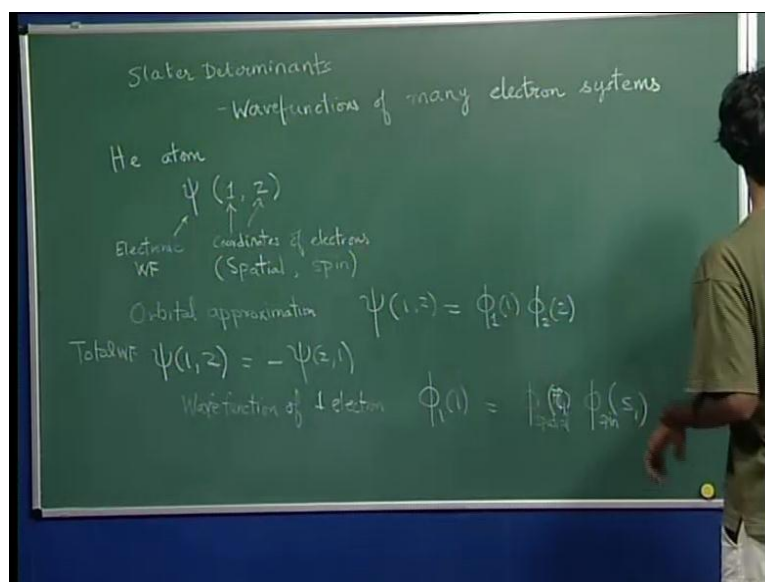


**Mathematics for Chemistry**  
**Prof. Dr. M. Ranganathan**  
**Department of Chemistry**  
**Indian Institute of Technology, Kanpur**

**Lecture - 13**

Today's class we will look at 2 examples of applications of all that we have learned so far in linear algebra, specially an application of matrix methods. The two applications that we will talk about today are Slater determinants and Huckle molecular orbital theory. Now, Slater determinant is the first application that we will talk about.

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And Slater determinants are used to express wave functions of many electron systems, and by many electron we mean more than one electron. So, system with more than one electron, the wave function of that system is expressed in terms of Slater orbital's in terms of Slater determinants. So, how does this work, so for this let us consider the case of a helium atom. So, the helium atom has 2 electrons, so the wave function of the helium atom the electronic wave function of the helium atom is a function of the coordinates of the both electron 1 and electron 2.

So, this is the total electronic wave function and 1 is the coordinates, 1 and 2 are coordinates of electron. And when I say coordinates I mean both the spatial coordinate that is what where it is located in space and the spin coordinates and what it spin is. So, for example, and electron one could be located at  $r_1$  with spin with spin alpha or it

could be located in  $r_2$  spin  $\beta$  and so the coordinates of the electrons have both the spatial and the spin part.

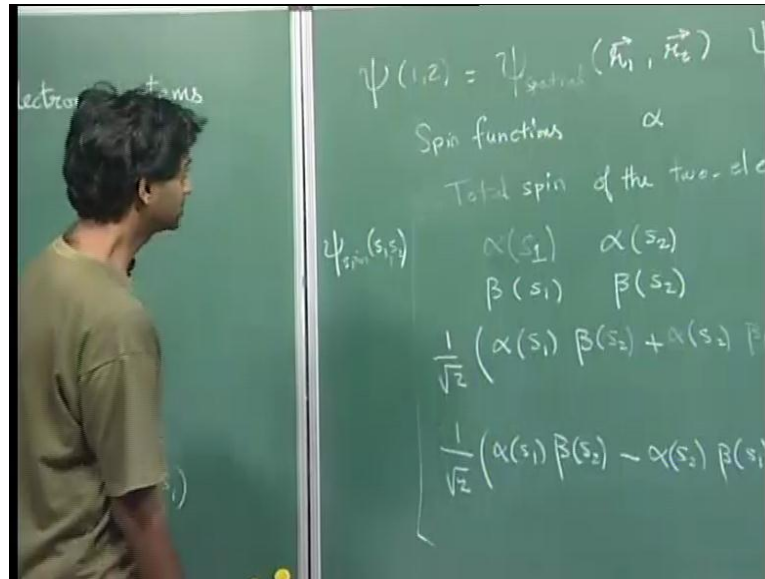
So, now in order to write the wave function of a helium of a many electron system the first approximation that we make is called the orbital approximation. So, the orbital approximation consists of saying that this wave function which is a function of both the coordinates can be written as a product of coordinates of first electron and the coordinates of the second electron. So, in other words you can write here wave function of 1 and 2 as a product of wave functions for the first electron  $\phi_1$  of first electron  $\phi_2$  of second electron.

And so we say that each electrons stays in its own orbital. So, electron 1 is in orbital corresponding to  $\phi_1$  electron 2 is in orbital corresponding to  $\phi_2$ . And so this is the first approximation this is called the orbital approximation. Now, these need not be the same as the orbitals of the hydrogen atom but this is some orbital some atomic orbital's of that particular species of helium atom in this case. Now, there is a fundamental principle that says that your wave function  $\psi$  of 1 2 should be anti symmetric to permutation of 1 and 2.

So, this is the total wave function has to satisfy the property that  $\psi$  of 1 2 equal to minus  $\psi$  of 2 1 this has to do with the fact that the electrons are what are called as fermions or spin half particles. And all spin half particles have to be anti symmetric to interchange of the 2 particles. So, this is the fundamental property of the system and it is because we are looking at electrons that interchange of electrons should give the same wave function with the opposite sign.

Now, what we are going to do is to we are going to try to construct various orbitals that satisfy this property or various wave functions that satisfy this property. Now, be further more we write this total wave function of 1 electron. So, the single electron wave function  $\phi_1$  of 1 this is factored into a spatial part and a spin part. So, I will call it  $\psi$  spatial times  $\phi$  spin this is the and the spatial coordinate of one is  $r_1$  and the spin coordinate I will call it  $s_1$ .

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So, this is written in this form and. So, your total wave function your psi of 1 2 can be written as psi spatial of 1 2 of rather of  $r_1$  and  $r_2$  times psi spin of  $s_1 s_2$ , these are the spin coordinates. So, just as you have spatial coordinates, you have spin coordinates for each of the electrons. And it is this total wave function that should satisfy this anti symmetric property, so let us start with this helium atom. Now, since we can factor the orbital into a spatial and a spin part.

We can say that the spin functions spin functions are denoted by there are only 2 possibilities for these spin functions. The 2 possibilities are alpha and beta. So, the spin function of any electron can either be alpha or beta these are the 2 spin functions corresponding to you can think of them as spin up and spin down. So, there are only 2 possibilities for the spin functions. So, now if you look at the total spin of the system of the 2 electron system, now there are various possibilities. So, for example, you could have the first electron in alpha.

So, the first electron is in spin state alpha and the second electron is also in spin state alpha. Now, both the electrons are in spin state alpha alternatively you could have both the electrons in spin says beta or you could have one electron in alpha and the other electron in beta. So, you could have electron one in alpha or and electron 2 in beta but because the electrons are in distinguishable this is should be the same as electron 2 in alpha and electron one in beta.

So, these 2 should or actually you cannot distinguish between them so this sort of representation is not valid as a representation of the spin function of the 2 electron system. And you have to consider either a linear combination of this form or a linear combination of this form. And this wave this function is symmetric to interchange of  $s_1$  and  $s_2$ . So, if switch  $s_1$  and  $s_2$ . This remains the same whereas, here if I switch  $s_1$  and  $s_2$  this change as sign.

So, this is anti symmetric to exchange of  $s_1$  and  $s_2$ . What we mean by anti symmetric is that if I change  $s_1$  and  $s_2$  then this whole wave function will change  $s_2$  beta  $s_1$  minus alpha  $s_1$  beta  $s_2$  that is negative of this wave function. Whereas, these 3 wave functions if I change  $s_1$  and  $s_2$  they are symmetric  $s_1$  and  $s_2$ . And we could not use this as a wave function we could not use this as a valid wave function because it is neither symmetric now anti symmetric to exchange of  $s_1$  and  $s_2$ .

And so we have to construct a we have to construct 2 combinations one which was symmetric and the other which is anti symmetric. So, these are the 4 allowed spin functions. So, the allowed spin functions are these 4, so if you say  $\psi$  spin of  $s_1 s_2$  can take any of these values. So, these are allowed values for  $\psi$  spin of  $s_1$  and  $s_2$ .

So, now what we will do is we use this in a combination with a spatial wave function. Now, since the product of the spatial times a spin part has to be anti symmetric. Since, this product has to be anti symmetric it follows that in if you take a spin part which is symmetric then the spatial part has to be anti symmetric. And if you take a spin part to be anti symmetric the spatial part has to be symmetric. So, since this product has to be symmetric; that means, one of these has to be anti symmetric the other has to be symmetric.

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$$\text{He } 2e^- \text{ GS} \rightarrow \text{Both electrons are in } 1s \text{ orbital}$$

$$\psi_{\text{spatial}}(\vec{r}_1, \vec{r}_2) = 1s(\vec{r}_1) 1s(\vec{r}_2)$$

$$\psi(1, 2) = 1s(r_1) 1s(r_2) \frac{1}{\sqrt{2}} (\alpha(s_1) \beta(s_2) - \alpha(s_2) \beta(s_1))$$

$$= \frac{1}{\sqrt{2}} \left[ (1s(r_1) \alpha(s_1)) (1s(r_2) \beta(s_2)) - (1s(r_2) \alpha(s_2)) (1s(r_1) \beta(s_1)) \right]$$

$$= \frac{1}{\sqrt{2}} \left[ 1s_{\alpha}(1) 1s_{\beta}(2) - 1s_{\alpha}(2) 1s_{\beta}(1) \right]$$

$$= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s_{\alpha}(1) & 1s_{\alpha}(2) \\ 1s_{\beta}(1) & 1s_{\beta}(2) \end{vmatrix} \quad \text{Slater determinant}$$

Now, there are 3 choices of taking symmetric spin part, spin functions and there is only one choice of an anti symmetric spin function. So, let us go and try to write the spatial part now, for helium atom in the you have 2 electrons you know that the ground state corresponds to ground state both electrons are in 1s orbital. And since both the electrons are in the same spatial orbital's there for both electrons are the same.

So, the spatial orbital, so you can write  $\psi_{\text{spatial}}(r_1, r_2)$  is equal to  $1s$  of  $r_1$  times  $1s$  of  $r_2$ . So, the spatial parts are the same and so the since each electron is in the  $1s$  orbital. So, the wave function in the orbital approximation can be written of a product of wave functions. This is  $1s$  for  $r_1$  this is  $1s$  for  $r_2$ . Now, if both the electrons are in the same spatial orbital since, the product of the wave functions has to be anti symmetric you can immediately see that this is the only allowed spin function.

So, only one spin function is allowed that is the anti symmetric spin function. So, you can immediately write that  $\psi(1, 2)$  is equal to  $1s$  of  $r_1$   $1s$  of  $r_2$  into  $1/\sqrt{2}$   $\alpha$  of  $s_1$   $\beta$  of  $s_2$  minus  $\alpha$  of  $s_2$   $\beta$  of  $s_1$ . You can immediately write this form and you can write this in a slightly different form. Suppose I take the  $1s$  inside I can write this as  $1/\sqrt{2}$   $1s$  of  $r_1$  into  $\alpha$  of  $s_1$  times  $1s$  of  $r_2$   $\beta$  of  $s_2$  minus  $1s$  of  $r_2$   $\alpha$  of  $s_2$  times  $1s$  of  $r_1$   $\beta$  of  $s_1$ .

So, you can write it in this form and notice that this depends only on electron 1 this depends only on coordinates of electron 1. So, I can write this as  $1s$   $\alpha$  of 1 so I just

denote this is the spin orbital of electron 1. So, this says that the spatial orbital is  $1s$  and the spin orbital is  $\alpha$ . So,  $1s\alpha$  of 1 I can write this as  $1s\beta$  of 2 minus  $1s\alpha$  of 2,  $1s\beta$  of 1 and this whole thing times  $1/\sqrt{2}$ .

And this can be written as  $1/\sqrt{2} (1s\alpha_1 1s\beta_2 - 1s\beta_1 1s\alpha_2)$  hmm sorry I will put it slightly differently I will write  $1s\alpha_1 1s\alpha_2 1s\beta_1 1s\beta_2$  and. So, the first row I have  $1s\alpha$  and the second row I have  $1s\beta$  and what I am going to put here is in the first column I will put 1 second column I will put 2. So, it is  $1s\alpha_1$  times so this determinant gives me the allowed wave function. This determinant is called a Slater determinant.

So, the Slater determinant notice that I put all the spin orbital's on the rows and I put the coordinates of the electron on the columns. So, the first column corresponds to coordinates of electron 1 the second column corresponds to coordinates of electron 2. Now, writing the wave function in the Slater determinant form is very useful and it ensures that.

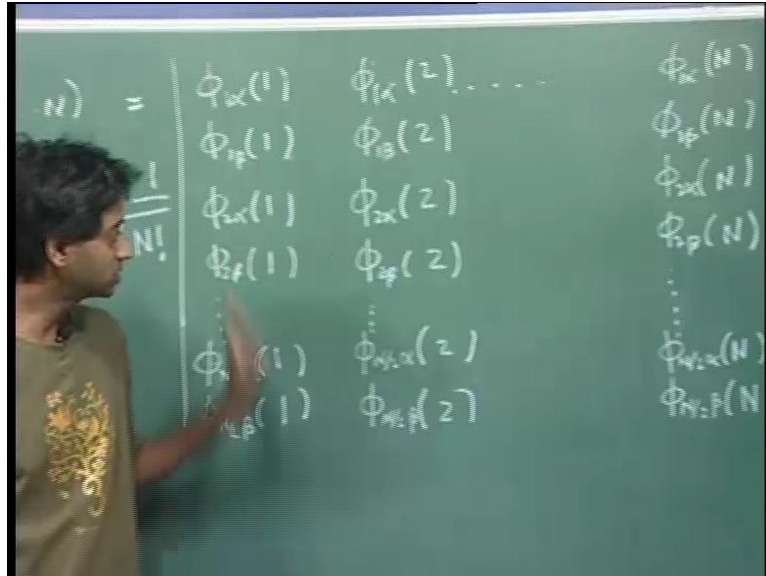
If I switch 1 and 2 if I switch the coordinates of 1 and 2 it is like switching 2 rows of a determinant it says exactly equivalent to switching 2 rows of a determinant and. So, when I interchange one and 2 then I am changing the sign of the determinant. So, the Slater determinant it ensures that your wave function is anti symmetric. So, it ensures that the wave function that you have is anti symmetric, and you can do this even for you know this need not be it can be if both the electrons.

So, I can do this even for other this does not need to be  $1s\alpha$  and  $1s\beta$ , it can be  $1\alpha$  and  $2s\beta$ . So, you can do this for more complicated systems rather than just helium atom. So, it ensures because of the nature of this of these determinants it ensures that it is that the total wave function will be anti symmetric. And the reason it will be anti symmetric is that switching the coordinates of any 2 electrons is like changing 2 rows of the determinant.

So, this can be extended to a many electron system and you can easily show how to extend this to a to a many electron system and that is what we will do next. So, incidentally you notice that the moment we said, that the spatial parts of the 2 electrons have to be identical. When the 2 electrons are in the same spatial orbital because of the anti symmetric condition their spins have to be different. So, having 2 electron in the in

the same spatial orbital ensures that the spins are different and this is an illustration of Pauli's exclusion principle.

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So, Pauli's exclusion principle says that if 2 electrons are in the same orbital then their spins have to be opposite and so these 2 electrons are in the same spatial orbital and spins are opposite. And that is the only allowed state, only allowed wave function. Now, suppose you had a many electron system how do you write this so suppose you had psi of 1 2 up to n and for convenience let's assume that this is a closed shell system.

So, closed shell system; that means, n is an even number and all the electrons are paired in their orbitals. So, in this case what you have is you have various you can write this determinant in this form one over square root of N factorial. That is the normalization constant and then if the various orbitals corresponds to phi 1 alpha phi 1 beta phi 2 alpha phi 2 beta all the way up to phi n by 2 alpha phi n by 2 beta. So, all the electrons are paired in their respective orbitals and these are the various orbitals. So, we can write the Slater determinant very easily. So, you write all the orbitals in this way similarly, you will write the same orbitals beta and. So, on all the way up to you will write it n times. Now, we have to write the various arguments you have to write the various what is the, what is it a function of...

So, we have to fill in these things and following the prescription for the Slater determinant on the first column I will put 1 corresponding to electron 1. Second column I

will put 2 corresponding to electron 2 and. So, on I will go all the way in the  $n$  th column I will put  $n$  corresponding to electron  $n$ . So, there are  $n$  electrons in  $n$  by 2 orbital's. So, there are  $n$  electrons and the total number of orbital's is  $n$  by 2 and. So, you follow this prescription and you can write the wave function.

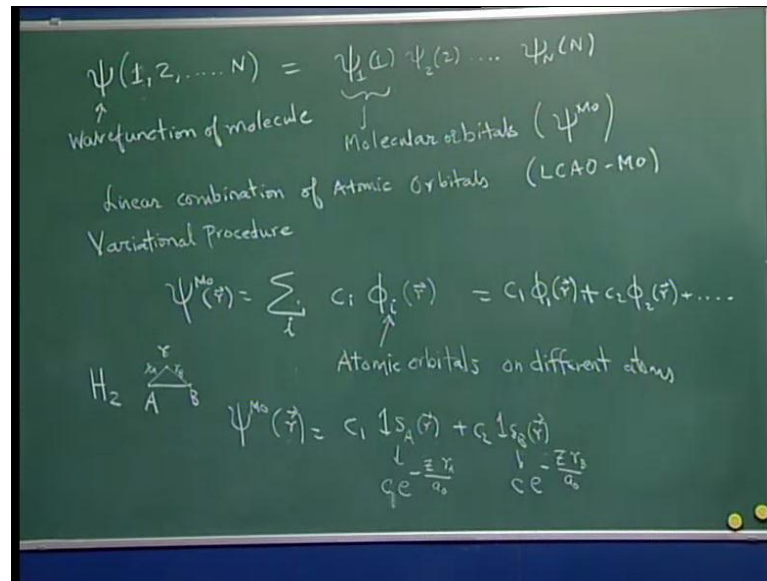
And this is anti symmetric to interchange of any 2 electrons so I can switch one and 2 I will get it will be anti symmetric I can switch one and  $n$  again the determinant will change sign. So, if I change any 2 rows of the determinant. Then the determinant changes sign and the way we have written the Slater determinant we have ensured that the coordinates of only one electron appear in one column coordinates of only one electron appear in any column.

And that ensures that switching 2 columns is like changing the coordinates of 2 electrons. So, this way of writing determinant is extremely useful for closed shell systems and it is not just atoms for which this is useful this is also useful for molecules with which have a closed shell configuration. And so this is a very simple and very useful application of this idea of determinants. The next application that we will do is what is called as Huckle molecular orbital theory.

And this is another application of determinants and in fact, in general of matrix methods and linear algebra. Now, in order to introduce the Huckle molecular orbital theory I will first tell about molecular orbital theory and in particular about what is called as linear combination of atomic orbital's leading to molecular orbital's. So, if you have a molecule suppose you have molecule a Molecule has many electrons a molecule typically has many electrons and So, you have you have coordinates 1 2 or to some number there are  $n$  electrons.



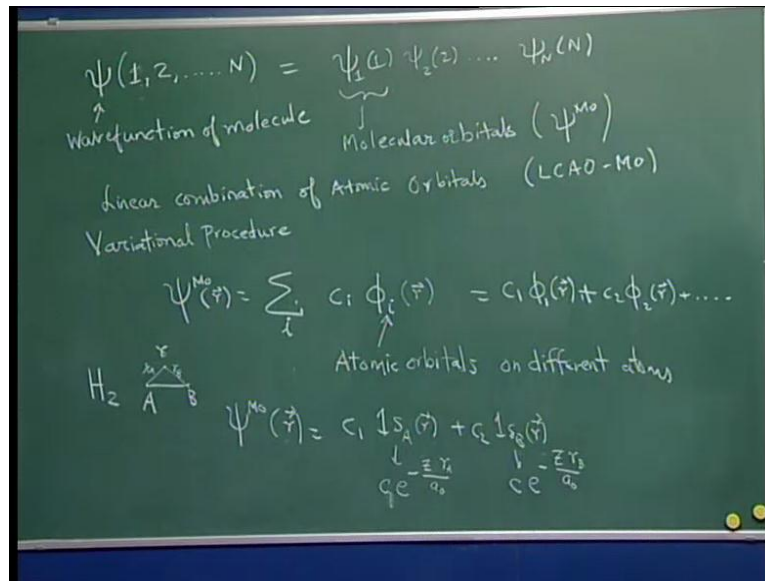
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So, this is a molecular wave function. So, this is the wave function of the molecule and in particular I should say this is the electronic wave function of the molecule. And the first thing you do is to write this as a product of one electron wave functions. So, you write this as a product of  $n$  and these are single electron wave functions these are called orbital's. And in particular these are called molecular orbital's. So, this is the under the orbital approximation.

So, we use the approximation that the total wave function can be written as a product of these orbital's or single electron wave functions. Now, the molecular orbital's are actually incredibly complicated objects to calculate and what is typically done is the procedure called linear combination of atomic orbital's it is called LCAO hyphen MO. So, Linear Combination of Atomic Orbital's giving Molecular Orbital's. And this is implemented in something called a variational procedure.

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So, what are the main steps in this procedure so your molecular orbital your I will call this psi M o. So, your molecular orbital psi M o is written as a sum of c i phi i. This is a coordinate of the electron and I am restricting only to the spatial part. So, restrict only to the spatial part. So, the molecular orbital is a function of coordinates of one electron I will just call that coordinate r and that is written as a linear combination of various functions.

These are various function and so it is written as linear combination of various function. So, you can write this as c phi 1 of r plus c 2 phi 2 of r plus and so on. So, you are summing over r. So, this is the basic idea that you write a molecular orbital as a linear combination of various functions and these functions we choose as atomic orbital's. So, these functions are chosen as the atomic orbital's and typically when you have a bond then you choose them as the orbital's of the atoms corresponding to the produce the bonds.

So, if you have a bond between 2 hydrogen atoms you choose these to be atomic orbital's center on the 2 hydrogen atoms. So, for example, if you have H 2 so I can write this as the first atom I show as A second atom is B and if you have an the if you have an electron whose coordinate is r. Then the wave function of this electron in a it is in a molecular orbital and it is wave function is written as c 1. Now, corresponding to the atomic orbital's at A. So, the atomic orbital's these are all different atoms.

So, this is linear combination of atomic orbital's on different atoms. So, for a hydrogen molecule the lowest energy state will correspond to overlap between  $1s$  of A and  $1s$  of B so you write this as  $c_1 \psi_{1s}^A(r) + c_2 \psi_{1s}^B(r)$ . So, this is this basically corresponds to A  $1s$  orbital centered at A. So, it is a  $1s$  orbital assuming that the nucleus is at A. So, and this corresponds to A  $1s$  orbital assuming that the nucleus is at B. So, assuming that the nucleus is at B what does  $1s$  look like and what is the value of that at  $r$ .

So, this is how you write a molecular orbital wave function. So, you notice that these are this is a sum of atomic orbital's there is only coordinate  $r$  because this is a single electron wave function and so the coordinate of that electron appears. So, there is only one coordinate  $r$  that appears but these atomic orbital's are centered on different atoms. So,  $1s$  centered at A will depend on will be some constant. So, this will be some constant times  $e^{-Zr_A/a_0}$  I will say  $r_A$  divided by a naught a naught is a bore radius.

So,  $r_A$  is the distance of  $r$  from A. So, this is  $r_A$  and if this is  $r_B$  so the other similarly, this will be  $c_2 e^{-Zr_B/a_0}$ . So, they are different I mean they are since they are centered at different atoms their resulting function will be different. So, this will depend on this distance whereas, that will depend on the  $1s$  A will depend on this distance  $1s$  B will depend on this distance. So, this is the general linear combination of atomic orbital procedure.

Now, the question is how do you calculate your  $c_1$  how do you go about calculating you are your  $c_1$  and  $c_2$  what is the choice of  $c_1$  and  $c_2$  that you should take and the choice of  $c_1$  and  $c_2$  is given by something called a variational procedures. So, the variational Procedure will give you choice of  $c_1$  and  $c_2$ . So, the choice of  $c_1$  and  $c_2$  is given by a variational procedure.

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Choice of  $c_1$  and  $c_2$  given by variational procedure

$$\langle E \rangle = \frac{\int \psi_{MO}^*(\vec{r}) \hat{H} \psi_{MO}(\vec{r}) d\vec{r}}{\int \psi_{MO}^*(\vec{r}) \psi_{MO}(\vec{r}) d\vec{r}}$$

$$= \frac{\int (c_1^* 1s_A^*(\vec{r}) + c_2^* 1s_B^*(\vec{r})) \hat{H} (c_1 1s_A(\vec{r}) + c_2 1s_B(\vec{r})) d\vec{r}}{\int (c_1^* 1s_A(\vec{r}) + c_2^* 1s_B^*(\vec{r})) (c_1 1s_A(\vec{r}) + c_2 1s_B(\vec{r})) d\vec{r}}$$

$$\int 1s_A^*(\vec{r}) \hat{H} 1s_A(\vec{r}) d\vec{r} = H_{AA}$$

$$\int 1s_B^*(\vec{r}) \hat{H} 1s_B(\vec{r}) d\vec{r} = H_{BB} = H_{AA} = \int 1s_A^*(\vec{r}) \hat{H} 1s_B(\vec{r}) d\vec{r}$$

So, how does this work. So, this is based on something called a variational theorem that says that if you calculate the energy of any trial wave function then it is always greater than or equal to the true ground state wave function. So, then the best choice of  $c_1$  and  $c_2$  will be that choice of  $c_1$  and  $c_2$  that gives you the minimum energy. So, the choice of  $c_1$  and  $c_2$  that gives the lowest energy turns out to be best choice of  $c_1$  and  $c_2$ .

So, we calculate the energy of this of an electron on this molecular orbital and. In fact, you have to calculate the expectation value of energy. The expectation value of energy is given by  $\int \psi_{MO}^*(\vec{r}) \hat{H} \psi_{MO}(\vec{r}) d\vec{r}$  divided by  $\int \psi_{MO}^*(\vec{r}) \psi_{MO}(\vec{r}) d\vec{r}$ . So, you just this is the definition of the expectation value of energy and. So, you go about you go ahead and you calculate this now wherever I have  $\psi_{MO}$ .

I substitute this value and if I go ahead and do that then I will get here I have  $c_1 1s_A$  plus  $c_2 1s_B$ . So, I will have  $c_1^* 1s_A^*(\vec{r}) + c_2^* 1s_B^*(\vec{r})$ . So, that is the  $\psi_{MO}^*$  times Hamiltonian operated on  $c_1 1s_A$  or plus  $c_2 1s_B$  divided by the same thing as the numerator without this H. So, I will just write it as  $d\vec{r}$ . So, it is exactly the same as the numerator without this H. Now, we have 4 terms in the numerator and 4 terms in the denominator.

The numerator will consist of terms of the form if I exclude the constants it will contain terms like  $\int \psi_A^*(\vec{r}) \psi_A(\vec{r}) d\vec{r}$ . So, this term we call it as  $H_{AA}$  it is independent of  $r$  it is just some number we call this  $H_{AA}$ , similarly if you have  $\psi_A$  and  $\psi_B$  we will call it  $H_{AB}$  so if you had  $\psi_A^* \psi_B$  we will call it  $H_{BA}$   $\int \psi_A^*(\vec{r}) \psi_B(\vec{r}) d\vec{r}$ . This is  $H_{BA}$  and this is the same as  $H_{AB}$  which is  $\int \psi_B^*(\vec{r}) \psi_A(\vec{r}) d\vec{r}$ .

So, because your Hamiltonian is a hermitian operator it satisfies this property similarly, we can define  $H_{BB}$  also. So, then your expression for  $E$  at least the numerator part we can write in terms of  $H_{AA}$ ,  $H_{BB}$  and  $H_{AB}$  for the denominator we will use exactly as similar notation but if there is no  $H$  we will call it  $S_{AA}$ .

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$$\int \psi_A^*(\vec{r}) \psi_B(\vec{r}) d\vec{r} = S_{AB}$$

$$\int \psi_A^*(\vec{r}) \psi_A(\vec{r}) d\vec{r} = 1$$

$$\langle E \rangle = \frac{c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}}{c_1^2 + c_2^2 + 2c_1 c_2 S} = \frac{N}{D}$$

$$\frac{\partial \langle E \rangle}{\partial c_1} = 0 = \frac{D(2c_1 H_{AA} + 2c_2 H_{AB}) - N(2c_1 + 2c_2 S)}{D^2}$$

$$= \frac{2c_1 H_{AA} + 2c_2 H_{AB} - \langle E \rangle (2c_1 + 2c_2 S)}{D} = 0$$

So, if you had  $\int \psi_A^*(\vec{r}) \psi_A(\vec{r}) d\vec{r}$  if you had  $\psi_A$  and  $\psi_A$  that is  $S_{AA}$  which is just 1. So,  $r$  equal to 1 similarly, if you had  $\psi_B$  it will be 1. So, now you can write your expectation value of  $E$  as  $c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}$ . So, the first term will be  $c_1^2 H_{AA}$  the second term will be  $c_2^2 H_{BB}$  and you will have a term that  $2c_1 c_2 H_{AB}$ . So, you have  $c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}$  and if  $c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}$  is the same as  $c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1 c_2 H_{AB}$  so you can write it as  $2c_1 c_2 H_{AB}$ .

So, let us for simplicity I have assumed that  $c_1$  and  $c_2$  are both real. So, if  $c_1$  and  $c_2$  are real I can write it in this form divided by, now in the denominator, I will get  $c_1^2 + c_2^2 + 2c_1 c_2 S$ ,  $S_{AB}$  I am just denoting as  $S$ . So, the variational

theorem says that this energy should be minimum. So, you should choose your  $c_1$  and  $c_2$  such that this energy is minimum. So, in other words your  $\frac{d\langle E \rangle}{dc_1} = 0$ .

And if you calculate  $\frac{d\langle E \rangle}{dc_1}$ , so we will go ahead and do this, we will just call this some numerator divided by denominator we will call this denominator and this as numerator. So, you can use the usual rule for differentiation and you can write this as denominator into derivative with respect to  $c_1$  of this is  $2c_1 H_{AA}$  and you have  $c_1$  here also, you have plus  $2c_2 H_{AB}$  minus numerator into derivative of denominator in this case will just be  $2c_1$  plus  $2c_2 S$ .

Divided by denominator square and what I can do is I can take 1 of the square of the denominator up I will take. So, I will get  $2c_1 H_{AA}$  plus  $2c_2 H_{AB}$  and then I have a  $\frac{d\langle E \rangle}{dc_1}$  is nothing but this  $\langle E \rangle$ ,  $\langle E \rangle$  times I will have  $2c_1$  plus  $2c_2 S$  divided by denominator. And if this has to be equal to 0 then basically you will say that this numerator has to be equal to 0. So, this has to equal 0. So, if this has to equal 0 I can write this as  $c_1$  times  $H_{AA}$  minus  $\langle E \rangle$  plus  $c_2$  times  $H_{AB}$ .

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The image shows a green chalkboard with handwritten mathematical equations. The equations are as follows:

$$c_1(H_{AA} - \langle E \rangle) + c_2(H_{AB} - \langle E \rangle S) = 0$$

$$c_1(H_{AB} - \langle E \rangle S) + c_2(H_{BB} - \langle E \rangle) = 0$$

Condition for nontrivial soln is

Secular determinant =  $\begin{vmatrix} H_{AA} - \langle E \rangle & H_{AB} - \langle E \rangle S \\ H_{AB} - \langle E \rangle S & H_{BB} - \langle E \rangle \end{vmatrix} = 0$

$$(H_{AA} - \langle E \rangle)(H_{BB} - \langle E \rangle) - (H_{AB} - \langle E \rangle S)^2 = 0$$

$$\langle E \rangle^2(1 - S^2) + \langle E \rangle(-H_{BB} - H_{AA} + 2H_{AB}S) + H_{AA}H_{BB} - H_{AB}^2 = 0$$

Minus  $\langle E \rangle S$  equal to 0. So, I can write this in this form so I cancel the 2 I cancel the denominator. So, I have  $c_1$  times  $H_{AA}$  minus  $\langle E \rangle$  and I have  $c_2$  times  $H_{AB}$  minus  $\langle E \rangle$  times  $S$  and if you do the same for  $\frac{d\langle E \rangle}{dc_2}$  what you will get is the following you will get  $c_1$  times  $H_{AB}$  minus  $\langle E \rangle S$  plus  $c_2$  times  $H_{BB}$  minus  $\langle E \rangle$  equal to 0. So, if you do the same for  $\frac{d\langle E \rangle}{dc_2}$  you will get this equation below. Now, you have 2

equations and you have 2 unknowns of  $c_1$  and  $c_2$  but the right hand side of both the equations is 0.

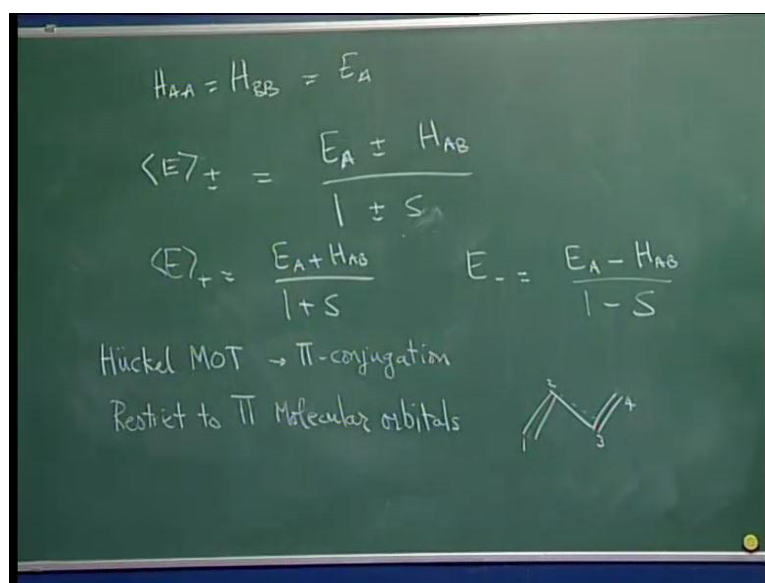
Now, these equations have a trivial solution  $c_1$  equal to  $c_2$  equal to 0. So, if I put  $c_1$  and  $c_2$  as both 0 then I satisfy this equation but that is not really a useful solution because  $c_1$  equal to  $c_2$  equal to 0 means your wave function is 0 and there are no electrons. So, non trivial solutions. So, the condition for non trivial solution is that this determinant the secular determinant equal to  $H_{BB} - E$  as to equal to 0. So, the condition for non trivial solution is that this determinant has to equal 0.

Now, this gives a simple so if you go ahead and multiply out this determinant what you will get it is a quadratic equation in  $E$ . So, you will get this into this minus this into this. So, minus  $H_{AB} S$  the whole thing square equal to 0. So, this is a quadratic equation in  $E$  in expectation value of  $E$  and if you solve this you will get the expression  $E$  is equal to you will 2 solutions. So, the 2 solutions are  $E$  plus and  $E$  minus and  $E$  plus and  $E$  minus are related by this way. So, this  $E = A \pm$ .

So, let us go work this out so if you take this you will get  $E^2$  and from here you have a  $E^2 - S^2$ . So,  $E^2$  into  $1 - S^2$  plus  $E$  and the terms containing  $E$  are given by. So, you have a minus  $H_{BB} - H_{AA}$  and you have. So, you have minus  $H_{BB} - H_{AA}$  minus now in this case will have plus twice  $H_{AB} S$ . So, these are the terms multiplying  $E$  and then the terms that do not have any  $E$  are given by, so plus  $H_{BB}$ .

So, you have one term  $H_{AA} - H_{BB}$  and then from here you will get  $H_{AB}^2$ . So, minus  $H_{AB}^2$  equal to 0. So, this is a quadratic in  $E$  and you can solve this to write the value of  $E$  now we would not do this in detail but you can solve this and you will get 2 values for  $E$  we will take this for the specific case when. In this case since both the atomic orbital's were one s orbital's. So,  $H_{AA} = H_{BB}$ .

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So, in the case  $H_{AA}$  equal to  $H_{BB}$  and we will just call this  $E_A$ . So, if  $H_{AA}$  equal to  $H_{BB}$  equal to  $E_A$  then you can write  $E$  there are 2 solutions plus and minus solutions. And this is given by  $E_A$  plus minus  $H_{AB}$  divided by  $1 \pm S$ . So, there are 2 solutions and the 2 solutions are related this way so in other words you can write  $E_{+}$  is  $E_A + H_{AB}$  divided by  $1 + S$  and  $E_{-}$  is  $E_A - H_{AB}$  divided by  $1 - S$ . Now, usually  $S$  depending on the sign of  $s$  one of these is lower and the other is higher.

And so depending on the sign of  $S$  and  $H_{AB}$  one of these is higher or lower. So, now what Huckle has done was to use this molecular orbital theory and in a very creative way to describe  $\pi$  conjugation in automatic systems. So, now we will see an application of this in what is called as Huckle molecular orbital theory. Molecular orbital theory and this is used to describe  $\pi$  conjugation so systems that have  $\pi$  conjugation.

So, this Huckle molecular orbital theory is used to describe these systems. So, in Huckle molecular orbital theory you restrict to  $\pi$  molecular orbital's. So, for example, if you have butadiene so you have a  $\pi$  conjugated system now Huckle molecular orbital theory gives a simple way to calculate the energies of the  $\pi$  molecular orbital's of the only the  $\pi$  molecular orbital's not the sigma orbital's. And these are actually simply related to the highest occupied molecular orbital's.

So, that is a reason why Huckle molecular orbital theory is so useful. So, in order to see how to do Huckle molecular orbital theory, there are just 2 ingredients that we need. First



is we need to write the secular determinant for a system so in Huckle molecular orbital theory. You write various atomic orbital's centered at each of the atoms. So, if you call it 1 2 3 4 atoms you have atomic orbital's centered at each of these atoms.

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$$0 = \begin{vmatrix} H_{11} - \langle E \rangle & H_{12} - \langle E \rangle S_{12} & H_{13} - \langle E \rangle S_{13} & H_{14} - \langle E \rangle S_{14} \\ H_{12} - \langle E \rangle S_{12} & H_{22} - \langle E \rangle & H_{23} - \langle E \rangle S_{23} & H_{24} - \langle E \rangle S_{24} \\ H_{13} - \langle E \rangle S_{13} & H_{23} - \langle E \rangle S_{23} & H_{33} - \langle E \rangle & H_{34} - \langle E \rangle S_{34} \\ H_{14} - \langle E \rangle S_{14} & H_{24} - \langle E \rangle S_{24} & H_{34} - \langle E \rangle S_{34} & H_{44} - \langle E \rangle \end{vmatrix}$$

And if you follow the molecular orbital prescription you can write a wave function and you can write the secular determinant. So, following the molecular orbital theory you write the secular determinant. So, for example, if you have butadiene one 3 butadiene you will write as H I will say 1 1 minus E H 1 2 minus E S 1 2 H 1 3 minus E S 1 3 H 1 4 minus E S 1 4 and these are S is a overlap of the phi atomic orbital's of 1 and 4.

So similarly, the second row will be H 2 1 which is same as H 1 2 minus E S 1 2 the second row second column will be H 2 2 minus E H 2 3 minus E S 2 3 H 2 4 minus E S 2 4. This is H 1 3 minus E S 1 3 H 2 3 minus E S 2 3 H 3 3 minus E H 3 4 E S 3 and this will be H 1 4 minus E S 1 4 H 2 4 minus E S 2 4 H 3 4 minus E S 3 4 and finally, H 4 4 minus E. So, notice that the 2 all off diagonal elements are identical in this picture and this has to be equal to 0.

So, you said this equal to 0 and you get some polynomial in E and you solve for the energy now in huckel molecular orbital theory. So, huckel approximations H 1 1 equal to H 2 2 equal to H 3 3 equal to H 4 4 equal to alpha and H i j equal to beta if i and j are bonded. So, 1 and 2 H 1 2 will be beta and equal to 0 otherwise but H 1 3 because 1 and 3 are not bonded will be 0 and then S i j equal to 0. So, S i j is always 0.

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

Calculate  $\langle E \rangle =$

- $\alpha + 1.62\beta$       Lowest Energy
- $\alpha + 0.62\beta$
- $\alpha - 0.62\beta$
- $\alpha - 1.62\beta$       Highest Energy

4e<sup>-</sup> Total Energy =  $2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$

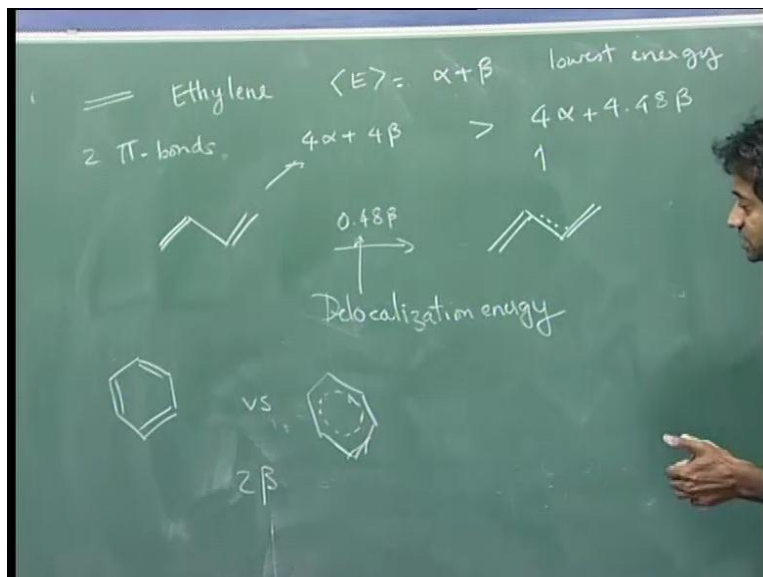
So, this was the simple basis of Hückel with this simple approximation this determinant simplifies to it can be written as alpha minus E beta 0 0 beta alpha minus E beta 0 0 beta alpha minus E beta 0 0 beta alpha minus E. And this will be equal to 0. So, notice that alpha minus E along the diagonals and beta is just next to the diagonals you have this beta. So, everywhere else you have 0. And this theory can be extended to much larger systems I just took 1 3, but diene, but you could extend it to benzene, you could extend it to other conjugated touelenes.

And this works and so what you can do is you can calculate E so if you said this E equal to 0 you will get a fourth order polynomial in E and you can easily calculate this and you can show that E is equal to alpha. So, it has 4 values, one value is alpha plus 1 point 6 2 beta the other is, alpha plus 0 point 6 2 beta, alpha minus 0 point 6 2 beta, alpha minus 1 point 6 2 beta so you get 4 values. Now, it turns out that beta is negative for this system. So, this is the lowest energy.

And this is a highest energy. Now, what is so interesting about these values is the following now butadiene has four electrons. So, 2 of them will have will be will be in the orbital corresponding to this and 2 of them will be in the orbital corresponding to this. So, the total energy is equal to twice alpha plus 1 point 6 2 beta plus twice alpha plus 0 point 6 2 beta this is equal to 4 alpha plus 4 point 4 8 beta. This will come out to this

value now, this 4 point 4 8 is actually quite interesting and the way to understand. Why this is. So, interesting is a following remember beta is negative.

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To see the significant of this 4 point 4 8 you ask yourself what will happen if you just had ethylene. And if you do the calculation for ethylene you will get the lowest energy is alpha plus beta this is lowest. So, you do the same calculation you will get you will have only this term. So, you can have alpha plus beta or alpha minus beta and the lower energy corresponds to alpha plus beta. So, if you had 2 phi bonds the energy if you had if you just had 2 phi bonds then the energy would have been 4 alpha plus 4 beta.

So, this energy is actually is greater than 4 alpha plus 4 point 4 eight beta so; that means, the energy of butadiene is lower than that of 2 separated phi bonds. So, if you had 2. Separated phi bonds the energy would have been 4 point 4 8 beta but this is lower than 2 separated phi bonds. So, it is not as though so this would have energy of 4 point 4 8 whereas, in this case because the electrons are delocalized there is some delocalization and that allows you to have an additional lower energy.

So, the difference in these 2 is 0 point 4 8 beta this is the called the delocalization energy. So, Huckel molecular orbital theory gives you a simple way to see this idea of delocalization and this delocalization energy or sometimes it is even called resonance energy, and you can take this one step further you can calculate all kinds of atoms for example, you can do for benzene this versus where the electrons are truly delocalized.

And in this case you will get a stabilization of  $2\beta$ . And so benzene has a very large delocalization energy. So, this is a simple application of the idea of determinant and linear algebra and we will this completes the linear algebra part of this course and starting from the next lecture we will start differential equations.