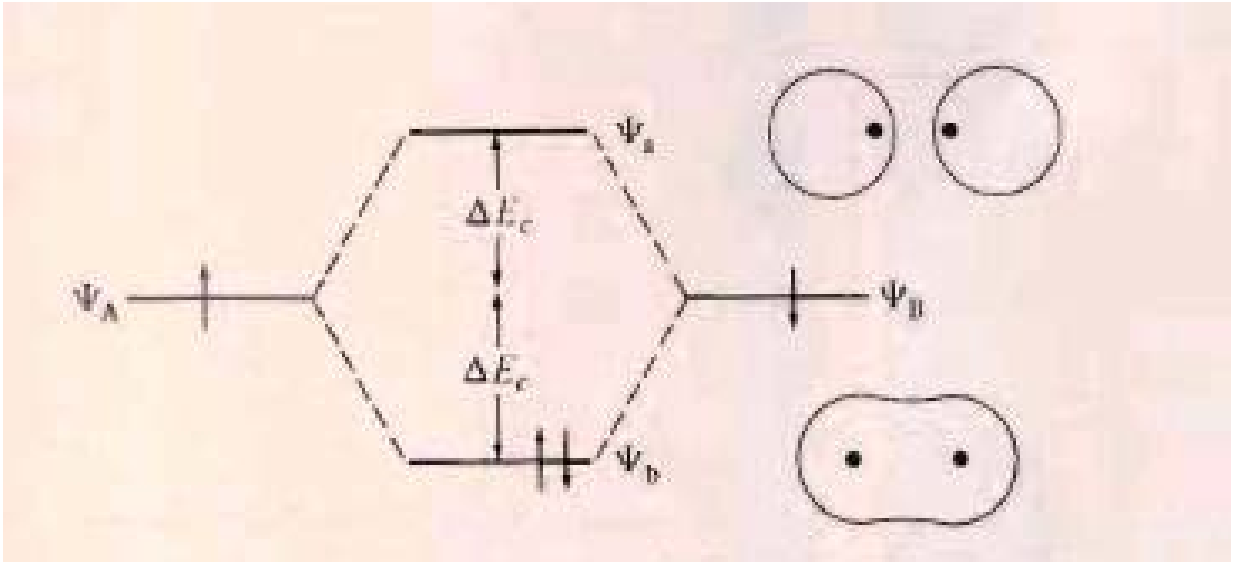
$\psi_m = \psi_{bond(1)}\,\psi_{bond(2)} = [\psi_{A(1)} + \psi_{B(1)}]\,[\psi_{A(2)} + \psi_{B(2)}]$

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

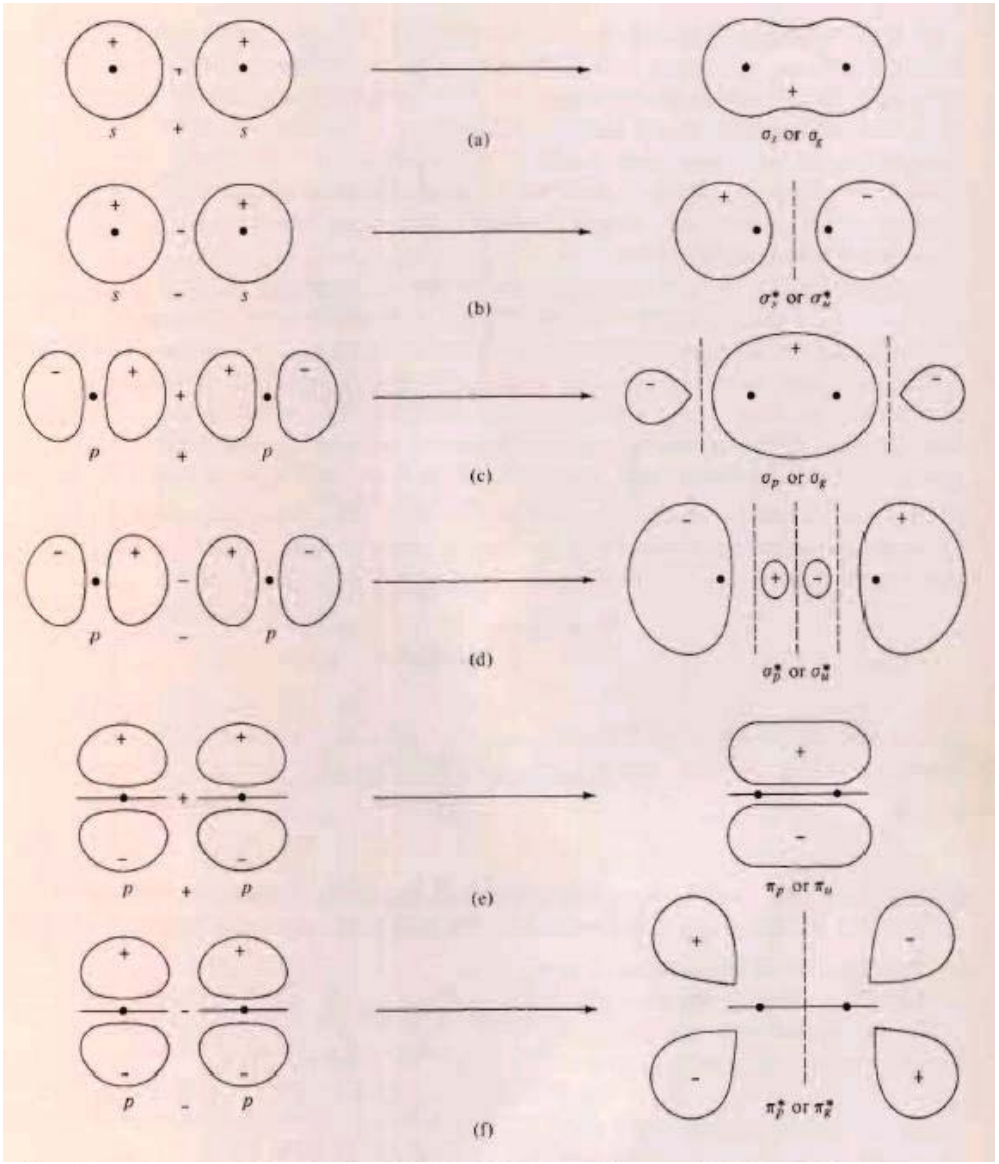
MOT

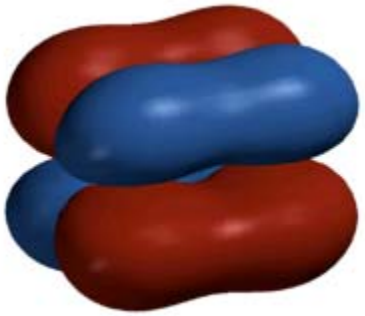


MO Diagram



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

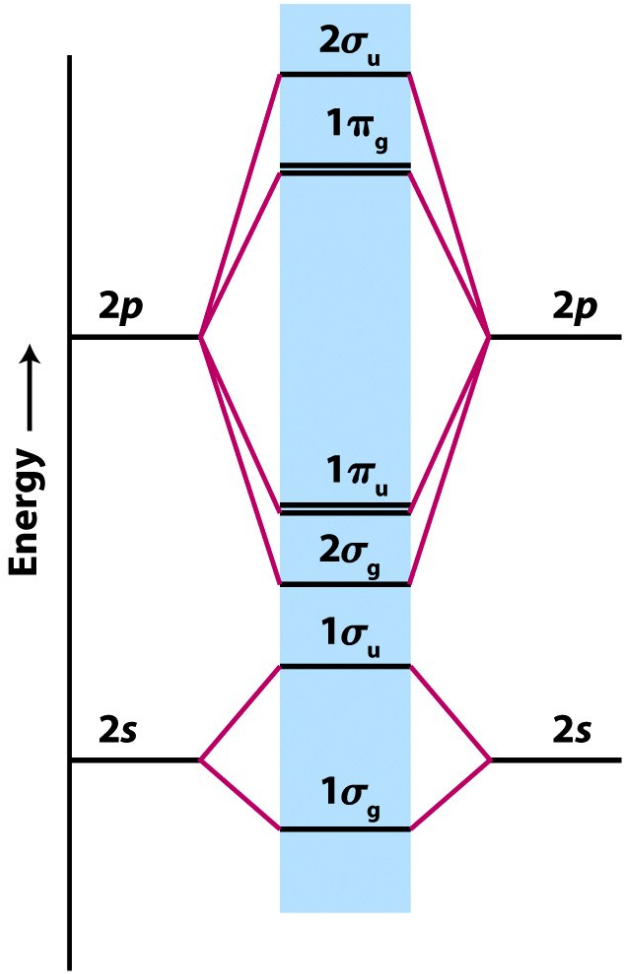


Figure 2-14
Shriver & Atkins Inorganic Chemistry, Fourth Edition

MOT-Homonuclear Diatomics

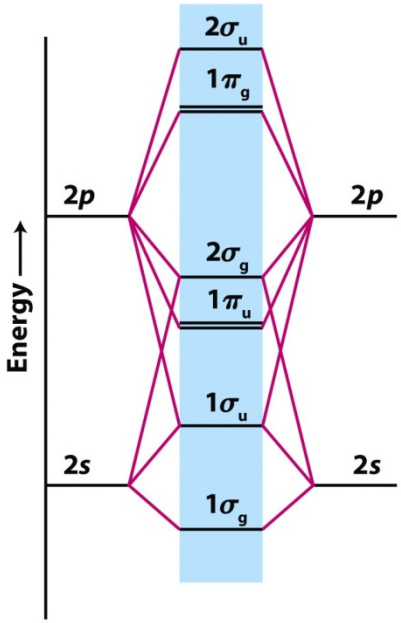


Figure 2-18
Shriver & Atkins Inorganic Chemistry, Fourth Edition

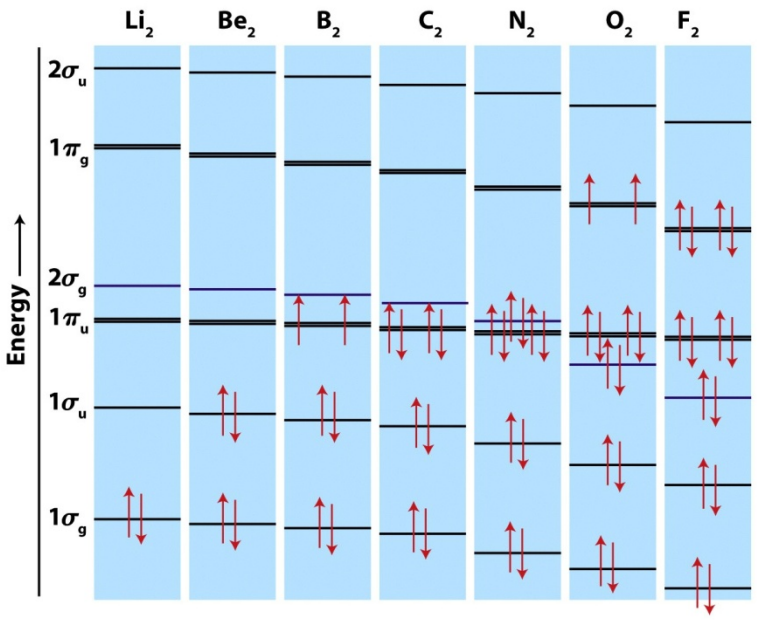


Figure 2-17
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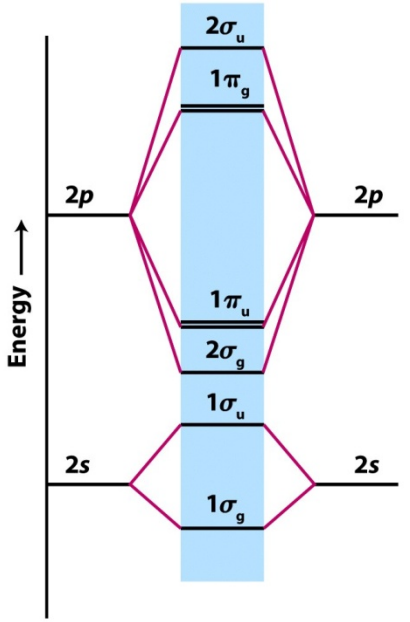
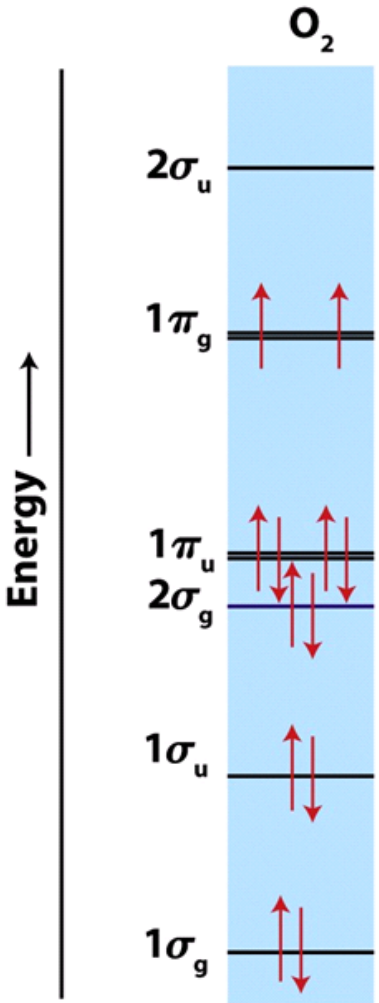


Figure 2-14
Shriver & Atkins Inorganic Chemistry, Fourth Edition

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

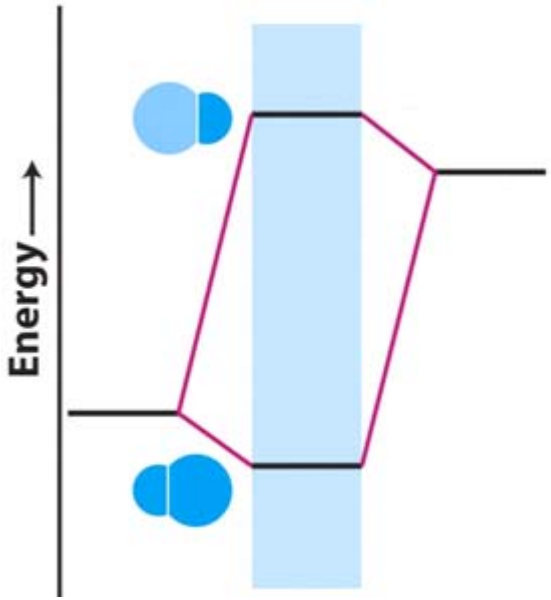
HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital
SOMO = Singly Occupied Molecular Orbital
SLUMO

MOT-Heteronuclear Diatomics

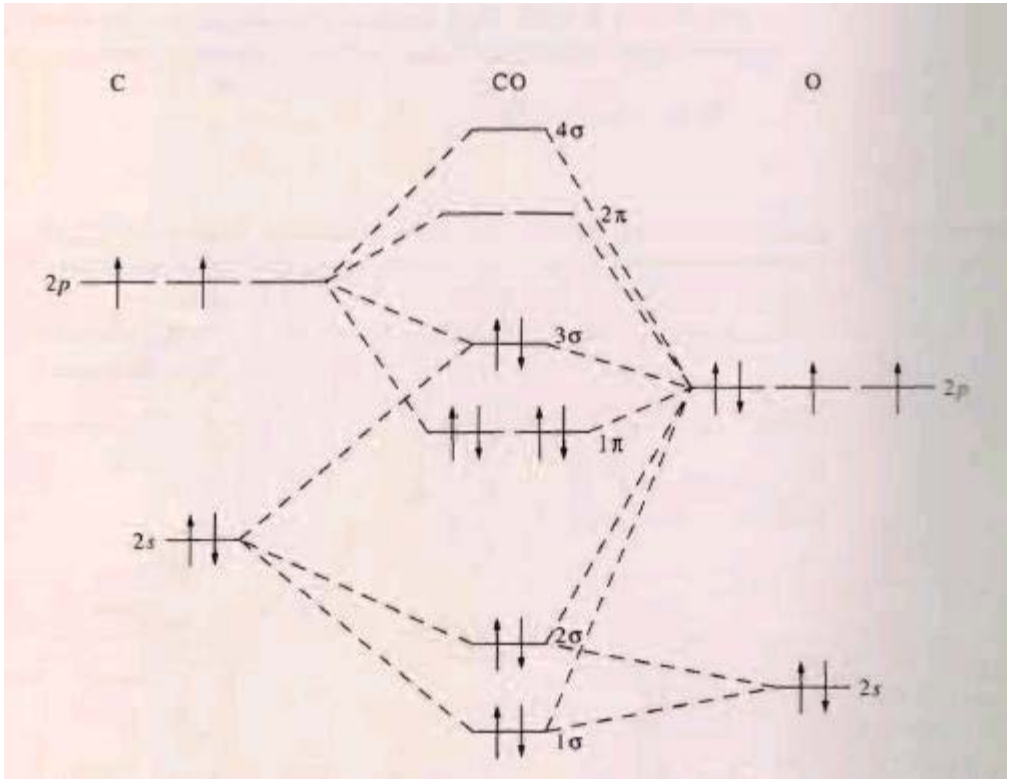
- Differences from Homonuclear case:
  - for $\psi_{bond(1)} = \psi_A + \psi_B$, ψ_A does not = ψ_B
  - Electrons will be drawn to the more electronegative element . Thus bonding orbitals will have more of that element character and antibonding orbitals will have more AO character from the more electropositive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

The molecular orbital will be closer in

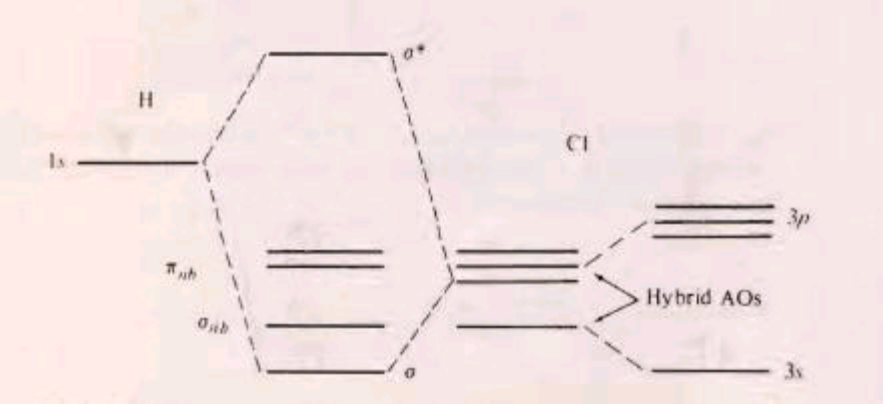
Energy to the AO of A.



Consider CO



Consider HCl



MOT-predicting bond order, bond length and bond strength

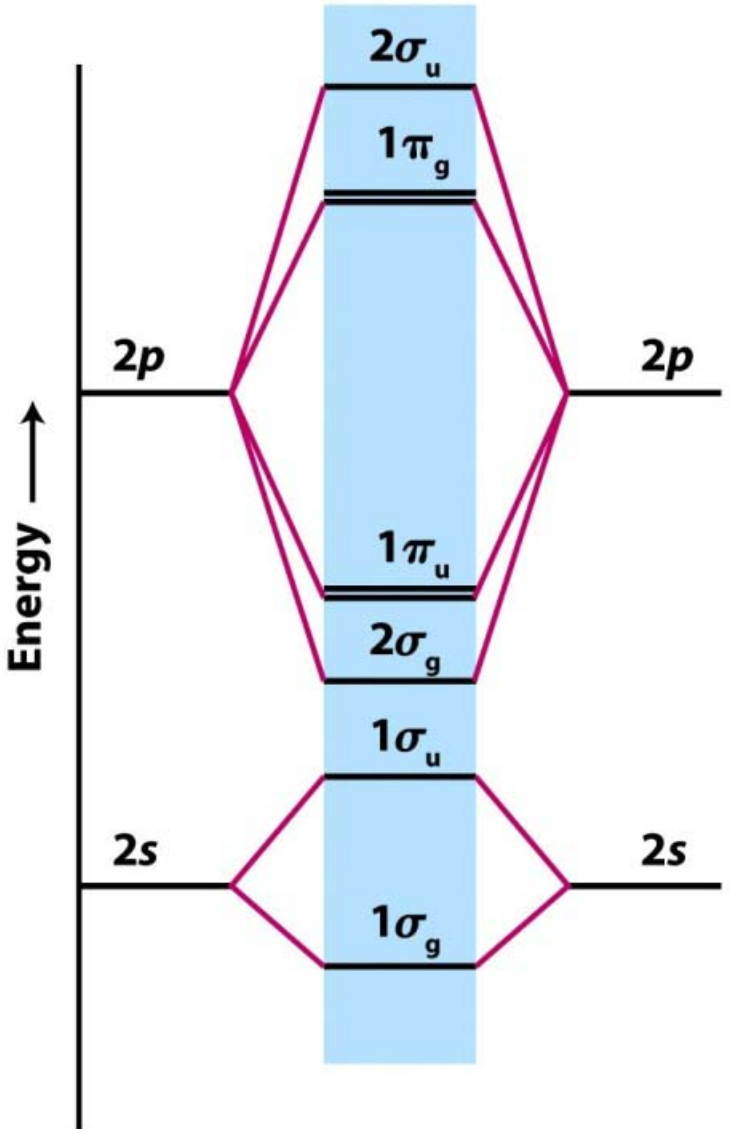
- Consider O_2, O_2^-, O_2^{2-}, O_2^+
- Bond Order b= ½(bond – anti)

$\nu_{o\text{-}o}$ = 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.