Concepts of Chemistry for Engineering

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Lecture No. 20

Hückel's MOT for ethylene

We are discussing Hückel MOT for ethylene. We have formulated the problem, we have identified these integrals H_{11}, H_{12}, S_{11}, S_{12} and we have obtained this secular equation where this determinant is equal to 0. Now, the next thing is to try and find solutions for this secular equation.

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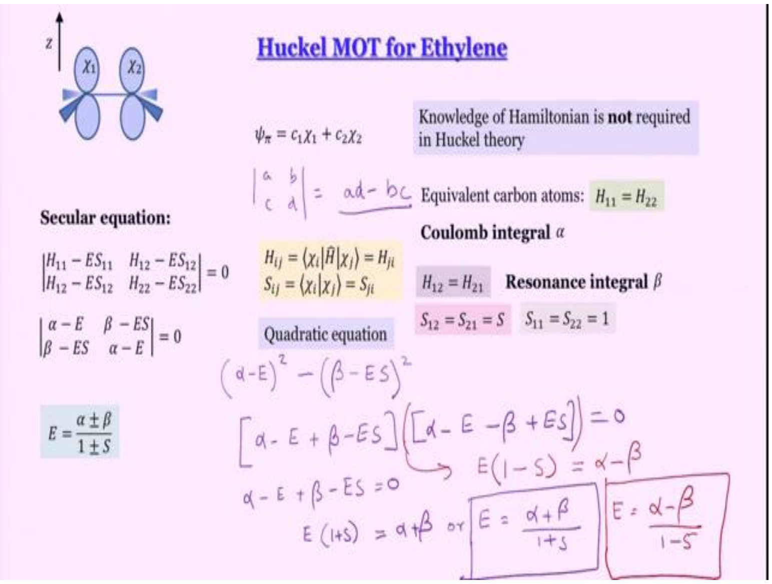

Huckel MOT for Ethylene

$\psi_\pi = c_1\chi_1 + c_2\chi_2$

Knowledge of Hamiltonian is **not** required in Huckel theory

$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = \underline{ad - bc}$

Equivalent carbon atoms: $H_{11} = H_{22}$

Coulomb integral α

Secular equation:

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

$H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle = H_{ji}$

$S_{ij} = \langle \chi_i | \chi_j \rangle = S_{ji}$

$H_{12} = H_{21}$ **Resonance integral** β

$S_{12} = S_{21} = S$ $S_{11} = S_{22} = 1$

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

Quadratic equation

$(\alpha - E)^2 - (\beta - ES)^2$

$[\alpha - E + \beta - ES]([\alpha - E - \beta + ES]) = 0$

$\rightarrow E(1 - S) = \alpha - \beta$

$\alpha - E + \beta - ES = 0$

$E(1+S) = \alpha + \beta$ or $\boxed{E = \frac{\alpha + \beta}{1+S}}$ $\boxed{E = \frac{\alpha - \beta}{1-S}}$

$E = \frac{\alpha \pm \beta}{1 \pm S}$

Once again, remember, that H_{ij}, where i and j can be 1 and 2 in this case, this is equal to H_{ji} and this is the form $H_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle = H_{ji}$. Sij=$\langle \chi_i | \chi_j \rangle$=Sji and this is the form. Now, let me remind you of this interesting aspect of Hückel MOT. We do not have to write the Hamiltonian. We try to formulate without doing it explicitly. Also, we remember that for equivalent carbon atoms H_{11} must be equal to H_{22}, Hii is the same, Hii equal to Hjj, even though i and j can be different for equivalent hydrogen atom.

Why, because, remember, this is just the Hamiltonian is formulated considering an electron to move in the joint field of the nuclei and the other electrons, and electrons are indistinguishable. We will come back to this later on. But let us say that this equivalent carbon atoms H_{11}, H_{22}, we write this as alpha and α is called coulomb integral.

Why, now we can perhaps continue that discussion. It is called coulomb integral because it is all about electrostatic interaction of this electron in the joint field of nucleus and nuclei and the other electrons. So, that H_{11} and H_{22} in this secular equation, we are going to add α here and we are going to write α here, we are left with H_{12} and S_{11}, S_{12}.

Well, H_{12} and H_{21} are written resonance integral β. It is something that should remind us of our discussion of H_2^+ problem. Here we have one orbital, one atomic orbital in the bra vector, another atomic orbital in the ket vector Hamiltonian in middle. So, this is a quantum mechanical quantity that is called resonance integral. So, H_{12} equal to H_{21}, as we said earlier, you are going to call it β. And beta is actually a negative quantity as we will discuss later on as well.

So, how have we simplified this? This is α-E multiplied by, well, S_{11} as we know is actually 1. You do not have to worry about it. So, this will become the first term will become α-E, second one H_{12}, what is that, β, β-E×S. This one is H_{12}, what is H_{12}, that is β, β-ES and this α-E. So, this is the secular equation. This is what it boils down to α-E, β-ES, a nice symmetric determinant that equal to 0.

If you expand the determinant, what do you get? You get a quadratic equation. And let me try to write that quadratic equation for you. What is the quadratic equation? $(\alpha\text{-}E)^2 - (\beta\text{-}ES)^2$. Remember, if I have a determinant like this $\begin{vmatrix} a & b \\ c & d \end{vmatrix}$, that is actually ad-bc. I am sure we all know this, but I thought I will write it just in case.

Now, what kind of integration is this? X square minus y square. And what is $x^2 - y^2$ It is $(x + y)(x - y)$. Let me write it in this form. So, I get $(\alpha - E + \beta - ES)(\alpha - E - \beta + ES) = 0$. Considering the first term, I write $(\alpha - E + \beta - ES) = 0$. So, from here what do I get? I get $E(1 + S) = \alpha + \beta$, or, $E = \frac{\alpha+\beta}{(1+S)}$

See what just happened? I did not try to solve Schrodinger equation exactly. I have not written the Hamiltonian at all. Yet, I have an expression for the energy E in terms of integrals, which I do not know, but let us see whether we can figure out what they are. Meanwhile, let us try to work out the second integral also, this one, the second term also. When I equate that $(\alpha - E - \beta + ES) = 0$ what do I get?

Similarly, I get, $\mathrm{E}(1-\mathrm{S})=\alpha-\beta$, or, $\mathrm{E}=\frac{\alpha-\beta}{(1-\mathrm{S})}$

We have two expressions, two routes of energy. And together we can write $\mathrm{E}=\frac{\alpha\pm\beta}{(1\pm\mathrm{S})}$. We have got the expression. Now, we will start worrying about what alpha, beta, S all these are.

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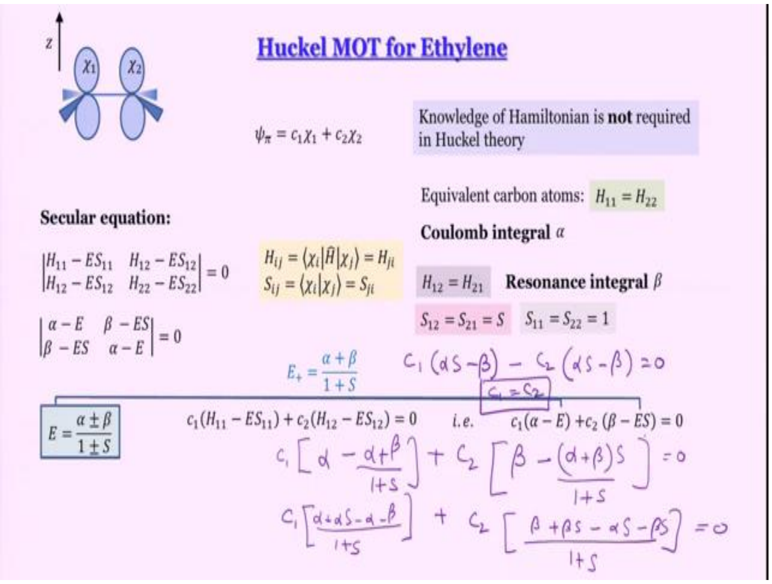

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$H_{12} = H_{21}$ **Resonance integral** β

$S_{12} = S_{21} = S$ $S_{11} = S_{22} = 1$

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

$E_+ = \frac{\alpha+\beta}{1+S}$

$c_1(\alpha S-\beta) - c_2(\alpha S-\beta) = 0$

$\boxed{c_1 = c_2}$

$\boxed{E = \frac{\alpha\pm\beta}{1\pm S}}$

$c_1(H_{11}-ES_{11}) + c_2(H_{12}-ES_{12}) = 0$ i.e. $c_1(\alpha-E) + c_2(\beta-ES) = 0$

$c_1\left[\alpha - \frac{\alpha+\beta}{1+S}\right] + c_2\left[\beta - \frac{(\alpha+\beta)S}{1+S}\right] = 0$

$c_1\left[\frac{\alpha+\alpha S-\alpha-\beta}{1+S}\right] + c_2\left[\frac{\beta+\beta S-\alpha S-\beta S}{1+S}\right] = 0$

So, to start with, let us just put back this expression$c_1(H_{11}-ES_{11})+c_2(H_{12}-ES_{12})$ into the first equation that we got. We will now formally determine what is c_1, what is c_2. So, put it in $i.e.\, c_1(\alpha-E)+c_2(\beta-ES)=0$. This is what we can get easily, because H_{11} is α and H_{12} is β. S_{11} is equal to 1, S_{12} equal to S.

Now, what we will do is we will put in these expressions for energy, here as well as here. And there are two expressions. I am going to work out one, you work out the other. I will work out this one, $E_+=\frac{\alpha+\beta}{(1+\mathrm{S})}$. When I put it there, what do I get? This equation, I get $c_1(\alpha-\frac{\alpha+\beta}{(1+\mathrm{S})})+c_2(\beta-\frac{\alpha+\beta}{(1+\mathrm{S})}\times S)=0$. Expand it a little bit, $c_1(\frac{\alpha+\alpha\mathrm{S}-\alpha-\beta}{(1+\mathrm{S})})+c_2(\frac{\beta+\beta\mathrm{S}-\alpha\mathrm{S}-\beta\mathrm{S}}{(1+\mathrm{S})})=0$. Actually, there is no need for me to work it out like this. You can do it yourself.

But what am I got from here?$c_1(\alpha\mathrm{S}-\beta)-c_2(\alpha\mathrm{S}-\beta)=0$.

From here, what do I get? Do not I get $c_1 = c_2$? And is not this the result that we had guessed already, just from symmetry. We just proved it a little more formally, that is all.

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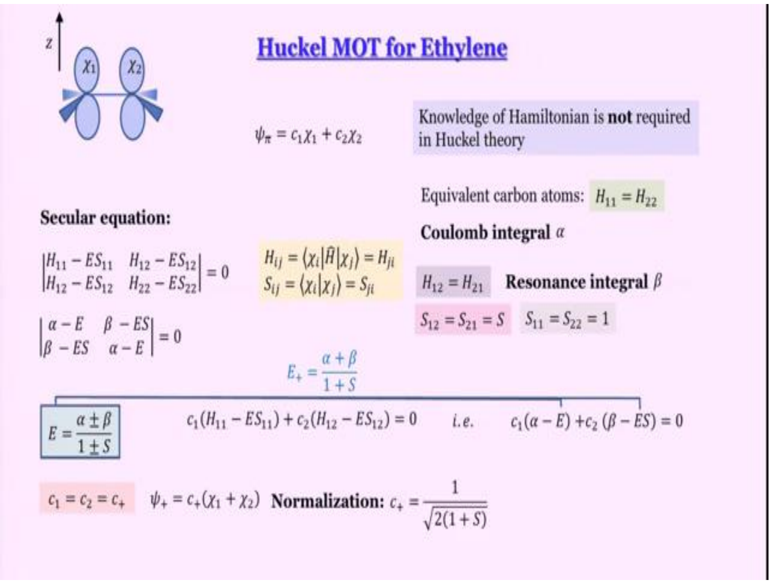

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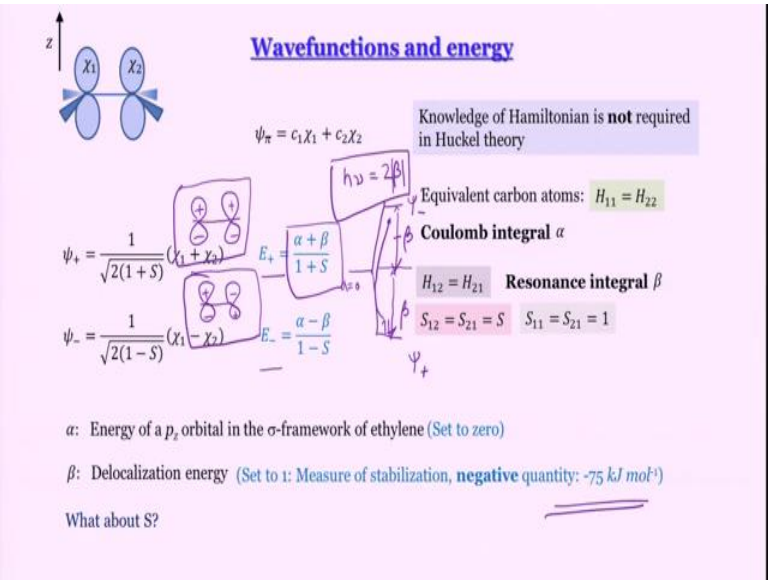
$E_+ = \dfrac{\alpha + \beta}{1 + S}$

$\boxed{E = \dfrac{\alpha \pm \beta}{1 \pm S}}$ $c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$ *i.e.* $c_1(\alpha - E) + c_2(\beta - ES) = 0$

$c_1 = c_2 = c_+$ $\psi_+ = c_+(\chi_1 + \chi_2)$ **Normalization:** $c_+ = \dfrac{1}{\sqrt{2(1+S)}}$



Wavefunctions and energy

$\psi_\pi = c_1\chi_1 + c_2\chi_2$

Knowledge of Hamiltonian is **not** required in Huckel theory

Equivalent carbon atoms: $H_{11} = H_{22}$

Coulomb integral α

$\psi_+ = \dfrac{1}{\sqrt{2(1+S)}}(\chi_1 + \chi_2)$ $E_+ = \dfrac{\alpha + \beta}{1 + S}$

$H_{12} = H_{21}$ **Resonance integral** β

$S_{12} = S_{21} = S$ $S_{11} = S_{21} = 1$

$\psi_- = \dfrac{1}{\sqrt{2(1-S)}}(\chi_1 - \chi_2)$ $E_- = \dfrac{\alpha - \beta}{1 - S}$

α: Energy of a p_z orbital in the σ-framework of ethylene (Set to zero)

β: Delocalization energy (Set to 1: Measure of stabilization, **negative** quantity: -75 $kJ\ mol^{-1}$)

What about S?

So, we get $c_1 = c_2$ and since we got this by taking the plus combination, we call it c_+. So, your wave function becomes $\Psi_+ = c_+(\chi_1+\chi_2)$. Please work out the other one and see, convince yourself Ψ_- that is going to be $\Psi_- = c_-(\chi_1-\chi_2)$. When you normalize this, that is very is. I will not work it out, because we have done something similar for H_2^+. We get $c_+ = \frac{1}{\sqrt{2(1+s)}}$

This is what we have got $\Psi_+ = \frac{1}{\sqrt{2(1+s)}}(\chi_1+\chi_2)$, corresponding energy $E_+ = \frac{\alpha+\beta}{(1+S)}$,

Ψ_- $\frac{1}{\sqrt{2(1-s)}}(\chi_1-\chi_2)$, your homework is, $E_- = \frac{\alpha-\beta}{(1-S)}$

Now, let us remind ourselves that alpha really is the energy of a p_z orbital in the σ framework of ethylene considering ethylene to be in xy plane, energy of p_z orbital in σ framework of ethylene. So, whatever energy we calculate should be with respect to this. What is the stabilization? What is the destabilization? What is β? β is $\int \chi_1 \chi_2$ that is the interaction energy, delocalization energy.

So, we set σ to 0, and we write β to be 1. So, we write everything in terms of 1. But experimentally you can find out that the value is minus 75 kilojoules per mole. How can you find out experimentally? Using spectroscopy, you see where the transitions are and you can work out easily. What is this S? S is at best a small number. As you will see, in the simplest version of Hückel molecular orbital theory, S is conveniently set to 0. But we will talk about that in a little more detail when we discuss the next problem, when we add two more carbon atoms here.

Before we conclude our discussion of ethylene, let us try to think what kind of energy level diagram we are going to get, E_- and E_+ , which one is lower and which one is higher. And also let us try to draw the wave functions, very simple. The, what will Ψ_+ be?(χ_1+χ_2) It is that means something like this. What is Ψ_-? It is going to be? (χ_1-χ_2). So, if I write it like this plus minus this will minus plus. Who has said this is plus minus, this is minus plus? Nobody has said. If you want it in a different way, please do it yourself.

So, this one really is the bonding orbital, bonding π orbital. This one is the anti-bonding π orbital. And I would now like you to remind yourselves of these orbitals π_u and π_g, π_u and π^*_g that we had drawn in one of the earlier lectures and you can understand that there is a buildup of electron density between the atoms in the bonding situation, there is a depletion in anti-bonding situation. So, this energy is higher, this energy is lower. And also, from the expressions you can see, we said that β is a negative quantity -75 kilojoules/mol.

So, E_+ is going to be lower energy, E_- is going to be higher energy. So, if we set α to be equal to 0, if we draw like this, I will write α equal to 0, then energy level diagram is such that this is the lower energy corresponding to Ψ_+ bonding orbital is higher energy corresponding to the Ψ_- anti-bonding orbital. What are the energy gaps? This one is β, this one is -β. And that brings us to the question how do we know it is - 75 kilojoules per mole?

Well, see, how many π electrons are there in ethylene? There are two. Where will they reside? They will reside here. If you can bring about a π to π^* transition, you can see what energy is absorbed, the energy of that photon $h\nu = 2\beta$. And you can find out, well, $2|\beta|$ is what I want to write, from there you can find out what β is.

Remember, in this case this is actually $-\beta$. β is a negative quantity. So, $-\beta$ is a positive quantity. And this is how you can determine it experimentally. This is how it has been determined that β is -75 kilojoules per mole. We will discuss this in more detail when we go to the next problem that is Hückel theory of Butadiene.