Quantum Mechanics – I
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Lecture - 39
Perturbation Theory – IV

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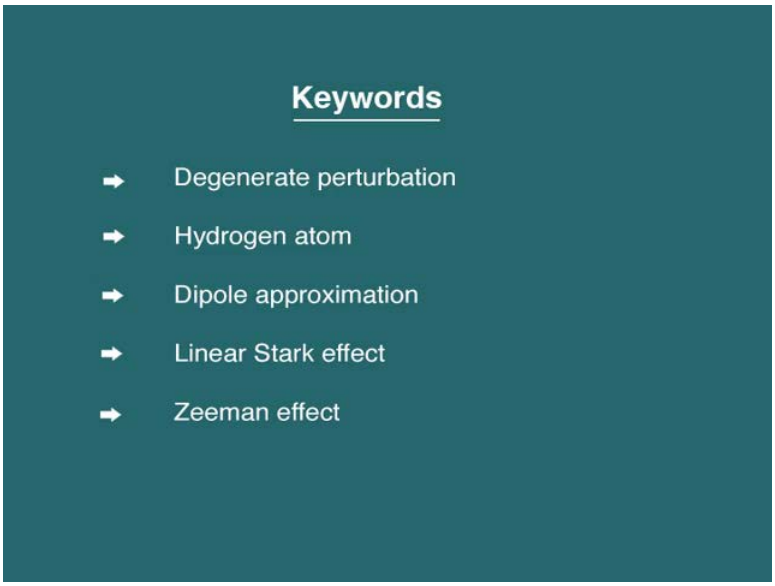

We have been discussing stationary perturbation theory and in the last lecture I have been looking at the degenerate case so just by the way of recapitulation, some salient features and the terminology.

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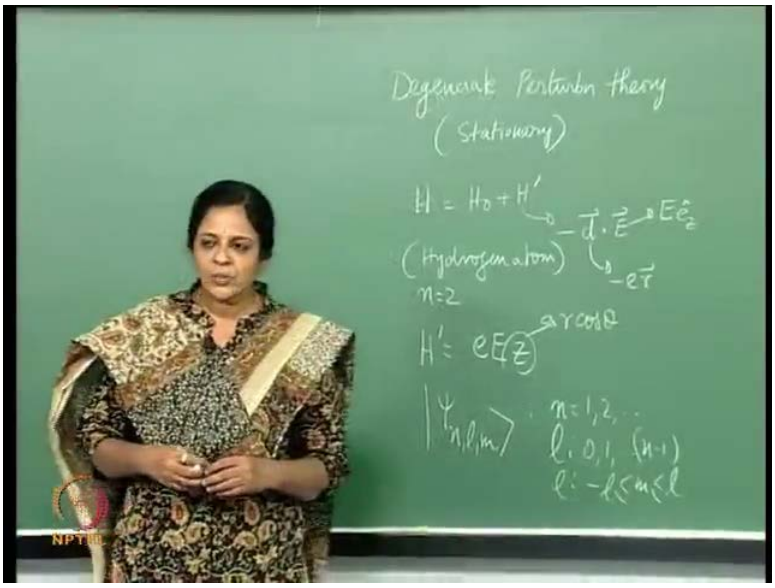

Let me put down the notation again and this is stationary perturbation theory. The total Hamiltonian is H naught plus H prime. The example that we select is where H prime is a constant electric field along the z axis and we work in the dipole approximation. Therefore, H prime is minus d dot E where d is the atomic dipole operator and indeed we have been looking at the hydrogen atom problem.

So, the problem considered is hydrogen atom and the states that we consider correspond to n equals 2 and therefore, there are four states, all of them with the same energy value. The dipole operator itself is minus e r and this electric field is modulus of E times e z because I have selected a constant electric field along the z axis. Therefore, H prime is simply e E z because it is only the z component of r that is going to give a contribution here. Notice that, z is r cos theta if you want to write it in spherical polar coordinates which indeed is what I would do, because in this problem a typical wavefunction of the hydrogen atom is given by specifying three quantum numbers: n, l and m.

So, for a given n and we have chosen n equals 2, l takes values: 0 to n minus 1 and for a given l, m takes values: plus l to minus l, in steps of 1. So, these are the three quantum numbers. Then of course, I will recall for you couple of expressions that we derived. We have this expression for the 1st order contribution to the energy.

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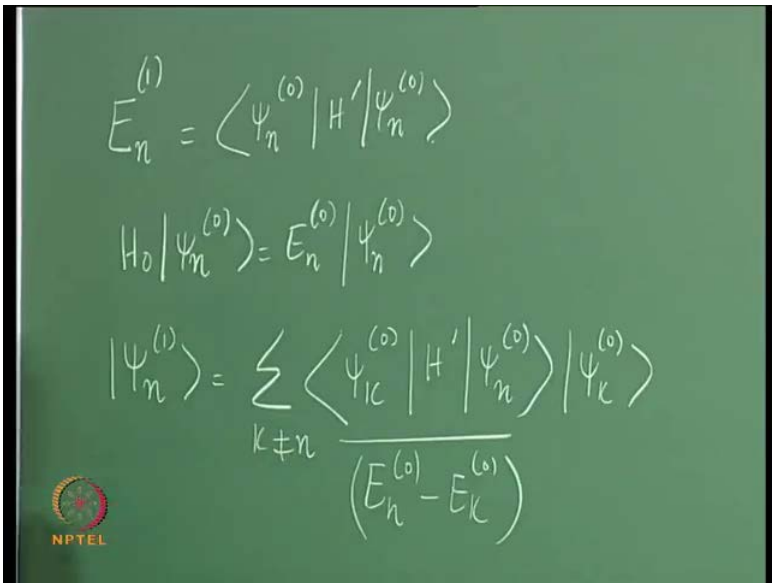

So, if you are talking about the discrete level n. I could use the same n here and here (Refer Slide Time: 00:27) because E sub n depends upon the value of n. So, E n 1 is simply psi n 0 H prime psi n 0 and what psi n 0? They are the Eigenstates of the unperturbed Hamiltonian with the corresponding Eigenvalues E and 0.

So, the 1st order contribution to the energy or the correction to the energy once we put in the perturbation and only worry about the 1st order term in the perturbation is this. The corresponding contribution to the wavefunction, I call that psi n 1, summation over all k not equal to n psi k 0 H prime psi n 0. That is a number. So, there is a ket here, psi k 0 divided by E n 0 minus E k 0. And, to quickly recapitulate what we had, problem arises when there is a degeneracy because then the denominator becomes 0 and that is ok provided the numerator becomes 0 and we are only interested in all k not equal to n.

So, now let us return to the problem of the hydrogen atom. (Refer Slide Time: 00:27) What are the states that are involved?

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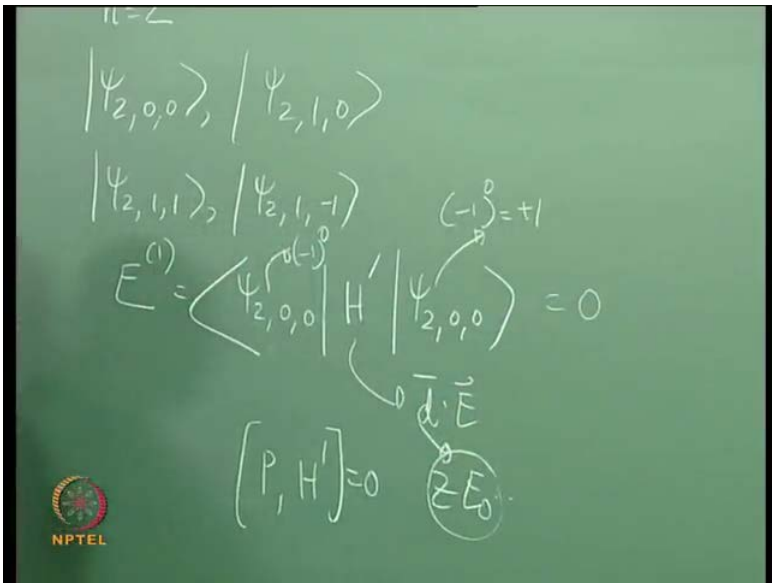

You have selected n equals 2. In fact, there are four states: psi 2, 0, 0, psi 2, 1, 0, psi 2, 1, 1 and psi 2, 1, minus 1. This is n, that is l and that is m and remembers that l takes values: 0 to n minus 1. So, that is 0 to n minus 1 and for a given l, m takes values: minus l to plus l in steps of 1. So, we have these four states. Then what is the 1st order contribution to the energy in these states? So, what is E 1? For instance, if you take the state psi 2, 0, 0 I need to compute this object. Now, H prime is essentially of the form d dot E and we have selected the electric field to be along the z axis. So really, this gives me z and that is some E naught. Look at this: electromagnetic interactions and strong interactions conserve parity.

Now, what does that mean? If you look at the parity of this state, this is minus 1 to the l and l is 0, which is plus 1. When you say that electromagnetism conserves parity it means that the parity operator commutes with the Hamiltonian. So, look at this. The net state, the net matrix element of the Hamiltonian if you take it, here there is a z and under parity that changes sign. So, there you pick up a minus 1 here and that is a plus 1 but the net parity must be plus 1 because of this and therefore, this state whatever I put here in the bra should have odd parity, because that had even parity.

So, there is no way I can use a psi 2, 0, 0 here because if I did that, this is parity plus 1, that has parity plus 1 that makes it even parity. But, you see there is a contribution here

to parity which is minus 1 and parity is a multiplicative quantum number and therefore, this contribution is 0.

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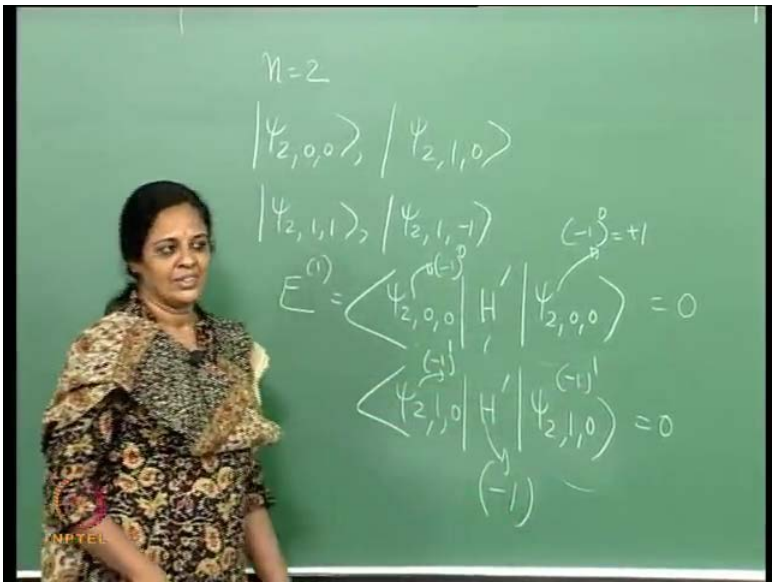

Now, I will use the same argument to show that the contribution psi 2, 1, 0 H prime psi 2, 1 0, this matrix element is also 0, same argument. Here the parity is minus 1 to the 1 and here to minus 1 to the 1, but this provides another minus 1 and therefore, the net parity is minus 1 which is not 1.

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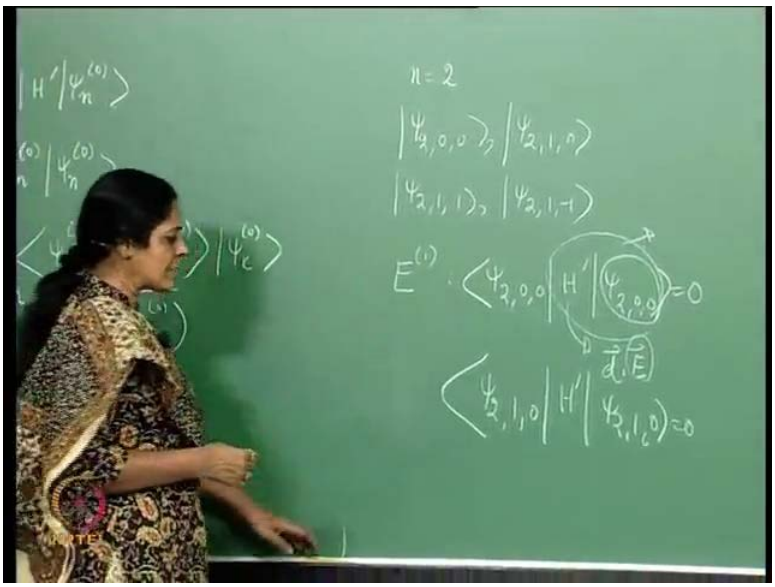

How do I get out of this problem? So, if you want to lift the degeneracy and in the 1st order produce different contributions to the energy of these states. We try to use a superposition.

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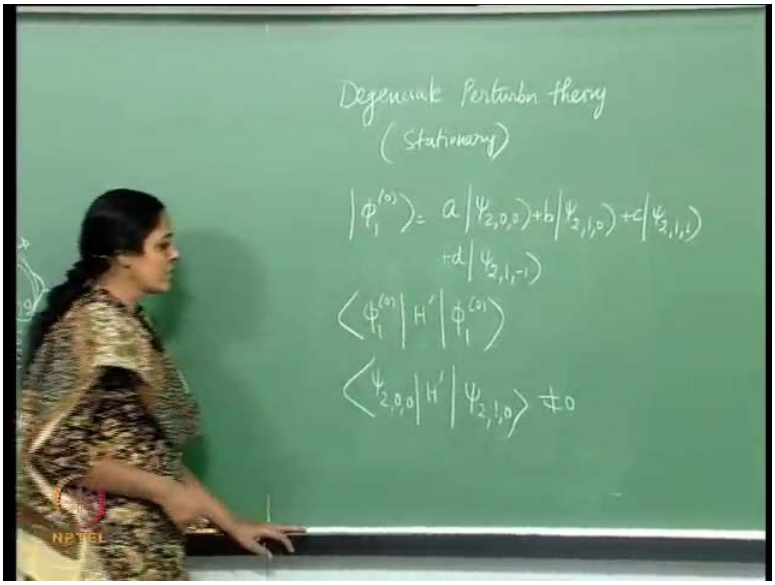

In other words, we construct new states. For instance, I could construct a state phi 1 0 which is a linear combination of all the states. Now, if I did this and I say I work with this and suitable combinations of this kind, the relevant contribution to energy to the 1st order would really be this object and so on. I would construct a phi 2, 0 which is another superposition, a phi 3 0 which is another superposition and a phi 4 0. And here, I would expect that the contribution would be non-vanishing because clearly there will be terms of this form.

Such a contribution would in general be non-vanishing, because this is parity minus 1 to the 1, it is minus 1 and that again produces another minus 1. So, the total parity there is plus 1 which matches with the parity here, which is minus 1 to the 0. And since, such matrix elements do not vanish. I would imagine that the 1st order contribution to the energy would be different for different superpositions, thus lifting the degeneracy.

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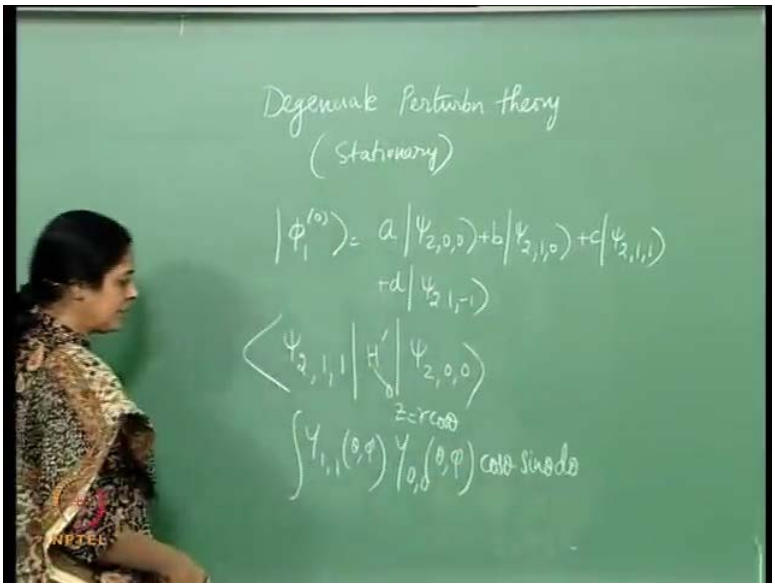

But, what are these contributions? I can only include such contributions where the matrix element of a Hamiltonian between the unperturbed states is non-vanishing but you consider a thing like this. Consider psi 2, 1, 1 H prime psi 2, 0, 0. This contribution is 0 because if you look at the angular integration H prime has a z in it which is r cos theta apart, from the magnitude of electric field, the electric charge and so on. It has a z which is r cos theta and then this angular integral would be a Y 1, 1 of theta phi from there, a Y 0, 0 of theta phi from here and these are all real functions of theta and phi. So, I do not put a star, times a z which gives me a cos theta and then the angular integration sin theta d theta. I am not looking at the phi integration.

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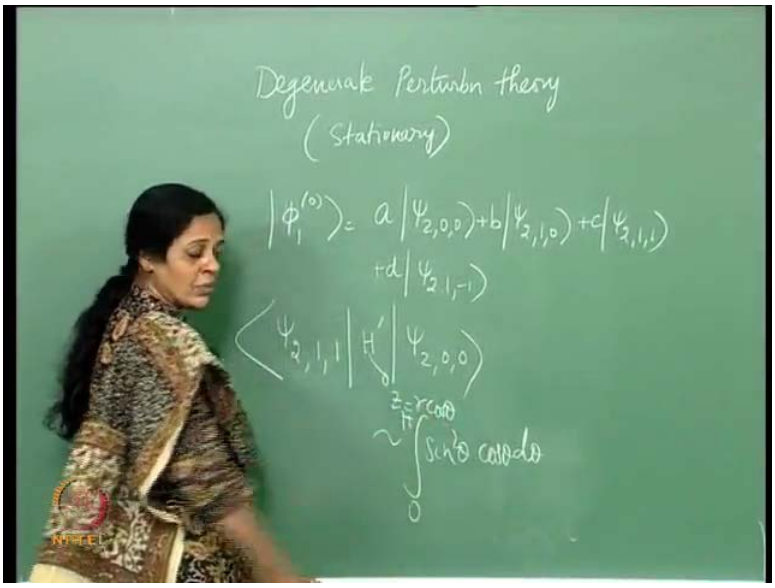

Now, Y 0, 0 is merely a number. It is a constant. So, I can remove that and Y 1, 1 of theta phi is proportional to sin theta. So, this is essentially integral sin square theta cos theta d theta and that vanishes because theta goes from 0 to pi. Substitute sin theta as u. And therefore, I have a u square d u when I integrate I get a u cubed by 3 where u is sin theta and therefore, such terms do not contribute.

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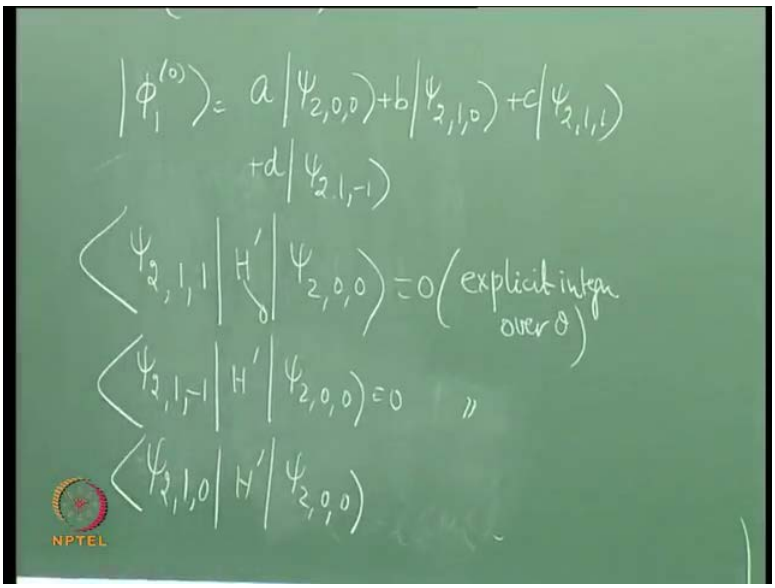

Similarly, this is by explicit calculation, integration over theta. Similarly, if you look at psi 2 1 minus 1 H prime psi 2 0, 0 that is also 0 explicit integration now, if you look at

psi 2, 1, 0 H prime psi 2, 0, 0, parity is conserved. Because, this has got even parity that has odd parity the combination has odd parity and this as odd parity. But, if you look at this term theta integration you would just have the following.

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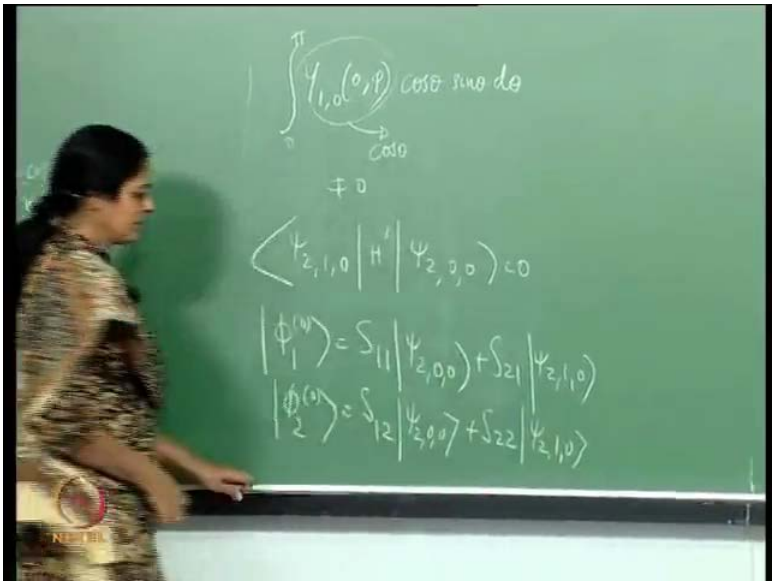

You would have integral Y 1, 0 of theta phi cos theta from H prime because there was a z, which was r cos theta. Y 0, 0 which is a constant, sin theta d theta and this Y 1, 0 of theta phi is actually proportional to cos theta and therefore, this integration from 0 to pi is not equal to 0. So, the only terms that would contribute in a superposition like this (Refer Slide Time: 12:47) that would make intelligent contributions, nonzero contributions, would come from matrix elements of H prime with the state psi 2 0, 0 here and psi 2, 1, 0 there or vice versa.

And therefore, there is no point in producing superpositions which include psi 2, 1, minus 1 and psi 2, 1, 1. If you consider the contribution of this type this is also 0 by parity arguments. Hence, the only non-vanishing contribution comes from this, in this specific example. And therefore, I define phi 1 0 is some S 1 1 psi 2, 0, 0 plus S 2 1 psi 2, 1, 0 and I define another combination phi 2, 0 is S 1 2 psi 2, 0, 0 plus S 2 2 psi 2, 1, 0. So, what do I have for the initial states now? I have the following.

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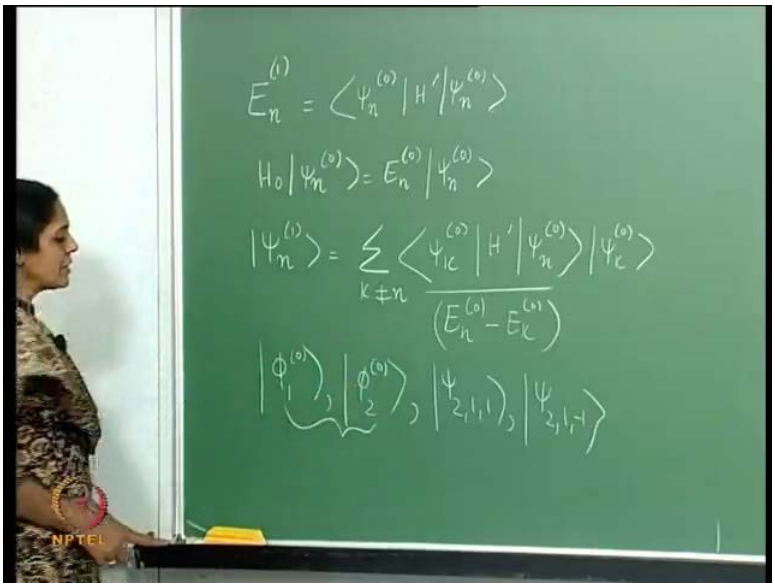

I have phi 1 0 phi 2 0 instead of psi 2, 0, 0 and psi 2, 1, 0. (Refer Slide Time: 13:47) I have made the superposition and then of course, I have psi 2, 1, 1 and psi 2, 1, minus 1. These are my four states. Now, this superposition hopefully lifts the degeneracy between two of these states. There was a fourfold degeneracy and what about the other two states? They continue to have the problem and one has to go to a higher order in the perturbation theory in order to lift the degeneracy between psi 2, 1, 1 and psi 2, 1, minus 1.

So, for the moment we will only worry about the mechanism that lifts a degeneracy in this sector. The sector which involves (Refer Slide Time: 13:47) psi 2, 0, 0 and psi 2, 1, 0. So, what do we have here?

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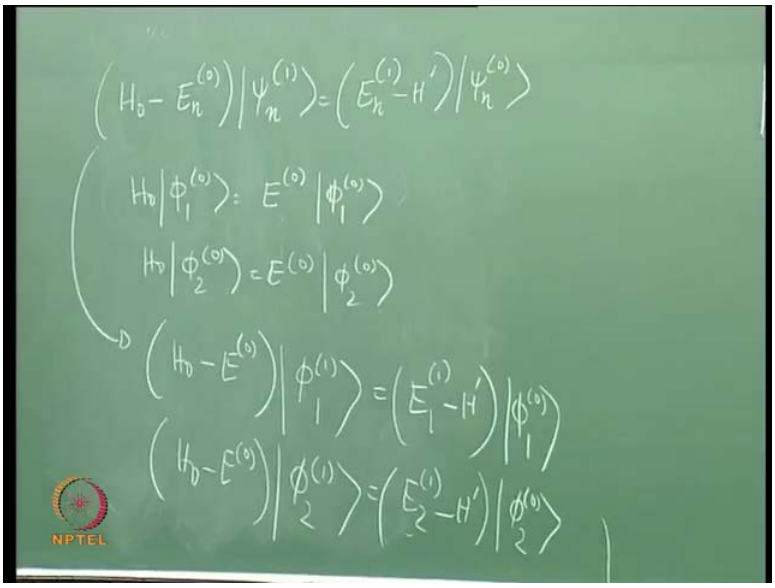

Remember that, when we derived the expressions for contributions to 1st order we showed that H naught minus E n 0 psi n 1 was E n 1 minus H prime psi n 0. In fact, this was our starting point for 1st order perturbation theory. So, in this case I would have H naught. Let us first look at what we get when H naught acts on phi 1 0. That is the same as E 1 0 phi 1 0. But, there is a degeneracy and therefore, H naught acting on phi 2 0 which would normally be some E 2 0 phi 2 0. E 1 0 and E 2 0 are the same and I am going to represent them as E 0.

So, in this case I merely have H naught minus E 0 phi 1 1. That is the 1st order contribution to the state phi 1 (Refer Slide Time: 13:47) where the zero-th order contribution was written like this. That is E 1 1 minus H prime phi 1 0. That is my 1st equation. Then my 2nd equation is H naught minus the same E 0 because there was a degeneracy phi 2 1 is E 2 1, the 1st order contribution minus H prime phi 2 0.

These are the two equations that I should be dealing with. So, I am really working in a two dimensional subspace of the original space. A crucial input would be this. What would be (Refer Slide Time: 15:51) the 1st order contribution to the wavefunction? Well, we are not going to worry about psi 2, 1, 1 and psi 2, 1, minus 1 anymore. We are merely going to look at the two dimensional subspace.

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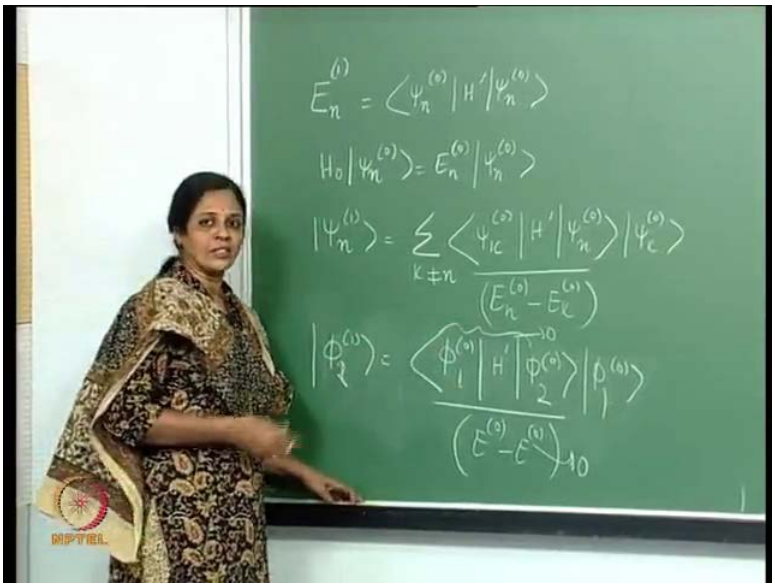

So, phi 1 1 would be, there are exactly two states: phi 1 1 and phi 2 1. So, this would just be phi 2 0 H prime phi 1 0 times phi 2 0 by E 0 minus E 0 in my notation. And since, the denominator goes to 0, I would want the numerator to also go to 0 in order to get a nonzero value, a finite nonzero value. Similarly, if I look at phi 2 1 I would have a phi 1 0 here, a phi 2 0 there and a phi 1 0 here. So, essentially one has this requirement that this matrix element become 0 because the denominator blows up and I would expect the numerator also to go to 0 in order to extract a nonzero finite contribution to the wavefunction in the 1st order. So, let me look at these equations. (Refer Slide Time: 13:47)

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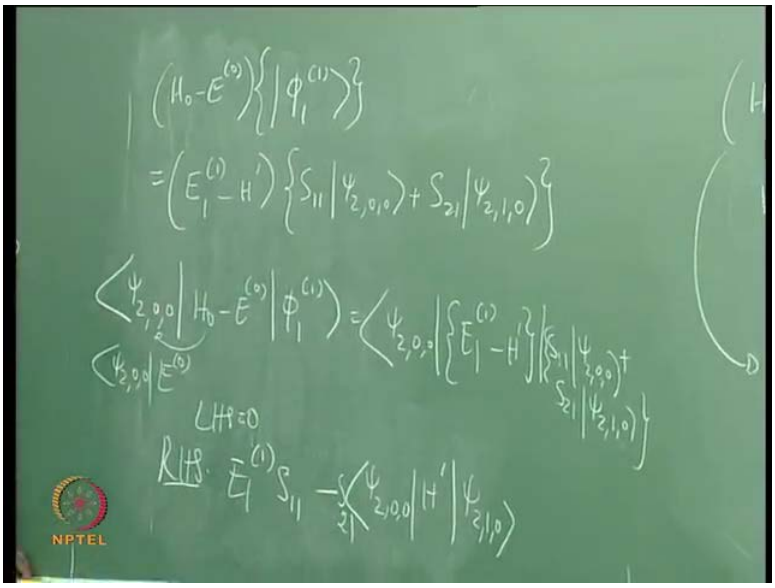

So, I have H naught minus E 0 S 1 1 psi 2, 0, 0 plus S 2 1 psi 2, 1, 1 a 1, 0. That is what I have here. That is E 1 1 minus H prime S 1 1 psi 2. I have phi 1 1 right. So, let me start with phi 1 1. This is S 1 1 psi 2, 0, 0 plus S 2 1 psi 2, 1, 0. This is my 1st equation. Let me do the following. Let me flank it on this side with psi 2, 0, 0. What do I get? I have the following expression and this is what I have. That gives me an E 0 psi 2, 0, 0 and therefore, the E naught cancels out. The left hand side is 0. Look at the right hand side. The 1st term is E 1 1 and remember psi 2, 0, 0 is orthogonal to psi 2, 1, 0.

So, the contribution is really E 1 1 S 1 1 which is just a number, minus psi 2, 0, 0 H prime. H prime cannot connect states of the same parity. So, I can only work with psi 2, 1, 0 on this side and there is a coefficient S 2 1. So, that is the 1st equation that I have.

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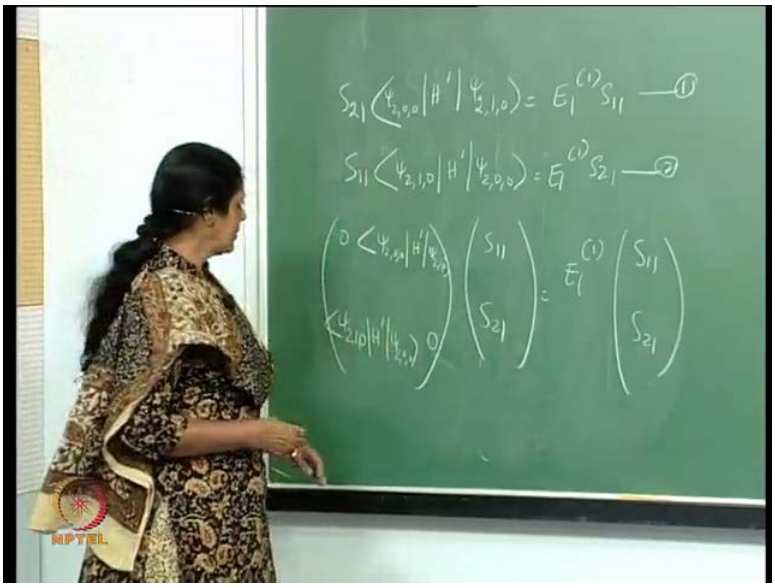

In other words, I can well write it as follows, S 2 1 and then this matrix element H prime sandwiched between psi 2, 0, 0 and psi 2, 1, 0 is E 1 1 S 1 1. So, that is the 1st equation I have. Now, instead of working with (Refer Slide Time: 21:05) psi 2, 0, 0 let me work with psi 2, 1, 0.

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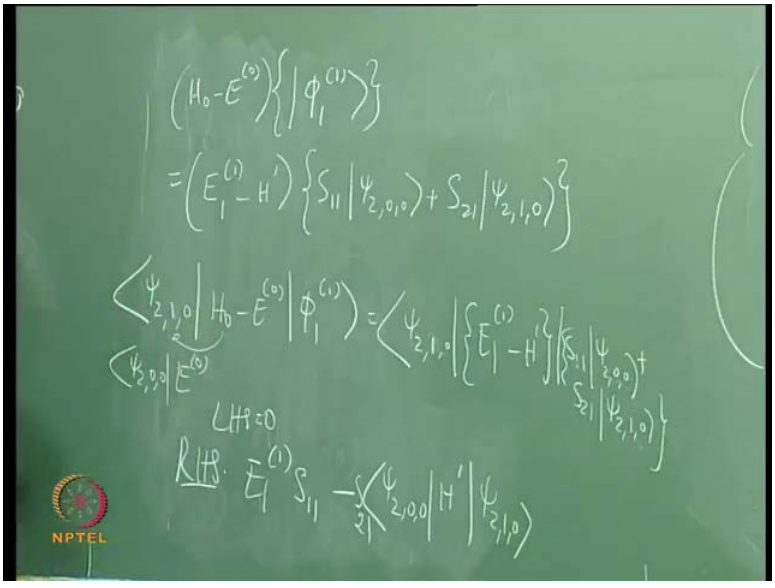

Now, if I did that let me start with psi 2, 1, 0. This step continues because H naught on psi 2 1 0 is E naught. To zeroth order, these are degenerate states. They have the same energy value and therefore, the left hand side is 0.

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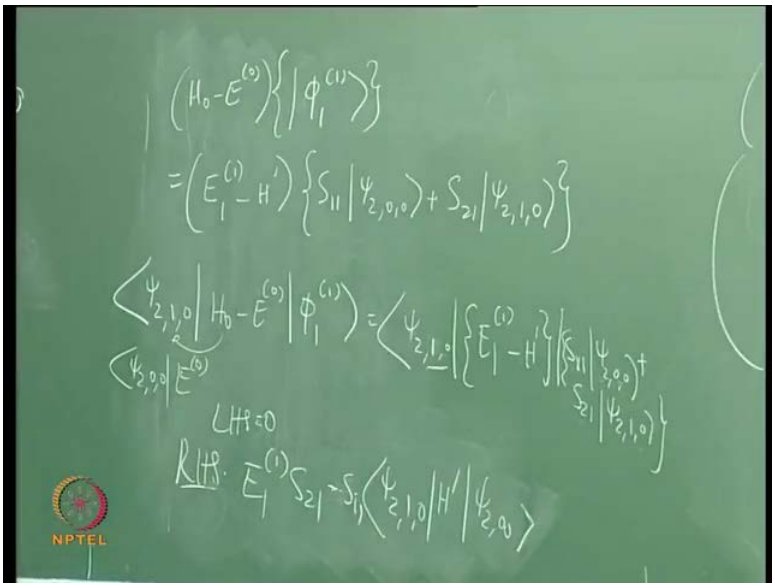

As far as the right hand side is concerned I have E 1 1 H prime connects states of opposite parity. So, the contribution will come from S 1 1 psi 2, 0, 0 and not from S 2 1 psi 2, 1, 0. Therefore, I have E 1 1 times S 2 1. This state is orthogonal to that state not to this minus psi 2, 1, 0 H prime psi 2, 0, 0 and there is an S 1 1 out there. So, I will write it as minus S 1 1. This is the right hand side which tells me that S 1 1 psi 2, 1, 0 H prime psi 2, 0, 0 is E 1 1 S 2 1. That is my 2nd equation.

To remind you I started with this (Refer Slide Time: 17:10) equation and I flanked it with bra psi 2, 0, 0 first and got this equation then with bra psi 2, 1, 0 and got this equation. What is that tell me? It tells me that if I wrote this as an Eigenvalue equation I have 0 psi 2, 0, 0 H prime psi 2, 1, 0 psi 2, 1, 0 H prime psi 2, 0, 0 here and 0. These are the matrix element; there is a 0 and then this matrix element. This is the complex conjugate of that but we are dealing with real functions.

So, if I compute this matrix element, that is the same as this and there is a 0. I have an Eigenvalue equation. The job is to solve this. First explicitly evaluate this matrix element, solve for the Eigenvalue and the corresponding Eigenvectors which means I get S 1 1 and S 2 1 and therefore, I have phi 1 0. So, that is the 1st of these equations. Now, let us look at the matrix element.

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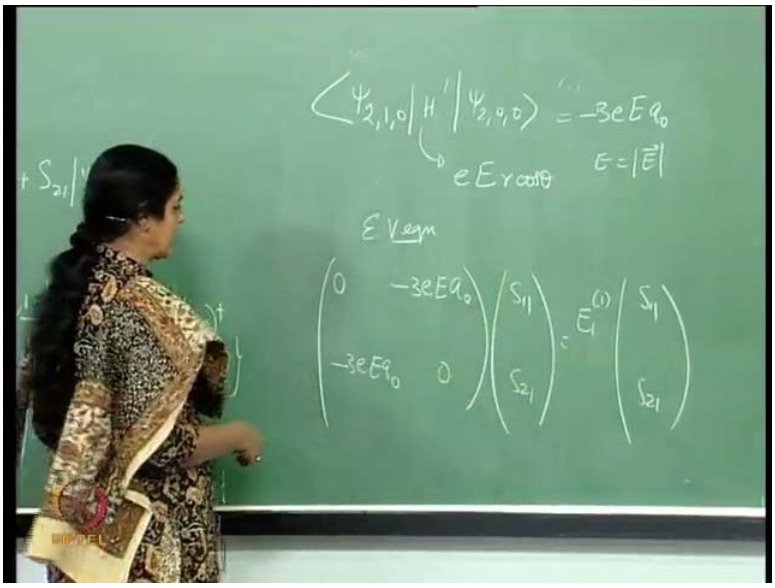

So, if you wish to compute psi 2, 1, 0 H prime psi 2, 0, 0, have to feed in everything now.

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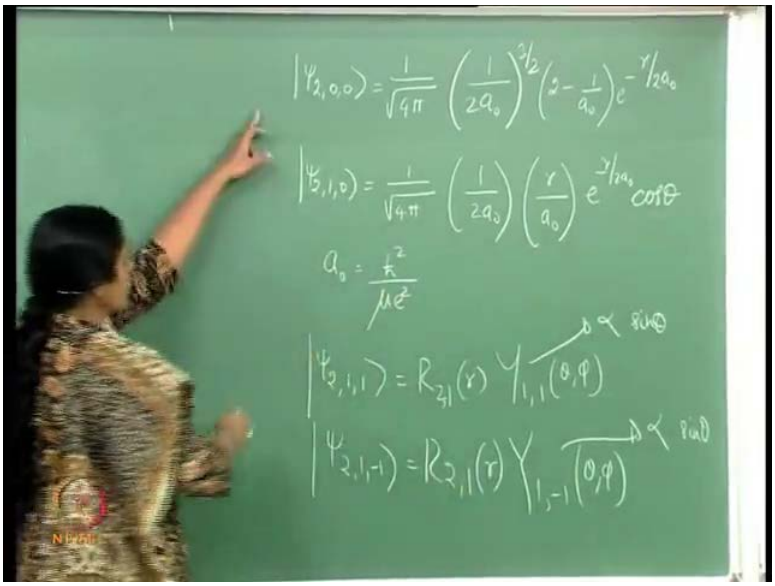

The expressions are here, psi 2, 0, 0 has a Y 0, 0 and then there is an r dependence r 2, 0 of r, r n l of r and that is out here. Notice, the exponential fall of e to the minus r by 2 a 0 where a 0 is simply h cross squared by mu e square, mu being the reduced mass. These are expressions that we derived when we looked at the hydrogen atom problem. After all these are the unperturbed wavefunctions for the hydrogen atom.

Now, if you look at psi 2, 1, 0 apart from the radial dependence which is different from this but which certainly has that exponential fall off to match boundary conditions. There is a cos theta because Y 1, 0 is proportional to cos theta.

Now, these two have to be substituted in calculating this matrix element and for H prime we have an electric field whose magnitude is given to us and a z which is r cos theta. This integration has to be done. The integral over r goes from 0 to infinity, theta 0 to pi and phi 0 to 2 pi. I leave it to you as an exercise to show that this is minus 3 e E a 0, where e is the magnitude of vector E. Remember that was a constant electric field in the z direction.

So, I can now go back and write down that equation. The Eigenvalue equation is therefore, 0, minus 3 e E a naught, minus 3 e E a naught, 0, S 1 1, S 2 1 is E 1 1 S 1 1, S 2 1. What is it that we are trying to do? We are diagonalizing the perturbing Hamiltonian in the superposed basis. So, we are using components S 1 1 and S 2 1 and working in that basis.

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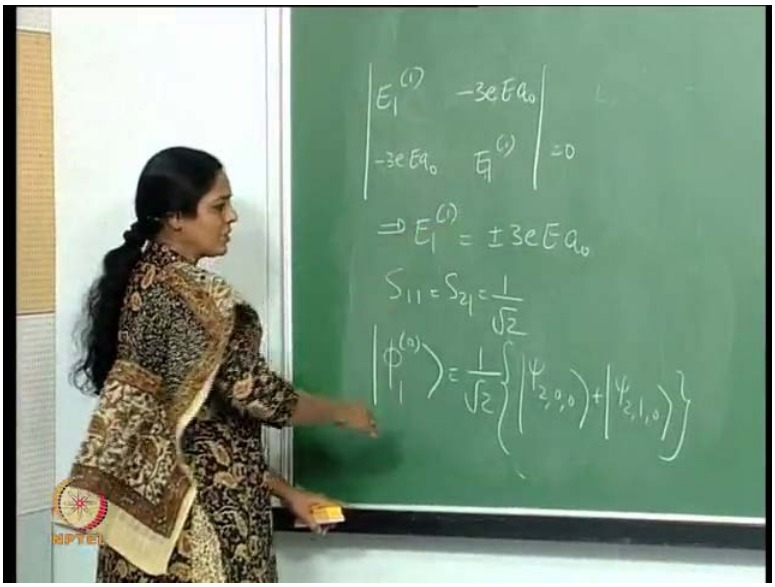

Now, the Eigenvalues can be got. You will get a quadratic because this implies that E 1 1, determinant of this object in order to get the Eigenvalues and therefore, the Eigenvalue, the contribution to 1st order is plus or minus 3 e E a 0.

Now, suppose I had worked not with this (Refer Slide Time: 24:41) but with the other equation, the equation for phi 2. What would I have got? To complete this story before we get there I can now substitute this (Refer Slide Time: 27:20) Eigenvalue and find out S 1 1 and S 2 1 and it turns out. It is a trivial matter to show that S 1 1 equals S 2 1 is 1 by root 2 and therefore, I have this normalized state phi 1 0 is 1 by root 2 psi 2, 0, 0 plus psi 2, 1, 0. And therefore, I have found out the energy Eigenvalues could be plus or minus. But, remember that there is an E 2 1 as well. So, let us see what that gives us.

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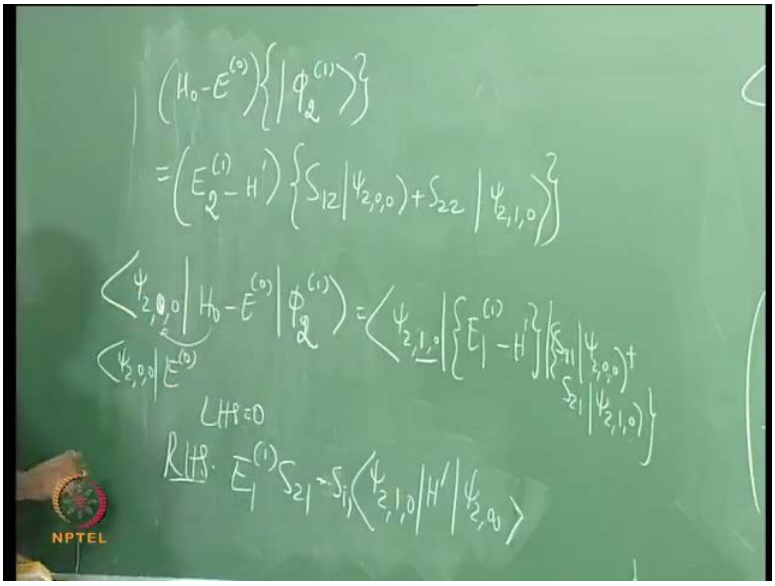

Should give us pretty much the same thing because, if you now go back and redo the calculation. You will have the following equation: H naught minus E naught on phi 2 1 is E 2 1 minus H prime phi 2, 0 and phi 2, 0 in terms of the unperturbed basis was this. Once more I can flank it with psi 2, 0, 0 to begin with.

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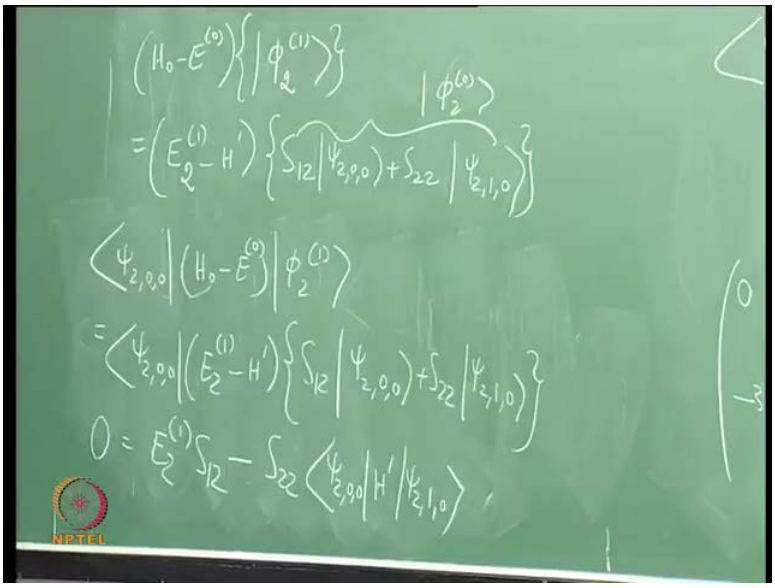

So, let us redo this psi 2, 0, 0 H naught minus E naught phi 2 1 is psi 2, 0, 0 E 2 1 minus H prime S 1 2 psi 2, 0, 0 plus S 2 2 psi 2, 1, 0. It is evident that in this case the corresponding Eigenvalue equation would be used to determine S 1 2 and S 2 2 and therefore, phi 2 0. This is phi 2 0. Once more the left hand side is 0, because psi 2, 0, 0 is an Eigenstate of H naught with Eigenvalue E naught.

So, the left hand side is 0 and the right hand side gives me 0 is E 2 1. What is the non-vanishing element here? Its S 1 2 because psi 2, 0, 0 is orthogonal to psi 2 1 0. So, I have S 1 2 minus, use the fact that H prime only connects states of opposite parity. So, I have s 2 2 psi 2, 0, 0 H prime psi 2, 1, 0.

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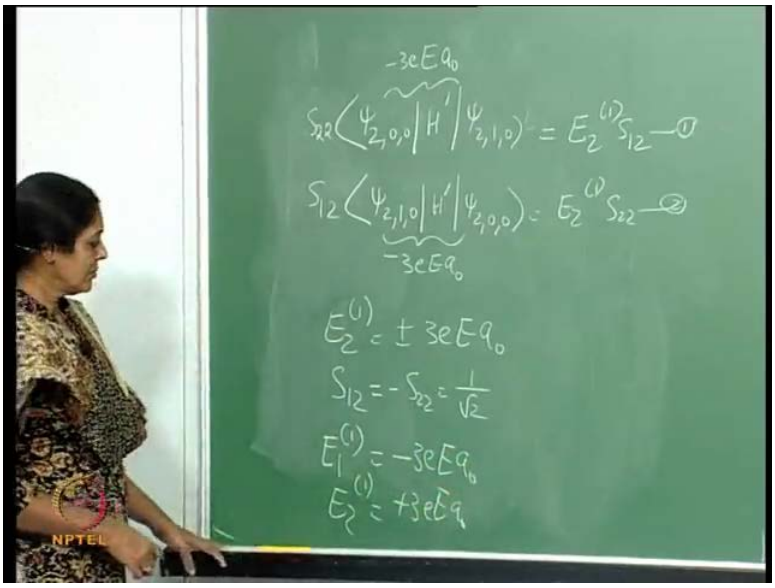

So, I have the first of my equations: S 2 2 psi 2, 0, 0 H prime psi 2, 1, 0. Remember this was minus 3 E, magnitude of the electric field times a naught. This (Refer Slide Time: 32:34) quantity is E 2 1 S 1 2. So, that is the first of my equations.

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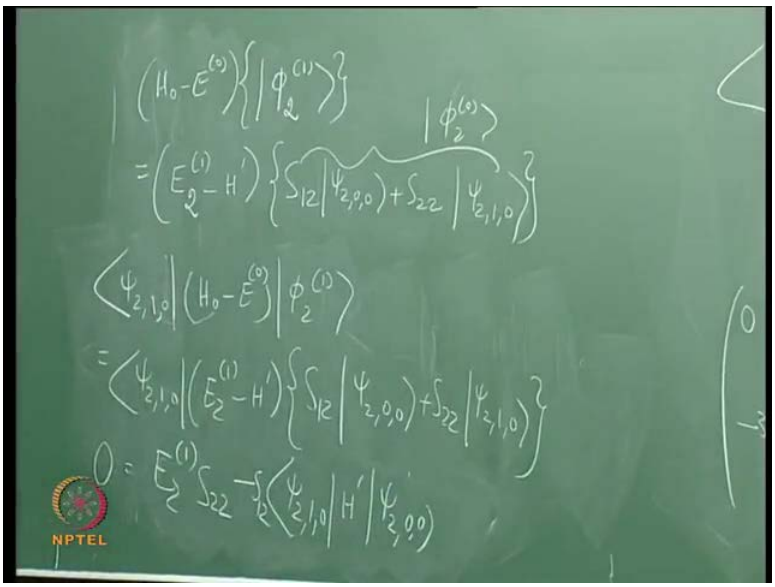

Instead, I now work with bra psi 2, 1, 0. As before, the left hand side is 0. As far as the right hand side is concerned I have an E 2 1 and the non-vanishing contribution comes from here that is an S 2 2 minus psi 2, 1, 0 H prime psi 2, 0, 0 with an S 1 2.

So, this is what I have and therefore, I have S 1 2 psi 2, 1, 0 H prime psi 2, 0, 0 is E 2 1 S 2 2. It is the same thing as before. It is the real matrix element. Diagonalize this matrix and you will retrieve E 2 1 is plus or minus 3 e E a 0. You will also get S 1 2 equals minus S 2 2 equals 1 by root 2. The degeneracy is obviously lifted because I have E 1 1 is say minus 3 e E a 0 and E 2 1 is plus 3 e E a 0.

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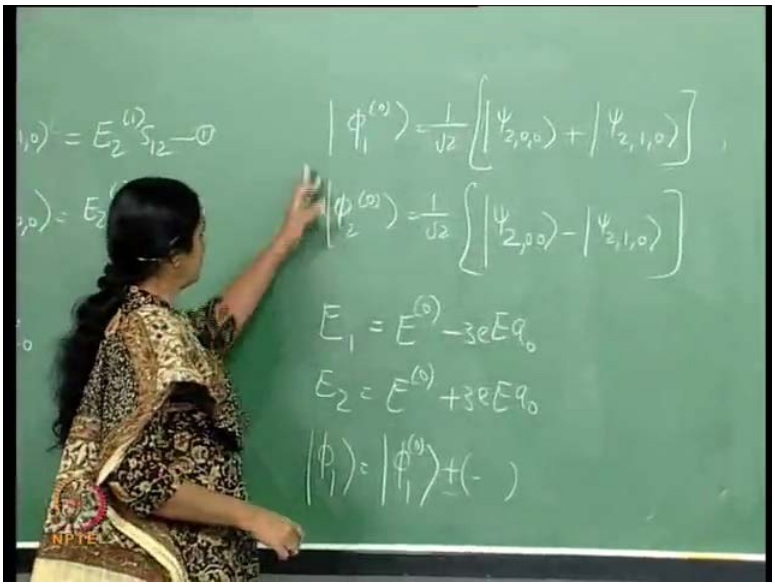

I also have the orthogonal states phi 1 0 and phi 2 0, because phi 1 0 was 1 by root 2 psi 2, 0, 0 plus psi 2, 1, 0. That is what I had and I have phi 2 0 is 1 by root 2. Remember (Refer Slide Time: 34:14) there is a relative negative sign here, psi 2, 0, 0 minus psi 2, 1, 0. This is what I have.

The corresponding energy is therefore to 1st order, the energy E 1 is E 0 which was common to both states minus 3 e E a 0 and E 2 was E 0 which was common to both states plus 3 e E a 0. And, as to the wavefunctions phi 1 is phi 1 0 plus contribution from 1st order and phi 2 is phi 2 0 plus contribution from 1st order and that is a simple matter to settle.

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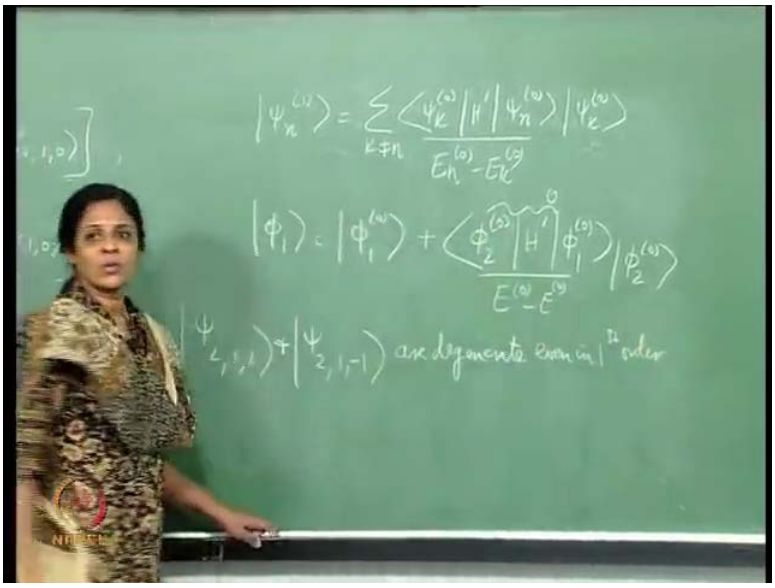

Remember, that in the original notation the 1st order contribution to the state psi n is summation k not equal to n psi k 0 H prime psi n 0 times psi k 0 with the denominator E n 0 minus E k 0. And therefore, we now have phi 1 is phi 1 0 and we know what is phi 1 0. That was this (Refer Slide Time: 36:40) superposition of the unperturbed states plus phi 2 0 H prime phi 1 0 by a denominator which was just E 0 minus E 0 phi 2 0. The only thing we need to check out is that, this matrix element is 0 which indeed it is because if you feed in (Refer Slide Time: 36:40) phi 2 0 is 1 by root 2 psi 2 0, 0 minus of this and phi 1 0 is 1 by root 2 psi 2, 0 plus this.

It will be evident that in the superposition the only contribution will be from psi 2, 0, 0 here and psi 1, 0, 0 there, psi 2, 1, 0 there or vice versa. You will simply get a 1 by root 2 times 1 by root 2 for the 1st term and a 1 by root 2 times minus 1 by root 2 for the 2nd. Therefore, the numerator is 0 and this is all that I have. The numerator is 0, the denominator is 0. We can get a sensible expression out of this and I have the 1st order contribution. I also realize that to 1st order the degeneracy has been (Refer Slide Time: 36:40) lifted between these two states. The other two states continued to be degenerate. The state psi 2, 1, 1 and psi 2, 1, minus 1 are degenerate even in 1st order. So, as I indicated earlier one goes to higher order perturbation theory to lift that degeneracy.

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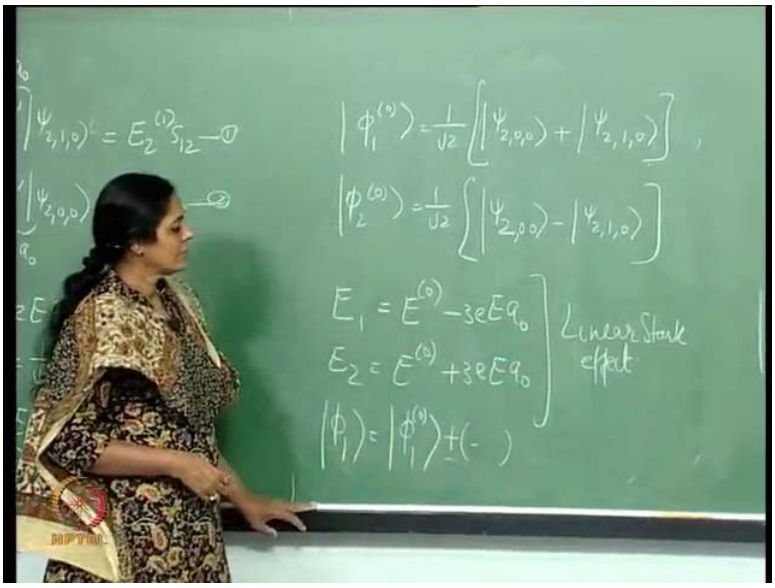

So, what you have seen is called the Linear Stark effect. This is the Stark effect where you use an electric field to lift the degeneracy between two of the hydrogen atom states corresponding to n equals 2. It is the 1st excited state, linear because it is proportional linearly e E appears not as a quadratic. But, as a linear object to power 1 in a and therefore, it is called the Linear Stark effect. There is an counterpart to this which is the Zeeman effect. Instead of using an electric field to lift the degeneracy you could have used a uniform magnetic field to lift the degeneracy. So, let us look at that.

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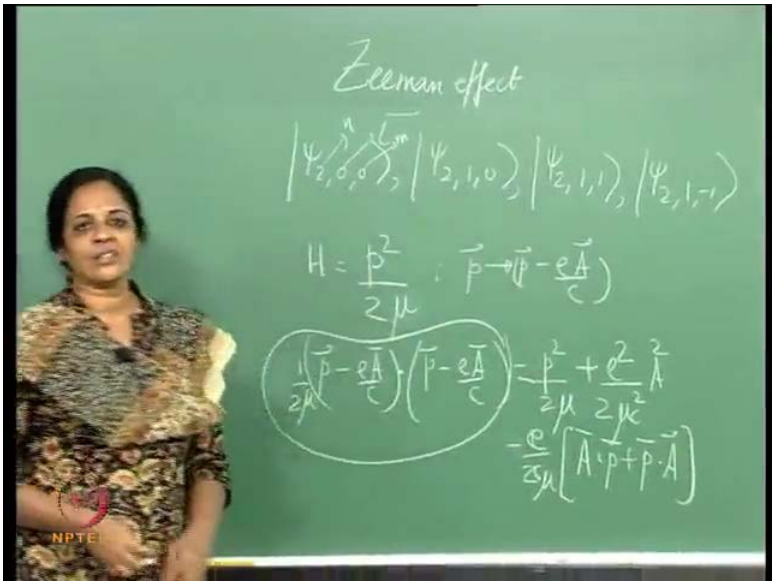

So, that is the next example of degenerate perturbation theory. There are certain striking differences between using a magnetic field and an electric field. So, let me look at the Zeeman effect. Once more I have the same states: psi 2, 0, 0, psi 2, 1, 0, psi 2, 1, 1 and psi 2, 1, minus 1 and, I now consider the electron with momentum P, the free Hamiltonian of course, is P squared by 2 m. But, let us be careful about the notation. This is n, that is l and that is m, the quantum number. So, what I want here is really the, we are looking at the hydrogen atom problem. So, this would be the reduced mass. So, mu is the reduced mass. So, I write H as P squared by 2 mu and now I couple it to a magnetic field.

So, that means that P goes to P minus e A by C and therefore, the Hamiltonian itself is P minus e A by C dotted with P minus e A by C and the whole thing has a 1 by 2 mu outside. So, what are the various terms? This is my new Hamiltonian. This has the old Hamiltonian P squared by 2 mu as the 1st term. Then, I have plus e squared by 2 mu C square A squared, that comes from here. Obviously, there is no term which involves P dot A or A dot P here. However, there is a cross term coming up now and that is plus 1 by 2 mu or minus 1 by 2 mu.

So, this quantity is expanded out here minus 1 by 2 mu e by C A dot P. So, let us also put the e by C outside, A dot P that is from here and this gives me an e by C, P dot A and A dot P is not the same as P dot A. We have to be careful.

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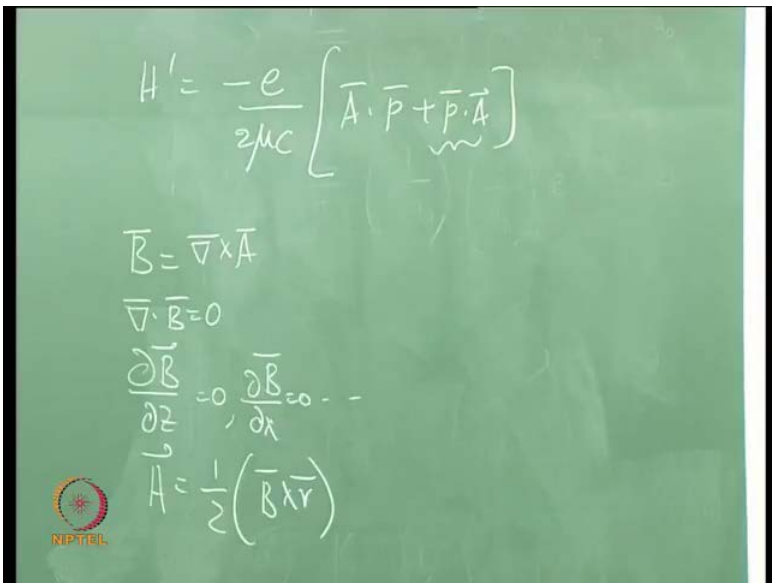

Look at H prime. It is minus e by 2 mu C A dot P plus P dot A. The magnetic field B is itself is del cross A, came out because del dot B is 0. I use the uniform magnetic field say along the z axis and therefore, delta B by delta Z equals 0, delta B by delta X equals 0 and so on. And therefore, I can write A as half B cross r. We will use this later but look at P dot A.

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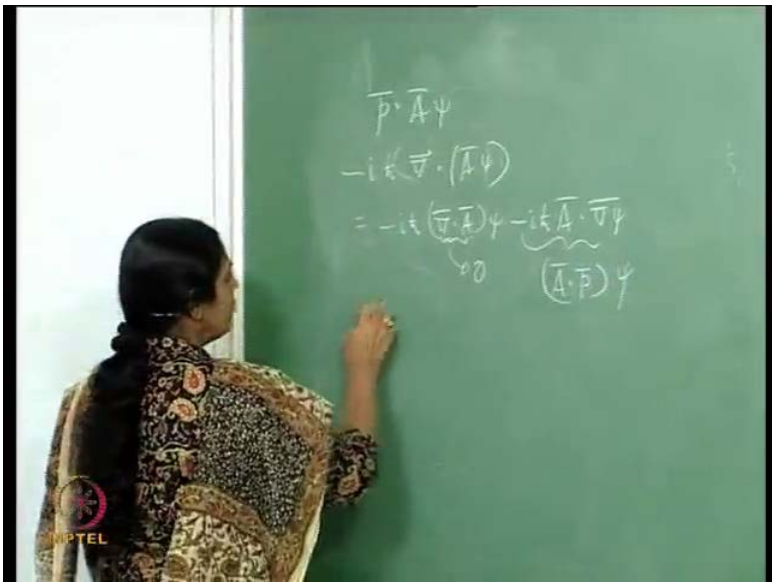

Consider P dot A. That is minus i h cross say P dot A psi is minus i h cross del dot A psi and that is minus i h cross del dot A psi minus i h cross A dot grad psi. That is what I get. This thing with A being given (Refer Slide Time: 44:56) by half B cross r del dot A becomes 0 and this object is simply A dot P psi and therefore, what is left of P dot A. What I need to use is simply A dot P, (Refer Slide Time: 44:56) the contribution from here is simply A dot P.

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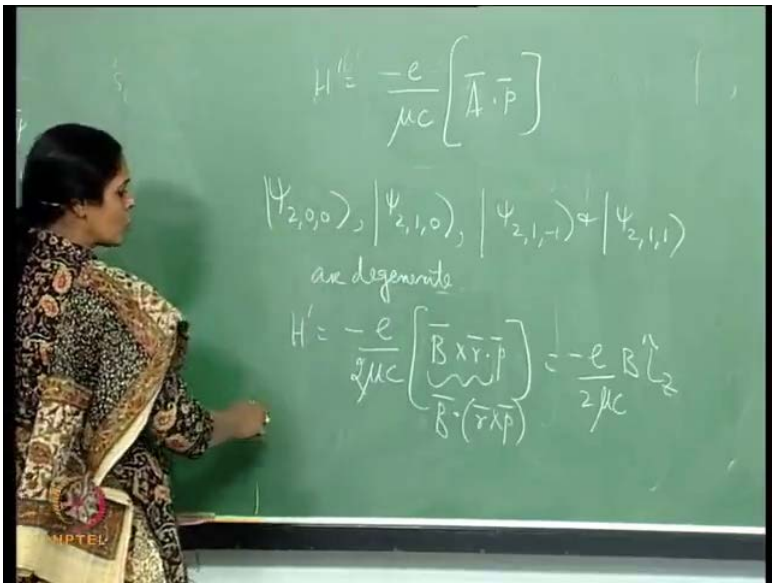

And therefore, H prime simplifies and we have the following expression for H prime minus e by mu C where mu is the reduced mass A dot P. That is all. So, this is the perturbing Hamiltonian. Now, what happens? How do I find the energy Eigenvalues? To begin with I know that these states and psi 2, 1, 1 are degenerate because the energy simply depends upon the n value. The idea is to use the fact that there l and m values are different and see what we can get. So, let me substitute for A. So, it's minus e by mu C, A is the half B cross r dot P. I can just write this as B dot r cross P. But, B is along the z axis. I have chosen the uniform magnetic field along the z axis, the magnitude B. And therefore, that is minus e by 2 mu C magnitudes B L z because I need to worry about the z component of the orbital angular momentum. It is clear that I have not put in spin.

So, I am trying to address this problem with just the orbital angular momentum put in excluding spin for the movement and seeing what exactly I get. So, this is the operator that I have. This is H prime, this is H prime. I do not need to consider superpositions anymore because if you look at the expectation value of H prime in any one of these states. It amounts to L z acting on these states and pulling out an Eigenvalue. These are Eigenstates of L z with Eigenvalue m h cross. So, it is pretty clear what is going to happen. There is no need to consider superpositions. Let us look at the contribution to the energy.

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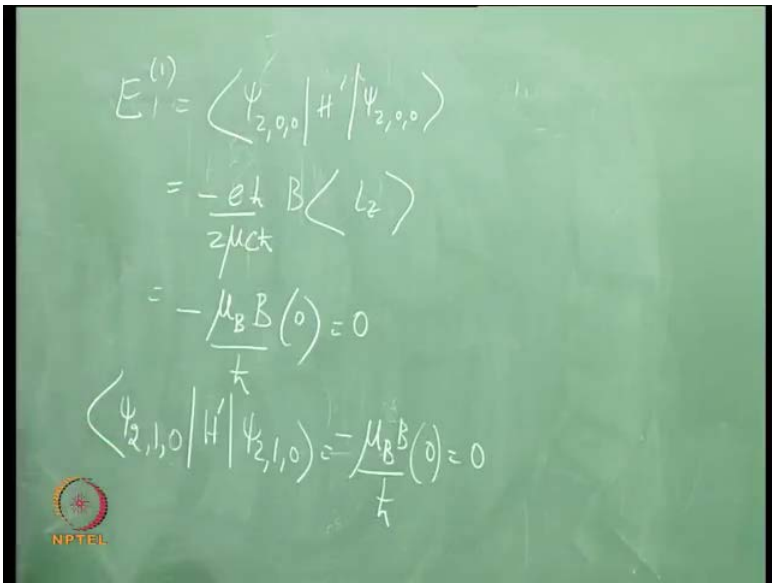

So, E 1 the 1st order contribution in one case is psi 2, 0, 0 H prime psi 2, 0, 0 and what is that? That is minus e by 2 mu c. I will put an h cross there because e h cross by 2 mu c is the Bohr magneton. Expectation value of L z in the state so that is minus the Bohr magneton. Let me call that mu B by h cross, B expectation value of L z in the state is 0. Remember L z acting on psi 2, 0, 0 is 0 h cross psi 2, 0, 0. So, the answer is 0. Now, if I consider psi 2, 1, 0 H prime psi 2, 1, 0 by a similar token I get minus mu B by h cross times 0 because the m value is 0. And therefore, they still continues a degeneracy between psi 2, 0, 0 and psi 2, 1, 0 even in the 1st order analogous to the Linear Stark effect.

But, in contrast to the case of the electric field, the Stark effect case I do not need superpositions. I work with the original states. But, I can see that I cannot lift the degeneracy fully. On the other hand, this is certainly true.

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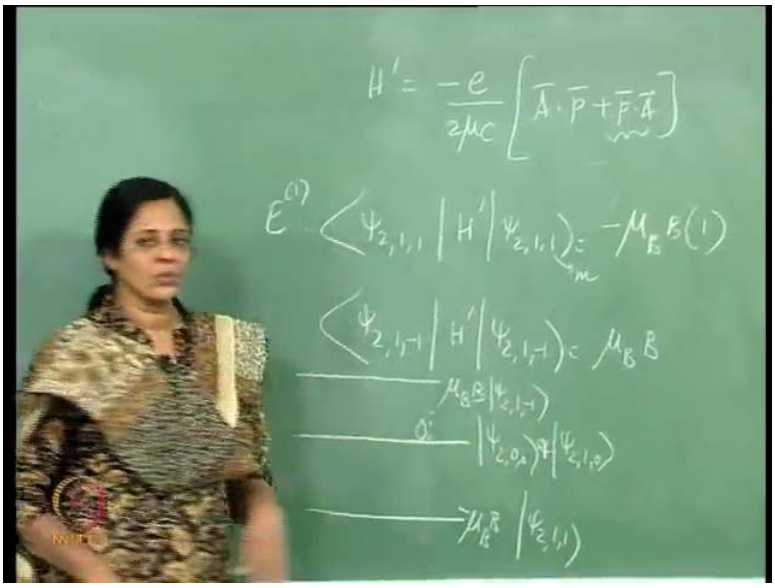

If I look at the 1st order contribution psi 2, 1, 1 H prime psi 2, 1, 1 this is minus mu B B. Let us forget that h cross (Refer Slide Time: 50:09) because L z pulls out an m h cross and the h cross will cancel out times 1. That is the m value and if I look at psi 2, 1, minus 1 H prime psi 2, 1, minus 1 that is mu B B. So, (Refer Slide Time: 50:09) this is what I have. Normally, I should have written it as minus mu B B m that is the energy, the 1st order contribution. But, as you can see the degeneracy between psi 2, 1, 1 and psi 2, 1, minus 1 have been lifted in contrast to the case of the Stark effect where the degeneracy between psi 2, 0, 0 and psi 2, 1, 0 was lifted.

So here, I now have two states: psi 2, 0, 0 and psi 2, 1, 0 with energy 0 and then I have two states: one of them with energy mu B B and the other with energy minus mu B B. So, one of them is psi 2, 1, 1 and the other is psi 2, 1, minus 1. So, the other two states not the ones where the degeneracy was lifted in the case of the constant electric field but the other two states, their degeneracy have been lifted. Whereas, these states continued to be degenerate and this is called the Zeeman effect. You have to go to higher orders to lift the degeneracy between psi 2, 0, 0 and psi 2, 1, 0.

So, these are two examples of degenerate perturbation theory. Essentially, in the 1st example that I worked out for you I showed you how super posing states helped. And, you could lift the degeneracy at least partially that is in a subspace in the 1st order of perturbation. Whereas, in the Zeeman effect there was no point doing a super posing. On

the other hand, the fact that these were Eigenstates of L z helped us lift the degeneracy again only partially, because we used an external magnetic field. In general, in a more complicated example you might have to superpose more states and work in a higher dimensional space to remove the degeneracy. So, that extent you will have to diagonalize a bigger matrix and see what you get to 1st order in the perturbation theory.

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