Chemistry Atomic Structure and Chemical Bonding
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Lecture – 39
Variational Method: Method of Lagrange Multipliers

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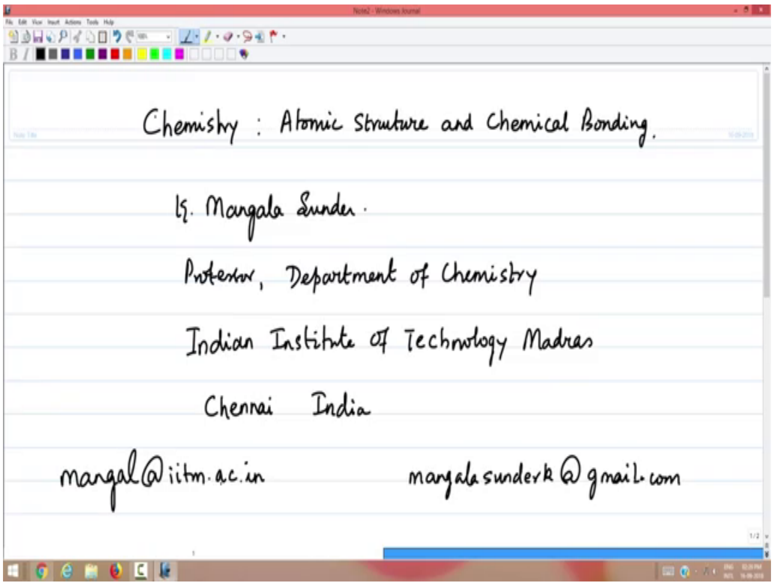

Chemistry : Atomic Structure and Chemical Bonding.

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Welcome back to the lectures in Chemistry and the Structure of Atomic and the topic of Atomic Structure and Chemical Bonding ok. My name is Mangala Sunder; and I am a in the department of Chemistry, Indian Institute of Technology, Madras. My email addresses are given here for reference, and for contact. The lecture, now we will continue from the last one on the variational method, but I shall discuss a little bit on the variational principle or variational minimization of the energy using the method of Lagrange a multipliers in between the lecture.

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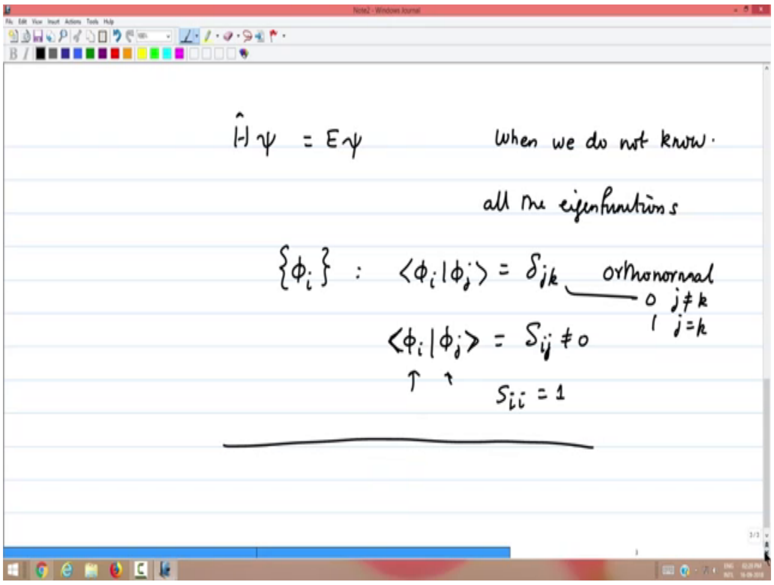

$\hat{H}\psi = E\psi$ When we do not know

all the eigenfunctions

$\{\phi_i\}$: $\langle\phi_i|\phi_j\rangle = \delta_{jk}$ orthonormal

$0 \quad j \neq k$

$1 \quad j = k$

$\langle\phi_i|\phi_j\rangle = S_{ij} \neq 0$

$S_{ii} = 1$

Now, recall that we were trying to solve the Schrodinger equation H psi is equal to E psi, when we do not know all the eigen functions even some. Therefore, we could use an arbitrary basis function set phi i such that the basis functions are preferably orthogonal, and this is an orthonormal set.

And if the basis functions are not orthogonal, then we use the overlap between them call it as S i j not equal to 0. This is delta j k means j equal to k, j not equal to k, this is 0 0 - j not equal to k; and 1- j equal to k right. If the functions are orthogonal, we can define an overlap matrix with normalization as a possibility, so that S i i they can always set into 1 by redefining the wave functions.

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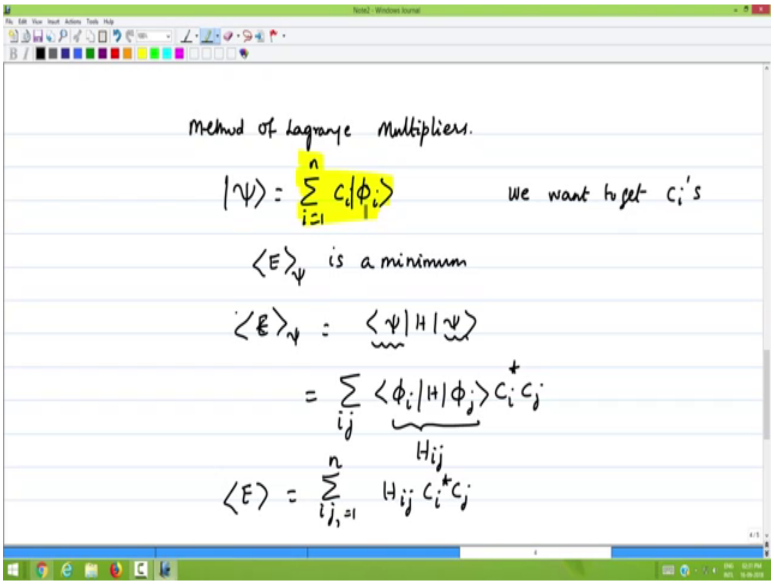

Method of Lagrange Multipliers.

$|\psi\rangle = \sum_{i=1}^{n} c_i|\phi_i\rangle$ we want to get c_i's

$\langle E\rangle_\psi$ is a minimum

$$\langle E\rangle_\psi = \langle \underset{\sim}{\psi}|H|\underset{\sim}{\psi}\rangle$$

$$= \sum_{ij} \underbrace{\langle\phi_i|H|\phi_j\rangle}_{H_{ij}} c_i^{*} c_j$$

$$\langle E\rangle = \sum_{ij=1}^{n} H_{ij}\, c_i^{*} c_j$$

So, this was mentioned in the last lecture, but let us see it in the from the variational theorem using what is known as the method of Lagrange multipliers Lagrange multipliers ok. Now, if we write the wave function in terms of linear coefficients C i phi i, we want to write this you can always write this as a kit. And we want to obtain the Ci’s such that get C i’s such that the energy is a minimum the average value for the energy.

The average value for the energy in the state is if you write the integral formula, it will be psi H psi. And using the expansion of the wave function in terms of all the basis sets i equal to 1 to n if you do that, you get the sum i j phi i H phi j, you get C i star and C j, because, this is of course, C i star phi i, this is C j phi j and Hamiltonians in is and which between the two. And you write to this usually as the Hamiltonian matrix element H i j. And therefore, this expression for the energy is expressed given as i j both giving going from 1 to n. You have H i j C i star C j ok.

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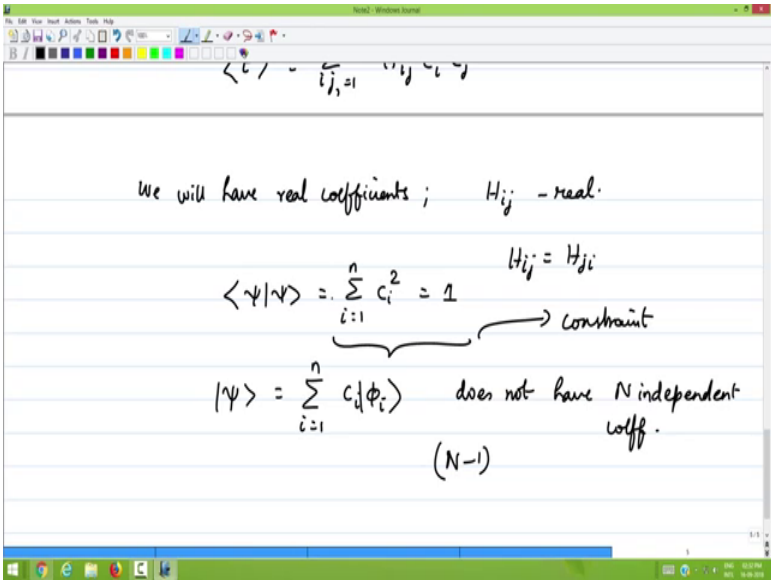

We will have real coefficients ; H_{ij} - real.

$H_{ij} = H_{ji}$

$$\underbrace{\langle\psi|\psi\rangle = \sum_{i=1}^{n} c_i^2 = 1} \xrightarrow{} \text{constraint}$$

$|\psi\rangle = \sum_{i=1}^{n} c_i|\phi_i\rangle$ does not have N independent coeff.

$(N-1)$

First let us make some simple assumptions, which are generally valid for the problems we deal with that we will have real coefficients. And we will also have H i j all elements of the Hamiltonian real ok. Therefore, H i j due to the Hermiticity property it will be H j i ok. And the condition for the wave function psi to be normalized is the sum over i with 1 to n. The absolute values of C i square of course, we are now using real values, therefore C i square is equal to 1 ok. This is the constraint in the choice of the C i's here.

Now, if you look at it carefully there are n coefficients, which are not determined, and which we want to know. Therefore, if you think that all the n coefficients are independent of each other, and we want to minimize the energy as a function of these n coefficients. We have to remember that all these coefficients are connected by this relation that the sum of squares of these coefficients is equal to 1. Therefore, the expansion psi is equal to i 1 to n C i phi i does not have n independent coefficients, but has only N minus 1 of them because of the constraint this is called the constraint that the sum of squares of the coefficient is equal to 1.

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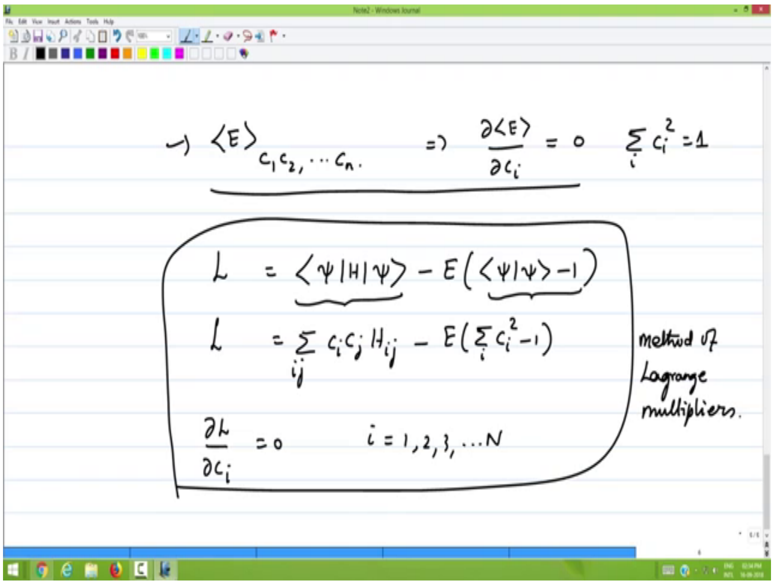

$$\rightarrow \underline{\langle E \rangle_{c_1 c_2, \cdots c_n.} \quad \Rightarrow \quad \frac{\partial \langle E \rangle}{\partial c_i} = 0} \qquad \sum_i c_i^2 = 1$$

$$\boxed{\begin{aligned} L &= \underbrace{\langle \psi | H | \psi \rangle} - E\big(\underbrace{\langle \psi | \psi \rangle} - 1\big) \\ L &= \sum_{ij} c_i c_j H_{ij} - E\Big(\sum_i c_i^2 - 1\Big) \\ \frac{\partial L}{\partial c_i} &= 0 \qquad i = 1, 2, 3, \ldots N \end{aligned}}$$

method of Lagrange multipliers.

For a minimization of such problems of the energy as a function of the C 1, C 2, the C n what you want to do is to write dou E dou C i is equal to 0. Therefore, to do this with the constraint that C i square is equal to 1. The method of Lagrange multiplier defines, what is known as and L function Lagrange function L, which is the energy itself psi H psi, but which includes the constraints namely that E times psi psi minus 1 ok.

Therefore, what you have is the matrix the Hamiltonian with the E multiplied by the constraint that psi psi is equal to 1, therefore technically this is 0. But, remember now if you write this in terms of coefficients, you will see that this is i j C i C j H i j minus E times sum over i C i square minus 1 this is called the L function. And the minimization for the energy is done by taking the dou L by dou C i to 0 for all C i i is equal to 1, 2, 3 up to n. This is called the method of Lagrange multipliers Lagrange multipliers.

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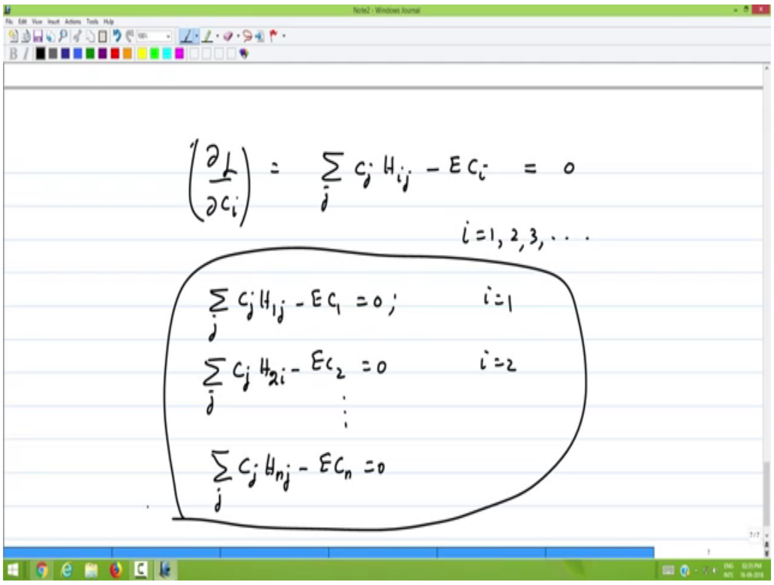

$$\left(\frac{\partial L}{\partial c_i}\right) = \sum_j c_j H_{ij} - E c_i = 0$$

$i = 1, 2, 3, \ldots$

$\sum_j c_j H_{1j} - E c_1 = 0;$ $\quad i = 1$

$\sum_j c_j H_{2i} - E c_2 = 0$ $\quad i = 2$

$\vdots$

$\sum_j c_j H_{nj} - E c_n = 0$

Therefore, let us do the following. If L is as we have, you can just go back to the previous page L is given by this. Therefore, if you take the derivative of L with respect to C i, you will see that there is a C j H i j, but it will be twice and this is 2 c i E. Therefore, what you would get is when you take the derivative of this expression, you will get this forms j C j H i j minus E c i that should be 0, this is dou L by dou C i ok.

And this is valid for i is equal to 1, 2, 3, 4. So, you have essentially the kind of expressions namely sum over j C j H 1 j minus E C 1 is equal to 0, this is for i equal to 1. And for i equal to 2, you have C j H 2 j minus E C 2 is equal to 0, and likewise you will have n equations namely j C j H n j minus E C n is equal to 0. Now, if you look at this equation carefully, see this is the same thing as the matrix eigenvalue equation we wrote down in the previous lecture on variational method, because what you have is essentially C 1 H 1 1 minus E plus C 2 H 1 2 plus C 3 H 1 3 plus C 4 H 1 4 and so on. This is 0 right.

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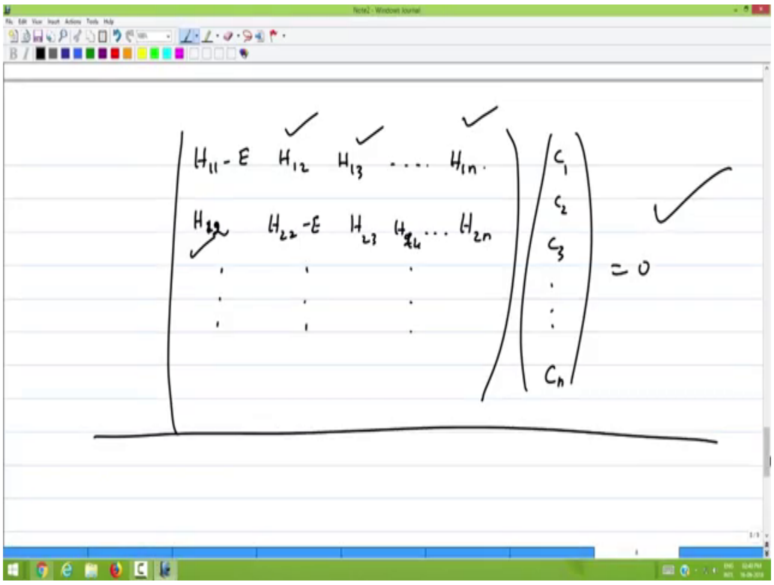

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots & H_{1n} \\ H_{12} & H_{22}-E & H_{23} & H_{24} \cdots & H_{2n} \\ \vdots & \vdots & & \vdots & \\ \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{pmatrix} = 0$$

And for it is easy to write this down as C 1, this one H 1 1 minus E H 1 2, H 1 3, H 1 n; H 2 1 or H 1 2 because they are both equal H 2 2 minus E H 2 3 H 2 4 all the way have to H 2 n. You can see that this multiplied by C 1, C 2, C 3 up to C n is equal to 0, you can write this down right all equations. This is exactly what we had earlier. Therefore, the method of Lagrange multipliers is give it I mean it gives you identical results in within this limitation of a real basis functions, and real coefficients, and the Hamiltonian matrix elements being real, but this can be extended to complex quantities, I do not think it is the problem the Hamiltonian is a Hermitian matrix.

You only have to make sure that you take the right derivatives, but what is important is that this has already been identified. And the method of the multipliers gives you the same namely the determinant of this should be 0. And therefore, you will have n eigenvalues and the lowest of the eigenvalues for various values of C there is what is called the variationally minimized energy. The only change is that if the basis functions are chosen, as you see here which was the basis functions are orthonormal (Refer Time: 11:31) where I have written that down, let me see where I have it ok.

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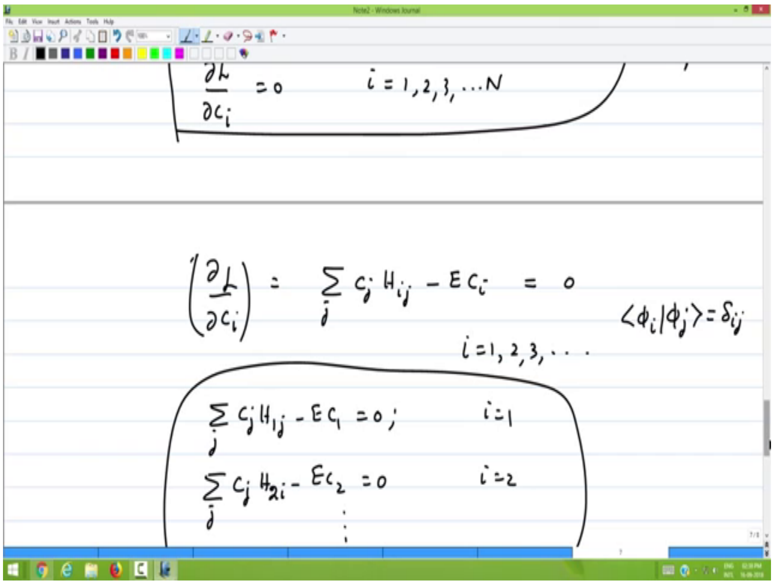

$$\frac{\partial L}{\partial c_i} = 0 \qquad i = 1,2,3,\ldots N$$

$$\left(\frac{\partial L}{\partial c_i}\right) = \sum_j c_j H_{ij} - E c_i = 0 \qquad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

$i = 1,2,3,\ldots$

$$\sum_j c_j H_{1j} - E c_1 = 0; \qquad i = 1$$

$$\sum_j c_j H_{2i} - E c_2 = 0 \qquad i = 2$$

$$\vdots$$

The basis functions phi i phi j where assumed to be delta i j and if you did not have that condition, then the energy expression that you have. The average value for the energy here, the average value for the energy will also contain an S i j sorry this is H i j. The eigenvalue expression E will contain here this one this will also contain an s i j because the coefficients and a corresponding C j. Therefore it will not be limited to one see's, but it will be there will be many. What is the form of that equation if the eigen function the basis functions are not orthogonal, but they have an overlap between them.

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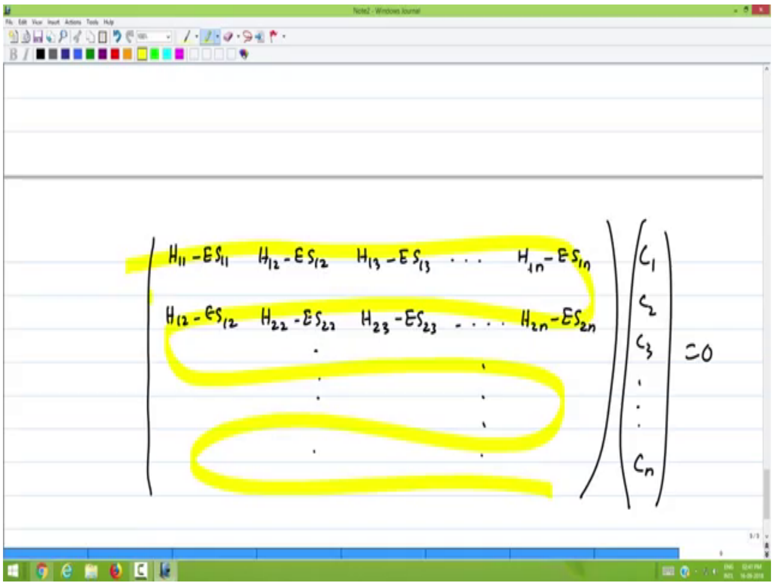

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & \cdots & H_{1n} - ES_{1n} \\ H_{12} - ES_{12} & H_{22} - ES_{22} & H_{23} - ES_{23} & \cdots & H_{2n} - ES_{2n} \\ & \vdots & & & \vdots \\ & \vdots & & & \vdots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Then the Hamiltonian that we have to write will be H 11 minus E S 1 1 would be 1, but then you will have H 1 2 minus E S 1 2, H 1 3 minus E S 1 3 all the way up to H 1 1 minus E S 1 n. And likewise, you will have H 1 2 minus E S 1 2, because the overlaps are also symmetric H 2 2 minus E S 2 2 H 2 3 minus E S 2 3 and so on, H 2 n minus E S 2 n, all of this multiplied by C 1, C 2, C 3, up to C n that would be 0 this goes all the way down to the nth element ok.

So, either we use this if we are able to choose the basis functions to be orthogonal, but if the basis functions are not orthogonal. And they have some numerical reasons for choosing them, that it is possible to calculate. All these quantities H 1 2, H 1 3 all these things much more efficiently using functions, which are not numerical numerically, which are not orthogonal right. If that is the case, then you have actually calculate the overlap integrals between the basis functions. And you ensure that the Hamiltonian that is diagonalized is this Hamiltonian what you see here is this Hamiltonian equation ok, (Refer Time: 14:17) the whole of it.

The choice of Gaussian functions in the numerical calculations of the entire quantum chemical, this I mean the quantum chemistry, the entire quantum chemistry; the use of Gaussian functions is precisely for this reason that they may not have a zero overlap that is they may not be orthogonal. It is possible to bring some orthogonal functions into them, but if they are not orthogonal, it is still possible for us to use them by ensuring that we calculate the overlaps appropriately, and then numerically diagonalize the whole process.

Now, for real problems the n has to be a finite number, because computers cannot take n to be infinite. Therefore, the choice of basis functions is very very carefully made, and the n which is the total number of basis functions that one has to choose is also control, so that you have numerical efficiency in using computer time in using the computer memory, and in getting the right result, which is close to what you think should be the experimental result, how closely you can align yourself with the experimental results. All these things are important factors, but the variational principle is fundamentally to all of that ok.

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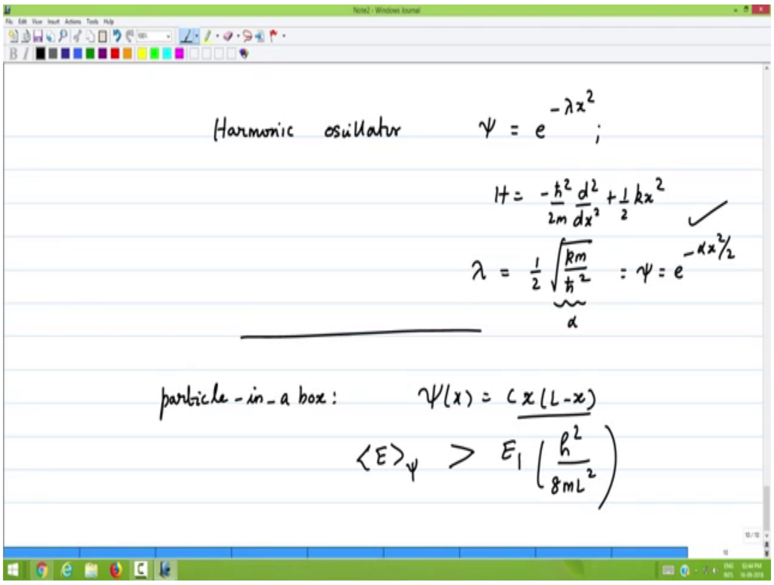

Harmonic osillatur $\psi = e^{-\lambda x^2}$;

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad ✓$$

$$\lambda = \frac{1}{2}\underbrace{\sqrt{\frac{km}{\hbar^2}}}_{\alpha} \; : \psi = e^{-\alpha x^2/2}$$

particle-in-a box: $\psi(x) = c\,\underline{x(L-x)}$

$$\langle E\rangle_\psi > E_1\left(\frac{h^2}{8mL^2}\right)$$

Now, just two simple examples of this process and one example is already something that you have done. The harmonic oscillator, example you have already done in the last class or the last lecture, please recall that we chose an arbitrary function for the wave function psi to be an exponential minus lambda x square. And we found out that for the Hamiltonian minus H bar square by 2 m d square by dx square plus half k x square. We found out that lambda turned out to be square root of 1 by 2 square root of k m by h bar square ok, and this 1 by 2, which is usually written as alpha. And therefore, you see psi is e to the minus alpha x square by 2. We have done this we have verified this for the variation method.

Today, we shall also look at this time, we shall also look at one more simple problem namely a particle in the box. If we have the wave function psi of x, which merely satisfies the boundary conditions that it is a constant times x times L minus x, so that the wave function is 0 at both the boundaries. But, otherwise it is an arbitrary wave function what will be the average value for the energy using this wave function, variational theorem tells you that this will be greater than or equal to E 1. But in this case of course, it is quite clear that this is not the eigen function, therefore we will see that this is actually greater than the E 1, which the exact solution for the particle in the box gives you as h square by 8 m L square that L is the box length. Let us see that very quickly.

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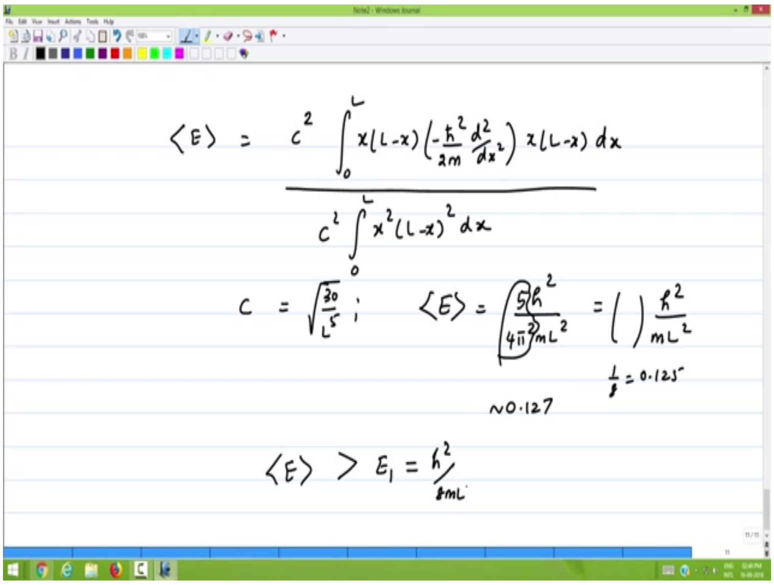

$$\langle E \rangle = \frac{c^2 \int_0^L x(L-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) x(L-x)\, dx}{c^2 \int_0^L x^2 (L-x)^2\, dx}$$

$$c = \sqrt{\frac{30}{L^5}}\ ; \quad \langle E \rangle = \frac{5\hbar^2}{4\pi^2 mL^2} = (\ )\frac{\hbar^2}{mL^2}$$

$$\frac{1}{8} = 0.125$$

$$\sim 0.127$$

$$\langle E \rangle > E_1 = \frac{h^2}{8mL}$$

The average value for E is to be obtained with C square the integral x into L minus x minus h bar square by 2 m d square by d x square times x into L minus x dx, but since the wave function is not normalized and these are the C square, we should have it as the integral C square times the integral x square into L minus x whole square. It is C square times the integral x square into L minus x square 0 to L dx ok.

Now, this is such an elementary calculation if you have done it several times, therefore let me write down the final answer for this the energy. The C is given as root 30 by L raise to 5, you have already calculated this in some of the examples. The E is calculated as 5 h square the average value 5 h square by 4 pi square m L square. So, if you have to write this as h square by m L square, whatever the number you get here should be greater than 1 by 8 1 by 8 is 0.125.

If you calculate this number 5 by 4 pi square, you get approximately 0.127. Therefore, you see that the average value E is greater than the exact eigenvalue E 1, which is h square by 8 m L square. So, this is a simple example of a variational method. When you have an arbitrary wave function, what you do is you calculate the energy; of course here we did not have any parameter.

Therefore, there was no requirement for the parameter to be minimized, whatever we got was essentially the average value as defined in quantum mechanics. So, it does not seem to be like anything to do variation what kind of variation we did or what we varied it does not seem to be coming out. But, in the case of harmonic oscillator, of course you saw that lambda itself was the parameter.

And therefore, we minimize to the energy calculation as a function the derivative of that energy with respect to lambda was said to 0. And then, we try to obtain the minimum and predict that that is the energy that we should get from variation theorem ok. There are quite a few examples, what I would do is in an assignment or in the in a handout. I should gives you a few more problems directly using the variational method, but let me give you one slightly more complicated example.

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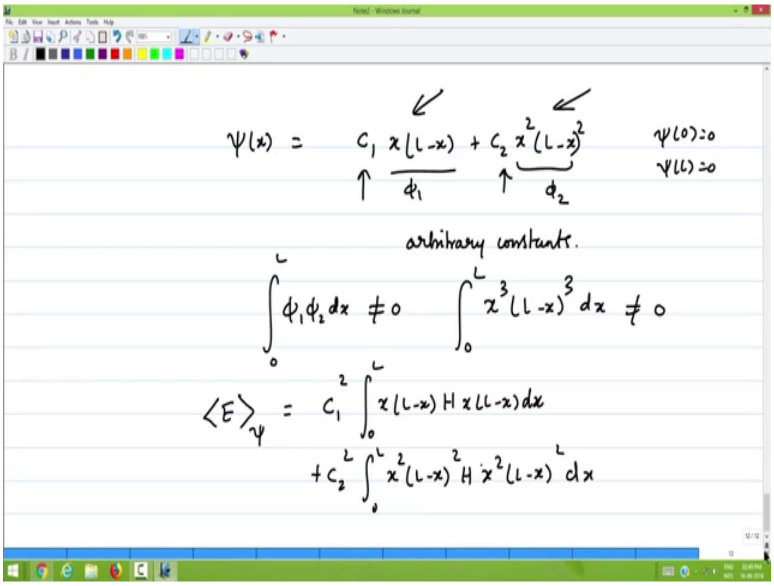

$$\psi(x) = \overset{\swarrow}{\underset{\uparrow}{C_1}}\ \underbrace{x(L-x)}_{\phi_1} + \overset{\swarrow}{\underset{\uparrow}{C_2}}\ \underbrace{x^2(L-x)^2}_{\phi_2}$$

$\psi(0)=0$
$\psi(L)=0$

arbitrary constants.

$$\int_0^L \phi_1\phi_2\,dx \neq 0 \qquad \int_0^L x^3(L-x)^3\,dx \neq 0$$

$$\langle E\rangle_\psi = C_1^2\int_0^L x(L-x)\,H\,x(L-x)\,dx$$
$$+\,C_2^2\int_0^L x^2(L-x)^2\,H\,x^2(L-x)^2\,dx$$

Suppose, the wave function for the particle in a one-dimensional box is given by two constants C 1 whose function is x into L minus x, and another one C 2 whose function is x square into L minus x square whole square; C 1 and C 2 or arbitrary constants. And the functions x into L minus x, and x square into L minus x whole square both satisfy the particle in the boundary particle in the box boundary condition namely psi of 0 is 0, psi of L is 0.

But, remember these two functions are not orthogonal to each other, because if you take the orthogonality property call this as phi 1, and you call this as phi 2. Phi 1 star phi 2 d tau dx 0 to L phi 1 phi 2 dx that is not 0 ok, it is 0 to L x cube into L minus x whole cube dx ok. Therefore, these wave functions are not orthogonal.

Now, if we calculate the energy of the particle in a box as a function of this psi you will get the following namely C 1 square the integral x into L minus x times the Hamiltonian operator times x into L minus x dx divided by we will we will do the division later sorry this integral minus x plus C 2 square this is 0 to L 0 to L x square into L minus x whole square H x square into L minus x whole square dx, this is the second term. This is C 2 square.

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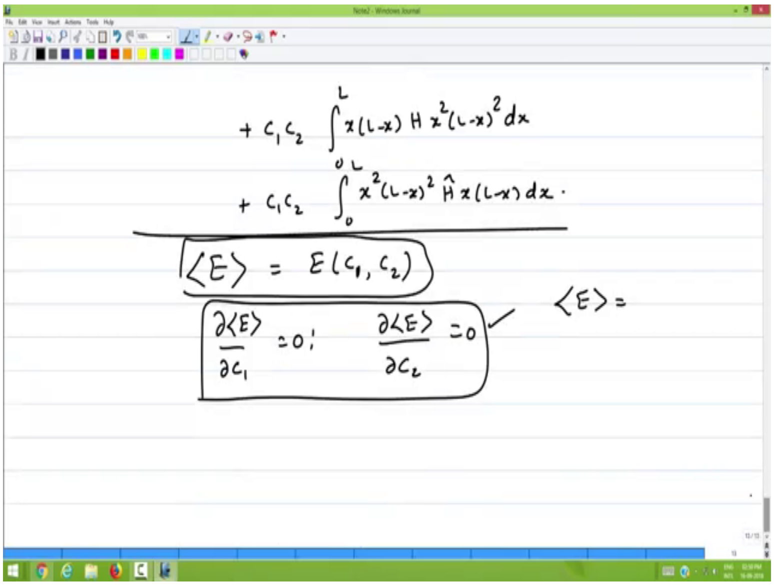

$$+ c_1 c_2 \int_0^L x(L-x)\, H\, x^2 (L-x)^2\, dx$$

$$+ c_1 c_2 \int_0^L x^2 (L-x)^2\, \hat{H}\, x(L-x)\, dx \,.$$

$$\boxed{\langle E \rangle = E(c_1, c_2)}$$

$$\boxed{\frac{\partial \langle E \rangle}{\partial c_1} = 0 ; \qquad \frac{\partial \langle E \rangle}{\partial c_2} = 0} \checkmark$$

$$\langle E \rangle =$$

And then, you have C 1 C 2 plus C 1 C 2 the integral 0 to L x into L minus x H acting on x square into L minus x whole square dx plus C 1 C 2 the integral 0 to L x square into L minus x whole square with the Hamiltonian acting on x into L minus x dx. Now, you see that the energy that you obtain is a function of the coefficients C 1 and C 2.

So, the variational principle here is that if you want this energy to be minimum, then we calculate dou E by dou C 1 to be 0 the cept is equal to 0. And find out the value by also having simultaneously the second equation dou E by dou C 2 is equal to 0, because the energy is a function of two parameters, and you have two conditions you will get a value for C 1 and C 2 by solving this equation. Dou C 1 and C 2 if you substitute in the expression for the energy above in all these four 1, 2, 3 and 4 terms, then you get what is called the variationally minimized energy.

This is a trivial example for which we already know the solutions exactly, but the point is the exercise of how you should do for functions. And for systems for which if you do not know the exact eigenvalue, the procedure is identical that is why, this matrix formulation was done a little earlier. When we do not know the correct eigen function, we only make a proportion. And we have a lot of coefficients, and we try to minimize these coefficients. Either the minimization or the matrix diagonalization, they both we will give you identical results from there we can get to the energy eigenvalue.

So, there are many other examples, and you will see more and more; when you move on to the next course, in quantum chemistry. And you want to compute numerically the properties and also start using numerical routines; you will see more of this. I have not given any mathematical concept here, but probably in the lecture nodes that I might come wide in this course, I will do a little bit of formal mathematical work.

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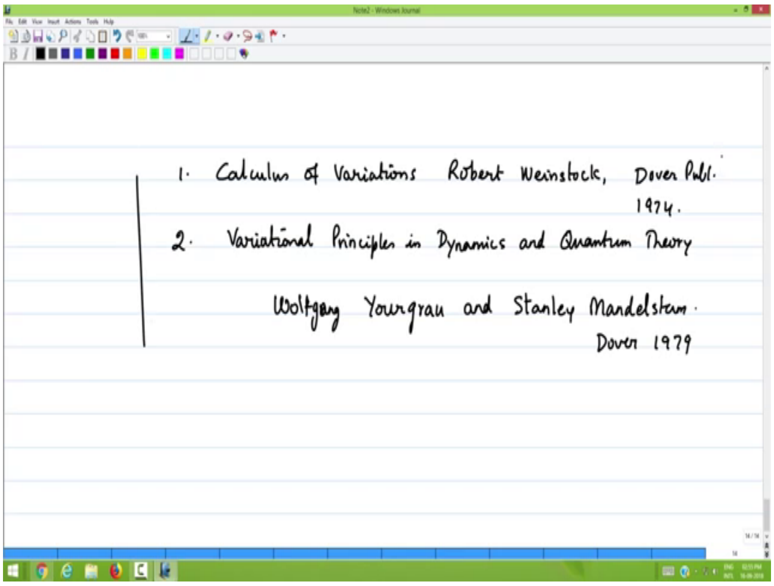

1. Calculus of Variations Robert Weinstock, Dover Publ. 1974.
2. Variational Principles in Dynamics and Quantum Theory
Wolfgang Yourgrau and Stanley Mandelstam.
Dover 1979

There are two beautiful books for those of you who are interested in looking at to the variational method in detail ok. Let me write down those books two books for you ok. The first one is Calculus of Variations and the author is Robert Weinstock, it is a Dover publications book, 1974. The second book is a little more into the mathematics of it, it is called Variational Principles in Dynamics and Quantum Theory, it is also an advanced book. And the author is Wolfgang Yourgrau g a r e u, and Stanley Mandelstom even known physicist, this is also a Dover book, 1979.

They are both quite advanced, but variational method is an extremely important method. I will say much more of this in an advanced course. But, in the introductory course, I think it is important to here to some elementary principles, but for those of you who want follow this in more detail; these two books will provide you some of the best state of the art variation methods used in quantum theory ok. We will continue this with to the first lecture in the next lecture on the chemical bonding, and there we will start with the hydrogen molecule ion as the first example.

Until then, thank you very much.