ELEMENTS OF MODERN PHYSICS

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Lec 13: Variational Theory

We shall be doing variational theory. This is one of the approximate methods that is used to deal with problems in quantum mechanics. To distinguish it from the perturbation theory that we have done, there are in fact two of these approximate methods. There is another semi-classical method that we have not talked about, which is called the WKB approximation. Now, this perturbation theory that we have talked about in detail is applicable to systems where there is a small parameter available, such that you can expand the Hamiltonian in terms of this small parameter, with the understanding that when this parameter is equal to 0, the problem is exactly solvable.

So, if you have H equal to H0 plus lambda H prime, where lambda is a small parameter, and not keeping terms which are of the order of lambda squared, lambda cubed, and other higher powers of lambda, then the solution to the H0 problem is completely known. And the understanding is that the system, because of this introducing this lambda H prime, the system doesn't go too far away from the state from its, you know, the unperturbed states. And we can calculate the corrections to the energy in first order in lambda or second order in lambda. And also we can find out the corrections to the wave function in these, you know, first and second powers of lambda and so on.

Two approximate methods:

1. **Perturbation Theory**: Applicable for systems where a 'small parameter' is available. The underlying assumption is that the Hamiltonian is exactly solvable when the small parameter goes to zero. Examples: Stark Effect, Zeeman Effect etc

$H = H_0 + \lambda H'$

2. **Variational Theory**:
   (a) No need to have a small parameter.
   (b) Any general Hamiltonian can be solved.
   (c) Most suitable to obtain the ground state (with limited efficiency, works for the excited state as well.
   (d) Examples: Fractional Quantum Hall Effect (FQHE), BCS Theory..

These are called first and second order perturbation theory and so on. There is another approximate method where there is no need for a small parameter. In fact, there is no division between this H that is known. There is an H that is known, but we do not know how to distinguish it or rather split it into two terms, which are H0 and lambda H prime, such that the solution to H0 is known, and that facility is not there.

So, in a way to say that this H comes as a, you know, a compound problem or rather as a compound Hamiltonian, which has no such splitting available that we have seen for the perturbation theory. So it has it can be any general Hamiltonian can be solved even if there is a strong term which or rather strong term in the Hamiltonian which cannot be dealt with perturbatively. And it's actually this theory that we are going to discuss is most suitable to obtain the ground state. But of course, if you extend the formalism to the excited state, you'll not be doing too much of mistake. In fact, it works as we'll see in some problems.

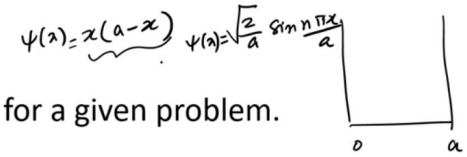
And these have been used in some really classic problems, which are known as this fractional quantum Hall effect, which was introduced by Laughlin. So he introduced a variational state and he got these energy of these, this problem or other energy of these electrons interacting electrons. to be very, very close to the actual energy. Actual energy means which is done or rather obtained by exact diagonalization of the problem. There is another classic problem in superconductivity where again variational method is used and one has obtained the using a variational ground state for the problem.

One has obtained the equation for the gap, the energy gap that separates the, you know, the field Fermi sea. to the superconducting gap. So basically it gives you a relationship between how the gap behaves with temperature and as you increase temperature of course these electrons which are formed a cooper pair will dissociate and they'll no longer be superconducting state. So when does this energy gap due to this superconducting state that sort of vanishes with temperature.

So, that even that is a variational theory. So, there are a few caveats, there are a few warnings so to say and one needs to have a good guess wave function for a given problem because we do not know anything about the H, the splitting of H, neither we know how to solve H. So, we need to have a guess And the better that the guess you have, the better estimate that you would have for the energy. And so this goodness of the guess wave function will decide how tight the upper bound to the ground state energy is. Okay.

which means that you will always get an upper bound to the ground state energy and not something, you will not get an energy which is lower than the ground state energy by doing a variational calculation. So, you will get something which is above the ground state energy, but how close you get to the actual ground state energy would depend on the choice of the wave function or the guess wave function. And this guess wave function has some scientific name called as, you know, either you call it an Ansatz or you call it a trial wave function. But nevertheless, it remains as a guess wave function. And how do you choose the goodness of these guess or how appropriate is your guess?

Caveat:



One needs to find a 'good' guess wavefunction for a given problem.

The 'goodness' will decide how 'tight' is the upper bound to the ground state energy.

The 'goodness' will be decided by the symmetries and boundary conditions of the problem.

There is in principle no way to judge how close the result is to the 'true' result.

Probably many different 'guesses' should be tried to zero in on a given wavefunction.

How would you decide on that? Is there any guiding principle? I mean, there is really no guiding principle, but you have to look at the problem and imbibe all the symmetries or the conditions that are there. So, for example, you have done this problem of particle in a box. So, the particle is between 0 and a.

And we know that the solutions are root over 2 by a sine n by x by a. These are the ground. I mean, these are different energy eigenstates for different n and n can take values 1, 2, 3, etc. And we know the corresponding energy as well. Now suppose we do not know this problem and we simply say that you know this is a trial wave function. So, this is Psi of X instead of this Psi of X which is a known problem.

Now you see that even though this looks very very different than the sinusoidal difference that you or sinusoidal variation that you have in the wave function. but it still has the two basic symmetries of the problem is they are covered. So, at x equal to 0, the

wave function goes to 0 and at x equal to a, the wave function goes to 0 as well. So, this is a guess wave function which is not too bad because it really respects the parent symmetries that the wave function has to vanish At both the walls, because these walls are infinitely high and the particle cannot escape.

So this is what I meant by the boundary conditions or really the symmetries and and the conditions that are imposed on the problem in order to solve it. So there is really no way to judge how close this result to be to the true result. Like if you use this wave function and calculate the ground state energy, etc. by, you know, operating it by with the Hamiltonian and then calculate the expectation value of energy. It is not very clear that whether this will give a better estimate to the ground state energy which is given by say pi square h cross square by 2 m a square or something else will give a better estimate.

So, there are many different cases that would have to be, you know, tried out in order to arrive at the one which gives you the tightest bound to the ground state energy or which lies closest to the ground state energy. So, let us do the formalism as briefly as we can and then try to do one or two problems. So, let us say that this is the formalism part that we need here. Okay, so let you know psi 0 be the ground state. Let me write true ground state.

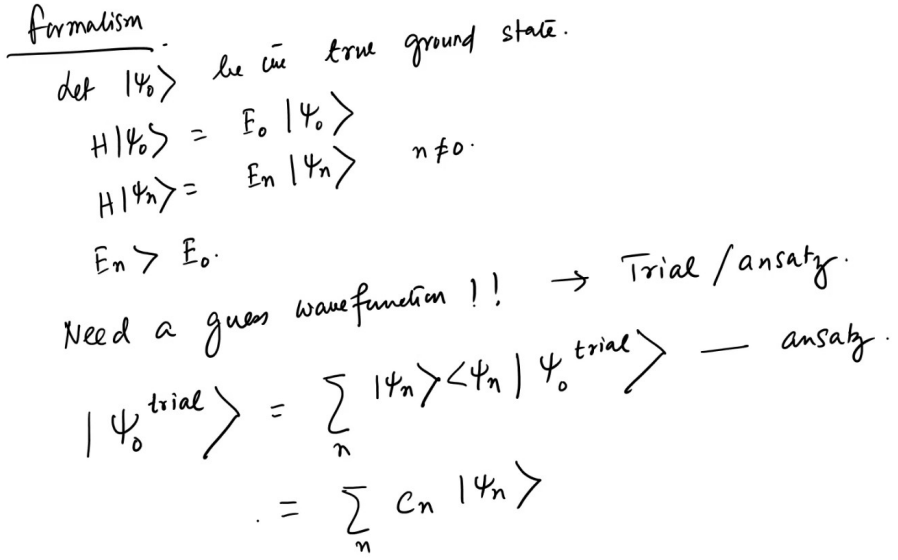
So, we will say many things with this word called true and guess or true and trial or true and ansatz. These trial, ansatz, guess, they all mean the same thing: that is, we are making sort of an assumption for the wave function that we think is suitable for a given problem. We do not know this, of course, this psi 0, but let this be the true ground state. So, H acting on psi 0 will give E 0, which is the ground state energy, and returns me this wave function, okay. And it is also true that if you make it act on any of the excited states, which are these E n and n not equal to 0.

So, this will give all the excited state energies. So, the Hamiltonian acting on any state will return the energy of that state and will return the wave function itself. And it is very clear that E n is greater than E 0 because E 0, by definition, is the ground state energy, which is the lowest energy of the system. So, we now resort to this guess wave function or trial wave function for this H because we do not know what is going to be the ground state or what is going to be even the excited states, any of the states, basically the eigenstates of H, we do not know. So, we need a guess wave function.

And so, let us call this trial wave function or, alternatively, you can call it an ansatz; you make an ansatz about the wave function. And let us call this psi 0 trial. Because this is a

ground state, we do not know what psi 0 is, so we take a trial wave function, okay. And so, what is the trial wave function that is going to look like? So this would be, you know, different from the actual psi 0, but it could very well be a linear combination of all the eigenstates of the system.

So how do we write that? The true eigenstates of the system. We do not know either of them; that is, we do not know psi n, but we can say that it is basically a linear combination of all these. Excited or, rather, all the eigenstates of the system. So, this is a linear combination.



So, this trial wave function—this is the ansatz that we make—is actually a linear combination of all the different eigenstates of the problem. This can now be written as Cn and Psi n, okay, and sum over n, with n including everything, okay. And so, this will tell us that the ansatz is exact. If C0 equals 1 and all the other Cn are equal to 0 for n not equal to 0. So, which means that you are trying to find out the ground state and you expand it in terms of all the eigenstates—available eigenstates of the problem—and if you are really making an ansatz for the ground state.

Then the C0 coefficient, which corresponds to the ground state, should be equal to 1 or as close to 1 as it can get, and all the other Cn's will nearly vanish. So that it becomes the best guess for your system. And of course, the normalization would demand that your C0 squared plus all the n not equal to 0, Cn squared, this should be equal to 1. So, that is a

normalization. Let me write this: it is demanded by the normalization, okay. So, what will happen to the expectation value of energy?

And this will be with this trial wave function that you have. It is psi 0 trial. There is no problem in calculating this because you know the Hamiltonian. And then you can calculate this expectation value. And this would simply be equal to C0 mod squared E0 plus all these n not equal to 0, Cn mod squared En.

And this certainly, because of this second term, will be greater than or equal to E0. OK, because with your C0, the ideal situation—the equality will prevail when C0 equals 1 and all other Cn's are 0. But suppose for a moment that C0 is less than 1, and all the other Cn's will account for whatever is less than 1. And then this would give a ground state energy, which is basically this. The left-hand side is greater than or equal to the ground state energy.

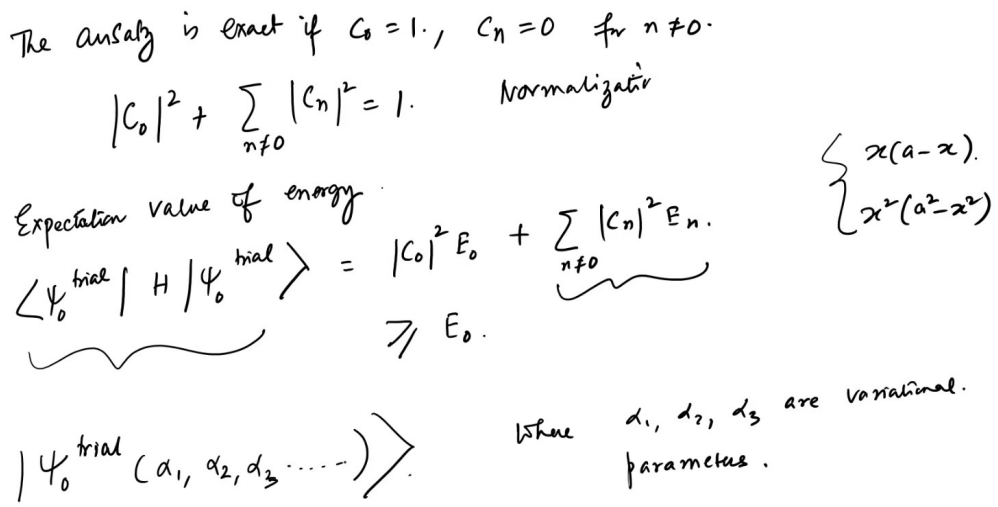
And that's what you get. This is what we were trying to say by saying that that you get a tightest bound or an upper bound to the ground state energy. So you don't get the ground state energy exactly. but you get an upper bound and how close it is to the actual easy row will depend upon how good your trial wave function is. And as we have said that there is no a priori way of knowing that even two wave functions having you know they obeying all symmetries will give different these expectation values or the estimate of the ground state energy.

and the one that's actually closer to the actual energy would prevail, or the one that's lower in these two, because you don't know what's the exact ground state energy, the one which is lower. Say, for example, we have given this particle in a box at x into a minus x, but you can have a x square into a square minus x square as well. this also goes to 0 at x equal to 0 and at x equal to a and both of them will have different energies. We of course you do not see a variational parameter here but this variational parameter can be you know put in fact in these problems it is always put in the exponent for the particle in a box but we will do some other problems where you see that you can actually minimize it with respect to the these variational parameter.

So, what you need to do is that you would get this quantity to be a function of the variational parameter, minimize it with respect to the variational parameter. I say minimize, but it is actually extremize which means the see the derivative with respect to the parameter that is variational parameter is equal to 0 and then get that out, put it back into the wave function and that will give you the variational ansatz or that is the trial

wave function that you get. So, once again coming back to the context is that you get an upper bound to the true ground state energy. And sort of a better estimate will give these, you know, the C0 squared to be very, very close to 1.

And that will make these, you know, the equality gradual or inequality gradually becoming equality. In fact, the converse is also true that states with lower, you know, energy or expectation value of this Hamiltonian, they have better overlap with the ground state. Okay. So, based on this, let us propose that these, you know, psi 0 trial that we are talking about is really a function of these, you know, variational parameters, let us call them alpha 1, alpha 2, alpha 3, and all that.



And so, these alpha 1, alpha 2, alpha 3 are variational parameters. which are tunable and which are tunable means that which values of alpha 1, alpha 2 and alpha 3 would minimize this energy that is expectation value of H between these states, the trial states would have to be, you know, those are the ones that are going to be important for our discussion and they would have to be put back into this I0 trial to get this variational wave function. So, your E0 trial is going to be a function of all these alpha 1, alpha 2, and so on, and this is nothing but this psi 0 trial, and you have these alpha 1, alpha 2, and all that, and then H, and then psi 0 trial alpha 1, alpha 2, and all that. So, this is your trial energy and all that, and then what you do is that these alpha 1, alpha 2 can be found out by putting this del E0 trial del alpha 1 equal to del E0 trial del alpha 2, and so on, all

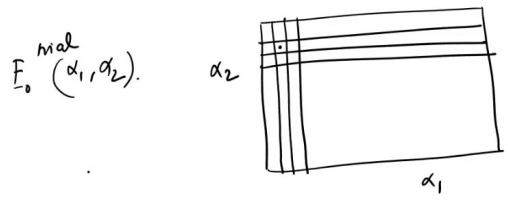
these equal to 0. Calculate alpha 1, alpha 2, put them back into psi 0 trial, and that will be your variational wave function.

There is one problem as far as, you know, the working out of these expressions goes, that suppose we talk about two variational parameters. Let us talk about just alpha 1 and alpha 2. And if you think about it, your E0 is a function of that. So E0 trial is a function of that. which means that you have to simultaneously, you know, find out the zeros of these two quantities, that is, del E0 trial del alpha 1 has to be 0, and at the same time, the del E0 trial del alpha 2 equal to 0 as well.

So, this simultaneous vanishing of that means that you have to actually find a minimum of this energy. In a space that is spanned by, say, alpha 1 and, say, alpha 2. That's a very difficult task because then you have to make grids here, and these grids you have to calculate these E0 values, E0 trial values at each point, either at the corner of the grid or at the center of the grid, and so on and so forth, and see where this energy is minimum. So, this is a huge computational task, and you need to make these grids finer and finer in order to get these alpha 1, alpha 2 values to be the ones that really minimize this E0 trial. And if you do not do that, then these alpha 1 and alpha 2 are really a little far away from where the E0 is truly a minimum, then that will defeat the purpose, and the corresponding psi 0 trial that you get would not be a good wave function to give you the tightest bound to the ground state energy.

$$E_0^{trial}(\alpha_1, \alpha_2, \dots) = \langle \psi_0^{trial}(\alpha_1, \alpha_2 \dots) | H | \psi_0^{trial}(\alpha_1, \alpha_2 \dots) \rangle.$$

$$\frac{\partial E_0^{trial}}{\partial \alpha_1} = \frac{\partial E_0^{trial}}{\partial \alpha_2} = \dots = 0.$$



So, it is always a problem if you have more than one variational parameter. So, in fact, we will try to—we will, of course, do examples where there is just one variational parameter, but I still explain that if you have more than one, then you sort of look for

another condition that connects alpha 1 and alpha 2. And this is precisely the thing that has been done by BCS theory. There were two variational parameters, but the normalization actually demanded that

they are connected or, rather, you know, there's some other condition that connected them, and hence you only had one variational parameter with which you were required to minimize the energy and put it back then into the variational problem or, rather, the trial state. So, uh, Having done this part, it is small and simple, easy to understand, but sometimes the working principle is quite difficult. And, in fact, we will see that—let us take an example of, so let us do the ground state of the hydrogen atom. And let us take a variational wave function as—so just to remind you that the actual, it is a true ground state.

So, just to, for your reference, let me write down the true ground state. This is equal to root over pi a0 cube exponential r over a0, a0 is the Bohr radius, okay. And suppose we do not know this. We are for, you know, for demonstration purpose, we will only take problems that are known. But of course, you can apply these formalism to Hamiltonian or a system where you, you know, do not know this, the true wave function at all.

All right. So, and just to tell you that the energy is given by minus, you know, E square by 2 a0 and which is as a value which is minus 13.6 electron volt. Okay. So, let us take a psi 0 trial. So, suppose for the moment we do not know this.

So, we are not aware of this and we need to solve the problem. We need to get an upper bound to the ground state energy of the hydrogen atom. So, we propose that your psi trial is that has a form which is say root over pi alpha cube minus e to the power r over alpha. okay even though it looks very similar to the actual wave function what we have done is that we have introduced a variational parameter here and written down a state which is which is very similar in fact it is like an exponentially decaying state but that you know, can be written down because we know that the electronic wave function would decay and essentially would go to 0 at r equal to infinity.

So, with this premise, we can write down this variational parameter, and this is actually a function of alpha, which you see and which is the variational parameter that we are talking about. Do not mind at this moment that they are nearly the same, so we should get the same values or energy values, but this is for demonstration purposes only, to show how a variational method works. We have this Hamiltonian to be equal to p square over 2m. And minus e square over r. So, if you have this, then we can calculate p square over

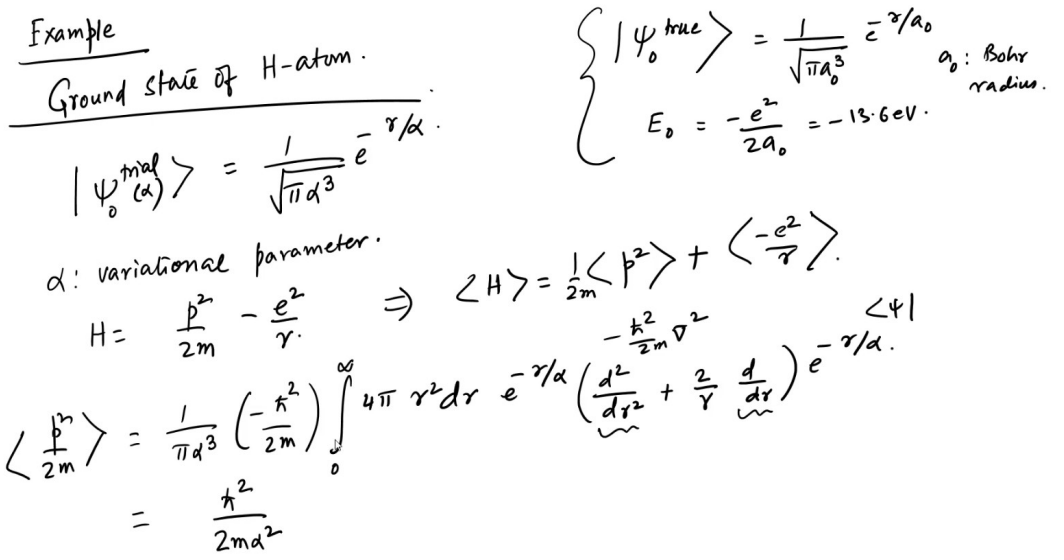
2m, the expectation value, which we are calculating. So basically, this tells us that the expectation of H is p square 1 over 2m expectation plus these.

Minus E square by R expectation, and what do we use for calculating these expectation values? These wave functions. So, these trial wave functions are what we use here, and we can do that. This actually looks like we use term by term, and then, you know, there is a 1 over pi alpha cube. Minus h square over 2m. Remember that this p square is minus h square over 2m, and then there is a del square, but now this del square has got a r term and a theta phi term, and these r terms will, you know, have to be considered here.

And because the wave function, the trial wave function that we have taken, does not depend on theta and phi, okay. So, they will simply, the integration of them will give, you know, the sine theta d theta d phi, which is equal to 2 pi into 2, 2 pi coming from the phi integral and 2 coming from the theta integral, and that will give you 4 pi. And so, this is equal to a 4 pi r squared. dr e to the power minus r over alpha, that is the psi star, that is, you know, this bra psi is what we have written here, including the energy integral. Sorry, there is no pi square, so it is 4 pi.

And now, the radial part of this del square term is d square d2 dr2 plus 2 by r d dr, and this is going to act on exponential r minus alpha, okay. So, that is what you have to calculate. And if you do it patiently, there are, you know, terms that you need to. So, on the right-hand side, there is an exponential minus r by alpha. For this term, you have to take a double derivative.

For this term, you have to take a single derivative and then finally calculate these terms. Integral from 0 to infinity, and so you need a gamma function integral which has already been told. So, this is equal to h square by 2 m alpha square. So, that is the expectation value of the kinetic energy term. Now, we will see the potential energy.



So, now you have a minus e square over r. And this is equal to, again, pi alpha cubed and a minus e squared. And once again, a 4 pi r dr. There's no r squared because there was a 1 over r that cancels with r. So it's r dr and exponential minus 2r over alpha. There's a simpler term because this term does not do any operation. There's only a 1 over r.

So, this integral if you evaluate again using a gamma function integral it becomes E square by alpha. So, that tells you that your E 0 which is a function of alpha E 0 trial function of alpha which becomes this H square. over 2m alpha square and minus E square over alpha. So, if you minimize this E0 trial, that is DE0 trial alpha D alpha, put that equal to 0 and so this becomes equal to so d d alpha of this term.

So, it is h cross square over 2 m alpha square minus e square by alpha. This is equal to 0. That, you know, gives alpha equal to h cross square over m e square. And if that is true, then, of course, your psi becomes equal to 0. 2 over pi this alpha square that we have just got hold to the power.

In fact, this is you know the psi trial, psi 0 trial. Now, this thing was what we have started with is this 1 by pi alpha cube. e to the power minus r by alpha. So, put this alpha there. So, I do not write it, but you can write it.

So, you can write e to the power minus r over alpha. So, put this alpha here, and that will give you the trial wave function and so on. Okay, and suppose, so actually you get a ground state energy which is exact because you have taken something as a variational parameter, your A0, the Bohr radius was actually taken as a variational parameter and

you landed up by, you know, minimizing the energy with respect to alpha, you landed up with an alpha which is exactly like that, which is nothing but the Bohr radius and so on. So, this gives you exactly 1 by pi a0 cube e to the power minus r by a0 and this is the exact result, exact wave function, ground state wave function, okay. and the reason is that that you did not you know play around much with the wave function and you have been quite in a bid to sort of preserve the symmetries you have taken it exactly the one that comes you know the true ground state basically and then you get this result.

$$\left\langle -\frac{e^2}{r} \right\rangle = \frac{1}{\pi\alpha^3}(-e^2)\int_0^\infty 4\pi r\,dr\, e^{-2r/\alpha} = -\frac{e^2}{\alpha}$$

$$E_0^{trial}(\alpha) = \frac{\hbar^2}{2m\alpha^2} - \frac{e^2}{\alpha}$$

$$\frac{dE_0^{trial}(\alpha)}{d\alpha} = 0 \Rightarrow \frac{d}{d\alpha}\left(\frac{\hbar^2}{2m\alpha^2} - \frac{e^2}{\alpha}\right) = 0$$

$$\alpha = \frac{\hbar^2}{me^2} = a_0$$

$$|\psi_0^{trial}\rangle = \frac{1}{\sqrt{\pi\alpha^3}} e^{-r/\alpha}$$

$$= \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \longrightarrow \text{Exact wavefunction.}$$

Let us say you try out a different one, okay. So, let us say you try out a Psi of alpha, something different, and maybe wildly different, and so this could be like 2 by pi alpha square. So, hold to the power 3 by 2 and exponential minus r square by alpha square. Okay.

How do you get this factor? This factor is obtained from this psi, psi equal to 1. In fact, what I did not say is that your expectation value of H or the energy that you get—so this is E0 trial—you need to actually do the normalization. So, it is psi 0 trial, H psi 0 trial, and this divided by psi 0 trial, psi 0 trial, okay.

So, this normalization has to be done. So, this normalization gives this. But you see, interestingly, we have taken something which is completely wrong and we should not have taken it in the first place because it is a Gaussian and the form of a Gaussian really looks like this, okay. So, this does not exclude the possibility that the electron can

actually penetrate inside the nucleus because this R square by alpha square will have finite extent on both the positive and negative sides of R.

But the negative side of R, which means inside the nucleus, it cannot penetrate. And this is visibly wrong. But let us start with a wrong variational state, calculate the energy, and see how close that energy could be. So once again, we repeat this procedure, and I will simply write down the results here. So, you can try it out exactly the way you have done it.

So, 2 by pi alpha square whole to the power, you know, this is 3, and you have a minus h square over 2m and then we have a 4 pi r square dr e to the power r square by alpha square. So, then you have this d2 dr2 plus 2 by r d dr and then you have this e to the power minus r square by alpha square from 0 to infinity. If you calculate that, you get 3 h cross square by 2 m alpha square. So, that is your p square over 2m expectation, and the expectation of minus e square over r is simpler; that gives you minus 2 root 2 by pi root pi, and one gets e square over alpha. So, now if you do a del E0 trial,

del alpha, then what you get and put that equal to 0, this will give us an alpha equal to 3 root over pi h cross square divided by 2 root over 2 m e square. Now, I leave that for you to do this algebra, but this is what you get for the alpha that is the variational parameter and this variational parameter interestingly gives the ground state energy or the estimate for the ground state energy to be equal to minus 4 over 3 pi and e to the power 4m and h cross square and this really is 0.85 times the E0. So, E0 is minus 13.6.

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

$\langle \psi | \psi \rangle = 1$.

$\left\langle \frac{p^2}{2m} \right\rangle = \left(\frac{2}{\pi\alpha^2}\right)^3 \left(-\frac{\hbar^2}{2m}\right) \int_0^\infty 4\pi r^2 dr\, e^{-r^2/\alpha^2} \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) e^{-r^2/\alpha^2}$

$\langle H \rangle = E_0^{trial} = \frac{\langle \psi_0^{trial} | H | \psi_0^{trial} \rangle}{\langle \psi_0^{trial} | \psi_0^{trial} \rangle}$

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

$\left\langle -\frac{e^2}{r} \right\rangle = -\frac{2\sqrt{2}}{\sqrt{\pi}} \frac{e^2}{\alpha}$.

$\frac{\partial E_0^{trial}}{\partial \alpha} = 0 \Rightarrow \alpha = \frac{3\sqrt{\pi}\hbar^2}{2\sqrt{2}me^2}$

$E_0^{trial} = -\frac{4}{3\pi}\frac{e^4 m}{\hbar^2} = 0.85\, E_0$.

So, it comes as close as, you know, 85% of that. So, you are only off by 15%. By taking a very wrong wave function, okay, the wave function which does not obey the basic symmetry of the problem, you still get something which is as good as that, okay. All right, so it works well, 85% is not a great estimate, but it is nevertheless with trial wave function without any thought, it is giving that, you know, as close to the actual ground state energy is also something that is interesting. Let us see whether how well it works for the excited states.

We have said that with limited efficiency, but it may actually work better than that, provided you take the correct symmetries and so on. So the whole thing is that if you make an ansatz for the excited state, say the first excited state, it should correspond to a different quantum number as compared to the ground state. And that condition would make it to be orthogonal with the ground state. So, which means that now, even if there is no quantum number associated with the first excited state, it will still be, you know, I mean, distinct quantum number, it will still be orthogonal to the ground state. And let us see the, as an example, see the 2P state of hydrogen atom.

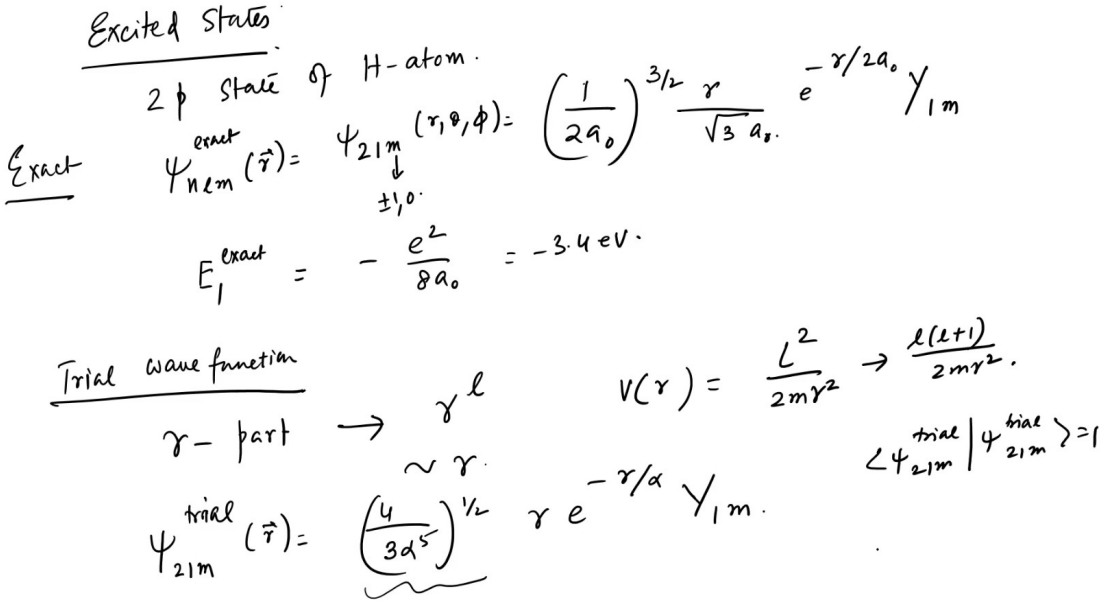
And this 2p state is n equal to 2, so it's like 4-fold degenerate and all that, and so the true wave function for this is psi nlm, this is r, this is equal to psi 2, and because we are talking about a p state, it's a 2, 1. Now, this 2, 1, then we can have m, which I leave it, and this m can be equal to plus minus 1 or 0. So, this and r theta phi, this is equal to 1 over 2 a0, this is the exact one, this is not the variational one. So, this is 3 by 2 and r divided by root over 3 a0. And e to the power minus r over 2a0, and then there is a y. Now, I just leave m as m, so it is a ylm, it is l is equal to 1, and m can take three values that we just saw, plus minus 1 and 0.

And again, the exact energy for this, so this is exact energy. And the exact energy for this is equal to minus e square over 8 a0 and that has an energy which is close to minus 3.4 electron volt. So, that is the exact problem and this exact problem lets you know make an ansatz for the trial wave function. So, let us take the trial wave function to be. I mean just make some ansatz that because this R part of the trial wave function, it must be something like R to the power L because you know this radial part has this L dependence and where it comes from is that there is a part of this.

The potential term which is like L square by 2m R square and this is L into L plus 1 divided by 2m R square. So, we make an ansatz that the r part is given as r to the power l or now since we are talking about l equal to 1, so the r part here goes as r and we will not

make too much of. Change otherwise this equation that this part of the, this exponentially dying part of the wave function. So, we make an ansatz that psi, now it is 2, 1, m trial. So, this is trial and as a function of r is 4 by 3 alpha to the power 5.

to the power half r e to the power r by alpha and y1 m. We have not changed much. Apart from that, we have introduced a variational parameter. And this term that you see is coming from the normalization, as I said. So you take some normalization A and then do a demand that this is equal to 0.



That is, this 2 1 m trial with an overlap with itself is equal to 0. Sorry, it is equal to 1, not 0. pardon me, this is equal to 1 and then this constant will or rather this coefficient will come out and now we have this important part of the wave function which looks like this and if we go ahead and calculate again the expectation value of the kinetic energy term that will give us so this is like now you have a h square over 2m now you need an additional term in the this r part of the kinetic energy which is coming from these potential terms. So, there was a V effective which is when we write this is this V effective I mean this one part of that.

So, let us not you know some V part which is coming from the radial part of the kinetic energy. And so, this 2 by r d dr minus l into l plus 1 r square, this term was not there for these equations. for the L equal to 0, that is the ground state. So, you have to calculate this and this one again with this Ansatz wave function and calculating this expectation

value will give us h cross square divided by 2m alpha square. This part of this calculation, like this part, they are already done and this is simple because it is just getting multiplied with 1 over r square.

So, it is not going to be difficult. So, this is h cross square by 2m alpha square. And for the potential energy term, which is minus e square by r, is equal to minus e square over 2 alpha. And so, once again, what we do is take the derivative. of this dE, now it is 1 trial d alpha that is equal to 0, and this gives us alpha equal to h cross square by 2 m e square, and that gives an E min equal to E square m by 8 h cross square, and once again, this is exact. And why is it exact?

So, this is really the trial E1 trial. So, this is exact, and the reason it is exact is clear to you because we have taken nearly the same wave function obeying all the symmetries. So, that is pretty much what one does in these variational calculations. These are not too difficult calculations, but they are lengthy at times because you need to calculate the expectation value of the kinetic energy and the potential energy. And here, the potential energy is simpler to calculate because it does not involve any operation.

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle -\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right)\right\rangle$$

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

$$\left\langle -\frac{e^2}{r} \right\rangle = -\frac{e^2}{2\alpha}.$$

$$\frac{dE_1^{trial}}{d\alpha} = 0 \Rightarrow \alpha = \frac{\hbar^2}{2me^2}.$$

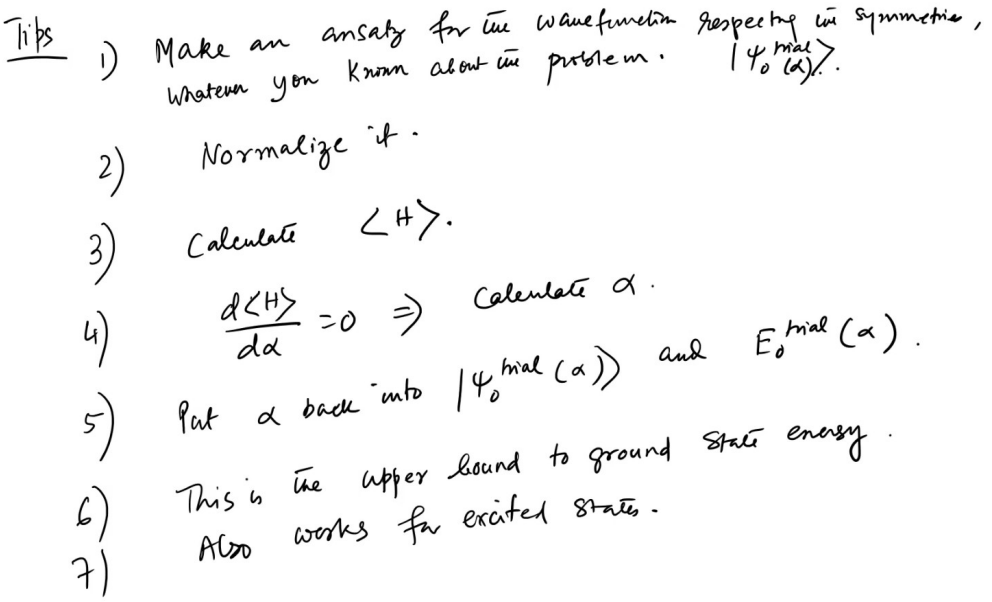
$$E_1^{trial} = -\frac{e^2 m}{8\hbar^2} \quad : \text{Exact}.$$

But because of the complexity of the kinetic energy term, that is the del square operator written in the radial coordinates. Well, I mean, radial coordinates means that you have some coordinates there, I mean, which is a theta coordinate there, but that has been taken care of. And So, you should remember that this expectation value has a dependence on theta. So, this Y1m has a theta dependence and, of course, a phi dependence.

So, they cannot be taken out. As a 4π, as opposed to when we did it for the ground state. So, with all these conditions in mind and doing it correctly because it is laborious but not difficult. So, one needs to do it carefully and without making any mistakes. So, one also needs to normalize the trial wave function.

Because that is needed to calculate the expectation value. So, for a given problem, the suggestion is that you make an ansatz. So, this is like tips. So, make an ansatz for the wave function, respecting the symmetries and, importantly, whatever you know about the problem.

So, use all that information in order to, you know, write down this wave function, normalize it, If you normalize it, then you do not have to, you know, calculate the expectation value of H. Okay? So, calculate this dH, put dH/dα equal to 0, calculate α. So, this will give you a Ψ_0 trial, which is a function of α. Put α back into Ψ_0 trial(α) and E_0 trial(α). This is the upper bound to ground state energy, which also works for excited states, okay?



We do not want to say much about the excited states for the reason that talking about an upper bound to a particular or other first excited state energy, one has to see how well it gives a tighter bound and so on. So, let us keep it for the ground state mainly and follow these steps in order to solve a given problem. We are given a few examples, mostly related to the hydrogen atom, but that conclusively sets the platform for you to solve

more problems. So, we will stop here for today and continue with some more approximate methods in the next session.