Approximate Methods in Quantum Chemistry
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Lecture 15
Topic – Molecular Orbital Treatment of Diatomics and Polyatomics

Hello students! Welcome to this lecture. In the last lecture we discussed a few applications of linear variational method in chemical bonding. Within that we discussed the molecular orbital theory and its application in hydrogen molecule. We discussed that molecular orbital theory suggests to construct trial wave function for the molecule as a linear combination of the atomic orbitals.

In this lecture we will extend our discussion from hydrogen molecule to other larger systems. In case of hydrogen molecule, we had only 1s electrons, for molecules with heavier atoms, we need to consider electrons in other orbitals. First, we will discuss molecular orbital treatment of diatomics and then extend our discussion to polyatomics.

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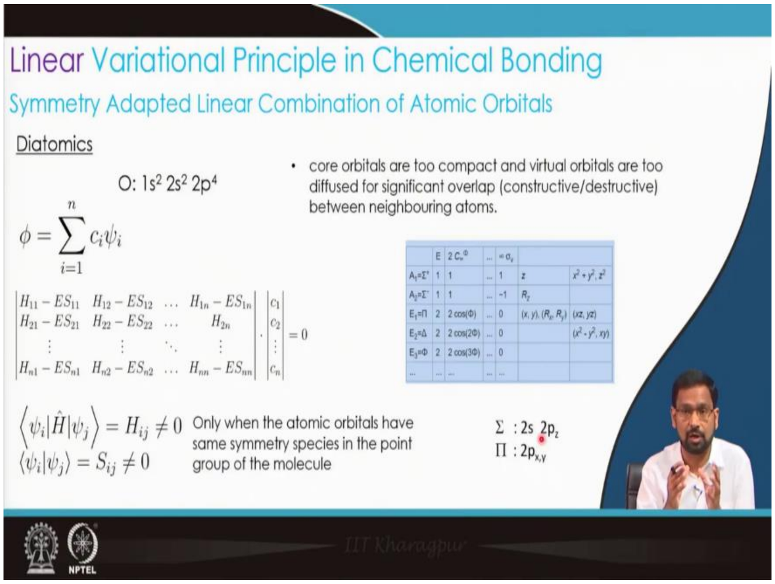

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Diatomics

O: $1s^2\,2s^2\,2p^4$

- core orbitals are too compact and virtual orbitals are too diffused for significant overlap (constructive/destructive) between neighbouring atoms.

$$\phi = \sum_{i=1}^{n} c_i \psi_i$$

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

	E	$2C_\infty^\Phi$	...	$\infty\sigma_v$		
$A_1=\Sigma^+$	1	1	...	1	z	x^2+y^2, z^2
$A_2=\Sigma^-$	1	1	...	-1	R_z	
$E_1=\Pi$	2	$2\cos(\Phi)$	...	0	$(x, y), (R_x, R_y)$	(xz, yz)
$E_2=\Delta$	2	$2\cos(2\Phi)$	...	0		(x^2-y^2, xy)
$E_3=\Phi$	2	$2\cos(3\Phi)$	...	0		
...	...	...	...	...		

$$\langle \psi_i | \hat{H} | \psi_j \rangle = H_{ij} \neq 0$$
$$\langle \psi_i | \psi_j \rangle = S_{ij} \neq 0$$

Only when the atomic orbitals have same symmetry species in the point group of the molecule

Σ : 2s $2p_z$

Π : $2p_{x,y}$

Let us consider any diatomic molecule from atoms in the 2nd row of the periodic table. For example, O atom, whose electron configuration is $1s^2 2s^2 2p^4$. When O atom takes part in a molecule (O_2, CO, NO etc.), it does so by using its electron in various orbitals. These atomic orbitals are the eigenfunctions of the Hamiltonian of O atom. They form a complete set of orthonormal eigenfunctions (1s, 2s, 2p, 3s, 3p, 3d, …), although in the ground state only the lowest 2 shells carry electrons. The higher energy orbitals which do not carry electrons (the so-called virtual orbitals) are diffused and hence can be ignored from our trial function (although for accurate treatment of the system, these orbitals need to be considered). On the other hand, the low-energy orbitals (such as 1s in O) are too compact to participate in chemical bonding. Hence, the core orbitals can also be ignored from our trial function. This leaves us with the valence orbitals (2s, 2p in O), which are important for chemical bonding and hence will be included in our trial function. If we consider O_2 molecule, each oxygen will be described by 4 atomic orbitals (2s, 2px, 2py, 2pz) and hence the trial function of the molecule will have total 8 atomic orbitals. We can proceed to do a linear variational calculation, which in case of O_2 will be an 8 x 8 problem.

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

Before solving the above secular equations, we need to evaluate to overlap integrals (S_{ij}) and the Hamiltonian matrix elements (H_{ij}). We can see there are several integrals to be evaluated. But we would now use molecular symmetry to reduce the number of integrals we need to evaluate.

Hamiltonian of a system is invariant to any symmetry operation of the molecule. This means, when I construct the matrix element H_{ij}, the integral survives only when it is totally symmetric.

$$\left\langle \psi_i \middle| \hat{H} \middle| \psi_j \right\rangle = H_{ij} \neq 0$$
$$\langle \psi_i | \psi_j \rangle = S_{ij} \neq 0$$

From symmetry arguments, we can see that the above integrals are totally symmetric only when both ψ_i and ψ_j span the same irreducible symmetry in the molecular point group. We should keep in mind that the energy integrals and the overlap integrals become 0 when the concerned atomic orbitals do not belong to the same irreducible presentation. By referring to a character table of the point group of the molecule of interest, we can easily find out symmetry of the atomic orbitals. For example, for a heteronuclear diatomic molecule, we can check the character table for $C_{\infty v}$ point group and find out that the 2s and 2pz orbitals belong to Σ^+ irreducible representation, while the 2px and 2py orbitals belong to Π symmetry. Since the orbitals of different symmetry would not mix with each other, we can reduce the complex 8 x 8 problem to separate small problems, corresponding to each symmetry representation. In the case O_2, we can treat 2s and 2pz of both O atoms separately from the treatment of the 2px and 2py orbitals of the atoms. In this case, 8 x 8 problem reduces to two 4 x 4 problems.

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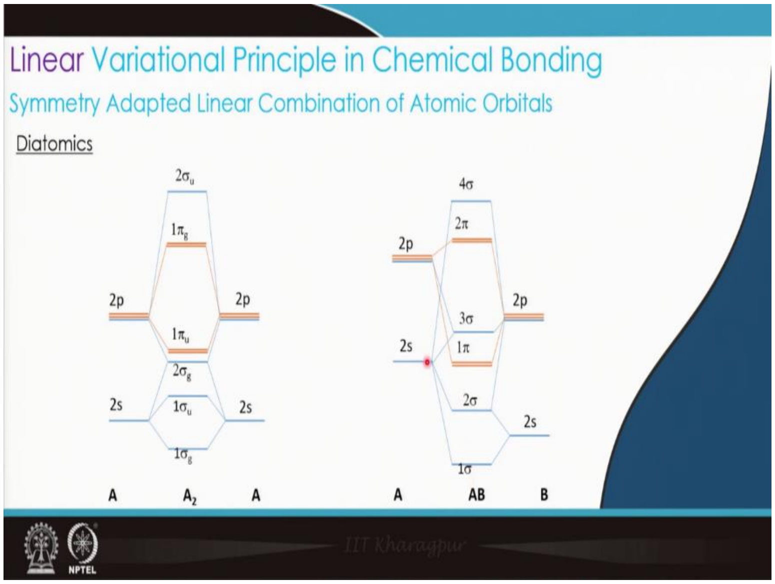

Linear Variational Principle in Chemical Bonding

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Diatomics

If we carry out the abovementioned two 4 x 4 variational problems, we would obtain the energies and the wave functions of the diatomic molecules. The wave functions are expressed as linear combination of the constituent atomic orbitals. The final result of this exercise is often expressed in terms of the very familiar molecular orbital diagrams, as shown above. The connecting lines between the atomic orbitals and the molecular orbitals indicate the linear combination of atomic orbitals to form molecular orbitals.

Let us consider the molecular orbitals arising from the 2s and 2pz orbitals – called the sigma orbitals. Among the four σ orbitals, two molecular orbitals arise from the positive combination of the atomic orbitals that gives rise to 'bonding' molecular orbitals. The bonding molecular orbitals, for a homonuclear diatomic molecule, is symmetric with respect to the centre of inversion and hence is called σ_g (sigma – gerade (even)) molecular orbital. Similarly, the negative combination of the orbitals give rise to the antibonding σ_u (sigma – ungerade) (odd)) molecular orbitals.

Similarly, we can consider the 2px and 2py orbitals of the two atoms, which form four molecular orbitals of π symmetry. Since 2px and 2py orbitals are degenerate, the resulting molecular orbitals are also two-fold degenerate. One pair of these π orbitals is a positive (bonding) combination and the other pair is a negative combination (antibonding). For π orbitals in homonuclear diatomic molecules, the bonding orbitals are anti-symmetric with respect to centre of inversion (hence π_u) while the antibonding orbitals are symmetric (π_g).

Using symmetry arguments, we obtained the 4 σ and 4 π orbitals from two independent calculations. For electronic configuration, we can arrange the obtained molecular orbitals according to their energy and fill the available electrons following aufbau principle. For diatomic molecules, the exact value of the molecular orbital energy depends on the exact value of the 2s-2p separation energy of the atom, and the inter-nuclear distance. From accurate calculations, it is seen that the $1\pi_u$ and $2\sigma_g$ orbitals switch their relative position. For oxygen and heavier atoms (in the 2nd row) the corresponding diatomic molecular orbitals show $2\sigma_g$ having lower energy $1\pi_u$, while the opposite is true for diatomic molecules with lighter elements (such as, N_2, etc.). Please keep in mind, that accurate estimation of the energy and orbital composition requires explicit solution of the corresponding linear variational problem. The qualitative, diagrammatic representation of the molecular orbitals are quite useful in giving us an insight to chemical bonding, bond order, bond distance etc.

Now, we can extend our discussion to heteronuclear diatomic systems, where the two atoms have different electronegativity, which affects the relative energies of the atomic orbitals. For example, in the diagram shown above, the 2s orbital of B is much lower in energy than that of the 2s orbital of A (when B is more electronegative). In such a case, the extent of mixing of the two orbitals is reduced, which influences the energies of the molecular orbitals. The final orbital energies and the wave functions can be obtained in a similar symmetry-adapted linear combination formalism within the linear variational method.

In the next lecture, we will consider molecular orbital treatment of larger molecular systems.

Thank you for your attention.