

1. VALENCE- BOND METHOD

In this method, atoms are assumed to maintain their individual identity in a molecule and the bond arises due to the interaction of the valence electrons when the atoms come closer. It amounts to considering molecules as composed of atomic cores and bonding valence electrons. Thus, VB method considers bringing the atoms with their associated electrons together and allowing them to interact to form the bond.

HYDROGEN MOLECULE-HEITLER LONDON THEORY

The application to valence problems was first considered by Heitler and London in 1927. The idea was later extended by Slater and Pauling to give a general theory of chemical bonding and the theory is known as the Valence Bond (VB) method.

Consider two hydrogen atoms far apart so that there is no interaction between them. Labeling the electrons as 1 and 2, the nuclei as a and b and the electron nucleus distances by r_{a1} and r_{b2} ,

Writing the Schrodinger equations:

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

Where $E_a = E_b = E_H$, the ground state energy of the hydrogen atoms and $\Psi_a(1)$ and $\Psi_b(2)$ are the 1s hydrogenic wave function.

$$H_a(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{a1}}, \quad H_b(2) = -\nabla_2^2 - \frac{e^2}{r_{b1}}$$

When the two atoms are brought closer and there is no interaction between the two, the

$$H = H_a(1) + H_b(2)$$

It amounts to assuming that electron 1 is moving about proton 'a' and electron 2 is moving about proton 'b'. The system of two hydrogen atoms can be described by the wave function

$$\Psi_1(1,2) = \Psi_a(1) \Psi_b(2)$$

With energy eigenvalue $E_a + E_b$

$$\begin{aligned} [H_a(1) + H_b(2)] \Psi_a(1)\Psi_b(2) &= H_a(1) \Psi_a(1)\Psi_b(2) + \\ &H_b(2) \Psi_a(1)\Psi_b(2) \\ &= E_a\Psi_a(1) \Psi_b(2) + E_b\Psi_a(1) \Psi_b(2) \\ &= (E_a + E_b) \Psi_a(1) \Psi_b(2) \end{aligned}$$

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' , hence the wave function,

$$\Psi_2(2,1) = \Psi_a(2) \Psi_b(1)$$

$\Psi_1(1,2)$ and $\Psi_2(2,1)$ are eigenfunctions of the description $H_a + H_b$ with eigenvalue $(E_a + E_b)$. The two functions differ only in the interchange of the two electrons between the orbitals. Hence, this degeneracy is referred to as the **exchange degeneracy** and the wave functions of the two electron system, must be a linear combination of $\Psi_1(1,2)$ and $\Psi_2(2,1)$.

Now considering the hydrogen molecule, the Hamiltonian of the system

$$H = H_a(1) + H_b(2) + H' + \frac{e^2}{R}$$

Where

$$H' = -\frac{e^2}{r_{b1}} - \frac{e^2}{r_{a2}} + \frac{e^2}{r_{12}}$$

Evidently, the term e^2/R is independent of electronic coordinates, its contribution may be incorporated at the final stage as an additional term e^2/R .

The problem can be solved either by using the perturbation method or the variation method. Heitler and London followed the perturbation method. As the Hamiltonian H is unchanged on exchange of the two electrons, the wave functions must either be symmetric or antisymmetric with respect to such an exchange. So, the symmetric Ψ_s and Ψ_{as} antisymmetric combinations are:

$$\Psi_s = N_s[\Psi_a(1)\Psi_b(2) + \Psi_a(2) \Psi_b(1)]$$

$$\Psi_{as} = N_a[\Psi_a(1)\Psi_b(2) - \Psi_a(2) \Psi_b(1)]$$

Where N_s and N_a are normalization constants and the Normalization conditions gives

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

Where S is given by the overlap integrals.

The inclusion of electron spin and Pauli's leads to the Heitler-London wave functions corresponding to a singlet (S=0) and a triplet (S=1)

$$N_s[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)] \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$N_a[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)] \left\{ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \right. \\ \left. \beta(1)\beta(2) \right\}$$

Since the Hamiltonian does not contain spin terms. The energy is not affected by the inclusion of spin part. The space parts alone can then be taken as the unperturbed wave functions for the evaluation of energy.

Let H' be the perturbation applied to the system and the first order correction to the energy E' is the diagonal matrix element of the perturbing Hamiltonian corresponding to the unperturbed wave functions, so that

$$E'_1 = N_s^2 \langle \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1) | H' | \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1) \rangle \\ = \frac{(2J+2K)}{2(1+S^2)} = \frac{J+K}{1+S^2}$$

Where J and K are called **Coulomb and exchange integrals** respectively and are

$$J = \langle \Psi_a(1)\Psi_b(2) | H' | \Psi_a(1)\Psi_b(2) \rangle \\ K = \langle \Psi_a(1)\Psi_b(2) | H' | \Psi_a(2)\Psi_b(1) \rangle$$

The Ψ 's are hydrogen 1s wave function. The energy of the singlet state corrected to first order

$$E_s = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{R}$$

The first order correction to the triplet state

$$E' = 2 \frac{J+K}{1+S^2}$$

and the energy of the triplet state

$$E_a = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{R}$$

The **Coulomb integral** represents the interaction of the classical electron charge clouds 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 when these are in contact is unity. K and J both tend to zero for large R , while both are negative for intermediate values. The magnitude of K is several times larger than that of J . Thus E_s can have a value less than $2E_H$, whereas E_a is always shows a minimum for the Ψ_s combination corresponding to the formation of the stable molecule. The state characterized by the Ψ_{AS} combination corresponds to repulsion for all values of R . The equilibrium internuclear distance r_0 is the one corresponding to the minimum of the Ψ_s curve. The theoretical value of 0.85 \AA for r_0 is high compared to the experimental value of 0.74 \AA . The binding energy corresponding to 0.85 \AA is about 72 kcal/mol whereas the experimental value is 109 kcal/mol .

In case, the exchange degeneracy is not considered one would have got a binding energy of about 6 kcal/mol . The additional binding energy of 66 kcal/mol is referred to as **exchange energy**.

Figure Energies E'_1 and E'_2 versus internuclear distance R .

The structures given by Ψ_S and Ψ_{AS} are referred to as covalent structures as one electron is associated with one nucleus and the second one with the other nucleus. The agreement between experimental and theoretical values can be improved further by considering two additional structures in which both the electrons are associated with only one nucleus. These are the ionic structures. H_a^- H_b^+ and H_a^+ H_b^- with wave functions $\Psi_a(1) \Psi_a(2)$ and $\Psi_b(1) \Psi_b(2)$ respectively. Inclusion of these structures gives a binding energy that agrees fairly well with the experimental value.

2. Valance Bond **METHOD OF HYDROGEN MOLECULE ION**

The Hydrogen molecule ion is the system consisting of a single electron and two nuclei and the Schrodinger equation for the H_2^+ ion is

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + \left(-\frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{R} \right) \Psi = E\Psi$$

Consider the system initially with the two nuclei very far apart with the electron associated with the nucleus a . This leads to the structure of $H_a H_b^+$ and the wave function for this structure be assumed as Ψ_a .

When the electron is associated with the nucleus b , the structure is described by $H_a^+ H_b$ with wave function Ψ_b .

Both these structures correspond to the same energy and the electron wave function will be the same as the hydrogenic 1s wave function.

Further when the two nuclei are brought closer, they repel one another but the electron gets attracted to both the nuclei thereby creating a bond. A hydrogen molecule ion is formed when the energy of the system is minimum. That is, the wave function of the system is described by a linear combination of Ψ_a and Ψ_b .

$$\Psi = c_1 \Psi_a + c_2 \Psi_b$$

$c_1 = \pm c_2$ As both the states have the same energy they contribute equally to Ψ . The two possible linear combinations are

$$\Psi_1 = \frac{1}{\sqrt{2+2S}} (\Psi_a + \Psi_b), \quad \Psi_2 = \frac{1}{\sqrt{2-2S}} (\Psi_a - \Psi_b)$$

$$S = \langle \Psi_a | \Psi_b \rangle$$

The charge density is proportional to Ψ^2 .

The increased electron charge density in the case of Ψ_1 is concentrated in the region between the nuclei. However, in the case of Ψ_2 the electron charge density is pushed away from the internuclear region.

In Figure, the variation of energy of the states Ψ_1 and Ψ_2 is plotted against the internuclear distance. The calculations lead to energy and bond length values same as that obtained on the basis of simple Molecular Orbital theory. This is understandable since Ψ_a and Ψ_b are 1s atomic orbitals.

3. Difference between Molecular orbital (MO) method and valence bond method(VB):

The MO method considers that the electron pairs forming the bond gets delocalized and not concentrated between the nuclei. While, in the **Valence Bond** picture the electrons in a molecule occupy atomic orbitals and the overlap of atomic orbitals results in the formation of a bond.

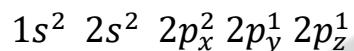
Larger the overlap stronger is the bond. Thus, the VB theory represents a localized picture of the chemical bond. However, the localized and delocalized pictures of the chemical bond are equivalent as the charge distribution in each molecular orbital when added up over the region where the bond is extended gives the same total charge density as that given by the VB theory.

In this localized picture, the direction in which maximum overlap occurs will be the direction of the bond.

4. Visualizing the Shape of Polyatomic Molecules:

It is easier to visualize the shape of polyatomic molecules with the electron pair concept.

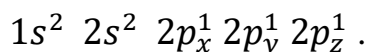
Consider the structure of water molecule. The electron configuration of the oxygen atom is



The two unpaired electrons in the $2p_y$ and $2p_z$ orbitals that are at right angles are available for bonding with the $1s$ orbital of hydrogen atoms. The s -orbital can overlap to the same extent in all directions as it is spherically symmetric whereas the p orbitals have certain preferred directions. Therefore, one gets a water molecule with HOH angle 90°

However, the actual value is 104.5° . When the water molecule is formed, the electrons in the OH bond are drawn towards the oxygen atom making the hydrogen atom slightly positive. That means the mutual repulsion between the hydrogens is partly responsible for the increases in the angle. Note that the angles are 91° and 93° in the case of H_2Se and H_2S , respectively.

NH_3 molecule, the central nitrogen atom has the electron configuration

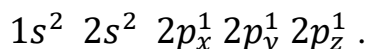


The maximum overlapping of the three p orbitals with the 1s hydrogen orbitals are possible along the x,y and z direction.

The bond angle in this case is 107.3° that is again partly due to the mutual repulsion between the hydrogen atoms. Note that in the related molecules PH_3 , AsH_3 and SbH_3 the observed angles are 93.3° , 91.8° and 91.3° respectively which is close to 90° .

5. Hybridization and Shape of Molecules

There is a limitation of the above concept of directed valence as it could explain bond angles only in certain molecules and it failed in large number of cases especially with carbon compounds. The electronic configuration of the carbon is



As the lobes of the two valence electrons are perpendicular, it is expected that the carbon atom will form two bonds at right angles to each other. While in a molecule like CH_4 it is found to form four equivalent bonds directed towards the corners of a tetrahedron. This is possible only if one of the $2s$ electrons is promoted to the vacant $2p_z$ orbital giving the excited electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$.

The four orbitals available now for bonding will not be equivalent. However, if there is mixing of the energy of the $2s$ and $2p$ orbitals, four orbitals of the same shape and energy is possible. The process of mixing of pure orbitals is called **hybridization** and the resulting mixed orbitals are called **hybrid orbitals**. Obviously, the resulting hybrid orbitals do not retain the characteristics of the original orbitals.

Generally, three types of hybridization are possible between s and p orbitals:

(i) sp hybridization (ii) sp^2 hybridization and (iii) sp^3 hybridization.

The figure depicts the polar representation of sp hybrid orbitals:

(a) $\Psi_{sp}(i)$, (b) $\Psi_{sp}(ii)$, (c) $\Psi_{sp}(i) + \Psi_{sp}(ii)$.

SP Hybridization

A linear combination of s and p orbitals in proper proportion gives hybrid sp orbitals. The angle between the directions of the maxima of the two resulting orbitals is 180° .

Thus, the two sp hybrid wave functions are:

$$\Psi_{sp}(i) = \frac{1}{\sqrt{2}} [\Psi(s) + \Psi(p_x)]$$

$$\Psi_{sp}(ii) = \frac{1}{\sqrt{2}} [\Psi(s) - \Psi(p_x)]$$

Figure shows how these hybrids which point in opposite directions arise from the two combinations. The combination $\Psi_{sp}(i)$ has a large lobe with positive sign since the positive signs of both $\Psi(s)$ and $\Psi(p_x)$ orbitals coincide.

In $\Psi_{sp}(ii)$ the large lobe with positive sign is on the other side because of $-\Psi(p_x)$ appears in the expression.

As the orbitals $\Psi_{sp}(i)$ and $\Psi_{sp}(ii)$ protrude more than the s and p orbitals, stronger bonds results due to considerable overlapping.

Formation of BeCl_2 molecule using sp hybrid orbitals of Be ($\Psi_{sp}(\text{i})$, $\Psi_{sp}(\text{ii})$ and $3p_x$ orbitals of chlorine) has been shown in the figure.

sp^2 Hybridization

The functions involved in sp^2 hybridization are s , one p_x and one p_y . Their linear combination results in three equivalent orbitals which are coplanar and oriented at 120° to each other. Equations for the three sp^2 orbitals are:

$$\Psi_{sp^2}(\text{i}) = \frac{1}{\sqrt{3}}\Psi(s) + \sqrt{\frac{2}{3}}\Psi(p_x)$$

$$\Psi_{sp^2}(\text{ii}) = \frac{1}{\sqrt{3}}\Psi(s) - \frac{1}{\sqrt{6}}\Psi(p_x) + \frac{1}{\sqrt{2}}\Psi(p_y)$$

$$\Psi_{sp^2}(\text{iii}) = \frac{1}{\sqrt{3}}\Psi(s) - \frac{1}{\sqrt{6}}\Psi(p_x) - \frac{1}{\sqrt{2}}\Psi(p_y)$$

Figure illustrates the formation of sp^2 hybrid orbitals from the component orbitals. Boron atom has an electronic configuration $1s^2 2s^1 2p_x^1$. The promotion of one $2s$ electron gives the excited state $1s^2 2s^2 2p_x^1 2p_y^1$ resulting in the formation of three sp^2 hybrid orbitals. In boron trichloride molecule, the sp^2 hybrid orbitals of boron

overlap with the $3p_x$ atomic orbitals of the chlorine atoms and gives the coplanar structure with bond angle 120° .

Figure sp^2 hybrid orbitals from component orbitals: (a) unhybridized $2s$, $2p_x$ and $2p_y$ orbitals, (b) hybridized sp^2 orbitals.

sp^3 Hybridization

The Hybridization of one $2s$ and three $2p$ orbitals results in four equivalent hybrid orbitals concentrated along the tetrahedral axes. This process is sp^3 Hybridization and the angle between the direction of the maxima of any two orbital being $109^\circ 28'$. The four orbitals do not retain their individual s and p characteristics.

The four combination which are mutually orthogonal and normalized are:

$$\Psi_{sp^3}(i) = \frac{1}{2}\Psi(s) + \sqrt{\frac{2}{3}}\Psi(p_z)$$

$$\Psi_{sp^3}(ii) = \frac{1}{2}\Psi(s) + \sqrt{\frac{3}{2}}\Psi(p_x) - \frac{1}{2\sqrt{3}}\Psi(p_z)$$

$$\Psi_{sp^3}(iii) = \frac{1}{2}\Psi(s) - \frac{1}{\sqrt{6}}\Psi(p_x) + \frac{1}{\sqrt{2}}\Psi(p_y) - \frac{1}{2\sqrt{3}}\Psi(p_z)$$

$$\Psi_{sp^3}(iv) = \frac{1}{2}\Psi(s) - \frac{1}{\sqrt{6}}\Psi(p_x) - \frac{1}{\sqrt{2}}\Psi(p_y) - \frac{1}{2\sqrt{3}}\Psi(p_z)$$

The carbon in CH_4 is sp^3 hybridized and each one of the tetrahedrally directed lobes overlaps with the s orbital of hydrogen giving rise to four equivalent carbon hydrogen σ bonds. The overlap is very effective and the charge distribution is symmetrical along the CH internuclear axis.

Other Hybridization

In addition to the three types discussed above, there are number of different types of h Hybridization giving rise to different spatial arrangements of orbitals. Table lists some of the Hybridizations along with molecular examples. The directional and overlapping properties of hybrid orbits are different from those of the constituent atomic orbitals. In short the concept of Hybridization helps us to understand shape and structure of molecules in a better way.

Table Certain Hybrid Orbitals

No. of Orbitals	Atomic-orbital combinations	Spatial arrangement	Example
2	sp	Linear	C ₂ H ₂ , CO ₂ , CN ⁻
3	sp ²	Trigonal	BCl ₃ , C ₂ H ₄ , NO ₃ ⁻
4	sp ³ OR d ³ s	Tetrahedral	CH ₄ , C ₂ H ₆ , MoO ₄ ²⁻
4	dsp ²	Square planar	PtCl ₄ ²⁻ , Ni(CN) ₄ ²⁻
5	dsp ³	Trigonal bipyramid	PCl ₅ , Fe(Co) ₅
6	d ² sp ³	Octahedron	PF ₆ ⁻ , SF ₆ , Fe(CN) ₆ ³⁻

Hybridization and shape of Molecules

Consider the case of ammonia and water molecules.

- The five outer electrons of the central nitrogen ($2s^2 2p^3$) of ammonia used the four tetrahedral orbitals formed by sp^3 Hybridization in the following way:

Three electrons occupy three orbitals singly and two electrons with opposite spins occupy the fourth orbital. The two electrons occupying the fourth orbital are referred to as **lone pair electrons**. The two electrons occupying the fourth orbitals with 1s electron of hydrogen leads to 3 bonding orbitals and one lone pair of electrons in ammonia.

- In the same way the six outer electrons of the oxygen atom ($2s^2 2p^4$) in water can occupy the four tetrahedral orbitals, two occupied by single electrons and the other two by lone pair of electrons. The singly occupied orbitals can

then accommodate the electrons of hydrogen atoms forming the water molecule.

The bonding pair of electrons is under the influence of two nuclei whereas the lone pair electrons are under the influence of only one nucleus. Therefore, the order of repulsion between electron pairs is likely to be as

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

- In CH_4 there is no lone pair whereas there is one in NH_3 and two in water. This accounts for the decrease in the bond angle as one goes from $\text{CH}_4(109.5^\circ)$ to $\text{NH}_3(107.3^\circ)$ to $\text{H}_2\text{O}(104.5^\circ)$