

**Quantum Chemistry of Atoms and Molecules**  
**Prof. Anindya Datta**  
**Department of Chemistry**  
**Indian Institute of Technology – Bombay**

**Lecture-44**  
**Variational Method- Continued**

We are discussing the variational method and we have presented an introduction to it. We have said that what we do is we write a functional  $\epsilon_0$  which has more or less the same form of as the ground state energy. The only difference is that the ground expression for ground state energy would involve the actual wave functions that we do not know and for  $\epsilon_0$  we have some trial guess wave function that we have given.

And then we said that this wave function would have some associated parameters which are called variational parameters.

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**The Variational Method**

**Ground state of an arbitrary system:**  $\hat{H}\psi_0 = E_0\psi_0$       $E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$

Trial/ guess wavefunction:  $\phi$       $\epsilon_0(\phi) = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$      *Functional*

**Upper limit theorem:**  $\epsilon_0(\phi) \geq E_0$

**Strategy:**

- Start with an arbitrary trial function
- Calculate energy
- Vary parameters of the function
- Recalculate
- Continue until convergence to a value of calculated energy):

$\phi = e^{-kr}$   
 $\phi = e^{-kr^2}$

What we do is we vary these parameters change the values of this parameters calculate  $\epsilon_0$  and upper limit theorem tells us that whatever minimum value we get for  $\epsilon_0$  is the maximum possible value for  $E_0$  or the upper bound or upper limit of  $E_0$ . So, let us demonstrate this by going back to our old friend the hydrogen atom.

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### An illustration: Hydrogen atom

Ground state:  $\hat{H} = -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r}$        $E_0 = -0.500 \left( \frac{\mu e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)$

Trial/ guess wavefunction:  $\phi = e^{-\alpha r^2}$ ;  $\alpha =$  Variational parameter       $\epsilon_0(\phi) = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$

$$\langle \phi | \hat{H} | \phi \rangle = \int_0^\infty e^{-\alpha r^2} \left( -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d e^{-\alpha r^2}}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r^2} \right) dr = \frac{3\hbar^2 \pi^{3/2}}{4\sqrt{2}\mu\alpha^{1/2}} - \frac{e^2}{4\epsilon_0\alpha}$$

$$\langle \phi | \phi \rangle = \left( \frac{\pi}{2\alpha} \right)^{3/2}$$

$$\therefore \epsilon_0(\phi) = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{3\hbar^2 \alpha}{2\mu} - \frac{e^2 \alpha^{1/2}}{\sqrt{2}\epsilon_0 \pi^{3/2}}$$

$$\therefore E_{min} = -\frac{4}{3\pi} \left( \frac{\mu e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right) = -0.424 \left( \frac{\mu e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)$$

- $E_{min} > E_0$
- More parameters: closer match
- Optimization with respect to each parameter
- Iterative methods: Computational Chemistry
- Lose sight of exact solutions?



Of course we do not have to do this variation treatment for hydrogen atom because you already know the solutions. But since we know the solutions this hydrogen atom provides a very good test system because we know the expression for energy we know that this Hamiltonian is like this and its ground state so since its ground state I am only bothered with the r part of the Hamiltonian I do not bother about the theta and phi Hamiltonian because I know that in the ground state wave function there is node theta phi dependence.

Also I know the ground set energy this is something that well I am not sure if I have written exactly in this form earlier but it is the same as what we have written earlier. I know the energy now the good thing is I should be able to use variation method and get something that is close. We have not really derived the theorem yet we will do that but right now we are taking it axiomatically for the next 15 minutes or so and we are working it out.

And when I say we are working it out I am lying because I will not work out anything. I hope you remember our rule you have to sit in front of the computer with a pen and paper you are going to work out. I am not going to do so much of integration and all because then it will take a lot of time and its quite mundane you can do it. So, we will try to see whether we get a similar expression first of all and we will try to see whether the minimum value of epsilon 0 that I get is more than E 0.

If it is so how much more let us proceed. So, let us say I take a trial or guess wave function  $\psi$  equal to  $E$  to the power  $-\alpha r^2$ . So,  $\alpha$  is the variational parameter I am not using this  $q$  as variational parameter just as yet let us see what happens if I just vary  $\alpha$ . If it is not good then of course I want to try with  $3/4$  and so on and so forth in the exponent but we will see what happens. And why am I choosing this  $E$  to the power  $-\alpha r^2$  all of a sudden.

Two reasons first of all this is a well behaved wave function is not it because it goes to 0 at  $r$  equal to infinity the Gaussian function. Secondly I am cheating a little bit because I already know the solution I know what the one is wave function is that is  $E$  to the power  $-k r$  sort of is an exponential decay. So, Gaussian decay and exponential decay how different are they what I am saying is an exponential decay is something like this I goofed sorry not bad this is let us say an exponential decay something like  $E$  to the power  $-k r$ .

And what is the Gaussian decay is something like this. So, I might as well play around with this parameter  $\alpha$  and try to see whether I can bring this Gaussian down here as close to this exponential decay as possible. There will always be some mismatch in near  $r$  equal to 0 I will normalize and get it as close as possible. It will never be exactly the same but it is not very different I mean if we close one eye and shut the other a little bit we will we can live with this and we will see whether we can really live with this or not.

So  $\psi$  equal to  $E$  to the power  $-\alpha r^2$ ; so,  $\alpha$  here is the variational parameter that we have discussed already great. So, now this is the expression for  $\epsilon_0$  ok we know this so what I will do is I just write down but not solve I will only give you the final solution you solve if you want and you should solve and convince yourself that this is correct. This treatment is from Macquarie's quantum chemistry book not Mcquarie and Simon physical chemistry Macquarie only Macquarie quantum chemistry.

So I just plug in the expression for Hamiltonian and I write the value I write the expression for the trial wave function and all I have to do is just see what I get? And this is what I get I am giving you the answer please work it out yourself you will have to use a standard integral association. This is what I get. What is the denominator? Denominator is simpler  $E$  to the power

-  $\alpha r^2$ . So, multiplied by  $E$  to the power -  $\alpha r^2$  what is it and then integrate from 0 to infinity this is what you get.

So when you divide the numerator by the denominator you get the value with the expression for  $\epsilon_0$  function of  $\phi$  as  $3 h^2 \alpha^2 \mu - E^2 \alpha$  to the power half divided by  $\sqrt{2 \epsilon_0 \pi}$  to the power 3 by 2 fantastic what is the next step? What am I looking for? I am looking for what is the value of minimum value of  $\epsilon_0$ . How do I change the value of  $\epsilon_0$  the only thing that I can play around with here is  $\alpha$  variation parameter.

So I keep on changing the value of  $\alpha$  and I have to look for the minimum. So, essentially I have to again well even though we have said it earlier I will draw that curve once again. Let us say this is the value of  $\epsilon_0$  with respect to  $\alpha$  and to keep things simple I just show one minimum. Let us say this here is the plot I seek to find the value of  $\epsilon_0$  at this value of  $\alpha$  so to do that I have to first find this value of  $\alpha$  where  $\epsilon_0$  is minimum.

Now let us think of what we have learnt in high school calculus. I have a plot, how do I find the minimum of a plot or the maximum of a plot? For that matter differentiate and equate it to 0. For maximum as well as minimum the slope here is something like this the slope here is 0 is not it. So, what we have to do is we have to know what happened we have to find the minimum value of  $\epsilon_0$  to do that we simply differentiate  $\epsilon_0$  with respect to  $\alpha$  and equate it to 0 first derivative has to be 0 that is all.

How do you differentiate between a minimum and a maximum by the way yeah for minimum as well as maximum this is the first derivative is equal to 0. What about the second derivative? Second derivative is it 0 or positive or negative for maximum and minimum? I leave it to you to refresh your memory on that here at least in the curve that I have shown I do not have to worry because I have not even shown a maximum only minimum point is there.

So differentiate this and equate it to 0 what will you get you will get a value of  $\alpha$  is not it that value of  $\alpha$  turns out to be  $\mu^2 E^2$  to the power 4 by  $18 \pi^3 \epsilon_0^2 h^2$

to the power 4 I have given you the answer you should not be satisfied with that. You should differentiate it equate to 0 see what value of alpha you get and convince that whatever we get you convince yourself that what we have written here is indeed correct. Please do it.

So we plug in this value of alpha here in the second term and in the first term what will happen I will get some expression for  $E_0$  is a function of phi and that expression turns out to be  $-4$  by  $3 \pi \mu E$  to the power 4 by  $16 \pi^2 \epsilon_0^2 h^2$  and I am calling this  $E_{\min}$  perhaps I should have called it epsilon min but then I am using a different convention than my query I wanted to get back and be at par with him.

So I have written  $E_{\min}$  which is what is written in Macquarie's book  $E_{\min}$  turns out to be  $-4$  by  $3 \pi \mu E$  to the power 4 by  $16 \pi^2 \epsilon_0^2 h^2$  that turns out to be equal to  $-0.424 \mu E$  to the power 4 by  $16 \pi^2 \epsilon_0^2 h^2$  yeah I just clean it up a little bit for you. So, this is what we have get  $-0.424$  multiplied by this factor and this is what we have got from the exact solution  $-0.500$  multiplied by the same factor.

So is that good or is that good? It is good. First thing we see is that this is a demonstration of the upper limit theorem  $E_{\min}$  is greater than  $E_0$  it is close. Since it is close I say the agreement is good but it is still greater than  $E_0$  it is not less than a 0 that is point number one. This is not a proof by the way it is an illustration. Now we can think that we have got  $0.424$  and here it is  $0.500$  how can I get closer to  $0.500$ ?

And the answer would be by playing introducing some other parameter. I have taken a Gaussian parameter so instead of 2, I can write  $q$  and I can play around with  $q$  and you know what will happen if  $q$  goes closer to 1 and I am saying this because I know what way 1S wave function is if  $q$  goes closer to one then the match should be better. So, the energy that I get should be closer to the energy that I get from the exact solution.

Besides I could multiply this by a number maybe so that you get the correct form but that may not make any difference. So, I can play around with the exponent here. So, if you put in more parameters I get a closer match. Well when you do this kind of what I should say curve fitting if

you use more parameters you always get a better match and sometimes there is this stranger which is called over parameterization.

Here we do not have to worry about over parameterization that is great because remember that cartoon on the cover page of the previous module we cannot do better than the best. Whatever we get is always more than the actual value of energy. So, even if you over parameterize it is not a problem it is a beautiful consequence of the upper limit theorem. So, I can actually increase the number of parameters I can have trivial parameters eventually but does not matter.

So if you can if you have the time and you have the capability you can just keep on increasing the parameter, number of parameters. So, what we have to do is we have to optimize this epsilon 0 function that is related to energy with respect to each and every parameter. So, you need to do iterations and you can understand that here we are looking at a very simple system we are working with only one parameter.

For larger systems there will be many, many parameters. So, if I try to do it by hand it will take me so much of time that by the time I am done the problem may not be relevant anymore, so you have to use computers. So, requirement of this excessive large number of calculation requires an interfacing of chemistry with computers. Conventionally when you see think chemistry when you talk about chemistry you think of color, smell many times bad smell, beaker, conical flask weighing balance. yeah

But now we see that computers turn seem to have an important role to play in chemistry because you cannot do this computers any longer without sorry you cannot do this calculations any longer without using good computers. So, this iterative method is sort of our introduction to the requirement of computational chemistry of course we are nowhere close to the actual thing yet I mean in this course.

Computational chemistry nowadays has developed into a huge field will not get into computational chemistry but we are taking baby steps towards it. So what I am saying is that this is the first baby step or introduction to iterative method. The first baby step towards this fast field

of computational quantum chemistry and in doing so one thing that might happen is that we might lose sight of exact solutions; is that good or is that bad?

See here we use some arbitrary function  $E$  to the power  $-\alpha r^2$  Gaussian function not really the exact solution yeah but still we got it. And then we said that will introduce more parameters so will deviate further and further and further from the exact solution is that good is that bad? But it is good in the sense that sometimes we do may not even know the exact solution that is the reason why you want to do variational method rather than perturbation theory.

So if you can forget about the exact function that is great yeah just change the number of parameters do not bother about the wave function bother about the energy that is a good part of it. The bad part of it is that we might lose a little bit of physical insight. So, you see all these orbitals that we talked about after some time these orbitals may not be necessary anymore. We can just construct the wave function here I have used one Gaussian function I can take a linear combination of many Gaussian functions.

I can take exponential functions I can take introduce some asymmetry factor so this way I can actually synthesize the wave function by using mathematical functions, simpler mathematical functions which is great because I can with enough computational power I can find the energy. And from the point of view of a conventional physical chemist you might be a little sad because you will not be able to perhaps after a while say much that is in relation to your good old one is  $2s$ ,  $2p$  orbitals or maybe you can we will see.

Now that we have illustrated that this upper limit theorem works for hydrogen atom let us move forward to a formal proof of the theorem.

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**Proof of Variation theorem**

$\hat{H}\psi_i = E_i \psi_i$       $\psi_i$ : Complete, orthonormal, unknown;  $i = 1, 2, 3, \dots, n$

Let  $\phi = \sum_i c_i \psi_i$       $\hat{H}(c_1 \psi_1) = c_1 E_1 \psi_1$       $\hat{H}(c_2 \psi_2) = c_2 E_2 \psi_2$       $\sum_i c_i E_i \psi_i$

$$\varepsilon_0(\phi) = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\langle (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) | \hat{H} (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) \rangle}{\langle (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) | (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) \rangle}$$

$$= \frac{\langle (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) | (c_1 E_1 \psi_1 + c_2 E_2 \psi_2 + c_3 E_3 \psi_3 + \dots + c_n E_n \psi_n) \rangle}{\langle (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) | (c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \dots + c_n \psi_n) \rangle}$$

$$= \frac{c_1^2 E_1 + c_2^2 E_2 + c_3^2 E_3 + \dots + c_n^2 E_n}{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2} = \frac{\sum_i c_i^2 E_i}{\sum_i c_i^2}$$

$$\varepsilon_0(\phi) - E_0 = \frac{\sum_i c_i^2 E_i}{\sum_i c_i^2} - E_0 = \frac{\sum_i c_i^2 E_i - \sum_i c_i^2 E_0}{\sum_i c_i^2} = \frac{\sum_i c_i^2 (E_i - E_0)}{\sum_i c_i^2} \geq 0$$

$\varepsilon_0(\phi) - E_0 \geq 0$

$E_0$ : Ground state, lowest energy

Let us say once again that we can write this kind of Schrodinger equation for this arbitrary system and let us say psi i's are considered the complete orthonormal unknown complete orthonormal set of unknown wave functions let us say there are n such wave functions. Here again I deviate a little bit from Macquarie's treatment Macquarie's has written n I am rewriting i because I thought that you use n for a particular value and then use n as an index you might get confused.

So I am using i which is an index. So, now let us define an arbitrary wave function that will work with remember phi we define phi and this time I say that I can write phi as a sum of c i psi i is this valid actually it is because see what are psi i's we are taking an orthonormal set a complete orthonormal set. So, they are like the coordinates of the function space. I take some arbitrary function in that function space I want to work in that function space because system is same.

I should be able to express it in terms of the coordinates of that space the norm the modes of that phase space that is why it is perfectly valid to write phi equal to sum over i c i psi i I construct the arbitrary wave functions that way and as we have discussed earlier we define epsilon 0 to be integral phi star h phi divided by integral phi star phi over the entire function space. So, far so good I hope you can proceed yeah.

Let us go proceed so what I will do now is I will write it out and I have written it out completely I should have animated little bit more please do not get scared I will go term by term well I should have ideally written a summation but I myself get confused sometimes if there are too many summation signs. So, I have actually opened the summation. So, this is what will happen  $\phi$  is what  $\phi$  is this summation.

So I have just opened it up  $c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3$  so on and so forth until  $c_n \psi_n$  so the general term here  $c_i \psi_i$  sum over  $i$ . So, actually I am work with this complex conjugate remember of a function or function in the bra vector is actually its complex conjugate. If left this left multiplies  $H$  operating on  $\phi$  which is  $H$  operating on  $c_1 \psi_1 + c_2 \psi_2$  same thing. In the denominator we have integral  $c_1 \psi_1 + c_2 \psi_2$  etcetera, etcetera complex conjugate multiplied by  $c_1 \psi_1 + c_2 \psi_2$  etcetera, etcetera integrated over all space.

Now what will I do now I remember that  $H \psi_i$  is equal to  $E_i \psi_i$  so what happens when  $H$  operates on this let me write. So, what this means essentially is say  $H \psi_1$  is equal to  $E_1 \psi_1$  why we put the arrow there this so what is  $H$  operating on  $c_1 \psi_1$  that will be equal to  $c_1$  into  $E_1 \psi_1$  remember we are working with linear operators. But I have written it so horribly I think I will erase it and I will write the whole thing once again.

What I am saying is this Schrodinger equation is something like this  $H$  operates on  $\psi_1$  to give me  $E_1 \psi_1$  so what happens when  $H$  operates on  $c_1 \psi_1$  that is the same as  $c_1$  multiplied by  $H \psi_1$  is not it linear operator so this will be simply  $c_1 E_1 \psi_1$ . Similarly  $H$  operating on  $c_2 \psi_2$  will be  $c_2 E_2 \psi_2$  so on and so forth. So, essentially this state vector will become sum over  $i$   $c_i E_i \psi_i$  perhaps you understand I perhaps I do not need to explain in such meticulous as detail but I still will in case somebody does.

So this is what it is I have not worked with the denominator yet I hope I have not made any mistake anywhere yeah so this is what I get. In the bra vector I have  $c_1 \psi_1 + c_2 \psi_2$  etcetera etcetera sum over  $i$   $c_i \psi_i$  this in the  $k$  vector I now have sum over  $i$   $c_i E_i \psi_i$ . Now let us remember that these  $\psi_i$ 's are all orthonormal. So, what happens when I try to simplify this numerator or denominator a little further.

First let me take this term  $c_i \psi_i$  and this so I will write this  $c_i \psi_i$  and  $c_i E^{-1} \psi_i$  so this will give me  $\int c_i \langle \psi_i | \psi_i \rangle$  sorry  $c_i \langle \psi_i | \psi_i \rangle$  in bra vector yeah is this anything else well let us not forget that I have  $\psi_i$  here as well I can take these coefficients out of the integral they are constant. So, that becomes  $c_i \langle \psi_i | \psi_i \rangle$  this is actually  $c_i$  in bra vector remember its actually  $c_i$ .

So  $c_i \langle \psi_i | \psi_i \rangle$  comes out and inside the integral you are left with  $\int \psi_i^* \psi_i d\tau$  what is that that is equal to 1 because they are normalized. Similarly if I take this term and this term what will I get I will get  $c_i \langle \psi_i | \psi_j \rangle$  but then orthonormal right orthonormal. So, these are all orthogonal to each other. So, this integral must be equal to 0 so I am only left with  $c_i \langle \psi_i | \psi_i \rangle$  multiplied by  $\int \psi_i^* \psi_i d\tau$ .

Similarly I will get sorry  $c_i \langle \psi_i | \psi_i \rangle$  multiplied by  $\int \psi_i^* \psi_i d\tau$ . Similarly I will get  $c_j \langle \psi_j | \psi_j \rangle$   $\int \psi_j^* \psi_j d\tau$ . So, the general term here will be  $c_i \langle \psi_i | \psi_i \rangle$   $\int \psi_i^* \psi_i d\tau$ , so  $i, j$  kind of term will not be there and it will be a summation over  $i$ . What will the denominator be similarly denominator also has to become sum over  $i$   $c_i \langle \psi_i | \psi_i \rangle$  because take these 2 terms again maybe I will take these  $c_2 \langle \psi_2 | \psi_2 \rangle$  and  $c_2 \langle \psi_2 | \psi_2 \rangle$  here that gives you  $c_2 \langle \psi_2 | \psi_2 \rangle$   $\int \psi_2^* \psi_2 d\tau$  all space.

And if I take say  $c_3 \langle \psi_3 | \psi_3 \rangle$  and well  $c_n \langle \psi_n | \psi_n \rangle$  then I get  $c_3 \langle \psi_3 | \psi_3 \rangle$   $\int \psi_3^* \psi_3 d\tau$  over all function space which is equal to 0. So, this is what I get did I goof up a little bit in the numerator actually I did. See here what I have written is I have forgotten something I forgotten that I have  $E^{-1}$  also  $E$ , so numerator turns out to be  $c_1 \langle \psi_1 | \psi_1 \rangle E^{-1}$  because the integral of  $\psi_i^* \psi_i$  over all function space is  $0 + c_2 \langle \psi_2 | \psi_2 \rangle E^{-2}$  so on and so forth.

Denominator is  $c_1 \langle \psi_1 | \psi_1 \rangle + c_2 \langle \psi_2 | \psi_2 \rangle + c_3 \langle \psi_3 | \psi_3 \rangle$  so on and so forth. So, I will write it as summation that I have written here and I made a mistake while writing the numerator. So, this is  $\sum_i c_i \langle \psi_i | \psi_i \rangle E^{-i}$  divided by  $\sum_i c_i \langle \psi_i | \psi_i \rangle$ . Now what do I actually want I am trying to prove the variation theorem upper limit theorem. So, what I want to know is whether this  $\epsilon - E_0$  is greater than equal to 0 or not.

So let me subtract  $E_0$  from left hand side then I have to subtract it from hand side also so this is what I get yeah and these steps are simple so I will just rush through. So, this is basically one summation minus another summation. So I can just make 1 summation and in both the cases coefficient of  $E_i$  is  $c_i^* c_i$  so I can write like this  $E_i$  and  $E_0$  both coefficient is  $c_i^* c_i$  so I get this numerator is sum over  $c_i^* c_i$  multiplied by  $E_i - E_0$  divided by  $c_i^* c_i$ .

Now please remember what is  $E_0$ ?  $E_0$  is our definition of ground state energy what is  $E_i$ ?  $E_i$  is the energy of some excited state some excited state for  $i$  is not equal to 0. So, will you agree with me that  $E_i - E_0$  has to be positive or at most 0 when  $i$  equal to 0 yeah because energy of the ground state is the lowest for all values of  $i$  other than 0 energies are higher and higher that is why it is called ground state.

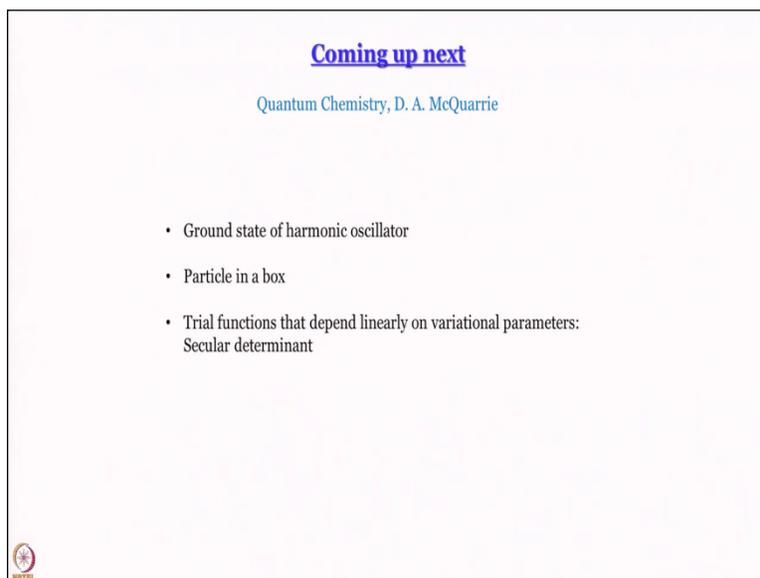
The ground state cannot be above the excited state well in case of some human being cities but they are not quantum mechanical systems fine. So,  $E_i - E_0$  has to be greater than equal to 0 because  $E_0$  is the lowest value of energy among all the  $E_i$ 's that are possible. Remember  $i$  is the general index I should have perhaps written 0 here also. If I define  $i$  to be 1, 2, 3 so one and so forth I am not writing 0 well whatever well 0 means ground state that is point number one.

Point number 2 is what is  $c_i^* c_i$ ? Some complex number multiplied by its complex conjugate yields a real number can it ever be negative? Never, complex conjugates are defined in such a way that when they multiply each other you are going to get a positive real number is not it yeah if there is any confusion please go back to some basic book of complex numbers 11, 12 level book your doubt will be cleared.

Otherwise just believe me when I say that  $c_i^* c_i$  has to be a positive real number. So, this is also 0. So, in the denominator I have something that is positive. In the numerator  $E_i - E_0$  is positive and I just said that  $c_i^* c_i$  is also positive so this  $E_i - E_0$  is a positive quantity divided by a positive quantity which is a positive quantity. Hence we have been able to prove the variation theorem or upper limit theorem which says that  $E_i - E_0$  is greater than equal to 0.

Or in other words the functional epsilon that we calculate by varying the parameters of phi can never be less than the actual energy and that is a saving grace that is why variation theorem is so useful.

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So, that is what we have learnt today we have done it from quantum chemistry's book by Donald Macquarie we are going to use Pillars book also in this context. What we will do next is that now that we have proved this theorem we are going to see how we can get an expression for ground state of harmonic oscillator? How we can get an expression for the energy levels of particle in a box using variation method and somewhere in the line may be before this or after this we will show that for trial functions that depend linearly on variational parameter we get a secular determinant and the moment we get a secular determinant.

The solution becomes very simple and that becomes a cornerstone in trying to solve variational problems. And then finally we are going to use the variation method and also perturbation method in multi electron atom. So, all this is coming up in the next few modules as I say in fm channels stay tuned.