**CH101**

Class 11-12; Physical Chemistry

Molecule:

Born-Oppenheimer Approximation

In a molecule, the nuclei can be considered as stationary as it moves much slowly compared to the electrons. For example, by the time the nucleus moves by 1 pm the electron moves by 1000 pm. Hence assuming the nucleus to be stationary generates small error in calculating the energies of electrons in molecules.

In simple terms, when considering the energetics of molecules we can consider the internuclear separation to be constant.
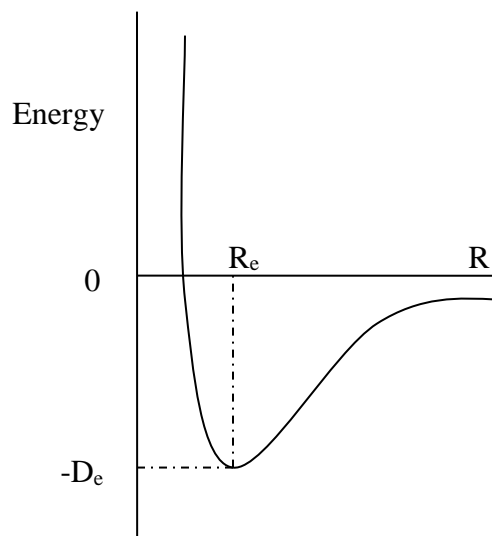
A molecular potential energy curve. The potential energy calculation is performed by setting R as a parameter. In other words, the energy is calculated for every R. The equilibrium bond length corresponds to the energy minimum. The bond dissociation energy $D_0 = D_e - \frac{1}{2} \hbar\omega$

Valence-bond Theory

How does one find out the wavefunctions of hydrogen molecule, H_2.

　Spatial Wavefunction

The wavefunction for an electron on each of the two widely separated H atoms is

$\Psi' = \Psi_{H1S_A}(r_1)\Psi_{H1S_B}(r_2)$; where $\Psi_{H1S_A}(r_1)$ is the wavefunction of electron 1 in

atom A and $\Psi_{H1S_B}(r_1)$ is the wavefunction for the electron 2 in atom B

This sets the electron 1 to be in atom A and electron 2 to be in atom B.

However, an equally likely option is the electron 1 to be in atom B and electron 2 in atom A.

Then the wavefunction is $\Psi'' = \Psi_{H1S_B}(r_1)\Psi_{H1S_A}(r_2)$

However, in keeping with the tradition of Quantum Mechanics, one can write a better form of wavefunction, which takes care of each electron in either of the two atoms.

$$\Psi = \Psi_{H1S_A}(r_1)\Psi_{H1S_B}(r_2) \pm \Psi_{H1S_B}(r_1)\Psi_{H1S_A}(r_2)$$

It turns out that the lower energy option is the one with the positive sign; i.e.

$\Psi = \Psi_{H1S_A}(r_1)\Psi_{H1S_B}(r_2) + \Psi_{H1S_B}(r_1)\Psi_{H1S_A}(r_2)$. This function is symmetric

and thus the spin function would be antisymmetric.

$\sigma_-(1,2) = \dfrac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$. Thus the overall function would be

$$\Psi = [\Psi_{H1S_A}(r_1)\Psi_{H1S_B}(r_2) + \Psi_{H1S_B}(r_1)\Psi_{H1S_A}(r_2)][\dfrac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}]$$

Thus in the ground state the electrons are spin-paired.

The valence bond theory also has the concept σ of π and bonds and also hybridization.

The concept of σ of π and bonds have been dealt extensively in your earlier classes.

Hybridization:

Consider for example the case of CH_4. The central carbon has electronic configuration $1s^2 2s^2 2p^2$. The angle between each H-C-H bond is 109.47^0. Simple bonding between the 2s and 2p orbitals of carbon atom and 1s orbitals of H-atoms would not be able to explain the bond angle. The concept of hybridized orbital is invoked, where the valence shell orbitals of the central carbon can generate four hybridized orbitals as a result of interference between component orbitals. They are

$$h_1 = (s + p_x + p_y + p_z)/2 \qquad\qquad h_2 = (s - p_x - p_y + p_z)/2$$

$$h_3 = (s - p_x + p_y - p_z)/2 \qquad\qquad h_4 = (s + p_x - p_y - p_z)/2$$

The bond angle can be calculated. It is arcos $(-1/3) = 109.47^0$.

Each of these hybridized orbital can form a bond with the 1s orbital of a hydrogen atom and thus four hybridized orbitals forming four bonds separated at 109.47^0.

$$\Psi = h_1(r_1)\Psi_{H1S}(r_2) + h_1(r_2)\Psi_{H1S}(r_1)$$

All four bonds would be identical.

Valence Bond Theory (Continued)

In $HC \equiv CH$, the carbon atoms are sp hybridized. The central carbon atoms have electronic configuration $1s^2 2s^2 2p^2$. Find out the hybridized orbitals.

$h_1 = (1/2)^{1/2} \{s + p_z\}$

$h_2 = (1/2)^{1/2} \{s - p_z\}$

Schematically draw the skeleton of the molecule and then show that these orbitals generate a bond angle of 120°.

In $H_2C=CH_2$, the carbon atoms are sp^2 hybridized. The central carbon atoms have electronic configuration $1s^2 2s^2 2p^2$. Find out the hybridized orbitals.

$h_1 = (1/3)^{1/2} \{s + 2^{1/2}p_y\}$

$h_2 = (1/3)^{1/2} \{s + (3/2)^{1/2}p_x - (1/2)^{1/2}p_y\}$

$h_3 = (1/3)^{1/2} \{s - (3/2)^{1/2}p_x - (1/2)^{1/2}p_y\}$

Schematically draw the skeleton of the molecule and then show that these orbitals generate a bond angle of 120°.

Molecular Orbital Theory

In valence bond theory we have learned that electrons are shared between the atoms forming a chemical bond. In molecular orbital theory this is not the case. In a molecule, electrons are spread throughout the molecule rather than a particular bond.

Simplest system

Hydrogen molecule-ion, H_2^+.

It has two nuclei and one electron. Thus the Hamiltonian can be written as
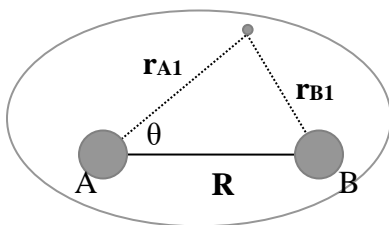
$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V ; \text{ where } V = -\frac{e^2}{4\pi\varepsilon_0}\{\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\}$$

Here $\mathbf{r_{A1}}$ is the distance of electron from the nucleus A,

$\mathbf{r_{B1}}$ is the distance of electron from the nucleus B,

and R is the internuclear separation.

$$r_{B1} = \{r_A^2 + R^2 - 2r_{A1}R\cos\theta\}^{1/2}$$

The one-electron wavefunctions can be obtained by solving the Schrödinger wave equation

$$H\Psi = E\Psi$$

The solutions, Ψ, are called molecular orbitals (MOs).

$|\Psi|^2$ provides the probability of finding the electron in a molecule.

Just like the wavefunction of electron in an atom is a measure of the probability of finding the electron in an atom; the wavefunction of an electron in a molecule also provides the probability of finding the electron in the entire molecule.

If one considers the Born-Oppenheimer approximation (To keep the internuclear separation term as a parameter; i.e. make it a constant and then solve the Schrodinger wave equation) then the Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V \text{ , where } V = -\frac{e^2}{4\pi\varepsilon_0}\{\frac{1}{r_{A1}} + \frac{1}{r_{B1}}\}$$

Solution of the above equation is possible but difficult. The solutions cannot be generalized for polyatomic molecules.

An easier way is to start from atomic orbitals and systematically build molecular orbitals from them.

Linear combination of atomic orbitals (LCAO) to form molecular orbitals (MO).
In the above case electron belongs 'equally' to two nuclei. This means that we can imagine that electron belongs to nucleus A (i.e. atom A) and also nucleus B (i.e. atom B).
This means the overall function of the electron can be considered as the superposition of atomic orbtial wavefunctions. These orbitals are called LCAO-MO.

$$\Psi = N(\Psi_{H1S_A} + \Psi_{H1S_B})$$

Here Ψ_{H1S_A} is the wavefunction of the electron belonging to atom A (H-atom)

And Ψ_{H1S_B} is the wavefunction of the electron belonging to atom B (H-atom)

N is the normalization constant.

Find the normalization constant N in the above molecular orbitals.

$$\int \Psi^* \Psi d\tau = N^2 \left\{ \int \Psi^*_{H1S_A} \Psi_{H1S_A} d\tau + \int \Psi^*_{H1S_B} \Psi_{H1S_B} d\tau + 2 \int \Psi_{H1S_A} \Psi_{H1S_B} d\tau \right\}$$

$$= N^2 \{1 + 1 + 2S\} = N^2 \{2(1+S)\} = 1$$

$$\therefore N = \frac{1}{\{2(1+S)\}^{1/2}}$$

Here $S = \int \Psi_{H1S_A} \Psi_{H1S_B} d\tau$

For wavefunctions are from H-atoms; hence their forms

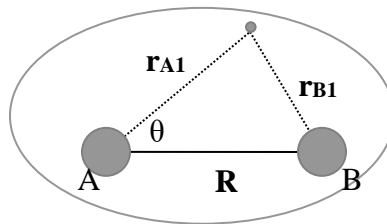$$\Psi_{H1S_A} = \frac{e^{-r_A/a_o}}{(\pi a_o^3)^{1/2}} \text{ and } \Psi_{H1S_B} = \frac{e^{-r_B/a_o}}{(\pi a_o^3)^{1/2}}$$

Molecular Orbital Theory (Continued)

H$_2$-molecule

Bonding Orbital

$$\Psi = N(\Psi_{H1S_A} + \Psi_{H1S_B})$$

Here Ψ_{H1S_A} is the wavefunction of the electron belonging to atom A (H-atom)

And Ψ_{H1S_B} is the wavefunction of the electron belonging to atom B (H-atom)

N is the normalization constant.

$$\therefore N = \frac{1}{\{2(1+S)\}^{1/2}}$$

Here $S = \int \Psi_{H1S_A} \Psi_{H1S_B} d\tau$

For wavefunctions are from H-atoms; hence their forms

$$\Psi_{H1S_A} = \frac{e^{-r_A/a_o}}{(\pi a_o^3)^{1/2}} \text{ and } \Psi_{H1S_B} = \frac{e^{-r_B/a_o}}{(\pi a_o^3)^{1/2}}$$

H-atom; Antibonding orbitals

$$\Psi = N(\Psi_{H1S_A} - \Psi_{H1S_B})$$

N is the normalization constant.

$$\therefore N = \frac{1}{\{2(1-S)\}^{1/2}}$$

Here $S = \int \Psi_{H1S_A} \Psi_{H1S_B} d\tau$

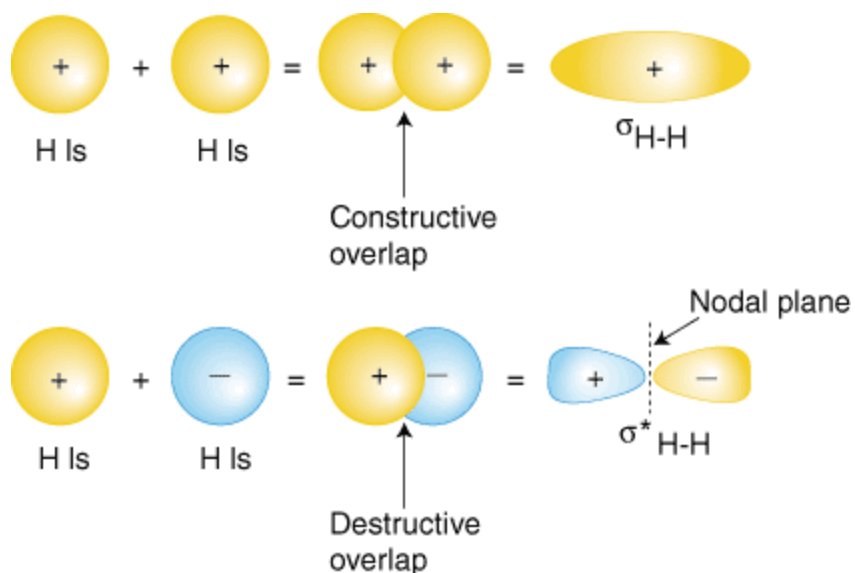http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.html

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Figure: Two 1s orbitals combine to form a bonding and an antibonding M.O.

If one looks carefully at the σ (bonding) orbital, it becomes obvious that there is a overlap region between two H-atom orbitals and thus bonding occurs. Thus the approximation in wavefunction is a good one.

If one looks carefully at the σ* (anti-bonding) orbital, it becomes obvious that there is no overlap region between two H-atom orbitals and thus no bonding occurs. Thus the approximation in wavefunction is a good one.
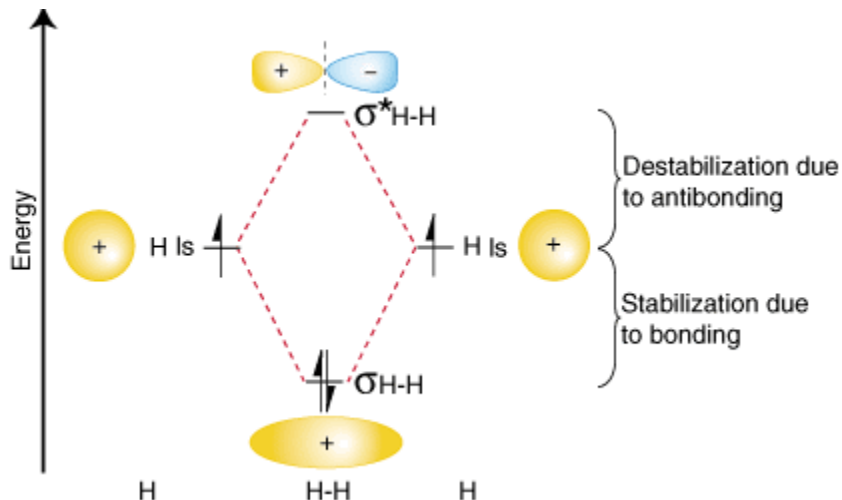

Figure: An orbital correlation diagram for hydrogen

H_2 bond order = ½ (No. of bonding electrons – no. of antibonding electrons**)**

$$= ½ (2\text{-}0)=1$$

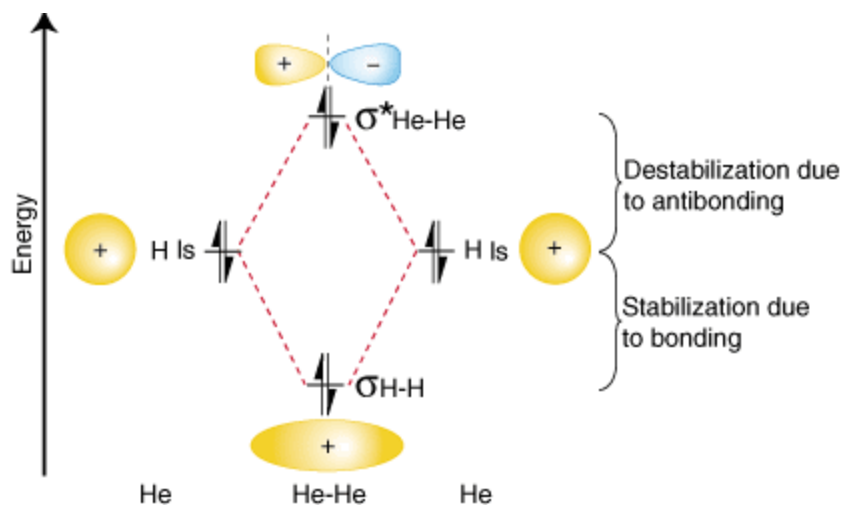*Figure: An orbital correlation diagram for a hypothetical He-He molecule*

He$_2$ bond order = ½ (No. of bonding electrons – no. of antibonding electrons**)**
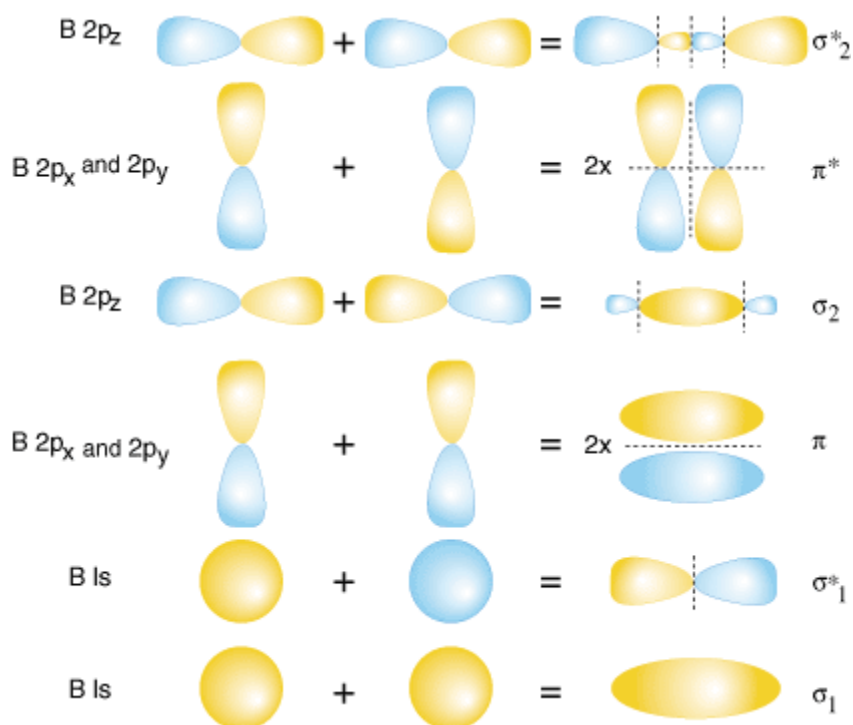
$$= \frac{1}{2}(2\text{-}2)=0$$

*Figure: The molecular orbitals of diboron (In the figure read **1s as 2s; it is a mistake, otherwise**).*