CHEM F111 : General Chemistry
Semester II: AY 2017-18

Lecture-11, 05-02-2018

Notice: Assignment Test-01

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI
II Semester, 2017-2018

Course No.: CHEM F111 Course   Title: General Chemistry

Seating arrangement for Assignment-01 Test

Date: 08-02-2018   Time: 17.30 hrs.

Tutorial Section	Room No	Invigilator
T-1	3249	Dr. Anil Kumar
T-2	3250	Dr. Paritosh Shukla
T-3	3215	Dr. Shamik Chakraborty
T-4	3156	Dr. Inamur R. Laskar
T-5	3253	Dr. Rajeev Sakhuja
T-6	3158	Dr. Madhushree Sarkar
T-7	3247	Dr. Bibhash R. Sarkar
T-8	3201	Dr. Surojit Pande
T-9	3248	Dr. Subit K. Saha
T-10	3203	Dr. Saumi Ray
T-11	3160	Dr. Indresh Kumar
T-12	3245	Dr. Ajay K. Sah

Syllabus: L-4 to L-12

Notice: Extra Class

For Lecture Section-01 (Morning class: 10.00 – 10.50 hrs)

Purpose: To discuss remaining portion of L-10

Date: **05-02-2018**

Time: 17.15 hrs

Room No: 5106

For Lecture Section-02 (Afternoon class: 14.00 – 14.50 hrs)

Purpose: To discuss remaining portion of L-10

Date: **06-02-2018**

Time: 17.15 hrs

Room No: 5106

Notice: Extra Class

## For Tutorial Section-08 (Thursday class: 3.00 – 3.50 hrs)

Date: **05-02-2018**

Time: 17.10 hrs

Room No: 3253

Summary: Lecture 10

- Stern-Garlach experiment: Intrinsic spin of electron
- Spin quantum number: $s = \frac{1}{2}$;
- Spin magnetic quantum number: $m_s = \pm \frac{1}{2}$
- Magnitude of spin angular momentum: $\sqrt{s(s+1)}\,\hbar$
- Z-component of spin angular momentum: $S_Z = \pm \frac{1}{2}\,\hbar$
- Possible spin states with $s = \frac{1}{2}$ is two (α, β)
- Spin multiplicity: $(2s+1)$

$m_s = +\frac{1}{2}$ $\quad \frac{\sqrt{3}}{2}\,\hbar$

$m_s = -\frac{1}{2}$ $\quad \frac{\sqrt{3}}{2}\,\hbar$
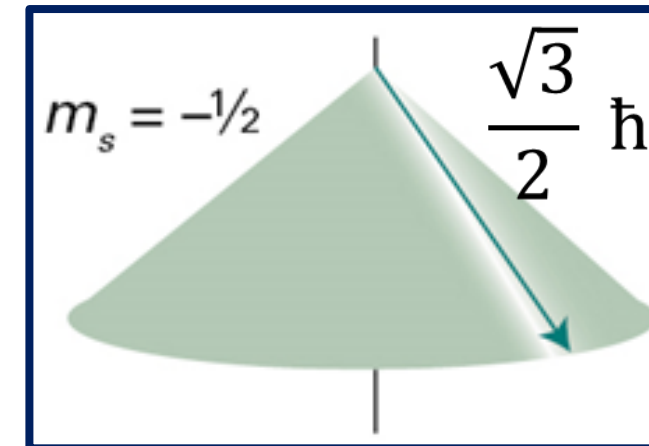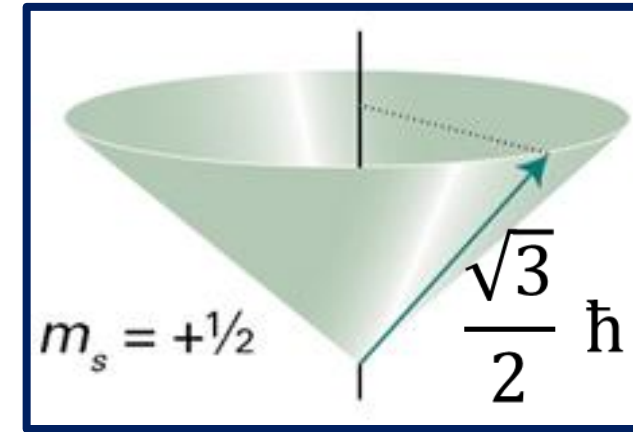
We can consider normalized linear combination:

$$\frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) \pm \beta(1)\alpha(2) \right]$$

Spin orbitals:

$\psi(1,2) = \phi(1)\phi(2)\ \alpha(1)\alpha(2)$

$\psi(1,2) = \phi(1)\phi(2)\ \beta(1)\beta(2)$

$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\ \{\ \alpha(1)\beta(2) + \beta(1)\alpha(2)\ \}$

Symmetric

$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\ \{\ \alpha(1)\beta(2) - \beta(1)\alpha(2)\ \}$

Anti-symmetric

Orbital and spin angular momenta

Are they independent?

Magnetic moment from spin

Electron has spin angular momentum

Moving charges generate magnetic fields

Magnetic field generated from spin

Magnetic moment from orbital angular momentum

Electron has orbital angular momentum ($l>0$)

In effect a circulating current

Magnetic field generated from orbital momentum

Spin orbit coupling/interaction

- Spin-orbit coupling is a magnetic interaction between spin and orbital magnetic moments.

- Total angular momentum of an electron - quantum number j.
- Z-component of total angular momentum – quantum number m_j.

$$j = l + s$$
High j

High energy

$$j = l - s$$
Low j

Low energy
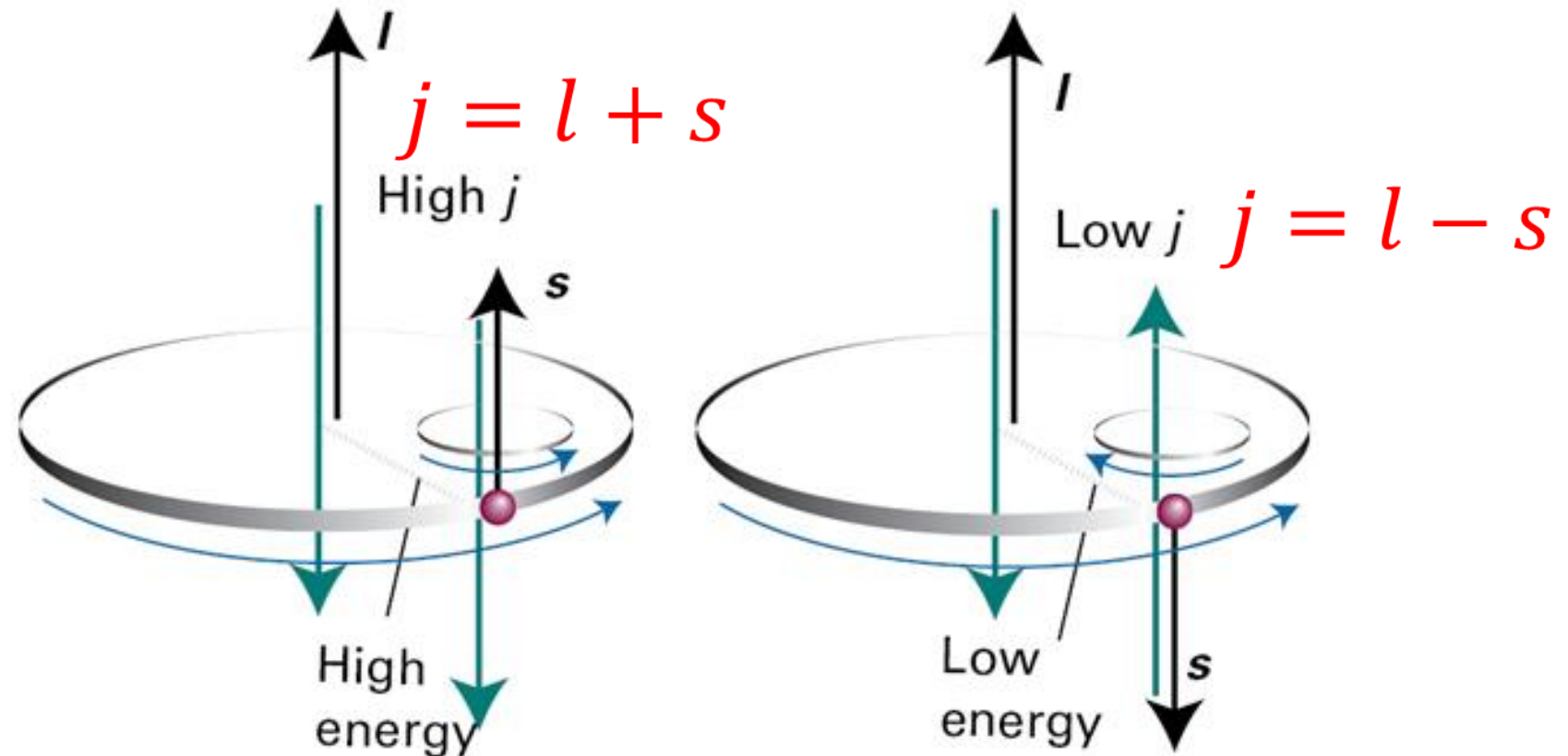
Spin-orbit coupling energy

Energy of the spin-orbit coupling depends on

$E \propto \{j(j+1) - l(l+1) - s(s+1)\}$

For electron, s= ½; $E \propto \{j(j+1) - l(l+1) - ½(½+1)\}$

If orbital ang. momentum is zero *l* =0, *j = s =*½

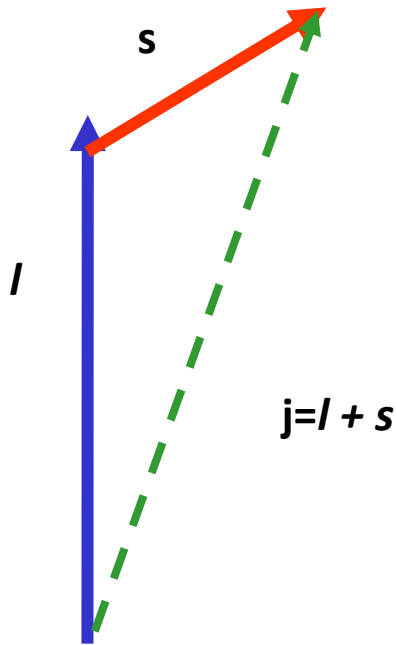$E \propto \{j(j+1) - l(l+1) - s(s+1)\} = \{½(½+1) - 0 - ½(½+1)\} = 0$

No spin orbit coupling.

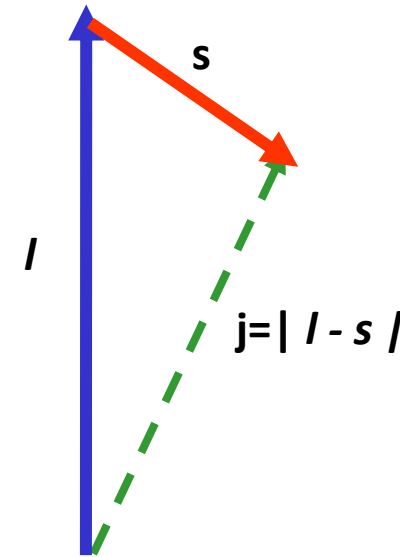In other cases, coupling can happen : energy will vary: different levels

Spin orbit interaction – one electron

Two angular momenta adding

s

l

j=*l* + s

Total angular momenta

j = |*l* ± *s*|

Two angular momenta opposing

s

l

j=| *l* - s |

For an *s*-electron: *l* = 0, s = 1/2; j = 1/2 only
For a *p*-electron: *l* = 1, s = 1/2; j = 3/2 or 1/2
For a *d*-electron: *l* = 2, s = 1/2; j = 5/2 or 3/2

Term symbols

A term represents the energy level of an atom.

The notation used to specify a term is called term symbol.

A term symbol tells us about the angular momentum of the electrons in the atom and it looks like

$$^{2S+1}L_J$$

Here, S = Total spin angular momentum quantum number.

L = Total orbital angular momentum quantum number.

J = Total angular momentum quantum number.

Can we explain the formation of Na D lines?

Many electron system

Extensive discussion will be on extra class

Chemical Bond

Description of electronic structure of molecules

Ionic bond: Transfer of electron(s) from one atom to another, and the consequent interaction (electrostatic) between the ions so formed.

Covalent bond: Two neighboring atoms share a pair of electrons. Identified by G. N. Lewis.

Major approaches to the calculation of molecular structure:
1. **Valence Bond Theory** (a simple qualitative understanding of bond formation)
2. **Molecular Orbital Theory**

Electronic structure of Molecules

How does quantum mechanics treat "Molecular Orbitals"?
Rather than being localized on individual atoms – an electron in a molecules has wavefunctions that extends over the entire molecule.

There are several mathematical procedures for describing molecular orbitals: [to construct the wavefunction for electrons in molecules]
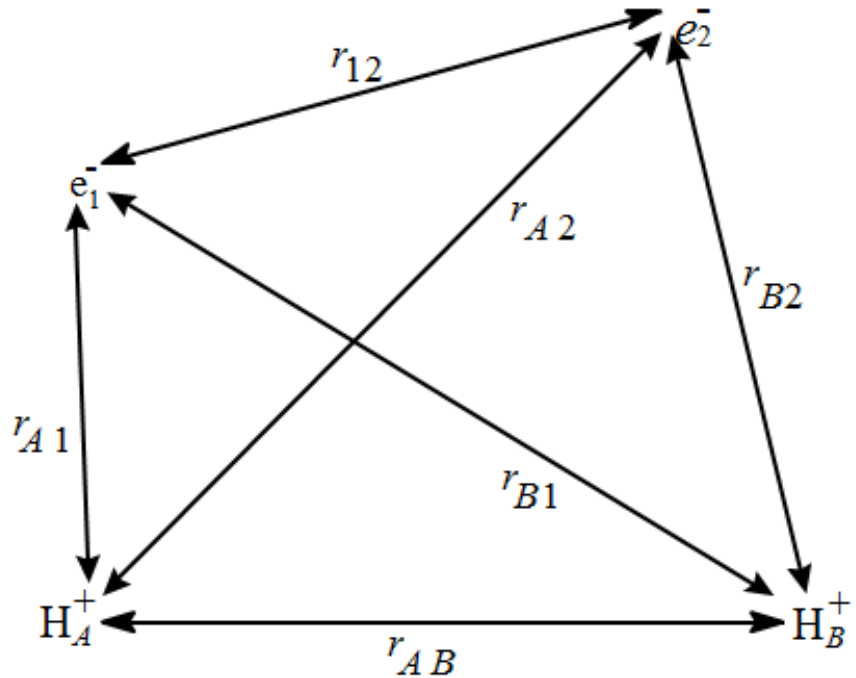1. Valence Bond Theory
2. Linear Combination of Atomic Orbitals – Molecular Orbitals (LCAO-MO)

Electronic structure of Molecules

All properties of a molecule (<u>M nuclei + n electrons</u>) can be evaluated if we find the wavefunction by solving the Schrödinger equation:

$$H\Psi = E\Psi$$

$$H = T_{tot} + V_{tot} = (T_N + T_e) + (V_{eN} + V_{ee} + V_{NN})$$

The Born-Oppenheimer approximation

◆ Born-oppenheimer approximation, it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move in their field.

◆ Therefore, the nuclei as fixed at arbitrary locations and then solve the Schrodinger equation for the wavefunction of the electron alone.

Molecular potential energy curve
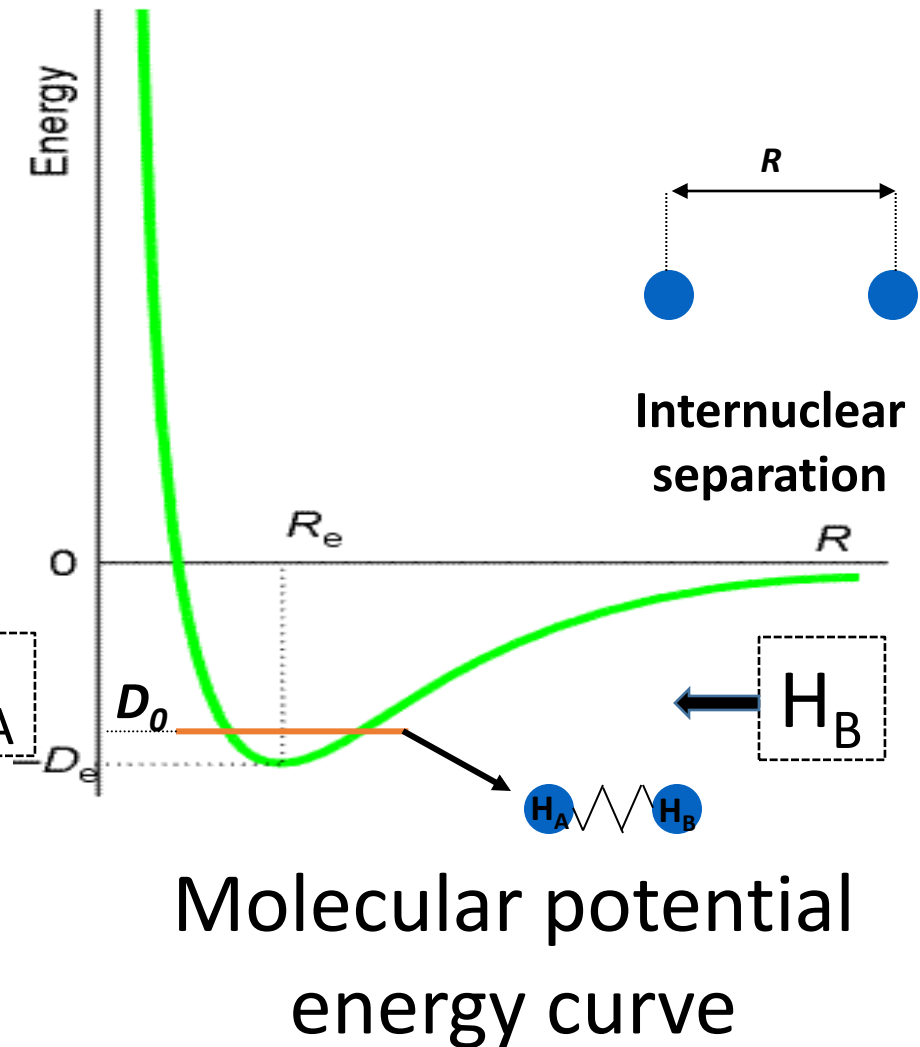
Valence bond theory

Valence Bond theory consider the molecular wavefunction in terms of <u>product</u> of atomic orbitals

<u>Hydrogen molecule as an example</u>

At infinite inter atomic separation, each hydrogen atom (H_A and H_B) has its own independent wavefunctions

$\psi_{HA} = 1s_{HA}(1)$ and $\psi_{HB} = 1s_{HB}(2)$ (<u>Electrons are labeled as 1 and 2</u>)

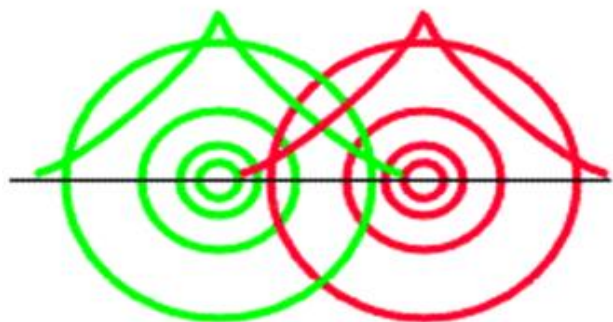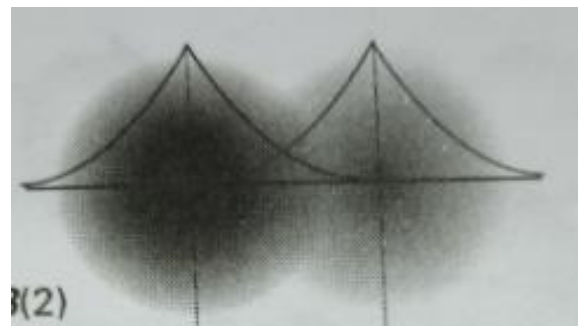The wavefunction is: $\Psi = \psi_{HA}\ \psi_{HB} = 1s_{HA}(1)\ 1s_{HB}(2)$

Another possible wavefunction is $\Psi = \psi_{HA}\ \psi_{HB} = 1s_{HA}(2)\ 1s_{HB}(1)$
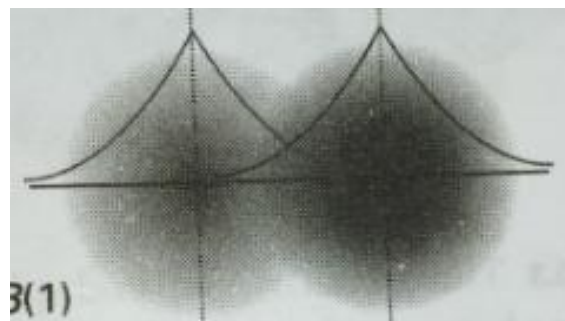
Valence bond theory
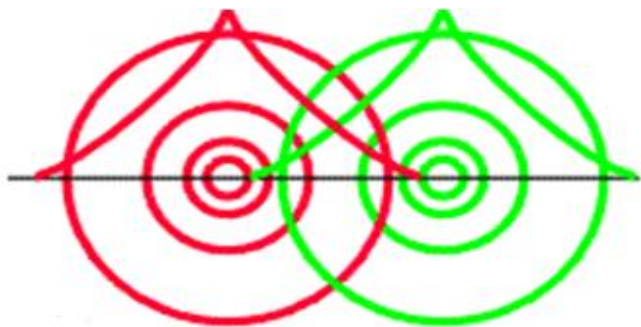
$1s_{HA}(1)\ 1s_{HB}(2)$

$1s_{HA}(2)\ 1s_{HB}(1)$
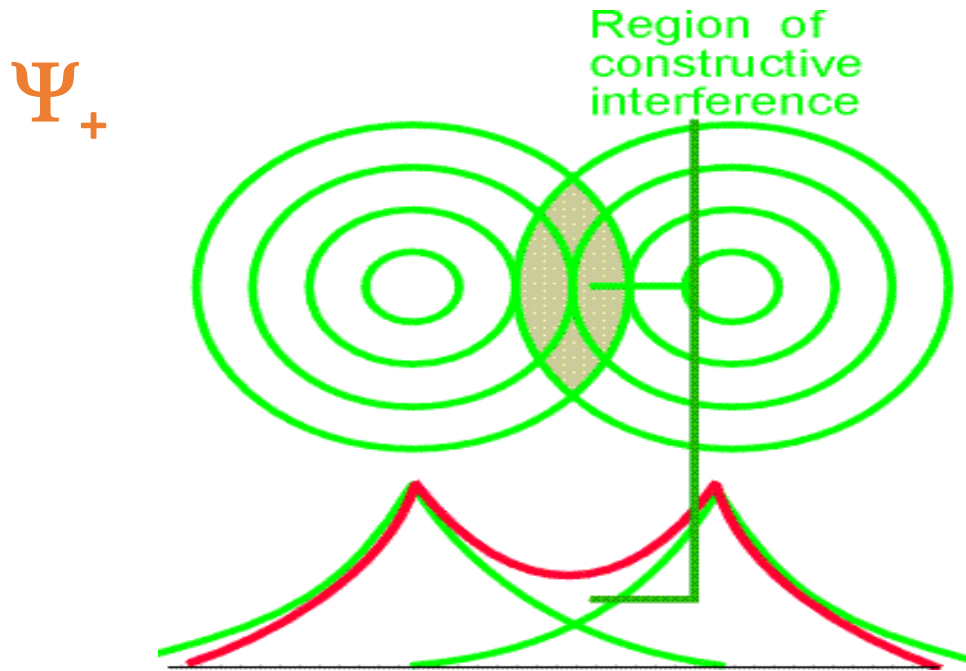
Linear combination of the individual wavefunctions

Enhanced electron density
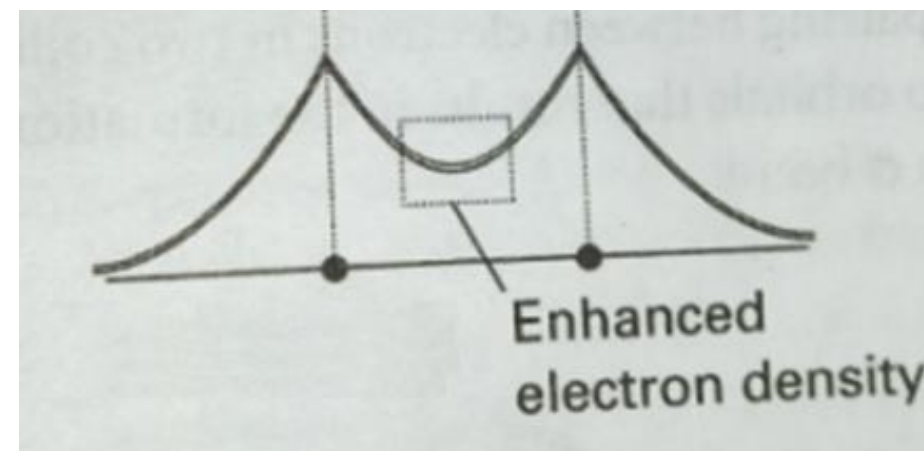
Superimposed contributions

The wavefunction is:
$$\Psi = 1s_{HA}(1)\ 1s_{HB}(2) \pm 1s_{HA}(2)\ 1s_{HB}(1)$$

Valence bond theory

Ψ_+

$$\Psi_- = 1s_{HA}(1)\ 1s_{HB}(2) - 1s_{HA}(2)\ 1s_{HB}(1)$$

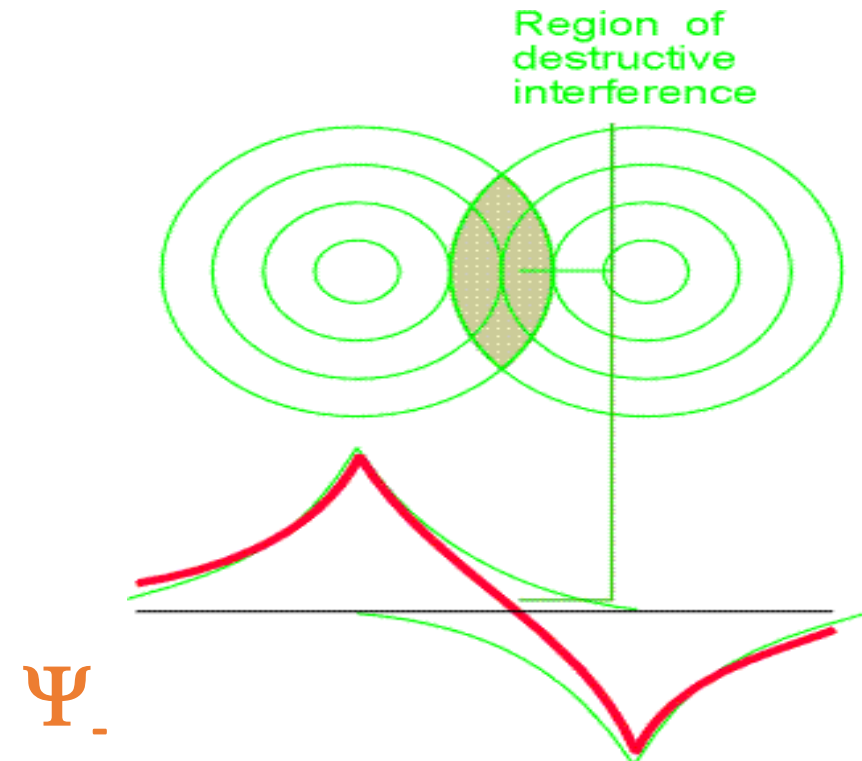→ between the two nuclei, Ψ_- changes sign → $|\Psi_-|^2 = 0$ → creation of a σ^* bond described by a "**_antibonding molecular orbital_**".

$$\Psi_+ = 1s_{HA}(1)\ 1s_{HB}(2) + 1s_{HA}(2)\ 1s_{HB}(1)$$

→ between the two nuclei: $|\Psi_+|^2 > 0$ creation of a σ bond described by a "**_bonding molecular orbital_**"

Ψ_-

VBT: spin of 2 electrons

The overall VB wavefunction for two electrons is

$$\Psi(1,2) = \{1s_{HA}(1)\ 1s_{HB}(2) + 1s_{HA}(2)\ 1s_{HB}(1)\}\ \sigma(1,2)$$

By changing the labels,

$$\Psi(2,1) = \{1s_{HA}(2)\ 1s_{HB}(1) + 1s_{HA}(1)\ 1s_{HB}(2)\}\ \sigma(2,1)$$
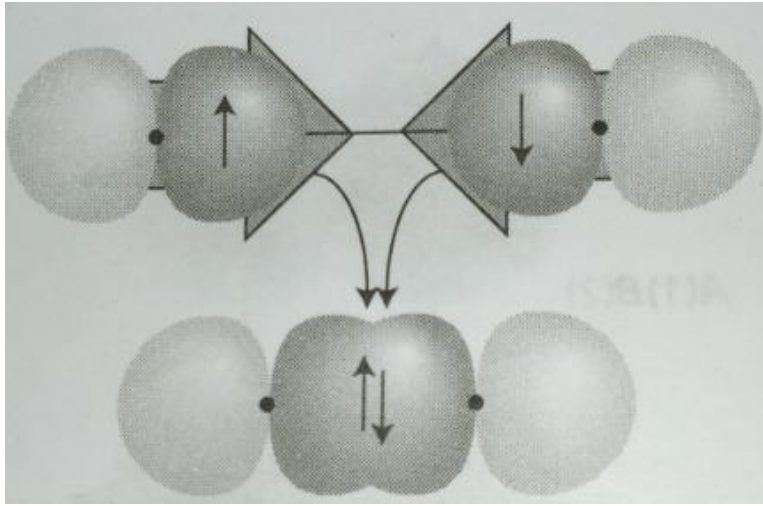$$= \{1s_{HA}(1)\ 1s_{HB}(2) + 1s_{HA}(2)\ 1s_{HB}(1)\}\ \sigma(2,1)$$

The Pauli principle requires that $\Psi(2,1) = -\Psi(1,2)$, which is satisfied only if $\sigma(2,1) = -\sigma(1,2)$ (The total electronic wavefunction of H_2 must be ***antisymmetric***)

The combination of two spins that has this property is

$\sigma_-(1,2) = (\tfrac{1}{2})^{1/2}\ \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$, Which corresponds to paired electron spins

➔ The formation of a bond is achieved if the electron spins are paired

Homonuclear diatomic molecule (N₂)

EC of N: $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

σ Bond (2pz)

π

σ

π

Nodal plane

Internuclear axis

π Bond (2px & py)

The remaining N2p orbitals can't merge to give σ bonds as they don't have ***cylindrical symmetry*** around <u>the</u> <u>internuclear axis</u>

N₂: 3 bonds are formed by combining the 3 different 2p orbitals of the 2 nitrogen atoms. This is possible because of the symmetry and the position of those 2p orbitals wrt each other.
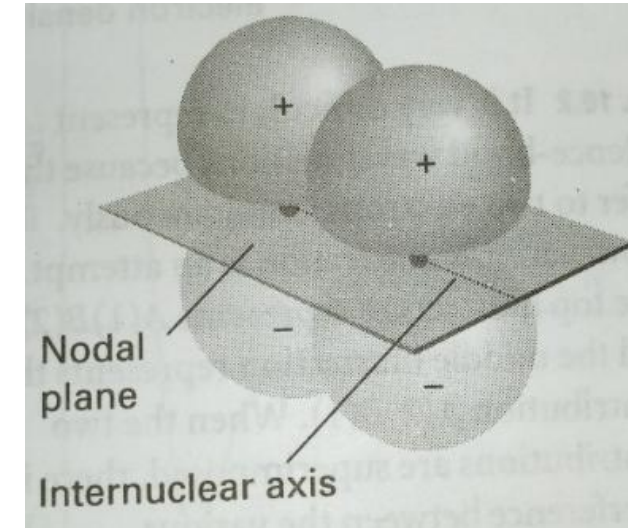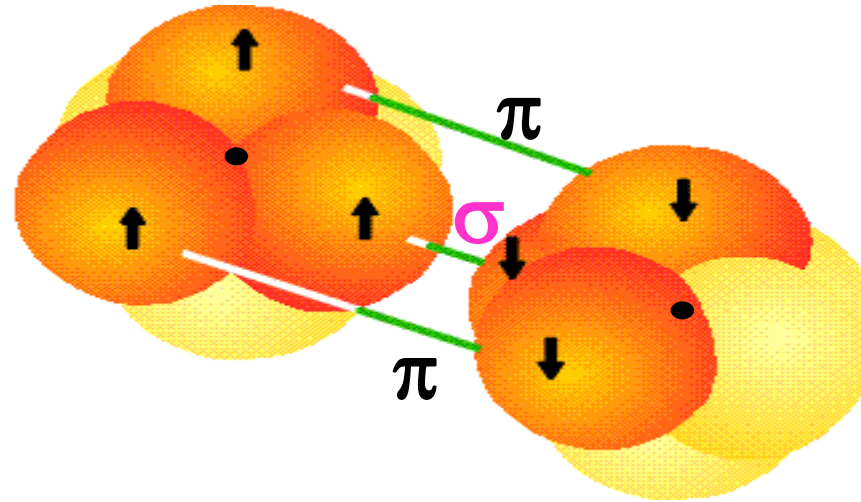
Discussed topics……

- ➢ Spin-orbit coupling, Idea of Term-symbol

- ➢ Electronic structure of molecule

- ➢ The Born-Oppenheimer approximation (PE curve)

- ➢ Valence bond theory of H_2 and N_2