

# CH 107 Week 5 - Summary

Ashwin Abraham

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We started the lectures for this week by looking at Valence Bond Theory, which was an extension of the Lewis electron dot model. We constructed the Hamiltonian for the  $H_2$  molecule which came out to be very large. In order to simplify the massive Hamiltonian, we used the Born-Oppenheimer Approximation, in which we ignore the motion of and Potential Energies of the Nuclei and focus only on the electrons. We can do this as the Nuclei are much more massive than the electrons. Still, the Hamiltonian was not separable. Therefore, we need a method to get approximate solutions.

In order to find the approximate Energy of this system, Heitler and London wrote  $\Psi(1, 2)$  as:

$$\Psi(1, 2) = c_1\psi_A(1)\psi_B(2) + c_2\psi_A(2)\psi_B(1) \quad (1)$$

Here we represent  $\psi_A(1)\psi_B(2)$  as  $\psi_1$  and  $\psi_A(2)\psi_B(1)$  as  $\psi_2$ .

Therefore, on putting  $c_1\psi_1 + c_2\psi_2$  in the Hamiltonian, we get:

$$\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2) \quad (2)$$

In order to simplify this equation and get the coefficients  $c_1$  and  $c_2$ , we take the inner product on both sides with  $\psi_i$ , where  $i = 1$  or  $i = 2$ . Representing  $\langle\psi_i|\hat{H}\psi_j\rangle$  as  $H_{ij}$ , we get:

$$c_1(H_{11} - E) + c_2(H_{12} - ES^2) = 0 \quad (3)$$

$$c_1(H_{21} - ES^2) + c_2(H_{22} - E) = 0 \quad (4)$$

Where  $S$  represents the overlap integral  $\langle\psi_A|\psi_B\rangle$ . On evaluating this, for  $H_2$  it comes out to be:  $e^{-R}(1 + R + \frac{R^2}{3})$ .

Since  $c_1$  and  $c_2$  cannot both be 0, the determinant of the system of linear equations must be 0.

Hence we get the Secular Determinant equation:

$$\begin{vmatrix} H_{11} - E & H_{12} - ES^2 \\ H_{21} - ES^2 & H_{22} - E \end{vmatrix} = 0 \quad (5)$$

On solving these equations, using the fact that:

$$H_{11} = H_{22} = -1 + J \quad (6)$$

and

$$H_{12} = H_{21} = -S^2 + K \quad (7)$$

where  $J$  is the Coulomb Integral and  $K$  is the Exchange Integral, we get 2 possible values of Energy:

$$E_{\pm} = \frac{J \pm K}{1 \pm S^2} \quad (8)$$

These energies correspond to a singlet ground state and a triplet excited state.

We then talked about Hybridization, which originated in Valence Bond Theory. Here it was concluded that linear combinations of Atomic Orbitals lead to better bonding than the pure Atomic Orbitals.

We then constructed the  $sp$  and  $sp^2$  hybrid orbitals and drew their graphs and saw their nodal surfaces. For the  $sp$  orbital

$$\psi_1 = \frac{1}{\sqrt{2}}(\psi_s + \psi_p) \quad (9)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\psi_s - \psi_p) \quad (10)$$

For the  $sp^2$  orbital

$$\psi_1 = \frac{1}{\sqrt{3}}\psi_s + \sqrt{\frac{2}{3}}\psi_{p_y} \quad (11)$$

$$\psi_2 = \frac{1}{\sqrt{3}}\psi_s + \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y} \quad (12)$$

$$\psi_3 = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{2}}\psi_{p_x} - \frac{1}{\sqrt{6}}\psi_{p_y} \quad (13)$$