Approximate Methods in Quantum Chemistry
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Lecture 16
Molecular Orbital Treatment of Polyatomics

Hello students! Welcome to this lecture. In the last lecture we discussed about the molecular orbital treatment for diatomic molecules and in this lecture will extend our discussion to the molecular orbital treatment of polyatomic molecules.

Molecular orbital theory proceeds with one basic prescription, that is: the molecular orbitals are formed by linear combination of the atomic orbitals. While discussing the molecular orbital treatment of diatomics we took molecular symmetry into account, where we showed that atomic orbitals of same irreducible representation (under the molecular point group) can mix to give rise to molecular orbitals. This symmetry-adapted linear combination of atomic orbitals reduces the complexity of the linear variational problem to be solved. Let us now extend our discussion to polyatomic systems and see how symmetry-adapted molecular orbitals can be formed.

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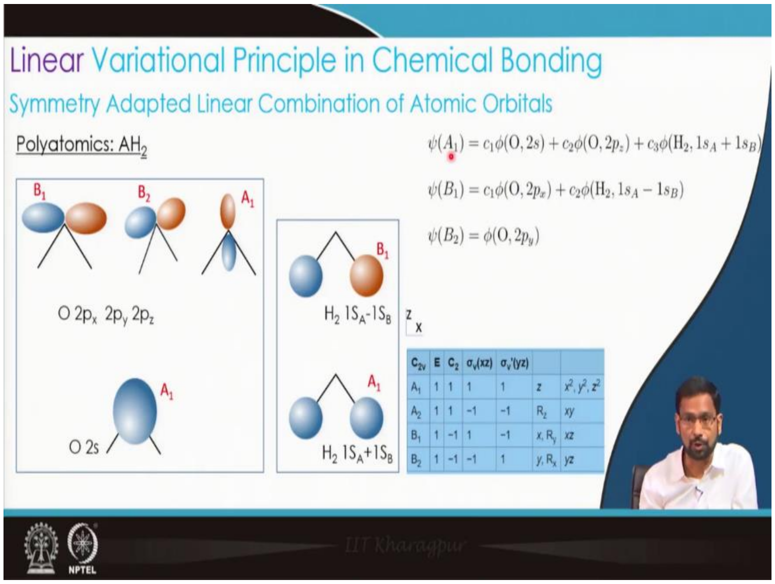


Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2

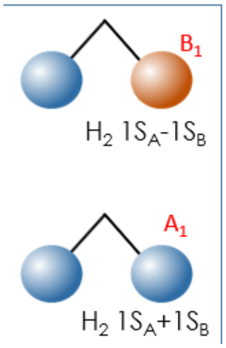
$$\psi(A_1) = c_1\phi(\mathrm{O},2s) + c_2\phi(\mathrm{O},2p_z) + c_3\phi(\mathrm{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\mathrm{O},2p_x) + c_2\phi(\mathrm{H}_2, 1s_A - 1s_B)$$

$$\psi(B_2) = \phi(\mathrm{O},2p_y)$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Let us consider a simple AH_2 system, where A can be any element in the second row of the periodic table. Here, we have three atoms, two hydrogen atoms and one A (N or O, for example). Each atom will participate in the chemical bonding using its valence orbitals. Here, instead of



considering each atom, let us treat the molecule as two fragments: A and H_2. We already know the molecular orbitals of H_2. One of them is a positive combination of the two 1s atomic orbitals (the bonding orbital) and the other one is the negative combination of the two (the antibonding orbital). The sign of the coefficients are indicated by the color of the orbitals. The AH_2 molecule belongs to C_{2v} point group. Hence, the symmetry of these fragment orbitals have to be determined within the same point group. In C_{2v} point group, there are four symmetry elements: E, C2 rotation around z-axis, σ_v along the xz and yz planes. By applying these symmetry operations on the fragment orbitals of H2, it can be shown that the bonding orbital spans A_1 and the antibonding orbitals spans B_1 irreducible representation (character table for this point group is given in the slide above).

Now, let us consider the central atom A, whose valence orbitals are 2s, 2px, 2py, and 2pz. We can find out from the character table that these orbitals span A_1, B_1, B_2, and A_2 irreducible representation, respectively. Taken together, we have now 6 orbitals which will take part in the linear combination for molecular orbital formation. If we do not use symmetry, the problem will be a 6 x 6 problem. However, when we consider symmetry we can see that 3 of these 6 orbitals have A_1 symmetry, 2 of them have B_1 symmetry and 1 is of B_2 symmetry. If we follow symmetry-adapted linear combination, we can write down three trial functions as given below:

$$\psi(A_1) = c_1\phi(\mathrm{O}, 2s) + c_2\phi(\mathrm{O}, 2p_z) + c_3\phi(\mathrm{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\mathrm{O}, 2p_x) + c_2\phi(\mathrm{H}_2, 1s_A - 1s_B)$$

$$\psi(B_2) = \phi(\mathrm{O}, 2p_y)$$

Here, the coefficients (c_i) are unknown and will be determined from the solution of the corresponding secular equations. It can be seen that instead of solving a 6 x 6 problem, we need to solve three simpler problems, one of which is a 3rd order problem and one is a 2nd order problem, while the third one does not require any additional calculations.

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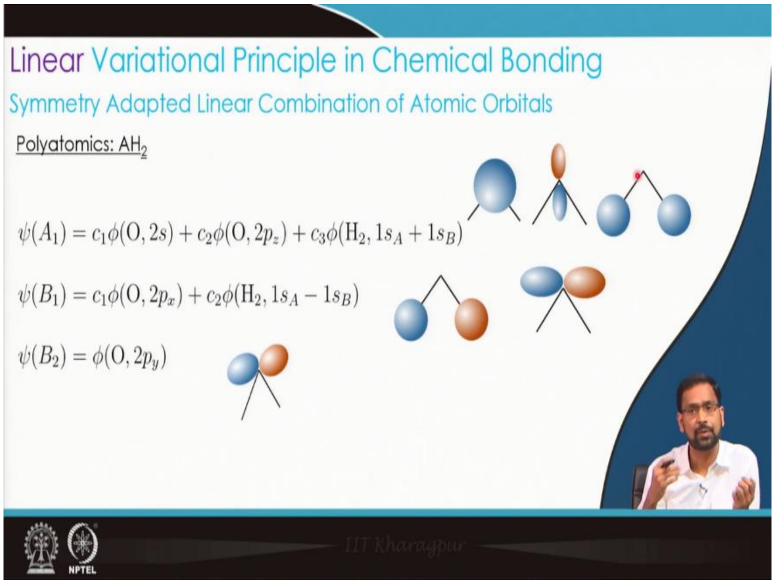

Linear Variational Principle in Chemical Bonding

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Polyatomics: AH_2

$$\psi(A_1) = c_1\phi(\mathrm{O}, 2s) + c_2\phi(\mathrm{O}, 2p_z) + c_3\phi(\mathrm{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\mathrm{O}, 2p_x) + c_2\phi(\mathrm{H}_2, 1s_A - 1s_B)$$

$$\psi(B_2) = \phi(\mathrm{O}, 2p_y)$$

The orbitals to be used for linear combination in each symmetry is shown above. For B2 symmetry, since there is a single orbital this orbital remains as a non-bonding orbital. In B1 symmetry, where we have two orbitals, the final molecular orbitals will be (similar to H2 case) of positive and negative combination of the two fragment orbitals. Similarly, within A1 symmetry, we need to mix three orbitals and the resulting molecular orbitals will be some linear combination of these fragment orbitals. For each of these problems, we can set up the secular equations, determine the overlap integrals, and energy integrals. The exact values of these integrals will depend on the molecular structure (A-H_1, A-H_2 bond distances and H_1-A-H_2 angle). Using these integrals, the secular equations can be solved and the eigenvalues and wave functions can be obtained. We are here skipping the numerical details of the linear variational calculations and focus instead on the final results.

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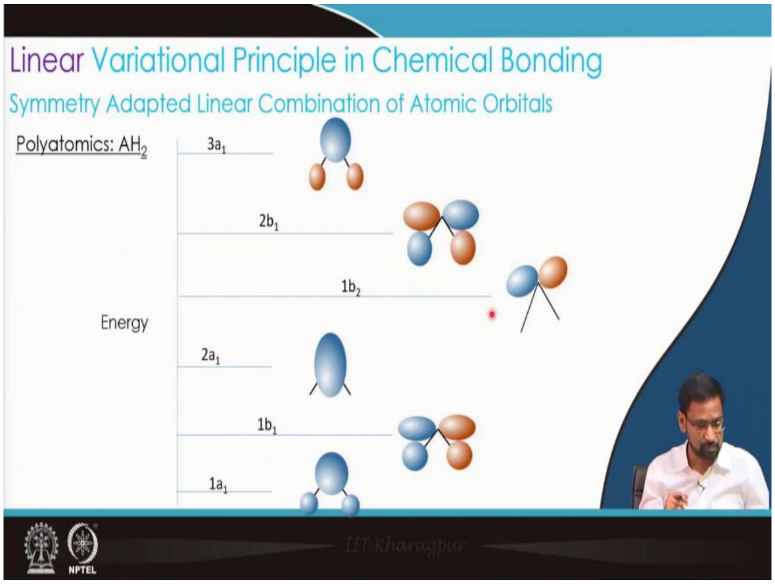

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2

Let us now arrange the final molecular orbitals according to their energy. We can immediately identify the non-bonding $1b_2$ molecular orbital (the first – and only – molecular orbital of b2 symmetry). We have two molecular orbitals from b1 symmetry: the lower energy one is the bonding combination ($1b_1$) and the upper energy one is the antibonding combination ($2b_1$) of the two fragment orbitals belonging to B_1 irrep. The third set of orbitals constitute three molecular orbitals of a_1 symmetry. Of these, $1a_1$ and $3a_1$ orbitals are the bonding and antibonding combinations of the orbitals of A with H_2 fragment, whereas $2a_1$ is a non-bonding orbital primarily composed of a 2p orbital of A. Keep in mind that the b_2, b_1 and a_1 molecular orbitals are obtained from three independent calculations and these orbitals are arranged according to their energy. Based on the number of electrons available, we can fill the molecular orbitals. For example, for an 8-(valence) electron AH_2 (A=oxygen), the electronic configuration is $1a_1^2\,1b_1^2$, $2a_1^2$, $1b_2^2$. One can perform a similar analysis for AH_3, AH_4 systems and derive various molecular properties from the molecular orbital theory.

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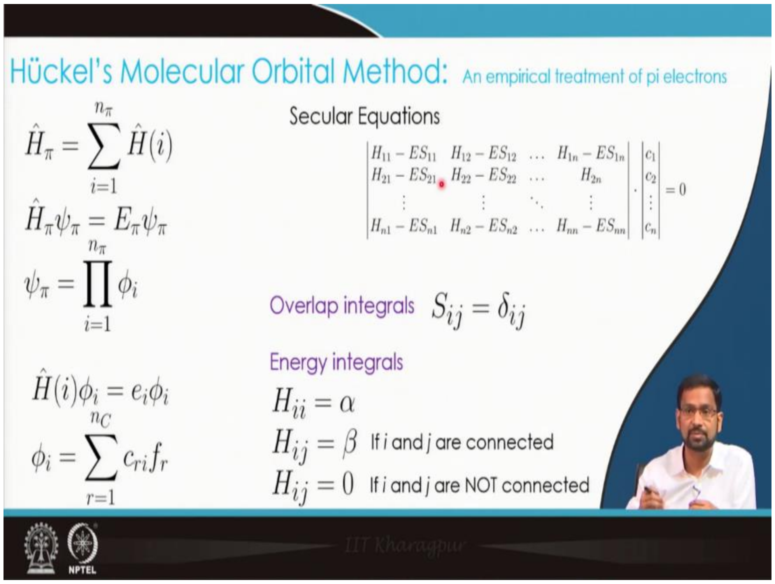


Hückel's Molecular Orbital Method: An empirical treatment of pi electrons

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{H}(i)$$

$$\hat{H}_\pi \psi_\pi = E_\pi \psi_\pi$$

$$\psi_\pi = \prod_{i=1}^{n_\pi} \phi_i$$

$$\hat{H}(i)\phi_i = e_i \phi_i$$

$$\phi_i = \sum_{r=1}^{n_C} c_{ri} f_r$$

Secular Equations

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

Overlap integrals $S_{ij} = \delta_{ij}$

Energy integrals

$H_{ii} = \alpha$

$H_{ij} = \beta$ If *i* and *j* are connected

$H_{ij} = 0$ If *i* and *j* are NOT connected

Let us now extend our discussion to even larger systems. Here, we will discuss the molecules with pi electrons. Consider ethylene, where you have carbon-hydrogen sigma bonds and carbon-carbon sigma bond along with C-C pi bond. We can follow a similar approach of symmetry-adapted linear combination of atomic orbitals to obtain the sigma and pi orbitals of ethylene. From symmetry point of view, the sigma and pi orbitals do not mix and hence can be obtained from independent calculations. We can extend this observation to even larger pi-conjugated systems, such as, butadiene or benzene, etc. In essence, we can separately treat the pi-orbitals from the rest. This has further helped from energy arguments, where a clear sigma-pi separation is often noticed. Since the pi-orbitals often constitute the chemically significant frontier molecular orbitals, In the rest of the discussion, we will ignore the sigma bonds and focus only on pi bonds, following the approach of Hückel, popularly known as Hückel's molecular orbital theory (H-MOT).

There are a few fundamental approximations in H-MOT. First, we consider only the pi-electrons in the Hamiltonian ($\widehat{H}_\pi$), where the total Hamiltonian of the pi system is now considered as the sum of several one-electron Hamiltonians ($\widehat{H}_i$). The solution of the pi Hamiltonian is achieved by expressing the wave function as a product of the 1-electron wave functions. For a n_π electrons system, the total wave function is simply given as a product of n_π one-electron wave functions.

$$\hat{H}_\pi = \sum_{i=1}^{n_\pi} \hat{H}(i)$$

$$\hat{H}_\pi \psi_\pi = E_\pi \psi_\pi$$

$$\psi_\pi = \prod_{i=1}^{n_\pi} \phi_i$$

The one electron wave functions ϕ_i are the solution of one electron Hamiltonians, where the one-electron functions ϕ_i are expressed as linear combination of $2p_z$ orbitals of the carbon atoms in the pi system with n_c number of C-atoms.

$$\hat{H}(i)\phi_i = e_i\phi_i$$

$$\phi_i = \sum_{r=1}^{n_C} c_{ri} f_r$$

Given the choice of the trial function as a linear combination of several atomic orbitals, we can now carry out a linear variation calculation by evaluating the overlap integrals (S_{ij}) and energy integrals (H_{ij}). With increasing number of C-atoms in the molecule of interest, the number of integrals to be evaluated increases. In Huckel's molecular orbital theory, however, we do not explicitly evaluate these integrals. Rather, we use some empirical estimations for these integrals based on some simple guidelines (or rules) as following:

Overlap integrals $S_{ij} = \delta_{ij}$

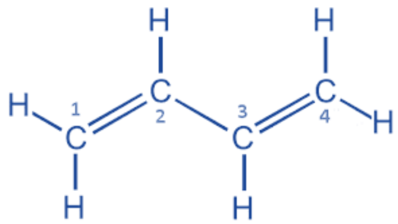
Energy integrals

$H_{ii} = \alpha$

$H_{ij} = \beta$ If *i* and *j* are connected

$H_{ij} = 0$ If *i* and *j* are NOT connected

The overlap integrals between any two (normalized) orbitals centred on two different atoms are approximated as 0. This approximation can be justified from the fact that the overlap integrals between two p_z orbitals are small and nearly constant. Furthermore, the energy integrals are also not explicitly calculated. Rather, some empirical constants (α and β) are used in their place, as shown above.



Consider betadine. C3 and C1 are not connected. Hence from the above rule, $H_{13} = 0$. On the other hand, $H_{12} = \beta$ (a negative constant, called bond integral or resonance integral), as C1 and C2 are connected. Additionally, $H_{11} = H_{22} = H_{33} = H_{44} = \alpha$. So, instead of calculating any of these integrals we are just taking some standard empirical values and putting them into the secular equations.

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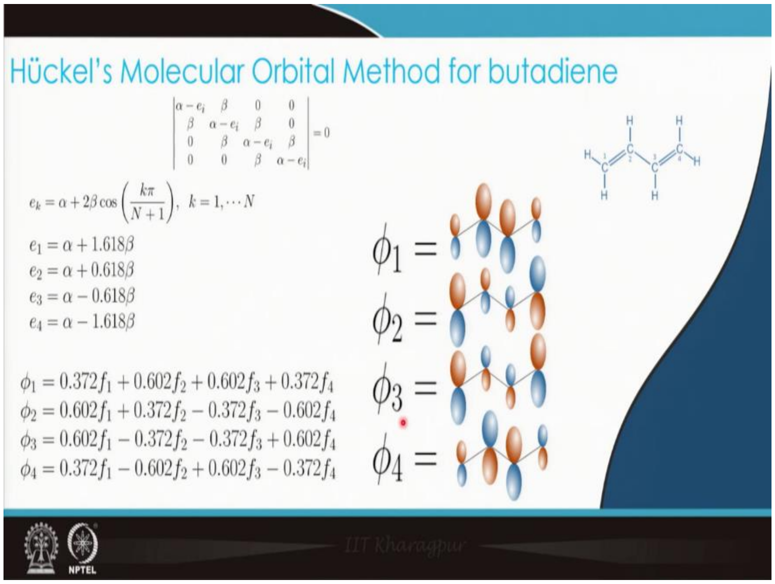


Hückel's Molecular Orbital Method for butadiene

$$\begin{vmatrix} \alpha - e_i & \beta & 0 & 0 \\ \beta & \alpha - e_i & \beta & 0 \\ 0 & \beta & \alpha - e_i & \beta \\ 0 & 0 & \beta & \alpha - e_i \end{vmatrix} = 0$$

$$e_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right), \quad k = 1, \cdots N$$

$$e_1 = \alpha + 1.618\beta$$
$$e_2 = \alpha + 0.618\beta$$
$$e_3 = \alpha - 0.618\beta$$
$$e_4 = \alpha - 1.618\beta$$

$$\phi_1 = 0.372 f_1 + 0.602 f_2 + 0.602 f_3 + 0.372 f_4$$
$$\phi_2 = 0.602 f_1 + 0.372 f_2 - 0.372 f_3 - 0.602 f_4$$
$$\phi_3 = 0.602 f_1 - 0.372 f_2 - 0.372 f_3 + 0.602 f_4$$
$$\phi_4 = 0.372 f_1 - 0.602 f_2 + 0.602 f_3 - 0.372 f_4$$

Based on the rules discussed above, the secular equations for the linear variational problem appears as

$$\begin{vmatrix} \alpha - e_i & \beta & 0 & 0 \\ \beta & \alpha - e_i & \beta & 0 \\ 0 & \beta & \alpha - e_i & \beta \\ 0 & 0 & \beta & \alpha - e_i \end{vmatrix} = 0$$

The eigenvalues of the tridiagonal matrix are given by a general formula

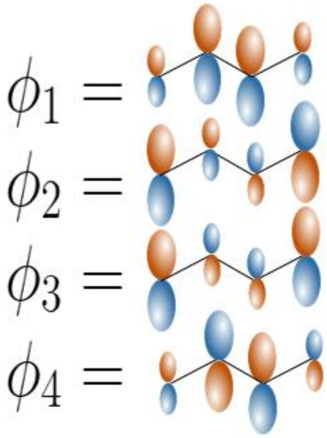
$$e_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right), \quad k = 1, \cdots N$$

$$e_1 = \alpha + 1.618\beta$$
$$e_2 = \alpha + 0.618\beta$$
$$e_3 = \alpha - 0.618\beta$$
$$e_4 = \alpha - 1.618\beta$$

Since beta is a negative constant, e_1 is the lowest energy orbital and e_4 is the highest energy orbital. Now, corresponding to each energy value, we can get a set of coefficients which can be used in the linear combination to express the (Hückel) molecular orbitals:

$$\begin{aligned}
\phi_1 &= 0.372f_1 + 0.602f_2 + 0.602f_3 + 0.372f_4 \\
\phi_2 &= 0.602f_1 + 0.372f_2 - 0.372f_3 - 0.602f_4 \\
\phi_3 &= 0.602f_1 - 0.372f_2 - 0.372f_3 + 0.602f_4 \\
\phi_4 &= 0.372f_1 - 0.602f_2 + 0.602f_3 - 0.372f_4
\end{aligned}$$

The above wave functions can be pictorially represented as the following:



Here the lowest energy orbital (ϕ_1) has no nodes, while the higher energy orbitals have increasingly greater number of nodes (1, 2, 3 for ϕ_2, ϕ_3, ϕ_4, respectively). Once the molecular orbitals are determined, the electron configuration can be obtained by filling the available $\pi-$electrons starting from the lowest energy orbitals. For example, in butadiene, the $\pi -4$ electrons can be filled in $\phi_1\ and\ \phi_2$. Thus, ϕ_2, ϕ_3 become the HOMO and LUMO, respectively, of this molecule. We can use these results to discuss the stability, reactivity of the concerned molecules. But we must always be aware of the approximations we have made to get these results. For quantitative accuracy we require accurate calculations, with explicit evaluation of the integrals.

In this lecture we discussed how we can use linear variational principle to describe the famous Hückel molecular orbital theory.

Thank you for your attention.