The Structure of Molecules
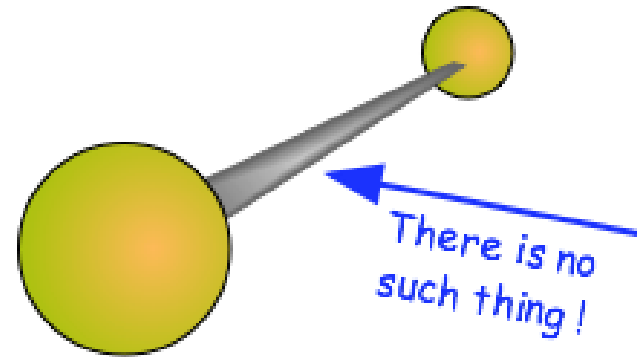
Focus 9

R. N. Behera
Department of Chemistry

The Chemical Bond

A link between atoms?
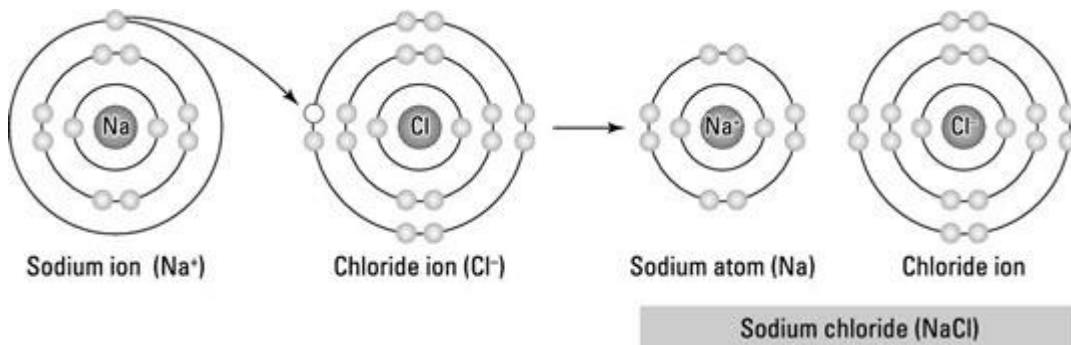
There is no such thing !

- Central to all aspects of Chemistry
- Reactions make them &/or break them

Major approaches for calculation of molecular structure:

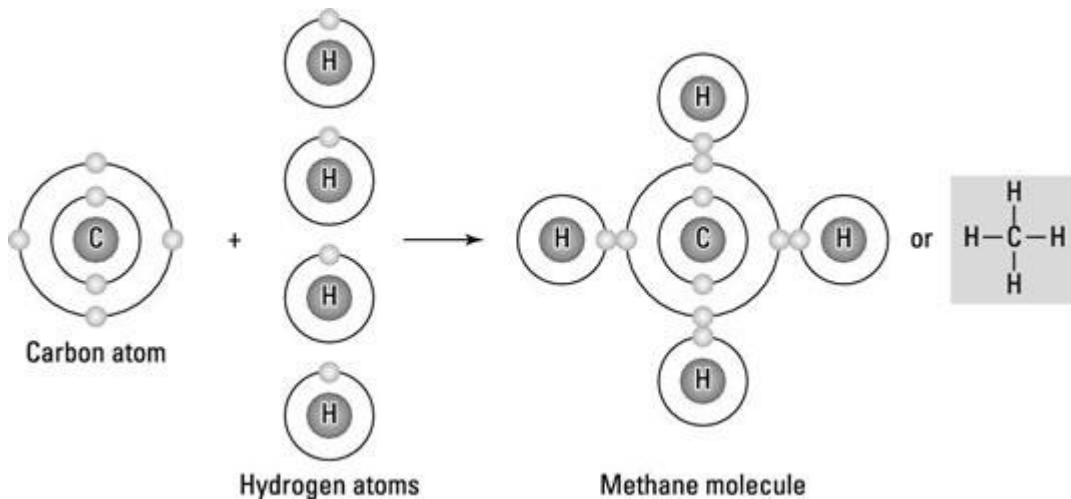- Valence Bond Theory (VBT)
- Molecular Orbital Theory (MOT)

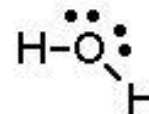# The Chemical Bond: classification

Ionic bond:

Sodium ion (Na⁺)   Chloride ion (Cl⁻)   Sodium atom (Na)   Chloride ion

Sodium chloride (NaCl)

Covalent bond:

Carbon atom   +   Hydrogen atoms   →   Methane molecule

Lewis Concept: Octet rule

Lewis Diagrams

Water H_2O

O =   6 e
H = 2 x 1e = 2e
total =   8e

Carbon Dioxide CO_2

C =   4 e
O = 2 x 6e = 12e
total =   16e
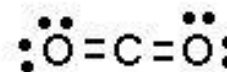
C. Ophardt, c. 2003

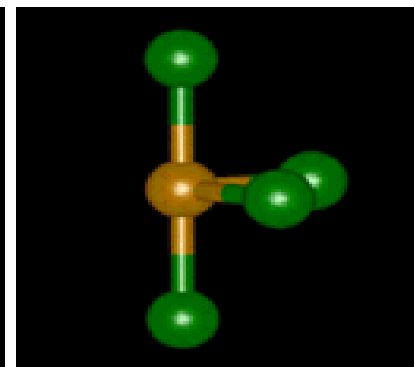## VSEPR model: Shape of Molecules

VSEPR model: Shape of Molecules
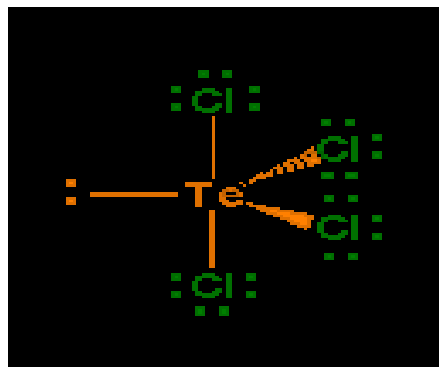
❑ Predicts shape of molecules from Lewis dot structure

❑ The shape of the molecule is determined by repulsion between valence shell electrons (VSE).

❑ Strength of repulsion:

lp-lp > lp-bp > bp-bp;   TB > DB > SB
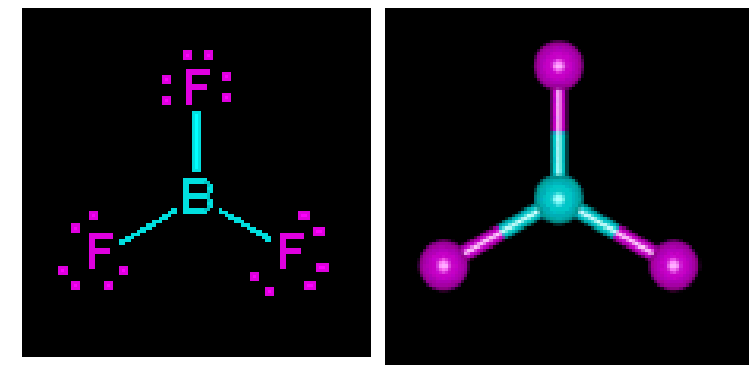
VSEPR model: Shape of Molecules

STRUCTURE   SHAPE   VSE   STRUCTURE   SHAPE   bp+ lp=VSE

H—Be—H
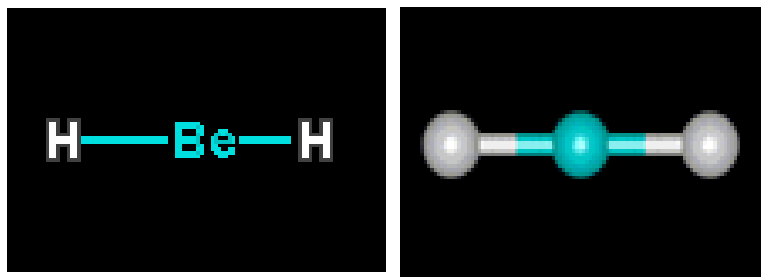
2

4+1=5

3
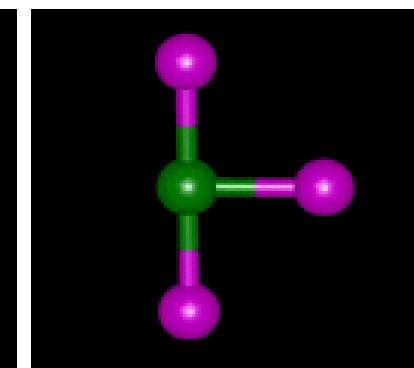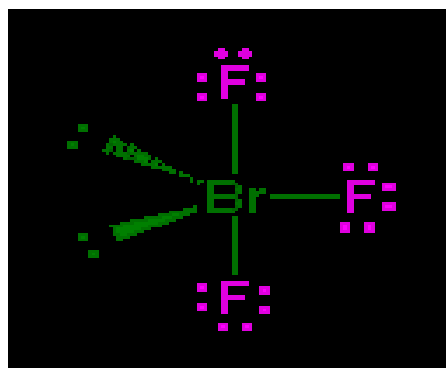
3+2=5
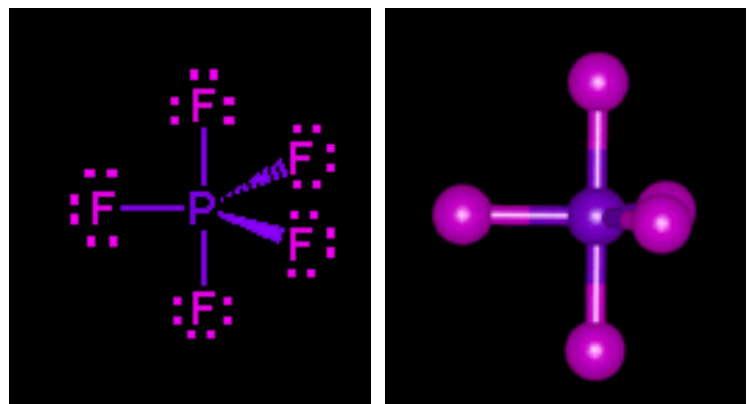
5

2+3=5

Solution of SE for Molecules

Based on **Born–Oppenheimer Approximation:** *nuclei being much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move around them.*

Enable to solve Schordinger equation for the electron alone at a fixed location of nuclei.

R_e: Equilibrium Bond Length
D_e: Depth of the minimum

Potential Energy Surface

The valence bond theory

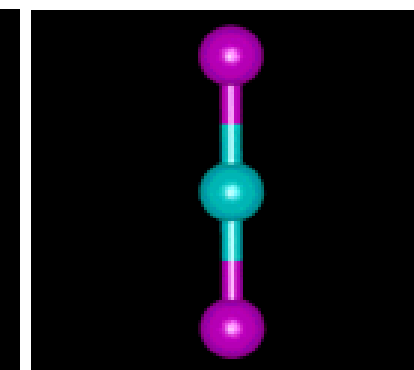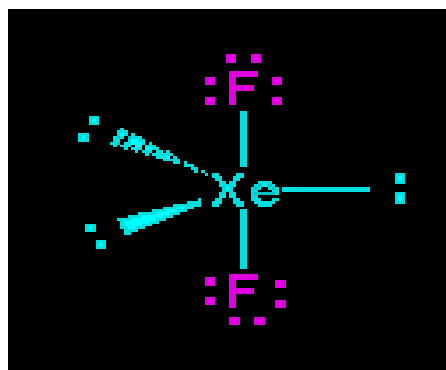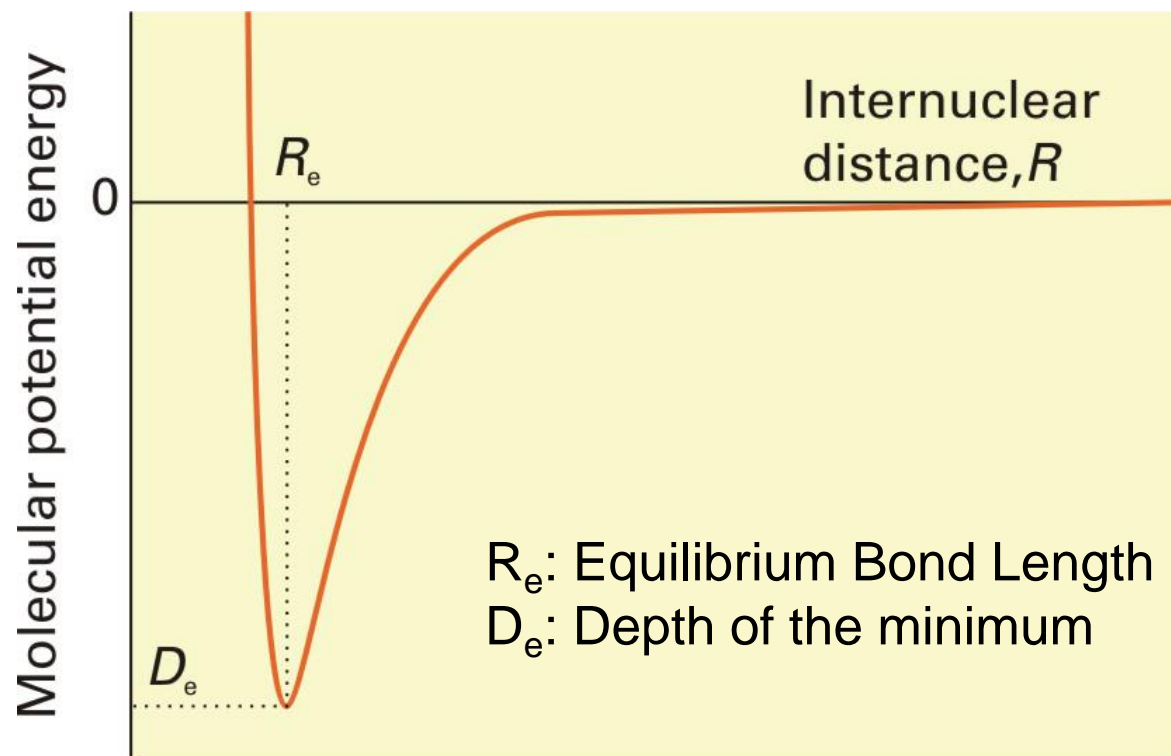*A bond is formed when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on an another atom.*
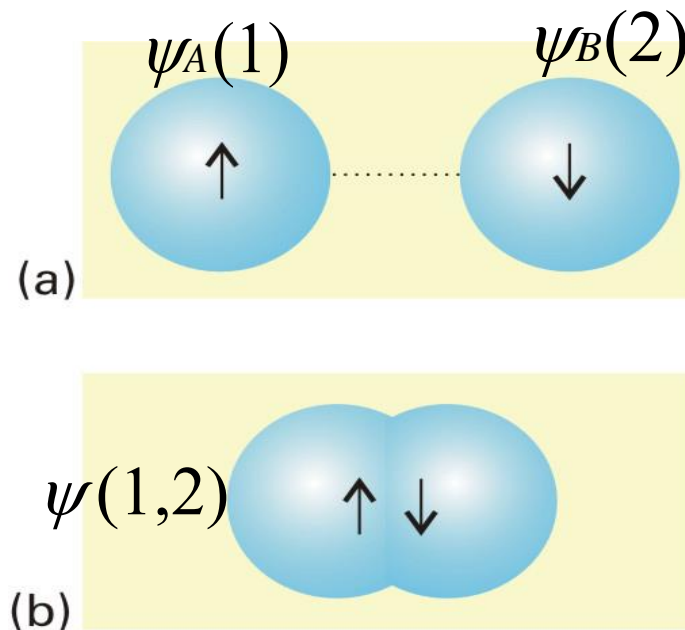
For non-interacting atoms: $\psi(1,2) = \psi_A(1)\psi_B(2)$

Taking indistinguishablity of electron, the (spatial) wavefunction:

$$\psi_{H-H}(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$$

Total Wavefunction : $\psi_{Total} = \psi_{H-H}(1,2) \times \psi_{spin}$

where $\psi_{spin} = \alpha(1)\beta(2) - \beta(1)\alpha(2)$

The valence bond theory

VB Spatial Wave function for an A-B Bond:

$$\psi_{A-B}(1,2) = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$$
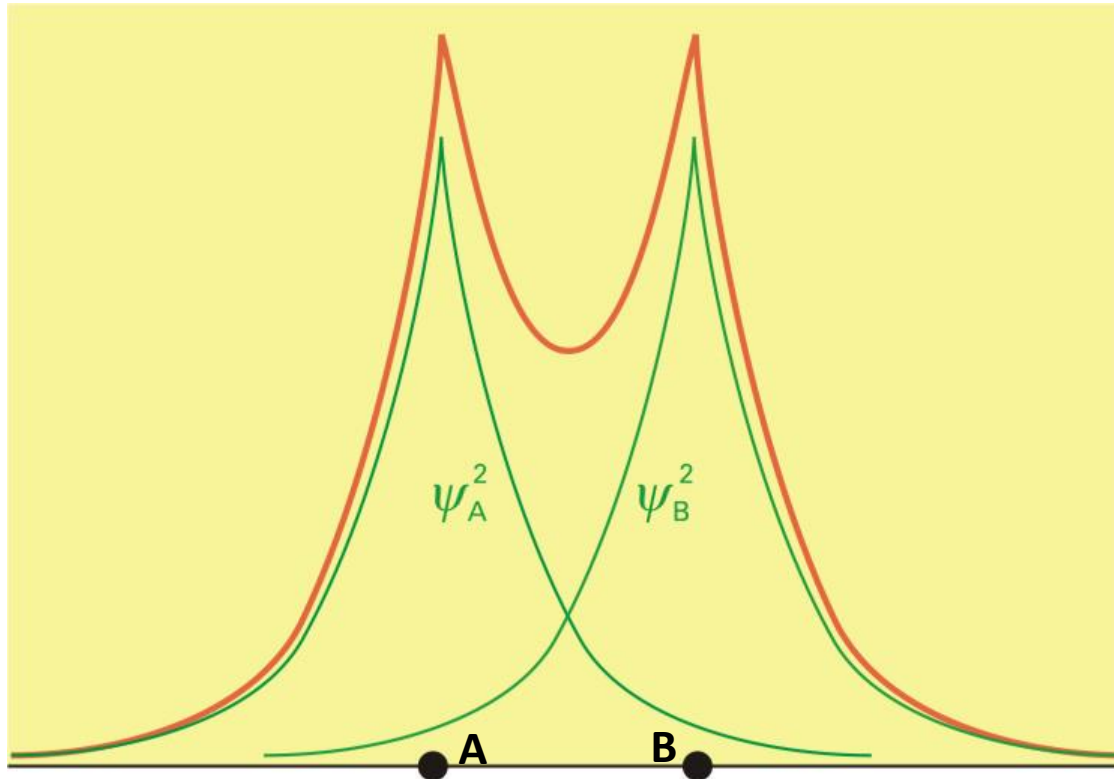
VB Electron Density of H_2

- Accumulation of electron density b/w the two nuclei
- Wave function with cylindrical symmetry (σ-bond)

The valence bond theory of N_2

Valence Electronic configuration: $2s^2 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$

Bonding in N_2

- Nitrogen $2p_z$ orbitals pair

  Cylindrical Symmetry: σ bond

- Nitrogen $2p_x$ and $2p_y$ orbitals

  No cylindrical symmetry: π bond
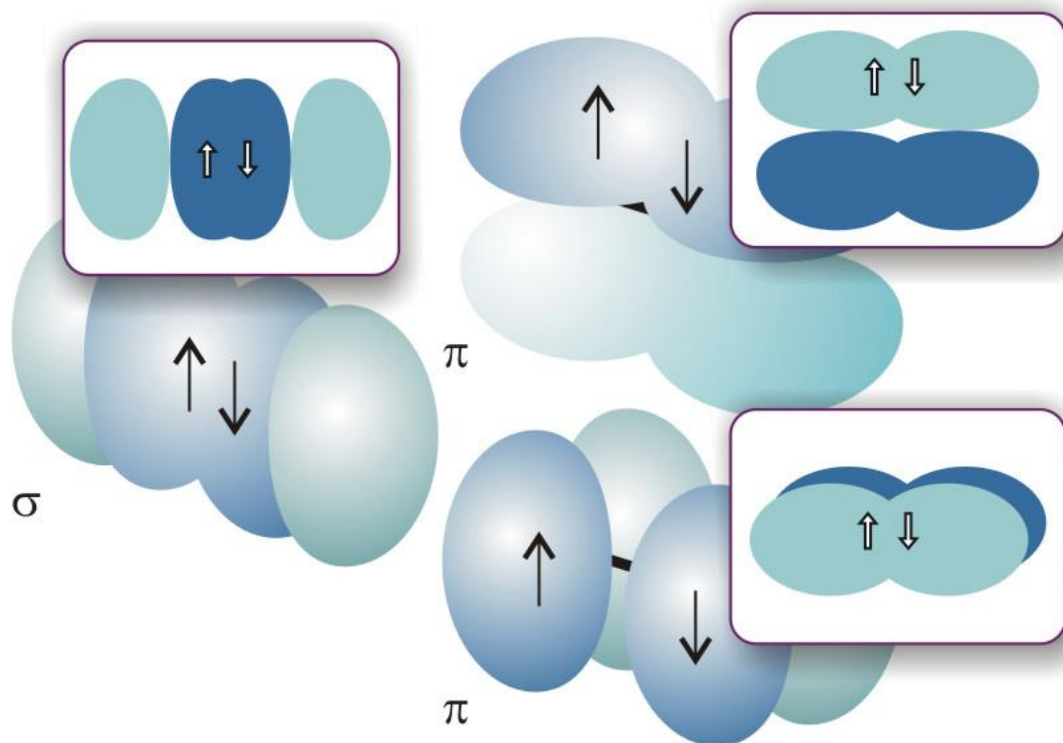
Sigma and Pi bond formation N_2

VB Theory of polyatomic molecules

e.g. H_2O molecule: $O-atom : 2p_x^2 2p_y^1 2p_z^1 + H-atom : 1s^1$

Figure 11-6
Atkins Physical Chemistry, Eighth Edition
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2p orbitals of oxygen form σ bonds with H1s

Predicted bond angle: 90°

Deficiencies of VB

- Poorly estimates bond angle
- Number of bond formation, **e.g. $C(2s^2p^2)$**

VB Theory of polyatomic molecules
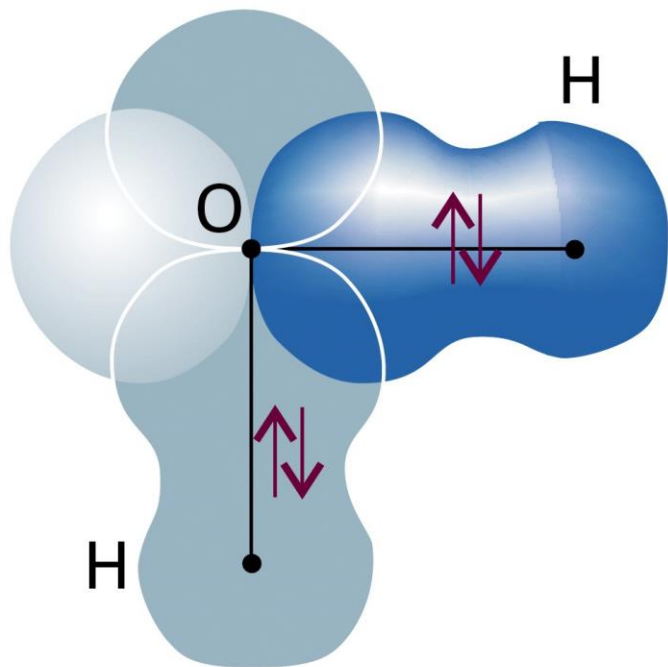
e.g. Methane CH_4 C: $2s^2 2p_x^1 2p_y^1 2p_z^0$
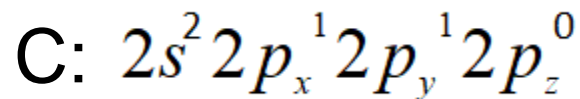
H: $1s^1$ $\Rightarrow$ Two Bonds

- Promotion of one e from 2s to 2p orbital:
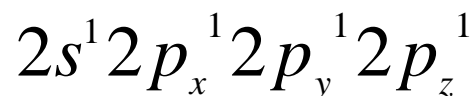
$$2s^1 2p_x^1 2p_y^1 2p_z^1 \Rightarrow \text{Resulting 4 Bonds}$$

- Atomic orbitals inter-mix to give rise four new orbitals called Hybrid orbitals

Intermixing of orbitals: Hybridization

- Promotion of e from 2s to 2p orbital : $2s^1 2p_x^{\ 1} 2p_y^{\ 1} 2p_z^{\ 1}$

- Atomic orbitals inter-mix to give rise four new identical orbitals called Hybrid orbitals

$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y + p_z$$
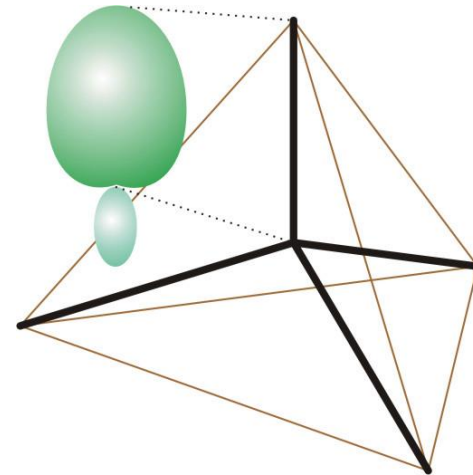
$$h_4 = s + p_x - p_y - p_z$$

(sp^3 hybrid orbitals)

Regular Tetrahedron Formation

σ bond   sp^3 hybrid
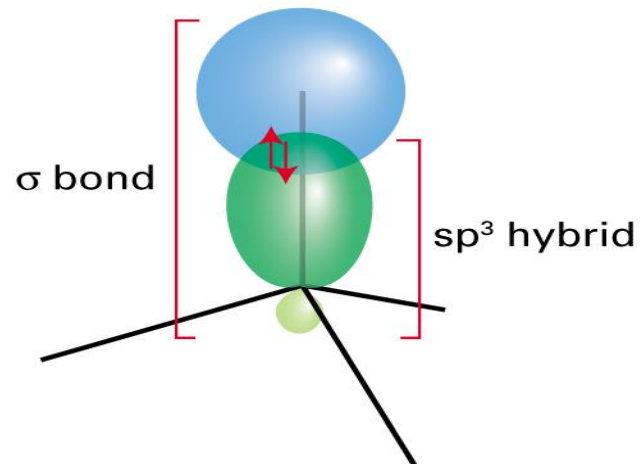
VB Theory of Alkenes

Sp^2 Hybridization; Trigonal Planar; Bond angle: 120°
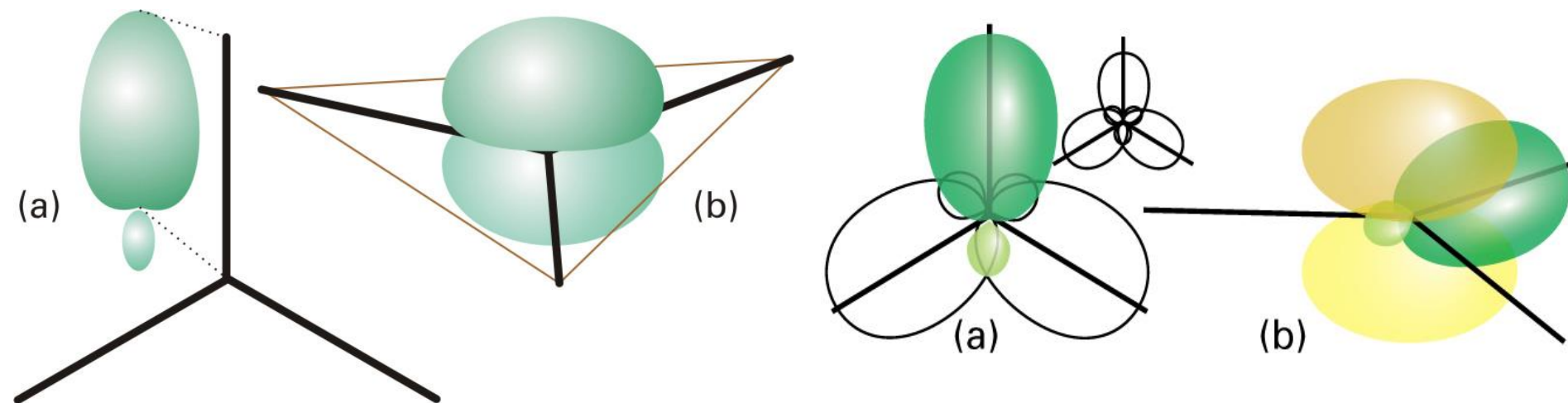
sp^2 hybrid orbitals:

$$h_1 = s + \sqrt{2}\, p_x \quad ; \quad h_{2,3} = s \pm \sqrt{(3/2)}\, p_x - \sqrt{(1/2)}\, p_y$$

- The coefficients indicates directional properties
- Squares of the coefficients indicates proportion of atomic orbitals

VB Theory of Alkynes

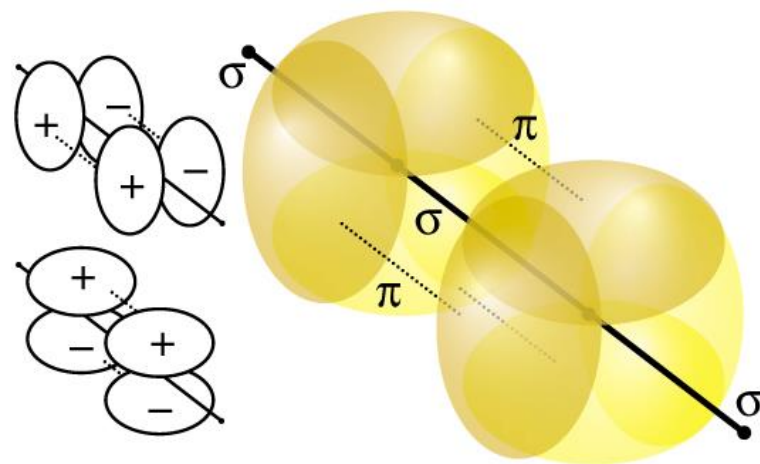Sp Hybridization; Linear;
Bond angle: 180°

$$h_{\frac{1}{2}} = s \pm p_z$$

Two π bonds perpendicular
to molecular axis

Hybridization: summary

Number	Shape	Hybridization*
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

Hybridization of N atomic orbitals always results in the formation of N hybrid orbitals.

* Other combinations are possible.

Resonance

For purely covalent *H–Cl*: $\psi_{H-Cl}(1,2) = \psi_H(1)\psi_{Cl}(2) + \psi_H(2)\psi_{Cl}(1)$

For Ionic *H⁺Cl⁻*: $\psi_{H^+Cl^-}(1,2) = \psi_{Cl}(1)\,\psi_{Cl}(2)$

Superposition of ionic & covalent H–Cl: $\psi_{HCl} = \psi_{H-Cl} + \lambda\psi_{H^+Cl^-}$

$$\text{In General, } \psi = \psi_{\text{covalent}} + \lambda\,\psi_{ionic}$$

λ^2 denotes proportion of Ionic Contribution: smaller λ implies lesser ionic (or greater covalent) character of ψ

The superposition of wave functions with different electron distributions in the same nuclear framework is called **Resonance**
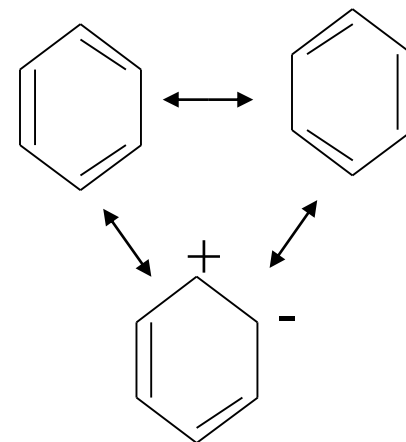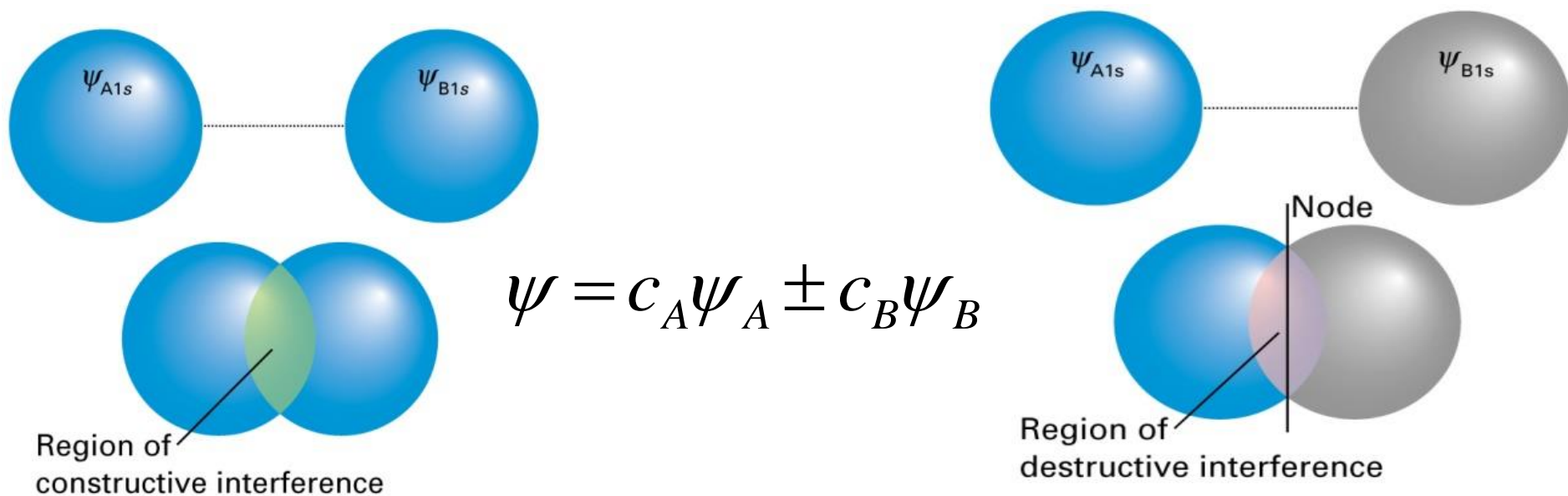
VBT: summary

❑ **The names of bond types:** σ and π bonds are formed by spin pairing of electrons and are distinguished by their symmetry around the interneuclear axis.

❑ **Promotion:** valence electrons may be promoted to empty orbitals if overall that results in lowering energy.

❑ **Hybridization:** atomic orbitals may be hybridized to match the observed geometry of the molecules.

❑ **Resonance:** the superposition of individual structures distributes multi-bond character over the molecules and lowers the overall energy.

Molecular Orbital Theory

-Electrons spread through out the entire molecule

-Every electron contributes to the strength of every bond

The ψ of the molecule is written as the Linear Combinations of Atomic Orbitals (LCAO)

$$\psi = c_A \psi_A \pm c_B \psi_B$$

ψ_{A1s} ψ_{B1s}

Region of constructive interference

ψ_{A1s} ψ_{B1s}

Node

Region of destructive interference

$C_A{}^2$ and $C_B{}^2$ are proportion of AO corresponding to MO

MO Theory of Diatomics

For Homonuclear diatomics, $C_A{}^2 = C_B{}^2$

$$\psi = \psi_A + \psi_B \; (Bonding)$$
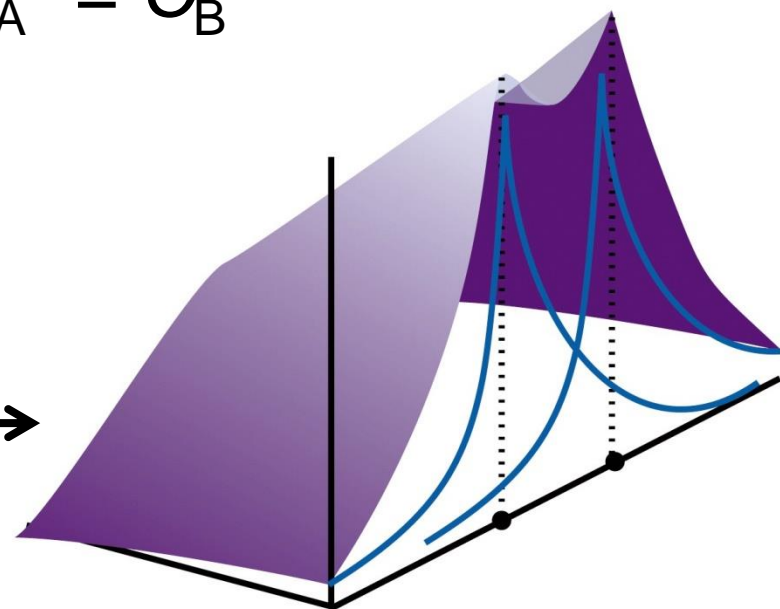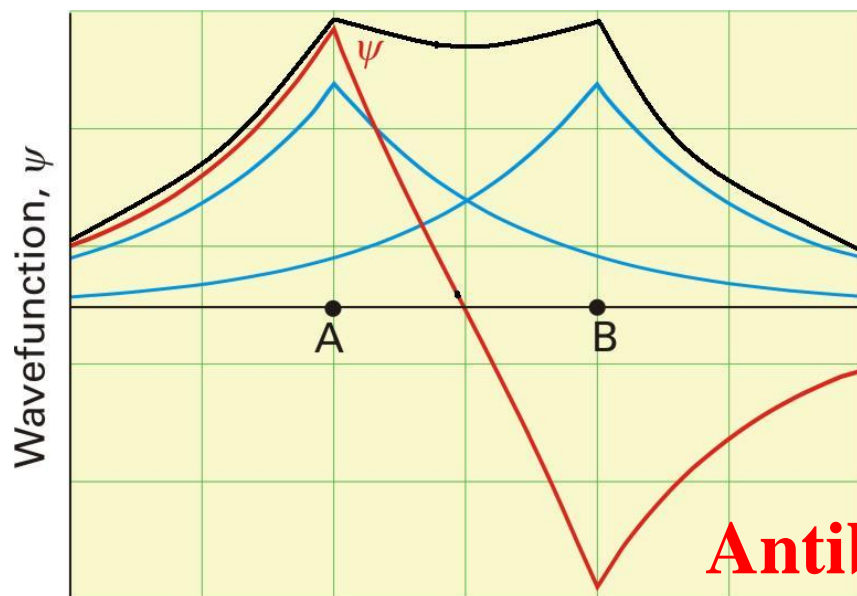
$$\psi = \psi_A - \psi_B \; (Antibonding)$$

Bonding $\longrightarrow$

Figure 11-13a
Atkins Physical Chemistry, Eighth Edition
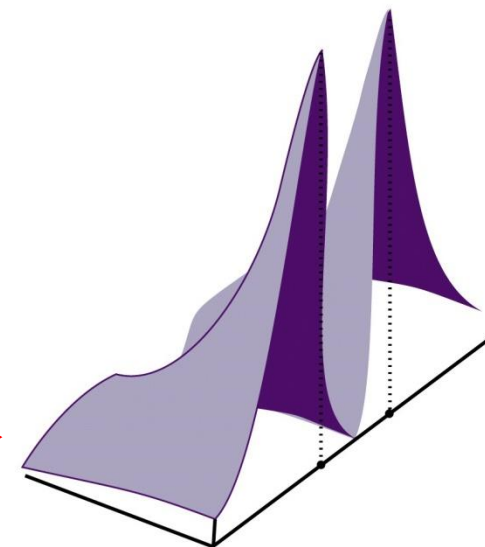© 2006 Peter Atkins and Julio de Paula

Antibonding $\longrightarrow$

Figure 11-20
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Orbital Symmetry

Bonding

$$\psi = \psi_A + \psi_B$$
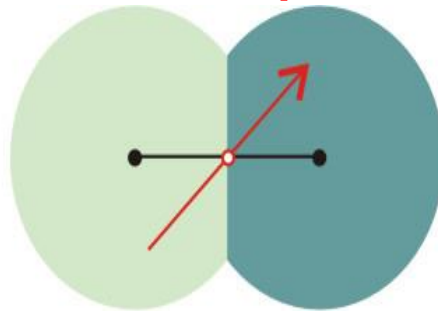
Antibonding

$$\psi = \psi_A - \psi_B$$

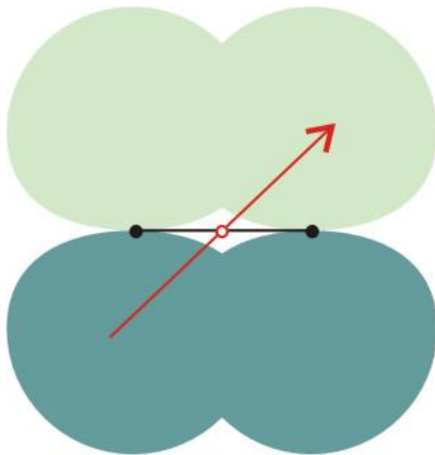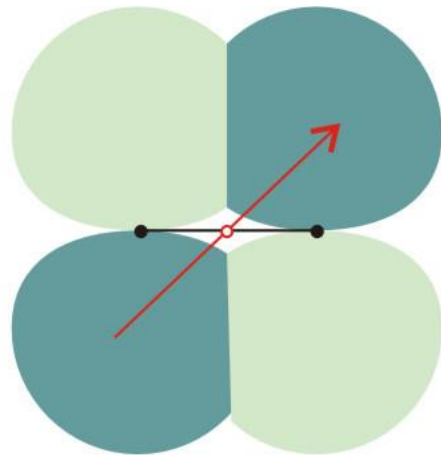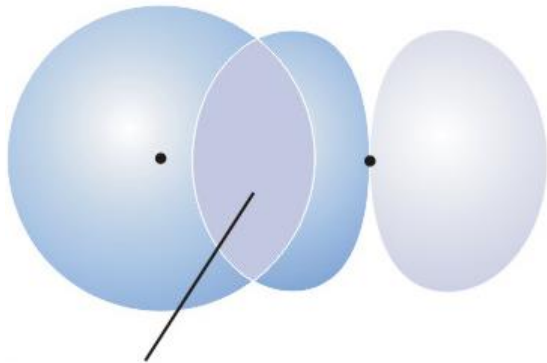**(For s-s combination)**
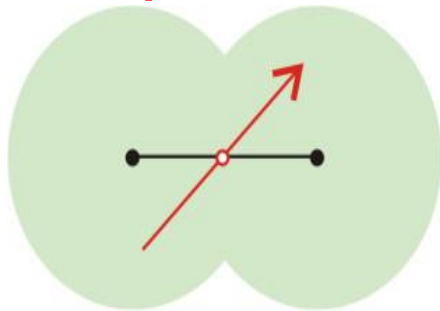
Inversion Symmetry

- Identical sign of Ψ (Gerade Symmetry)
- Opposite sign of Ψ, (Ungerade Symmetry)

(For p-p combination)
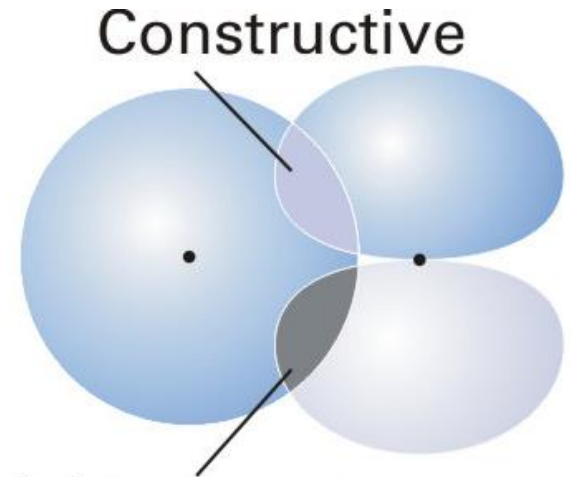
Symmetry and Overlap
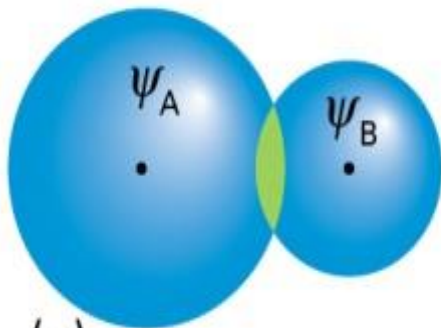
e.g. S and p overlap
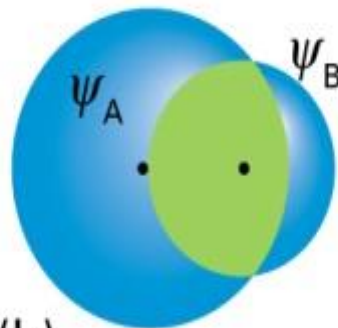

(a) Constructive

Constructive

(b) Destructive

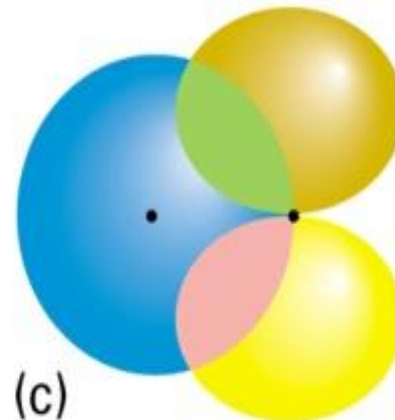- non-zero overlap
- axially symmetric σ orbital

- No net overlap
- No bonding

(a)   (b)   (c)

Overlap Integral
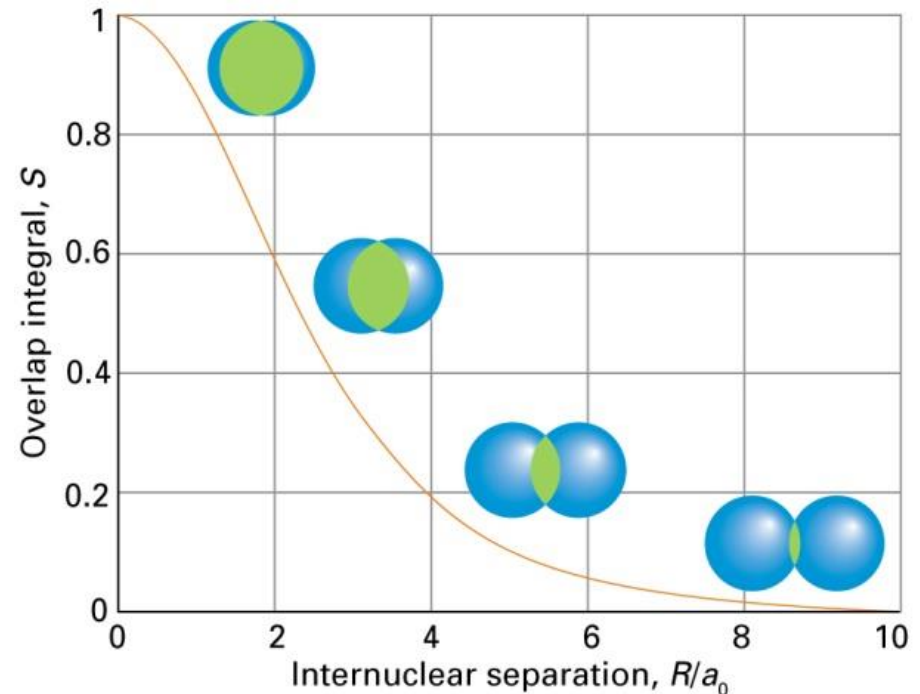
The extent of overlap b/w two orbitals Ψ_A and Ψ_B is given by the overlap Integral S:

$$S = \int \psi_A \psi_B d\tau$$

$$d\tau = \mathrm{dxdydz}$$
$$= r^2 \,\mathrm{drsin}\theta d\theta d\phi$$

The overlap Integral b/w two H1s orbitals separated by R:

$$S = \left\{ 1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2 \right\} e^{\frac{-R}{a_0}}$$

Building up molecules

- **C**onstruct MO by LCAO of all suitable valence atomic orbitals.

  N atomic orbitals results in N molecular orbitals

- **A**ccommodate the valence electrons supplied by the atoms so as to achieve the lowest overall energy subject to Pauli exclusion principle

- **I**f more than one molecular orbital of the same energy is available, add the electrons to each individual orbital before doubly occupying any one orbital (Hund's rule)

Structure of homonuclear diatomics

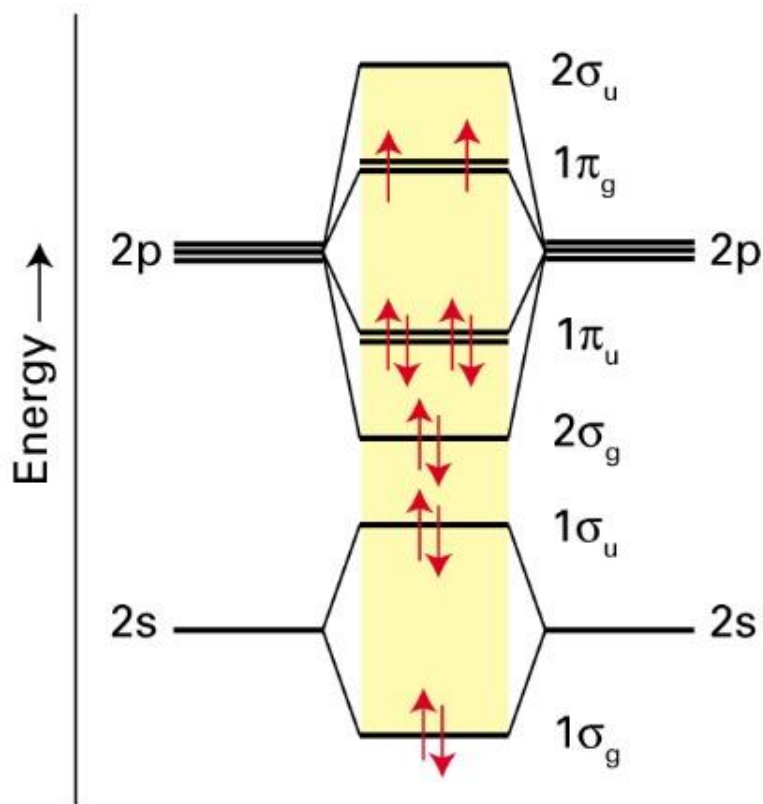Two atomic orbitals (*AOs*) forms two molecular orbitals (*MOs*): 1σ (bonding) and 1σ* (anti-bonding).
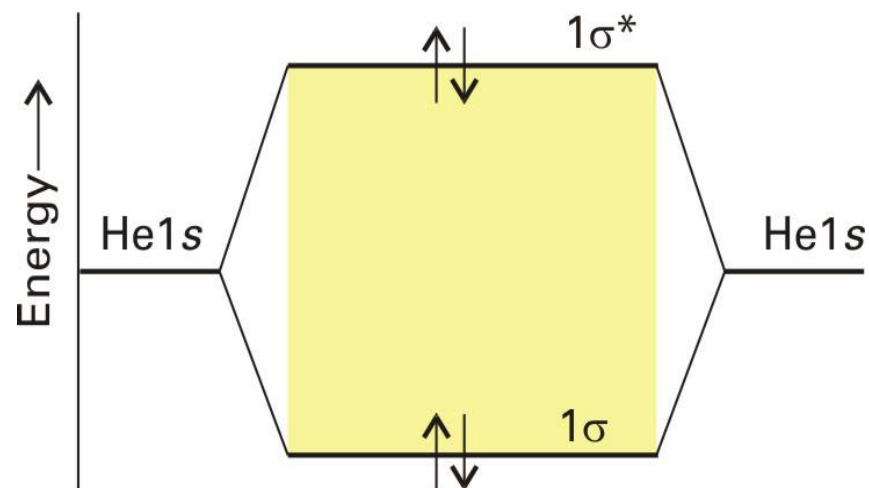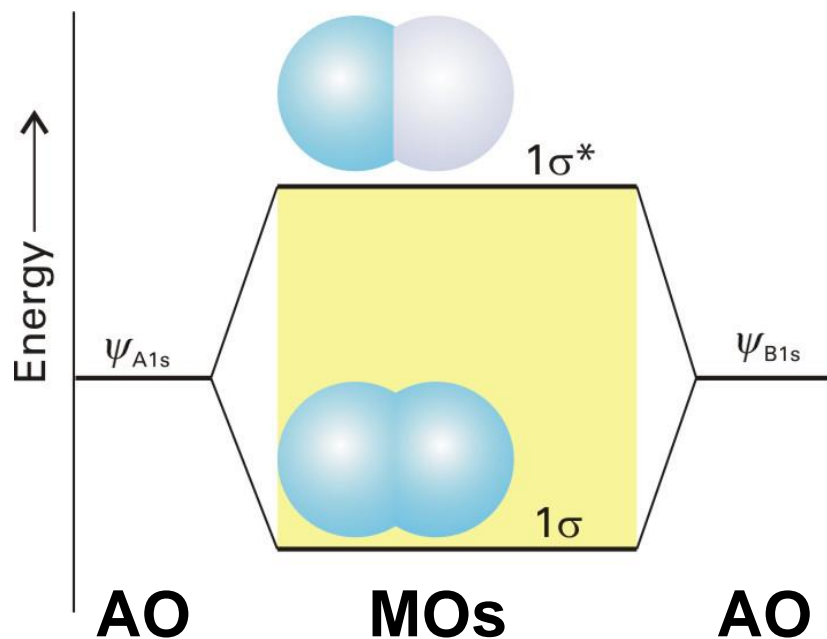
The energy gain while occupying the 1σ* is more than the energy lowering in occupying the 1σ. Thus, Helium atoms do not form a bond.

Structure of homonuclear diatomics

AOs on A or B of $2s$ and $2p$:

$$\psi = c_1 \psi_{A2s} + c_2 \psi_{B2s} + c_3 \psi_{A2p_z} + c_4 \psi_{B2p_z} + \cdots \text{(LCAO)}$$

Electronic Configuration of O_2

- No. of Valence Electrons: 12
- Ground-State

  $1\sigma_g^2\, 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2 1\pi_g^2$

- Bond Order

  b= (½)(n-n*)   (For O_2 , b=2)
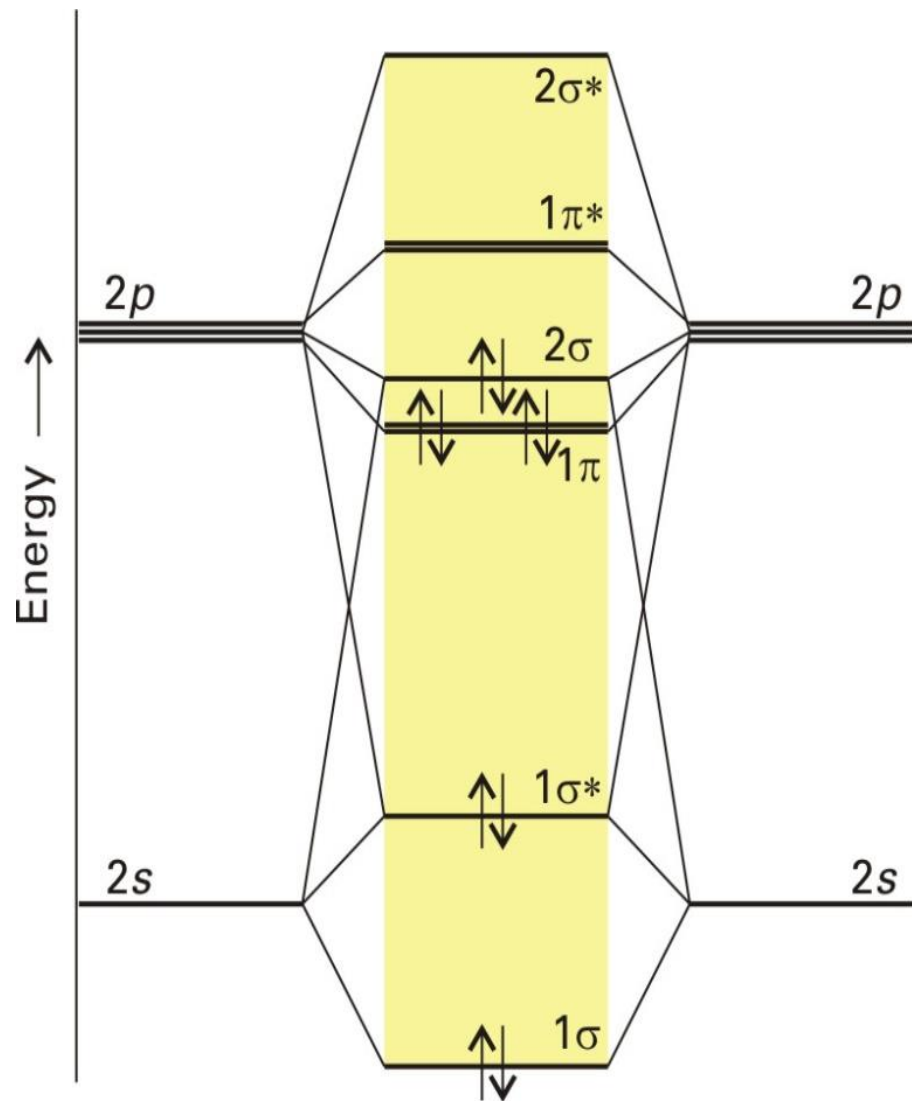
Configuration of B_2 and C_2

No. of Valence Electrons: 6 & 8

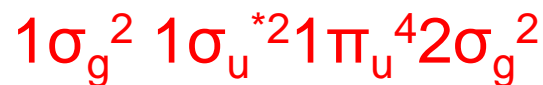B_2 : diamagnetic ?

C_2 : paramagnetic ?

However, B_2 is paramagnetic while C_2 is diamagnetic !

Structure of homonuclear diatomics

Electronic Configuration of N_2

- No. of Valence Electrons: 10
- Ground-State

  $1\sigma_g^2 \, 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2$

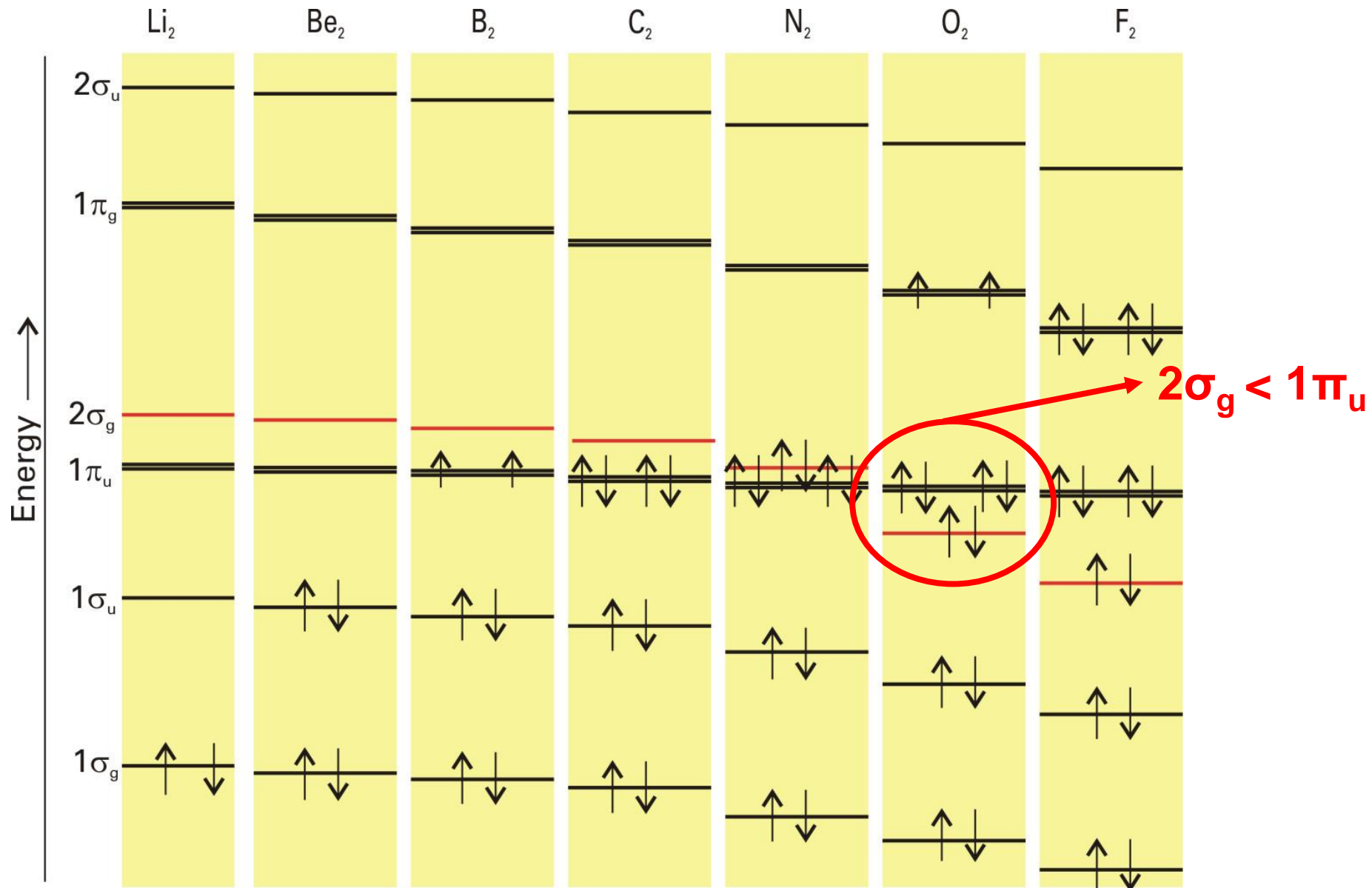- Bond Order

  b= (½)(n-n*)   (For N_2 , b=3)

Correctly explain the configuration of B_2 and C_2

No. of Valence Electrons: 6 & 8

B_2 is paramagnetic

C_2 is diamagnetic

Variation of orbital energies

Heteronuclear diatomics

The bonding electron pair is shared unequally by two atoms resulting Polar Bond. e.g: CO and HCl

LCAO gives

$$\psi = c_A \psi_A \pm c_B \psi_B$$

with $c_A^2 \neq c_B^2$

Relative Contribution of Atoms in a Polar Bond

Polarity depends on electronegativity (χ)

$For\ \chi_A > \chi_B :$

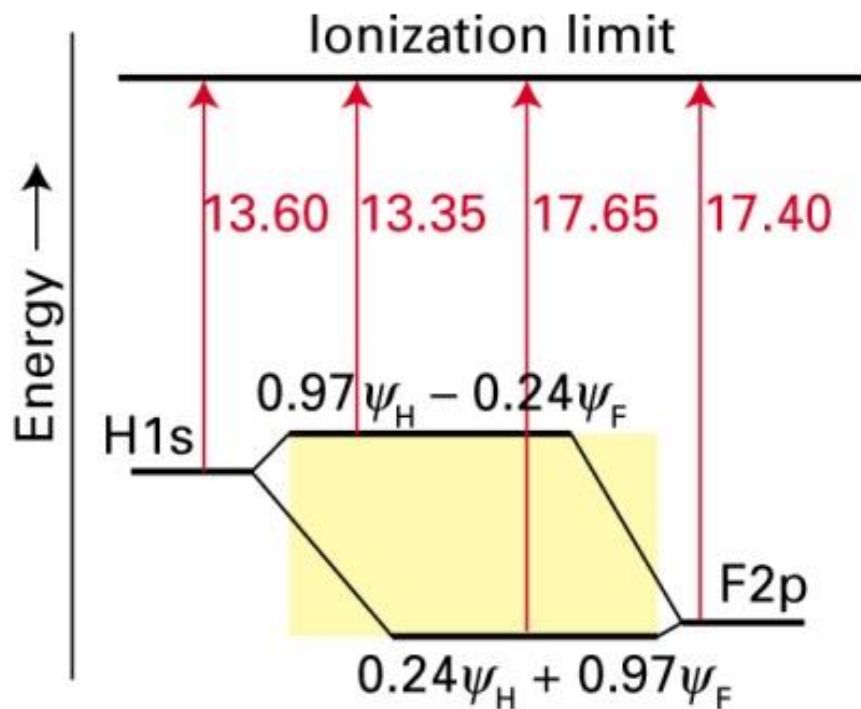$$c_A^2 > c_B^2\ (bonding),\ c_A^2 < c_B^2\ (antibonding)$$

Electronegativity Scale

Pauling: $|\chi_A - \chi_B| = [D_0(AB) - 1/2\{D_0(AA) + D_0(BB)\}]^{1/2}$

Mulliken: $\chi = 0.5(I + E_{ea})/eV$

MO Diagrams: HF & CO

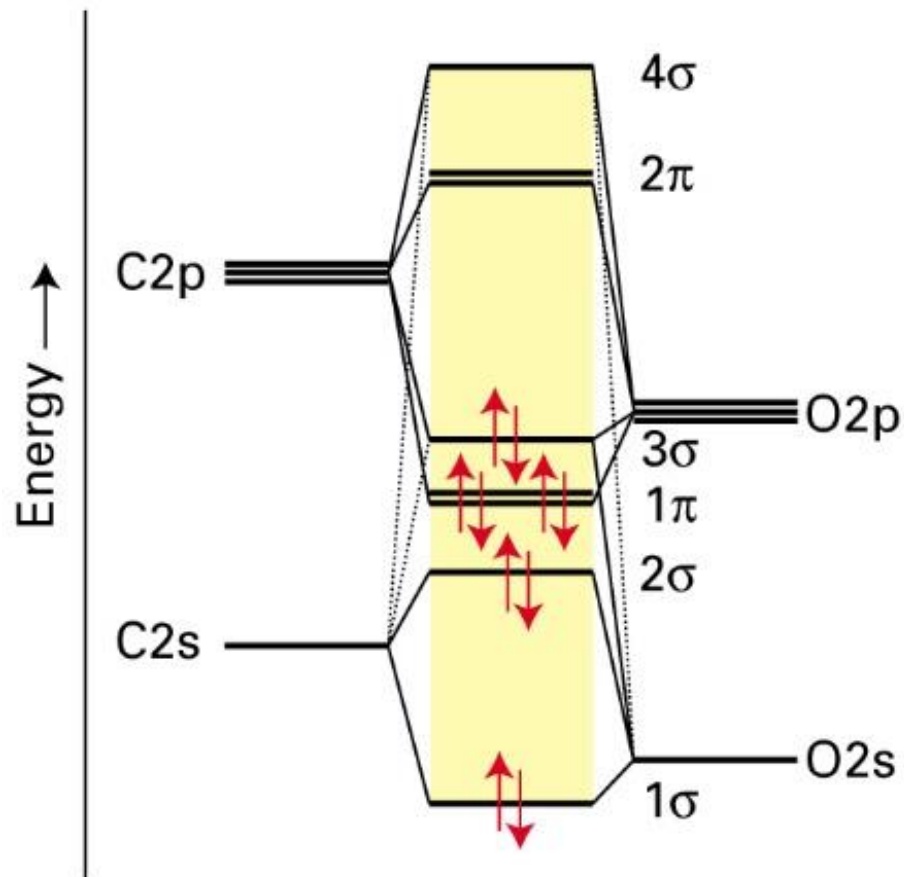Ionization limit

13.60 13.35 17.65 17.40

H1s

$0.97\psi_H - 0.24\psi_F$

F2p

$0.24\psi_H + 0.97\psi_F$

C2p

C2s

4σ

2π

O2p

3σ

1π

2σ

O2s

1σ

Atom having higher electronegitivity have usually higher ionization energy

HOMO: 3σ (nb) on C

LUMO: 1π (2p) mostly on C

Forms many carbonyl compounds