

Born - Oppenheimer approximation

In order to calculate the electronic energy, we need to solve the electronic Schrodinger equation. The complete Schrodinger equation covers both the nuclear and the electronic motions.

For a system of n nuclei and P electrons whose co-ordinates are collectively denoted as R and r respectively, Hamiltonian is given by the equation.

$$\hat{H} = -\sum_{i=1}^n \frac{\hbar^2}{8\pi^2 M_i} \nabla_i^2 - \sum_{j=1}^P \frac{\hbar^2}{8\pi^2 m} \nabla_j^2 + V(r, R) \quad \text{--- (1)}$$

And the Potential energy $V(r, R)$ is given by

$$V(r, R) = -\sum_{k=1}^n \sum_{j=1}^P \frac{Z_k e^2}{r_{jk}} + \sum_{n \neq j} \frac{e^2}{r_{nj}} - \sum_{k \neq l} \frac{Z_k Z_l e^2}{R_{kl}} \quad \text{--- (2)}$$

In equation (1) and (2), M_i is the mass of the i^{th} nucleus, m that of an electron, Z_k is the atomic number of the k^{th} nucleus, r_{jk} is the distance of the j^{th} electron from the k^{th} nucleus, r_{nj} is the distance between the n^{th} and j^{th} electrons and R_{kl} is the distance between k^{th} and the l^{th} nuclei.

The first term in equation (1) represents the nuclear kinetic energy operator \hat{T}_N and second and third terms together make up the electronic Hamiltonian operator \hat{H}_e i.e.

$$\hat{H} = \hat{T}_N(R) + \hat{H}_e(r, R) \quad \text{--- (3)}$$

The electronic operator describes the motion, of the electrons for fixed position of nuclei i.e. it depends on the position (and not the momenta) of the nuclei.

The Schrodinger equation due to electronic motion, Max Born and Robert Oppenheimer assumed that since the nuclei are much more heavier than the electrons, the former may be assumed to be stationary when the latter move. So the electronic wave function can be obtained by solving the electronic equations for some fixed position of the nuclei. Each choice of nucleus co-ordinate (R) will lead to a different potential energy and hence a different electronic Schrodinger equation.

Thus while the electronic wave function ψ_e will depend on r as well as R , the nuclear wave function will depend on R only. The complete wave function in equation (3) can be written as,

$$\Psi = \psi_e(r, R) \cdot \Psi_N(R) \quad \text{--- (4)}$$

Substituting eq (4) for \hat{H} and eq (5) for Ψ in eq (3), we get,

$$\left[-\sum_{i=1}^n \frac{\hbar^2}{8\pi^2 M_i} \nabla_i^2 - \sum_{j=1}^P \frac{\hbar^2}{8\pi^2 m} \nabla_j^2 + V(r, R) \right] \psi_e(r, R) \cdot \Psi_N(R) = E \psi_e(r, R) \Psi_N(R) \quad \text{--- (6)}$$

two separate equations are obtained by solving equation (6) first equation being:

$$-\sum_{i=1}^n \frac{\hbar^2}{8\pi^2 M_i} \nabla_i^2 \Psi_N(R) + E(R) \Psi_N(R) = E_T \Psi_N(R) \quad (7)$$

$$\text{or, } [\hat{T}_N + E(R)] \Psi_N(R) = E_T \Psi_N(R) \quad (8)$$

Equation (8) is the nuclear Schrödinger Equation in which $\hat{T}_N = -\sum_{i=1}^n \frac{\hbar^2}{8\pi^2 M_i} \nabla_i^2$ is Kinetic energy operator and $E(R)$ is potential energy operator, making

$$\hat{H}_N \Psi_N(R) = E_T \Psi_N(R)$$

Equation (8) is the nuclear Schrödinger Equation in which $\hat{T}_N = -\sum_{i=1}^n \frac{\hbar^2}{8\pi^2 M_i} \nabla_i^2$ is Kinetic energy operator and $E(R)$ is potential energy operator, making \hat{H}_N the nuclear Hamiltonian

$$\text{Similarly } -\sum_{j=1}^n \frac{\hbar^2}{8\pi^2 m_j} \nabla_j^2 \Psi_e(r, R) + V(r, R) \Psi_e(r, R) = E(R) \Psi_e(r, R)$$

$$[\hat{T}_e + V(r, R)] \Psi_e(r, R) = E(R) \Psi_e(r, R)$$

$$\hat{H}_e \Psi_e(r, R) = E(R) \Psi_e(r, R) \quad (9)$$

This is the electronic Schrödinger equation.

Solution of equation (9) gives the electronic energy $E(R)$ and the wave function $\Psi_e(r, R)$ for a particular value of R . Such separation of nuclear and electronic functions describes Born-Oppenheimer approximation, according to which the true wave functions of systems of moving electrons and nuclei will differ very slightly from those calculated assuming nuclei to be stationary.

The approximation holds good for ground state of molecules and may break down for excited states.

~ ~ ~

Normalised VB wave function and MO wave function for H₂ molecules: -

H₂ molecules contains two electrons labelled 1 and 2 and two Hydrogen nuclei labelled A and B. The pairing of electrons leads to the formation of a covalent bond.

In the VB approach, if electron 1 is on nucleus A then electron 2 would be on nucleus B and vice-versa. Thus however the two electrons are distinguishable, therefore the VB wave function for H₂ molecule can be written as,

$$\psi_{VB} = \left(\frac{1}{\sqrt{2}}\right) [\phi_A(1) \phi_B(2) + \phi_A(2) \phi_B(1)] \quad \text{--- (1)}$$

where $\frac{1}{\sqrt{2}}$ is the normalization constant obtained by normalizing ψ_{VB} .

In MO theory, the MO wave function for H₂ molecule is given by

$$\psi_{MO} = \psi_1 \psi_2 \quad \text{--- (2)}$$

where ψ_1 and ψ_2 are the normalized wave functions for MO's of H₂ given by

$$\psi_1 = \left(\frac{1}{\sqrt{2}}\right) [\phi_A(1) + \phi_B(1)] \quad \text{--- (3)}$$

$$\psi_2 = \left(\frac{1}{\sqrt{2}}\right) [\phi_A(2) + \phi_B(2)] \quad \text{--- (4)}$$

Multiplying ψ_1 and ψ_2 we get ψ_{MO} as

$$\psi_{MO} = \frac{1}{2} [\phi_A(1) + \phi_B(1)] [\phi_A(2) + \phi_B(2)] \quad \text{--- (5)}$$

$$= \frac{1}{2} [\phi_A(1) \phi_A(2) + \phi_B(1) \phi_B(2)] + \frac{1}{2} [\phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2)] \quad \text{--- (6)}$$

In eqⁿ (6) the first two terms represent the probability of finding both the electrons on the same atom at the same time.

In other words, these terms represent the ionic structure of H₂ molecule which may be written as $H_A^- H_B^+$ and $H_A^+ H_B^-$.

The last two terms represents the covalent structure of H₂ molecule.

Comparing ψ_{VB} and ψ_{MO} . We observe that while the wavefunction in VBT does not give any weightage to ionic structures, the MOT gives equal weightage to covalent and ionic structures.

— > —

Application of LCAO for H_2^+

Using the LCAO-MO approximation, the wave function for H_2^+ is written as.

$$\psi = N (c_1 \phi_A + c_2 \phi_B) \text{ where } N \text{ is normalisation constant. — (1)}$$

According to the normalisation condition for real ψ (Using Dirac's bra and ket notation)

$$\int \psi^2 dz = \langle \psi | \psi \rangle = 1 \quad \text{————— (2)}$$

Incorporating the value of ψ from eqn (1) in eqn (2) we have

$$N^2 \langle c_1 \phi_A + c_2 \phi_B | c_1 \phi_A + c_2 \phi_B \rangle = 1$$

$$\text{or, } c_1^2 [\langle \phi_A | \phi_A \rangle] + c_2^2 [\langle \phi_B | \phi_B \rangle] + 2c_1 c_2 [\langle \phi_A | \phi_B \rangle] = \frac{1}{N^2} \quad \text{— (3)}$$

Assuming ϕ_A and ϕ_B are normalised, i.e.

$$\langle \phi_A | \phi_A \rangle = \int \phi_A^2 dz = 1 \text{ and } \langle \phi_B | \phi_B \rangle = \int \phi_B^2 dz = 1$$

We have, $c_1^2 + c_2^2 + 2c_1 c_2 S = \frac{1}{N^2}$, where S is the Overlap Integral — (4)

$$\text{define as, } S = \langle \phi_A | \phi_B \rangle = \int \phi_A \phi_B dz \quad \text{———— (5)}$$

$$\text{So that } N = (c_1^2 + c_2^2 + 2c_1 c_2 S)^{-1/2} \quad \text{———— (6)}$$

Hence from eqn (1)

$$\psi = (c_1^2 + c_2^2 + 2c_1 c_2 S)^{-1/2} (c_1 \phi_A + c_2 \phi_B) \quad \text{———— (7)}$$

But we know that for BMO (Bonding Molecular Orbital)

$$c_1 = c_2 \text{ and ABMO, } c_1 = -c_2$$

Hence from equation (7)

$$\psi_{\text{BMO}} = \frac{1}{\sqrt{2(1+S)}} (\phi_A + \phi_B)$$

and for ABMO (Anti Bonding Molecular Orbital)

$$\psi_{\text{ABMO}} = \frac{1}{\sqrt{2(1-S)}} (\phi_A - \phi_B)$$

————— \times —————

Comparison between VBT and MOT

- (1) In VBT, the electronic structure of a molecule is described in terms of atomic orbitals while in MOT, it is described in terms of Molecular Orbitals which are formed as a result of linear combination of atomic orbitals.
- (2) In both the theories, emphasis is laid on the overlap of atomic orbitals and the cause of bonding is said to be the displacement of electron-density into inter-nuclear region. Here Molecular Orbital theory puts greater electron-density between the nuclei than the Valence bond theory.

- (3) Each of the two theories attributes the stabilisation of the molecule to exchange integral. In MOT the exchange integral is defined as

$$\int \phi_A \hat{H} \phi_B \phi_2$$

which refers to the exchange of an electron between two atomic orbitals ϕ_A and ϕ_B . In VBT the exchange integral,

$$\int \phi_A(1) \phi_B(2) \hat{H} \phi_B(1) \phi_A(2) \phi_2$$

it refers to the exchange of a pair of electrons between the two atomic orbitals. Thus VBT retains the concept of electron-pair bond between two atoms, it is lost in MOT, there being a continuous electron density distribution over the whole molecule with no localisation of electron pair.

- (4) The typical Valence bond function for a bond in homonuclear molecule like H_2 in ground state is

$$\psi^{VB} = \phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2)$$

while the corresponding Molecular orbital function is

$$\psi^{MO} = [\phi_A(1) + \phi_B(1)] [\phi_A(2) + \phi_B(2)]$$

$$\text{or } \psi^{MO} = \phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2) + \phi_A(1) \phi_A(2) + \phi_B(1) \phi_B(2)$$

The first two terms in ψ^{MO} corresponds to the ψ^{VB} and the last two terms represent ionic bonds, $H_A^- H_B^+$ and $H_A^+ H_B^-$ i.e. ψ^{MO} is an equal combination of covalent and ionic functions. The VBT completely ignores the ionic functions.

- (5) The two wave-functions ψ^{MO} and ψ^{VB} represent the two extremes of situation. For small values of the internuclear distance R , when there are greater chances of finding the two electrons in one orbital, MOT applies better. For larger value of R , Valence bond theory gives better result.

- (6) In the ultimate analysis, the MO and VB theories are equivalent and lead to almost similar results. They have been used equally well but with respect to the treatment of large molecules, the MOT has gained an edge over the VBT.