

Quantum Chemistry of Atoms and Molecules
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Lecture-66
Huckel MOT-2

This is the last lecture of the business end of this course we are going to talk about wave functions of butadiene pi wave functions of butadiene.

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Huckel MOT for butadiene

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

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

Coulomb integral α (Set to zero)

Resonance integral β

$H_{ij} = H_{ji} = S$ $S_{ii} = S_{jj} = 1$ For adjacent atoms and zero for others

$S=0$ for all; Simplest version of Huckel theory

The slide also displays a 4x4 secular determinant with elements $H_{ii} - ES_{ii}$ on the diagonal and $H_{ij} - ES_{ij}$ for adjacent atoms.

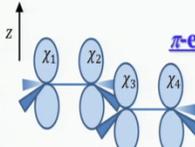
So we are developing a Huckel MOT treatment for butadiene we have expressed the pi wave functions pi molecular orbitals as a linear sum of the p z orbitals of the 4 participating carbon atoms and we have written the secular equation. In this circular equation we have realized that since the carbon atoms are equivalent H_{ii} has to be equal to H_{jj} that has been equal to coulomb integral and for all practical purposes all measurement will be with reference to this coulomb integral so this is really our 0 for measurement.

If you remember what we discussed in the last lecture alpha is really the energy of a p z orbital in the sigma framework of the molecule. So whatever stabilization destabilization takes place has to be done with from with respect to that so it will always be alpha plus something alpha minus something. And overlap integral we for our purpose we set it to 0 it is not set to 0 for all all pairs of atoms in a little more advanced vocal treatment.

But today well we are at the end of the course we are not going to start a new discussion now so we are going to set it to be equal to 0. And the justification for setting s equal to 0 or nearly equal to 0 is that we are talking about pi interaction. So overlap is po overlap integral is going to be small.

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π -electronic energies for butadiene



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

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

$\alpha - E$	β	0	0	$= 0$	x	1	0	0	$= 0$
β	$\alpha - E$	β	0		1	x	1	0	
0	β	$\alpha - E$	β		0	1	x	1	
0	0	β	$\alpha - E$		0	0	1	x	

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

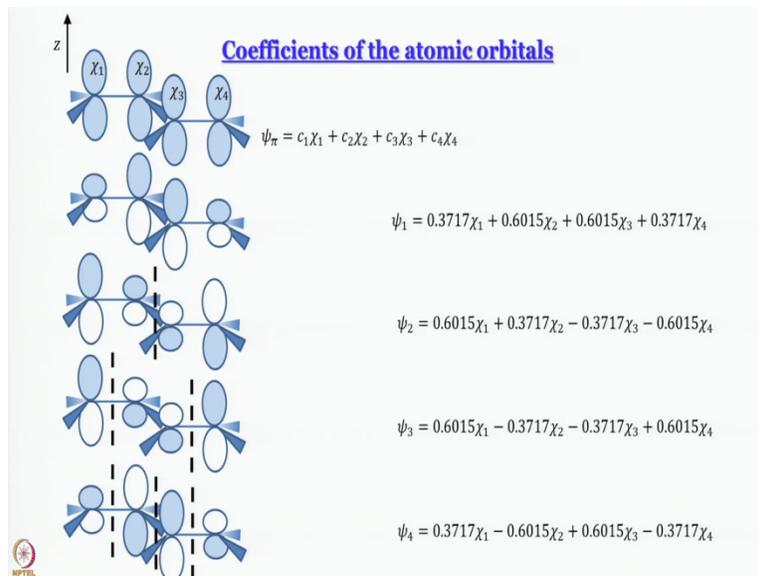
$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

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

So when we apply all these in this secular determinant it simplifies and we simplify it further by substituting x equal to alpha minus C by beta and we say that x then is essentially negative of energy in terms of beta in units of beta. We find out what x is and hence we have obtained what the energy levels are. The next thing we want to do is we are going to find we are going to write down will not find you know how to find it.

We did it for ethylene we know that we can go back to the equations for the coefficients and substitute these values of alpha beta everywhere in the integrals and you can determine C 1 C 2 C 3 C 4 keeping in mind additionally that each of these molecular orbitals have to be normalized and each of the participating atomic orbitals are of course normalized. So will not do it I encourage you to do at least one by yourself.

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But here I just show you the results and I will write here E 1 E 2 E 3 E 4 to remind you that as you go higher up we are we are calling the lowest energy level to be E 1 and do not forget that plus well 1.16804 beta really means a negative energy because beta itself is negative. So these are the coefficients that one obtains if one does the treatment that we just discussed. What we will do is we like to draw pictures do not.

We so we will try and draw pictures cartoons qualitative pictures well semi quantitative pictures you can say of these molecular orbitals. So what we see is that look at the first one there are 2 things to see first of all signs are plus and second thing is the coefficients are not equal. So there is a smaller contribution from chi 1 greater contribution from chi 2 equally greater contribution from chi 3 smaller contribution from chi 4.

So what will this m1 look like? To do that what we will do is we are going to draw these p orbitals showing the signs of wave functions in each loop so we are going to and I am not going to tell you which is which we are going to draw 1 lobe with solid color 1 lobe with white and you can decide which 1 is plus which 1 is minus. As you know this plus minus sign of a function is just relative. But in the first wave function first is that on top of this x y plane in direction of plus z all the lobes have the same wave function of same sign.

The lobes below have opposite sign to that but same sign among themselves and I have also drawn the heights of these orbitals proportional sort of proportional to the square of the coefficients or coefficients the coefficients actually.

0.3717 is a smaller number than 0.6015 that is why chi 1 looks small here chi 2 looks bigger and coefficients of chi 2 and chi 3 are same so they are of the same height. Coefficient of chi 4 is the same as chi 1 so chi 1 and chi 4 they are of the same height but smaller than chi 2 and chi 3. What will happen if I want to draw a similar diagram; before that at the risk of sounding repetitive the solid lobe is it plus or minus I do not know and I do not care you decide.

Can be plus can be minus as long as you stick to the same convention throughout. The crux of the matter is that top of the on top of the x y plane the wave functions are all wave functions at the same sign below the plane they also have the same sign but this sign is opposite to the sign of the wave functions above the x y plane. What about psi 2 .6015 chi 1.3717 chi 2 so now it is a turn of chi 1 to be larger chi 2 to be smaller beside there is a sign change between 2 and 3 - 0.3717 chi 3 -0.615 chi 4 so this is the diagram.

I hope it is not very difficult to understand and will come back to this sign change business. What about psi 3 0.615 chi 1 -0.3717 chi 2 so sign change already -0.3717 chi 3 so no sign change between 2 and 3 but another sign change between 3 and 4 and change in sign as well as size as well. This is what psi 3 would look like what is psi 4 + 0.3717 -0.6015 + 0.6015 -0.3717 this is what it will be like.

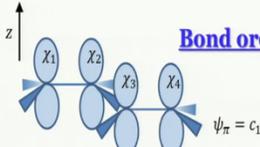
So now one thing that is very useful is to see where the nodes are of course in the first one except for that x y plane which is already there for p orbitals there is no new node that comes in as a result of formation of the MO's for the second one psi 2 however you see between 2 and 3 there is a sign change so you have a nodal plane here. I am drawing a dashed line but it is really a nodal plane.

What about psi 3 between 1 and 2 there is a sign change between 2 and 3 there is no sign change between 3 and 4 there is a sign change in the opposite direction. So, 1 node here another node

here what about psi 4 sign change between 1 and 2 and between 2 and 3 and between 3 and 4 so how many nodes are there? 1 2 3. So if you remember the energies energy of psi 4 is highest energy of psi 1 is lowest. So this is in line with something that we have said several times more the number of nodes higher is the energy. So that is what we learn first thing that we learn from the wave functions that it is in keeping with this nice model that we built.

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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_r, 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 ,

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

$$P_{12}^{\pi} = 2c_{11}c_{12} + 2c_{21}c_{22} = 0.8942$$

$$P_{23}^{\pi} = 2c_{12}c_{13} + 2c_{22}c_{23} = 0.4473$$

$$P_{34}^{\pi} = P_{12}^{\pi} \quad \text{by symmetry}$$

$$\psi_1 = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$$

$$\psi_2 = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$$

$$\psi_3 = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$$

$$\psi_4 = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$$

Now we learn to determine 2 very important quantities 2 varied important properties of the molecule. First is charge distribution as you know charge distribution may or mu may not be uniform if you take H 2 charge is distributed uniformly if you take HF that is not the case. So now we learn a little more quantitative way of determining charge distribution from coefficients of atomic orbitals and this is something that is done at in higher level quantum chemical calculations as well using software's like Gaussian or Gammas or something like that.

So first thing that I want to say here is sum over n equal to 1 by 4 C_i^2 is equal to 1 where i is a molecular orbital. So i would be 1 2 3 and 4 and n is carbon atom number this also is 1 2 3 and 4 but do not get confused between this set of 1 2 3 4 and this set of 1 2 3 4 I should have perhaps written roman numeral or something or dev nugget numeral to differentiate between the 2 but I have not. So please bear with me all this treatment is available in Macquarie's quantum chemistry book as usual.

So C_{in} , what is that C_{in} is a coefficient of the i th molecular orbital in the n th carbon atom. So for example this minus 0.3717 is the coefficient of molecular orbital number 3 very bad example in carbon atom number 3 so it is C_{33} . Let us take this one that is better minus 0.6015 is the coefficient of molecular orbital number 4 in carbon atom number 2 so it is going to be C_{42} I hope you have understood. Now this sum over i for some over n C_{in}^2 that has to be equal to 1 is not it because this sum of squares is like this over the atoms.

And if you remember that this χ_1 and χ_2 this χ_1 the χ_1 is there is no χ_2 when you sum like this the χ_1 is normalized. So what happens when you take the squares just square and add well you get something like this the sum of squares turns out to be 1 just do it yourself 2^2 into 0.3717^2 plus 2^2 into 0.6015^2 will turn out to be 0.999 something 1, great. So what does that have to do with charge distribution well the total pi electronic charge on the n th carbon atom is q_n is equal to sum over i equal to 1 to 4 $n_i C_{in}^2$.

Now what did I just say let us see, n_i is the number of electrons in the i th MO what is the number of electron in ψ_1 ? 2 what is the number of electrons in ψ_2 ? 2 what is the number of electrons in ψ_3 and ψ_4 is 0. So this n_i is 2 for ψ_1 , 2 for ψ_2 , 0 for ψ_3 , 0 for ψ_4 . Now so you have to multiply that number by C_{in}^2 , C_{in}^2 remember i th coefficient of i is molecular orbital in n th carbon atom or the other way round whatever you want. So this is the if you take $n_i C_{in}^2$ what is it.

C_{in}^2 is the contribution population you can say and n_i is the number of electrons so multiply them together you get the contribution of charge for that MO in this in this atom and you sum over all the electrons you get the total charge distribution on the n th atom. So, let us do that for one for all values of n take any value of n so take n equal to 2 for example second carbon atom what I am asking you to do is 2 multiplied by 0.6015^2 plus 2 multiplied by 0.3717^2 square that turns out to be 1.

Do it for any carbon atom it will turn out to be 1. So what that tells us is that this uniform distribution of pi electrons over the 4 carbon atoms there is no polarization that is the first thing that we had said from valence bond theory and from common sense but this is something that we

arrive at using the charge distribution calculated from the coefficients of atomic orbitals. The second thing that we want to talk about is bond order.

See C_{ir} multiplied by C_{is} remember C_{ir} is a contribution of the i th MO in the r th atom C_{is} is the contribution of the i th MO in the s th atom when you take a product of these coefficients that gives us the π electron charge in the i th MO between adjacent atoms r and s . So if you want to find out π bond order between adjacent atoms r and s they are adjacent 1 and 2, 2 and 3, 3 and 4 that is all then this will write this bond order to be $p_{rs}^{\pi} = \sum_{i=1}^4 n_i C_{ir} C_{is}$ where n_i is the number of electrons in the i th MO.

So if I want to find say p_{12}^{π} what will it be what is C_{ir} in that case what is the first C_{ir} C_{11} then what is C_{is} C_{12} so that multiplied by 2 because we said that ψ_1 has a population of 2 electrons are there in ψ_1 so 2 into C_{11} plus 2 into C_{12} then again ψ_2 also has 2 electrons so 2 into C_{21} into C_{22} we do not go any further because there is no need of considering ψ_3 and ψ_4 because they are not even populated.

So what is C_{11} ? 0.3717 What is C_{12} ? 0.6015 What is C_{21} ? 0.6015 What is C_{22} ? 0.3717 so you multiply them together multiplied by 2 and this is what you get p_{12}^{π} turns out to be 0.8942 so the π bond order remember π bond order between 1 and 2 is 0.8942 remember there is already a sigma bond. So overall bond order will be 1.8942 so what do you expect it to be in a valence bond picture you draw in some resonating structures you draw double bond between 1 and 2 in some resonating structures you draw double bond between 2 and 3.

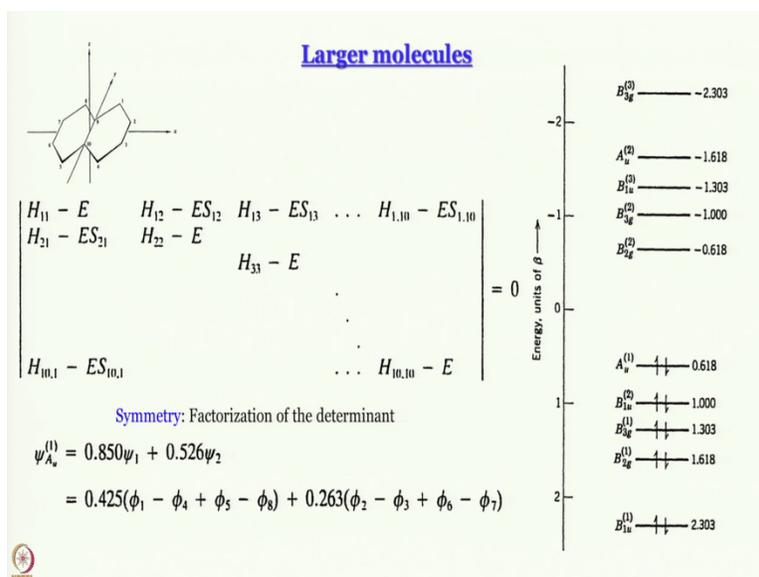
So not in all the resonating structures do you have a double bond between 1 and 2 that is why the overall bond order is less than 2 or if you want to talk only about overall π bond order that is less than 1 and that is something that comes out very nicely p_{12}^{π} turns out to be 0.8942. Similarly let us find out what is p_{23}^{π} ? p_{23}^{π} would be $C_{12} C_{13}$ we want to find the bond order between atom 1 and atom 2 but let us not forget that only ψ_1 and ψ_2 are populated.

So we have to worry about coefficients of psi 1 well we have coefficient we have to worry about the coefficient of the first and the second MO's in these atoms. So 2 into C 12 C 13 plus 2 into C 22 C 23 that turns out to be 0.4473 please work it out yourself. What does that mean that means that pi bond order of well let us finish the story its not very difficult to understand that p 3 4 pi has to be equal to p 1 2pi because of symmetry there all integral.

If I just flip the molecule then 1 and 4 will change positions so and 2 and 3 will also change positions. So what we see is that for these bonds 1 3 1 2 and 3 4 pi bond order is 0.8942 a little less than 1 and for 2 3 pi bond order is little less than half does this agree with the valence bond pictures that you drew? Please draw the resonating structures and convince yourself that this pi bond order is actually in agreement with what you get from valence bond theory using resonance structure as well.

So now we have discussed small molecules. We have discussed ethylene we have discussed butadiene. So in Macquarie's book benzene is not worked out but the solution is provided I have not written it down because you might have instead of reading from the slides you read it from the book but if you want to handle bigger molecules you do not want to stop you have such a beautiful easy theory semi empirical theory.

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Of course we do not want to stop at butadiene we want to go to big molecules we want to talk about naphthalene. The problem is in case of even naphthalene the secular determinant is taunting is a 10 what is the order of the determinant? 10 so who is going to solve this it becomes a very, very tedious problem that is where see remember we have talked about symmetry earlier. We have said by symmetry coefficients must be either equal to well C 1 has to be equal to plus minus 2. We have said by symmetry this pi bond order of 1 3 has to be the same as that of 1 2 has to be the same as that of 3 4.

So, symmetry actually has a big role to play in simplifying problems of quantum mechanics. So one can use symmetry to factorize this determinant break this determinant down into smaller ones and from there very elegantly you can find out the expressions you see this is an expression for one of the molecular orbitals of naphthalene. And one can work out all the energies from this equal approximation without having to use a computer actually using this symmetry factorization.

This is discussed nicely in Cotton's book on chemical applications of group theory among other books in fact all this whatever I have written here the diagram everything is copied from Cotton book. So we need to learn symmetry before we can talk about larger molecules. But we do not have time to do this I will give you some pointer in the concluding lecture which is to follow but for now this is the end of our discussion of a Huckel treatment of conjugated bimolecular systems.