Advanced Quantum Mechanics with Applications
Prof. Saurabh Basu
Department of Physics
Indian Institute of Technology, Guwahati

Lecture – 25
Application of Variational method, Hydrogen, Helium atom, Comparison with perturbation theory

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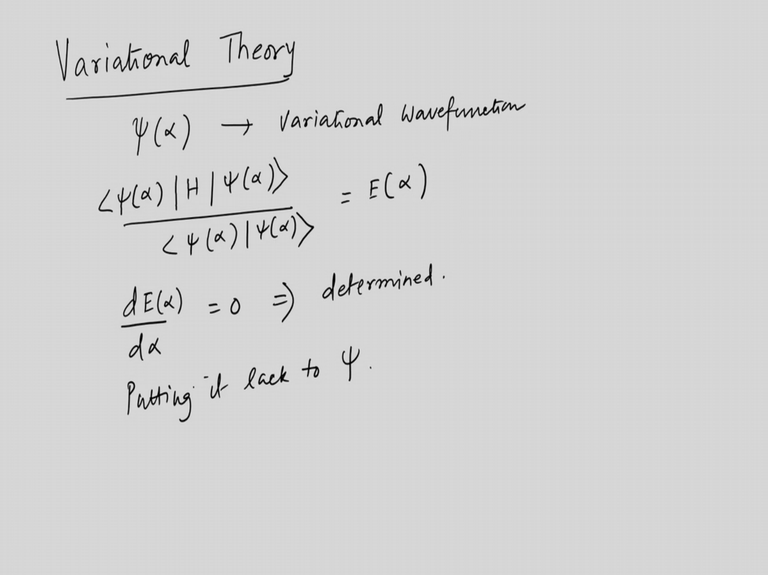

Variational Theory

$\psi(\alpha) \rightarrow$ Variational Wavefunction

$$\frac{\langle \psi(\alpha) | H | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle} = E(\alpha)$$

$$\frac{dE(\alpha)}{d\alpha} = 0 \Rightarrow \text{determined.}$$

Putting it back to ψ.

So, let us recapitulate the variational calculations of the variational theory that we were talking about. So, what we did is that we apriori did not know how to split the Hamiltonian into unperturbed and a perturbation Hamiltonian. So, we were given a Hamiltonian whose exact solution is not known. And we had taken a variational wave function, and so this is the variational wave function.

And hence we went ahead and calculated this the variational energy with and called that as E alpha. Now, this E alpha was minimized with respect to alpha, and determined alpha was determined. Putting it back into psi that is the variational state that we have obtained.

So, two comments are in order. One is that the trial wave function of the variational wave function is of course chosen with the boundary conditions kept in mind. If you completely disregard the boundary conditions, the variational calculation can still be done. But, you will get a estimate of energy, which is much larger than the actual energy, the real energy of the system or the exact energy of the system.

Now, the second point is exactly in that line that the variational calculation yields the maximum or the upper bound to the lowest energy possible for that system. And we mostly carry out the calculation for the ground state though it is not impossible. It is it may be complicated, but not impossible to do the calculation for excited states. So, let us tell the results of a few (Refer Time: 03:13) problems in the context of variational theory.

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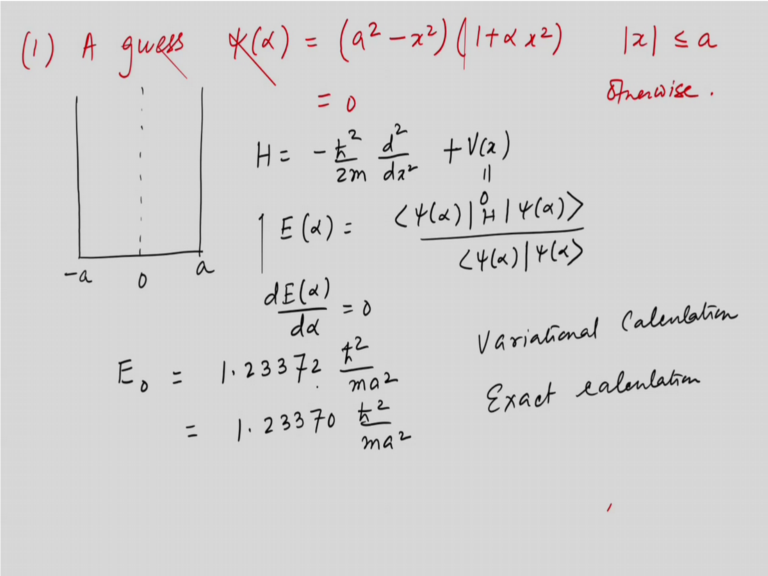

(1) A guess $\psi(\alpha) = (a^2 - x^2)(1 + \alpha x^2)$ $|x| \leq a$

$= 0$ otherwise.

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \underset{\overset{\|}{0}}{V(x)}$$

$$E(\alpha) = \frac{\langle \psi(\alpha) | \overset{0}{H} | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle}$$

$$\frac{dE(\alpha)}{d\alpha} = 0$$

$E_0 = 1.23372 \frac{\hbar^2}{ma^2}$ Variational Calculation

$= 1.23370 \frac{\hbar^2}{ma^2}$ Exact calculation

Let us take the first problem. So, a guess such as psi of alpha, it is equal to a square minus x square 1 plus alpha x square for x less than equal to a. Now, this is for a particle in a box and it is 0 otherwise, so that is the problem that is chosen. Alpha is of course the variational parameter. Now, look at it that the box is from 0 to a. So, at x equal to a, the wave function is equal to 0. And of course at x equal to 0 x equal to minus a, again the wave function is equal to 0. So, this is at the well is like this minus a to a. And this is the 0.

And for that the variational function is taken as this. I will not do the calculation, but you can do it. You can you know that the Hamiltonian is written as minus h square by 2 m d 2 dx 2 plus V of x, which is equal to 0. So, it is simply the non-interacting problem, where the particle has mass m, and it is a confined within this well. You can calculate the energy which is equal to psi alpha H psi alpha. And then of course you can normalize the wave function.

And then put a d E d alpha equal to 0. The exactly what we have said in the last slide, put that equal to 0, and put alpha back into that. And an estimate of the ground state energy is equal to so this is E 0 that is from the variational calculation its 1.23372 h cross square by ma square that is the variational calculation. And the exact calculation is very very close, it is 23370 h cross square by m a square. So, this is the exact.

So, you see that the wave function as arbitrary as this, which simply satisfies the boundary conditions that this is equal to 0 at x equal to plus a and x equal to minus a. And then we have gone ahead and calculated the variational energy the variational energy only differs from the exact energy in the 5th decimal place. So, it is that good, because the wave function had followed the right or the correct boundary conditions.

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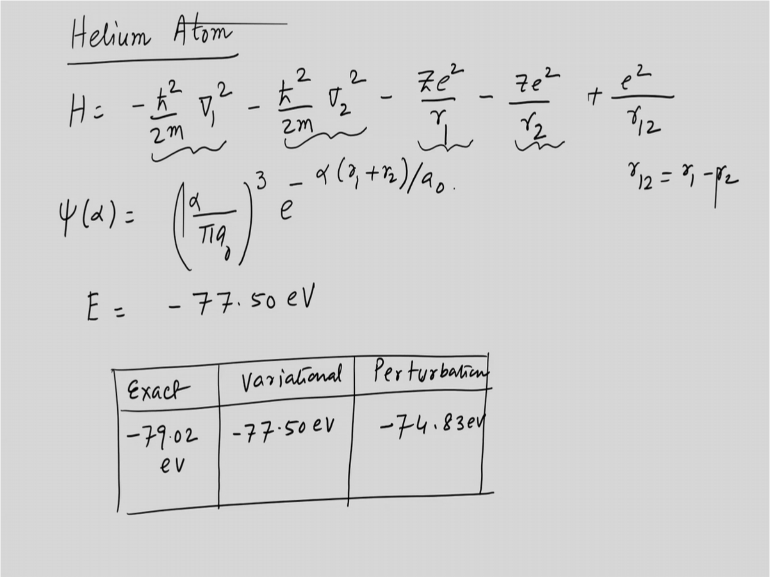

Helium Atom

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

$$r_{12} = r_1 - r_2$$

$$\psi(\alpha) = \left(\frac{\alpha}{\pi a_0}\right)^3 e^{-\alpha(r_1+r_2)/a_0}.$$

$$E = -77.50\ \text{eV}$$

Exact	Variational	Perturbation
-79.02 eV	-77.50 eV	-74.83 eV

So, let us look at this problem of helium atom; this is a famous problem in this context. So, we are going to talk about helium atom, which consists of two electrons. And there is a nucleus, and there is and also because there are two electrons. There is an electron-electron interaction.

So, the Hamiltonian could be written as, it is minus h square by 2 m del 1 square. So, this corresponds to electron 1, we can write the same mass for the electrons. So, it is minus h square by 2 m del 2 square minus, now of course this is z is equal to 2. So, it is z e square by r 1 that is the distance between the nucleus and the first electron. And then there is a z e square by r 2. And of course, there is also term which is the electron-electron interaction, and which could be written as simply equal to plus e square divided by r 1 2, where r 1 2 is given by r 1 minus r 2.

So, this is the Hamiltonian for the helium atom. So, they are considered as this is for one electron, this is for the other electron. This is the between the interaction between the nucleus and the first electron, again the nucleus and the second electron, and that is the interaction energy with between the first and the second electron. So, the wave function let us take the wave function as, we can take it as alpha over pi a 0 whole cube, and then exponential minus alpha r 1 plus r 2 by a 0.

Now, this is a fairly accurate equation rather the wave function, because you see the ground state of the hydrogen atom has a simple exponential minus alpha r by a 0. There is no theta or phi dependence. So, this is a fairly good wave function. And with this wave function one gets the energy as minus 77.50 electron volt ok. And if I make a table of the exact energy versus this variational energy and also compare it with the perturbation energy, then that is so the exact is a minus 79.02 electron volt.

The variational has just said to this calculation I am skipping for now, but most likely we will be doing it in a tutorial problem. So, it is minus 77.50 electron volt. The perturbation theory on the other hand with this last term as the perturbation yields a minus 74.83 electron volt, which is far away from the actual exact energy.

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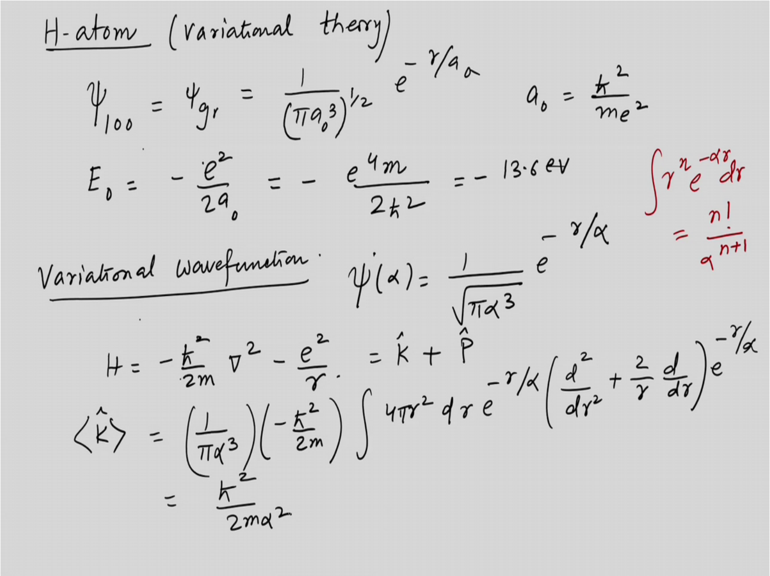

H-atom (Variational theory)

$\psi_{100} = \psi_{gr} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$ $\quad a_0 = \frac{\hbar^2}{me^2}$

$E_0 = -\frac{e^2}{2a_0} = -\frac{e^4 m}{2\hbar^2} = -13.6\,eV$

$\int r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}$

Variational wavefunction. $\psi(\alpha) = \frac{1}{\sqrt{\pi\alpha^3}} e^{-r/\alpha}$

$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} = \hat{K} + \hat{P}$

$\langle \hat{K} \rangle = \left(\frac{1}{\pi\alpha^3}\right)\left(-\frac{\hbar^2}{2m}\right) \int 4\pi r^2\, dr\, e^{-r/\alpha}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) e^{-r/\alpha}$

$= \frac{\hbar^2}{2m\alpha^2}$

Let us now talk about the some specific cases again. Let us talk about the hydrogen atom, which is most familiar to you. So, the ground state of the hydrogen atom, so we will use variational theory for the hydrogen atom and so you know that the wave function the ground state wave function, which is which corresponds to 1 0 0, which we call let us say we call it a psi g, which is equal to 1 by pi a 0 cube whole to the power half and exponential minus r by a 0 that is a ground state energy or ground state wave function.

So, so where a 0 equal to h cross square by m e square, m is the electronic mass, and e is the charge of the electron. And this gives that the E 0 is equal to minus e square by 2 a 0 which of course has a value, which is e 4 m divided by 2 h cross square, there is some spurious lines coming. And this has a value, which as all of you know that it is equal to minus 13.6 electron volt. And now suppose we take this wave function a variational wave function as a psi alpha equal to 1 by root over pi alpha cube exponential minus r by alpha.

Now, this is fairly exact. So, let us see that even with a fairly exact variational state what kind of energy do we land up with. So, h is nothing but by 2 m del square minus e square over r. So, the kinetic energy term. So, this is equal to the kinetic energy plus the potential energy. So, the kinetic energy term is written as 1 by pi alpha cube, and then minus h square over 2 m, and then 4 pi r square d r exponential minus r by alpha. And then of course we have a d 2 d r 2 plus a 2 by r d d r and exponential minus r by alpha, so that is the calculation for this for the kinetic energy expectation value of the kinetic energy.

Now, see that we have not written the theta and the phi dependence in del square term. And the reason being the ground state energy does not depend upon theta and phi. So, we have simply written down the del square for the r operator. And this can be as I said that it can be integrated by gamma function integral, which you should keep in mind. So, this looks like let me write it down with a different color.

So, it is a r to the power n exponential minus alpha r d r is equal to n factorial divided by alpha to the power n plus 1. So, when you do that this thing gives you a result, which is equal to h cross square by 2 m alpha square, so that is the kinetic energy.

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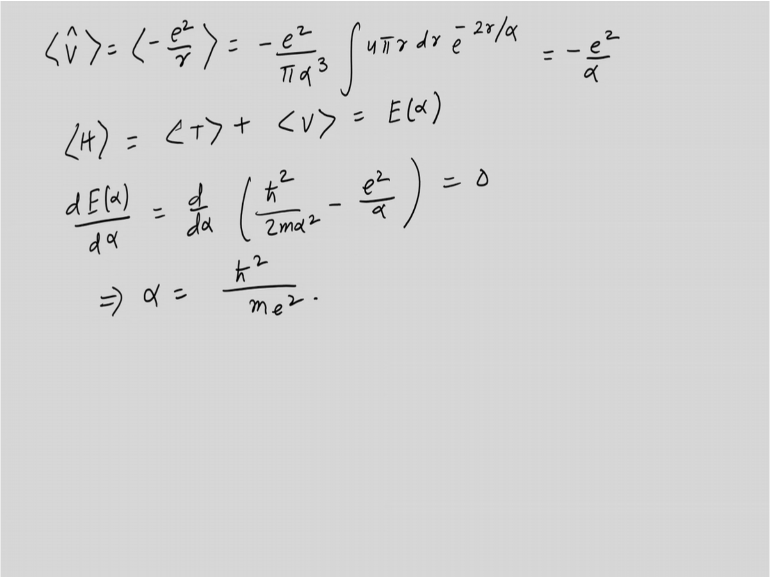

$$\langle \hat{V} \rangle = \left\langle -\frac{e^2}{r} \right\rangle = -\frac{e^2}{\pi\alpha^3}\int 4\pi r\, dr\, e^{-2r/\alpha} = -\frac{e^2}{\alpha}$$

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = E(\alpha)$$

$$\frac{dE(\alpha)}{d\alpha} = \frac{d}{d\alpha}\left(\frac{\hbar^2}{2m\alpha^2} - \frac{e^2}{\alpha}\right) = 0$$

$$\Rightarrow \alpha = \frac{\hbar^2}{me^2}.$$

And the potential energy is simply equal to minus e square over r, so that is equal to so that is equal to minus e square divided by pi alpha cube and the 4 pi r d r and exponential minus 2 r by alpha. And again this is another gamma function integral, which gives a minus e square over alpha. Now, by minimizing the energy, so this your total energy is of course equal to E equal to what is we write, so V.

So, your total energy is equal to T plus V. And d rather this is the Hamiltonian, and this is equal to the energy, which is E alpha. So, d E alpha d alpha equal to del alpha or we can there is simply one variational parameter. So, we can simply write it as d d alpha of h cross square by 2 m alpha square minus e square over alpha and then put that equal to 0. So, this gives a value of alpha that is equal to h cross square divided by m e square and that of course gives us the exact result, that one should get which is what is quoted here. So, this gives of course the exact energy that we are familiar with.

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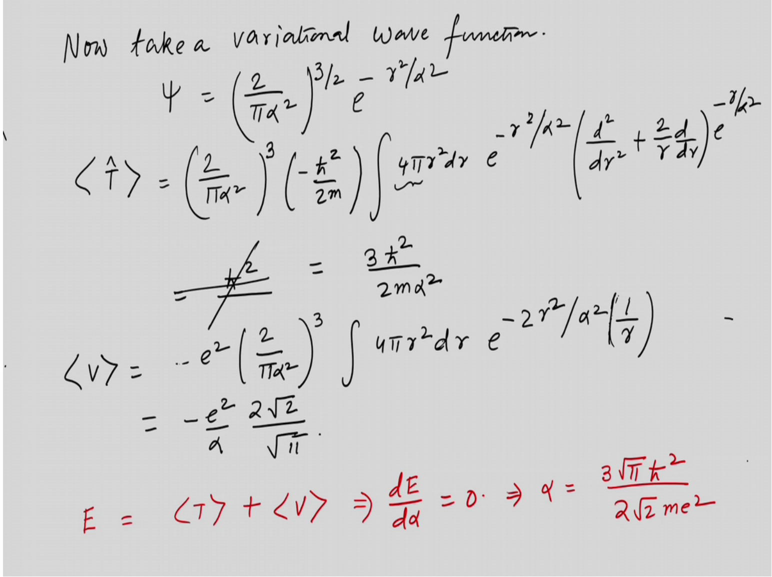

Now take a variational wave function.

$$\psi = \left(\frac{2}{\pi\alpha^2}\right)^{3/2} e^{-r^2/\alpha^2}$$

$$\langle \hat{T} \rangle = \left(\frac{2}{\pi\alpha^2}\right)^3 \left(-\frac{\hbar^2}{2m}\right) \int 4\pi r^2 dr\, e^{-r^2/\alpha^2} \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) e^{-r^2/\alpha^2}$$

$$\cancel{= \frac{\hbar^2}{}} = \frac{3\hbar^2}{2m\alpha^2}$$

$$\langle V \rangle = -e^2 \left(\frac{2}{\pi\alpha^2}\right)^3 \int 4\pi r^2 dr\, e^{-2r^2/\alpha^2} \left(\frac{1}{r}\right)$$

$$= -\frac{e^2}{\alpha} \frac{2\sqrt{2}}{\sqrt{\pi}}.$$

$$E = \langle T \rangle + \langle V \rangle \Rightarrow \frac{dE}{d\alpha} = 0. \Rightarrow \alpha = \frac{3\sqrt{\pi}\hbar^2}{2\sqrt{2}\, m e^2}$$

And then we can we can also take a variational wave function to be of this form. So, now take a variational wave function of a different form with is a completely different form actually. It is a 2 by pi alpha square this already is normalized. So, one does not have to worry about this. So, this is equal to r square by alpha square is very strange.

In fact, it should not be taken as the ground state wave function for the hydrogen atom, because it is Gaussian. And Gaussian only goes to 0 be at infinity at plus or minus infinity. However, this we know that the wave function has to go to 0 within a certain distance from the radius of the atom or maybe the Bohr radius. So, this is not a good choice of the wave function, but as we said that we can still calculate this.

So, we have again the minus h square by 2 m, so that is the kinetic energy let us write down the kinetic energy term. So, the kinetic energy is with this variational term, which is 2 over pi alpha square and there are two of them, so this becomes a cube. And there is a minus h square by 2 m, and there is a 4 pi r square d r and exponential r square by alpha square. Then you have that term which is d 2 d r 2 plus 2 by r d d r by exponential minus r square by alpha square.

And of course the theta and phi integrals have been done, and it is here in this 4 pi factor. So, the phi integral gives a 2 pi and the theta integral gives a 2, so that becomes a 4 pi. So, this if you calculate, it becomes equal to 3 h cross square by 2 m alpha square as I said that there is a simple integral, which is should try and do it. And all of them fall into this gamma function integral category, and then you can do it without a problem.

So, and then this V that is equal to minus e square, and then there is a 2 divided by pi alpha square and cube, and then there is a 4 pi r square d r exponential minus 2 r square by alpha square. And then there is a 1 over r that is coming from the form of the wave function, and it form of the interaction term all right.

So, if you perform this integral, this integral gives rise to minus e square by alpha and 2 root 2 divided by root pi again by taking a d E d alpha. So, the total energy is given by is T plus V. And so then the if we take this a d E d alpha, and put that equal to 0, one gets alpha equal to 3 root pi h cross square divided by 2 root 2 m e square.

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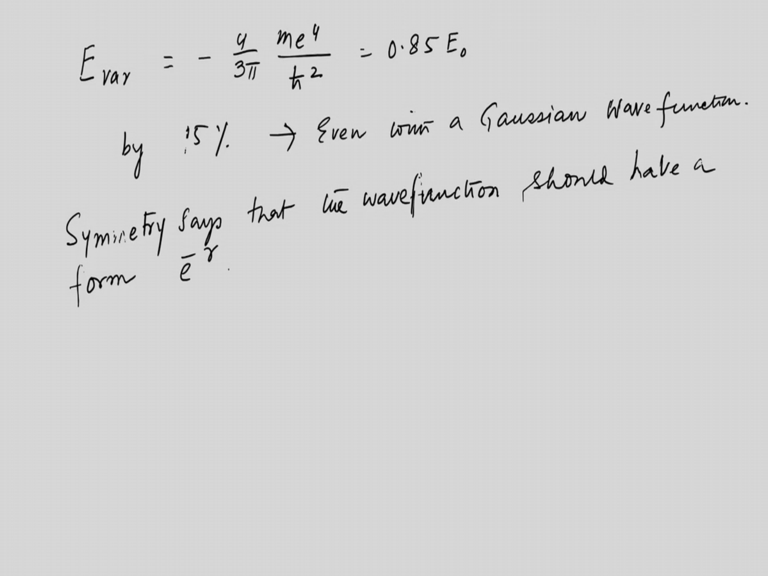

$$E_{var} = -\frac{4}{3\pi}\frac{me^4}{\hbar^2} = 0.85 E_0$$

by 15% → Even with a Gaussian Wave function.

Symmetry says that the wavefunction should have a form e^{-r}.

And with that the so this gives us that the energy the ground state energy is that is a variational energy. So, this is given by minus 4 by 3 pi and m e 4 divided by h cross square, and that comes out as 0.85 E 0. So, even with the wave function which does not obey the symmetry of the actual ground state wave function for a hydrogen atom, we still get accurate value to 85 percent of the actual value. So, we are only off by 15 percent ok. So, what it means is that we get a value which is 15 percent higher than the 13.6 electron volt, so even with a Gaussian wave function.

So, important thing is that that when the symmetry says that wave function should have a form, which is exponential minus r by or exponential minus r. We have taken it as a Gaussian, and then we are only off by 15 percent, which means that variational calculation at times works very well.

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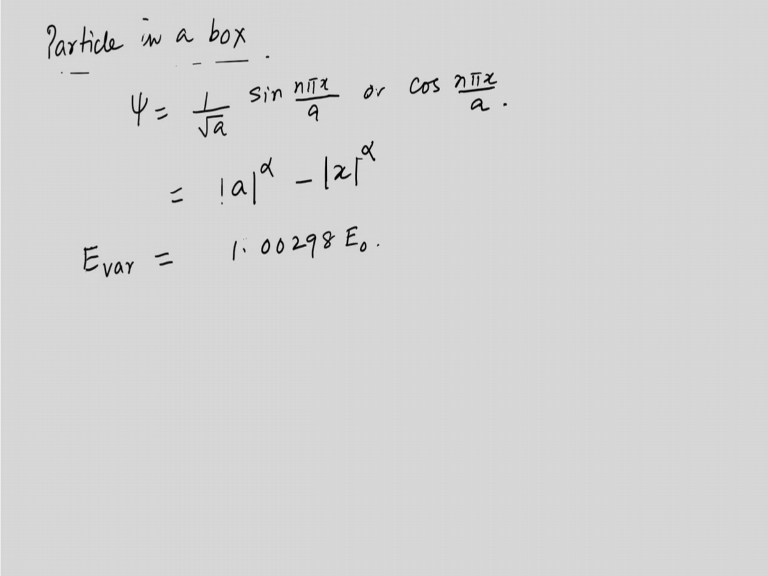

Particle in a box.

$$\psi = \frac{1}{\sqrt{a}} \sin \frac{n\pi x}{a} \text{ or } \cos \frac{n\pi x}{a}.$$

$$= |a|^{\alpha} - |x|^{\alpha}$$

$$E_{var} = 1.00298\, E_0.$$

Let me give another example that we know that the particle in a box has a wave function, which is like 1 by root over a sin n pi x by a or cosine n pi x by a. And one can actually take this one as well that it is a to the power alpha minus x to the power alpha. And then also we get the variational energy as let us call that as E var, which is equal to 1.00298 E 0. So, even with a polynomial function such as this the variational energy comes out to be fairly accurate, and it is extremely close to the actual energy.

So, the one important point is that that there is no hard and fast rule that what is a good wave function, in order to get a good bound on the or a very tight bound on the upper on the ground state energy. However, it should at least satisfy the boundary conditions that the wave function is supposed to satisfy. And in fact if you look at the quantum Hall effect rather the fractional quantum Hall effect, the wave function written by Laughlin.

Actually had (Refer Time: 27:10) all the other known wave functions at that time and clearly turned out to be a winner and deserved a noble prize for that. So, there are of course one has to be lucky. However, it also should obey the boundary conditions, that is supposed to obey.

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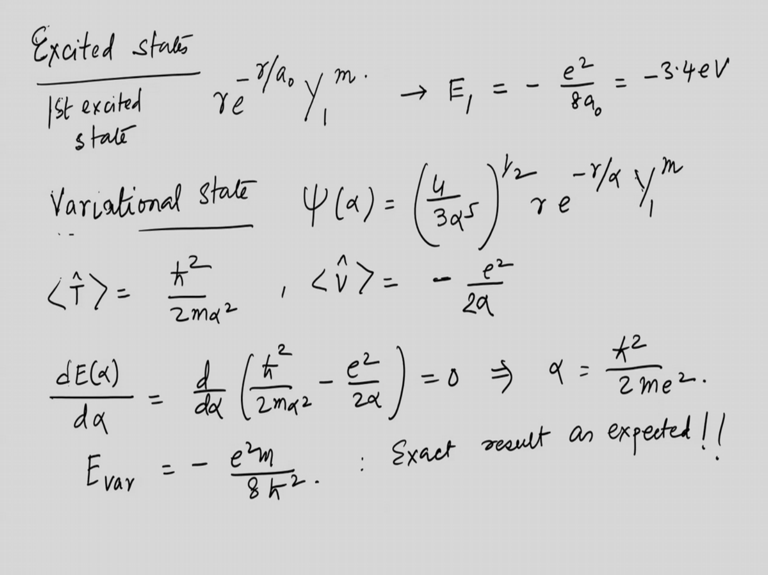

Excited states

1st excited state $\quad r e^{-r/a_0} Y_1^{m} \rightarrow E_1 = -\frac{e^2}{8a_0} = -3.4 eV$

Variational state $\quad \psi(\alpha) = \left(\frac{4}{3\alpha^5}\right)^{1/2} r e^{-r/\alpha} Y_1^{m}$

$\langle \hat{T} \rangle = \frac{\hbar^2}{2m\alpha^2} \quad , \quad \langle \hat{V} \rangle = -\frac{e^2}{2\alpha}$

$$\frac{dE(\alpha)}{d\alpha} = \frac{d}{d\alpha}\left(\frac{\hbar^2}{2m\alpha^2} - \frac{e^2}{2\alpha}\right) = 0 \Rightarrow \alpha = \frac{\hbar^2}{2me^2}.$$

$E_{var} = -\frac{e^2 m}{8\hbar^2}.$: Exact result as expected!!

Let me let me now go to another case. And give an example for the excited states. So, the excited state of hydrogen atom is the first excited states, so to say is of the form that we have r and exponential minus r by a 0 that is the exact one that I am talking about. And of course, there are Y 1 m is the form. And of course the energy of that is and energy is equal to minus e square by 8 a 0, which comes out to be minus 3.4 electron volt, so that is the known ground state energy.

Let us write down a normalized variational state as the following, remember that we had shown this the ground state has a is corresponds to the s state, which is l equal to 0 and has a spherical symmetry. However, the excited states correspond to l not equal to 0, and the spherical symmetry is broken, and they look like a dumble, and which is that theta dependence theta and phi dependences are taken care of by this Y 1 m.

It is actually really the theta dependence, the phi dependence only comes through an exponential plus minus i m phi, which comes as a phase the theta dependence of course comes from the Legendre polynomials anyway. So, this is we can take a variational state as follows. There is no necessity for you to start with a normalized wave function, but in any case you have to normalize it. So, I am writing down the normalized a variational wave function. It is r r my r by alpha and then Y 1 m, where m for l equal to 1 m can be minus 1 0 or plus 1.

Again the kinetic energy is given by h cross square by 2 m alpha square, I am not writing any longer the forms etcetera. But, they are of course had to be done in order to do it. So, this is a V, which gives a minus z e square, so z is equal to of course so 1. So, let us just write minus e square over alpha 2 alpha rather. So, when we do a d E d alpha, this is equal to del del alpha of h cross square by 2 m alpha square minus e square by 2 alpha, which when put equal to 0 or this is only one variational parameter.

There is no need for writing and del alpha, but so it is a d d alpha. This gives of course alpha equal to h cross square by 2 z, again z is not required. So, this is equal to m e square, and the minimum energy because of this so that is a variational energy comes out as e square m by 8 h cross square. So, this is the exact result as expected. The reason is that we have started with the exact wave function ok, so that is.

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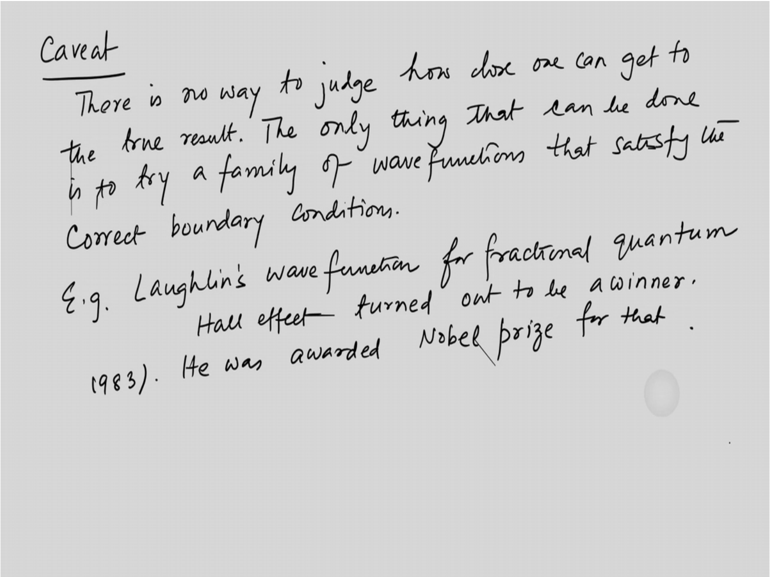

Caveat

There is no way to judge how close one can get to the true result. The only thing That can be done is to try a family of wave functions that satisfy the correct boundary conditions.

E.g. Laughlin's wave function for fractional quantum Hall effect turned out to be a winner. 1983). He was awarded Nobel prize for that.

Let us just write that caveat that we had just spoken that there is no way to justify a judge rather how close one can get to the true result. The only thing can be done is to try a family of wave functions that satisfy the correct boundary conditions. Once again Laughlin’s wave function for fractional quantum Hall effect turned out to be a winner. So, this was in 1983, and basically he was awarded Nobel Prize for that ok.

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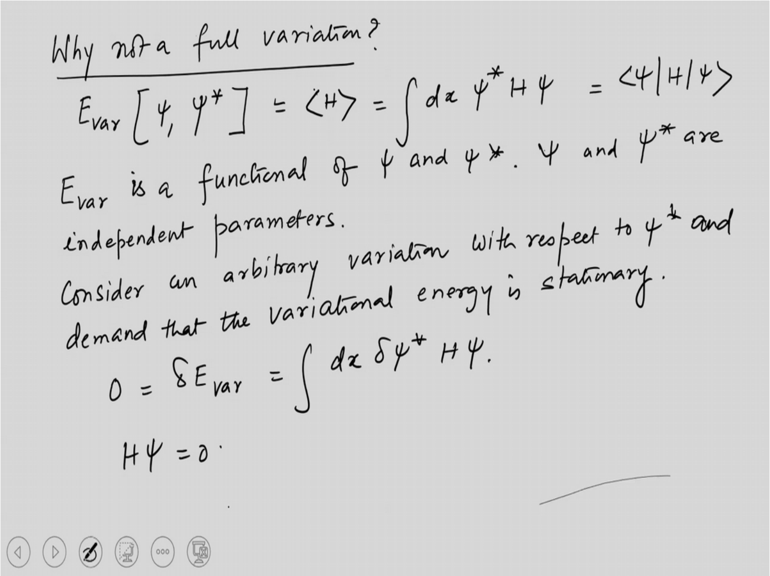

Why not a full variation?

$E_{var}[\psi, \psi^*] \doteq \langle H \rangle = \int dx\, \psi^* H \psi = \langle \psi | H | \psi \rangle$

E_{var} is a functional of ψ and ψ^*. ψ and ψ^* are independent parameters.

Consider an arbitrary variation with respect to ψ^* and demand that the variational energy is stationary.

$0 = \delta E_{var} = \int dx\, \delta\psi^* H \psi.$

$H\psi = 0.$

Let me end this discussion with a particularly important one that why not a full variation, and why a particular choice of the wave function. What we mean is that we can take the Hamiltonian. And take a wave function which satisfies the Schrodinger equation. And do a variation of the entire wave function of the family of wave functions not just choose one of them. And then minimize the energy with respect to the wave function not a particular variational parameter. And that would be much more accurate, but it turns out that that does not get us anywhere. In fact, we have brought to square one because of this following reason.

So, here our variational wave function is a functional of psi and psi star remember, because psi in general a complex quantity. Psi and psi star are linearly independent. So, this is the H the expectation value of H, which is nothing but a d x psi star H psi, and then we which is also written as psi H psi. So, E variational functional of psi and psi star. Here of course psi and psi star are independent parameters ok.

And we can consider an arbitrary variation with respect to psi star, I would it could be psi also, but just taking it with respect to psi star. So, this would give and demand that the variational energy is stationary. So, this is equal to 0 equal to delta E variational, and that is equal to d x delta psi star H psi, which gives H psi equal to 0 does not make sense, because this is the equation that we want to solve.

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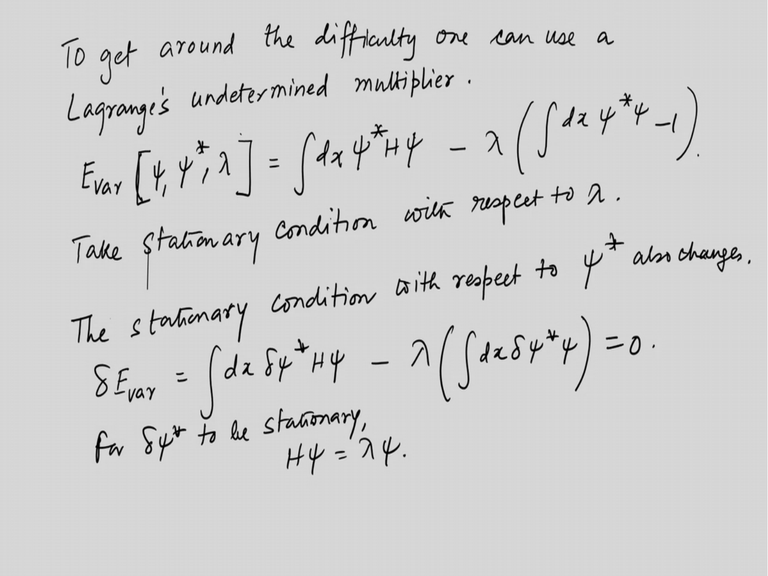

To get around the difficulty one can use a Lagrange's undetermined multiplier.

$$E_{var}[\psi, \psi^*, \lambda] = \int dx\, \psi^* H \psi - \lambda \left(\int dx\, \psi^* \psi - 1 \right).$$

Take stationary condition with respect to λ.

The stationary condition with respect to ψ^* also changes.

$$\delta E_{var} = \int dx\, \delta\psi^* H \psi - \lambda \left(\int dx\, \delta\psi^* \psi \right) = 0.$$

for $\delta\psi^*$ to be stationary,

$$H\psi = \lambda \psi.$$

So, one way to get around the difficulty is that one can Lagrange's undetermined multiplier, so that is called as lambda. So, now the variational energy is a functional of psi, psi star and that lambda. And that lambda is that enters, it is a psi star H psi minus lambda, and then there is a d x psi star psi minus 1. So, this is a functional of psi, psi star, and lambda; the stationary condition, now with respect to lambda and not with respect to psi or psi star. So, delta E variational, it is equal to d x delta psi H psi minus lambda.

So, so let me just explain this a little more clearly ok. So, if you take this stationary condition with respect to lambda, then the terms in the parenthesis that is this bracket would vanish. So, the properly normalized so for a properly normalized wave function there is an additional effect, which is the stationary condition with respect to psi star also changes, so that tells that delta E variational its equal to d x delta psi star H psi minus lambda d x delta psi star psi equal to 0, so that tells that for delta psi star to be stationary.

We get H psi equal to lambda psi. And in fact this is the one that we wanted to solve. This equation is same as the Schrodinger equation with the identification that the lambda is same as the energy. And we wanted to solve this, but this entire the variation with respect to the full psi or psi star leads to an equation that we are interested to solve, which means that we are back to where we were earlier. And hence, the utility of the variational method that is for a given a wave function with a single or you know even a number of variational parameters, but at least one class of them will have to be treated at one point of time.

If you are dissatisfied with that wave function, you can take another wave function, and can go ahead and do the calculation and see that whether that yields tighter bound to the ground state energy or the minimum energy exact energy that is possible. And as we said that it can also be done for the excited state energies provided you apply the correct boundary conditions.

And so this variational method in general is very powerful. And as we have said that in the a context of fractional quantum Hall effect, which could not have been solved using a perturbation theory or it is not a there is no perturbative solution corresponding to that. And same with BCS theory, these are non-perturbative problems. So, the variational theories came to the rescue.

And once one writes down a correct variational wave function, it is always possible to get good bound on the ground state energy. And as we said earlier that it could the energy obtained from a variational calculation could never be below the actual energy. However, it will give the amount that it is close to will be dependent on the choice of the wave function.