Chemistry Atomic Structure and Chemical Bonding
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 39
Introduction to Variational Principle in Quantum Chemistry

Welcome back to the lectures in Chemistry and the topic of Atomic Structure, and Chemical Bonding. My name is Mangala Sunder, and I am in the Department of Chemistry, Indian Institute of Technology Madras, in India. And my email addresses are given here for you to write to me on this or any other subject in related matter. This lecture will provide an elementary introduction to variational principle in quantum chemistry. And of course, I would try and make it as non-mathematical I wouldn't do any formal introduction to variational principle as a whole, but we will restrict to the most basic elements that we recognize in quantum chemistry.

A very good elementary account is given in 2 books that I have mentioned here, and both of which have influenced my own learning and applications of quantum mechanics to chemistry. One is the book by D A Mc Quarie, Quantum Chemistry and Fleur, I mentioned this earlier and the other is the book by Levine, I N Levine, also on quantum chemistry. They are both quite old, but they have very good learning materials.

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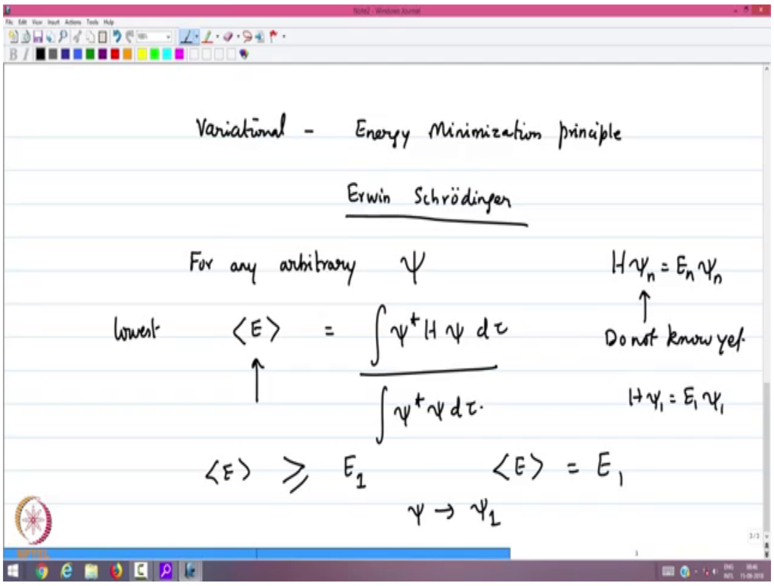

Variational - Energy Minimization principle

Erwin Schrödinger

For any arbitrary ψ

$H\psi_n = E_n\psi_n$

$\uparrow$

Don't know yet

lowest $\langle E \rangle = \dfrac{\int \psi^{+} H \psi \, d\tau}{\int \psi^{+} \psi \, d\tau}$

$\uparrow$

$H\psi_1 = E_1\psi_1$

$\langle E \rangle \geq E_1$

$\langle E \rangle = E_1$

$\psi \to \psi_1$

Now variational principle was introduced in quantum mechanics for energy, it is called the energy minimization principle. First my, because that have Erwin Schrodinger, whose equation we have been trying to understand for model systems. Namely, the time independent equation, it says they continue say that you have been working through this course hm.

This is one of the most significant contributions by professor Schrodinger himself on the energy minimization principle. In a nutshell, what it says is that for any arbitrary state psi of the system, that is may function psi, if he choose or if the system isn't in any arbitrary state psi, and it is not one of the Eigen states that we are trying to get by solving the equation H psi n is equal to E n psi n. We do not know this.

Yet for any arbitrary state psi be average value energy calculated the lowest or that state is psi star H psi d tau and the wave function is not normalized you also divided by psi star psi d tau. We average value calculated is always higher than the exact ground state, E is always higher than or greater than or equal to the exact ground state of the system, which we will denote by E 1.

As long as the wave function is arbitrary, and E will become exactly E 1, provided the wave function psi becomes the Eigenfunction psi 1, corresponding to the equation H psi 1 is equal to E 1 psi 1. That is no matter whatever you do, whatever approximation you provide, the average value for the energy through the calculation using the Hamiltonian, that you obtain will always be greater than the lowest exact Eigenvalue for that system.

And therefore, this lowest Eigenvalue or what is called the ground state Eigenvalue provides what is called the upper bound to all over calculations. We know that we are on the higher side of the error, not on the lower side of the error. This is a principal and I will immediately demonstrate this with a simple a statement of the Eigenfunctions and expressing wave function as a linear combination of Eigenfunction.

So, you will see that in the few minutes. This is an extremely important principle, because what it says is that if you want to get the exact ground state Eigenvalue, you have to search for the exact Eigenfunction the ground state Eigenfunction. Therefore, if you obtain or you provide Eigenfunction using some parameter and the energy is calculated as a function of that parameter, then you want to get the minimum for that energy. There is a mathematical method provided by the variational principle namely minimizing that energy as a function of the parameter. We will see these things in a right away.

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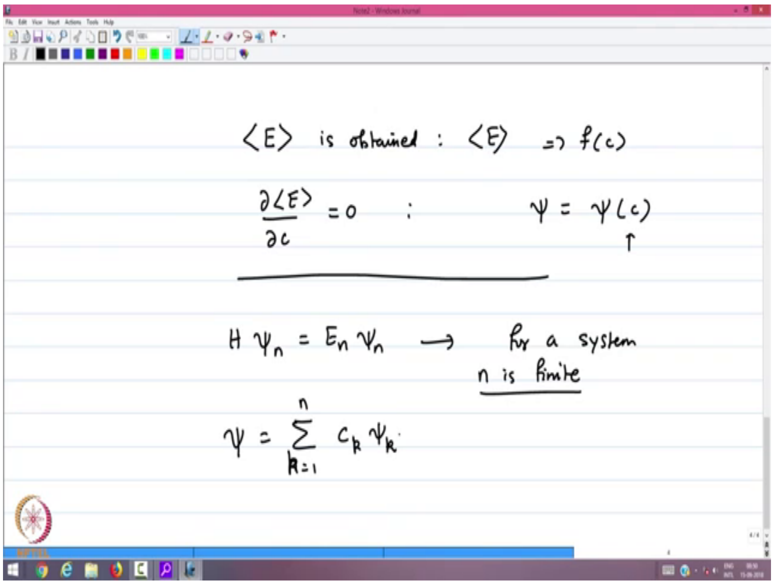

$\langle E\rangle$ is obtained : $\langle E\rangle \Rightarrow f(c)$

$$\frac{\partial\langle E\rangle}{\partial c} = 0 \quad : \quad \psi = \underset{\uparrow}{\psi(c)}$$

$$H\psi_n = E_n\psi_n \rightarrow$$ for a system $\underline{n \text{ is finite}}$

$$\psi = \sum_{k=1}^{n} c_k \psi_k$$

If the energy is obtained through a function, and the parameter C 1 parameter here, but it can be many this is the average value E. And therefore, the average value E is a function of the parameter c; then if you minimize the average value with respect to the parameter, and then calculate the average value.

You would see that that is the best you can get. And your idea of choosing the parameter is that the wave function that you choose, sorry, which is also a function of that parameter hm. The wave function that you choose should be chosen in such a way that it is closest to the possible exact Eigenfunction. I mean, depending on the system that you have with the system is close to harmonic oscillator. Types then you can use the linear combination of the Gaussian functions.

If the system is that of a columbic system like in the case of chemical in the case of molecules; obviously, columbic interactions are important not for the starting point could be something like the hydrogen atom wave functions for each and every electron, or it slightly better approximation and so on. But the point is no matter what you choose. The average value for the energy that you calculate is going to be higher than the exact ground state.

Let us look at this by a simple illustration ok. Let us assume that H of psi m is equal to E n of psi n or a system with some atoms and molecule whatever, it is ok? And let us assume that n is finite. It will never be, but and the state of the system let it be an arbitrary state, and in the same line as what we did in the last lecture. This will be k is equal to 1 to n some constants C k some k.

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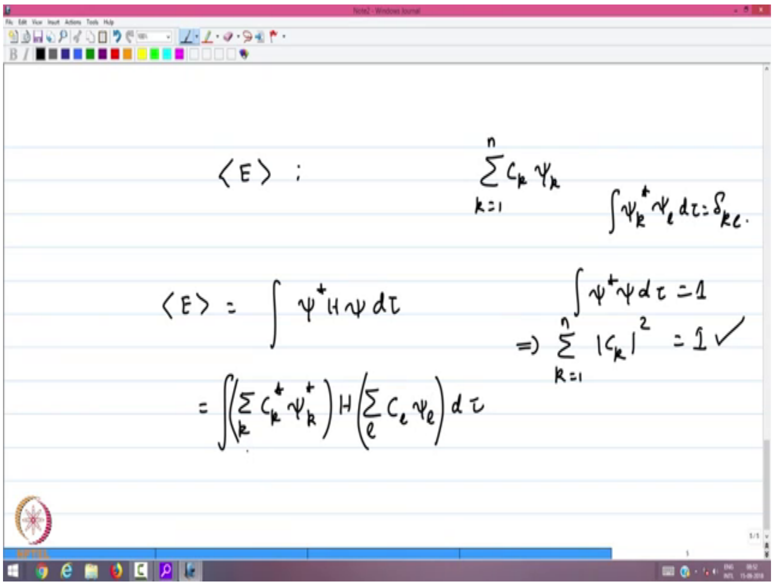

$\langle E \rangle$: $\sum_{k=1}^{n} C_k \psi_k$

$\int \psi_k^* \psi_l \, d\tau = \delta_{kl}$.

$$\langle E \rangle = \int \psi^* H \psi \, d\tau$$

$$= \int \left(\sum_k C_k^* \psi_k^* \right) H \left(\sum_l C_l \psi_l \right) d\tau$$

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

$\Rightarrow \sum_{k=1}^{n} |C_k|^2 = 1$ ✓

And let us calculate the average value for the energy using C k psi k wave functions. These are the Eigenfunctions one to n. And C is the linear combination coefficient, and remember that the psi k's are given by the, or they have this orthogonal orthogonality properties psi k star psi l d tau is delta kl; therefore, if you calculate the average value. This would be the integral psi star H psi d tau. And let us assume that the wave function itself is normalized, psi itself is normalized namely psi star psi d tau is one, which means that if we use the expansion of all the Eigenfunction.

This means that k is equal to 1 to n sum over C k square is one, let us keep this in mind. Therefore, the expectation value for the energy is given simply by this, and if you write this up explicitly, it is sum over k psi star is C k star psi star k. Sorry, H acting on sum l the same summation, but we will use a different index C l psi l d tau. This is psi, this is psi star.

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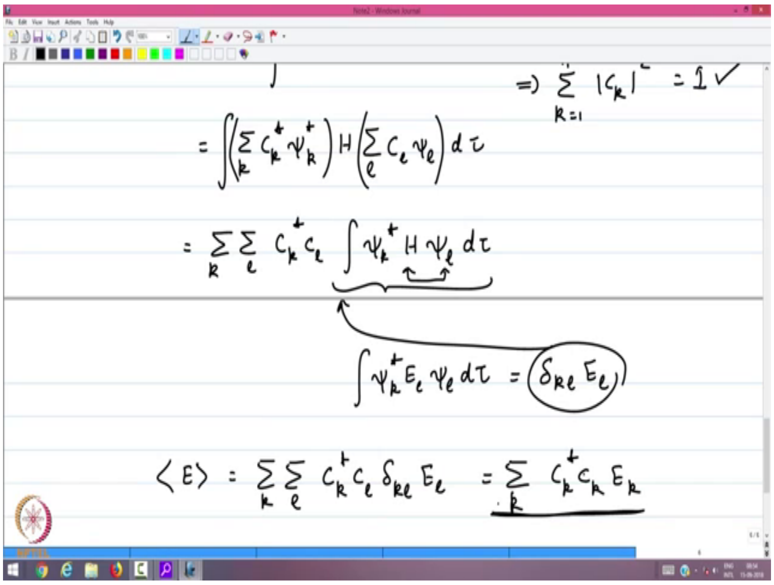

$$\Rightarrow \sum_{k=1} |C_k|^2 = 1 \checkmark$$

$$= \int \left(\sum_k C_k^* \psi_k^*\right) H \left(\sum_l C_l \psi_l\right) d\tau$$

$$= \sum_k \sum_l C_k^* C_l \underbrace{\int \psi_k^* H \psi_l \, d\tau}$$

$$\int \psi_k^* E_l \psi_l \, d\tau = \boxed{\delta_{kl} E_l}$$

$$\langle E \rangle = \sum_k \sum_l C_k^* C_l \delta_{kl} E_l = \underline{\sum_k C_k^* C_k E_k}$$

You expand this this is sum over k sum over l C k star C l integral psi k star H psi l d tau. And since the k psi k and psi l are all Eigenfunctions of the Hamiltonian, then this will give you E l psi l. Therefore, the integral is psi k star E l psi l d tau is this part alone. And that is equal to delta k l E l. So, if you substitute that here, then the average value for the energy is sum over k sum over l C k star C l delta k l E l. Because of the delta k l if you expand this sum k is equal to 1 to an l equal to 1 to n, k and l have to be the same.

Therefore, there' is only one sum which is sum over k or l whichever is the index you can choose, it is C k star C k E k because we have removed the sum over l with this orthogonality. You know, this is the average value for the energy,.

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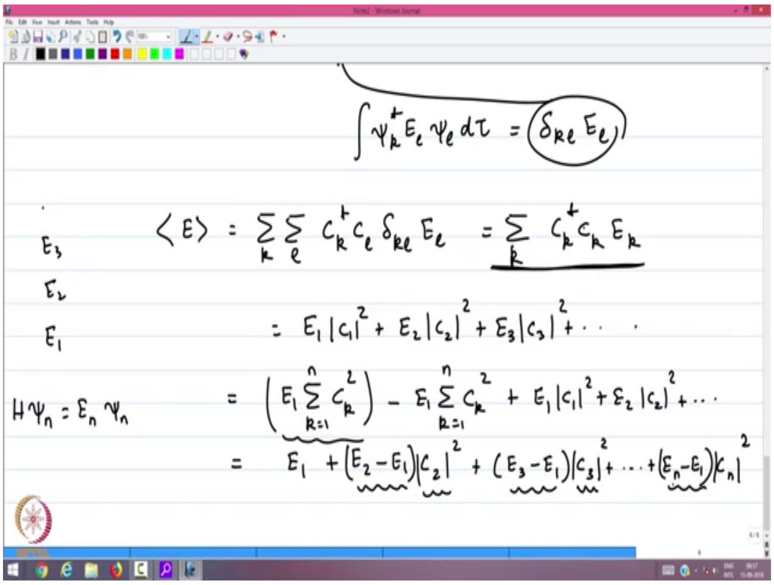

$$\int \psi_k^{+} E_l \psi_l \, d\tau = \boxed{\delta_{kl} E_l}$$

E_3

E_2

E_1

$H\psi_n = E_n \psi_n$

$$\langle E \rangle = \sum_k \sum_l c_k^{+} c_l \delta_{kl} E_l = \underline{\sum_k c_k^{+} c_k E_k}$$

$$= E_1 |c_1|^2 + E_2 |c_2|^2 + E_3 |c_3|^2 + \cdots$$

$$= \left(\underbrace{E_1 \sum_{k=1}^{n} c_k^2}\right) - E_1 \sum_{k=1}^{n} c_k^2 + E_1 |c_1|^2 + E_2 |c_2|^2 + \cdots$$

$$= E_1 + \underbrace{(E_2 - E_1)}\underbrace{|c_2|^2} + (\underbrace{E_3 - E_1})\underbrace{|c_3|^2} + \cdots + (\underbrace{E_n - E_1})|c_n|^2$$

So, let us write this, expand this, it is E 1 times C 1 square plus E 2 times C 2 square plus E 3 times C 3 square plus and so on. Let me introduce to this sum add and subtract that we add and subtract E 1 times the sum over k equal to 1 to n C k square. We are adding that and therefore, we also have to subtract the same thing E 1 sum over k is equal to 1 to n C k square plus all of those E 1 times C 1 square plus a 2 and C 2 square plus so on. Now you can rewrite this whole summation as follows, right.

This term is going to give you this is a particular term. This is going to give you E 1. Because the sum over k square is one, but now let us take this into this form. Therefore, this is E 1 C 1 square that is also an E 1 C 1 square, it gets cancelled out, but then the rest of it will be E 2 minus E 1 times C 2 square, plus E 3 minus E 1 C 3 square plus etcetera plus E n minus E 1 C n square.

The Eigenvalues are chosen in the order that E 1 is the lowest energy, E 2 is the next higher energy E 3 is the next higher and so on. Therefore, the energies H psi n the energies given by this equation x psi n is equal to E n psi n. Let us assume that the increasing order of energy is E 1, E 2, E 3 etcetera. Then you can see that all these coefficients are positive, all are positive. And this is definitely positive because of a choice of the E 1 and you can see that the average value for E is greater than E 1, because it has the additional terms.

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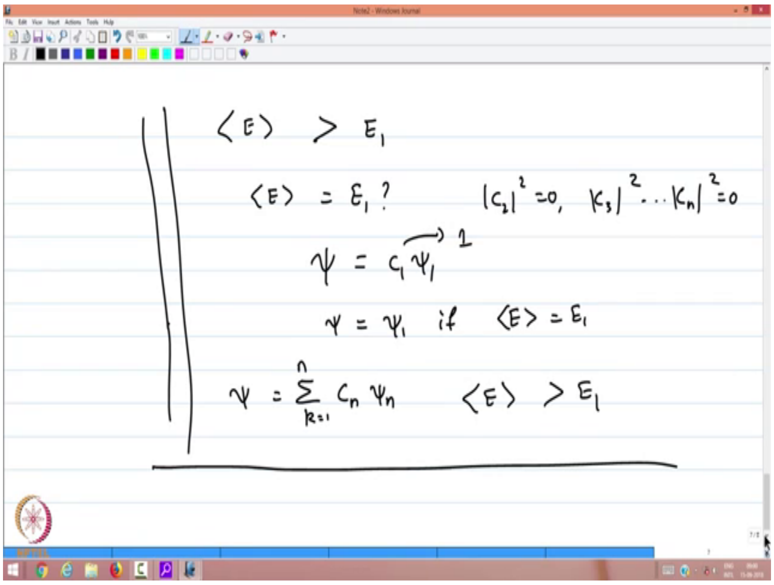

$$\langle E \rangle > E_1$$

$$\langle E \rangle = E_1 \,? \qquad |c_2|^2 = 0, \; |c_3|^2 \ldots |c_n|^2 = 0$$

$$\psi = \overset{\rightarrow 1}{c_1} \psi_1$$

$$\psi = \psi_1 \quad \text{if} \quad \langle E \rangle = E_1$$

$$\psi = \sum_{k=1}^{n} c_n \psi_n \qquad \langle E \rangle > E_1$$

When will be average value E become equal to E 1 ? Obviously, not when E 2 is equal to E 1 because these are different Eigenvalues; there never going to be equal. What is important is this will be this energy average value will be equal to E 1 if C 2 square is 0, C 3 square is 0, C n square is 0. Which means the psi that you have is now simply C 1 psi 1, and since psi is normalized C 1 is (Refer Time: 15:06), a phase factor is one we can remove that then organization coefficient.

Therefore, psi has to be psi 1 if the average value E is equal to E 1. For all other choices of psi ok, and for all others no matter what coefficients you choose psi n, the average value we will be greater than E 1.

So, this is a very simple illustration, but unless you happen to choose the trial wave function psi, which you think what represents the state of the system, and you want to find out all the coefficient C 1 C 2 C n etcetera by solving the equation right. Unless you choose the trial function by coincidence to the exactly the same as the ground state Eigenfunction, the energy Eigenvalue that you calculate will always be greater than the lowest exact Eigenvalue system, that is what this is this proof is about.

So, it is a very simple way of understanding that, that is our scale that is the bottom that we want to calculate, and very often in quantum chemistry, the calculation of the lowest or the ground state Eigenvalue of a stable system is called the search for the you know is a wholly grail. This is fundamentally important for all quantum chemist that, they should try and get the exact lowest eigenstate possible, and that will give you; obviously, the molecular geometry, and all the equilibrium properties can be calculated using the lowest Eigenvalue and the lowest Eigenfunction.

Therefore it is very important that variation theorem tells you, you can never do it unless you happen to accidentally get you are Eigenfunction to be the same as the lowest Eigenfunction. But variation theorem tells you, you do not have to worry no matter what you calculate all the calculations that you have done or greater than the lowest therefore, it is the upper bound.

That it is avoiding and we have to find fine tune our wave function parameterize our wave functions in such a way, that we minimize whatever energy that we get as a function of the parameter and try to get the best possible wave function that is closest to the Eigenfunction of the system. This is what the variation principle is. We will see some examples and therefore, it might be easier after seeing the examples to go back and the look at to the theorem again.

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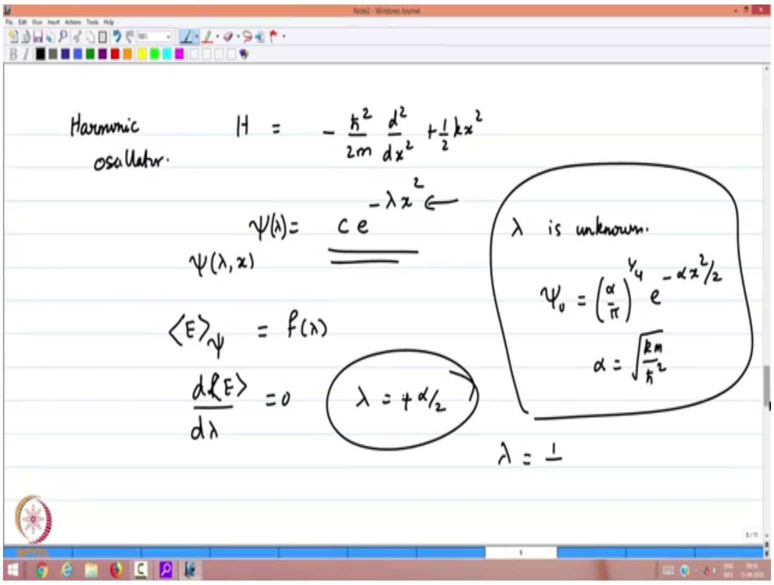

Harmonic osciallatr.

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

$$\psi(\lambda) = \underline{\underline{c\,e^{-\lambda x^2}}} \leftarrow$$

$$\psi(\lambda, x)$$

$$\langle E \rangle_\psi = f(\lambda)$$

$$\frac{d\langle E \rangle}{d\lambda} = 0$$

$$\lambda = +\alpha/2$$

λ is unknown.

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\alpha = \sqrt{\frac{km}{\hbar^2}}$$

$$\lambda = \frac{1}{}$$

Let us take a simple example H is a harmonic oscillator. It is a minus H bar square by 2 m d square by dx square plus half k x square. Now we will tweak this example, we know the exact solution for the harmonic oscillator. Therefore, how do we understand the variational principle? Let us choose an arbitrary wave function and calculate the energy, and minimize the energy as a function of the parameter of the arbitrary wave function.

What is meant by the parameter? Here psi is equal to let us assume that it is C e to the minus lambda k lambda x square lambda is unknown. And we want to find out wave function psi as a function of lambda as well as the x of course, lambda x. X is the coordinate for the whole wave function, but lambda is the parameter that which we evaluate different wave functions with different values of lambda to see what is the best value of lambda that would give you the exact Eigenvalue or will give you closest to the exact Eigenvalue.

But you know, that we have already guessed the wave function very close to that of the harmonic oscillator wave function. You know that the ground state wave function of the harmonic oscillator is alpha by pi 1 by 4 e to the minus alpha x square by 2.

Where alpha is obviously k m by H bar square root. You know that already, this is the exact solution we know. Therefore, if you do this average energy calculation using the psi, and if you get the average energy as a function of lambda, and if you minimize the average energy as a function of lambda is equal to 0, you will get; obviously, lambda is equal to minus alpha by 2, sorry plus alpha by 2 lambda there is already a minus psi here you will get that as the answer. But the illustration is to tell you the process by which variational principle is used in quantum mechanics right. Let us do that psi fx is equal to C e to the minus lambda x square

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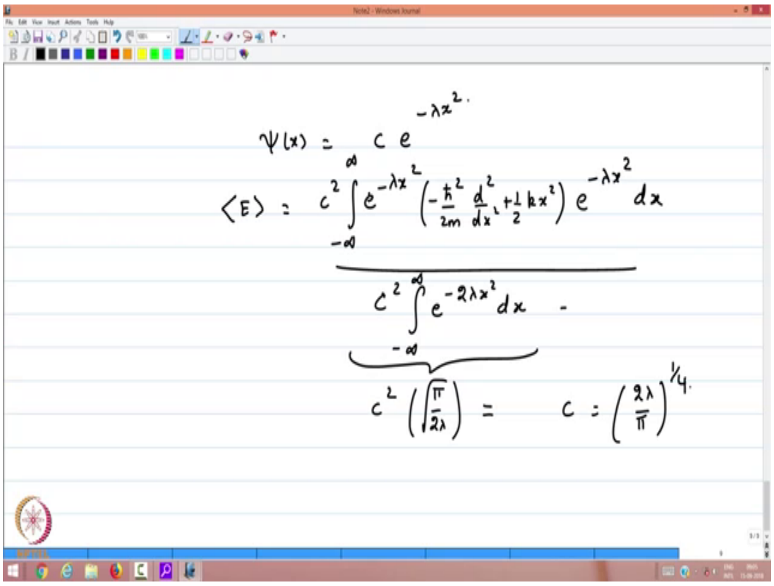

$$\psi(x) = c\, e^{-\lambda x^2}.$$

$$\langle E \rangle = \frac{c^2 \int_{-\infty}^{\infty} e^{-\lambda x^2} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 \right) e^{-\lambda x^2} dx}{\underbrace{c^2 \int_{-\infty}^{\infty} e^{-2\lambda x^2} dx}_{c^2 \left(\sqrt{\frac{\pi}{2\lambda}} \right) =}}$$

$$c = \left(\frac{2\lambda}{\pi} \right)^{1/4}.$$

C . The average value E is going to give you, the C star C square e to the minus lambda x square between minus infinity to plus infinity that is a harmonic oscillator coordinate, and then you have a minus H bar square by 2 m d square by dx square plus half k x square, e to the minus lambda x square dx divided by C square e to the minus 2 lambda x square d x from minus infinity to plus infinity.

This is let us first do this, because this normalization integral. You know the this has to be equal to 1. So, if you want to do that there will give you the value for c. This is C square times C to the minus 2 number 2 pi over a. So, it is root pi over 2 lambda. And that would be; that means, C is 2 lambda over pi 1 by 4, all right. This is the normalization constant.

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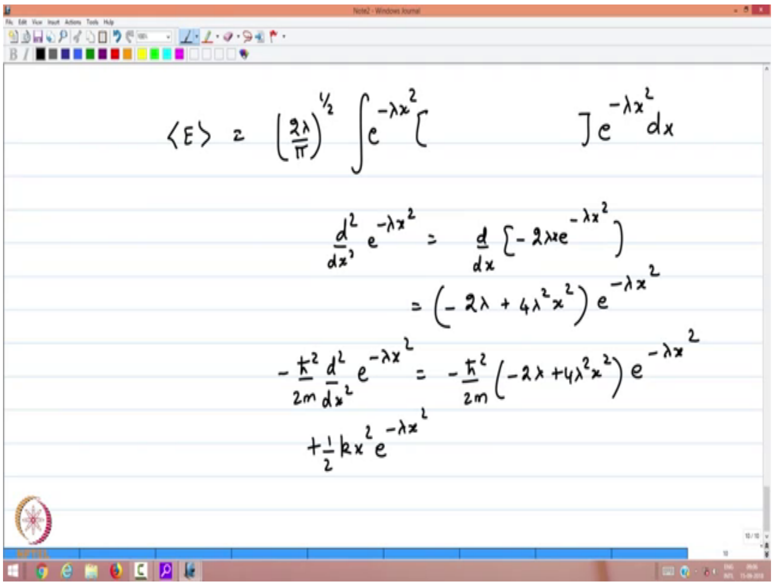

$$\langle E \rangle = \left(\frac{2\lambda}{\pi}\right)^{1/2} \int e^{-\lambda x^2} \Big[\qquad \Big] e^{-\lambda x^2} dx$$

$$\frac{d^2}{dx^2} e^{-\lambda x^2} = \frac{d}{dx} \left\{ -2\lambda x e^{-\lambda x^2} \right)$$

$$= \left(-2\lambda + 4\lambda^2 x^2 \right) e^{-\lambda x^2}$$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} e^{-\lambda x^2} = -\frac{\hbar^2}{2m} \left(-2\lambda + 4\lambda^2 x^2 \right) e^{-\lambda x^2}$$

$$+\frac{1}{2} k x^2 e^{-\lambda x^2}$$

Therefore, the average value e is 2 lambda by pi 2 1 by 2 which is E square, and then you have the integral e to the minus lambda x square, times the derivative acting on E 2 the minus lambda x square d x. Now you can do this d square by d x square on E 2 the minus lambda x square will be d by dx on minus 2 lambda e to the minus lambda x square lambda x e to the minus lambda where and that gives you minus 2 lambda plus 4 lambda square x square e to the minus lambda x square.

So, that is the derivative when you have if you multiply this by d minus H bar square by 2 m d square by dx square, on the same you get minus H bar square by 2 m minus 2 lambda plus 4 lambda square x square, times e to the minus lambda. Then you have a half kx square one to the minus lambda x square, ok.

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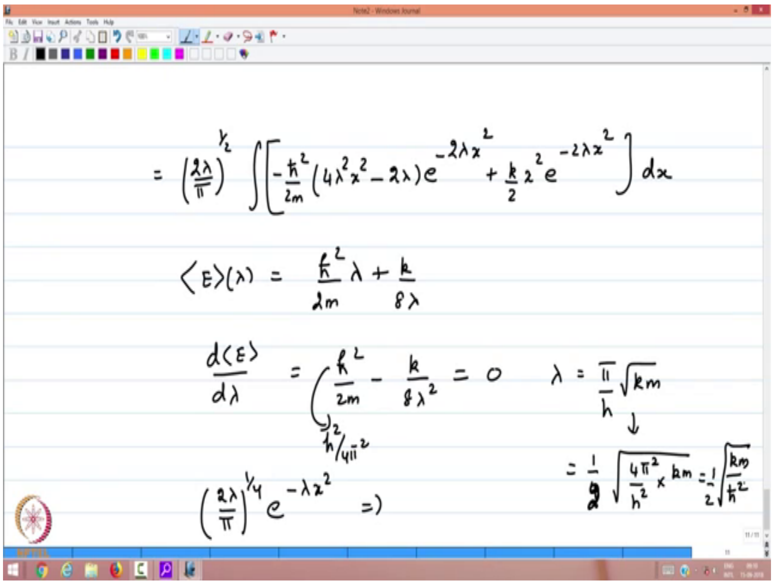

$$= \left(\frac{2\lambda}{\pi}\right)^{1/2} \int \left[-\frac{\hbar^2}{2m}(4\lambda^2 x^2 - 2\lambda) e^{-2\lambda x^2} + \frac{k}{2} x^2 e^{-2\lambda x^2} \right] dx$$

$$\langle E \rangle(\lambda) = \frac{\hbar^2}{2m}\lambda + \frac{k}{8\lambda}$$

$$\frac{d\langle E \rangle}{d\lambda} = \frac{\hbar^2}{2m} - \frac{k}{8\lambda^2} = 0 \qquad \lambda = \frac{\pi}{h}\sqrt{km}$$

$$\hbar^2 / 4\pi^2$$

$$\downarrow$$

$$= \frac{1}{2}\sqrt{\frac{4\pi^2}{h^2} \times km} = \frac{1}{2}\sqrt{\frac{km}{\hbar^2}}$$

$$\left(\frac{2\lambda}{\pi}\right)^{1/4} e^{-\lambda x^2} \Rightarrow$$

So, the integral that you have to now solve is 2 lambda by I 2 1 by 2 minus H bar square by 2 m, 4 lambda square x square minus 2 lambda times e to the minus lambda x square plus k by 2 x square e to the minus 2 lambda by x square. All of this differentiated.

The answer will turn out to be H bar square by 2 m times lambda plus k by 8 lambda ok. See the average value E as a function of lambda. Therefore, if you take the derivative of this with respect to lambda, you get H bar square by 2 m, minus k by 8 lambda square. And you minimize this by taking this to be 0, it gives you lambda is equal to pi by H is a root km. H bar square is H square by 4 pi 2.

So, use that if lambda is given by this therefore, the wave function is e to the minus lambda x square with the normalization constant 2 lambda by pi, 2 1 by 4. You can immediately see that this is 1 by 4 square root of 1 by 2, sorry, 1 by 2 square root 4 pi square, 4 pi square by H square into k m. And that is nothing but 1 by 2 square root km by H bar square. Km by H bar square is alpha. Therefore, you can see that lambda is equal to 1 by 2 alpha lambda is equal to 1 by 2 alpha.

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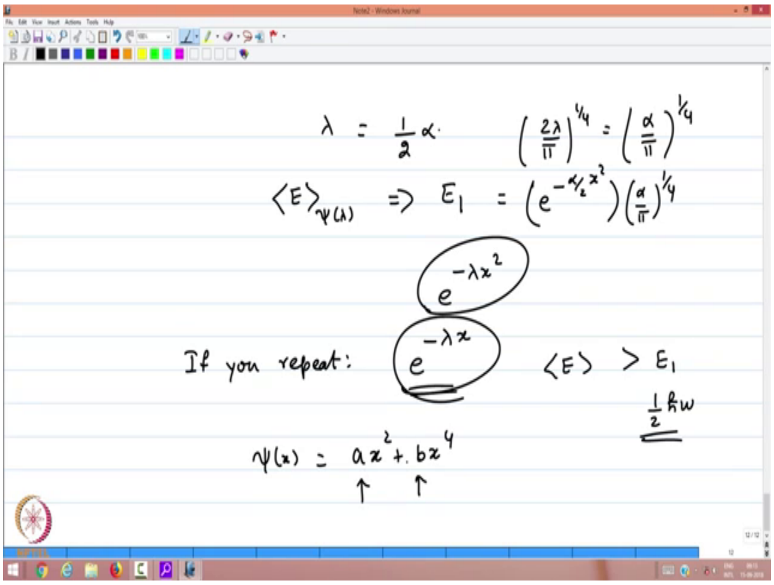

$$\lambda = \frac{1}{2}\alpha \qquad \left(\frac{2\lambda}{\pi}\right)^{1/4} = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\langle E\rangle_{\psi(\lambda)} \Rightarrow E_1 = \left(e^{-\alpha/2\, x^2}\right)\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$e^{-\lambda x^2}$$

If you repeat: $e^{-\lambda x}$ $\quad \langle E\rangle > E_1$

$$\frac{1}{2}\hbar\omega$$

$$\psi(x) = a x^2 + b x^4$$

$$\uparrow \qquad \uparrow$$

And 2 lambda by pi 2 1 by 4; obviously, becomes alpha by pi 1 by 4. Therefore, the exact wave function E psi lambda or the average value E to become E 1 is e to the minus alpha by 2 x square times the normalization constant alpha pi 1 by 4. How do you know that this is the exact value? You use this value of lambda in the expression for the energy.

The expression for the energy is H bar square by 2 m times lambda plus k by 8 lambda. You just showed that lambda is equal to pi by H k into square root km.

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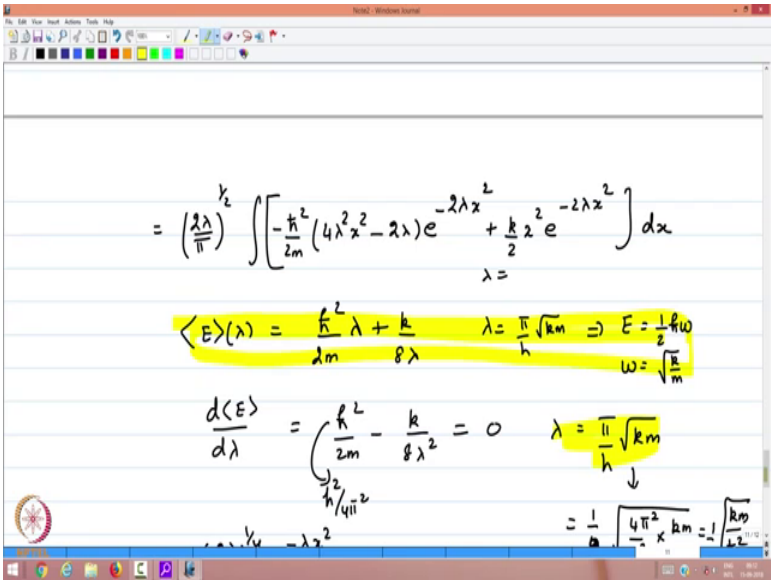

$$= \left(\frac{2\lambda}{\pi}\right)^{1/2}\int\left[-\frac{\hbar^2}{2m}\left(4\lambda^2x^2 - 2\lambda\right)e^{-2\lambda x^2} + \frac{k}{2}x^2 e^{-2\lambda x^2}\right]dx$$

$$\lambda =$$

$$\langle E\rangle(\lambda) = \frac{\hbar^2}{2m}\lambda + \frac{k}{8\lambda} \qquad \lambda = \frac{\pi}{h}\sqrt{km} \Rightarrow E = \frac{1}{2}\hbar\omega$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$\frac{d\langle E\rangle}{d\lambda} = \frac{\hbar^2}{2m} - \frac{k}{8\lambda^2} = 0 \qquad \lambda = \frac{\pi}{h}\sqrt{km}$$

$$\hbar^2/4\pi^2$$

Lambda is equal to pi by H into square root km ok. You can show that this gives you immediately the energy E is equal to half H bar omega, where omega is square root of k m, you can verify that. I mean with me therefore, you see that the energy Eigenvalue that you get when you minimize the energy as a function of lambda gives you the energy E is equal to half H bar omega, and gives you the parametric value lambda is equal to pi by H square root of km. And therefore, it recovers that the energy minimization as a function of this gives you the exact Eigenfunction and the exact Eigenvalue. That is because you started with your function which looks very close to the exact Eigenvalue, namely e to the minus lambda x square.

If you repeat this exercise without knowing that this is slightly to be the sort of Eigenfunction, but if you repeat this exercise with e to the minus lambda x; which is a problem that I will discuss in the video tutorial, you will get a different value for E and that will be greater than the E 1 in this case which is half H bar omega that we will be greater than this. Therefore, you see if you choose a different function, if you choose for example, psi of x is equal to a x square plus b x raise to 4, and now psi of x is expressed in terms of 2 variables a 2 constants a and b.

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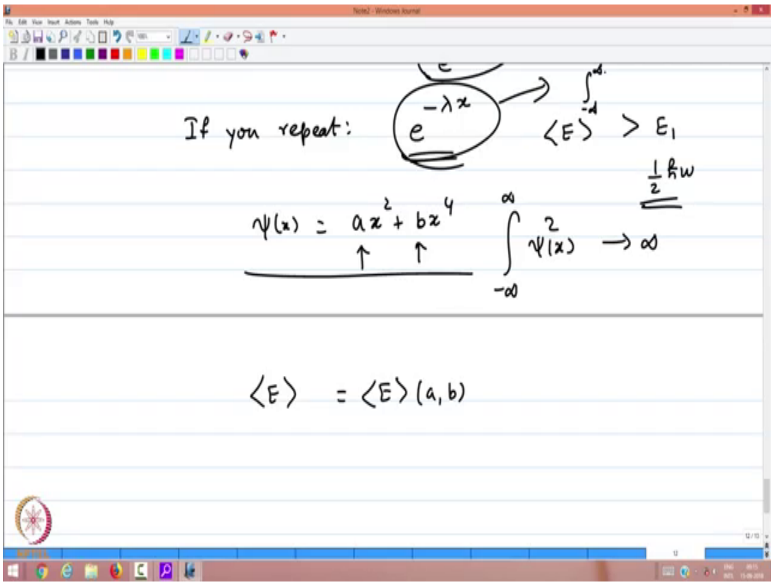

And if you calculate the energy using this form, then you will get E also as a function of a and b . But you have a problem with this function is not the correct function, why? Because the integral minus infinity to plus infinity of this psi of x psi square of x will give you infinity. What about this function? This will also give you a problem, because this cannot be normalized if you want to integrate from minus infinity to plus infinity. Therefore, you cannot choose random functions, the idea of choosing these random functions wrong, and then showing you that this is incorrect the correct function that you have to choose is one you have to choose a function that is normalizable.

Two you have to choose a function as a function of some parameters minimal set of parameters. And then minimize the average value of the energy as a function of all the parameters and then put the values of the parameters into the energy expression and get the energy Eigenvalue. If with all of that you will not get the exact Eigenvalue, unless the Eigenfunction happens to coincide with the exact Eigenfunction.

Therefore, variational principle always tries you that you go close to the minimal value of the energy, but never exactly until you hit the jackpot you got a function by some arbitrary choice you have got the exact Eigenfunction. But it always tells you that your error is always positive, minimize the error, quantum chemistry is fundamentally based on the advances of Hartree Fock, and later the DFT every method that you see in computational chemistry depends on this fundamental principle in the calculation of the ground state energy ok.

One last thing, what about other energies? The first excited state second excited state variational principle does not say anything about them. This is only true for the lowest energy E naught, nothing can be said about the first excited state or second excited state. We have to actually calculate those things using the best variationally minimized Eigenfunction and linear combinations of such Eigenfunctions to calculate the excited state, and hope that we are very close to the exact energy.

Therefore, the verification for all these things is the experimental spectroscopy which provides you differences between energies or frequencies as measurements that for computational chemistry must work very, very closely with experimental measurements to see what is best possible wave function, and what is a best possible Eigenvalue and so on. So, there is a lot more to learn, but let me start here this is only a cursory introduction. In the next part of this lecture, we will see one or 2 more example which are nontrivial, and then let me move on to the introduction of the chemical bonding as the series of lectures to follow ok.

Until then, thank you very much.