Symmetry and Group Theory
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Lecture -47
Molecular Orbital Theory

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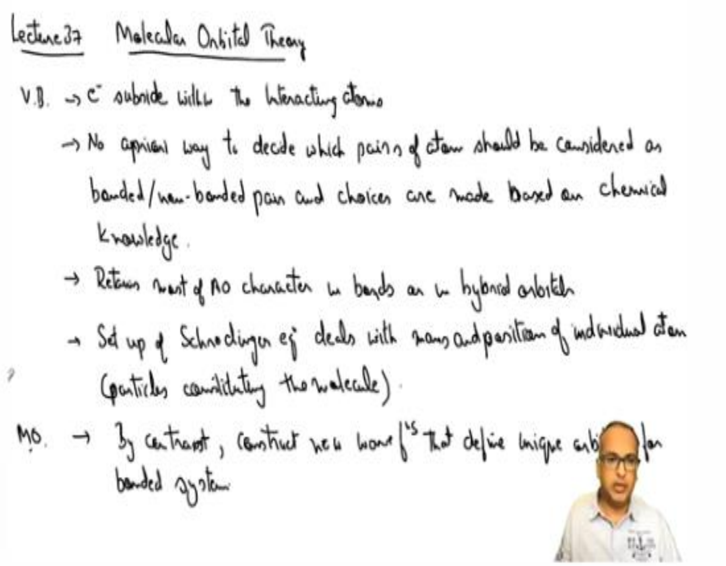

Lecture 37 Molecular Orbital Theory

V.B. → e^- subside within the interacting atoms

→ No apriori way to decide which pairs of atom should be considered as bonded/non-bonded pair and choices are made based on chemical knowledge.

→ Retains most of MO character in bonds or in hybrid orbitals

→ Set up of Schrodinger eq deals with mass and position of individual atom (particles constituting the molecule).

MO. → By contrast, construct new wave f^{ns} that define unique orbitals for bonded system

So, in the previous lecture we discussed Valance Bond theory and we tried to develop the picture for chemical bonding using symmetry and group theory. So now, let us continue the discussion of chemical bonding and move on to molecular orbital theory which is more generalized theory to explain the bonding picture. So, lets start with lecture 37, so today we will be discussing some aspects of Valance Bond theory and then we will try to compare it with MO theory.

And we will see what are the differences and then we will move towards linear combination of atomic orbital approach, which is used in MO theory. So, in case of VB Valance Bond theory, we had discussed that the electrons subside within the interacting atomic orbitals or within the interacting atoms you can say. So, also there is no apriori way to decide which pairs of atoms will form or should be considered rather as bonded pair.

And choices are made based on chemical knowledge. This is what we have seen earlier and these are the two main points. Also, if you see, it retains most of the atomic orbital character in bonds or we can say in hybrid orbitals, because hybrid orbitals are going to form bonds. And also, if we say that how do we set up the Schrodinger equation in this, so set up of Schrodinger equation deals with the, let us say if we want to calculate the energy of different orbitals and all.

So, then you need to set up and solve the Schrodinger equation and what you have to do is you have to set up the Schrodinger equation which deals with mass and position of individual atoms and then those atoms are actually considered as particles which constitute the molecule constituting the molecule. So, now let us see what happens and what changes in MO theory. So, MO theory by contrast we can say.

So, by contrast in MO theory, we construct new wave functions that define unique orbitals for bonded system, so this is in contrast to valence point where there is no a priori way to decide which pair of atoms should be considered as bonded pair.

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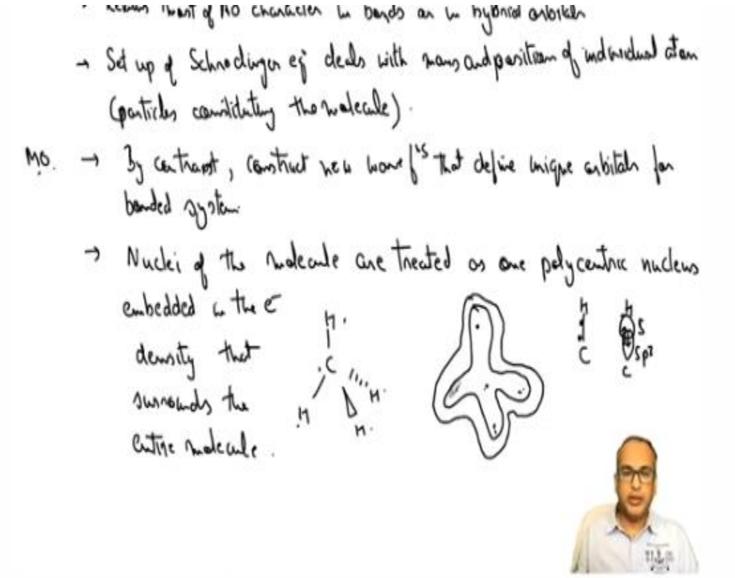

- retains most of AO character in bonds or in hybrid orbitals

→ Set up of Schrodinger eq deals with mass and position of individual atom (particles constituting the molecule).

MO. → By contrast, construct new wave f^{ns} that define unique orbitals for bonded system

→ Nuclei of the molecule are treated as one polycentric nucleus embedded in the e^- density that surrounds the entire molecule.

Further, if you look at the details of MO theory, so nuclei of the molecule are treated as so nuclei are treated as one polycentric nucleus, so all the nuclei taken together are treated as one polycentric nucleus. As if so let us say if I have CH4 here, and then I have a nucleus here, nucleus here, nucleus here, nucleus here, nucleus here, so instead of this I will be considering it as a nucleus something like this which will have centers like this.

So, this is how the nuclei are created as one polycentric, so this is one nucleus but which has many different charge centers, so it is one polycentric nucleus embedded in the electron density that surrounds the entire molecule. So, if these are the charged areas of a polycentric nucleus then this is also embedded into a electron density that surrounds the entire molecule. So, look at the bonding description which is different from valence bonds.

In case of valence bond, we had considered that a C-H bond there are two electrons which is one shared from here, one shared from here and then there is a bonding orbital which overlaps like this and then in this wave function there are two electrons which are staying, so this is 1s and then this is sp3 and this is s and then there is a overlap between proton and carbon orbital and then there are two electron.

One electron pair which is residing in this overlap bonding orbital, so this picture is totally different from what MO theory explains, MO theory says that there is a molecular orbital which covers the entire thing and then all the electron density is present surrounding this entire molecule.

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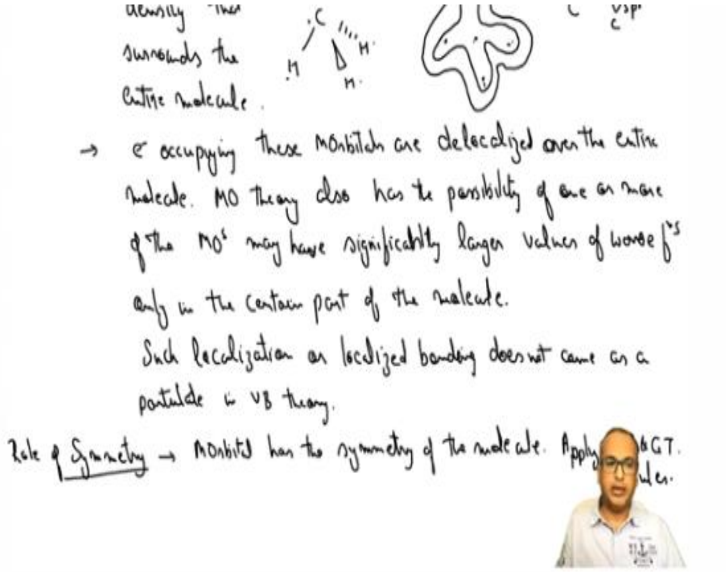

density that
surrounds the
entire molecule.

→ e^- occupying these MOrbitals are delocalized over the entire molecule. MO Theory also has the possibility of one or more of the MO's may have significantly larger values of wave f^n's only in the certain part of the molecule.
Such localization or localized bonding does not come as a postulate in VB theory.

Role of Symmetry → MOrbitals has the symmetry of the molecule. Apply GT.
les.

So, now let us also look at what is the basic idea? So, we can say that the electrons occupying these orbitals, we can say molecular orbitals, are delocalized over the entire molecule. MO theory also has the possibility of one or more of the molecular orbitals may have significantly larger values of wave functions only in the certain part of the molecule. What do I mean by that? So, it says that although the electron density is delocalized over the entire molecule over here.

But there are certain regions where the wave function has significantly larger values that mean the electron density is more stronger here, there is more probability of finding the electrons at certain places which are defined as bonds. So, it does say that there is electron density more in certain pictures but still it considers the delocalized picture overall. So, I hope the differences between the MO theory in Valence Bond theory should be very very clear.

So, we can say that such localization, or localized bonding you can say, does not come as a postulate in Valence Bond theory, so it does not say that there is a delocalization of electron density and there is localized electron density it only tells you that, Valence Bond theory only tells you that there is a bonding orbital which is formed by overlap of the hybrid orbital and one of the atoms and the electron density is subsided between those two.

But this picture is totally different. I hope the thing is very very clear now. So, now before actually going to develop the MO diagram using different examples by help of symmetry and group theory let us see that, what is the role of symmetry? How symmetry can play a role in MO theory? So, role of symmetry is, so imagine that the MO Molecular orbital has the symmetry of the molecule.

Why it has the symmetry of the molecule because it is spread around the complete entire molecule. So once we say that the molecular orbital has the same symmetry as the molecule so we can immediately think of applying symmetry and group theory rules. So, now we can say that there is a symmetry playing a role in formation of molecular orbitals. So, now before again we go on discussing the MO theory and how to apply symmetry and group theory to develop it further.

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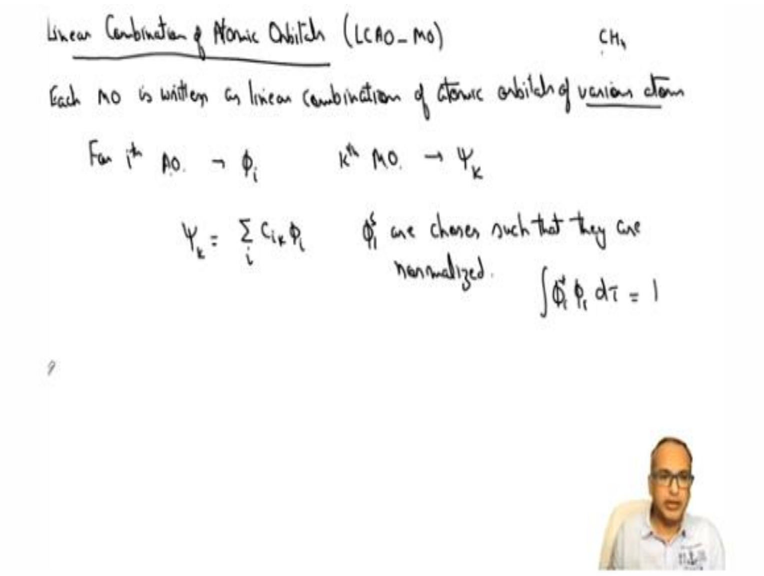

Linear Combination of Atomic Orbitals (LCAO – MO)

CH_4

Each MO is written as linear combination of atomic orbitals of various atoms

For i^{th} A.O. → ϕ_i k^{th} M.O. → ψ_k

$\psi_k = \sum_i c_{ik} \phi_i$ ϕ_i's are chosen such that they are normalized.

$\int \phi_i^* \phi_i \, d\tau = 1$

Let us see something called as Linear Combination of Atomic Orbitals which further leads to molecular orbitals, so it is a Linear Combination of all atomic orbitals which are taken. So unlike in Valance Bond theory where we were taking linear combination or symmetry adapted linear Combination of only the central atom, for example only carbon in CH4 was taken to form the hybrid orbitals. In this case we are taking linear combination of all the atomic orbitals this approach is called as LCAO or Linear Combination of Atomic Orbitals.

So, now let us start discussing this. So each molecular orbitals is written as Linear combination of Atomic orbitals, this is the basic start. So we will see that we can also start with let us say if you are talking about carbon and hydrogen, so we can start with carbon orbitals and hydrogen orbitals independently. Or we can also start with the hybrid orbitals of carbon and Atomic orbitals taken together, because if the atomic orbitals of carbon eventually would give rise to hybrid orbitals.

And that will combine with the atomic orbitals of Proton, will see how it goes. So, let us first start of various atoms. So one difference is that we are not talking about only central atom we are here we are including all that atoms. So, we can say for ith atomic orbital we can write it as phi i and kth can be written as psi k. This is the nomenclature which will be using. So if we now write psi k can be written as linear combination of atomic orbital.

So, I can say that summation over all i, c i k and phi i, I can say that. So, where phi i are the atomic orbitals and hence eigen functions of that particular atom atomic orbital this is the free atom we are talking about. Also, phi i are so chosen such that they are all normalized, otherwise we will have to normalize it and take, we will see how when we solve it, it will be required that we will normalize, that means that if you take the integration of phi i, star phi i over the space d tau this should be equal to 1, this is the normalization condition.

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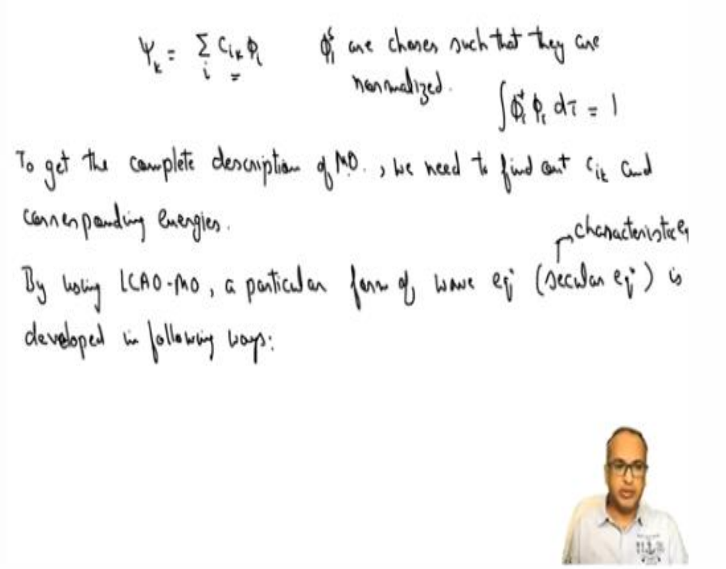

$\Psi_k = \sum_i c_{ik} \phi_i$ ϕ_i's are chosen such that they are normalized.

$\int \phi_i^* \phi_i \, d\tau = 1$

To get the complete description of MO, we need to find out c_{ik} and corresponding energies.

By using LCAO-MO, a particular form of wave eqⁿ (secular eqⁿ) is developed in following ways:

characteristic eq

So, now to get the complete description of MO what do we need, we need to find out these coefficients c ik and corresponding energies. So, by using Linear Combination of Atomic Orbitals, MO a particular form of wave equation called as secular equation is developed, in some books you will see that this is also written as characteristic equation, is developed in following ways.

So, let us try to develop secular equation which will be able to solve it for the energies of different molecular orbitals and the coefficients which are required for this Linear Combination.

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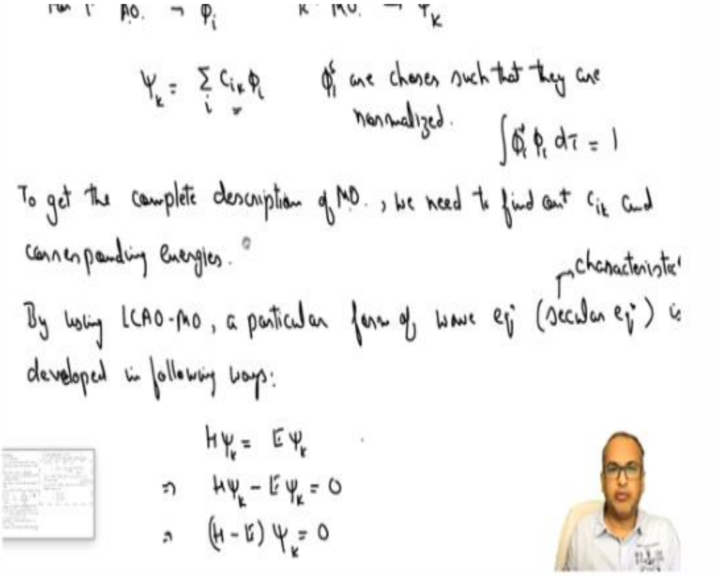

i AO → ϕ_i k MO → ψ_k

$\psi_k = \sum_i c_{ik}\phi_i$ ϕ_i's are chosen such that they are normalized.

$\int \phi_i^* \phi_i \, d\tau = 1$

To get the complete description of MO, we need to find out c_{ik} and corresponding energies.

By using LCAO-MO, a particular form of wave eqn (secular eqn) is developed in following ways:

characteristic

$$H\psi_k = E\psi_k$$
$$\Rightarrow H\psi_k - E\psi_k = 0$$
$$\Rightarrow (H - E)\psi_k = 0$$

So, let us start so we all know that we can write H psi is equal to E psi, this is the Schrodinger wave equation then we can also say so H is the Hamiltonian, E is the energy, psi is the state function for molecular orbital, this we have already discussed before so let us not spend time on this. So, we can now write it as like this also we can take out psi common. Now if we can write k over here now substituting the value of psi k from the above equation here which is the linear combination.

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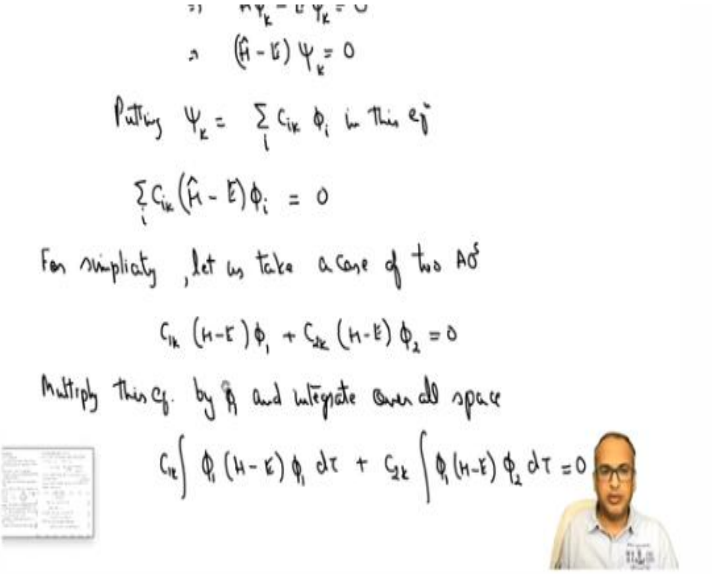

$$\Rightarrow H\psi_k - E\psi_k = 0$$
$$\Rightarrow (\hat{H} - E)\psi_k = 0$$

Putting $\psi_k = \sum_i c_{ik}\phi_i$ in this eqn

$$\sum_i c_{ik}(\hat{H} - E)\phi_i = 0$$

For simplicity, let us take a case of two AO's

$$c_{1k}(H - E)\phi_1 + c_{2k}(H - E)\phi_2 = 0$$

Multiply this eq. by ϕ_1 and integrate over all space

$$c_{1k}\int \phi_1 (H - E)\phi_1 \, d\tau + c_{2k}\int \phi_1 (H - E)\phi_2 \, d\tau = 0$$

So, what we can write is, so we can write putting psi k is equal to summation i, C i k, phi i in this equation, we get H – E, Phi i and C i k is outside summation i. So, H is operator which will act only on phi i and because this is the function and this the constant, so C i k will come out of this operator, I can write it like this H is the operator over here and this thing is equal to zero. So, now this is for i atomic orbitals.

So, let us take for simplicity only 2 atomic orbitals, so that we can see how to solve this equation. So, I will say for simplicity let us take a case of two atomic orbitals, so in that case our i will go from 1 to 2, so i will have 1 and 2. So, what do I say then I can say that this is my C 1k, H - E Phi 1 + C 2k, H - E Phi 2 equal to 0. So, I have just expanded this equation for two atomic orbitals, if there are more than two, so you can accordingly expand it.

Now how do we solve this equation, so now we have the energies and the coefficients how do we solve this? So, now if we multiply this equation by phi 1 and integrate over all space. So, when I say integrate over all space, I mean that integrates over the space within the boundary conditions of this atomic orbital. So, beyond which it will cease to act as Eigen functions, so only integrate within the boundary conditions not overall space.

But i in general we just write d tau so that we do not have to define the limits here. So, both sides by phi 1 and then integration. So what do we get? We will get C 1 k integral and we will have phi 1, H – E, Phi 1, d tau so this is integration over all space, then we have + C 2k integration phi 1, H – E, Phi 2, d tau equal to 0. So, let me go to next page.

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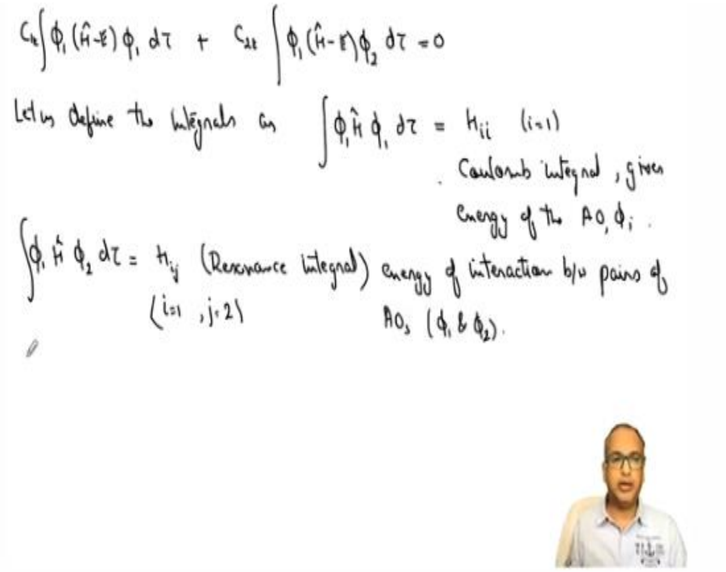

$$C_{1k}\int \phi_1 (\hat{H}-E)\phi_1 \, d\tau + C_{2k}\int \phi_1 (\hat{H}-E)\phi_2 \, d\tau = 0$$

Let us define the integrals as $\int \phi_1 \hat{H} \phi_1 \, d\tau = H_{ii}$ $(i=1)$

Coulomb integral, gives energy of the AO, ϕ_i.

$\int \phi_1 \hat{H} \phi_2 \, d\tau = H_{ij}$ (Resonance integral) energy of interaction b/w pairs of AOs (ϕ_1 & ϕ_2).

$(i=1, j=2)$

So, what do we have? So let me write that equation again, so we do not get confused, phi 1, H – E, Phi 1 d tau C 1k, C 2k integration phi 1, H – E, Phi 2 d tau equal to 0. Now, let us define, see all these integrals you do not need to solve because some of the integrals by the rules of symmetry in group theory, you should be able to simplify. How do we simplify that? We know that phi 1 will have will form basis for certain thing, H will form basis for certain things.

So, those irreducible representations can come in here and then we can take the direct products here, so we can simplify this equation. So, I am not going to do it right now, but when we are taking actual molecule, you should be able to do that. So, let us define these integrals. So we have so if we see here, there will be a term called phi 1, H phi 1 because H is going to operate it is an operator.

H is going to operate on phi 1 and phi 2, so we will have this integral Phi 1, H Phi 1, d tau and we will call this as H ii. So, in this case, i is equal to 1 where both the indices are same so this will be called as H ii and this is called as Coulomb integral. And basically, what it tells you it gives you the energy of, it gives you energy of the atomic orbital Phi i. So, if you want to estimate the energy of phi i you have to develop this integral;

And this will tell you the energy of phi i and this is called as H ii already. Now the second one which will come from here phi 1, H phi 2 integration d tau, this can be called as H ij and this is called as Resonance Integral. So, in this case i is equal to 1 and j is equal to 2 in this particular case, so this is called as Resonance Integral and what does it give you it gives you energy of interaction.

Energy of interaction between pairs of Atomic orbitals that are interacting in this case it is phi 1 and phi 2.

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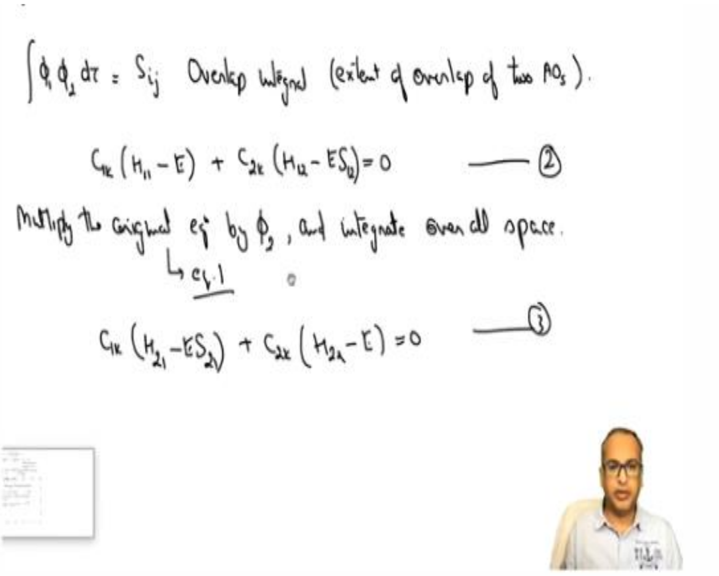

$\int \phi_1 \phi_2 \, d\tau = S_{ij}$ Overlap integral (extent of overlap of two AOs).

$$C_{1k}(H_{11} - E) + C_{2k}(H_{12} - ES_{12}) = 0 \quad \text{—— ②}$$

Multiply the original eq by ϕ_2, and integrate over all space.

$\hookrightarrow$ eq. 1

$$C_{1k}(H_{21} - ES_{21}) + C_{2k}(H_{22} - E) = 0 \quad \text{—— ③}$$

So, these are two integrals then we have we also have phi 1, Phi 1 d tau, which is equal to 1 we know that and this is a normalization condition, so we already started with normalized atomic orbitals. So, that is why we can substitute this as equal to 1, so this is normalization condition. We also have phi 1, Phi 2, d tau and this is called as S ij, which is called as overlap integeral. What is the extend of overlap?

It tells you about extent of overlap of 2 atomic orbitals in this case phi 1 and phi. So, that is very, very easy and now you can actually rewrite this equation double equation by assuming these indices. So, let us see that what we have got. We have C 1k and we can now write it as H 11 – E, so H 11 corresponds to the complete integral which I said, + C 2K. And we have H 12 - E equals to 0.

Now similarly if we multiply the original equation by phi 2, so initially we multiplied by phi 1 and integrated over all space now what we are doing is we will multiply the original equation by phi 2 and integrate it over all space. So, maybe it is better if I can write down the previous equation number, so that it is easier for you to understand let me go back to the previous page, so if I give this thing a name then let us call this equation 1.

So, we are multiplied this equation by phi 1 and integrated overall space, so now next what we are going to do is we are going to multiply equation 1 by phi. So, instead of original equation I will write this is equation 1, so that it is not confusing so if you do that, we will get a similar equation but now what we will get is, we will get to C 1 k then we have H 2 1 – E, there is one more term over here E into S 12, S 21 + C 2k and this will be H 22 – E equals to 0. So, now you have equation 2 and equation 3.

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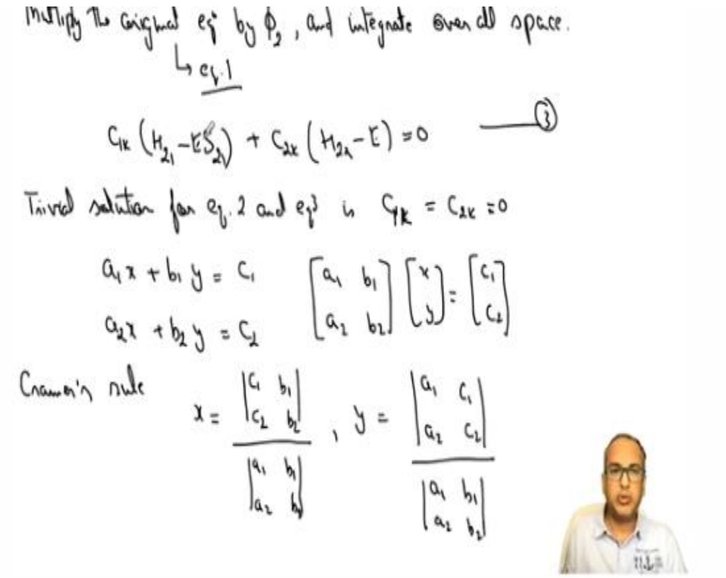

Multiply the original eq^n by ϕ_2, and integrate over all space.

↳ eq. 1

$$C_{1k}(H_{21} - ES_{21}) + C_{2k}(H_{22} - E) = 0 \quad \text{—③}$$

Trivial solution for eq. 2 and eq^n 3 is $C_{1k} = C_{2k} = 0$

$$a_1 x + b_1 y = C_1 \qquad \begin{bmatrix} a_1 & b_1 \\ a_2 & b_2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}$$

$$a_2 x + b_2 y = C_2$$

Cramer's rule

$$x = \frac{\begin{vmatrix} C_1 & b_1 \\ C_2 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}, \quad y = \frac{\begin{vmatrix} a_1 & C_1 \\ a_2 & C_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

Now trivial solution for this is, for equation 2 and equation 3 is, C 1k equals to C 2k equals to 0 and that will satisfy the whole thing. But we are not interested in putting all the coefficients equal to 0 that means there is no atomic orbital mixing, so that is the trivial solution which we are not going to take. Now let us see what is the non-trivial solution? Which will equate rest of the; things as equal to 0.

If you remember, let us call it as a 1 x + b 1 y equals to C 1 and a 2 x + b 2 y equals to C 2. So, you can convert this into matrix representation and write it as a 1 b 1, a 2 b 2 multiplied by x y and write it as C 1 C 2. In this case we can apply Cramer's rule, you must be remembering Cramer's rule from your class eleventh when the matrices and determinants were used and you would have solved set of linear equations using Cramer's rule.

So, what did we do there, so we had x can be written as solution as determinant where we will replace the first coefficients by C 1, C 2 and second will remain as such divided by the determinant of a 1, b 1, a 2, b 2, so this is how you can solve this equation. And similarly for y substitute C 1 C 2 at this column, so we have a 1, a 2, C 1, C 2 and at the bottom you have to determinant a 1, a 2, b 1, b 2 this should be clear so applying the same Cramer's rule to this equation what we have got?

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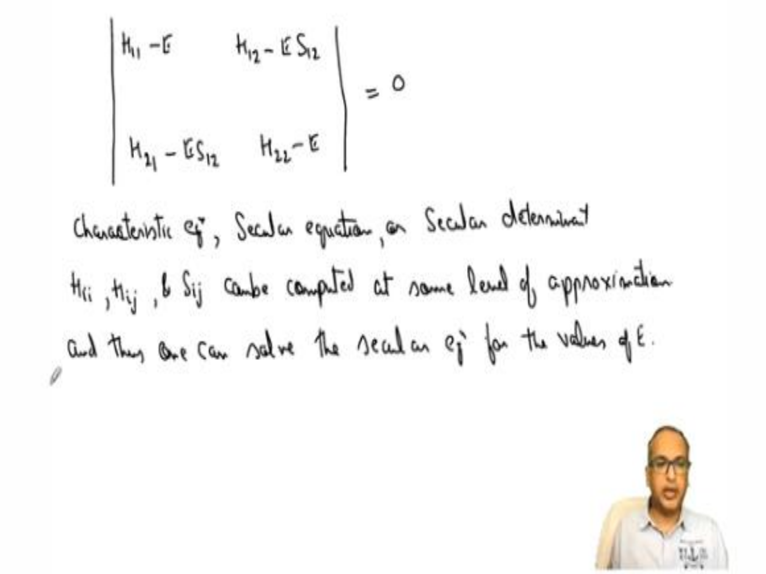

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{12} & H_{22} - E \end{vmatrix} = 0$$

Characteristic eq^n, Secular equation, or Secular determinant

H_{ii}, H_{ij}, & S_{ij} canbe computed at some level of approximation

and thus one can solve the secular eq^n for the values of E.

We will get H 11 – E, H 12 – E, S 12, H 21 – E, S 12, H 22 – E this determinant will go to 0, now this is called as characteristic equation or secular equation or secular determinant. If you need to know more details of it, so you can go back and look at the quantum chemistry course and there you will get it in more details. So, now we can say that the values of H ii, H ij and S ij can be computed at some level of approximation and thus one can solve.

So, again you can see that you can apply symmetry and group theory or direct product to be very precise to be able to save which of these integrals will go to 0 and which not and that will simplify your equation. So, one can solve the secular equation, for the values of E.

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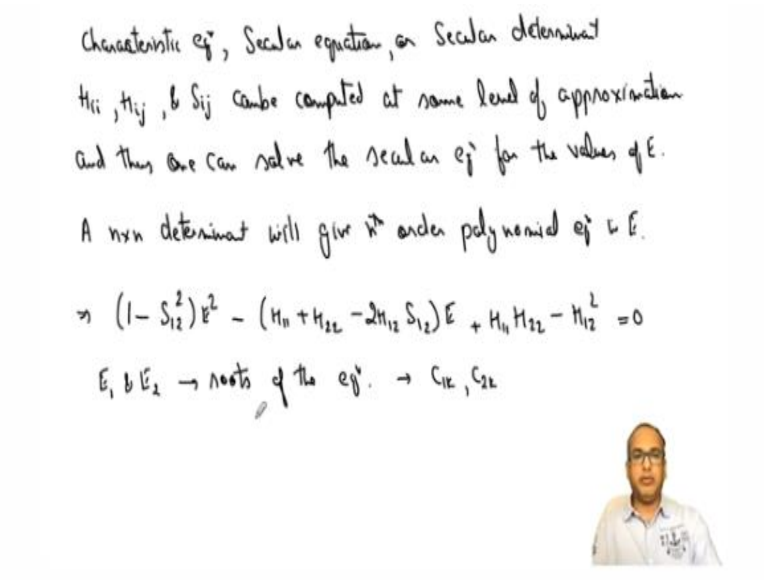

Characteristic eqⁿ, Secular equation, or Secular determinant

H_{ii}, H_{ij}, & S_{ij} can be computed at some level of approximation

and thus one can solve the secular eqⁿ for the values of E.

A n×n determinant will give nth order polynomial eqⁿ in E.

$\Rightarrow (1-S_{12}^2)E^2 - (H_{11}+H_{22}-2H_{12}S_{12})E + H_{11}H_{22} - H_{12}^2 = 0$

E_1 & E_2 → roots of the eqⁿ. → C_{1k}, C_{2k}

So, once you have got the values of E, let us see, in this case this is a two cross two matrix so it will give you quadratic equation if you have n atomic orbitals. So, we will get n cross n determinant will give nth order polynomial equation in E, so we get n values of E that means you will get n different molecular orbitals, when you combine n atomic orbitals, because you will have n different energy.

Some of them can be accidentally degenerate some of them can be similar because of symmetry they will be degenerate but you will get n different energies. So, in this particular example you have two cross two determinant so you will get quadratic equation, so let us see what we will get here if we solve the above determinant, we get 1 – S 12 square and we get E square – H 11 + H 22 – 2H 12 S 12 E + H 11 H 22 - H 12 square equal to 0.

Now this equation all these integrals can be calculated because you know the atomic orbital wave functions. So, you can set up the integrations simplify some of them by direct product some of them will go to zero.Tthose which will not go to zero put them here solve them and then you will get the values of energy, so you will get two values of energy. So, you will get roots will be E 1, let us say and E 2, these will be roots of the secular equation.

Further this will give you C1 k if you substitute these values into the original equation that was equation 1. One you will get the values of C 1 k and C 2 k. So, the coefficients will also be obtained once you have got the coefficients and the energies so you have developed yourself the picture for the molecular orbital. So, I think this is all for today so in the next class we will take up examples and see how actually using all these arguments which we have discussed today. How actually do we develop the molecular orbital diagram for a given molecule, thank you very much.