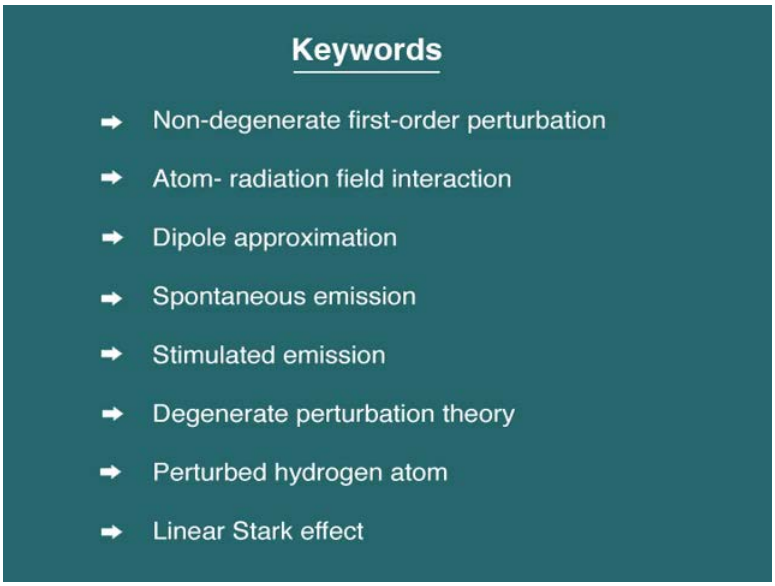
Quantum Mechanics - I
Prof. Dr. S. Lakshmi Bala
Department of Physics
Indian Institute of Technology, Madras

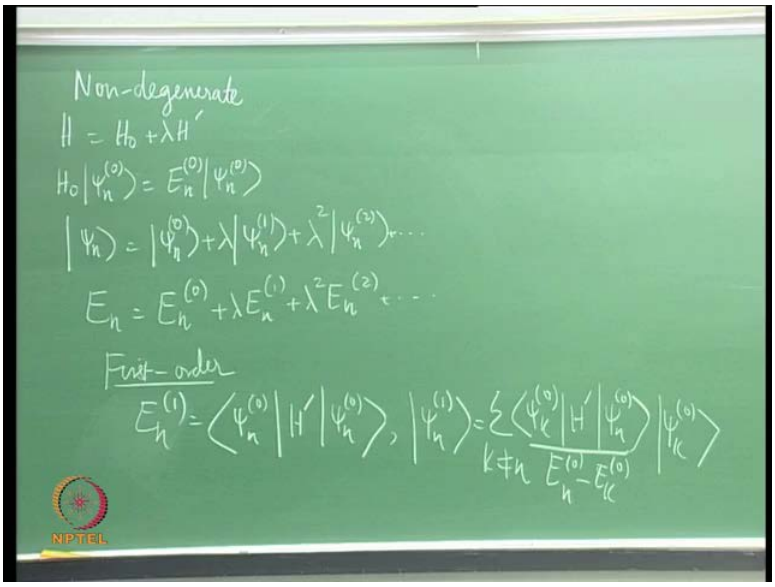
Lecture - 38
Perturbation Theory – III

(Refer Slide Time: 00:07)



We were looking at the Rayleigh Schrodinger a perturbation theory and just by way of recapitulation of the notation, let me put down here what exactly we had stated.

(Refer Slide Time: 00:23)

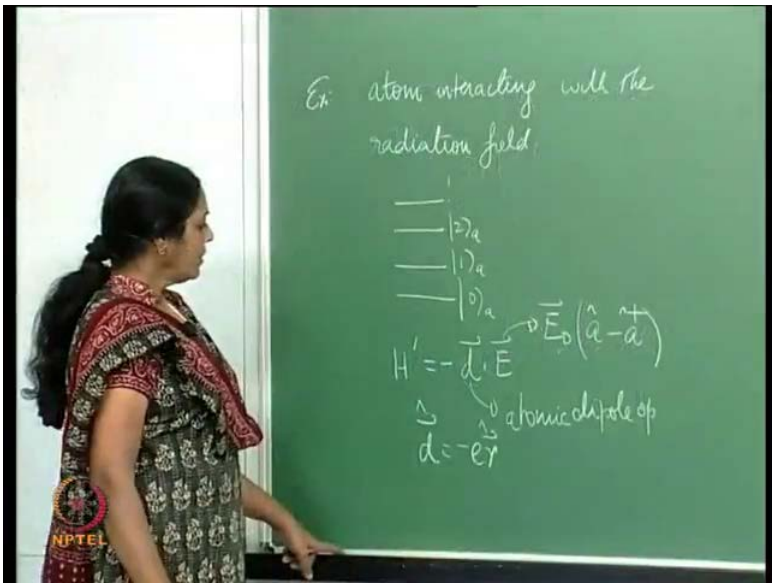


We were looking at the non degenerate case. I will discuss the degenerate case later by degenerate I mean that the energy has a g fold; the energy Eigen value is g fold degenerate. So, here we have the non degenerate case. And we had a total Hamiltonian which was H naught plus lambda H prime. There was a discrete spectrum and the Eigen functions the energy Eigen functions were represented by psi n 0 and the corresponding energy Eigen values by E n 0. And then because of the perturbing Hamiltonian H prime, the total wave function had this unperturbed form plus lambda psi n 1, and you could stop here if you were looking at the 1st order in the perturbation, or you could continue and get to the 2nd order in the perturbation and so on.

Depending on the context because you should decide where exactly it makes sense to truncate this series. Similarly, the energy Eigen values, get a contribution because of the perturbation to 1st order, there was a contribution E n 1 to 2nd order there was a contribution E n 2 and so on. And then we had these expressions we were looking at 1st order perturbation theory. And then we had the contribution to the 1st order, of the energy was the matrix element of the perturbing Hamiltonian in the zeroth order state psi n 0.

And then we had a very crucial expression, the contribution to the wave function to 1st order. That means just the 1st order contribution, I am neglecting the zeroth order contribution was summation over k not equal to n, psi k 0 H prime psi n 0 by E n 0 minus E k 0 it is good to pause here and understand what exactly this matrix element means. Now, look at the numerator the matrix elements there is the transition matrix element h prime takes this state psi n 0, to psi k 0 and we can in short form call that h prime subscript k n. So, transition matrix elements become extremely important in general. And it is after all the perturbing Hamiltonian, which is responsible for taking us from one state to another state.

(Refer Slide Time: 04:12)



So, let us look at an example and see what this means. The example that I am going to take is from optics. I have an atom interacting with the radiation field the atom has discrete levels. Could be a two level atom three level atom anything but, these are the atomic levels. I am looking at a situation where not only the atom is a quantum object, with discrete energy levels but, the radiation field is also quantized. Now normally in a situation where the atom interacts with a radiation field, a very popular perturbing Hamiltonian, the perturbation is because the radiation field is affecting the atom.

And is going to provide atomic transitions, because of the perturbation the atom could jump from a higher level to lower level releasing photons, or it can go from a lower level to a higher level by absorbing photons from the radiation field. And H prime a common example of H prime is minus d dot E where d is the atomic dipole operator and E is the electric field. Now, the atomic dipole like all dipoles is going to be represented by the charge e times r. And I am looking at a case, where E is spatially homogeneous.

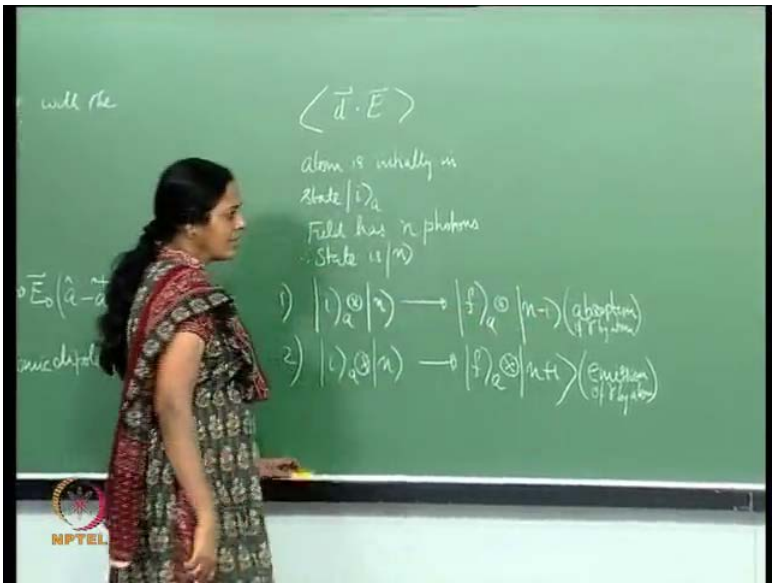
Now, this is reasonably good approximation is called the dipole approximation because the atomic dipole interacts with the radiation field. And E itself is taken to be spatially homogeneous, over atomic distances. In other words the size of an atom is typically of a few angstroms and I would assume that, if I use light electromagnetic waves, with wave length of the order of about say 500 nanometers then across the size of the atom across a stretch of a few angstroms, I do not expect the electric field to change terribly. So, the

electric field is taken to be independent of space it is a constant field the vector sin is because, there is a polarization vector E naught times I have quantized the electric field and if you go back to one of our discussions long time ago, where we were using the harmonic oscillator model the linear harmonic oscillator model to describe quantum optics.

We have realized that the energy density for the electromagnetic field is e squared plus b squared apart from constants like, permeability, permittivity overall factors and so on. Somewhat similar, to the quadratic Hamiltonian that you have in the case of the harmonic oscillator, which is essentially x squared plus p squared give or take some constants. And then we used the ladder operators of the harmonic oscillator. And we wrote the electric field as a plus a dagger, a minus a dagger and therefore, the magnetic field as a plus a dagger, this is apart from some constants. So, the constants become irrelevant here perhaps, I can even absorb the constants in E naught so E naught has the polarization vector and some overall constants.

And I have a minus a dagger, where a is the photon destruction operator, and a dagger is the photon creation operator. And there is no time dependence here. So, the perturbing Hamiltonian has no time dependence the polarization vector is the vector quantity here. So, there is dot product between the dipole which has vector r and this. There are operators here and those are the a's and a daggers. So, these are the operators relating to the radiation field a and a dagger. And this is the dipole operator, if you wish corresponding to the atom because it is the atomic dipole.

(Refer Slide Time: 09:55)



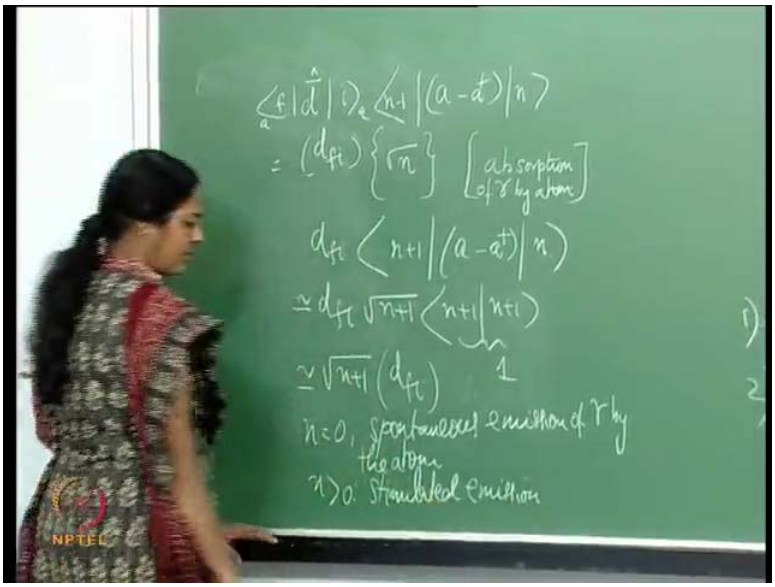
Now, in a situation like this, what it it that I will have? As far as the matrix elements of H prime go. Basically, I am looking at the matrix elements of d dot E because, that is the perturbing Hamiltonian. What are the initial states? Let us imagine that the atom is in an initial state is initially, in some state a or i if you wish that is the initial state of the atom, i a in my notation the suffix a means an atomic state. And the field has n photons initially. And therefore, the state of the radiation filed is n. So, my initial state would be i a direct producted with n. Now, this goes to a final state which is a final state of the atom.

Now, 2 cases are possible. the final state could have been reach by absorption of photons by the atom, let us say it absorbed 1 photon. And therefore, the photons in the radiation field at least 1 of them was used up. And I have a final state, which is given by f a clearly this is a higher energy level compared to i because, the radiation field has lost a photon and that photon has been absorbed by the atom to go to the state f. Now, this is one possibility, the 2nd possibility is where initial state of the atom becomes the final state f but, that is because the atom emitted a photon (Refer Slide Time: 04:12) and went from a higher state to a lower state.

The photon itself gets absorbed by the radiation field and while I had initially n photons it now becomes n plus 1. So, these are 2 possibilities where I only talk about going from one state to another of the atom by absorption of a single photon or by emission of a

single photon. Now, this process corresponds to absorption the atom has absorbed a photon. And this corresponds to emission of photon by atom. This is absorption of photon by atom. So, these are the possible processes that I have so if this is my initial state and that is the final state.

(Refer Slide Time: 13:25)



Let us look at case one, how do I go from one to the other? So, the matrix element is essentially the atomic dipole operator, taking an initial state i of the atom to a final state f. And then of course, I have a matrix element which is essentially a minus a dagger, coming from the electric field taking me from an initial state n, (Refer Slide Time: 09:55) in the 1st case to a final state n minus 1. Let me call this as the matrix element d f i and here I am with this object but, a on ket n, gives me root n ket n minus 1. And since the photon number states are orthonormal to each other that gives a contribution. The 2nd term that is a dagger on ket n takes it to n plus 1 and that does not therefore, make a contribution.

So, I have this (Refer Slide Time: 00:23) and this is the term H prime phi n psi k, for the transition element contributions that come from h prime in the case of absorption. Absorption of photon by atom, clearly this makes sense suppose I switched off the radiation field, that means there are no photons to be absorbed so if n is 0 this term drops out. That is common sense if there is no energy pumped into the atom. There is no way

by which is the atom can absorb energy and move to a higher state and therefore, such a transition is not possible so that is ok.

Now, you look at the 2nd case. (Refer Slide Time: 09:55) Once more I have the atomic dipole operators matrix element d f i. And then there is a situation, where the radiation field initially had n photons and finally had n plus 1 photons because, the atom emitted a photon. Now, what is this quantity equal to? This is d f i a on ket n is root n minus, it gives me ket n minus 1 and therefore, that does not make a contribution. But, a dagger forget the signs a dagger produces a root of n plus 1 ket n plus 1 and this is 1. And therefore, I have apart from signs constants and so on. I have a root of n plus 1, times the atomic part.

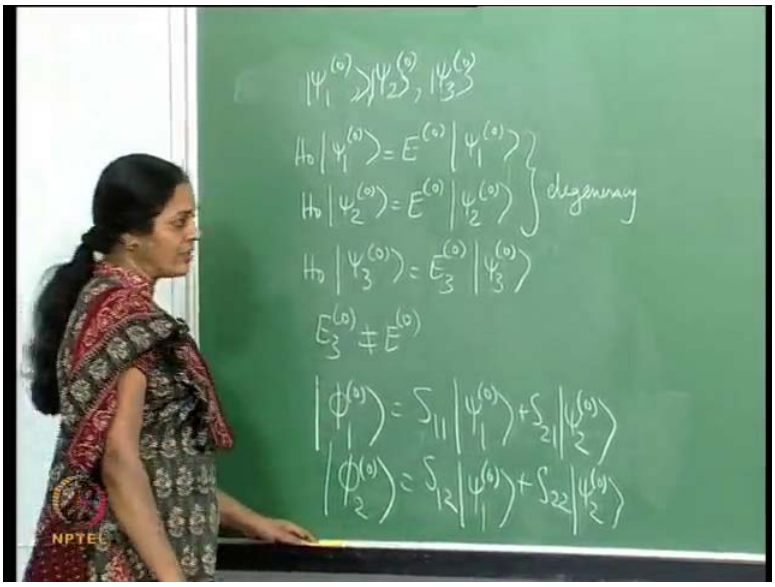
Now, this is a very important point it tells us that even if you switch off the perturbation, even if there are no photons supplied by the radiation field you switched off the radiation field that means you set n equals 0. You still have emission of photons by the atom. Clearly this is a very spontaneous emission of photons, because the atom spontaneously emits photons without the usage of an external radiation field. This is a purely quantum mechanical phenomena. You do not have a classical counterpart for spontaneous emission it therefore, becomes a very interesting feature of quantum physics. So, if n is 0 you have spontaneous emission of photons, by the atom if n is greater than 0, it is clear that the radiation field stimulates the atom to emit photons and that would be stimulated emission.

Spontaneous emission as I said has no classical analogs or classical counterparts. And that is a very interesting example of time independent perturbation theory, where I have used the fact that the energy levels are not degenerate because I have chosen energy levels where the initial state has a certain energy and the final state although energy is conserved, each state has a different energy so f has a higher energy compare to i and so on. So, this is a very interesting example of non degenerate stationary perturbation theory. (Refer Slide Time: 00:23) The next thing I wish to discuss is degenerate perturbation theory.

Now, look at the expression for psi n 1 in the denominator suppose there is degeneracy and E n 0 equals, some E k 0 the denominator blows up. And the perturbation formalism as such will not hold unless the transition matrix element in the numerator is also 0. How

do I alter this formalism to take care of the degenerate case? Clearly trouble comes in the 1st order contribution.

(Refer Slide Time: 20:06)

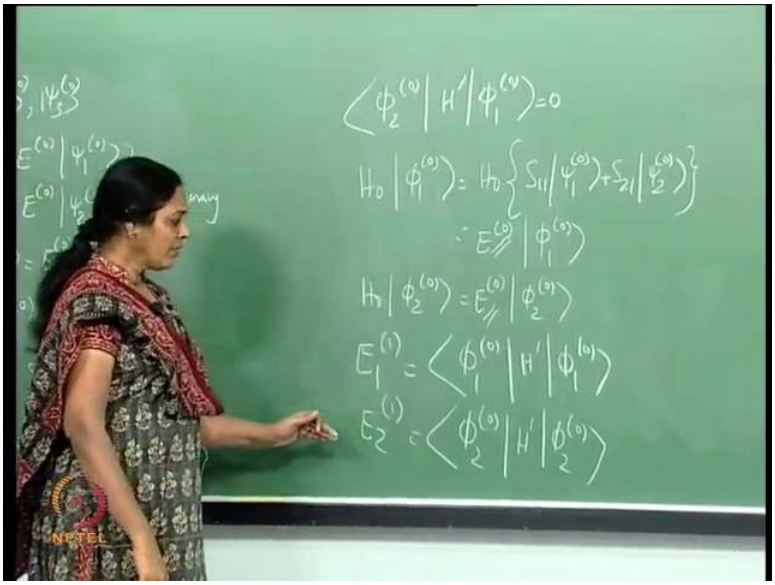


So, I go about it in the following fashion. Let me take an example, right now not an example from physics but, let me look at a situation, where there are 3 states psi 1 0, psi 2 0 and psi 3 0. Let us make kets out of them and let us say that psi 1 0 and psi 2 0 correspond to the same energy value. So I have H naught psi 1 0 is E naught psi 1 0 and H naught psi 2 0 is also E naught psi 2 0. On the other hand let us imagine that psi 3 0 is an Eigen state of H naught with a very different energy Eigen value such that, E 3 0 is not equal to E 0. So, in this problem there is a twofold degeneracy. The degeneracy is here corresponding to the energy value E 0 there are 2 independent linearly independent states psi 1 0 and psi 2 0 these are normalized states they are orthonormal to each other.

In that case, I could do the following thing. The trouble does not come from here, the trouble comes from here because in the denominator in the 1st order contribution (Refer Slide Time: 00:23) E 1 0 minus E 2 0 is 0. The way to handle this is by working in this space of degenerate states here I have twofold degeneracy and whatever I say is extendable to g fold degeneracy g being as large as you wish. So, I could define 2 objects phi 1 0 and phi 2 0, which are linear super positions of psi 1 0 and psi 2 0. So, let me say that this is S 1 1, psi 1 0 plus S 2 1 psi 2 0 and I have a phi 2 0, which is another super position S 1 2 psi 1 0 plus S 2 2 psi 2 0.

These 2 states are taken to be orthogonal to each other and they are normalized states. So, S 1 1 squared plus S 2 1 square is 1 S 1 2 squared plus S 2 2 squared is 1. So, these are normalized to unity. What are requirements that I have of these 2 superposed states?

(Refer Slide Time: 23:23)



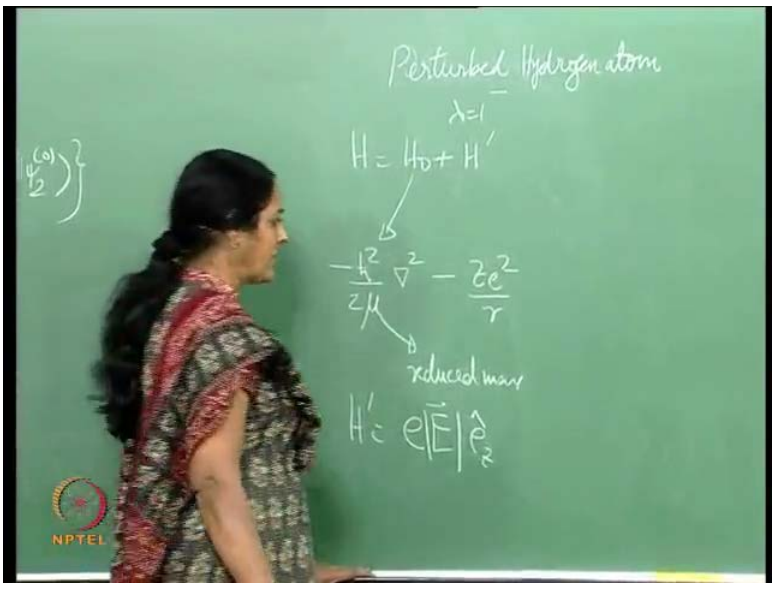
The requirements are the following: phi 2 0 H prime, phi 1 0 must be equal to 0. The reason is the following: H naught acting on phi 1 0 is H naught S 1 1 psi 1 0 plus S 2 1 psi 2 0. And that is the same as E 0 phi 1 0. Similarly, H naught phi 2 0 is also E 0 phi 2 0. (Refer Slide Time: 20:06) So, instead of looking at psi 1 0 and psi 2 0 if I worked with these combinations phi 1 0 and phi 2 0. (Refer Slide Time: 00:23) So, in this example k and n can only take values 1 and 2 and of course psi has to be replaced by phi appropriately. And now, since the denominator becomes 0 the matrix element in the numerator should also be 0.

So, this is certainly a requirement, I expect phi 2 0 H prime phi 1 0 to be 0. And therefore, it is complex conjugate phi 1 0 H prime phi 2 0 here to be 0. In general, if there is a g fold degeneracy I certainly expect phi k 0 H prime phi n 0 to be 0. Where phi k 0's and phi n 0's the phi's happens to be linear combinations of the original g fold degenerate states. Then what happens? Suppose I work with phi 1 0 and phi 2 0, it is clear that E 1 1, has to be of course, computed in the unperturbed bases but, now we have further degenerate states, the unperturbed basis states to be phi 1 0 and phi 2 0. So, E 1 1 is phi 1 0 H prime phi 1 0 and E 2 1 should be phi 2 0 H prime phi 2 0.

So, this is essentially what I need and the aim is to not just find out these energy values, which are hopefully different from each other. (Refer Slide Time: 20:06). We also need to find these states, which means we should be able to fix S 1 1, S 2 1, S 1 2 and S 2 2. Of course, if I worked with g fold degeneracy I should have g different energy values. Each of them, being the matrix element of the prime with respect to the appropriate linear combination of the original states. And in that I will have g of these, g linear combinations and I should work with them.

And I will demand that H prime phi k phi n, where k can take values 1 to g and n can take values 1 to g in this case, if k is not equal to n I demand that that is 0 in order to carry out, my perturbative calculation. So, in order do this it is best to illustrate it with an example. This is essentially what I wish to do, my example would be a perturbed hydrogen atom. So, let us look at the perturbed hydrogen atom. As you know the hydrogen atom the energy levels, except the ground state the energy levels are degenerate. And the perturbation which I will use in the 1st order perturbation theory, you find that a very interesting effect comes about it is called the linear stark effect and the degeneracy is lifted at least in some sector and we will see what that is.

(Refer Slide Time: 27:59)

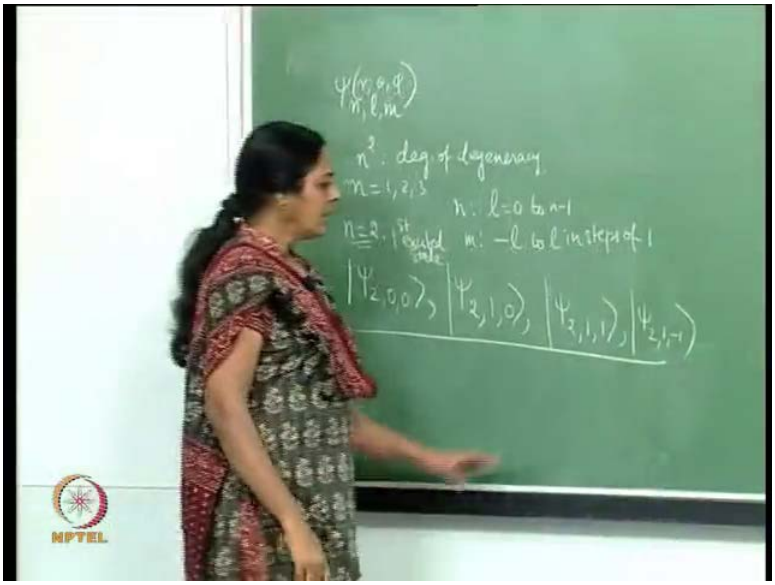


So, we will use the perturbed hydrogen atom to demonstrate what I say. So, the Hamiltonian as a free part I am going to set lambda equals 1 and a perturbation. Now, this free part this is what I have. This free part the hydrogen atom problem we had earlier

on reduced it to an effective one body problem. And H naught is minus h cross squared by 2 mu, where mu is the reduces mass Del squared, we work in spherical polar coordinates minus z e square by r. So that is the unperturbed part of the hydrogen atom.

I need to provide a perturbation, the perturbation could come in the form of an electric field I am going to consider an electric field perturbation has the electric charge e, times an electric field and this electric field is going to be modulus of e times e z. It is a homogeneous field, it is a constant field so this is what I have. Clearly I need to compute matrix elements.

(Refer Slide Time: 30:06)



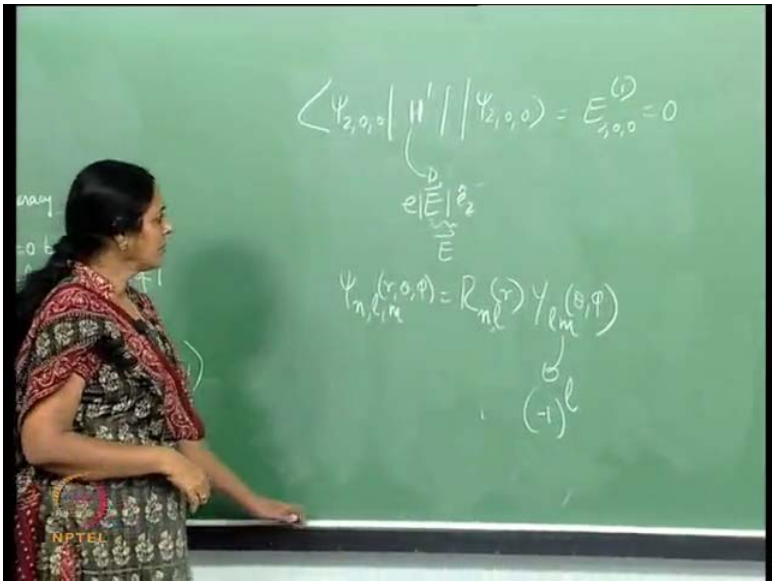
I need to 1st of all decide what level I am looking at, you will recall that in the hydrogen atom problem, the wave functions of the hydrogen atom carry with them three quantum numbers, n l and m. So, the generic wave function is psi n l m and for convenience, we could work in Spherical polar coordinates so I have psi n l m r theta of r theta phi. The degree of degeneracy is given by n squared, you will recall that n takes values 1 2 3 and so on. So, n is 1 there is exactly 1 state corresponding, to the hydrogen atom and that is the ground state.

However, when n is 2, for a given value of n l takes values 0 to n minus 1 and for a given value of l m takes values minus l to plus l, in steps of 1, these you will recall from our earlier discussion of the hydrogen atom. So, if I take n equals 2 there are 4 states corresponding to this energy level. So, there is a degeneracy and these 4 states I can

represent them by psi 2 l taking value 0 and therefore, m taking value 0, l taking value 1 and therefore, m taking value 0 or 1 or minus 1. Because m takes values minus 1 to plus 1 in steps of 1.

So, there is fourfold degeneracy and these are the various, wave functions each of them being a function of r theta and phi, corresponding to the 1st excited state of the hydrogen atom, this is the 1st excited state. We are interested in the matrix elements of H prime, the matrix elements which therefore, connect various initial states out of these to various final states.

(Refer Slide Time: 32:27)

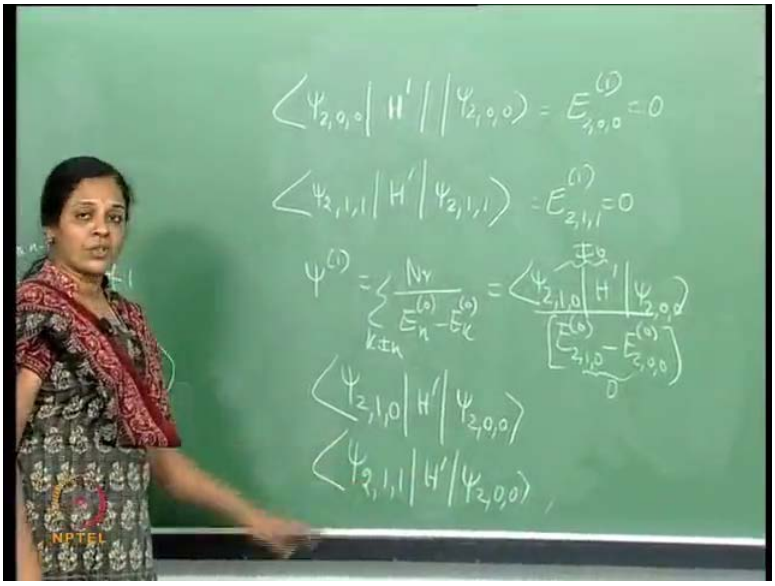


The typical matrix elements would be the following: I need to consider so if I am looking at that off diagonal elements of H prime I need to consider psi 2 0 0. Suppose I started with psi 2 0 0 and I did this, this object is going to correspond to the energy to 1st order. And that is 0, 0 for the following reason because as you can see this is the 1st order contribution to energy, take the unperturbed wave functions and find the expectation value of H prime in that state and that should give me the 1st order contribution. So, the 1st order contribution to this state is this object. But, H prime is e modulus of E times e z. I can well refer to this as vector E this is an electromagnetic process and electromagnetism conserves parity.

The electric field itself is a vector and therefore, it changes sin under parity. These wave functions the angular part of the wave function in general psi n l m of r theta phi in the

case of the hydrogen atom, has a redial part given by r n l of r and an angular part given y l m of theta phi and this is the object, that tells me that every Eigen state energy Eigen state of the hydrogen atom, has a definite parity given by minus 1 to the l. So returning to this, this quantum number is l this has even parity, H prime itself as the electric field E which changes sin under parity. So, this whole object is the state with odd parity but, that has even parity. And since electromagnetism is electromagnetic interactions are parity conserving, this object has a 1st order contribution which is 0.

(Refer Slide Time: 35:07)



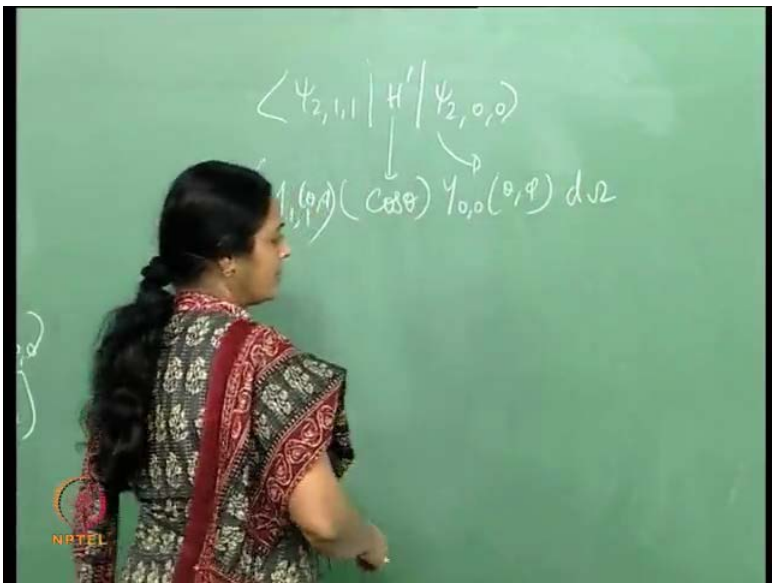
Similarly, if you look at for instance H prime psi 2 1 1, the same problem except that this state has odd parity because l is 1 and this also has odd parity so this entire state has even parity and that has odd parity. So, corresponding to the state to 1 1 the 1st order contribution is 0. Similarly, for all these 4 states as it stands the 1st order contribution is 0. And therefore, if I find out the 1st order wave function remember that that has a numerator by a denominator, which is E n 0 minus E k 0, summation over k not equal to n. And note that the numerator itself has matrix elements multiplying wave functions.

And since all these 4 states have the same energy there is a problem unless, the numerator becomes 0. So, let us look at the numerator. The numerator has the off diagonal elements of H prime. So, basically if I have a state here I should put in another of these 4 states on the other side. So, in the numerator as we know they are matrix elements multiplying wave functions. Let us not worry about the wave functions we will

look at the matrix element at this point. So, let me look at an element like psi 2 1 0 H prime psi 2 0 0 as it stands, the parity operation allows this, this has even parity with this this whole object has odd parity and this has odd parity.

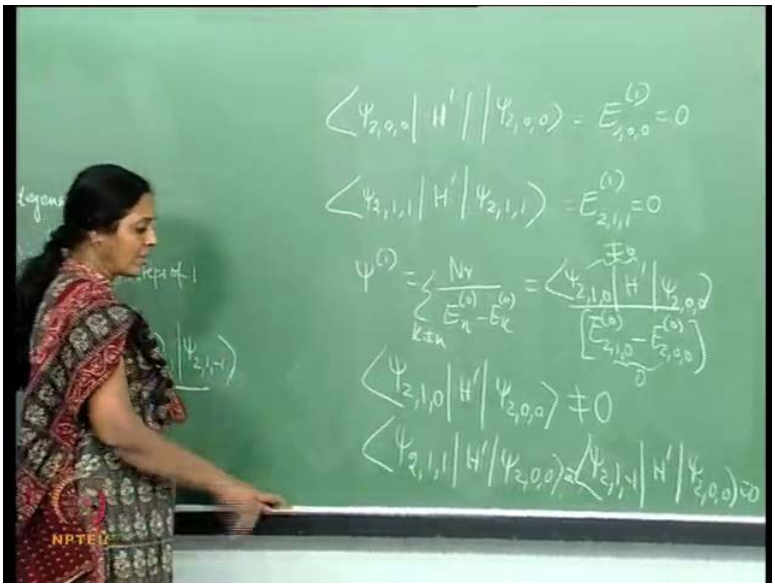
So, indeed I have a problem because in this expansion, there is a term psi 2 1 0 H prime psi 2 0 0 by E 2 1 0 0 minus E 2 0 0 0 this is 0 and this is non zero, I am putting down just one term in the summation. And there 2 I have not put down the appropriate wave function, that multiplies the matrix element but, this will do for my discussion. So, I do have a problem if I work with psi 2 0 0 as my initial state or with psi 2 1 0 as my initial state. Now, you would thing at the phase of it that the same problem will processed if I have this look at this matrix element, as far as the parity argument is concerned this would be non zero because, this has even parity the whole thing has odd parity and this has odd parity so it is fine. However, if you take these terms in and do an integration the answer is 0 you would find the following.

(Refer Slide Time: 38:26)



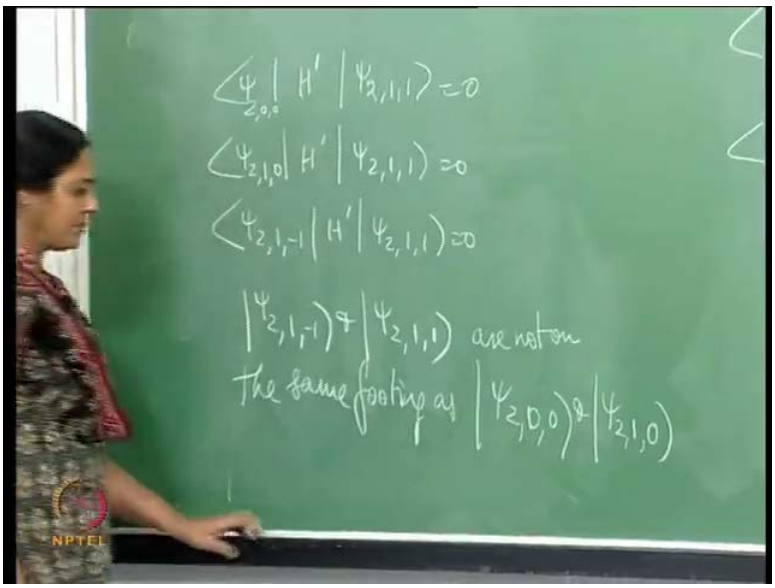
Let us look at psi 2 1 1, H prime psi 2 0 0, look at the angular part of the wave function this is Y 0 0 of theta phi, this h prime contributes just z which is cos theta and psi 2 1 1 has a Y 1 1 of theta phi. And this object has to be integrated essentially this amounts to integrating this over d omega.

(Refer Slide Time: 39:08)



Like psi 2 1 minus 1 H prime psi 2 0 0 that 2 0 so these 2 terms turn out to be 0. So, as far as the state psi 2 0 0 and psi 2 1 0 are concerned the problem does not come from, elements which involve psi 2 1 minus 1 and psi 2 1 1 but, this is the non zero element. So, this is where the problem is, now if you look at a state psi 2 1 1 and see what are the transition, what are the matrix elements of H prime?

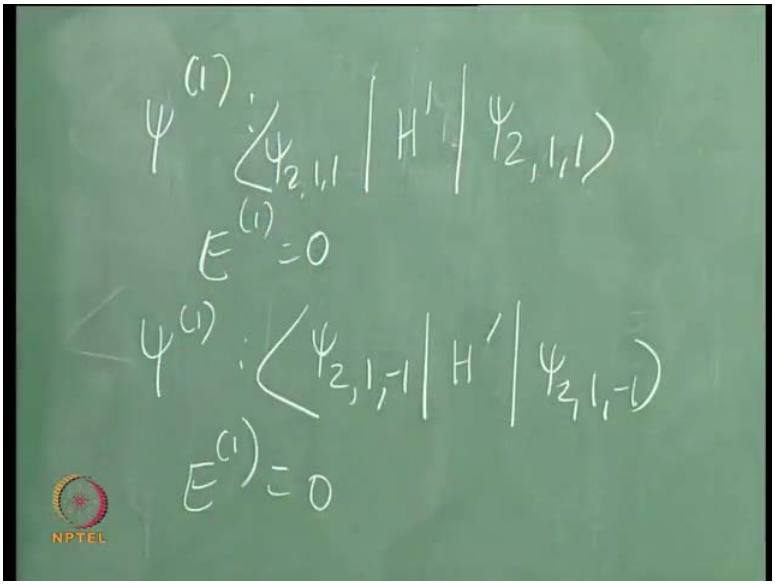
(Refer Slide Time: 40:01)



So, let us look at that. If I started with the psi 2 1 1 and I looked at all possible final states which are different from it, we have already shown that this is 0 this 2 is 0

because, of parity arguments and this 2 is 0 because, of parity arguments. Similarly, for psi 2 1 minus 1, they do not seem have any problems because are not on the same footing, as the s state term and the p state with m equals 0. So, you may imagine that these are really the analogs of the phi's that I wrote earlier, in other words you do not need to consider super positions of psi 2 1 minus 1 and psi 2 1 1. And you could do the 1st order of perturbation theory with no problems as such. So, let us look at these two states psi 2 1 minus 1 and psi 2 1 1, what is that I have.

(Refer Slide Time: 41:38)

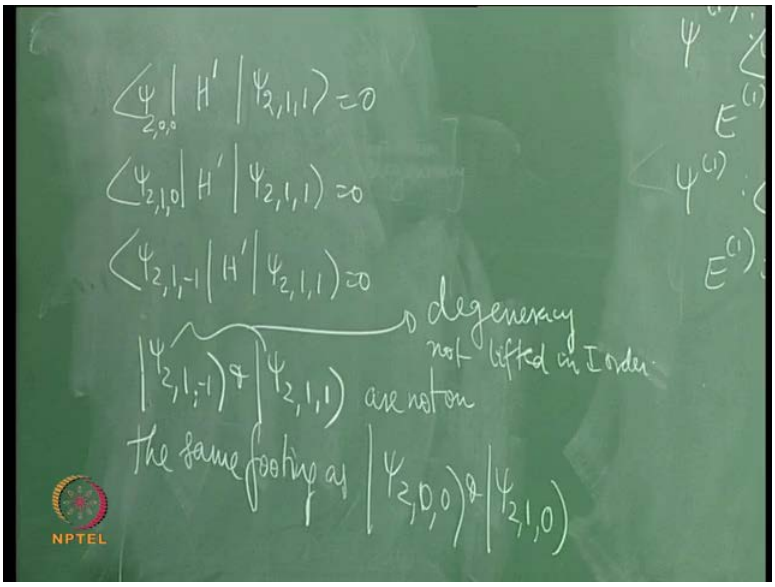


In the 1st order of perturbation if I look at this state psi 2 1 1 and it is energy Eigen value contribution, what is it that I have? Unfortunately this cannot connect these 2 states so; the energy contribution is 0 parity arguments. And then if you look at the 1st order contribution of this form by similar arguments the 1st order contribution of energy is 0. So, even to 1st order although the numerators that I was talking about, although they vanish it turn out that the energy Eigen values are the same and the degeneracy is not lifted. (Refer Slide Time: 40:01)

Let me retrace my argument. I found that the numerators in the 1st order contribution to the wave function were 0. And therefore, there was no need to look at super positions, analogous to the wave function phi that I was talking about earlier. However, look at the energy Eigen values, the energy Eigen values are 0 because, the physics of the situation does not let the Hamiltonian H prime connect have non zero matrix elements, diagonal

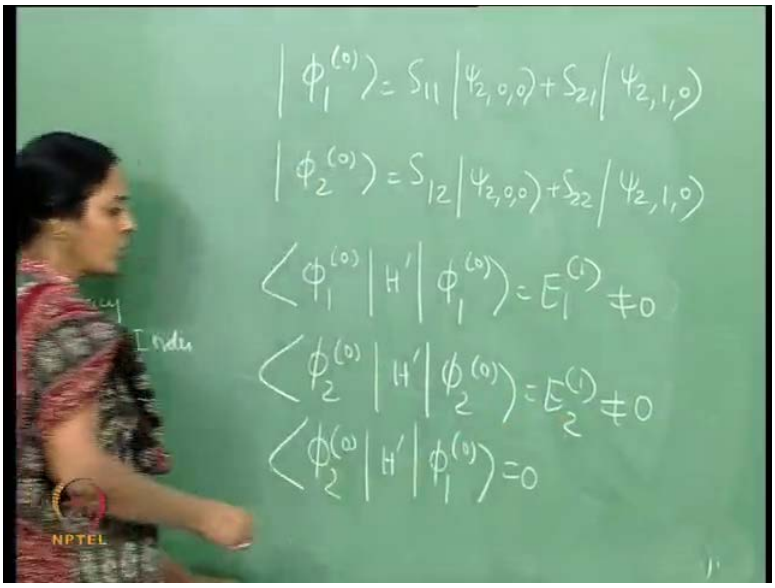
matrix elements of this kind. (Refer Slide Time: 40:01) And therefore, the degeneracy as far as these two states are concerned.

(Refer Slide Time: 43:26)



The degeneracy is not lifted, in the 1st order you have go to the 2nd order, in order to worry about how the degeneracy is lifted in this case. In general, if it not lifted in the second ordered in any general context, you will have to move to the third order. It is quite possible that the degeneracy process to large orders. However, in this problem at least, while these 2 states, there is no point thinking that the degeneracy would be lifted in the 1st order it does not happen as I have just now shown. It turns out that as far as these 2 states are concerned, I can produce super positions of psi 2 0 0 and psi 2 1 0, 2 linearly independent states orthogonal to each other, such that they have different energy Eigen values and they satisfy all the requirements of states that I expected from super positions of the degenerate states.

(Refer Slide Time: 44:50)



In other words as far as 1st order perturbation theory is concerned, the degeneracy between these 2 states is lifted because I will define a phi 1 0 which is some, S 1 1 psi 2 0 0 plus S 2 1 psi 2 1 0. Now, I will also define a phi 2 0 which is S 1 2 psi 2 0 0, plus S 2 2 psi 2 1 0, such that these states are normalized to 1 and my demands are the following. Phi 1 0 H prime phi 1 0 which is the contribution, E 1 1 is not equal to 0 phi 2 0 H prime phi 2 0, which is again the 1st order contribution to the other state is not equal to 0. And above all phi 2 0 h prime phi 1 0 this is 0 because, after all if I were to calculate the 1st order contributions to the wave functions it is this kind of term that is going to sit in the numerator.

And in the denominator of course, I have e 0 minus e 0 because, we have already seen that this phi 1 0 and phi 2 0 are Eigen states of the unperturbed Hamiltonian with Eigen values 0 and therefore, the numerator should be 0. So, these are the 3 conditions that I have to impose. The aim is to determine the 1st order contribution to the energy from both these states as also the wave functions which means, we need to determine these coefficients, S 1 1, S 2 1, S 1 2 and S 2 2. This is going to be done by diagonalizing H prime in the phi basis, finding the Eigen values and the Eigen vectors, a matter which I will discuss in further detail in the next lecture.

(Refer Slide Time: 47:04)