Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
Prof. Ranjan Das
Department of Chemical Sciences
Tata Institute of Fundamental Research, Mumbai

Lecture- 11
Quantum Mechanical Description of EPR – 1

Hello there, we have seen in our earlier class how a magnetic resonance transition take place. Today we are going to see the same thing from a quantum mechanical perspective, what we had seen earlier is something like this we keep a magnetic movement in a magnetic field.

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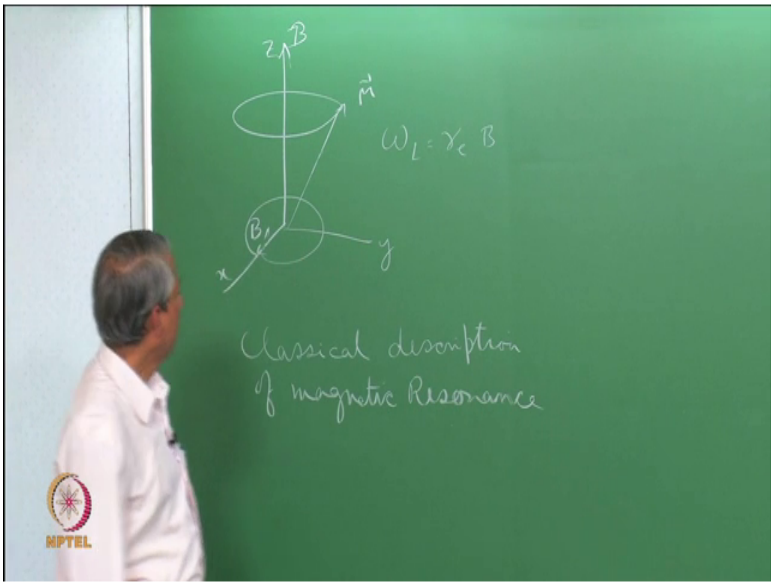

Magnetic field pointing on Z direction then the magnetic movement (Refer Time:00:53) around this magnetic field, this at the coordinate system and then we apply another magnetic field that is B 1 which rotates in the x y plane and then if the rotation of frequency of this is the same as the frequency of it is precision. Then the magnetic moment vector transform this to this and that is the transition. So, here the frequency of precision is given by normal frequency omega L gamma electron by B is the field. So, when this frequency same as this we get the resonance condition. So, this is the classical description of magnetic resonance.

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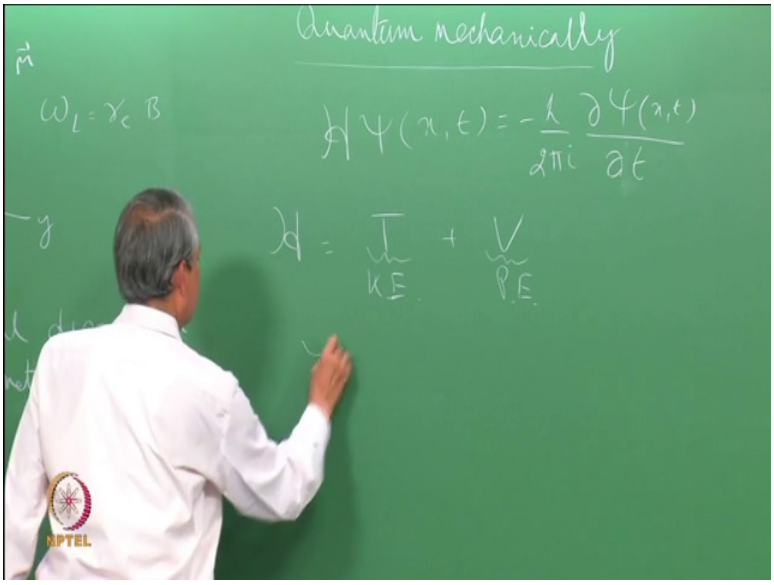

Today we will see what happens quantum mechanically. So, to get into the magnetic resonance from the quantum angle perspective let us review some basics of quantum mechanics. In quantum mechanics this the wave function which is a function of all coordinates and time this is a one (Refer Time: 02:32) coordinate expert one can have all the possible coordinate of the all the particles there. These has information that is that you can think of about the system and these follows this (Refer Time: 02:45) equation, this is the time dependent (Refer Time: 03:00) equation, where H is Hamiltonian operator because the kinetic energy operator plus potential energy operator. Now when the potential energy is not a function of time it depends only on coordinates.

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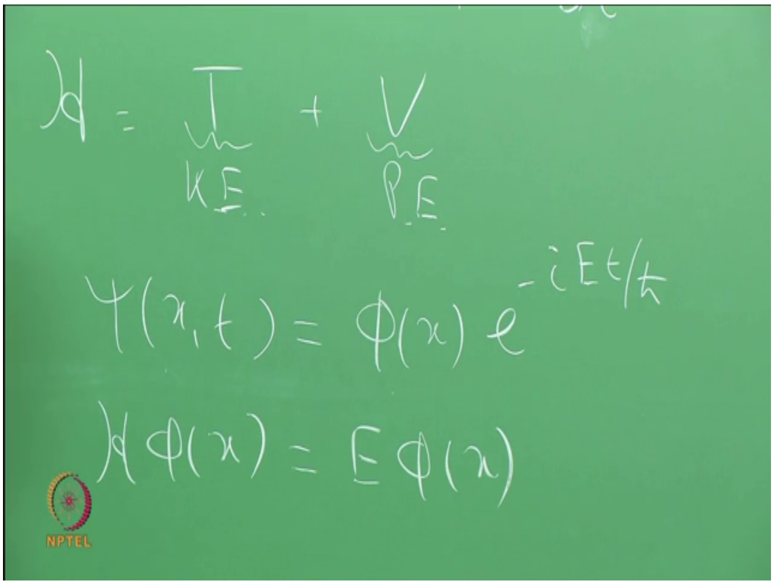

Then this wave functions psi can be written as function of only the space coordinate say phi of x and the energy term comes in this fashion, this is a time dividend part here and this phi x satisfies the same type of (Refer Time:03:46) equation, this called the time independent (Refer Time:03:55) equation. these the basis of quantum mechanics now this a particular case when the potential energy is independent of time then we get equation of this kind and the total wave function is a product of the space part and the time part and appears in this fashion and E is the energy of the system .

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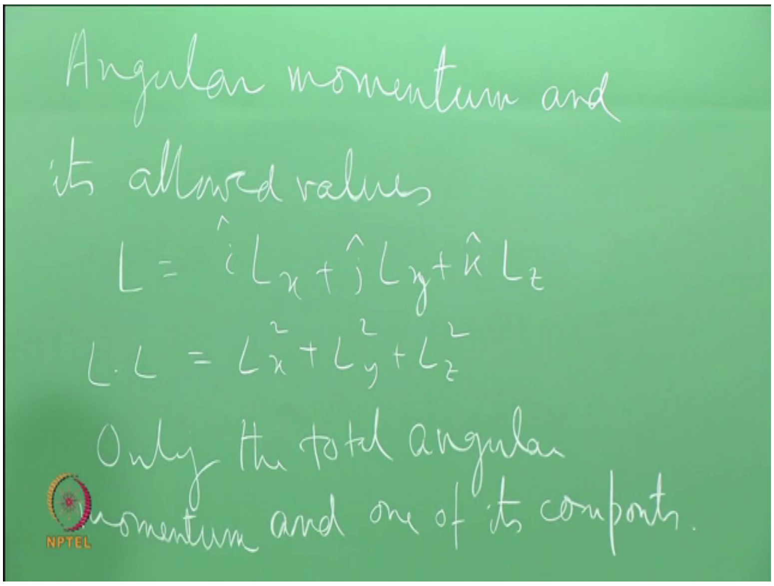

Now the other concept we need to revise is the angular momentum and it is allowed values, in quantum mechanics the L is the operator corresponding angular momentum, this is written as components i j k these three component angular momentum operator and magnitude of this is given as the product of this, which is L z square. It is so happened that the property of this three components of the operator and the total angular momentum square there a restrictions that restricts allowed values in this fashion, that we can have only the total angular momentum and one of it is component. So, you can choose whatever component you think of L x L I am sorry this will be L y, L x L y L z and the total magnitude of this is given by L square and that and all the component can be measured at the same time or these can have value of the same time that is a very important restriction here.

For example when have a picture of this kind it is shows that any instant time the magnetic movement is pointing this extend. So, it has value of the magnetic movement in all possible direction M x M y and M z and this in turn should be relate to the corresponding component of the angular momentum. Now this restriction say that that is not possible you can have only one component of the angular momentum and the total value of this. So, that puts a limit. So, this picture is not there for quite applicable if we strictly follow the quantum on mechanical principles.

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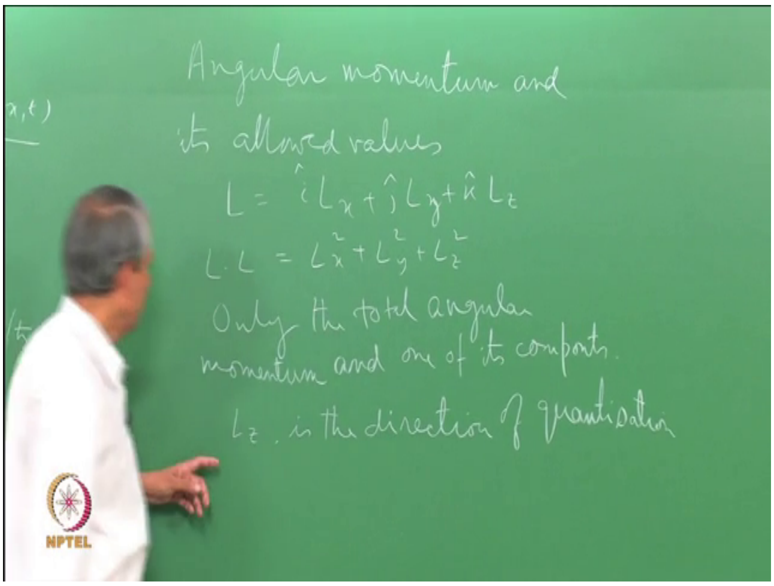

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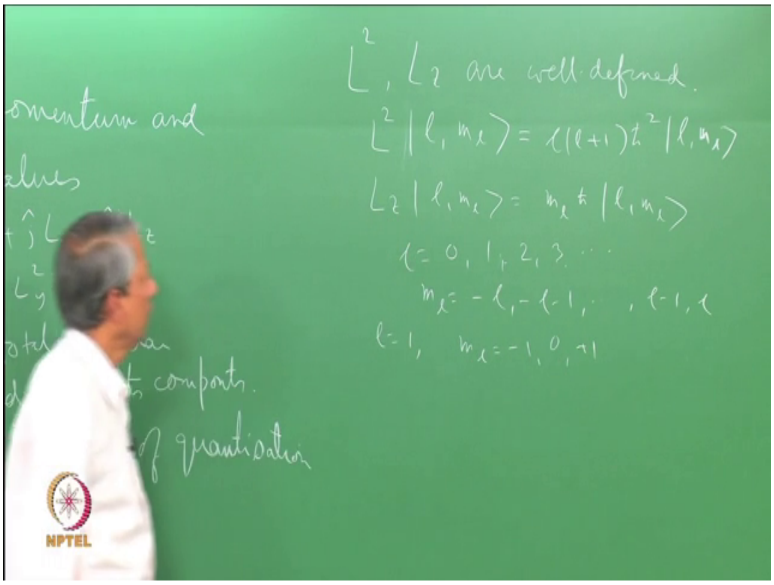

So, conventionally L z is taken to with the direction of quantisation is the. So, we can therefore, get a L square values and L z value, these are well define. For angular momentum the corresponding wave function or rather than again function of this operator written symbolically by that allowed values, let say L and m l such that L square operator gives the value of l into l plus 1, this the shorthand notation of saying that this represent a particular again function for a given L and given m l.

Similarly, L z gives the value m l, the restriction comes in this fashion that L can take value of this kind integral values and m l a takes again value integral values l. So, if l is equal to 1, then m l will minus 1 0 plus 1, see if you are dealing with spin angular momentum exactly similar properties hold there and we could write.

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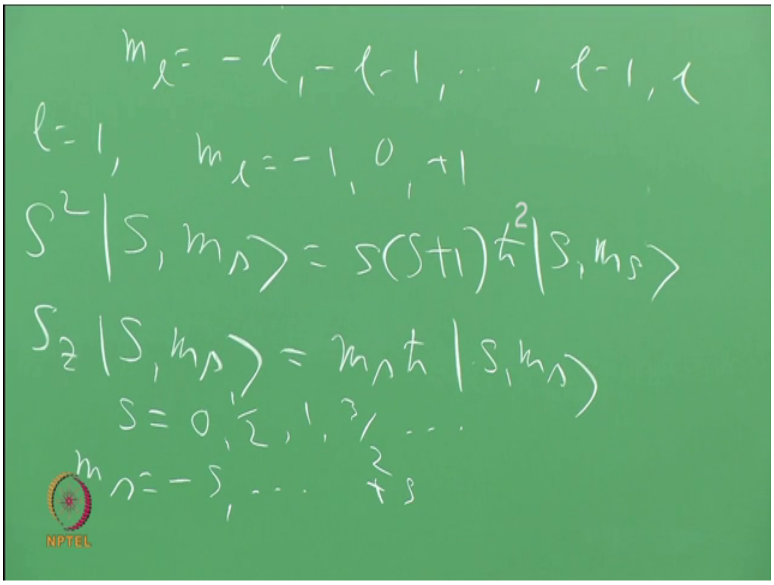

S square is the total angular momentum square and I can write S m s gives S into S plus 1, and S z is here there the restriction is that the quantum number S can take 0 half 1 3 by etcetera.

So, here half integral values are also allowed on then for L this will be strictly integral values, m s change from minus S to plus S in steps of 1.

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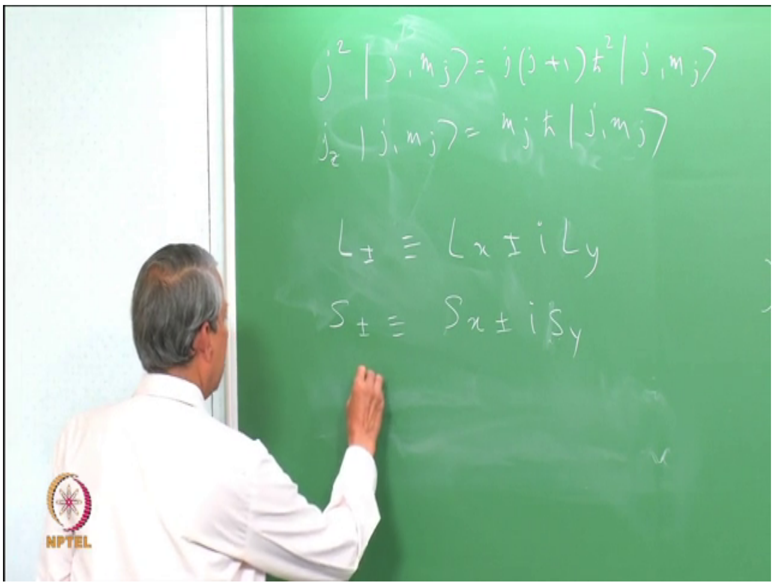

See in general if the angular momentum is let us take j then j square will give a value j into j plus 1 h square m j and j z gives m j. So, this is a very general expression, now we define another pair of operator in for angular momentum for example L, L plus minus is define to be L x plus minus I L y, similarly for spin angular momentum S plus minus define to be S y.

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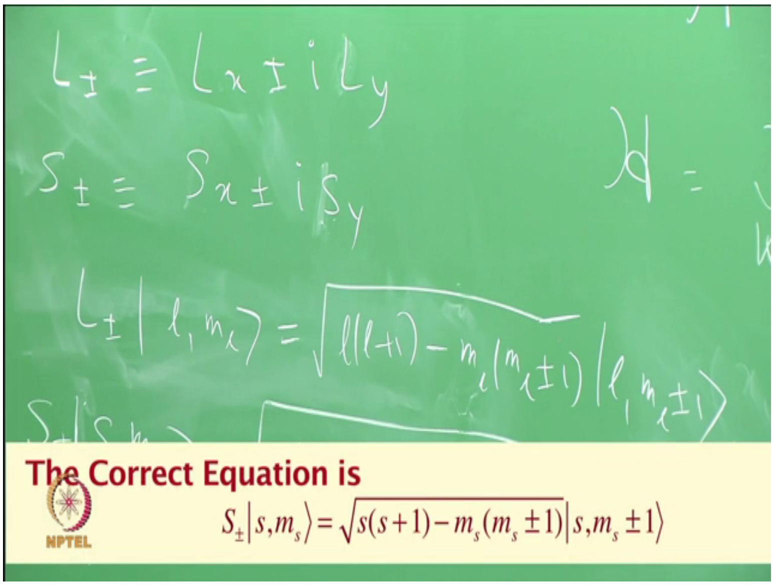

These are useful when you need to find out some integral that involves L x L y or S x S y. These are property of these are defined in terms of their behavior with respect to the again function of L square operator that is I have got l m l, this will give plus minus 1 similarly S plus minus S m s will be plus minus 1, Will find this expression is useful in deriving certain expressions. one importance consequence of this form of the wave function, that is when the potential energy does not depend on time, then the functional form of this is the product of the only space part times the energy part in this fashion this special properties is this.

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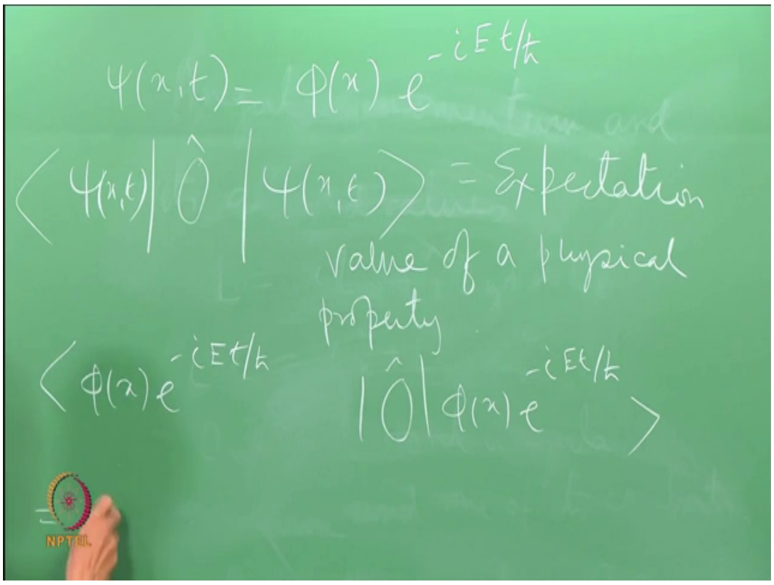

That, if you want to measure the physical property of any type that the system has in (Refer Time:13:09) variable, let us say kinetic energy, potential energy some other properties like, let us say now for moment for molecular bond length, bond angle all this properties is each of them there is a operator say operator, find out what the possible value that this particular system has the prescription is that we put the wave function in this fashion and then evaluate this integral where the operator is in the middle of that, this is called the expectation value of the of the physical quantity described by this operation O. Now here if the wave function of this kind then you see what happens this will look like, now this is just too many times here yes this is better.

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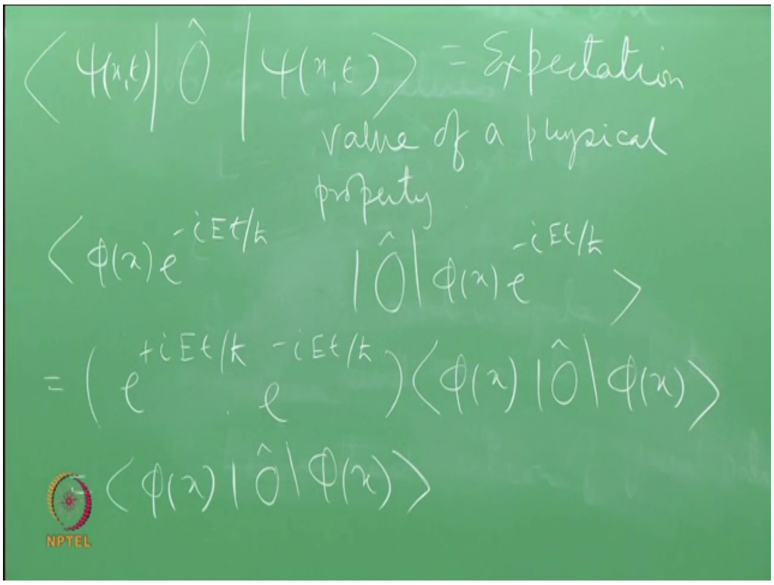

Now, here this is a (Refer Time: 14:58) of this. So, this can be taken out of the integral. So, this will be exponential plus i, this is a an allowed operation I can take this term out of the integral because this integral is respect to only the space coordinate, it does not involve indicator respected to time, this is a function of time, this is a function of time. So, this can come out of the integral to give rise to this term, now here see this accomplish consider to each other. So, this give raise to just one this is actually call to therefore, phi x to phi x. So, here there for these expectation value of any property that you can think of that becomes a function of only this kind (Refer Time:16:03) all special coordinate this become quantity which does not have any more time dependence.

So, that means that all physical properties of the system that you can think of for a wave function which is described by this becomes independent of time. So that means the system does not evolve does not change, we call that it has it is in a stationary state. So, all the properties therefore become independent of time. The key to that is that wave function, which function of space and time is a product of space part and time part and this is possible only if you go back this potential energy is independent of time then only such thing is possible. With this back ground now we try to see how much you can describe the magnetic resonance transition in terms of quantum principle.

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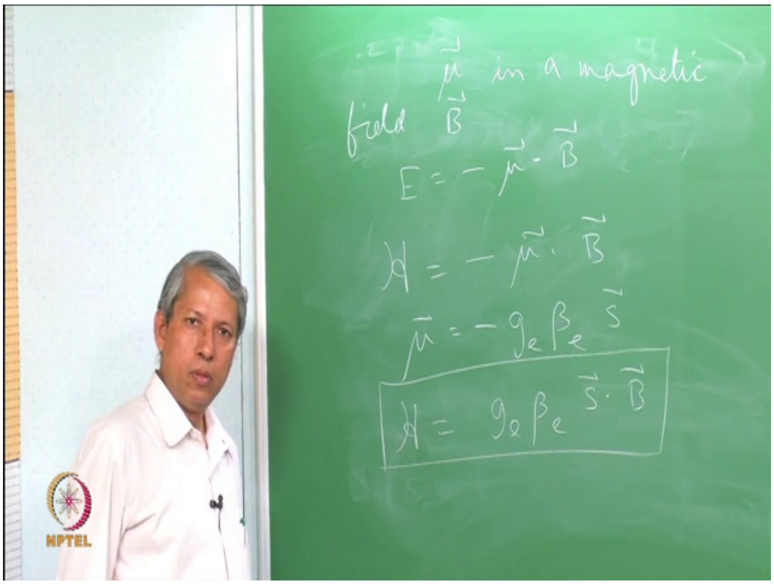

So, we start with this that magnetic moment let us say mu is placed in a magnetic field B. So, it is energy is given as minus mu dot B. So, here for quantum mechanics we replace all these by their corresponding operators, the Hamilton operator for this interaction could be given as similar to this, now the magnetic movement of a electron spin arises from it is angular momentum and that is given by minus g e b e S. So, here then the Hamilton operator becomes g e beta e S dot B. So, this is the Hamilton operator for the electron spin S put in a magnetic field. If there only one electron then it is allowed component of the spine angular momentum is S equal to half and m s is equal to plus minus half, now if the magnetic field is applied along the Z direction, then B is let us say B 0 K this is what Zeeman field.

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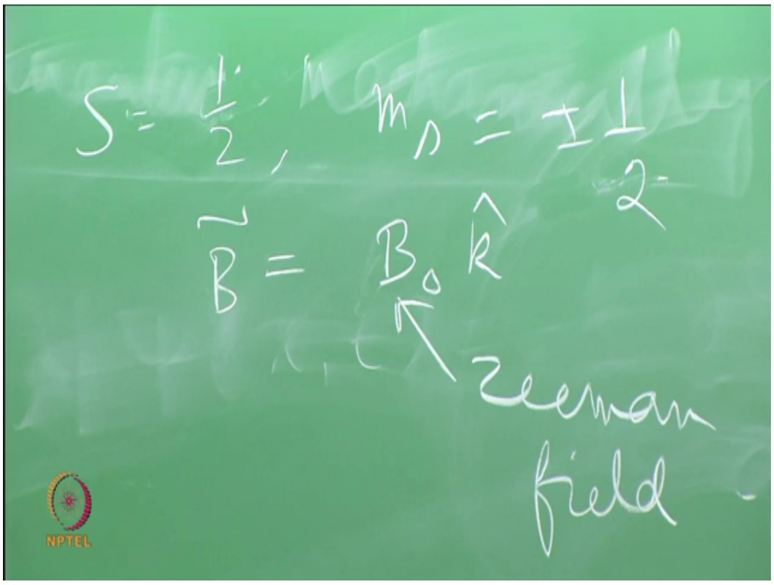

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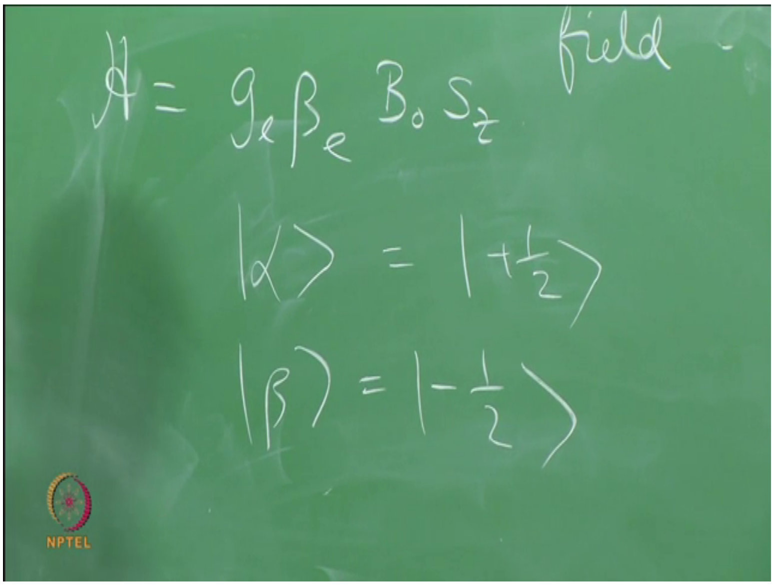

Then Hamilton becomes g e beta e B 0 S z. So, this is the Hamiltonian here the two component of the angular momentum is given by plus minus half I could design at the state of this by this symbol alpha which corresponds to plus half and beta which corresponds to minus half.

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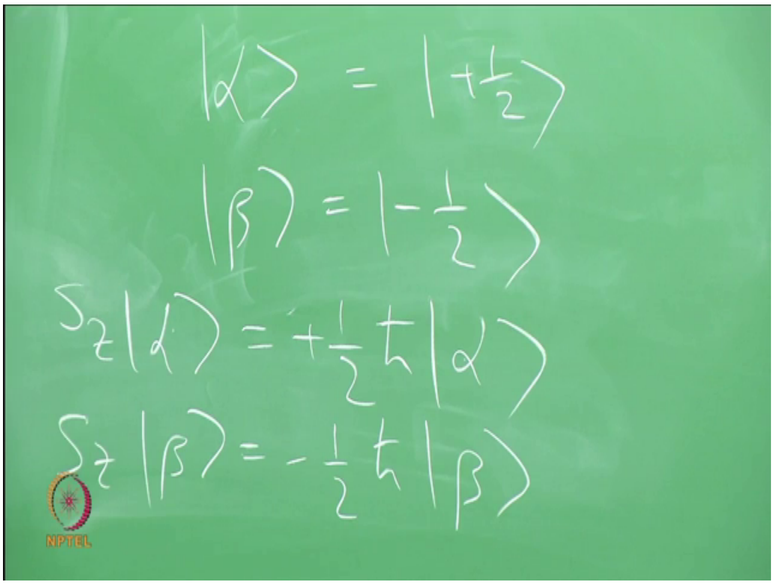

So, here there for S z alpha gives plus half h cross alpha, S z beta corresponds to minus half h cross beta. Then the energy can be now found out easy by operating h on these two states.

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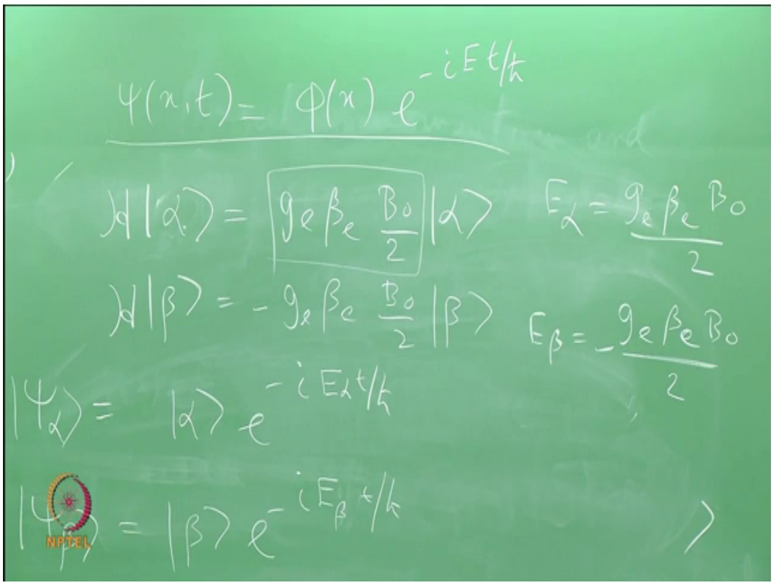

So, alpha gives this and similarly beta state gives minus B 0 by 2 beta. So, this is of course, something like a spatial part of this, space part symbolically spin is not quite any physical space, but we take it to the spine coordinate of the electron. So, to the total wave function which is of these kind will therefore look like, let us call it psi of alpha subscript alpha will be this. Alpha (Refer Time: 21:18) minus i E alpha by t h, where what is energy is given by this one. See again I can write E of alpha is equal to similarly energy for the beta state this. So, this is the total wave function for the alpha state similarly total (Refer Time: 21:57) beta state will be given by this is the subscript beta.

I hope there should be no confusion between the subscript beta and this beta E, this is (Refer Time: 22:19) beta subscript E this is the this alpha and beta corresponds to the spin state plus half and minus half. Just keep in mind that these two should not cause any confusion and no mix up takes place alright. So, there are the wave function that you found out for a spin which is kept in magnetic field and whose Hamiltonian is given by this fashion. These are against it of the Hamiltonian and also there are stationary states nothing pretty much happenes there that is system does not involve. So, we can write this in terms of energy level diagram.

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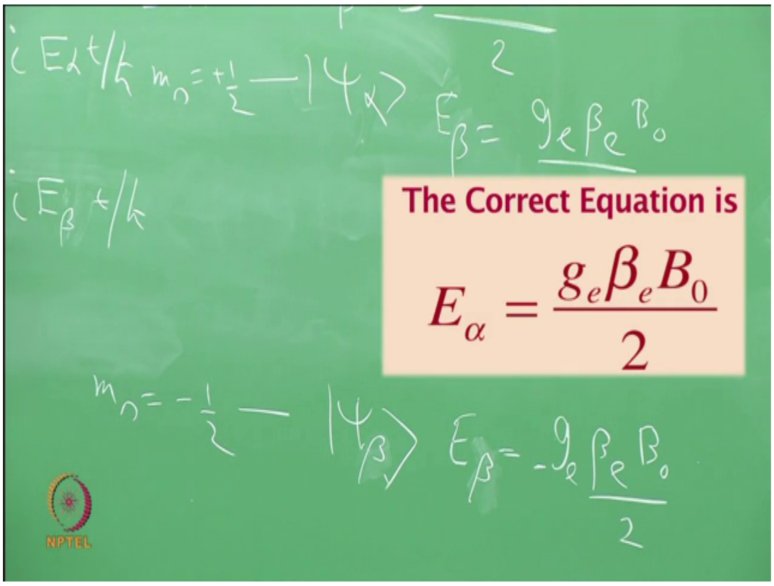

This is where psi alpha psi beta corresponding to m s equal to minus half, m s equal to plus half and this energy is given by this is alpha here beta here and E of alpha is g e beta e minus and here this is alpha beta is g e beta e by 2, this way you got complete description of the spin in a magnetic field.

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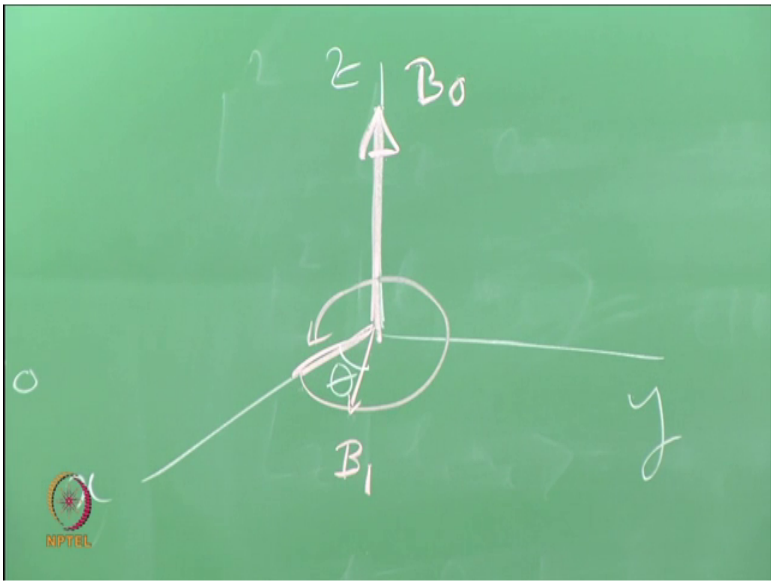

Now let us apply the small magnetic field along the x y plane, this x y z this is B 0 applied ground z direction, now we apply a small magnetic field which is moving in the x y plane this is magnitude is given B 1, and B 1 is very small compare to this one, how do we describe that suppose at time t called 0 the B 1 was exactly along the x direction then after sometime it is come here. So, this angle is theta and this angular velocity of B 1 around this z axis is omega, then omega will be omega times t is equal to theta t equal to 0 this was here now at a time t it has come here.

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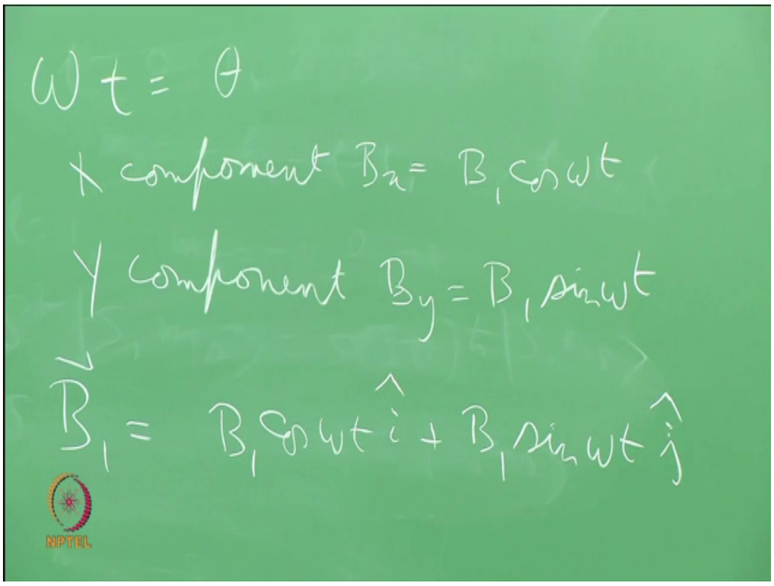

So, the component here is X component and this is the Y component. So, X component becomes this is B x becomes B o1ne cos omega t y component, B y is B 1 sin omega t. So, the this rotating magnetic field can be describe by this B vector it is B 1 vector is B 1 cos omega t i unit vector B 1 sin omega t j unit vector, this is the vector which describes the rotation of this b 1 field in x y plane with the angle of velocity omega. This is present what will be the Hamilton of the system we go back to this again here the B now total magnetic field that the spin is given by say B 0 in the z direction this Zeeman field, here plus i times B 1 cos omega t plus j times B 1 sin omega t.

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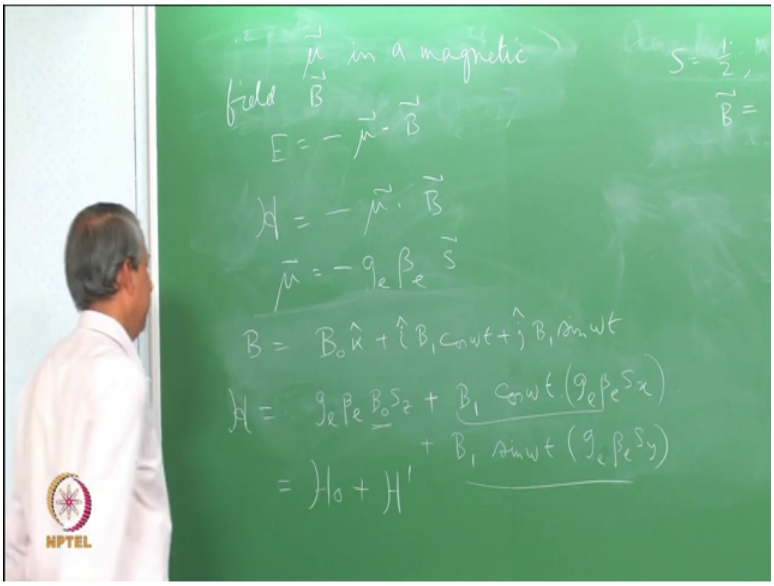

So, Hamilton becomes same way as this. So, this Hamilton becomes new Hamilton now in the presents of this B 1 field will be g e beta e B 0 S z which is a product of this and the z component of this, plus B 1 cos omega t x component and then g e beta e S of x B 1 sin omega t g e beta e S of y. This comes from the x component and y component of this one. So, this is the magnetic interaction that gives raise to this Hamilton of this kind. Now here as I said earlier that B 0 is Zeeman field which is much bigger than B 1 very small, we can treat this as a perturbation and this is the main Hamilton this could be written as the H 0 plus let us say H prime. H 0 is the g e beta e B 0 S z H prime is g e beta e B 1 S x cos omega t S y sin omega t.

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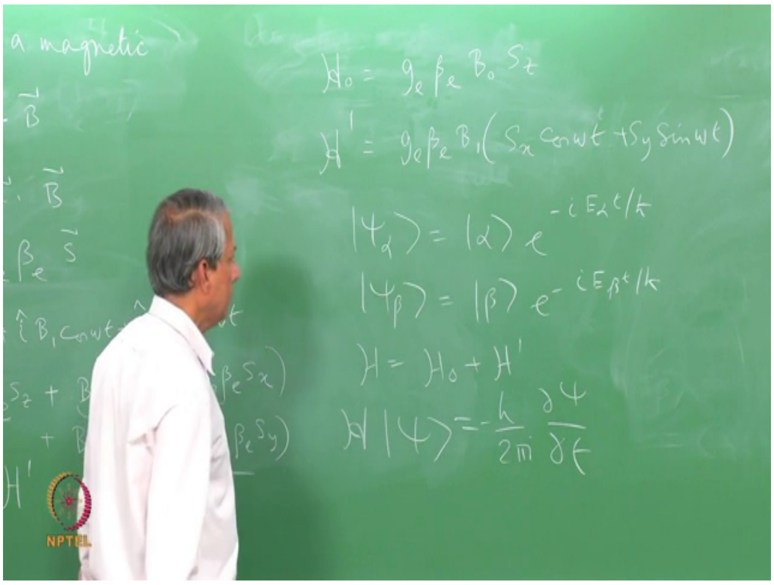

So, this is the perturbation this is the main un perturbation Hamilton, we know the solution to the time dependent (Refer Time: 29:36) equation gives this psi alpha is equal to alpha these are the solution for this Hamilton un perturbed Hamilton, this is un perturbed wave function therefore, now we want to find out the wave function that satisfies this total Hamilton now, H equal to H 0 plus H prime. So, here see this is a perturbation and these are the un perturbed wave function we can think of the wave function which satisfy this Hamilton, that this could be written as a linear combination of these two. In other words we take these two with the basis wave function and we expand the wave function corresponding to the total wave function total Hamilton in terms of these two basic.

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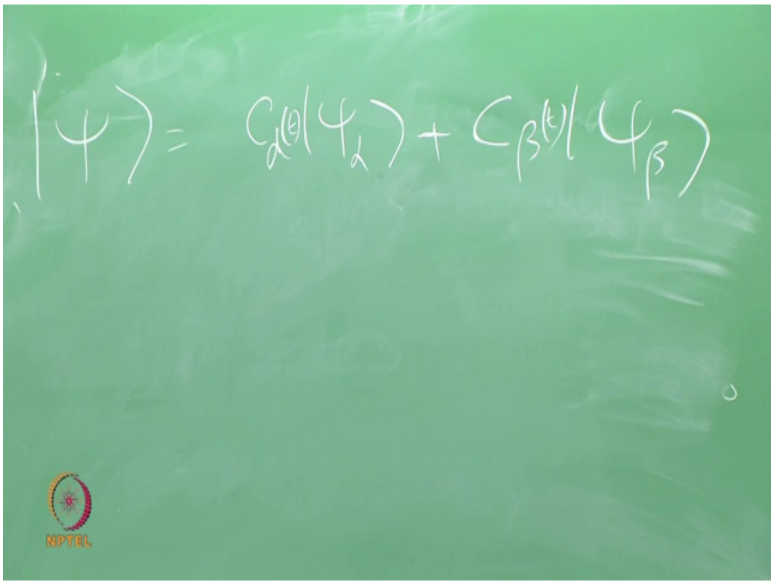

So, this becomes process C 1 C alpha these and these are these and these, now these (Refer Time:31:12) now time independent (Refer Time:31:14) equation and particular you see there is a time dependent part which is present here now, we expect this to be in general function of time. So, how to solve this we simply put this here and see what happens, put it here so this will give me H 0 C alpha t alpha plus H prime t is equal to in the right hand side.

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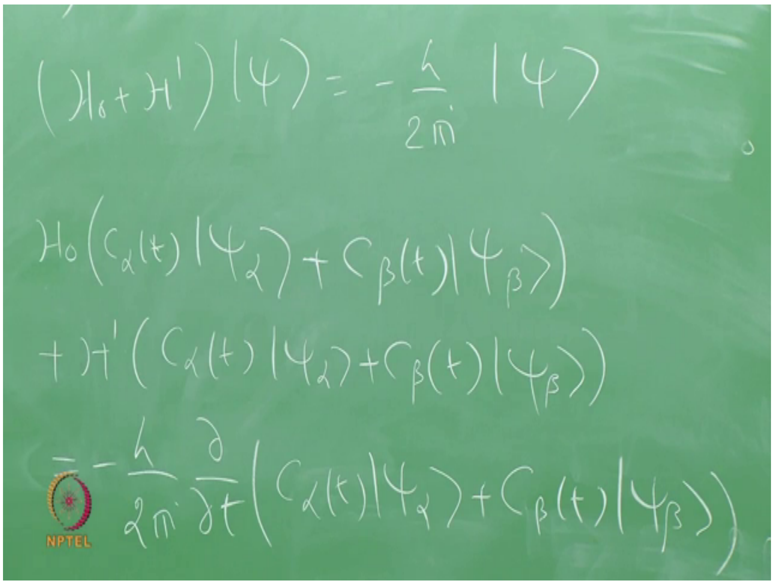

Here, now we noticed that this un perturbed wave function, psi alpha and H 0 the un perturbed Hamilton this operating on this gives H by 2 pi i delta psi t operating on this directly. Now this is a function of time this also could be a function of time. So, we can write in this fashion that h that is too much down.

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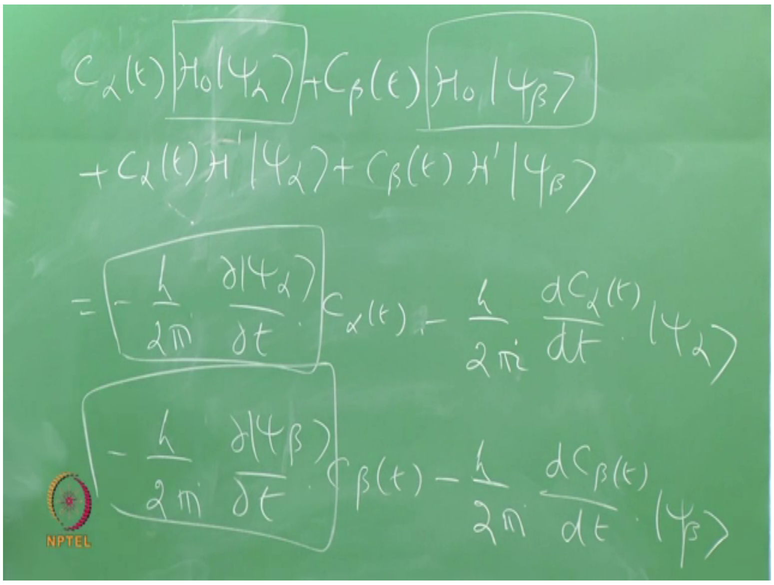

So, what we get here H 0. So, this term derivative will operate on this as well on this one. So, this gives, here so here this term is exactly equal to this term this comes from the un perturbed (Refer Time: 35:09) equation and un perturbed wave function. Similarly this term is exactly equal to this term we can therefore, cancel this from the two sides of the equation.

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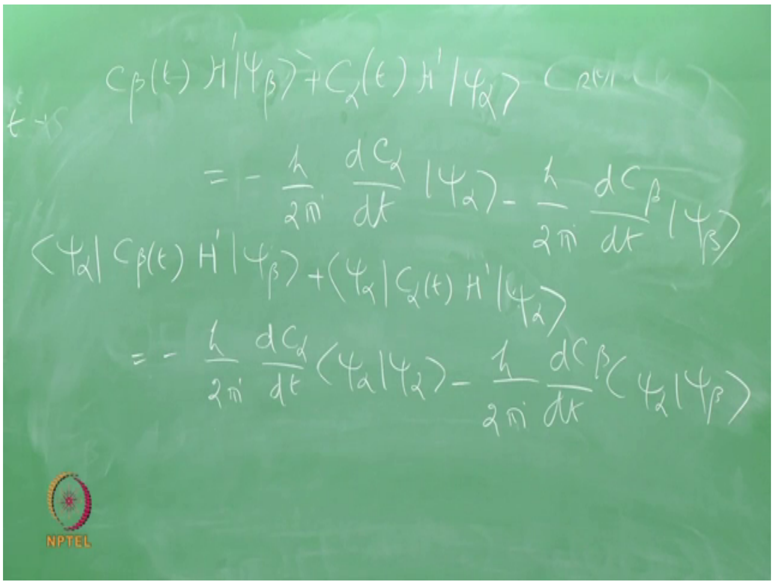

So, this gives me, ok now you our aim is to find out this coefficients C beta t and C alpha t because that is tells me how the system is revolving with time. To do that suppose we multiple on this side by psi alpha here. So, what I find here is that because of the orthogonality of these two wave functions psi alpha and psi beta this term goes to 0 and this is equal to 1. So, what I get is that minus h by 2 pi i this is one which is this can be taken out of integral.

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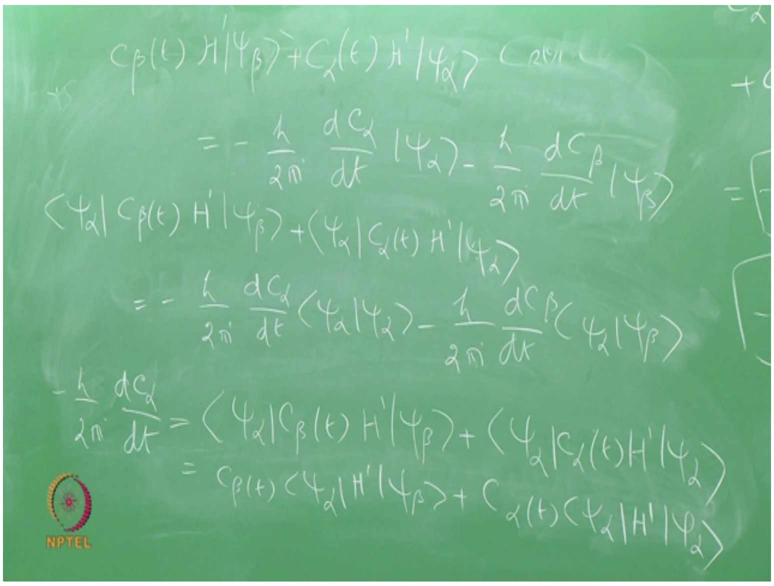

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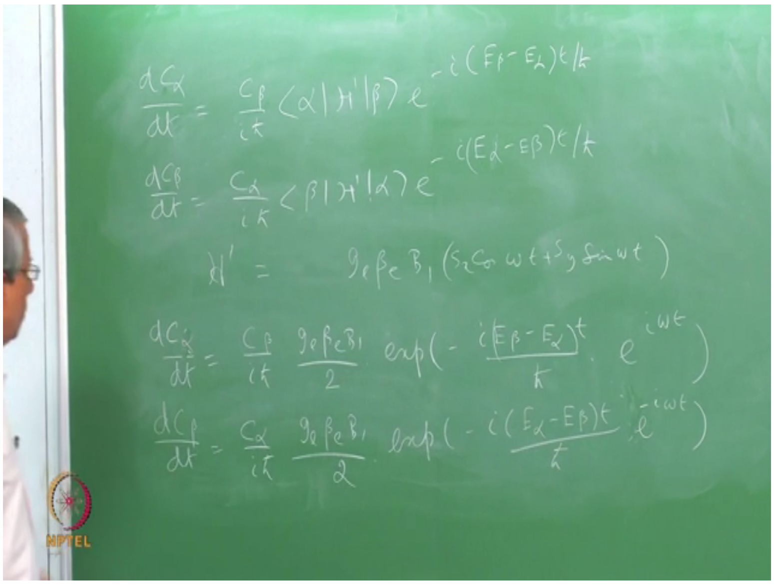

Ok, now these psi alpha and psi beta we know their form which we have it here this can be now simplified to write in this fashion. Similarly the coefficient d beta can be written as C alpha by these are very general form of equitation, where is C alpha is couple to C beta Cc beta is couple to alpha and a particular case. Now the Hamilton H is given as, so you put it here and then evaluate the integral with respect to the alpha and beta state.

So, that gives me and similar for beta it is ok; here you see that again that these are two couple differential equation and the way it this two energy levels alpha and beta comes is the energy different that comes in the picture here this omega is the frequency of the B 1 rotating around the x y plane.

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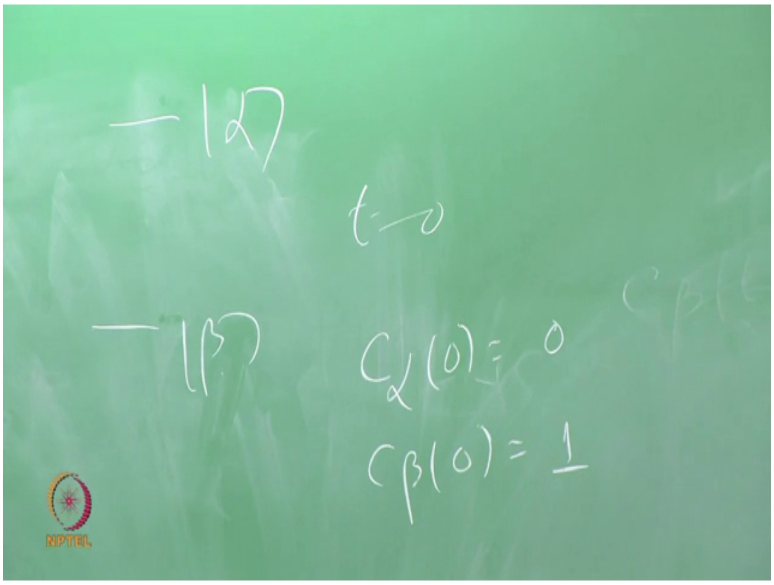

Now to solve this we can use the perturbation technique such that we assume that time t equal to 0 the system was in the beta state, t equal to 0 it was here (Refer Time:42:30) into C alpha at 0 was 0 and C beta time t equal to 1. So, we want to find out there for what is the probability that this will make a transfer here to there, that is C alpha becomes non 0. So, we will continue this derivation of this one in the subsequent lecture we stop at this moment now.