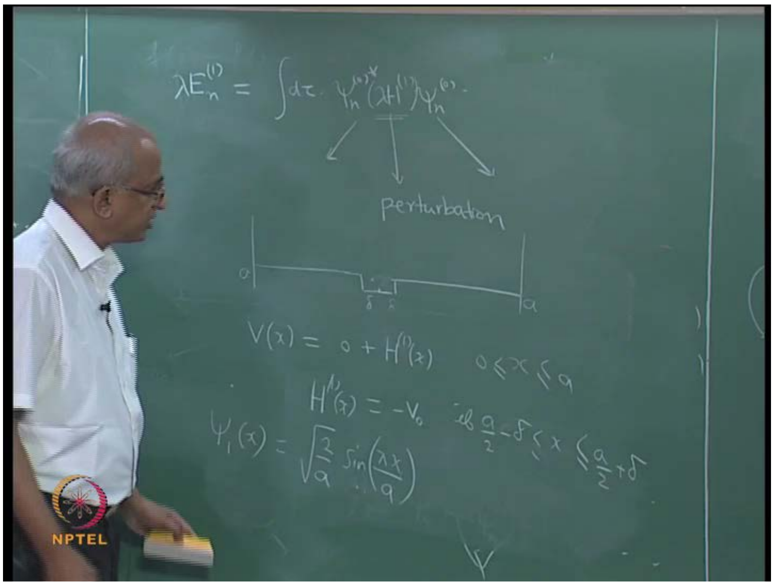
Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 37
Perturbation Theory – Continued

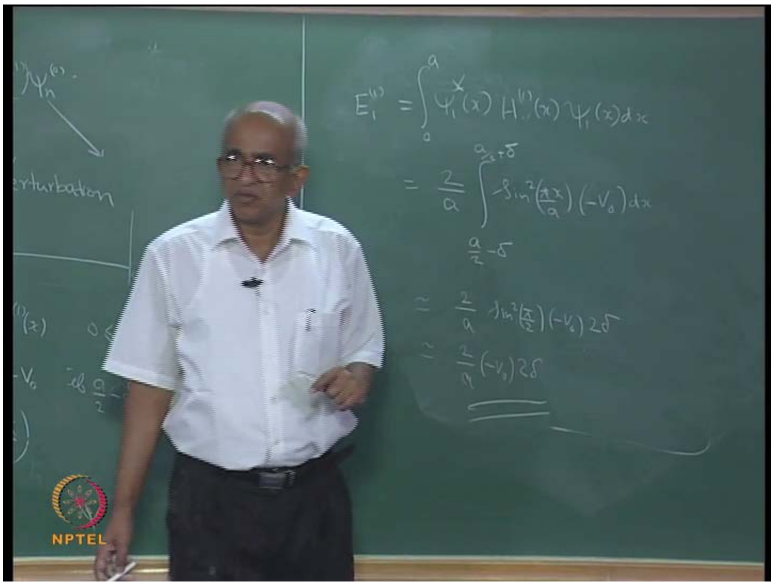
(Refer Slide Time: 00:20)



Just to illustrate; suppose I had a particle in a box. This is my particle in a box, it extends from 0 to a. And what I will do is, right in the middle, I will put a small well probably representing an hydrogen atom sitting there, if you feel like. And so how will I put the well or this one? The way to do that is, I will say that V – the potential energy is equal to 0 plus probably let me say some delta v of x. Zero was your original expression. See this is my delta v is the perturbation. So, it is 0 if x… If potential energy is 0; I mean if x is between 0 and capital A, this is how the potential is. What is the definition of delta v of x? It is equal to some minus – what do you want to call it? Probably minus v 0, if x is between a by 2 minus delta and a by 2 plus delta. All that I am saying is you see this is the middle of the box; let me modify this figure a little bit. This is the middle of the box. And you think of this length as delta. So, that the whole thing, this whole small well has a width of 2 delta, and within that region, the potential has the form minus v 0.

Maybe the best thing is to say that I do not use the symbol delta v. But, instead this is the perturbation. So, this is my H 1 of x, and so this is my H 1 of x. Correct? Therefore, if you wanted to calculate the first order correction to the energy of the lowest possible state; lowest possible state is what? In this case, it is actually what we have referred to as psi 1 of x; it will be equal to square root of 2 by a sin pi x divided by a. This is the eigenfunction for the lowest possible state for a particle in a box. So, what you will have to do is, you will have to calculate the expectation value of this H 1 using that psi 1. So, what will be the kind of expression that you would have, I can just write it down.

(Refer Slide Time: 03:41)



What is going to happen is, you will have psi 1 x; in principle, you should put a star; then H 1 of x psi 1 of x dx integrated from 0 to a. This will be the first order correction to the ground state energy. First order correction to the ground state energy is nothing but the expectation value of the Hamiltonian. This is the Hamiltonian. When I say Hamiltonian, I would mean the first order correction to the Hamiltonian. So, if you think about this integral, what will happen? I mean I can say psi 1 is given by that expression. Therefore, there will be square root of 2 by a occurring 2 times or 2 by a in total; then you will have sin square pi x divided by a. And you will have to put in H 1. What is H 1? H 1 is actually minus v 0 provided the x coordinate is between a by 2 minus delta and a by 2 plus delta. Therefore, you can say a by 2 minus delta to a by 2 plus delta into dx. This will be the first order correction to the energy. I mean if you wanted to… To know how much this is approximately, then you can say this interval delta is very small. If it is very small, then I can say this function is not going to change much over that small interval.

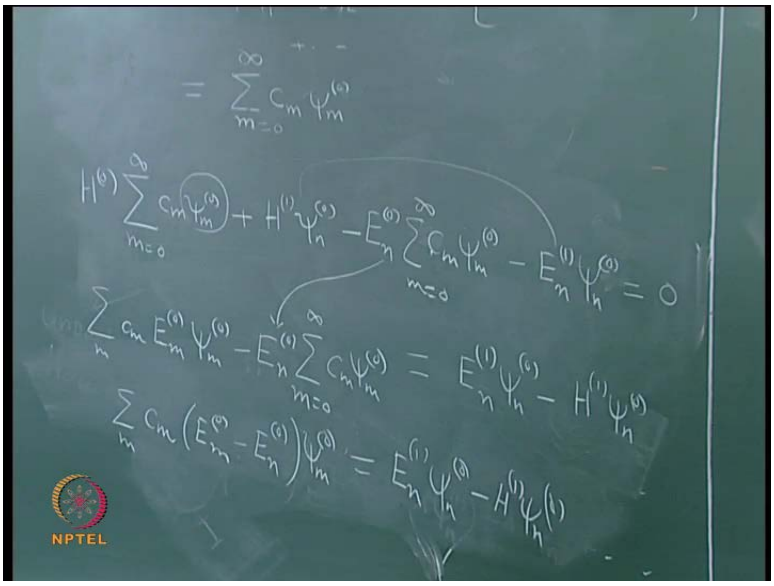
And therefore, I can replace the value of this by the value at the right at the middle of the box. And then what will happen, I will have 2 by a.

If you say you are in the middle of the box, x is actually equal to a by 2. Therefore, you would get sin square pi by 2 into minus v 0 into… If you did the integral, you are going to get the answer 2 delta. I wonder whether I am going fast, but this is a simple calculation. Therefore, what happens is, you will get 2 by a into minus v 0 into 2 delta as the answer. This is assuming that, delta is very small. Why did I get this sin square pi by 2? The reason is that, you see because delta is very small, I approximated the value of the wave function by its value at the middle of the box. This is actually… This one is sin square pi by 2 is coming from the value of the wave function at the middle of the box. And therefore, this is the correction to the energy.

But, suppose I was thinking of the first excited stage and did the same calculation; what would you expect? How is the first order wave function for the first excited state? It has a node right at the middle. See the wave function would look like that. And if you did the same kind of calculation, what will happen is that, you will have to evaluate the value of the wave function right at the middle. And right at the middle of the box, the wave function would have a value how much? 0. And therefore, within this kind of approximate calculation, what you would say is the first excited state wave function is having a value 0 right at the middle. And therefore, the correction to the energy will turn out to be… First order correction to the energy will turn out to be equal to 0.

Second excited state – there will be a nonzero correction again. For the third excited state, you will predict that, it should be 0. So, these are simple things. I mean as I said, you can use them to get rough idea. So, how the energy would change if you put a perturbation somewhere? For example, if you put a perturbation right where the node of the wave function is, the energy will be… Not surprising, energy would not be affected. So, now, I would also like to derive an expression for the correction to the wave function. So, I want to… What is it that I want to do? Unfortunately, I removed that equation, but I have it here. So, no need to worry.

(Refer Slide Time: 09:17)



$$= \sum_{m=0}^{\infty} c_m \psi_m^{(0)}$$

$$H^{(0)} \sum_{m=0}^{\infty} c_m \boxed{\psi_m^{(0)}} + H^{(1)} \psi_n^{(0)} - E_n^{(0)} \sum_{m=0}^{\infty} c_m \psi_m^{(0)} - E_n^{(1)} \psi_n^{(0)} = 0$$

$$\sum_m c_m E_m^{(0)} \psi_m^{(0)} - E_n^{(0)} \sum_{m=0}^{\infty} c_m \psi_m^{(0)} = E_n^{(1)} \psi_n^{(0)} - H^{(1)} \psi_n^{(0)}$$

$$\sum_m c_m \left(E_m^{(0)} - E_n^{(0)}\right) \psi_m^{(0)} = E_n^{(1)} \psi_n^{(0)} - H^{(1)} \psi_n^{(0)}$$

I want to calculate psi n 1. That is my aim now. So, how will I calculate psi n 1? So, to calculate psi n 1; this is an unknown function; I wanted to determine it. But, I know that the solutions of the Schrodinger equation for the unperturbed problem can be solved and I can find the eigenfunctions. These eigenfunctions actually form what is referred to as a complete set. Remember I told you this. What is the meaning of a complete set? Any arbitrary function can be expressed as linear combinations of this set. Therefore, if I have this unknown function psi n 1, I should be able to express this in terms of psi m 0. This is the complete set; that actually I am saying I have psi 1 0, psi 2 0, etcetera; I have this complete set. These functions are normalized; each one of them is normalized; and each one is orthogonal to all the remaining. That is how it is. Therefore, let me say that, I can write this psi n 1; as this is the first order correction to the n-th state wave function, it may be written as some c 1 psi 1 0 plus c 2 psi 2 0 plus etcetera.

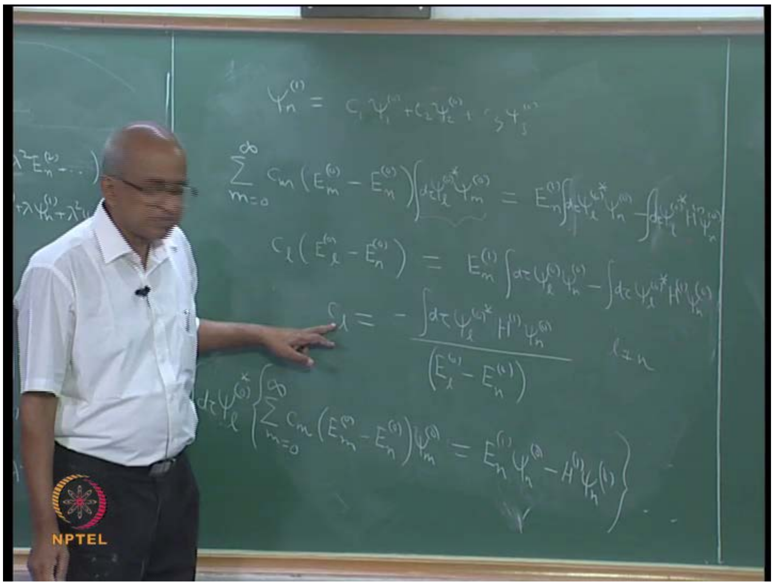
Now, I can use summation notation and say that, this may be written as sigma m c m psi m 0. Now, at this point, I suspect there may be a reason for questioning this expression, because strictly speaking, c 1, c 2, c 3, etcetera will depend up on which state I am thinking of. If I am thinking of the first state, that is, the ground state; then c 1, c 2, c 3, etcetera will have some value, which will be different from the values of c 1, c 2, c 3, etcetera if you are thinking of the second or the third or fourth state. So, strictly speaking, what I should do is I should put another subscript maybe n there; another subscript n here to indicate that, this will actually depend upon the state that you are thinking of. But, that will complicate the notation.

So, just remember that, I am thinking of the n-th state. And I will not write this subscript, which strictly speaking has to be there; it should not confuse you, because here this c is specific for the n-th state. If you are thinking of first state, you will have a certain value; if you are thinking of the second state, it will have some other value and so on. It will complicate the notation. And therefore, I am not doing it. So, this m what does it do? It varies from the minimum possible value of 0 to the maximum possible value, which of course, is infinity. So, what am I going to do? I am going to take that assumption and put it in here into this equation; which I had earlier, but I unfortunately rubbed off. But, that is not a problem.

Let us do that. What am I going to have? H 0 operating upon psi n 1. What will that be? That is actually equal to sigma m going from 0 to infinity c m psi m 0. H 0 operating up on this; then H 1 operating upon psi n 0 – that I do not have to do anything – minus E n 0 operating upon psi… E n 0 multiplying psi n 1; that is actually nothing but c m psi m 0 summed over all possible values of m running from 0 to infinity minus what do you have? E n 1. Correct? Please check; I would not like to make a mistake; I think it is OK. So, what I will do is I will… As I had done earlier, I will take these 2 terms to the other side and… Therefore, on the other side, I would have E n 1 psi n 0 minus H 1 psi n 0. That is what I would have if I took these 2 terms to the other side.

And, what is left on the left-hand side? I would have H 0 operating up on this. That is going to be there. But, H 0 is going to go and operate upon psi m 0. What would that be? This is an eigenfunction of H 0. Therefore, you will have the eigenvalue coming out. Therefore, this actually is going to be sigma m c m E m 0 – that will be the eigenvalue multiplied by psi m 0 plus… No, it is not a plus, but this is the term that is left. So, minus E n 0 sigma m going from 0 to infinity c m psi m 0. Correct? I mean it is obvious that, I can combine these two. So, what will I do? I will write this as sigma m c m E m 0, because you see the terms are actually rather similar. This is all that will happen. Now, you see you would be really worried, because on the left-hand side, I have a sum running from 0 to infinity; right-hand side of course, is very simple. But, you look at the left-hand side; what are the unknowns in this problem?

(Refer Slide Time: 17:30)



See we have assumed that, psi n 1 may be written as c 1 psi 1 0 plus c 2 psi 2 0 plus c 3 psi 3 0 plus etcetera. So, I actually have infinite number of unknowns, where… What are these c 1, c 2, c 3, c 4, etcetera? These are all unknowns. And I have only one equation. I mean you would not believe if I told you that, this one equation is enough for me to determine infinite number of unknowns. But, that is actually possible. The way to do that will be to take this equation and multiply it from the left-hand side with let us say psi l 0 if you like – star; and then the volume element d tau and integrate. This whole equation I will just multiply by psi l 0 star and integrate over the entire space. So, if you did that, what is going to happen let us see. I would have sum m going from 0 to infinity c m – c m is not affected by this integration process, because it does not depend upon position – multiplied by E m 0 minus E n 0 into psi m 0. This is already there, but you are going to multiply by psi l 0 star. So, psi l 0 star and the volume element d tau and integral. That is what you will get.

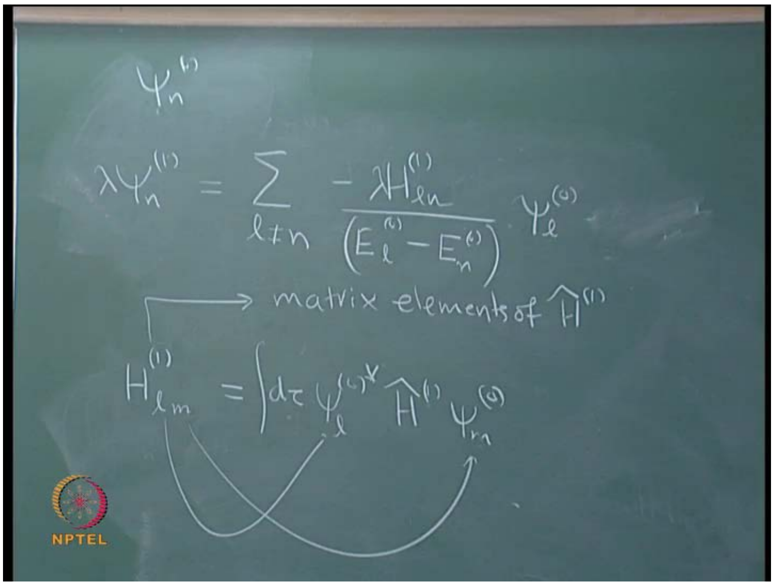
And, on the right-hand side, you are going to get E n 1 integral psi l 0 psi n 0 minus integral psi l 0 star H 1 psi n 0. I have to put in the d tau somewhere. So, d tau. So, this is what will happen. Still it appears very messy; but then if you look at this expression; and you will realize that, this integral that I have here; what is the value? It is actually equal to 0 unless m is equal to l. See here you have a sum over all possible values of m. Correct? For all values of m except m being equal to l, this integral is 0. So, out of this infinite sum, only one term is going to survive. And that will be the term with m equal to

l. Therefore, I need to write only that term; all the other terms are 0. So, if m is equal to l, what will happen? I will have c l E 0 l minus E n 0 l. And if l is… If m is equal to l, what will happen to this integral? It is unity. Therefore, that is one. And what about the right-hand side? You will have E n 1 integral psi… – integral d tau psi l 0 psi n 0 minus integral d tau psi l 0 star H 1 psi n 0. This is what you get. Correct? This is valid for all values of l. I mean I have just multiplied by psi l. So, psi l star is… I have just multiplied by this object. And l can be anything. This l I can choose to be to whatever I want.

In fact, if you say l is not equal to n, what will happen to this equation? All that will happen is that, if you put l is not equal to n, then this will vanish; this term will vanish if l is not equal to n. And so you will have an equation for c l. What will be the equation? c l will be… This will vanish. And therefore, you will have integral negative sign with psi l 0 star H 1 psi n 0 divided by E l 0 minus E n 0. So, when l is not equal to n, this is the expression for c l. Correct? Suppose I had put l equal to n here; then what will happen? This term actually vanishes. And what about the right-hand side? If you put l equal to n, you will have psi n 0 here; there is a star, which I should have put. So, this will be 1. And what about this one? It will be nonzero, but that we already have identified. That is actually equal to E n 1. We have already identified that. This term is actually equal to E n 1. Therefore, if you put l equal to n, this will vanish. And so naturally, the other side also has to vanish and it vanishes. So, there is absolutely no problem; everything is fine. And we have determined the value of c l when l is not equal to n. So, what is the result that we have obtained?

We have obtained that psi n 1 may be written as summation over all possible values of l. Actually, we have determined c l only when l is not equal to n; we have not worried about c l when l is equal to n. Therefore, what I will do is, I will say I am not having l equal to n, but all other values of l are fine; I know what the values are. The values are given by this expression. Now, this expression as you will see, it is tedious, difficult to write again and again and again.

(Refer Slide Time: 24:16)



$$\psi_n^{(1)}$$

$$\lambda\psi_n^{(1)} = \sum_{l\neq n} \frac{-\lambda H_{ln}^{(1)}}{\left(E_l^{(0)} - E_n^{(0)}\right)}\,\psi_l^{(0)}$$

$$H_{lm}^{(1)} = \int d\tau\, \psi_l^{(0)*}\, \hat{H}^{(1)}\, \psi_m^{(0)}$$

Therefore, it is best that I use a shorthand notation. This integral itself is difficult to write all the time. So, in quantum chemistry or in quantum mechanics, it is always usual to use… I mean in any branch of science, you would like to use shorthand notation, so that things will become simple. So, what we will do is I have this integral. I have this integral; I do not want to be writing this again and again and again. So, what I will do is; you see this is actually…

After all what is it having? This H has a hat; if you see I cannot put hats on top of H's; then it is better that you put them. But, you see now, we are fairly experienced and we know which are the operators and which are not the operators. So, as you get more experienced, you become very clever or you become very lazy; you can think of it whichever way you like. But, usually… I mean it is… I mean if I was doing a derivation myself, then I will never have that hat sitting on top. But, at a lower level in a class, it is always better that this hat symbol is there just to indicate that these are all operators. Everywhere H is occurring; you should actually… I mean even here I have not put it, but here it should be there strictly speaking. But, as I said, ((Refer Slide Time: 26:25)) you get more and more experienced, you do not normally write it down. But, better that it is there. Therefore, what will happen is that, you will have H hat with psi m 0 on this side, psi l 0 star on the other side. That is how it is. Therefore, the usual thing is you will say…

What is it that you have? You have something which involves the Hamiltonian operator. This is what H 1 operating upon psi m 0 multiplied by psi l 0 star and integrated over the entire space. So, this is a number. The answer that you are going to get is probably a complex number; it is not an operator anymore. And therefore, I will not put a hat, because it is just a number. And what happens? You have a psi m; it is… The H is operating upon psi m 0. Therefore, this object on the left-hand side will depend upon what the value of m is. And it will also depend upon what the value of l is. Therefore, this is the shorthand notation. And these are usually referred to as matrix elements – elements of H 1.

The reason for this word will become clearer as we proceed. Therefore, you see I have this very nice shorthand notation; this integral is just denoted as H 1 l m… The moment you see such a thing that, it implies that, psi m is occurring on the right-hand side of the operator. m is occurring on the right-hand side of the operator; while psi l 0 is occurring on the left-hand side. That is what you have to understand when you see such a notation. So, that is a general notation that I will adapt. Specifically if you are thinking of this particular thing that is occurring; that if I adapted this notation, it is going to be called H. There is a negative sign H 1 l n. That will be the name for it. This is our general notation for any l and m. Therefore, this is what it is; divided by… I am writing the expression for psi n 1. So, I have now written the expression for c l; it will contain E l 0 minus E n 0. This is just the coefficient c l. And that has to be multiplied by psi l 0. That will be the correction to the wave function.

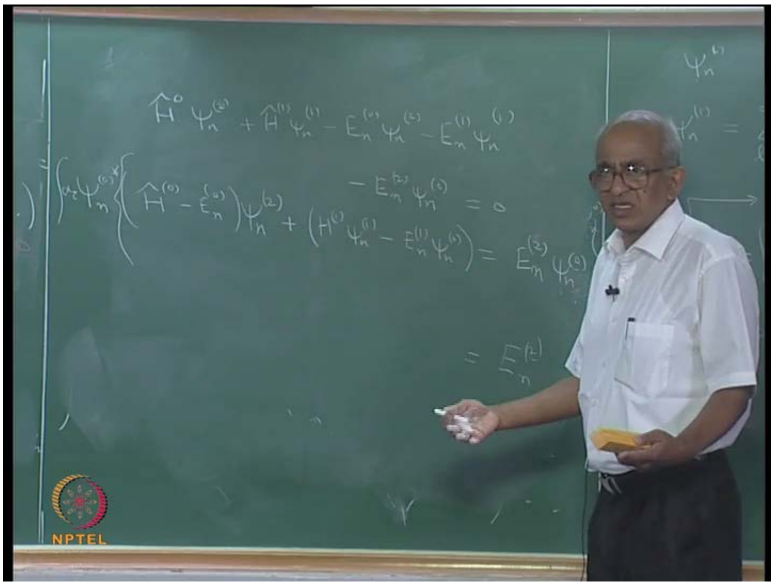
Now, you may say strictly speaking, you should have another term, which is actually of the form c n psi n 0 should be there, because this sum actually takes care of all the terms except l equal to n. Therefore, there should be c n times psi n 0. That is how strictly speaking, it should be. But, then you will think of the wave function – total wave function. What is the total wave function? This is only the correction to the wave function. Fine? Actually, strictly speaking, I should also add a lambda to say that, this is the correction, because that is the actual correction. And that actually means I would have a lambda here; that is also. Therefore, this is the first order correction to the wave function.

Now, this remember is going to be added to what? It is going to be added to psi n 0. It is going to be added to psi n 0. So, if we had taken this correction and added it to psi n 0, all that will happen is that, this term will get added on to psi n 0. And that will just modify the coefficient of psi n 0. Anyway you have to later on ensure that, the way function is normalized. Therefore, this term is not of great importance for us, because all that it does is, it multiplies psi n 0 by some factor, which you will eventually use normalization to determine anyway. So, you can assume that, the way function has to be normalized. And in fact, if you performed the operation of normalization up to first order in lambda, then what will happen is that, this will work out to be 0. You will have to believe me when I say that. Therefore, this term is of no importance. So, we have calculated the first order correction to the wave function; we have also calculated the first order correction to the energy.

And now, we would like to think of this equation, but this is rather messy looking what… Let me just see whether I can do something with this. It is possible to do something with it. Let us look at that. In fact, you see it is nice if I can get an expression for the second order correction to the energy. We will not worry about second order correction to wave function, but second order correction to the energy is important. The reason is actually simple. The reason is that, see for example, if you have 2 molecules approaching each other suppose; then there will be interaction between the 2 molecules. And this interaction between the 2 molecules can be treated according to perturbation theory. And if you calculated the second order correction to the interaction energy, then you will get this thing that you refer to as the Van der Waals interaction. So, the Van der….

What you refer to as the Van der Waals interaction actually comes from this particular term – E n 2… That is the one that is responsible. So, it would be nice; of course, I mean, in this set of lectures, I am not going to do this calculation, because it is a little bit lengthy. But, you should know. Suppose you wanted to use perturbation theory and calculate Van der Waals interaction; then you should have an expression, which hopefully you can use. And therefore, I can actually tell you how to get the expression for E n 2. This is the term that will give you Van der Waals interaction ((Refer Slide Time: 33:16)) if you are thinking of intermolecular interactions; which assumes that, the 2 molecules are rather apart. And if they are rather apart, what will happen? The effect of one molecule on the other is a small disturbance and vice versa also. So, how will I use this to get the expression for E n 2? All that you need to do is actually multiply throughout by psi n 0 star.

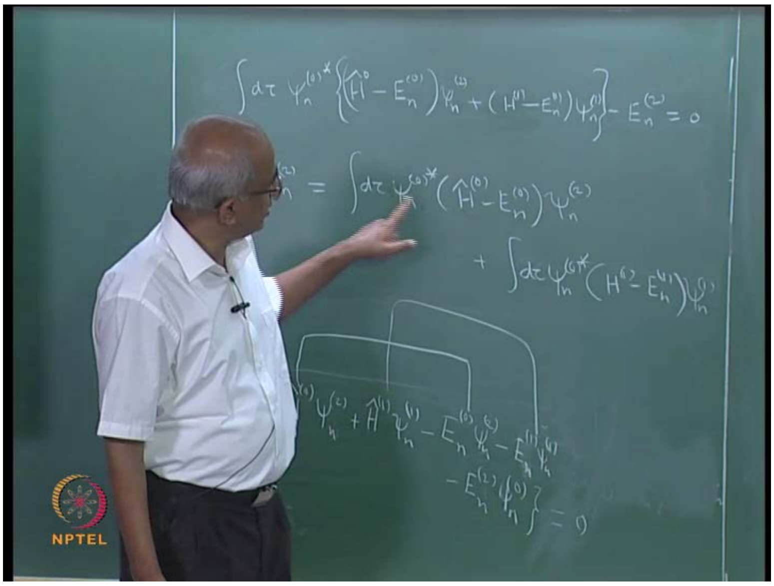
(Refer Slide Time: 34:08)



Where do I proceed? I have to do it here. H 0 psi n 2 plus H 1 psi n 1 minus E n 0 psi n 2 minus E n 1 psi n 1 minus E n 2 psi n 0 must be equal to 0. That is what ((Refer Slide Time: 34:54)) says; I hope I have not made a mistake. Rewrite this in a slightly different fashion. H 0 minus E n 0 into psi n 1 n 2 plus H 1 psi n 1 minus E n 1 psi n 0 is equal to E n 2 psi n 0. All that I need to do; I think I am going to run out of time. So, all that I need to do is I will just… I need to just multiply by psi n 0 star d tau everywhere. I take all these things everywhere; multiply it by psi n 0 star.

Now, you can see the reason for that. If you did that, this factor, this and those integrals will combine and it will give me 1. So, on the right-hand side, you are going to get E n 2, which is the object that I want? We will in the beginning of the next lecture, we will see what the left-hand side is. And the left-hand side will turn out to be rather simple, not a very complicated thing. Even though the equations appear quite complex; finally, the answers that you get are very physically understandable and the answers are simple.

(Refer Slide Time: 37:20)

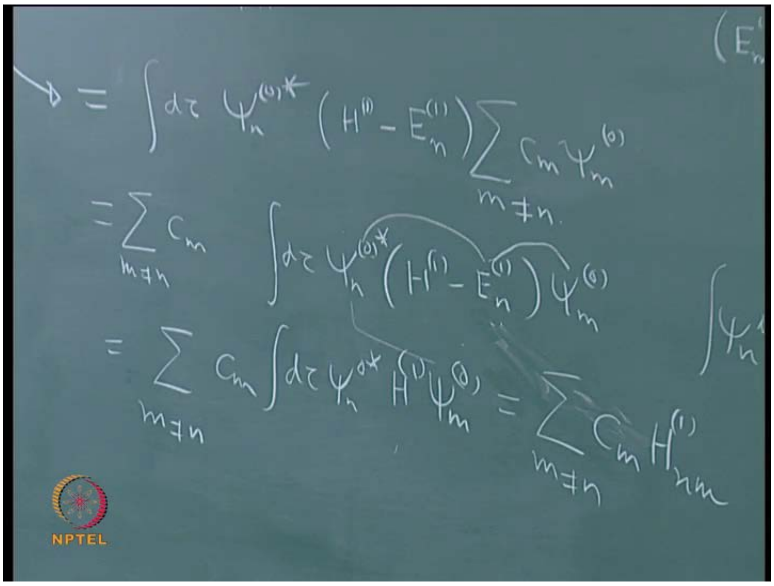


So, we want to determine the second order correction to the energy, which we have here. E n 2 is the quantity that we want to determine. And this can be determined from this equation, which says that, this term must be equal to… See the sum of all these terms should be equal to 0. And as I told you earlier towards end of the last lecture, what we will do is, we will multiply this by psi n 0 star; then the volume element d tau and integrate over the entire space. And that is what I am going to use to determine the value of E n 2. So, let us see what happens. You will have psi n 0 star multiplying by psi n 0 and being integrated over the entire space. Therefore, this term is going to be just minus E n 2.

And, I am going to write down the remaining terms. Integral of d tau psi n 0 star H 0… This term I will combine with that term, because you can see psi n 2 is common. So, H 0 minus E n 0 psi n 2… And this term I am going to combine with that term, because both have H 1. So, plus H 1 minus E n 1 psi n 1. Where should I put a bracket? Maybe the best thing is to put a bracket here. Or, I can rearrange this and write this as E n 2 is equal to this integral. Therefore, E n 2 is given by this expression. There seems to be 2 terms in the expression. But, when you think about this, you will realize; say H is a Hermitian operator.

So, I could do this trick of transferring the operation of H on to this psi n 0. Then what will happen? It is going to give me an E n 0 multiplied by psi n 0 itself. So, effectively, what will happen is that, this H 0 will get replaced with E n 0. So, this term actually is 0. Using the Hermitianness… Let me just repeat; using the Hermitian property of H, I can actually allow this H 0 to be transferred and it can operate upon psi n 0. We have done this in the morning. So, if it operates upon that, answer is going to be E n 0. So, E n 0 and that E n 0 will cancel. So, this term simply vanishes.

(Refer Slide Time: 41:03)



$$= \int d\tau\, \psi_n^{(0)*} \left(H^{(1)} - E_n^{(1)}\right) \sum_{m \neq n} c_m \psi_m^{(0)}$$

$$= \sum_{m \neq n} c_m \int d\tau\, \psi_n^{(0)*} \left(H^{(1)} - E_n^{(1)}\right) \psi_m^{(0)}$$

$$= \sum_{m \neq n} c_m \int d\tau\, \psi_n^{0*} H^{(1)} \psi_m^{(0)} = \sum_{m \neq n} c_m H^{(1)}_{nm}$$

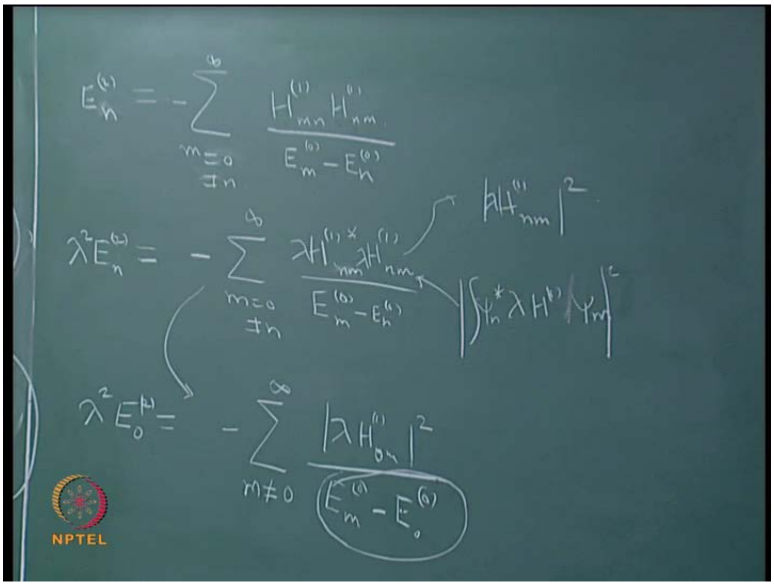
And, what do I have left? I have this expression. This is what I told you. I mean whenever you do this kind of things, the intermediate steps may appear complex, but the final answers appear to be very simple. So, this is the expression. And now, what is c n 1? c n 1 we already know; c n… What did I say? Not c n 1, psi n 1. Psi n 1 – what is the expression? It is actually sigma m c m psi m 0. If you like, you can put not equal to n; not necessary, but let it be there. And c m is how much? We have derived the expression for this actually – minus – correct me if I am wrong – H m n divided by… Is that correct? I suppose it is; there may be an error in the sign; just check it. So, it will…

So, we will use this value later. But, at the moment, I am going to use this expression, because you see I have to take this; I have to put this here. Then the expression looks very complicated. So, just keep things simple, I will just use this expression. I am going to substitute this in here. So, what will be E n 2? E n 2 I will continue. It is going to be integral d tau psi n 0 star H 1 minus E n 1 summed over all values of m c m psi m 0; m is not equal to n. Correct? Very simple things to do now. I can take this c m as well as a summation sign outside. So, I will get summation over m not equal to n c m integral d 2 psi. This was what? I have forgotten now. Psi n 0 star H 1 minus E n 1 psi m 0. That is what happens. Agreed?

Then, you look at this integral. See psi n 0 star into E n; E n is just a number. Look at the term involving E n; this into that into that. E n 1 is just a number. Therefore, this integral is nothing but integral psi n 0 star psi m 0 d tau. That is what this integral is. And what about this integral? The functions are orthogonal. And therefore, this has to be 0 unless m is equal to n. But, m is equal to n term is not there in the sum. Therefore, what will happen? This term involving E n does not contribute; it is identically equal to 0; I can just remove that.

And so what will happen? I shall get… This is actually the term involving this, is equal to 0. E n 1 is not zero, but the term involving that, is equal to 0. Therefore, you will get sigma m not equal to n c m integral d tau psi n 0 star H 1 psi m 0. Correct? That is all that you get. But, then we decided that, we do not want to be writing this term; it is tedious. Therefore, we will simply write this as sigma m not equal to n c m H 1 n m. Correct? We already know how much is c m. It is here now. So, I can directly take that and put it in here instead of that c m.

(Refer Slide Time: 46:33)



$$E_n^{(2)} = -\sum_{\substack{m=0\\ \neq n}}^{\infty} \frac{H^{(1)}_{mn} H^{(1)}_{nm}}{E_m^{(0)} - E_n^{(0)}}$$

$$\lambda^2 E_n^{(2)} = -\sum_{\substack{m=0\\ \neq n}}^{\infty} \frac{\lambda H^{(1)*}_{nm} \lambda H^{(1)}_{nm}}{E_m^{(0)} - E_n^{(0)}}$$

$|\lambda H^{(1)}_{nm}|^2$

$\left|\int \psi_n^* \lambda H^{(1)} \psi_m\right|^2$

$$\lambda^2 E_0^{(2)} = -\sum_{m\neq 0}^{\infty} \frac{|\lambda H^{(1)}_{0m}|^2}{\boxed{E_m^{(0)} - E_0^{(0)}}}$$

And so what is the result? The result is actually… m actually varies; m is equal to… m is actually varying from 0 to infinity, but it is not equal to n. This is the result. Fine? And now, this H 1 itself you see this is a part of Hamiltonian. And normally, what happens is that, even that part will be Hermitian operator; even the small part that you have. The perturbation that you are applying; it will be Hermitian operator, which actually implies that, this integral is nothing but the complex conjugate of that integral. That is what it means. You can actually use the definitions and show that. But, I am not going to do that. All that happens is that, this is the complex conjugate of that.

And therefore, this expression can be written as minus sum m going from 0 to infinity; m not equal to n; H 1 m n star H n m. Now, it is H n m star H 1 n m. I mean you take the matrix element; take its own complex conjugate and multiply the 2 together; you will get the numerator. Or, there is an even better way of writing this. This is nothing but magnitude of H n m 1 square. That is what this object is; the numerator. So, this is the expression.

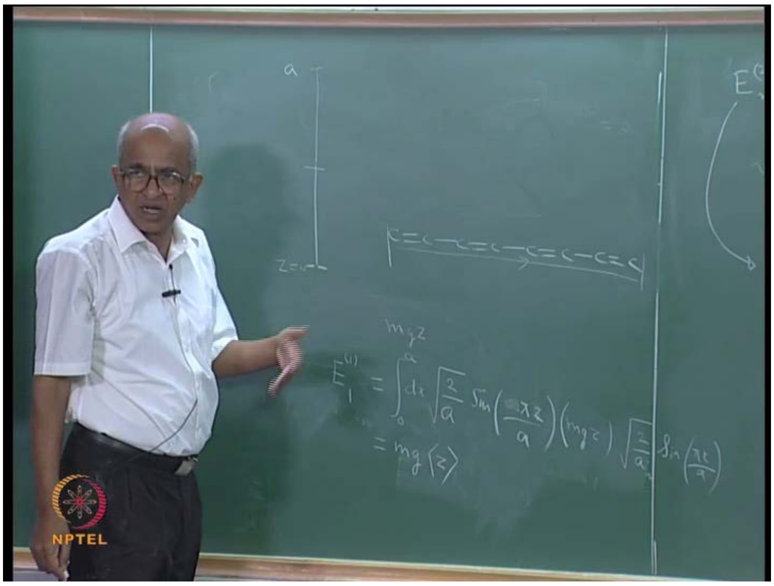
And, in fact, the correction to the energy is how much? It is actually lambda square times this. The correction to the energy is lambda square times this. Therefore, I will get a lambda here and a lambda there. Or, here you can say I will have a lambda square. And this is what? This is actually lambda H 1, is the perturbation. Remember lambda H 1 is the perturbation. So, you have to take the matrix element of this between psi m and psi n. Calculate that. Take its magnitude and square it. That is the term that is going to occur here. And you have this one – E m 0 minus E n 0. That is actually the difference between the different energy levels of the system.

Specifically, suppose I am thinking of the ground state of the system; most of the time, we are interested in the ground state. What happens to the ground state as a result of perturbation? So, if you are interested in the ground state, what will happen to the second order expression for energy? What you are going to get is you will have sigma. Now, you would not have m equal to 0, because you are thinking of the ground state; that is, we are thinking of the correction to the energy of the ground state; that means, lambda square E 0 2 is what I am calculating.

So, I will have to sum over m, but m is not equal to 0; but everything else… And that is going to be lambda H 1 n m magnitude square; n is actually 0; divided by E m 0 minus E 0 0. This will be the expression if you are interested in the ground state or a correction to the energy of the ground state. And this expression is quite interesting, because this is a magnitude square that is guaranteed to be positive; this expression. This is guaranteed to be positive. E m 0 minus E 0 0. This is the energy of the ground state. Any other energy is greater than that. And therefore, this also is positive. And therefore, what has happened to the second order correction to the energy? It is always negative. It is always negative. That is what this expression tells you.

If you are thinking of the ground state, the second order correction to the energy is always negative. So, this actually means the following. I mean if I had 2 molecules and if I think of interaction between the 2 as a perturbation; I mean I am assuming that, the molecules are in the ground state. And then what will happen? The interaction between the 2 molecules will always… This itself tells you that, it is going to be attractive, because energy is getting lowered because of this term. So, if you calculated Van der Waals interaction at large distances, it will always be negative irrespective of what the species is. It will be… This term will always be negative; which means that, there is always an attractive interaction at long distances. Now, as an example of these things, maybe I should do one more example. The example that I will give; I will not actually do the numerical calculations; but it is of no importance on earth. It is of no importance that whatever I am going to tell you; the physical problem that I am going to tell you.

(Refer Slide Time: 53:20)



Imagine I have a conjugated molecule. Maybe something like that; it is a particle in a box. And normally, we assume that, the conjugated molecule is horizontal. But, suppose

I had put it vertical; I mean this is the particle in a box; you see the electron can move from here to there. The electron can move from here to there. And if… The way we draw the molecule; it is horizontal. But, suppose the molecule is in the gaseous space and I rotate it, so that it is vertical; this molecule is like this. And there are electrons moving around; you may… I mean if I am crazy enough, I can say maybe the gravitational field of the earth is important. I want to see whether the gravitational field of the earth is important.

Further, how will it affect the motion of the electron? So, you can say that, there is a perturbation; what would be the contribution to the energy from the gravitational field? Quite simple; you would have m g into z. This point I will take it to be z is equal to 0; one end of the molecule. The other end is at what? At a height of a. Therefore, you will have a perturbation acting on the particle in a box. The perturbation will be of the form m g z. Here the perturbation will have the smallest value; at the other end, it will have the potential energy, will be the highest. And then of course, be the electron cannot go beyond that.

Now, what happens is that, in the case of earth, the gravitational field is so little that, the effect of this is of no significance. But, suppose as I said, I was crazy enough to do a calculation to find out how much does it affect the energy of the ground state of the system? Just one electron. So, how will you do the calculation? The calculation is extremely simple. I will calculate the first order correction to the energy. Now, in this case, you should remember that, the ground sate actually has the quantum number particle in a 1 dimensional box; n equal to 0 is not there; n equal to 1 is the ground state. So, I will put a subscript there – 1. And what will be the wave function? The wave function will be square root of 2 by a sin; normally we would write sin n pi x by a; but here you see I have put the box vertical. The molecule I have assumed it is vertical. So, I will put z there. And I am interested in the ground state. Therefore, n is 1. So, this is the wave function.

To calculate the first order correction, what should I do? I will have to take the perturbation, which would be m g z. Correct? And then I will have to multiply that by square root of 2 by a sin pi x by a once more. And then I will have to multiply it by d x and integrate it from 0 to a. Correct? So, this will be the first order correction to the energy due to the gravitational force of earth. And actually, you do not have to calculate this, because we can guess what the integral is going to be; it is actually nothing but m g into expectation value of z; m into g; g is the acceleration due to gravity; m is the mass of the electron. You take that out; what is left is expectation value of z.

We have actually argued about this kind of expectation values. What would be… I hope you remember what we did. The expectation value of z is actually a by 2, because you see in the box, the particle can be on this side or on that side; it can be in the upper half or lower half with equal likelihood. Therefore, the average has to be a by 2. And therefore, the correction to the ground state energy of the system will be m g into a divided by 2. So, as I said, if anybody wants to do this, I can do a calculation. And find that this is of no importance; we will never be able to see the difference. Actually this means that, if I had the molecule horizontal and if I were held it vertical, there is a slight ((Refer Slide Time: 58:15)) difference in the electronic energy, but of almost no importance. I should not say almost no importance; it is of no importance.

But, then I am told that on the surface of a neutron star, the gravitational field is enormous. And then this will make a difference. But, of course, on earth, it has no importance. So, with that example, we will pass on to the next approximation method. You see perturbation method is only one approximation procedure. In order to use the perturbation method, what should happen is that, the disturbance that you are causing should be small. It should not be large. If it is large, then it will breakdown; you cannot use it. Why? Because you see if it is large, the second order correction will turn out to be more important than the first order; and the third order will be even more important; and so on. And then it does not make sense, because we can calculate only the first few. So, if you had a situation where the disturbance that you are causing is large, what do you do? There is another procedure. This other procedure is referred to as the variation method.

So, thank you for listening.