

Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 56
LCAO Huckel Approximation

Okay, so today what we will do is we are going to revise what we know about LCAO and Huckel approximation and then we are going to talk about what are sometimes called term symbols. So it is going to be a revision of things that many of us know already, right? But we need this for the next stage. LCAO, Huckel approximation, and how to or what you can say is nomenclature of electronic states.

I was tempted to get into electronic spectroscopy of things like benzene and all but then I decided against it because that would be too much of a digression from what we want to do here. So tomorrow we are going to discuss naphthalene which is a kind of a longish discussion. What we will do is we will learn all that we can learn about naphthalene from symmetry, okay? What did we do last day?

We talked about benzene is it not so and then naphthalene is like a big brother of benzene, right? Two fused rings. How many p orbitals are there? 10 p orbitals, right? So we will learn how to symmetry classify them. I will talk a little bit about that today also and then we will see what we can say about the MOs, what we can say about the energies of the MOs and what we can say in a very preliminary manner about the spectroscopy of naphthalene, electronic spectroscopy of naphthalene.

And then next week, we go on to discuss unfortunately we do not have time for too much of discussion because last two classes I really want to derive great orthogonality theorem so we will discuss maybe a couple of inorganic systems. We will talk about MOT as applied in inorganic systems. We will not get time to get into Ligand field theory or crystal field theory as such, okay. So I think everybody knows the meaning of this, LCAO. What is the meaning of this?

Linear combination of atomic orbitals and as you know this is perhaps the most primitive form of molecular orbital theory. What is a molecular orbital? A molecular orbital is analogous to an atomic orbital, right? But the only difference is that here you consider the joint field of more than one nuclei instead of one nucleus that you consider in say hydrogen atom. So the question is how do you get the molecular orbitals?

It is impossible to solve the Schrodinger equation except for one molecule. For which molecule can you solve Schrodinger equation and generate the molecular orbitals? No. Helium is not even a molecule. H_2^+ . H_2^+ if you remember is a hydrogenic system. Hydrogenic system as in one electron system, right? So H_2^+ in principle we can actually solve Schrodinger equation and we can generate the molecular orbitals like what we did for hydrogen atom.

The only difference is that instead of one nucleus there will be two nuclei. So what complication will come in because of that? R_{ij} yeah, what is R_{ij} . No that is easily done. But then there will be a more fundamental change in the approach to the problem. Internuclear repulsion but then what I am asking for is even more fundamental here. How do we solve, now you are going further and further away, no. What was the first step in the formulation of the hydrogen atom problem?

What did we do? First step of course is to write Schrodinger equation. Then what did we do? We did some, yeah. No, before separation of variables. Okay, you separated the motion of the nucleus. Then what did you do. No, hydrogen atom orbital, yes. Yeah you converted into spherical polar coordinates. Why do we convert to spherical polar coordinates? Because it is a central field problem. It is a central field problem right? The attraction is towards the center.

That is why you can use spherical polar coordinates. Do you think you can use spherical polar coordinates for H_2^+ ? No. Because attraction due to this nucleus is there, attraction due to that nucleus is also there. So you have to use actually what is called elliptical coordinates which is bound to be a little more complicated than spherical polar coordinates. But it is still doable. But there is no need.

What we want to do is in any case we understand that whatever difficult formulation we develop using elliptical polar coordinates that is going to hold for H_2^+ and that is all, right? So it does not make sense. So it makes sense to go for the approximation right away. And the approximation that is simplest to use is that you consider that the MOs are made up of linear combinations or atomic orbitals. What is the advantage of this?

The advantage is that it is a direct extrapolation of the valence bond theory that we are so familiar with. In valence bond theory also you use atomic orbitals. What is your valence bond approach. You talk about overlap of atomic orbitals, right? You say that 1 s orbital, 1 p orbital another p orbital head on overlap that is sigma bond, side on overlap that is pi bond. Is that right or wrong? So you use almost a similar concept.

What you say is that the molecular orbital is made up of a linear combination of atomic orbitals. You retain the concept of atomic orbitals because they are easy for us to visualize and understand that is why okay.

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CAO $\psi_k = \sum_i c_{ik} \phi_i$

$H\psi = E\psi$

$(H - E)\psi = 0$

$\sum_i c_i (H - E)\psi \phi_i = 0$

$i = 1, 2$

$c_1 (H - E)\phi_1 + c_2 (H - E)\phi_2 = 0$

$\langle \phi_1 |$ Integrate $c_1 [\langle \phi_1 | H | \phi_1 \rangle - E \langle \phi_1 | \phi_1 \rangle]$

\downarrow H_{11}

$+ c_2 [\langle \phi_1 | H | \phi_2 \rangle - E \langle \phi_1 | \phi_2 \rangle]$

\downarrow S_{12}

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Now so what you do is you write the molecular orbital. It is the ψ_k , ψ_k is the k th molecular orbital as a linear sum of the atomic orbitals ϕ_i , right, okay? Please understand that this is only an approximation. After class Vibhav asked me last day and then the thing is there was a talk last week about coupled cluster theory and all so as the speaker said that there is no such thing as

orbitals. The orbitals are used only for so that we can visualize, we can do things easily which is a perfectly valid statement, right?

But the point is LCAO is an approximation. Approximations are the way to go for complicated problems. As long as we understand that this is only an approximation so it is going to work to a certain extent and no further, right? So as we will see today and tomorrow, LCAO does work for some systems like benzene or for naphthalene. It works fine. You do not need more complicated theory for that.

But if you want to talk about more complicated molecules or when you want to talk about more complicated phenomena like excited state processes there LCAO may or may not be sufficient. Usually, it is not sufficient. That is when you invoke higher levels of theory. Even when you run Gaussian, you have to choose a basis set and you have to choose a level of theory is it not? So generally what do you do? Do you start with the most complicated level? No.

Why because there is no point in using a Damascus sword to shave is it not? If you want to shave then a Gillette razor is good enough. There is no point of using a Damascus sword. If you have higher purposes then you use Damascus sword okay? So what we would like to do is we want to stick to the lowest level of theory that gives us the right answer, right? And here our purpose is to see how by using symmetry the problem becomes even more simplified for certain cases.

And we are going to restrict ourselves only for this benzene like systems right where you have pi bonds and the molecule is not very large. I just finished the response to the question you had asked after class yesterday. Fine. So this is the approximation that we are going to go by for the purpose of this course. The molecular orbital is a linear sum of the atomic orbital. If you have a wave function what is the next step?

The next step is to write Schrodinger equation, right in a simplest form. What is Schrodinger equation? $H \psi = E \psi$. But now the problem is we know that we cannot solve this equation, okay? So what we try to do is, we try to manipulate this equation and we see if we can work

around the problem and still find the values of energy. We have already approximated the wave function in a certain way. What is it that we do not know here in ψ_k , the coefficients.

You do not know the coefficients. So our problem is to find the coefficients and also to find the energy, alright. And we have to do it in a roundabout way because this equation cannot be solved so easily. It is not going to be separable unfortunately, okay. So you need a backdoor. So what we do now is we look for the backdoor. So what we do is, of course you people are all masters of manipulation.

You know very well that if you are given a problem you have to subtract 1 from 2 sides take cube root raised to the power of 2 and then take some terms from left to right and then the actual answer arises. We are going to do exactly that. It is just that we do not have so many steps in this problem. So let me write it like this. $H - E \psi = 0$. I think you agree, right? No problem with that? Why am I writing it this way?

Because by doing that what I will do is this is the first step of generating a system of linear equations and when I generate a system of linear equations I know how to solve it. How do I solve a system of linear equations? By Kramer rule, right? Cramer rule, secular determinant? That is where we are headed, okay? Of course, now you have only one equation. We will see how we can generate many equations from there.

So $(H - E) \psi = 0$. What is ψ ? You can use this value. So I can write $\sum_i C_i \psi_i = 0$. What is E ? E is the energy of what, ψ or ψ_i ? ψ , do not forget, ψ . $H \psi = E \psi$ no? Not $H \psi_i = E \psi_i$. So this E is the energy of the molecular orbital ψ , okay, fine. So you have got this equation. Now what do I do? First of all let me write it in a little simple manner.

Instead of, nobody like summations that has been established. So let me take a simple situation where i is equal to just 1 and 2. I will work with 2 terms to start with and then we will just write the other terms. So $C_1 (H - E) \psi_1 + C_2 (H - E) \psi_2 = 0$, alright. So from here I want to

generate a system of linear equations. At least two need to be there, right? How do I generate that linear equation? In quantum mechanics we always like to have triple products.

Say multiply by ϕ_1 and integrate over all space. Then in the next step what we will do? We will multiply by ϕ_2 and again integrate over all space. That way what we are going to do is we are going to generate a lot of integrals or in other words a lot of matrix elements, okay and then we will work with them. So let us see what we get. If we multiply by ϕ_1 and integrate then what is it that you get? You get $C_1 \phi_1 H \phi_1$ integrated over all space.

Everybody knows bracket notation, you have told me, right? Then next term is against minus C_2 . E is a constant and so can come out. And what is the integral. $\phi_1 \phi_1$ integrated over all space, okay. Then what is 1, what is 2? What is 1, what is 2? First atomic orbital, second atomic orbital, of the same atom or different atoms? Different atoms, right? One is for atom number 1, two is for atom number 2, okay? Let us be clear about that.

These are not the atomic orbitals of the same atom. Otherwise we can end in a little difficult situation. $+ C_2$ multiplied by, you are multiplying by ϕ_1 is it not? So integral $\phi_1 H \phi_2 - E$ integral $\phi_1 \phi_2$ over all space, alright? Now, let us write this in a little short form. What is this, integral ϕ_1, ϕ_1 over all space? That would better be 1, they are normalized. So I write 1. What is integral $\phi_1 \phi_2$ over all space? Not necessary.

That is why I asked the previous question. Do not forget that 1 and 2 are different atoms, right. If they are on the same atom then the orbitals, the wave functions have to be orthonormal. But if they are not on the same atom then they do not care about each other, right. So my 1 s does not have to be orthogonal to your 1 s, okay? They are in different galaxies. They are oblivious to each other. But let us think what is it going to be. Is it going to be 1 or 0 or something else?

So this is one orbital, this is one orbital. Let us say they are, the situation is like this. Then what do you have? You have overlap, okay? So what is that integral then? If this is what it is, this is one orbital, this is one orbital. That integral is just this area of intersection is it not? You are

multiplying phi 1 by phi 2 right? At this point for example, phi 1 has some value, phi 2 has no value. I mean phi 2 is 0. So phi 1 into phi 2 is 0. Here again phi 2 has some value, phi 1 is 0.

So only in the intersection do both of them have some value right? So you have to multiply them and integrate over all space. What we are talking about is we are focusing on this area, right of this product integrated over this area. Is this okay? So what is this going to stand for? I think you know this already. But this is a concept where we sometimes falter. So what would this integral stand for? Extent of overlap. S_{12} . It is called S_{12} . So I can name this S_{12} . What is this?

Integral phi 1 H phi 1 over all space? This is called H_{11} and what does it stand for? Expectation value, right? Expectation value of the hamiltonian for phi 1. What is this? It is called H_{12} and what does it stand for? Yeah? Suppose I say it stands for the interaction energy between phi 1 and phi 2. Is that, does that sound right? That is kind of like the interaction integral I can say. Exchange is right but I like to call it interaction.

Because the moment you say exchange, this idea of you know this thing going there, that thing coming here comes and that kind of becomes complicated. So what I want to say is that this stands for the interaction between 1 and 2, okay. Now can you write this equation in terms of those nicknames instead of writing those full integrals. What is it?

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

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - E) = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{vmatrix} = 0$$

→ E_1, E_2

$$\psi = (c_1 \phi_1 + c_2 \phi_2) N.$$

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C_1 multiplied by $H_{11} - E + C_2$ multiplied by $H_{12} - ES_{12}$, right? So you have got one equation. How will I get the second equation? Right. I only got the left hand side of one equation. Now I have got the whole thing. How will I get the second one? You already said multiply by ϕ_2 , integrate. What do I get? Work it out and again write it like C_1 multiplied by something plus C_2 multiplied by something. Okay this is the second equation.

You can work it out. Is $S_{12} = S_{21}$? $\int \phi_1 \phi_2 D\tau$ would better be equal to $\int \phi_2 \phi_1 D\tau$ also, alright? Now, so this is a system of linear equations in C_1 and C_2 , okay? When do we have nontrivial solutions? Secular determinant has to be equal to 0. Secular determinant is $H_{11} - E, H_{12} - ES_{12}; H_{21} - ES_{21}, H_{22} - E$. that determinant has to be equal to 0, okay? What is this called, equation? This equation is called secular equation, okay.

Now and then I think in quantum chemistry or bonding course you have studied of different methods by which you can evaluate this secular equation. Have you studied or no? How do I get H_{11} for example? See what is the unknown in this equation? H_{11} comprises of 2 wave functions and the Hamiltonian. So in principle they are known. If you do not even know the wave function then what are you talking about, right?

But do you know the wave function? Actually, you do. In this case, you are working with atomic orbitals, okay. $H_{12} - ES_{12}$ there also H_{12} is an integral. You know the 3 terms. You know S_{12} also. So the only unknown here is E , okay? The question is how do I know H_{11} , how do I know H_{12} , how do I know S_{12} ? How do I know them? Yeah. What is the energy of the orbital, where is the energy of the orbital? This E is the energy of the molecular orbital. I am trying to find it.

How will I know H_{11} . H_{11} is $\int \phi_1 H \phi_1$. So you can evaluate perhaps. If you know what is ϕ_1 , if you know what is the Hamiltonian, writing the Hamiltonian is not impossible, right? You can always write the Hamiltonian right or wrong? Whether you can use it and solve the equation that is a different question. But you can write the Hamiltonian and ϕ_1 is a relatively simple function.

You can make this Hamiltonian operate on ϕ_1 and then left multiplied by ϕ_1 see what you get. So you can in principle evaluate the integral, okay? But what I said of course is the rigorous pathway. Less rigorous pathway is that you can make an intelligent guess sum over the other and we will see an example of that intelligent guess in Huckel approximation. We know confusion here LCAO itself is an approximation, okay?

We are working within the ambit of that approximation. What else can I do? I can compute. Even if I cannot solve, I can work this out numerically. I can see some of the people who are present here who know how to do it. Using a computer you can do things numerically, right? Okay. So I can do it numerically. I can guess. I can take it from some table. I can work this out numerically. But once I know these integrals what I can do is I can expand this determinant.

What will I get? What kind of an equation will I get if I expand this determinant? I will get a quadratic equation in E , right? And when I solve it, how many roots will I have? I will have 2 roots, okay. So those will be the values of energy, alright. So, so far what have I used. I have used the atomic orbitals and I have used the Hamiltonian. What I have not used is the actual molecular orbital.

So see even without using the molecular orbital one can in principle work out the energy if you can have some idea of these integrals, alright. What will be the next step? Now see, look at the first equation. Suppose you can solve this equation and get the value of E . You get 2 values, right? 2 roots here, E_1 and E_2 . So what you can do is you can put in E_1 here, put in the value of E_1 there okay.

Then you get a simple equation in C_1 because if you can reach up to that means you already know what is H_{11} , what is H_{12} , what is S_{12} , okay. You just put in E_1 in both the equations. Now it becomes an equation in C_1 and C_2 that you can solve. You solve that and you find what is C_1 what is C_2 . Once you know what is C_1 what is C_2 what is it that you have worked out, the molecular orbital wave function ψ .

Do not forget $\psi = C_1 \phi_1 + C_2 \phi_2$, right? Yes, E is unknown. That is what I am saying. What you do is you find E from solving the secular equation. We are finding out 3 unknowns or more, it is actually 4 unknowns. 2 values of E do not forget. From our system of 2 linear equations okay which sounds counter intuitive per se but the only reason why we can do it is that we are saying that we know the values of H_{11} , H_{12} , H_{22} etc., okay?

So that is the power of your Cramer's method. So first work out E. Then insert the values of E here and then work out C_1 , C_2 and you can do that for E_1 as well as E_2 , right? Understand? So now see how many wave functions will you get? You will get 2 wave functions. One with the lower energy will be called the bonding molecular orbital. One with the higher energy will be called the anti-bonding molecular orbital, alright. So far so good.

“Professor - student conversation starts” Yes sir. We are talking about molecular orbitals. We have one equation $C_1^2 + C_2^2 = 1$. Yes. Talking about normalization, normalization becomes very easy in Huckel approximation, not here. Yeah. You have another equation by which you can find normalization constant that is right. But the problem is that normalization constant will come outside, right? So when you equate it to 0, the normalization constant goes. That is why we cannot use it. You have to do it this way. **“Professor - student conversation ends”**.

Okay. I think you have all read it somewhere or the other. I am just recapitulating at a very easy pace so that tomorrow when we talk about naphthalene we are all very comfortable. That is the reason. Okay, this is fine? So you can find out not only the energy but also what the molecular orbital looks like, okay? What is the basic assumption? See it is not as if you are doing it without an assumption.

We are doing it with the assumption that we know what is H_{11} , what is H_{12} , what is H_{21} , what is H_{22} , what are the overlapping details. Only with that knowledge can we use this method.