Concepts of Chemistry for Engineering
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Lecture No. 19
Introduction to Molecules with π bonds

Now that we have talked about methane, a polyatomic molecule with sigma bonds only, and now that we have got an idea that we can generate molecular orbitals that are delocalized over the entire molecule, but they can give you an idea about the electron density between two given atoms, the field is set for a discussion of molecules that have π bonds. And we will start with the simplest such molecule that one can think of and that is ethylene.

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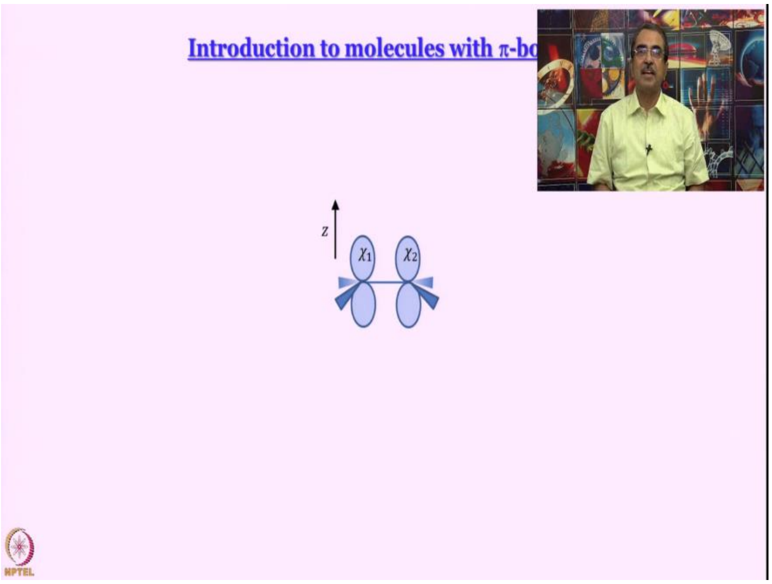
Introduction to molecules with π-bo

And here we are going to use this kind of a cartoon notation always. Here, we are actually drawing these constant probability surfaces the way they are usually drawn in textbooks. And our notation is going to be that we are going to denote the p orbitals, the atomic p orbitals as Xs, X_1 , X_2, X_3 whatever is required, and we are going to denote the molecular orbitals as Ψs.

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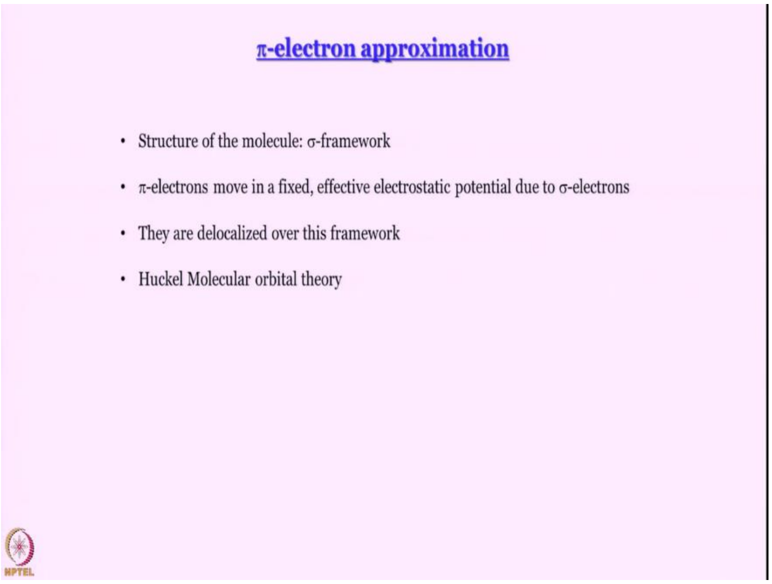

π-electron approximation

- Structure of the molecule: σ-framework
- π-electrons move in a fixed, effective electrostatic potential due to σ-electrons
- They are delocalized over this framework
- Huckel Molecular orbital theory

So, before we do that, let us discuss in very brief what π-electron approximation is. First of all, the structure of the molecule is considered to be built by the σ-framework. And while building this, it does not matter, whether one has used valence bond theory or molecular orbital theory, whether hybrid orbitals have been used or not. The structure of molecule is supposed to be in place.

So, π bonding comes into play only after a σ-bond is established. That is the realm of this theory. We are not talking about molecules that have exclusive π bonds only. So, the π framework has to be defined first, sorry the σ framework has to be defined first. And π electrons are considered to move in a fixed effective electrostatic potential involving σ electrons, not due to, but involving σ electrons. What does it mean? That means there are a number of nuclei.

So, if you take a pi electron, a given by electron, they are considered to move under the joint field of this nucleus, but this field is shielded by the remaining electrons. Remember, when we talked about particle in a box, we are said that we can approximately describe conjugated polyenes by a particle in a box model, free electron model, there are also the consideration was that there is shielding of the nuclear charge by the remaining electrons when we talk about any given electron.

Here, we are considering that the shielding is such that it is not complete, the electron does not become free as long as it is in the molecule the, potential energy is not equal to 0 necessarily, but there is shielding, effective electrostatic potential is there. And in this framework π electrons are delocalized all over. The method to do this, the simplest method is Hückel molecular orbital theory.

Hückel, u has actually two dots on top of it. And this is a semi-empirical approximate method. As you see, we will not make any attempt to write down the Hamiltonian completely. We will not make any attempt for an exact solution, because it cannot be achieved. Rather, we will use certain experimental conditions, experimental considerations to build our semi-empirical approximate description of these molecules in question.

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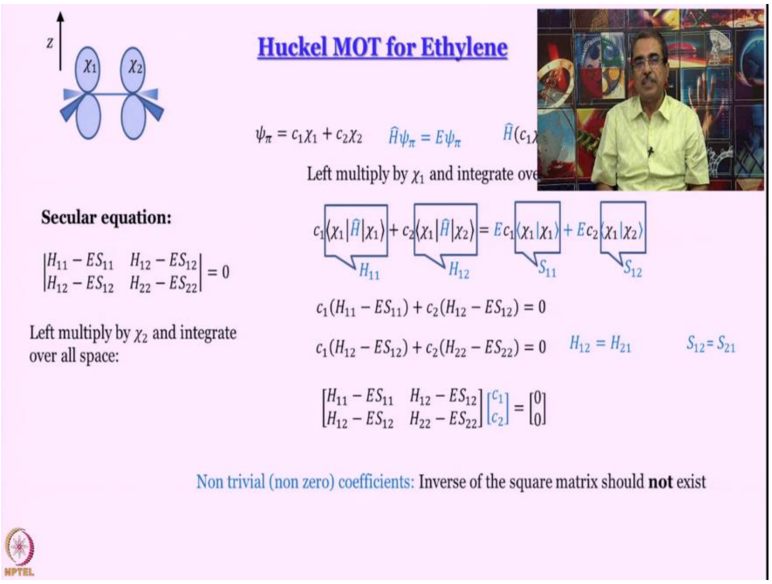

Huckel MOT for Ethylene

$\psi_\pi = c_1\chi_1 + c_2\chi_2$ $\quad \hat{H}\psi_\pi = E\psi_\pi$ $\quad \hat{H}(c_1\chi$

Left multiply by χ_1 and integrate ove

$$c_1\underbrace{\langle\chi_1|\hat{H}|\chi_1\rangle}_{H_{11}} + c_2\underbrace{\langle\chi_1|\hat{H}|\chi_2\rangle}_{H_{12}} = Ec_1\underbrace{\langle\chi_1|\chi_1\rangle}_{S_{11}} + Ec_2\underbrace{\langle\chi_1|\chi_2\rangle}_{S_{12}}$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

Left multiply by χ_2 and integrate over all space:

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0 \qquad H_{12} = H_{21} \qquad S_{12} = S_{21}$$

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

Non trivial (non zero) coefficients: Inverse of the square matrix should **not** exist

Secular equation:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

With this background, let us discuss ethylene. And remember when I say let us discuss ethylene, I mean, let us discuss the π electrons of ethylene. So, this is the cartoon that we have shown you earlier. The π wave function will be written as $\Psi\varphi$ is equal to $c_1\chi_1+c_2\chi_2$, but χ_1 and χ_2, as we said earlier, are the 2p orbitals of the two items here, c_1 and c_2 are the coefficients.

Before going further, is there any reason why the magnitude of c_1 should be any different than the magnitude of c_2? Actually, there is not. By symmetry, I mean, one and two are arbitrary levels we are using. We can interchange them. So, there is no reason why either of these coefficients will have more or less magnitude than the other. Remember, square of coefficient is a contribution of that p electron in the pi molecular orbital. Square of coefficient is the contribution of that p orbital in the molecular orbital, in the pi molecular orbital.

So, there is no reason really why MOT c_1 should be anything other than MOT c_2. So, we are going to work this out more formally, but I hope you understand this clearly. So, we might as well take c out and write c multiplied by $\chi_{1}\pm\chi_{2}$, that is the kind of wave function we are going to get. That is something we can sort of guess even before going into any further.

Now, let us write Schrodinger equation, $H\Psi_{\pi}=E\Psi_{\pi}$, very simply. In the next step, let us expand the wave function. Hamiltonian, what is the Hamiltonian here? Hamiltonian, remember, we are saying that the any electron that we talk about is considered to be moving in an effective potential provided by all the nuclei in question and the other electron. So, if I am talking about χ_1, well, if I am talking about electron in, on the first atom, then I am talking about this electron moving in the field of nucleus 1, nucleus 2 and electron 2. That is what the Hamiltonian is.

If you want you can write down the expression. We will not do it, because we are not going to make any attempt to actually solve it exactly. So, $\widehat{H}(c_1\chi_1+c_2\chi_2)=E(c_1\chi_1+c_2\chi_2)$. Is χ_1 or χ_2 an Eigen function of this Hamiltonian, no, they are not. They are Eigen functions of the hydrogen atom Hamiltonian, did not coordinates of 1 or 2. Is $c_1\chi_1+c_2\chi_2$ an Eigen function of the Hamiltonian $\widehat{H}$, yes, it is. The combination is an Eigen function. That is why we have been able to write the Schrodinger equation in this form.

The only trouble is that there is no direct way of solving this and finding E. So, we are going to try an indirect method that is used very commonly in quantum mechanical problems. What do we do? We left multiply chi 1 and integrate over all space. We are trying to generate two different equations. Why, because we do not know what the mixing coefficients are c1 and c2, two unknowns, we need two equations and this is how we generate them.

For the first equation, left multiplied by χ_1 integrate over all space. What do you get? $c_1\int\chi_1\widehat{H}\,\chi_1+c_2\int\chi_1\widehat{H}\,\chi_2=Ec_1\int\chi_1\,\chi_1+Ec_2\int\chi_1\,\chi_2$. In bracket notation this is what we get. Please make sure that you understand how we get this expression, how we get this equation, $c_1\int\chi_1\widehat{H}\,\chi_1+c_2\int\chi_1\widehat{H}\,\chi_2=Ec_1\int\chi_1\,\chi_1+Ec_2\int\chi_1\,\chi_2$

Do we know how to find out these integrals? We actually do not. But we can at least give them some names. So, the first one $\int\chi_1\widehat{H}\,\chi_1$, I call it H_{11}. In general, $\int\chi_i\widehat{H}\,\chi_i$ is going to be called $\widehat{H}_{ii}$. Then $\int\chi_1\widehat{H}\,\chi_2$ is given the name H_{12}. I hope you can see the pattern here. The name of the integral is H from Hamiltonian, subscript of the first wave function, then subscripts of the second wave function like that.

On the right-hand side, we call $\int \chi_1 \chi_1$ as S_{11}. Of course, I hope it is not very difficult for us to realize that this S_{11} is going to be equal to 1, because χ_1 is a p orbital that is normalized. And another thing, here we are working with real p orbitals. We are working with p_x, p_y, p_z. In this kind of a molecule, it is more convenient if you talk about the molecule in xy plane, and you consider χ_1 *and* χ_2 to be along z-axis.

So, of course, that is going to be 1. But for some time let us retain the notation S11, because then we get some nice good looking symmetric expressions. So, we will just keep it for now. And $\int \chi_1 \chi_2$ is S_{12} and that also you know. Overlap integral as we have encountered in our discussion of H_2^+. The only difference is that for $H_2^+$the overlap integral came from this kind of an overlap head on, here we are talking about this kind of an overlap side on.

So, let us write this equation in terms of these integrals and let us bring everything on the right hand to the left-hand side so that on the right-hand side we left with 0. What do we get, $c_1(H_{11}-ES_{11})+c_2\ (H_{12}-ES_{12})=0$. So, a linear equation in which the variables are c_1 and c_2 and their coefficients are $H_{11}-ES_{11}$ and $H_{12}-ES_{12}$, respectively.

So, that is the first equation that we sought. How do we get the second equation? Same thing, just left multiply by χ_2 and integrate over all space. I encourage you to please do it yourself and convince yourself that the expression you get is this $c_1(H_{12}-ES_{12})+c_2\ (H_{22}-ES_{22})=0$. And when you do that, one thing that should come to your notice is that here I have written H_{12} actually I should have written H_{21}, because I am left multiplying by χ_2.

So, the p orbital in the vector is actually χ_2 and not χ_1. Why have I written H_{12}? Well, without going into further detail, believe me when I say that utilizing the properties of Hermitian operators, H is a Hermitian operator, remember, H_{12} is equal to H_{21}. It comes from something called turnover rule. And S_{12}, of course, will be equal to S_{21}, because it is just integral of a product of two functions. $F_1\ F_2$ and $F_2\ F_1$ give you the same thing.

So, we got two equations and we have two unknowns, c_1 and c_2. So, we should be able to, in principle, solve this and get expressions and find out what c_1 and c_2 are. Let us write this system of linear equations as a matrix equation, like this, square matrix containing the coefficients multiplies a column matrix containing the variables to give us a column matrix, elements of which are 0 and 0.

Now, see, how do I solve this equation? One solution is that c_1 is equal to 0 and c_2 equal to 0. But if that is the case, then there is no mixing. There is no wave function, because $\Psi_\pi$is going to be $(0 \times \chi_1 + 0 \times \chi_2)$. So, there is no wave function. That is a trivial solution. What is, how can we hope to get a non-trivial solution, a non-zero value of c_1 and c_2? Well, this can exist if this matrix cannot be inverted. The square matrix here, if it is such that it cannot be inverted, that is the only hope of getting non-zero solutions for c1 and c2.

What is the condition for an inverse of a matrix to exist? The condition is that its determinant should not be equal to 0. Here we want the opposite thing. We want the inverse to not exist. So, the condition is that the inverse of the square matrix should not exist. Therefore, this determinant of the square matrix should be equal to 0. When this determinant equal to 0, the inverse does not exist, and that is the only hope of us getting c_1 and c_2 that are non-zero. So, this determinant is called the secular determinant. And secular determinant equal to 0 is called a secular equation.

For the rest of the discussion, we are going to try to see how one can solve for this secular equation.