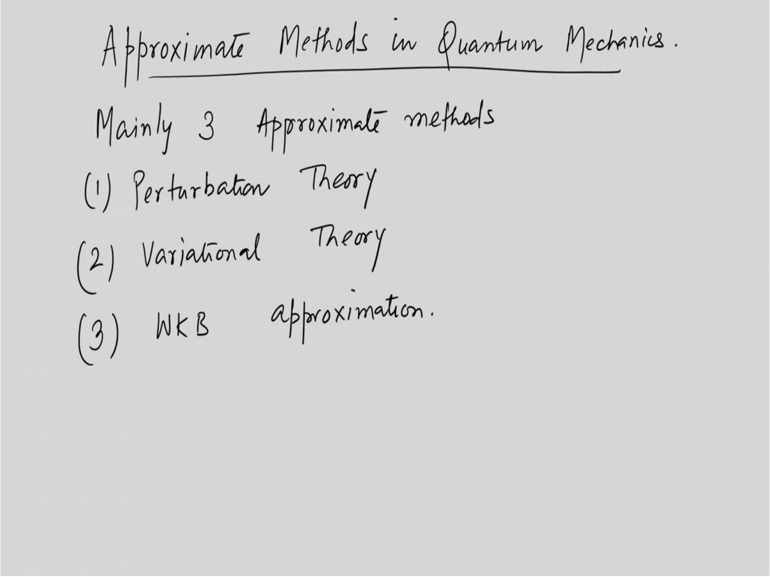
**Advanced Quantum Mechanics with Applications**
**Prof. Saurabh Basu**
**Department of Physics**
**Indian Institute of Technology, Guwahati**

## Lecture – 21
## Perturbation Theory

We are going to start a new chapter in the study of Advanced Quantum Mechanics and its Applications. This is called as the approximate methods in quantum mechanics.

(Refer Slide Time: 00:39)



Approximate Methods in Quantum Mechanics.

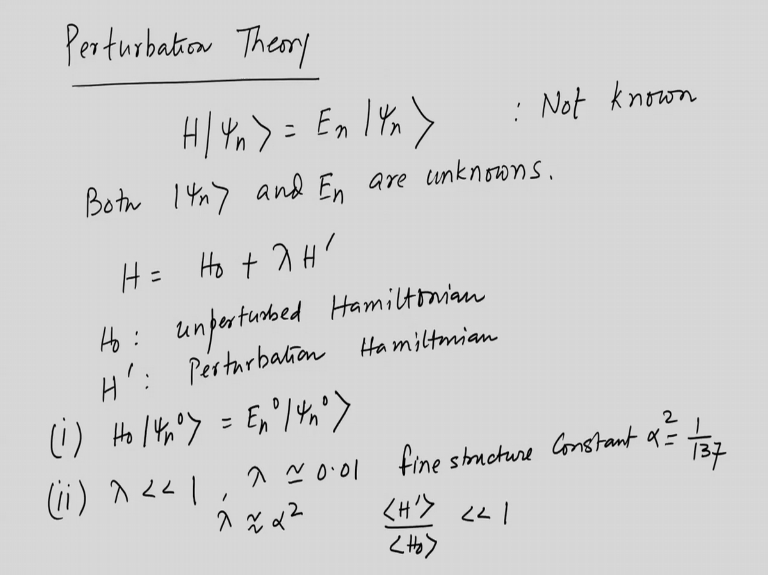
Mainly 3 Approximate methods
(1) Perturbation Theory
(2) Variational Theory
(3) WKB approximation.

So, most of these problems in the single particle quantum mechanics, that is obtained by the solution of Schrodinger equation. Most of them are actually unsolvable because of the complexity of this a mathematics involved, because the second order differential equation that we are trying to solve gets so complicated, that it is more often than not the closed solutions are not available. .

In which case the approximate methods are used in order to arrive at a solution and most of the time these approximation methods or the approximate methods play a very important role in the study of different quantum systems. So, we are going to look at a mainly 3 approximate methods. They are Perturbation theory, number 2 is Variation theory or a Variational theory and a number 3 is a WKB approximation.

Now, the first focus will be on the perturbation theory and let us see under what conditions perturbation theory works and it is applicable.

(Refer Slide Time: 02:52)



Perturbation Theory

$H|\psi_n\rangle = E_n|\psi_n\rangle$ : Not known

Both $|\psi_n\rangle$ and $E_n$ are unknowns.

$H = H_0 + \lambda H'$

$H_0$ : unperturbed Hamiltonian

$H'$ : Perturbation Hamiltonian

(i) $H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$

(ii) $\lambda << 1$ , $\lambda \simeq 0.01$ fine structure Constant $\alpha^2 = \frac{1}{137}$

$\lambda \approx \alpha^2$ $\quad \frac{\langle H'\rangle}{\langle H_0\rangle} << 1$

So, suppose there is a problem the Hamiltonian of which is represented by H for which the solution the exact solution is not known. So, we really do not know the solution of this problem. So, this is even I am writing it formally the solutions are not known which means that both psi n and E n are a unknown.

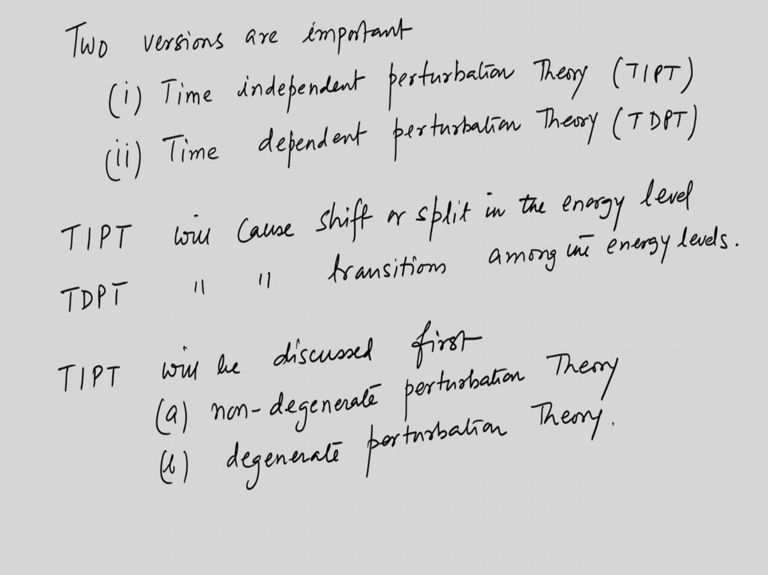
However, the H that we just saw, the Hamiltonian of the system can be represented in terms of a two terms the Hamiltonian is written in terms of these two terms which are H 0, which is called as the unperturbed Hamiltonian. And, H prime is called as the Perturbation Hamiltonian, it is important to realize that the system actually can be split in terms of these two Hamiltonians and that should be known. And, in addition to that there are two more conditions, one is that that the solution to this, the unperturbed problem is completely known which means that. So, by 0 we mean the unperturbed problem.

So, H 0 is the unperturbed Hamiltonian that is acting on the wave function gives me the energy spectrum which is E n 0 where n is some quantum number that is relevant to the problem could be momentum, could be spin, could be you know position etcetera; however, this problem is completely known to us. And the next condition, which is a very strict condition that this lambda has to be much smaller than 1, which means that the perturbation term is much smaller compared to the original Hamiltonian H 0.

And if you want a order of magnitude then lambda 1 is of the order of 0.01 at least or even lower than that. In fact, there is a the scale energy scale that is relevant to this discussion is that the fine structure constant, we will come back to this later which is called, which is written with alphas rather, alpha square which has a value 1 over 137. So, a lambda has to be comparable to this the fine structure constant and in order to have a and for the Perturbation theory to work this lambda has to be small.

So, the you know will it say that the expectation value of the Perturbation term divided by the expectation value of the unperturbed Hamiltonian is much smaller than 1. This is of course, assuming that we know how to calculate the expectation values and this is what we are going to learn. Now expectation values are taken with regard to some known states. In fact, we will see that these known states are nothing, but the unperturbed states of the system. In fact, we may not require the corrected wave function for most of the cases in order to have meaningful results, we could actually calculate the expectation values with the unperturbed wave functions themselves.

(Refer Slide Time: 07:41)



Two versions are important
(i) Time independent perturbation Theory (TIPT)
(ii) Time dependent perturbation Theory (TDPT)

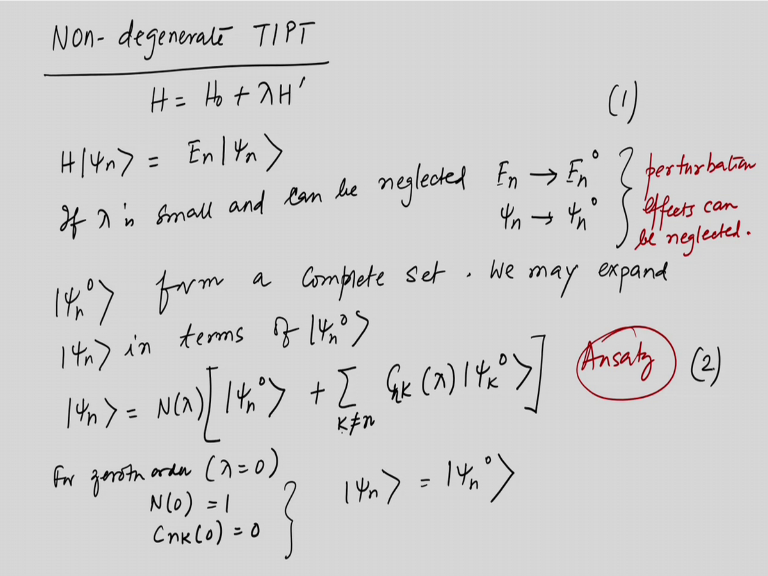
TIPT will cause shift or split in the energy level
TDPT " " transitions among the energy levels.

TIPT will be discussed first
(a) non-degenerate perturbation Theory
(b) degenerate perturbation Theory.

So, these are the requirements and we have the two a sort of versions of a perturbation theory which are important and one of them is called the time independent perturbation theory. And we will just call it or rather abbreviate it as a TIPT and the second one we will call it as, a time dependent perturbation theory and we will call it as TDPT ok. Now even in the time so if we begin with time independent perturbation theory or the TIPT as we said that will encounter there are again, you know degenerate and non degenerate perturbation theory.

But before we come to that let us tell you the features of this time independent perturbation theory. So, time independent perturbation theory, done on a system will a cause shift in the energy level or split in the energy level. And, time dependent perturbation theory will actually a cause transitions, among the energy levels and this the next, the second one that is a time dependent perturbation theory will be shown to be relevant for the discussion of a lasers or how lasing action takes place we will discuss that. So, we will first discuss the TIPT first, but then it has 2 variant as I said this is called as the non degenerate perturbation theory and b is a degenerate perturbation theory.

(Refer Slide Time: 10:57)



Non- degenerate TIPT

$$H = H_0 + \lambda H' \qquad (1)$$

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

If $\lambda$ is small and can be neglected $\left.\begin{array}{l} E_n \to E_n^0 \\ \psi_n \to \psi_n^0 \end{array}\right\}$ perturbation effects can be neglected.

$|\psi_n^0\rangle$ form a complete set. We may expand $|\psi_n\rangle$ in terms of $|\psi_n^0\rangle$

$$|\psi_n\rangle = N(\lambda)\Big[|\psi_n^0\rangle + \sum_{k\neq n} C_{nk}(\lambda)|\psi_k^0\rangle\Big] \qquad \text{Ansatz} \qquad (2)$$

For zeroth order $(\lambda = 0)$ $\left.\begin{array}{l} N(0) = 1 \\ C_{nk}(0) = 0 \end{array}\right\}$ $|\psi_n\rangle = |\psi_n^0\rangle$

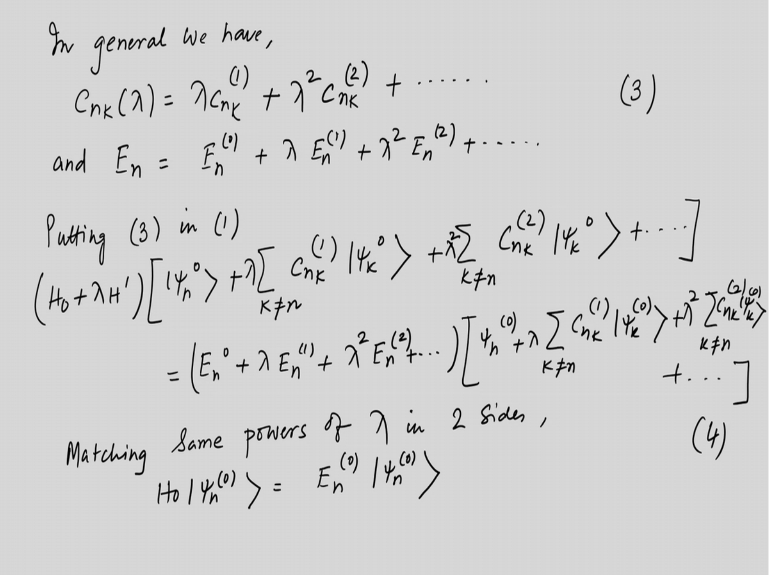
So, these are going to be discussed and we will start with a so, a non degenerate TIPT, we will start with that and so then, go over to the degenerate very quickly. Alright so, as we told that the total Hamiltonian is written as H 0 plus lambda H prime; remember that this separability of the Hamiltonian into two terms is very important for the perturbation theory to be applicable.

So, we just apply it on the wave function H psi n, without knowing what the E n and psi n are and we know that if a lambda is small and can be neglected then E n is nothing, but E n 0 and your psi n is nothing, but psi n 0 that is the perturbation effects can be neglected. Alright so, this is the zeroth order problem. Let us look at the first order or rather take into account the perturbation and see that how things can be calculated or how with the energy can be calculated, because of the inclusion of this H prime term.

And remember that your psi n, let us remove it psi n 0 form a complete set and we may expand, psi n in terms of psi n 0, what it means is that the full wave function including the perturbation term can be expanded in terms of the unperturbed wave function. So, this psi n is equal to some N lambda, this is the normalization can term. So, N lambda is normalization and then you have a psi n 0 which is a zeroth order term.

And then you have a, K not equal to n and the coefficient Cn K which of course, should be a function of a lambda and then a psi K 0. So, this is the basically the ansatz, that we start with ansatz it is the assumption that ok. So, this is your n a psi of n and of course, for the zeroth order which is not important at this moment, but still because this we have to build upon the zeroth order. For the zeroth order that is, lambda equal to 0, we are going to build up the perturbation theory in terms of or in powers of lambda. So, N of 0 is equal to 1 and Cn K 0 is equal to 0. So, which gives that the psi n is nothing, but equal to psi n 0, this is what we have seen; we have not yet taken into account the perturbation that will do it in the first order.

(Refer Slide Time: 15:25)



In general we have,

$$C_{nK}(\lambda) = \lambda C_{nK}^{(1)} + \lambda^2 C_{nK}^{(2)} + \cdots\cdots \qquad (3)$$

$$\text{and } E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\cdots$$

Putting (3) in (1)

$$(H_0 + \lambda H')\Big[|\psi_n^0\rangle + \lambda \sum_{K\neq n} C_{nK}^{(1)} |\psi_K^0\rangle + \lambda^2 \sum_{K\neq n} C_{nK}^{(2)} |\psi_K^0\rangle + \cdots\Big]$$

$$= \left(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\Big[\psi_n^{(0)} + \lambda \sum_{K\neq n} C_{nK}^{(1)} |\psi_K^{(0)}\rangle + \lambda^2 \sum_{K\neq n} C_{nK}^{(2)} |\psi_K^{(0)}\rangle + \cdots\Big] \qquad (4)$$

Matching same powers of $\lambda$ in 2 sides,

$$H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

So, in general we have C nK lambda equal to lambda C nK. So, this is 1, this 1 in the subscript or rather the superscript that indicates that we are doing or this involving first order of lambda or rather in technical terms it is called as we are doing the first order in the perturbation theory.

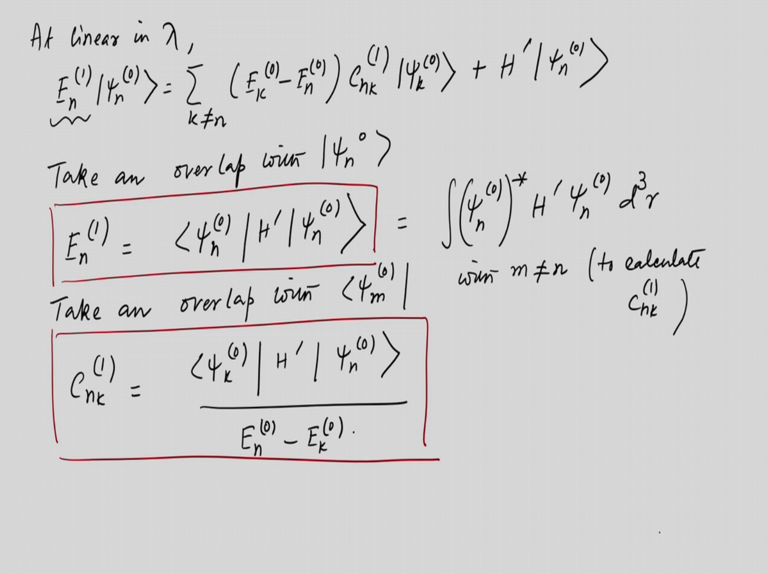
So, and then a lambda square a C nK C nK 2 and terms which are like this then they will be lambda cube C nK 3 and. So, on and also so this is the wave function the correction in the wave function, which are written in terms of the amplitude of the wave function and of course, your E n is the zeroth order which is what you know plus a lambda E n 1 and plus a lambda square E n 2, and so on. So, what we mean to say is that when we take a linear power of lambda, which is trying to do a first order perturbation theory and then there is a superscript of 1 in the bracket and then it is a lambda square as a 2 superscript 2 in the bracket and so on.

So, if we substitute these two into this equation, let us call this as the ansatz as equation 1 and let us call these two as equation 2. So putting 2 into 1, we have, H 0 plus a lambda H prime that acting on psi n 0 plus a sum over K, but that is not equal to n, lambda we can keep the lambda out. So, there is a C nK 1 psi K 0. So, psi K 0 psi n 0, the overlap between them is 0 because psi n 0 forms a complete set of states, plus there is a lambda square and then K not equal to n again and then there is a C nK 2 and then there is a psi K 0 and so on.

We are writing it without we were writing the wave functions without a bracket. So, let us just remove the bracket. Alright so, this is and then of course, you have terms now this is put in the so, this should be actually 1, these were way of putting it. So, maybe this will write it as 2. So, that is the ansatz and we will call this as 3. So, we will put actually 3 into 1 that is, what we are doing here. So, this is equal to E n 0 plus a lambda E n 1. Let us write it with a bracket this is it is up to you, whether you want to put the bracket, there is just you remember that the in the superscript those numbers 1 and 2 are written as that the order of perturbation theory that we are taking on just to make no mistakes that we are actually, when we write 2 it should not be in a square.

So, that is why we are a little conscious in writing them inside a bracket. So, this plus this and then of course, this wave function that we have just written a psi n 0 plus a lambda K not equal to n C nK 1 psi K 0 and a lambda square and a K not equal to n C nK 2 and psi K 0 and so on. So, this is the equation that we get by putting these two expansions into equation 1, that is the Schrodinger equation and now what we have to do is that we will have to match terms order by order in both the sides. So, which means that a same powers of lambda have to be matched. So, we will of course, I should recognize that a H 0 psi n 0 or which is equal to E n 0 psi n 0 and this is nothing, but the unperturbed equation.

(Refer Slide Time: 21:21)



At linear in $\lambda$,

$$\underset{\sim}{E_n^{(1)}} |\psi_n^{(0)}\rangle = \sum_{k \neq n} \left(E_k^{(0)} - E_n^{(0)}\right) C_{nk}^{(1)} |\psi_k^{(0)}\rangle + H' |\psi_n^{(0)}\rangle$$

Take an overlap with $|\psi_n^{0}\rangle$

$$\boxed{E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle} = \int \left(\psi_n^{(0)}\right)^* H' \psi_n^{(0)} \, d^3 r$$

Take an overlap with $\langle \psi_m^{(0)}|$ with $m \neq n$ (to calculate $C_{nk}^{(1)}$)

$$\boxed{C_{nk}^{(1)} = \frac{\langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}.}$$

The first order in lambda we have a E n 1 psi n 0, which is equal to sum over K not equal to n and we have a EK 0 minus E n 0 and a C nK 1 psi K psi K 0 and a plus a H prime psi n 0 just do not you know worry about that whether we are putting a bracket on the superscripts you can or you may not. But, just make sure that they do not mean a square and they are really talking about the powers of the perturbation theory that we are doing.

So, in order to get the energy correction that is this one, a E n 1 which essentially comes because of the perturbation term H prime we take an overlap with psi n 0. So, that immediately gives us, E n 1 which is equal to a psi n 0 H prime psi n 0 look the first term when you take the overlap of course, this is a number. So, it is just a psi n 0 psi n 0 which gives us 1, because we said that psi n 0 forms a complete set of states and when psi n 0 overlap is taken with psi K 0, since K is not equal to n because of the orthonormality condition this goes to 0.

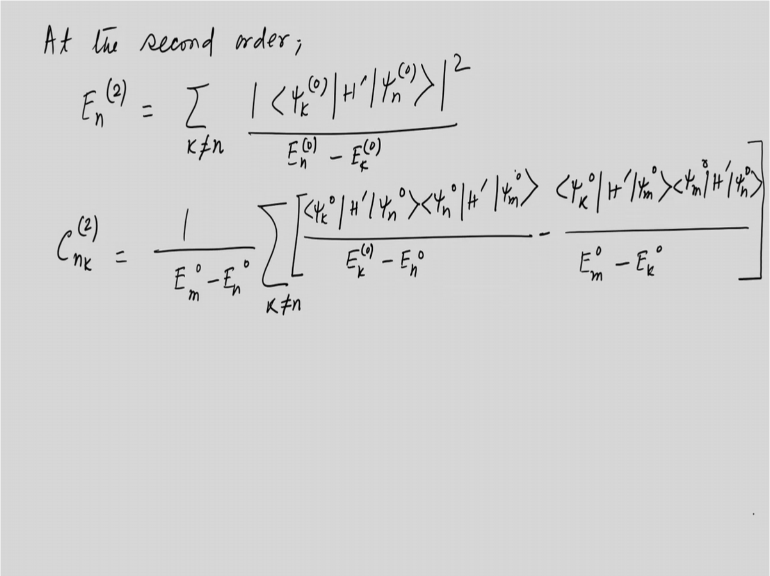
And the only term that survives is the last the term that is at the end in the RHS the right hand side and if you are interested in actually calculating this and then this is equal to in the integral form this is equal to that a psi n a 0, which are which could be functions of you know r theta phi or it could have additional indices such as, a spin. Or other you know quantum numbers, which are relevant to the problem it is this, and we are simply talking about maybe just talking about a integral which is a space integral.

So, this is the first order correction. So, the expectation value of the perturbation term needs to be taken between the unperturbed ground states and that gives you the first order correction and. So, that is one part of the story that is we now obtain the first order correction, what happens to the wave function that is the important thing. And the wave function can actually be obtained; we take the inner product with a psi m 0, where m is not equal to n. So, with m not equal to n and to calculate a Cn K 1, that is the first order correction to the wave function.

And this is equal to a C nK 1 equal to a psi K 0 H prime and then a psi n 0 and E K c En 0 minus EK 0 and so on. Ok. So, this is the first order correction to the wave function and we have already obtained the first order correction to energy. So, these are the important things let us just do a box of these important expressions and. So, one corresponds to the energy correction the other corresponds to the correction in the wave function.

And if you do it in the second order that is go back to this expression let us call it, expression or rather equation number 4. If you go to 4 and take the second order correction or rather second order in lambda and then equate powers in second order in lambda, remember the second order in lambda will also come from a lambda in the left hand side. And, the lambda in the right hand side or a lambda square on the right hand side with no power of lambda, lambda to the power 0 on the right and a vice versa.

(Refer Slide Time: 27:03)



At the second order;

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle \psi_k^{(0)} | H' | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$C_{nk}^{(2)} = \frac{1}{E_m^{0} - E_n^{0}} \sum_{k \neq n} \left[ \frac{\langle \psi_k^{0} | H' | \psi_n^{0} \rangle \langle \psi_n^{0} | H' | \psi_m^{0} \rangle}{E_k^{(0)} - E_n^{0}} - \frac{\langle \psi_k^{0} | H' | \psi_m^{0} \rangle \langle \psi_m^{0} | H' | \psi_n^{0} \rangle}{E_m^{0} - E_k^{0}} \right]$$

So, that all those combinations need to be taken you can do that and I will simply write down the expressions that are important. So at the second order, the second order correction in energy is simply equal to this and. So, a psi K 0 H prime a psi n 0 and a mod square of this and divided by E n 0 minus EK 0. So, this is the expression for the wave function or rather sorry the energy correction up to second order and which says that the matrix element has to be calculated between two different states.

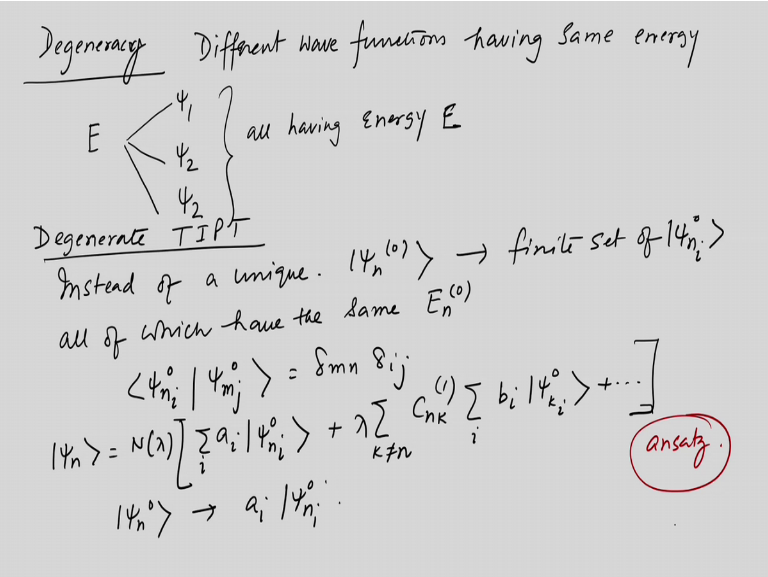
So, the H prime has to connect to two different states, that is K and n a 2 these are two orthogonal states if it does not connect then of course, the second order result is 0 and more importantly, why do you want to go to the second order perturbation theory? Sometimes it may happen which will show that the first order correction is 0. Now if the first order correction is 0 does not mean that the perturbation does not have any effect on the system, it could be showing up in the second order or in higher orders well.

So, this one and there is slightly complicated expression for the wave function the amplitude of the wave function, which is equal to 1 divided by E m 0 E n 0. Sometimes I am writing the brackets sometimes, I am not, there is a K not equal to n and now I have a psi K 0 H prime psi n 0 psi n 0 H prime psi m 0 and this divided by an energy denominator, which is EK 0 and E n 0 and a minus the psi K 0 H prime psi m 0 psi m 0 H prime psi n 0 and this again divided by EK or a Em 0 minus a Ek 0 and this is the expression for the second order correction in the amplitude of the wave function.

So, this would renormalize the wave function for the system in the at the second order. So, remember that it has an energy denominator and. So, is the energy denominator in the expression for the second order energy correction, which is En 0 minus EK 0 and. So, there is also an energy denominator in the Cn K term in the first order for the amplitude correction of the wave function.

Now, what happens if your E n 0 becomes equal to Ek 0, then all these things will the denominator will vanish and some denominator vanishing is not a good thing for any physics or rather anything that is happening because that will lead to divergences. And, these divergences are unwanted and hence we need to actually reformulate the problem when such a thing happens that is your En 0, becomes equal to EK 0 and needless you say that, we are actually talking about the degenerate cases.

(Refer Slide Time: 31:07)



Degeneracy Different wave functions having same energy

Degenerate TIPT

Instead of a unique. $|\psi_n^{(0)}\rangle \rightarrow$ finite set of $|\psi_{n_i}^{0}\rangle$

all of which have the same $E_n^{(0)}$

$$\langle \psi_{n_i}^{0} | \psi_{m_j}^{0} \rangle = \delta_{mn} \delta_{ij}$$

$$|\psi_n\rangle = N(\lambda) \left[ \sum_i a_i |\psi_{n_i}^{0}\rangle + \lambda \sum_{k \neq n} C_{nk}^{(1)} \sum_i b_i |\psi_{k_i}^{0}\rangle + \cdots \right]$$

ansatz.

$$|\psi_n^{0}\rangle \rightarrow a_i |\psi_{n_i}^{0}$$

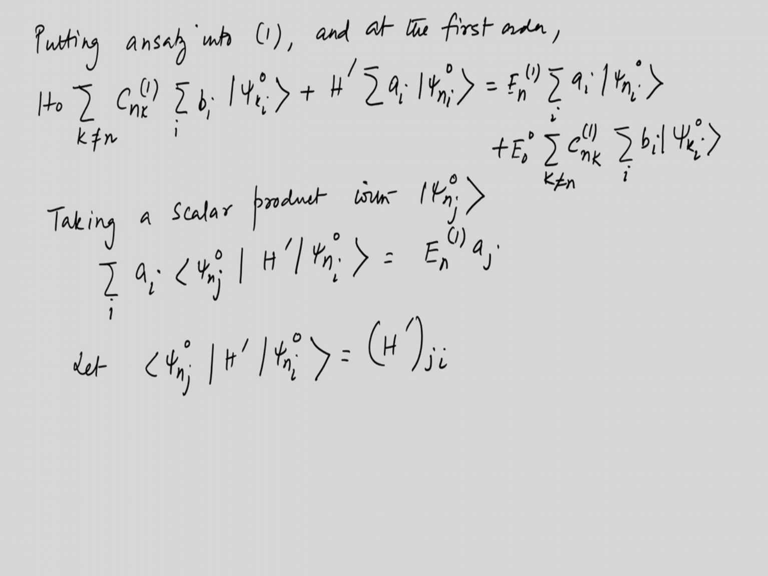
So, once again what is Degeneracy? Let me sort of. So, different wave functions having same energy. So, this is the definition of degeneracy. So, you have an energy which is say some E and this would correspond to you know say 3 wave functions having, psi 1, psi 2 and psi 3 all having the same energy, all having energy E. However, they are all distinct states and they could be orthogonal to each other and. So, this is what is called as degeneracy in case of degeneracy, one can actually have this EK 0 equal to En 0 or Em 0 equal to En 0, that is the two levels can be actually degenerate and then we have different wave functions etcetera corresponding to them.

So, what is the way to deal with such situations in which we have degeneracy in the perturbation theory? So, we have already said that the problem is with the energy denominator. So, instead of so we will talk about, the degenerate time independent perturbation theory. So, degenerate TIPT. So, instead of a unique psi n 0, we have a finite set of psi ni 0 and all of which have the same energy let us call it as E n 0. So, not only 1, but there are depending on how big i is that is i could be 2, 3, 4 or in many all of them have the same energy En 0 and this is what we mean by a degeneracy.

However, each of these you know these things are. So, psi n 0 and psi m j 0, so this is equal to a delta mn a delta ij. So, basically all this set is orthonormal. So, we now want to expand the wave function psi n, which is again just like earlier cases that we have a sum over i and a a i psi n i 0 plus a lambda a K not equal to n and a CnK 1 and sum over i and then there is a bi and a psi k i 0 and so on. So, this is the ansatz now let us call it.

Ok. So, if we put this ansatz into this equation 1, which is the Schrodinger equation then, we will get an equation of the form. So, we simply what we have done is that, we have a replaced our psi n 0 by a sum over i a i psi n i which is what we have there is a sum and so on ok.

(Refer Slide Time: 35:46)



Putting ansatz into (1), and at the first order,

$$H_0 \sum_{k\neq n} C_{nk}^{(1)} \sum_i b_i |\psi_{k_i}^0\rangle + H' \sum a_i |\psi_{n_i}^0\rangle = E_n^{(1)} \sum_i a_i |\psi_{n_i}^0\rangle$$

$$+ E_0^0 \sum_{k\neq n} C_{nk}^{(1)} \sum_i b_i |\psi_{k_i}^0\rangle$$

Taking a scalar product with $|\psi_{n_j}^0\rangle$

$$\sum_i a_i \langle \psi_{n_j}^0 | H' | \psi_{n_i}^0 \rangle = E_n^{(1)} a_j$$

Let $\langle \psi_{n_j}^0 | H' | \psi_{n_i}^0 \rangle = (H')_{ji}$

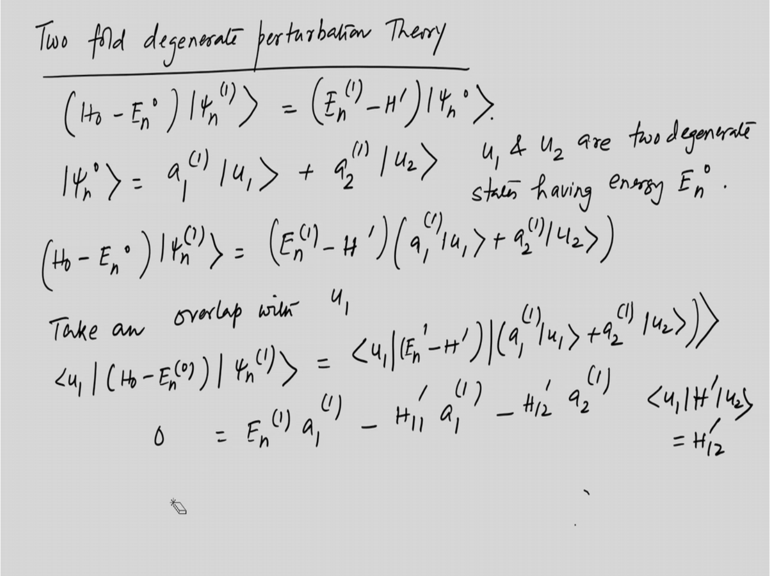
So, putting this putting ansatz into 1, we have a sum over or. So, let us just write it. So, this is a H 0, a K not equal to n. So, this is at the first order and at the first order assuming that the unperturbed problem is completely known and solved.

So, H 0 K not equal to n is CnK 1 sum over i bi psi k i 0 plus a H 1, not H 1 sorry this should be H prime. And we have a ai and a psi n i 0 and which is of course, we can continue that we are writing it in the first order. So, this is equal to a En 1 sum over i a i psi n i 0 plus E n 0 and there is a Cn. So, this K not equal to n and there is a Cnk nK be very careful with the, this indices and this I mean the basically the notation, you have to write it once in order to you know gain confidence.

So, this is equal to a sum over i and psi Ki 0. So, this is the first order equation and again in order to calculate the first order energy correction we take a scalar product. So, this gives the a i to be psi n j 0 H prime and psi n i 0, which is equal to E n 1 that is a first order energy and then it is a j the rest of the terms yield 0. So, it is a little more complicated than the non degenerate case that, we have just seen the only difference being that it is a finite dimensional problem, but still we have to recognize that it is a finite dimensional problem and should be solvable.

So your, so let you know I mean psi n j 0 H prime and psi n i 0. Let us call it as you know H prime j i. So, that is the matrix element and so on and let us just do it do this problem for a particular case that is say a twofold degenerate problem.

(Refer Slide Time: 39:29)



Two fold degenerate perturbation Theory

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle = (E_n^{(1)} - H')|\psi_n^0\rangle.$$

$$|\psi_n^0\rangle = a_1^{(1)}|u_1\rangle + a_2^{(1)}|u_2\rangle$$ $u_1$ & $u_2$ are two degenerate states having energy $E_n^0$.

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle = (E_n^{(1)} - H')\left(a_1^{(1)}|u_1\rangle + a_2^{(1)}|u_2\rangle\right)$$

Take an overlap with $u_1$

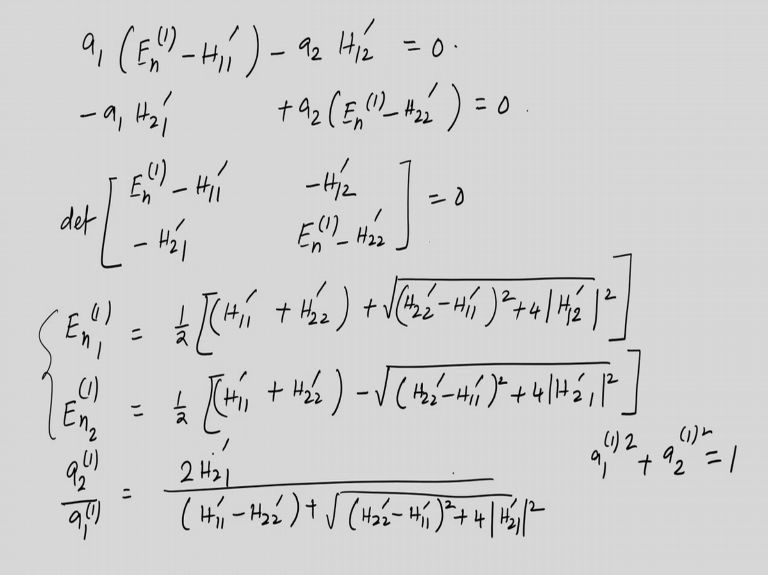
$$\langle u_1|(H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle = \langle u_1|(E_n^1 - H')|(a_1^{(1)}|u_1\rangle + a_2^{(1)}|u_2\rangle)\rangle$$

$$0 = E_n^{(1)}a_1^{(1)} - H'_{11}a_1^{(1)} - H'_{12}a_2^{(1)}$$ $\langle u_1|H'|u_2\rangle = H'_{12}$

So, alright so what is it? So, it is equal to H 0 minus E n 0; so, that and a psi n 0. So, whenever the superscripts actually denote the order that we are interested in. So, this is equal to E n 1 minus H prime and a psi n 0. So, let us now consider that psi n 0 equal to sum a 1 1 u 1 and a 2 1 and u 2, which are u 1 and u 2 are 2 degenerate states having energy E 0 E n 0 ok. So, if that is the case then your H 0 minus E n 0 multiplied or acting on this psi n 1, which is equal to E n 1 minus H prime and a 1 1 plus a 2 u 1 and let us write it clearly u 1 plus a 2 1 u 2. So, this is the equation.

Now, we take an overlap, overlap means the inner product so; that means, that you have a u 1 and a H 0 minus E n 0 a psi n 1 this is equal to a u 1 E E n 1, E n 1 minus H prime then this is a 1 1 u 1 plus a a 2 1 u 2 ok. So, this tells you that we have a any two equations which are 0 equal to E n 1 a 1 1 minus H 1 1 prime a 1 1 and H 1 2 prime a 2 1, remember that these H 1 1 prime and H 1 2 prime are basically. So, it is u 1 H prime u 2 and so on. So, that is equal to your H 1 2 prime and u 1 H prime u 1 is equal to H 1 1 and the other one would be minus a 1 H 2 1 prime. So, this one will be um.

(Refer Slide Time: 43:41)



$$a_1\left(E_n^{(1)}-H'_{11}\right)-a_2 H'_{12}=0.$$

$$-a_1 H'_{21}+a_2\left(E_n^{(1)}-H'_{22}\right)=0.$$

$$\det\begin{bmatrix} E_n^{(1)}-H'_{11} & -H'_{12} \\ -H'_{21} & E_n^{(1)}-H'_{22} \end{bmatrix}=0$$

$$\begin{cases} E_{n_1}^{(1)}=\frac{1}{2}\left[\left(H'_{11}+H'_{22}\right)+\sqrt{\left(H'_{22}-H'_{11}\right)^2+4\left|H'_{12}\right|^2}\right] \\ E_{n_2}^{(1)}=\frac{1}{2}\left[\left(H'_{11}+H'_{22}\right)-\sqrt{\left(H'_{22}-H'_{11}\right)^2+4\left|H'_{21}\right|^2}\right] \end{cases}$$

$$\frac{a_2^{(1)}}{a_1^{(1)}}=\frac{2H'_{21}}{\left(H'_{11}-H'_{22}\right)+\sqrt{\left(H'_{22}-H'_{11}\right)^2+4\left|H'_{21}\right|^2}}$$

$$a_1^{(1)2}+a_2^{(1)2}=1$$

So, we will have a two equations I will just write them in the next page. So, we have two equations which are a 1 E n 1 minus H 1 1 prime minus a 2 H 1 2 prime, it is equal to 0 and minus a 1 H 2 1 prime plus a 2 E n 1 minus H 2 2 prime it is equal to 0 as well. Now, this is a set of coupled equations you know that in order to have a non trivial solution for these coupled equations the determinant matrix should vanish. So, the determinant matrix is given by this secular equation, which is equal to so this is E n 1 minus H 1 1 prime, minus H prime 1 2 minus, H prime 2 1 E n 1 minus, H 2 2 prime and so on this is equal to 0. So, basically we are talking about the determinant equal to 0.

Now, you see it is like this that we are trying to calculate for this degenerate perturbation theory the first order energy correction, which involves the matrix elements of these H prime term that is a perturbation term between the non the unperturbed states. So, these are u 1 and u 2 are the degenerate unperturbed states and they are so, this is basically, so I will get two values of a E n ones may be, En 1 1 and En 2 1 that is these are the two values, which would give that how these two levels that is the energy levels will actually respond to this perturbation.

So um, in fact, the energy level which was earlier degenerate before the application of perturbation theory may actually respond differently to this perturbation and this is what most of the time it happens. So, that would be obtained by solving this secular equation, which is as I told that it is called let us call them as you would not know H 1 prime, H 1 2 prime and H 1 1 prime and h 2 1 prime and H 2 2 prime unless, you are given a specific problem, which is what we are going to see in a particular problem called as the stark effect.

So, let us at least write down the general form for this. So, it is H 1 1 prime plus H 2 2 prime. So, that is the value for 1 plus this H 2 2 prime and H 1 1 prime square plus a 4 H 2, this 2 1 not 1 2, they could be same they could be different for a Hermitian matrix H 1 2 is equal to H 2 1. So, this is the energy correction 1 and this is 2 at the first order level, which is equal to just having a minus sign in between. So, that is H 1 1 prime plus a H 2 2 prime minus H 2 2 prime minus a H 1 1 prime square plus a 4 H, this is prime amidst 2 1 prime or one of them is actually just check one of them should be 1 2 prime um.

So, this could be 1 2 prime we just check that it is just m in most of the cases, we are dealing with the Hermitian matrices. So, it really does not make any difference. So, these are the corrections in the energy E n 0. So, you see that because of this plus and minus sign here and here the two levels, which were earlier degenerate before the application of perturbation theory has now reacted differently. So, they will either shift or they will split on either side of the E n 0 and we are interested in finding out that and just that the two the first order correction in the wave function can be obtained by knowing this ratio which is equal to nothing, but 2 H 2 1.

We just all talking about solving a 2 by 2 secular equation; so, this is equal to H 1 1 prime minus H 2 2 prime plus H 2 2 prime minus H 1 1 prime square plus 4 H 2 1 prime square. And of course, this gives you the ratio, but there is a because of the normalization there is another condition that exists, which is the square of them should be equal to 1, now this is the full solution to this problem.

So, we have calculated the first order energy correction due to the perturbation term. So, these are the two of values of the correction. So, the two wave functions or rather which were degenerate before the perturbation was switched on such as, u 1 and u 2 they react or they respond to the perturbation in this particular fashion. And, the coefficients the first order change in coefficients of the wave function that corresponds to this kind of a correction which are subject to this normalization condition.

Now, the situation is that that we have done a perturbation theory, degenerate perturbation theory. Now, suppose this is not a twofold degenerate perturbation theory it is a fourfold degenerate, which is what we are going to see in stark effect then we have to solve a 4 by 4 secular equation. Just the complexity of the problem goes up a little, but you will see that because of the symmetry of the problem many of the terms, which are cancelled because of you know, because of the symmetry.

And the integrals if you before you actually calculate all the matrix elements such as H 1 2 H 2 1 etcetera; you can look at the symmetry of the problem. And, this quantum mechanics actually very importantly teaches us how to exploit the symmetry of the problem and reduce the complexity and you know in a way that is simplify a given problem. So, we will apply this degenerate perturbation theory to Stark effect, which is as I told you it is a fourth it is a you know degeneracy the level of degeneracy or the degree of degeneracy is 4 instead of 2, that we have just shown here.