Concepts of Chemistry for Engineering

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Lecture No. 22

Hückel's MOT for Butadiene-II

Now, we are going to discuss the wave functions of butadiene and we will see how we can arrive at some important information about the molecule from a knowledge of these wave functions.

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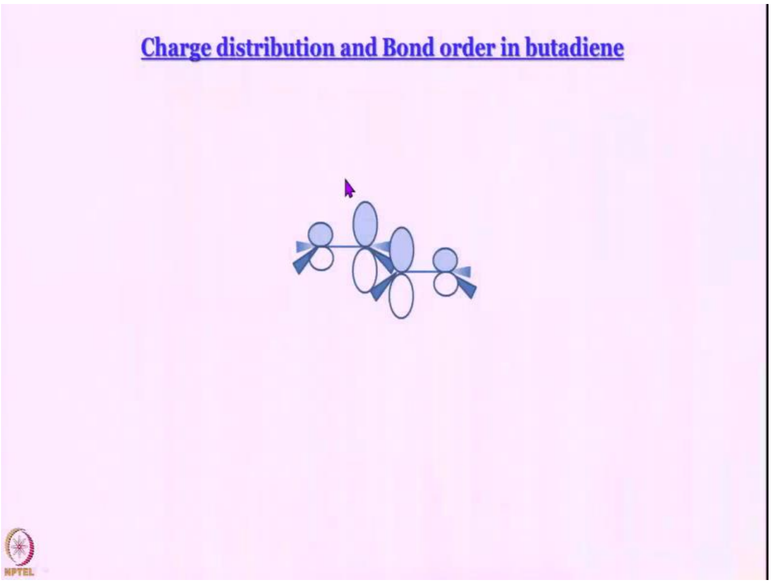

Charge distribution and Bond order in butadiene

What you see here is an example of one of the functions that we are going to encounter in a few minutes.

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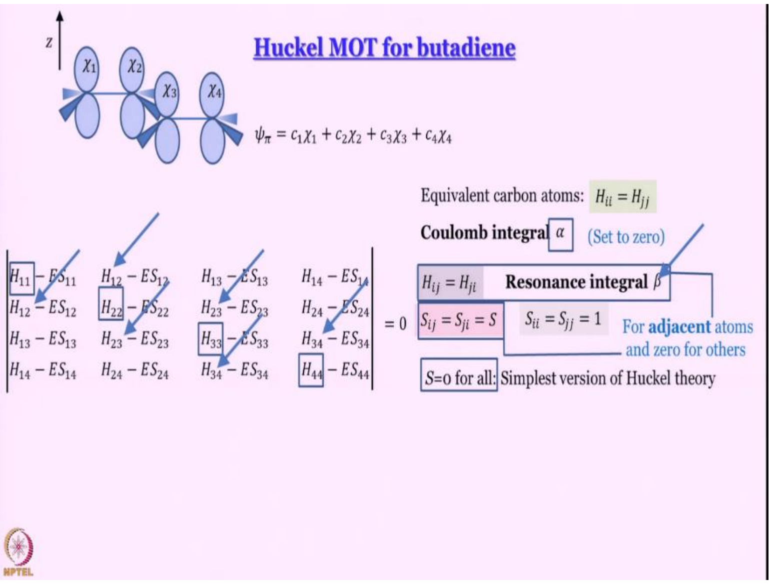

Huckel MOT for butadiene

$$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

$$\begin{vmatrix} \boxed{H_{11}} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{12} - ES_{12} & \boxed{H_{22}} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{13} - ES_{13} & H_{23} - ES_{23} & \boxed{H_{33}} - ES_{33} & H_{34} - ES_{34} \\ H_{14} - ES_{14} & H_{24} - ES_{24} & H_{34} - ES_{34} & \boxed{H_{44}} - ES_{44} \end{vmatrix} = 0$$

Equivalent carbon atoms: $H_{ii} = H_{jj}$

Coulomb integral $\boxed{\alpha}$ (Set to zero)

$H_{ij} = H_{ji}$ **Resonance integral** β

$S_{ij} = S_{ji} = S$ $S_{ii} = S_{jj} = 1$

For **adjacent** atoms and zero for others

$\boxed{S\text{=0 for all:}}$ Simplest version of Huckel theory

But before that, this is where we are. We have worked out the Huckel MOT formulation for butadiene. We have expressed the π molecular orbital as a linear sum of these four p orbitals on the four carbon atoms. And in the secular equation, what we have done is, we have said that equivalent carbon atoms have H_{ii} equal to H_{jj} equal to α and we have set that α to 0 and we make all the measurements from there, because, essentially, that denotes the energy of a p_z electron in the molecular framework.

We have said that this H_{ij} and H_{ji} they are equal to resonance integral when, only when i and j are adjacent to each other, so 1 and 2, 2 and 3, 3 and 4, no other combination. For all of the combinations, we set them to be equal to 0. And we have discussed why we are justified in doing that. And the overlap is set to 0 in all cases, because we are talking about a π overlap anyway, which is not all that strong. It is a fairly weak.

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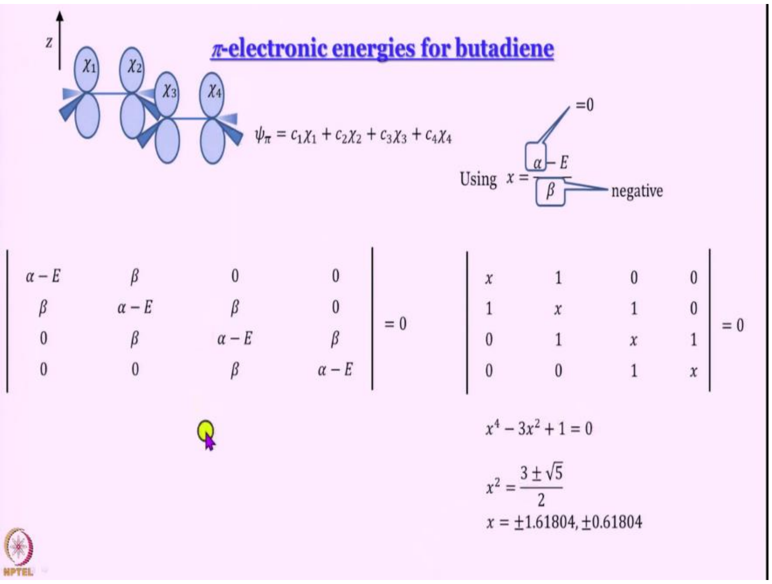

π-electronic energies for butadiene

$$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

=0

Using $x = \frac{\boxed{\alpha} - E}{\boxed{\beta}}$

negative

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$x^4 - 3x^2 + 1 = 0$$

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \pm 1.61804, \pm 0.61804$$

And then, we have simplified it a little bit. And we have written the determinant in terms of β. x is essentially energy in terms of β setting α to be equal to 0. That is how we can read it. And we have found some values of x. From there, we constructed the energy diagram. Once we know this energy diagram, from our knowledge of ethylene, we know that we can now plug this expression for energy back in the four linear equations that we had for the molecular orbitals and we can determine the coefficients.

We can, but will not do here because it is a little tedious. Whoever is interested is welcome to give it a try. It will take a little time, but you can do it, now that you know ethylene anyway. I am just going to show you the results.

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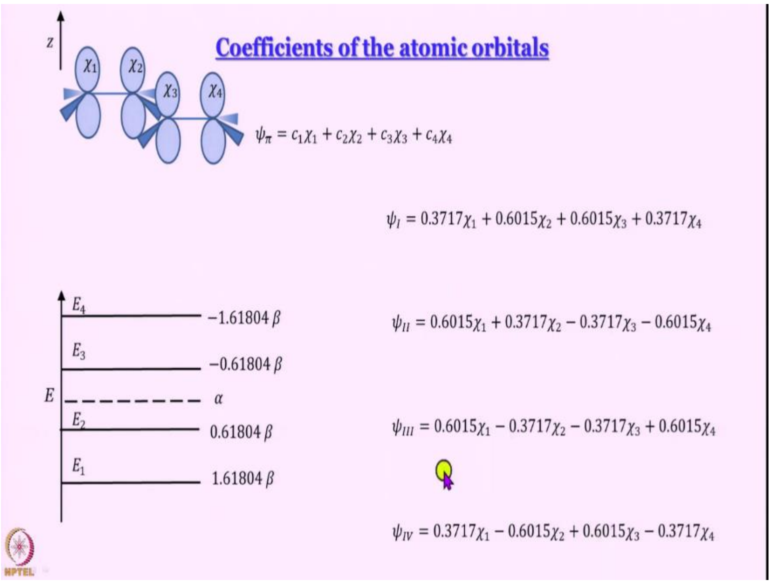


Coefficients of the atomic orbitals

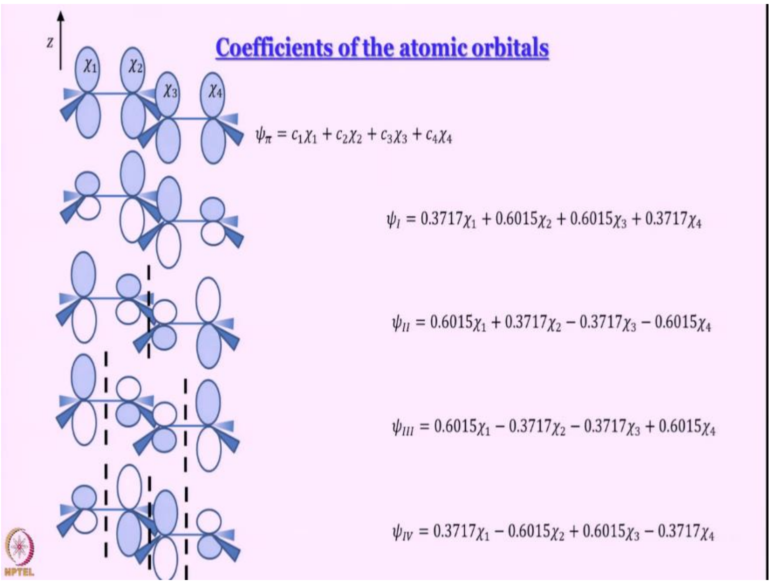
$$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

$$\psi_I = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$$

$$\psi_{II} = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$$

$$\psi_{III} = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$$

$$\psi_{IV} = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$$



Coefficients of the atomic orbitals

$$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

$$\psi_I = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$$

$$\psi_{II} = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$$

$$\psi_{III} = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$$

$$\psi_{IV} = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$$

And these are the results. These are the energy levels, E_1, E_2, E_3, E_4. Actually, in hindsight, I should have written them, E roman I, roman II, roman III, roman IV, because I have denoted the wave functions by Ψ_I, Ψ_{II}, Ψ_{III}, Ψ_{IV}, where I, II, III, IV are in roman numerals. This is just to differentiate the label for the molecular orbitals from the label of the atomic orbitals that participate in the linear combination or you can think labels of the atoms themselves. So, these are the coefficients that come out.

And once you look at the coefficient, you see this nice symmetry that was there in the secular determinant sort of reflected here as well. Modulus of the coefficient is just 0.3717 or 0.6015. And they just keep changing places. You always have two 0.3717s and two 0.6015s as coefficients, no matter which molecular orbital you take. It is just that, in the first one all of these coefficients have positive sign, in the other three two of them have positive sign, whereas two of them have negative sign, very nice, symmetric permutation combination kind of heavy situation.

So, now what we will do is we will draw the sort of cartoon representation. What we have drawn here is also a cartoon representation, a cartoon representation of these MOs. Here, you see, we have drawn χ_1, χ_2, χ_3, χ_4 as orbitals with the same height, because they are all independent p orbitals. Now, we are going to multiply their height by the coefficient. So, now the heights are going to change.

So, in Ψ_I, for example, the height of χ_1 will be little more than half of the height of χ_2. Height of χ_2 and χ_3 will be same, because both have coefficients 0.6015. Height of χ_4 is going to be same as height of χ_1, and once again, little more than half of the heights of χ_2 and χ_3. So, this is your χ_1. That is how we have drawn it. Of course, this is all approximate cartoon depiction. But we understand this very nicely.

And also, another thing that I have done here is since we have minus signs coming up later on, I have drawn two loops in two different colors. One of them is plus one of them is minus. Which one is plus which one is minus, I do not know and I do not care as long as we decide that solid ellipses are plus and empty, hollow ellipses are minus or the other way around as long as we stick to one convention throughout we are good.

Now, let us think of what will happen for Ψ_{II}. In Ψ_{II} the magnitudes are going to just get reversed, because now χ_1 is multiplied by 0.6015, χ_2 is multiplied by 0.3717. So, obviously, this χ_1 orbital will be bigger, χ_2 orbital will be smaller. Remember, when I say χ_1 orbital will be bigger or smaller, I mean actually χ_1 multiplied by coefficient.

One more thing will happen and that is we have two minus signs here. So, if I have taken it like this, for χ_3 and χ_4 I should have hollow lopes at the top and solid ropes at the bottom. So, this is your χ_2. I hope this is clear. Not difficult at all. What about χ_3? I encourage you to work out chi 3 yourself before going to the next step.

Well, first of all, we have alternate plus and minus signs and magnitude is more or less similar to χ_2, but signs are going to reverse not exactly alternatively between I and II and between III and IV.

There is no sign change between II and III. This is χ_3 and this is χ_4. There is a sign change after every atom. And when I say sign change, of course, we know that we are talking about nodes.

So, let us try and draw some nodes. One node is there already. The molecular plane itself is a node that comes from the basic properties of the p orbitals anyway. In addition, some nodes arise. Is there any node other than the molecular plane in Ψ_I? Not really, no node. What about Ψ_{II}? Do you have a node in Ψ_{II}? Yes, we do. There is a node. That is for the sign changes.

What about Ψ_{III}? We have two nodes. Here between I and II and here between III and IV. Between II and III there is no node. And if you are a little sorry that there is no node between II and III, well, our wish is fulfilled in the last one and we have a node between any pair of neighboring carbon atoms and that is why your signs keep on changing every time. We have drawn the wave functions. This is how it is drawn. And once you understand this, things like benzene should become cakewalk.

Now, let us see, can we get some idea about things like charge distribution? Can we get some idea about things like bond order from these coefficients from these orbitals?

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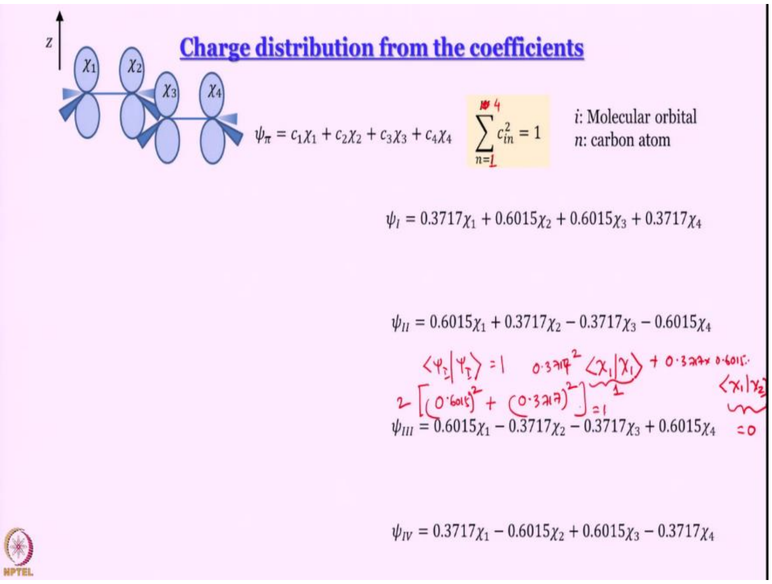


Charge distribution from the coefficients

$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$

$$\sum_{n=1}^{4} c_{in}^2 = 1$$

i: Molecular orbital
n: carbon atom

$\psi_I = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$

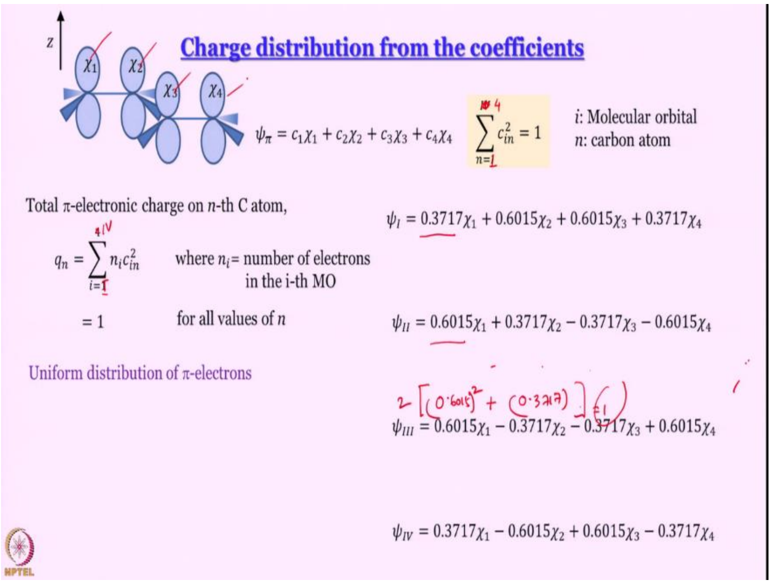
$\psi_{II} = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$

$\langle\psi_I|\psi_I\rangle = 1 \quad 0.3717^2 \underbrace{\langle\chi_1|\chi_1\rangle}_{1} + 0.3717 \times 0.6015 \underbrace{\langle\chi_1|\chi_2\rangle}_{=0}$

$2\left[(0.6015)^2 + (0.3717)^2\right] = 1$

$\psi_{III} = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$

$\psi_{IV} = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$



Charge distribution from the coefficients

$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$

$\sum_{n=1}^{4} c_{in}^2 = 1$

i: Molecular orbital
n: carbon atom

Total π-electronic charge on *n*-th C atom,

$q_n = \sum_{i=I}^{IV} n_i c_{in}^2$ where n_i = number of electrons in the i-th MO

$= 1$ for all values of n

Uniform distribution of π-electrons

$\psi_I = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$

$\psi_{II} = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$

$2\left[(0.6015)^2 + (0.3717)\right] = 1$

$\psi_{III} = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$

$\psi_{IV} = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$

So, first thing to remember is that if I sum over the, what am I summing over, n is carbon atom, so I am summing from left to right. If I sum from and here, I made a mistake, because n should be from, not roman I to roman IV, because roman I to roman IV, remember, is actually the designator for MO and not atom. So, this is 1 to 4. So, when we sum over all the atoms, then I should get 1, when I sum the square of coefficients. Why, that is the normalization condition, is not it? Because remember, it safe to write here, it is safe to write here I think.

This condition we have made sure that it is always fulfill. It is a $\langle \Psi_I | \Psi_I \rangle = 1$ What does that mean? It means that $(0.3717)^2$, I will just write it once, $\langle \chi_1 | \chi_1 \rangle$. Before going any further, what is this integral? This is equal to 1, because, $\chi_1,\ \chi_2$ these are all normalized by themselves plus what is the second term, second term I can write something like this 0.3717 ×0.6015 $\langle \chi_1 | \chi_2 \rangle$ multiplied by integral $\chi_1,\ \chi_2$, normalizing remember.

So, I have to integrate over all space. This, what is this? We have said that the overlap integral is equal to 0 in Hückel treatment. So, this is equal to 0. So, the only things have to, with that we have to worry about are $\langle \chi_1 | \chi_1 \rangle, \langle \chi_2 | \chi_2 \rangle, \langle \chi_3 | \chi_3 \rangle, \langle \chi_4 | \chi_4 \rangle$. So, that is what it is. So, and these integrals are 1 anyway.

So, essentially, what you get is $(0.3717)^2 + (0.6015)^2$, and again, you have $(0.6015)^2$ and $(0.3717)^2$, so I can just write $2\,[(0.3717)^2 + (0.6015)^2] = 1$. And you can see that that is actually the case. So, we have written these in normalized form. I keep this because this is something that is going to come handy right now. So, that is a first thing that comes from normalization condition.

Now, let us think about charge distribution. What is the meaning of charge distribution? If I think of a particular carbon atom, the π electronic charge on it is given by $\sum_{I=0}^{IV} n_i {C_{in}}^2$, where n_i is the number of electrons in the i th MO and here again I should write i equal to roman I to roman IV, $n_i {C_{in}}^2$. What does this actually mean? Well square of coefficient is the contribution of that orbital and n_i is the number of electrons in it.

So, what is the number of electrons in Ψ_I, it is 2. What is the number of electrons in Ψ_{II}, it is 2, once again. What is the number of electrons and Ψ_{III} and Ψ_{IV} , 0. This is what we have drawn earlier. So, that is what we have to find. That will give us the total pi electronic charge on nth atom. We can work with the first atom.

Let us work out what it is for the first atom. What will it be, 2 [$(0.3717)^2$ + $(0.6015)^2$], that we know already that that is equal to 1. You can, it is just plain arithmetic, you can do it. So, it does not matter which n you take, does not matter which atom you take 1, 2, 3 or 4. When I say 1, 2, 3 or 4, I mean, these, these $\chi_1, \chi_2, \chi_{3,} \chi_4$.

So, it does not matter which atom you take. π electronic charge is always 1, which means that the charge, the electrons are distributed uniformly across the molecule. So, this is a result that we know is correct. So, it is good that we have arrived at that. So, when we drew that valance bond theoretical picture, we had some charge separation. Does that mean that the charge density on electron number, carbon number 1 or number 4 is any different, not really?

The average value still comes out to be same. But here we get very elegantly the idea that we have uniform distribution of π electron, a situation that is sort of analogous to dihydrogen H_2, not HF. In HF you do not have a uniform distribution of electrons. Here, we have a uniform distribution of π electrons like the uniform distribution of σ electrons in dihydrogen that is what we see.

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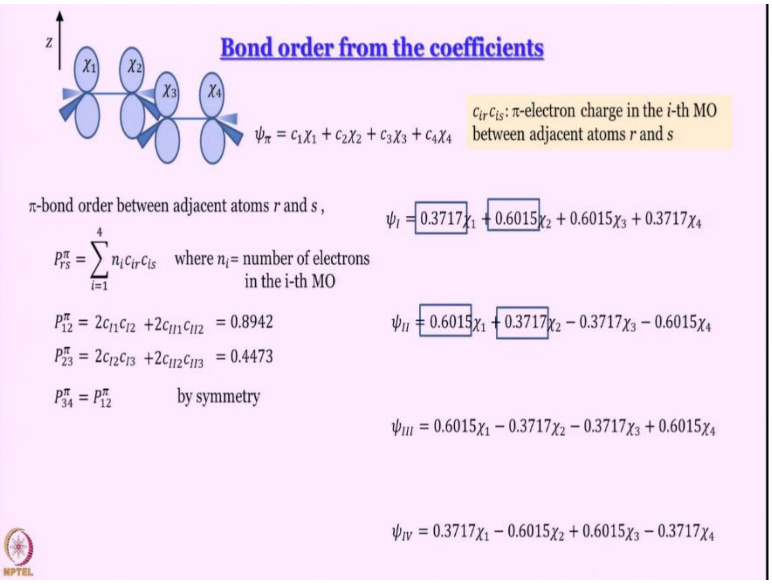

Bond order from the coefficients

$\psi_\pi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$

$c_{ir}c_{is}$: π-electron charge in the i-th MO between adjacent atoms r and s

π-bond order between adjacent atoms r and s ,

$P^\pi_{rs} = \sum_{i=1}^{4} n_i c_{ir} c_{is}$ where n_i= number of electrons in the i-th MO

$P^\pi_{12} = 2c_{I1}c_{I2} + 2c_{II1}c_{II2} = 0.8942$

$P^\pi_{23} = 2c_{I2}c_{I3} + 2c_{II2}c_{II3} = 0.4473$

$P^\pi_{34} = P^\pi_{12}$ by symmetry

$\psi_I = \boxed{0.3717}\chi_1 + \boxed{0.6015}\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$

$\psi_{II} = \boxed{0.6015}\chi_1 + \boxed{0.3717}\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$

$\psi_{III} = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$

$\psi_{IV} = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$

Another thing that we can work out is bond order from the coefficients. So, this c_{ir} × c_{is} gives you the π electron charge in the ith MO between adjacent atoms r and s. So, if I multiply 0.3717 by 0.6015 then I get an idea of pi electron charge density between 1 and 2. And the bond order is given by this, this product cir c_{is}× n_i, where n_i is the number of electrons in the ith MO, sum over i equal to 1 to 4. So, let us try to do that.

What is P^π_{12}, what do I multiply by 2c_{I1}, c_{12}, 0.3717 and 0.6015 plus 2c_{II1} c_{II2}. What are these 2s? These 2s are the number of electrons, n_i, and these are the coefficients for 1 and 2 that we get from orbital 1 and orbital 2. So, essentially 0.3717, 0.6015, 0.6015, 0.3717 and the product is added.

So, basically that gets multiplied by 4 actually, because 1, 2 comes from here and there are two such terms. The answer that you get is 0.8942, π bond order between 1 and 2, carbon 1 and carbon 2 is 0.8942. In fact, when I do the calculation, I get 0.8943. But I have gone with the value given in the book.

What about 2 and 3? Similarly, using the coefficients, this time which coefficients will use 0.6015, 0.6015, 0.3717 , -0.3717. Please remember that. It is not + 0.3717. When you multiply a positive quantity by a negative quantity, you get a negative quantity. So, you do that, 2 $c_{I2}c_{I3}$+ 2$c_{II2}c_{II3}$, then you get 0.4473. What is P_{34}? By symmetry, it is the same as P_{12}, 0.8942.

So, what is the total bond order that we get approximately? 0.9 + 0.9 is 1.8 +0.4 is a little more than 2, is not it? Well, but that comes because we have done the calculation this way. You will not get whole numbers here, because remember, the stabilization of bonding, destabilization of anti-boding these are also not exactly the same. So, we get approximately total bond order that is similar to what we get from valance bond theory.

But the more important picture that we get here is that the π bond order between 1 and 2, and 3 and 4 is about double the π bond order between 2 and 3. And that is what we expect from valence bond theory resonance picture as well, because in order to get the double bond between 2 and 3, you need to charge separation, which is not such a happy situation. So, we get a similar picture than what we could have got from valence bond theory. The good thing is we get it in a more mathematically rigorous way using Hückel approximation that can easily be extrapolated to bigger molecules, like this naphthalene.

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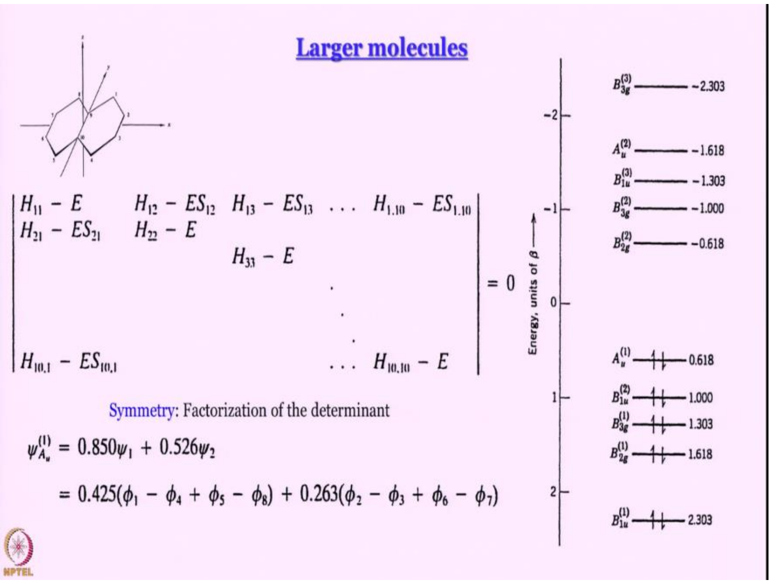

Larger molecules

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & \dots & H_{1,10} - ES_{1,10} \\ H_{21} - ES_{21} & H_{22} - E & & & \\ & & H_{33} - E & & \\ & & & \ddots & \\ H_{10,1} - ES_{10,1} & & & \dots & H_{10,10} - E \end{vmatrix} = 0$$

Symmetry: Factorization of the determinant

$$\psi_{A_u}^{(1)} = 0.850\psi_1 + 0.526\psi_2$$

$$= 0.425(\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.263(\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

In naphthalene the problem is that it is too larger molecule, the determinant is huge. So, what we do there is that we use symmetry to factorize the determinant and we get expressions like this. These Ψ_1, Ψ_2, Ψ_3, these are the p orbitals. And from there, one can work out the energy levels and you can work out, these are the wave functions anyway. What you see here, B_{3g}, A_u, so on and so forth these are, let us for now just say that these are the symmetry levels of these orbitals that are involved there. So, that opens up an entirely new angle altogether.

What we learn from there is that, using symmetry you can simplify quantum mechanical problems to a very great deal. Have we done that in a small way already actually? We have. Remember what we said, we said that $P_{34}^{\pi}$is equal to P_{12}^{π} by symmetry. So, this is just the tip of the iceberg. It is a hint that symmetry has an important role to play whenever we try to do a quantum mechanical treatment of these big molecules. But let that be the story for another day.

Today, we have learned that in butadiene using Hückel theory we can work out the energies, we can work out the wave functions, and from the wave functions, we can work out the electron distribution and it turns out that electron is distributed uniformly over the molecule. And also we can work out the bond order. When you go to bigger molecules like benzene and all similar treatment is extended.