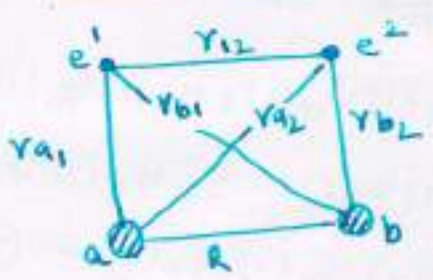# VALENCE BOND TREATMENT OF H₂

The first quantum-mechanical treatment of hydrogen molecule was by Heitler and London in 1927. Their ideas have been extended to give a general theory of chemical bonding, known as Valence-Bond theory. The VB method is more closely related to the chemists idea of molecules as consisting of atoms held together by localised bonds. The VB method views molecules as composed of atomic cores (nuclei plus inner shell electrons) and bonding valence electrons.

In this method, atoms are assumed to retain their individual identity in a molecule and the bond arises due to the interaction of the valence electrons when the atoms come closer. That is, a bond is formed when a valence electron in one atomic orbital pairs its spin with that of another valence electron in the other atomic orbital.

THE PROCEDURE (V.B TREATMENT - H₂)

The procedure adopted by Heitler and London was about treating ground state of H₂ molecule as two ground state hydrogen atoms.

We assume the two H atoms to be far apart so that there is no interaction between them. In the adjacent figure, electrons are labelled as 1 and 2, the nuclei as a and b along with distances between them.

The schrodinger equation for the system →

$$H_a(1)\,\Psi_a(1) = E_a\,\Psi_a(1)$$
$$H_b(2)\,\Psi_b(2) = E_b\,\Psi_b(2) \Bigg] \quad — ①$$

where $E_a = E_b = E_H$, the ground state energy of hydrogen atom and $\Psi_a(1)$ and $\Psi_b(2)$ are the 1s hydrogenic wavefunction.

$$H_a(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a_1}}$$
$$H_b(2) = \frac{-\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{b_2}} \Bigg] — ②$$

When the two atoms are brought closer and if there is no interaction between the two, the total hamiltonian of system

$$H = H_a(1) + H_b(2) \quad — ③$$

By assuming that electron 1 is moving about proton a and electron 2 is moving about proton b. This system of two hydrogen atoms can be described by the wavefunction:

$$\Psi_1(1,2) = \Psi_a(1)\,\Psi_b(2) \quad — ④$$

with energy eigen value $E_a + E_b$ since

$$[H_a(1) + H_b(2)]\,\Psi_a(1)\,\Psi_b(2) = H_a(1)\,\Psi_a(1)\,\Psi_b(2) + H_b(2)\,\Psi_a(1)\,\Psi_b(2)$$
$$= E_a\,\Psi_a(1)\,\Psi_b(2) + E_b\,\Psi_a(1)\,\Psi_b(2)$$
$$= (E_a + E_b)\,\Psi_a(1)\,\Psi_b(2) \quad — ⑤$$

The electrons are indistinguishable and therefore an equally good description of the molecule with the same energy is given by the structure in which electron 1 is associated

with atom b and electron 2 is associated
with atom a thereby giving wavefunction 2

$$\psi_2(2,1) = \psi_a(2) \, \psi_b(1) \quad — ⑥$$

In other words, $\psi_1(1,2)$ and $\psi_2(2,1)$ are eigen fns
of the Hamiltonian $H_a + H_b$ having eigen value
$(E_a + E_b)$. The two functions differ only in the
interchange of two electrons between the orbitals.
Hence, this degeneracy is referred to as the
<u>exchange</u> <u>degeneracy</u> and the wave functions
of two electron systems, must be a linear combination
of $\psi_1(1,2)$ and $\psi_2(2,1)$.

The Hamiltonian of hydrogen molecule ~~given by~~
~~can~~ can now be written as

$$H = H_a(1) + H_b(2) + H' + \frac{ke^2}{R} \quad — ⑦$$

where
$$H' = -\frac{ke^2}{r_{b1}} - \frac{ke^2}{r_{a2}} + \frac{ke^2}{r_{12}} \quad — 8$$

As the term ke^2/R is independent of electronic
coordinates, its contribution may be included
at the final stage as an additional term ke^2/R.

Now the problem can be handled either by
perturbation or variation method. H-L
followed perturbation method. Since an exchange
of the two electrons leave the Hamiltonian H
unchanged, the wavefunctions must either be
symmetric or antisymmetric wrt such an
exchange.

The symmetric ψ_s and antisymmetric ψ_{as} combinations are:

$$\psi_s = N_s \left[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \right]$$
$$\psi_{as} = N_a \left[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \right] \Big\} - 9(a,b)$$

where N_s and N_a are normalisation constants.

Normalisation condition gives

$$N_s^2 = \frac{1}{2(1+S^2)} \quad , \quad N_a^2 = \frac{1}{2(1-S^2)} \qquad - ⑩$$

where $\quad \langle \psi_a | \psi_b \rangle = \langle \psi_b | \psi_a \rangle = S$

The inclusion of electron spin and Pauli's principle leads to the Heitler London wavefunctions

$$N_s \left[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \right] \frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] - ⑪$$

$$N_a \left[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \right] \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right] \\ \beta(1)\beta(2) \end{cases} \Big\} ⑫$$

Eq⑪ corresponds to a singlet ($S=0$) and eq ⑫ is a triplet ($S=1$). Energy is unaffected by the inclusion of spin part as the Hamiltonian does not have spin terms. So we can take space part alone as the unperturbed wave function for calculating energy.

A perturbation calculation is then carried out with H' (eq8) as perturbation.

The first order correction to the energy E_1' is the diagonal matrix element of the perturbing Hamiltonian corresponding to the unperturbed wavefunctions. Then

$$E_1' = N_s^2 \langle (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)) | H' | (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)) \rangle$$

$$= \frac{(2J+2K)}{2(1+S^2)} = \frac{J+K}{1+S^2} \qquad\qquad (13)$$

where
$$J = \langle \psi_a(1)\psi_b(2) | H' | \psi_a(1)\psi_b(2) \rangle \qquad (14)$$
$$K = \langle \psi_a(1)\psi_b(2) | H' | \psi_a(2)\psi_b(1) \rangle \qquad (15)$$

J and K are called Coulomb and exchange integrals respectively. In these expressions, the ψ's are hydrogen 1s wavefunction.

The energy of the singlet state corrected to first order.

$$E_s = 2E_H + \frac{J+K}{1+S^2} + \frac{ke^2}{R} \qquad (16)$$

The first order correction to triplet state

$$E_2' = \frac{J-K}{1-S^2} \qquad\qquad (17)$$

The energy of triplet state

$$E_a = 2E_H + \frac{J-K}{1-S^2} + \frac{ke^2}{R} \qquad (18)$$
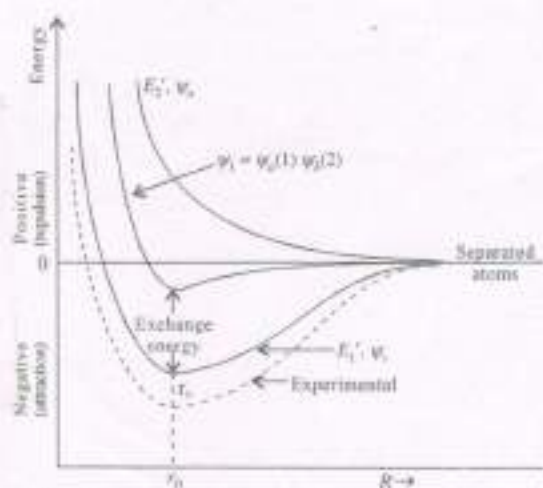
SIGNIFICANCE OF J AND K:

The coulomb integral represents the interaction of classical electron charge cloud about one nucleus with the charge in the other nucleus and the interaction of the two charge clouds with one another.

Exchange integral represents a non classical interaction It is a consequence of the inclusion of both $\psi_1(1,2)$ and $\psi_2(2,1)$, in the unperturbed wave function.

The two functions differ only in the interchange of the electrons between the orbitals ψ_a and ψ_b.

The overlap integral S is zero, when the two protons are far apart and is equal to 1 when they are in contact.

For large R, both J and K tend to zero. For intermediate values both are negative and the magnitude of K is several times larger than that of J. Hence E_S can have a value less than $2E_H$, while E_a is always above $2E_H$

Plot of energies E_1' and E_2' against internuclear distance R.

Fig 1

INTERPRETATION OF FIGURE 1

→ The figure shows the plots of E_1' and E_2' against the internuclear distance R

→ It shows the minimum of the ψ_s combination corresponding to the formation of a stable structure. Hence the normalised bonding valence bond molecular orbital is given by eq 9

→ The state characterised by the ψ_{as} combination corresponds to repulsion for all values of R.

→ The equilibrium internuclear distance R is the one corresponding to a min of ψ_s curve.

→ The Heitler-London treatment gives the value of De → 3·15 eV (dissociation energy) and equilibrium distance = 0·85 Å.

→ The agreement with the experimental value of De → 4·75 eV and equilibrium distance 0·74 Å is only reasonable.

→ The major contribution to the binding of molecule comes from the Exchange ~~degeneracy~~ degeneracy

COMPARISON OF MO AND VB THEORIES

Lets compare the molecular orbital and valence bond treatments of the H_2 ground state.

If ϕ_a symbolises an atomic orbital centered on nucleus a, the spatial factor of the unnormalised LCAO-MO wave function for H_2 ground state is

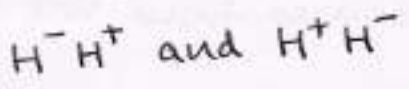$$[\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] \quad — \quad ①$$

In the simplest treatment, ϕ is a 1s at.orbital. The function given by ① equals to

$$\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) — ②$$

Now, what is the physical significance of the terms?

The last two terms have each electron in an atomic orbital centered on a different nucleus. These are covalent terms, corresponding to equal sharing of electrons between the atoms. The first two terms have both electrons in AOs centered on same nucleus. These are ionic terms, corresponding to the chemical structures

$$H^-H^+ \text{ and } H^+H^-$$

The covalent and ionic terms occur with equal weight, so this simple MO function gives a 50-50 chance as to whether the H_2 ground state dissociates to two neutral hydrogen atoms or to a proton and a hydride ion.

Actually, the H_2 ground state dissociates to two neutral H atoms. Thus the simple MO function gives the wrong limiting value of the energy as $R \to \infty$

NOW THE QUESTION IS HOW TO FIND THE SOLUTION

Since H_2 is nonpolar, chemical intuition tells us that ionic terms should contribute substantially less to the wave functions than covalent terms.

The simplest procedure is to omit the ionic terms of the MO function (eq 2) and this will give us

$$\phi_a(1)\,\phi_b(2) + \phi_b(1)\,\phi_a(2) \quad\text{——③}$$

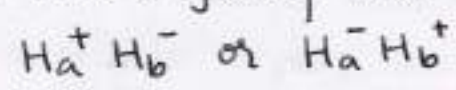if we see eq ③ carefully then we shall realise that is a Heitler-London function.

Although interelectronic repulsion causes the electrons to avoid each other, there is some probability of finding both electrons near the same nucleus, corresponding to an ionic structure

So therefore instead of dropping the ionic terms from eq 2 we might try

$$\phi_{VBimp} = \phi_a(1)\,\phi_b(2) + \phi_b(1)\,\phi_a(2) + \delta\left[\phi_a(1)\,\phi_a(2) + \phi_b(1)\,\phi_b(2)\right] \text{——④}$$

where $\delta(R)$ is a variational parameter and the subscript imp indicates an improved VB function. In the language of valence-bond theory, this trial function represents ionic covalent resonance

Let us now consider the role of ionic structures in VBT. For H_2 molecule, the ionic structures are those in which the electrons 1 and 2 are located on nucleus a or b giving rise to structures

$$H_a^+ H_b^- \text{ or } H_a^- H_b^+$$

↓

But these structures are unlikely since there is no electronegativity difference between two hydrogen atoms.

However such structures become important in heteronuclear diatomics. Thus the VB wave function can be written as composed of a covalent part and an ionic part.

$$\Psi_{VB} = \Psi_{cov} + \lambda \, \Psi_{IONIC}$$

$\lambda \rightarrow$ parameter whose value determines the polar character (ionicity of bond).

Q. assuming that the ionic character in H-Br bond is 11%. Calculate the fraction of contribution of ionic character to the VB wave function.

as per equation $\quad \Psi_{VB} = \Psi_{cov} + \lambda \, \Psi_{IONIC}$

% ionic character is given by $\dfrac{\lambda^2}{1+\lambda^2} \times 100$

$\therefore \quad 11 = 100\lambda^2 / (1+\lambda^2)$

or $\quad \lambda^2 = 11/89$

or $\lambda = 0.35$

Thus, the fraction of contribution of ionic character to Ψ_{VB} is 0.35