Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture - 12
Quantum Mechanical Description of EPR - 2

Hello. We have been discussing the Quantum Mechanical Description of a magnetic resonance condition. Let us recapitulate what we have done so far.

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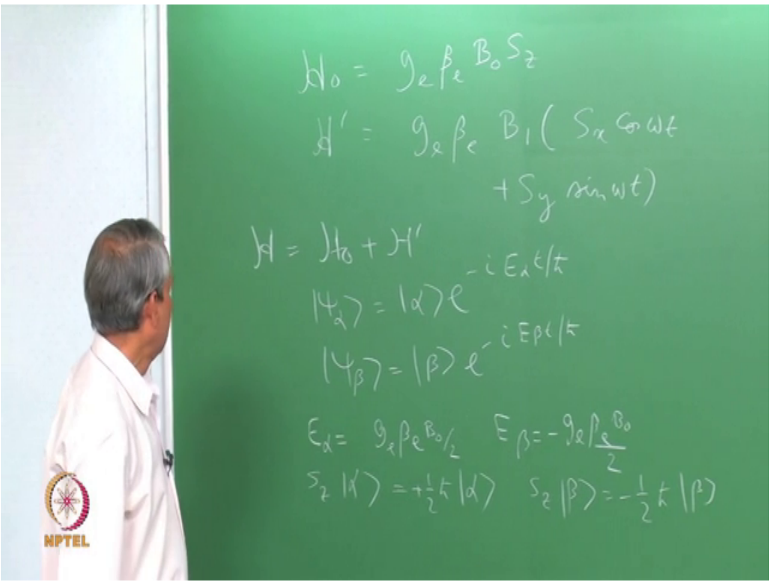

We have a Zeeman interaction which gives the main interaction given by this. This is the Zeeman magnetic field, this is a S z operator and the perturbation which is the small B 1 magnetic field applied in the x y plane that is given by is the way it is. So, the total Hamiltonian is H 0 plus H prime the wave function corresponding to the Hamiltonian H 0 is written as psi of alpha similarly psi of beta here E alpha and E beta are the energy corresponding the state of alpha and beta. And of course, alpha corresponds to this, I mean spin angular quantum number plus half and beta corresponds to the minus half component.

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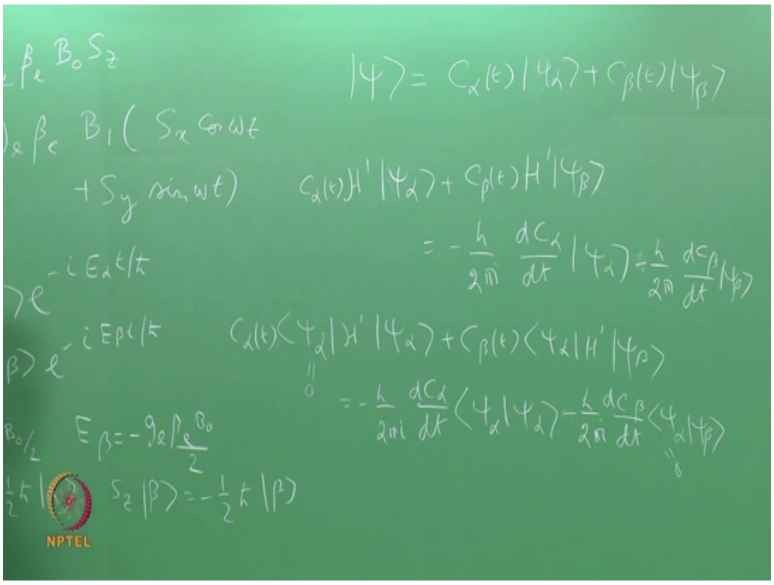

So, in the presence of this Quadra vision, we say the total wave function can be rewritten as a linear combination of this plus this I found that we can get equation of this kind, here our aim is to find out this coefficients here that tells the equation connecting evolution of the system from one state to the other. So, if you multiple on this side by let us say this one and complex conjugate of that. So, that I get psi alpha this gives now here because of the orthogonality of this wave function psi alpha and psi beta this give 0 and this term also will give 0, if I evaluate this integral using this form of the Quadra vision this goes 0.

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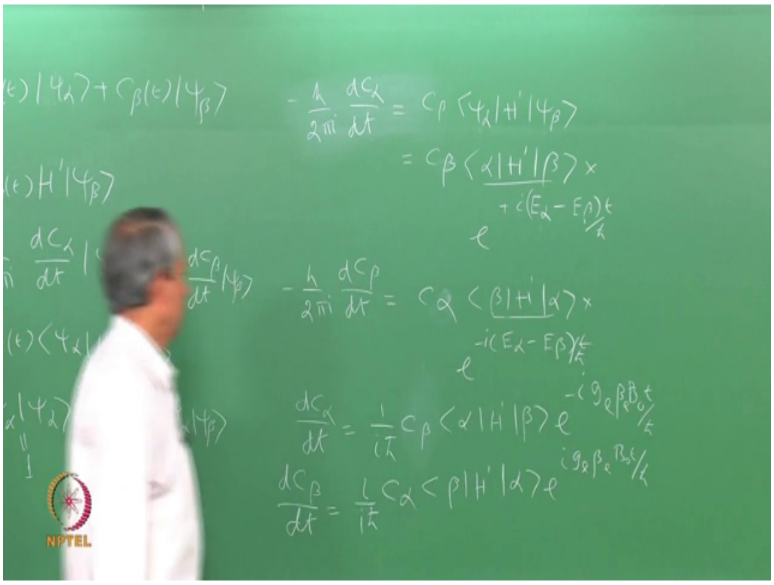

So, all I have here is this one is equal to 1.

Now, keeping in mind that this psi alpha and psi beta have this set of form that is space part is here and the time part involves the energy this can be written as into E to the power that is the way it looks like similarly for the other coefficient, we can write now that this equations are very important for that I have shown here in this slide.

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$$-\frac{h}{2\pi i}\frac{dc_\alpha}{dt} = c_\beta \langle \alpha | H' | \beta \rangle e^{-i(E_\beta - E_\alpha)t/h}$$

$$\frac{dc_\alpha}{dt} = \frac{c_\beta}{i\hbar} \langle \alpha | H' | \beta \rangle e^{-i(E_\beta - E_\alpha)t/h}$$

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Minus H by 2 pi i dc alpha by dt is equal to the functional form given here. Now this can be simplified by taking this H by 2 pi i as H cross and bring it in denominator. So, you got these 2 equations which are given here which shows the change of the coefficient alpha as a function of time and given by these. So, here it shows that if this term which is essentially same as that if this is 0, these are not going to change. In other words, for any change to take place or any transition from let us say state alpha to state beta to take place or from beta to alpha to take place; this must be non zero, in a sense, this decides the selection rule for transition.

Now we have got this to couple a differential equation; this got a mistake here and this got a mistake here. Now this E alpha minus E beta is nothing but the energy difference between the alpha state and beta state. So, this give rise to the higher energy and this is lower energy. So, this is actually equal to this was missing H cross was missing and other equation is dc. So, you got this coupled equation the C alpha connected to C beta C beta is connected to alpha. So, it is not easy to solve this equation simultaneously.

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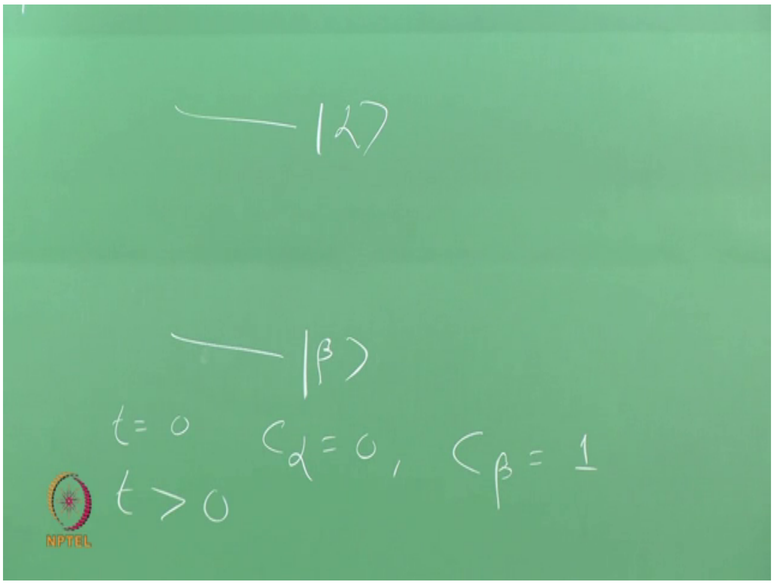

So, what you can do is to use a perturbative technique to get an approximate solution for that we start with this given initial condition that let us say condition is that the beta state is lower alpha state is higher. So, this spin system initially is here and then while the perturbation is applied can it make transition from here to there; that is we are going to find out.

So, t equal to 0 initial condition was that C alpha was 0 and C of beta equals to one and then what happens when t is greater than 0 S with this initial condition.

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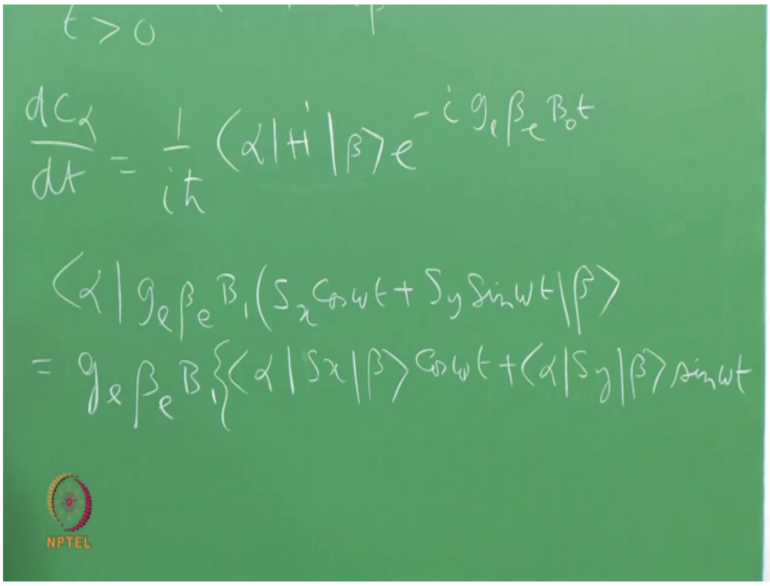

Now let us try to find out the value of let us say C alpha, then we can get d alpha by d t. Now here we have to find out this integral; now for that the integral is involves this perturbation expansion. So, this integral equal to cosine omega t plus sin omega t to evaluate this integral we can make use of the lowering operator or raising operator S plus S minus let see how that is done S plus 1 is S x plus minus i S y.

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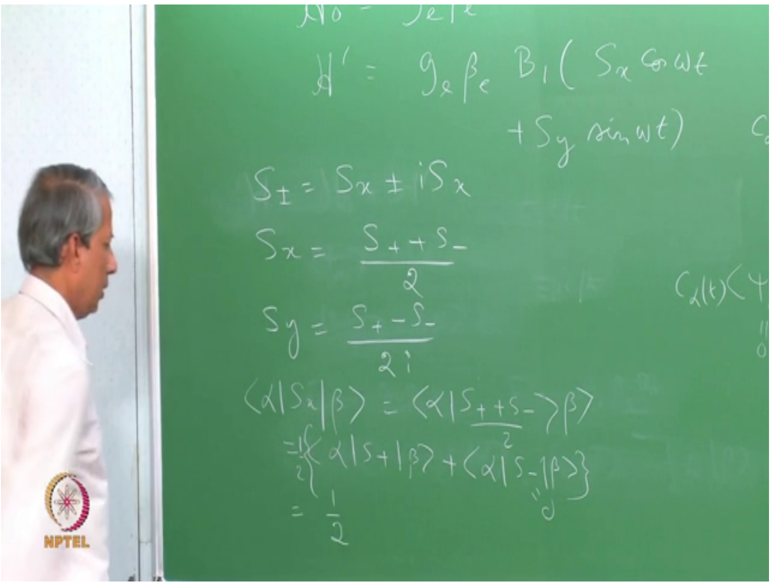

So, these gives S x is equal to S plus plus S minus by 2 and similarly S y S minus minus y; so alpha S x beta with alpha S plus plus S minus by 2 beta. So, this gives alpha half of here this is raising operator this is lowering operator.

So, when you raises it can raise beta to alpha and lowers lowering operator S minus operating on beta cannot lower it further where beta is the lowest ratio. So, this gives 0 then you can use the property of the operator. So, this you have to get the value this belongs exactly half S y component this alpha S y beta alpha S y beta.

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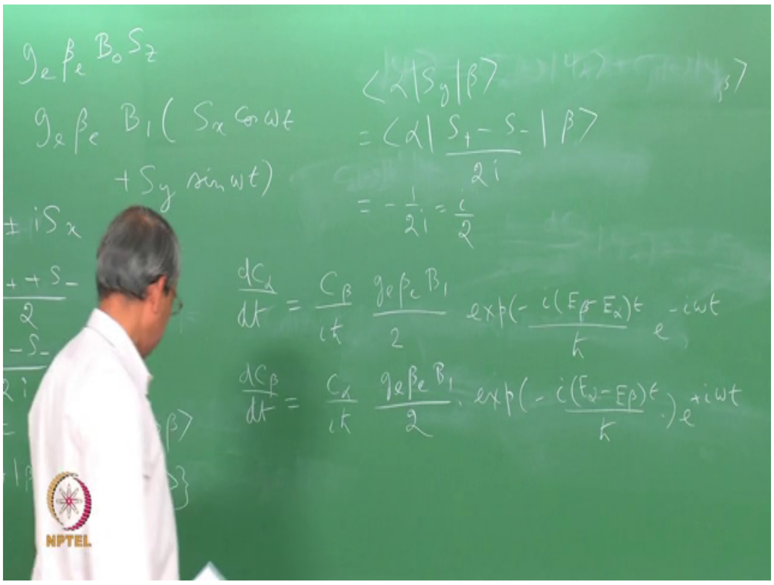

So, this can be written as alpha S plus minus S minus i twice i beta this will give minus 1 by 2 i or is equal to i by 2. So, from this I can get the expression of dc alpha by dt in terms of these values exponential minus minus i into E bar minus i omega t and similarly dc by dt gives C alpha by i H cross g E beta i B 1 by 2 exponential. This is alpha minus beta by t; that is the way it comes out to be.

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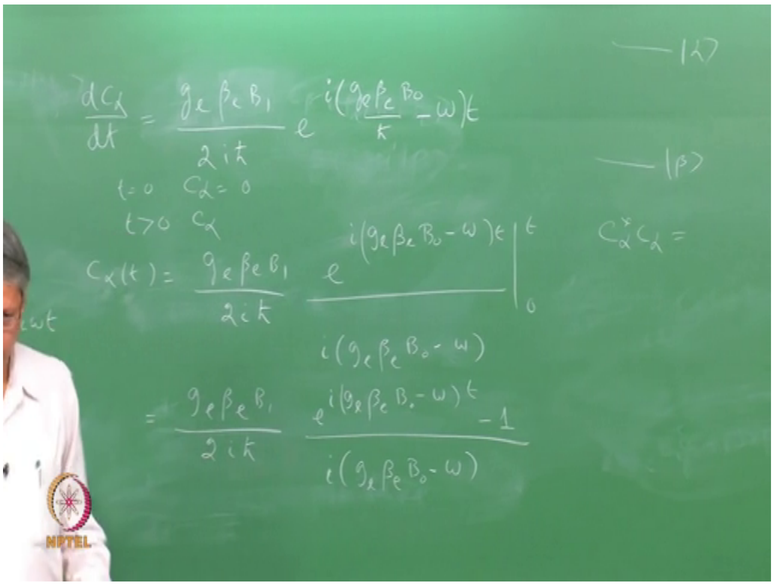

So, we have actually started with this equation and there found the solution w t; if we integrate this, now with respect to time, then at least t equal to 0 C alpha is equal to 0 and t is greater than 0 this is C alpha. So, this gives C alpha is function of time and if you integrate this; that is the way it comes out to be. Now with the limit put their value become.

So, these the expression of C alpha as function of time and how it changes and it changes in this fashion in this system. We assume that our spin system to start with was in beta and then this gives the probability that it will be applied here, but probability is not given by this number alone it will be a square of this number per se this is a complex number we take a modulus of that which is in this fashion C star alpha into C alpha.

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$$H' = g_e \beta_e B_1 (S_x \cos \omega t + S_y \sin \omega t)$$

$$\frac{dc_\beta}{dt} = \frac{c_\alpha}{i\hbar} g_e \beta_e B_1 e^{-i(E_\alpha - E_\beta)t/\hbar} \times \frac{e^{i\omega t}}{2}$$

$$\frac{dc_\alpha}{dt} = \frac{c_\beta}{i\hbar} g_e \beta_e B_1 e^{-i(E_\beta - E_\alpha)t/\hbar} \times \frac{e^{-i\omega t}}{2}$$

So, this will be retuning terms of the multiple this and its complex conjugate and simplify this, see, if have this here, this gives again dc beta by dt in this fashion similar by dc alpha by dt in this fashion and then you multiple this with complex conjugate and then simplify it; the equation looks like this.

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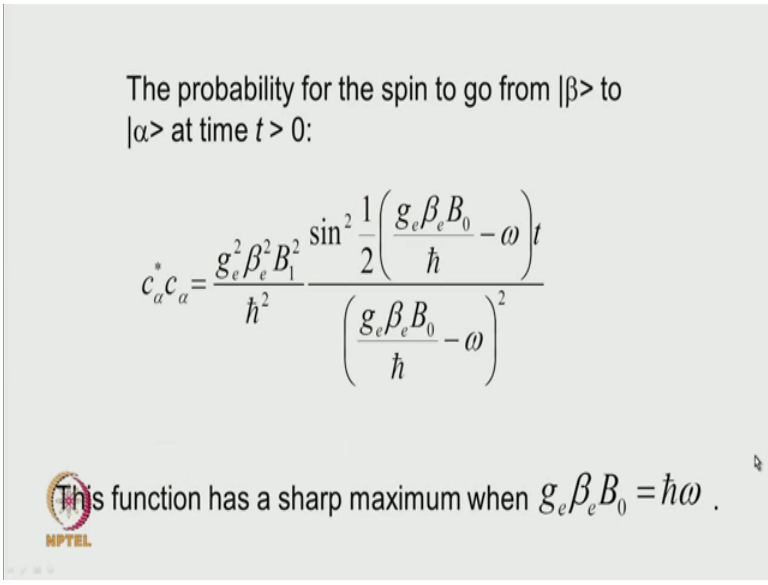

Now in this equation, see that sin square and this is the (Refer Time: 19:55) and the denominator also similar argument here. Now this function becomes very very large when omega is very nearly equal to this g E beta E B 0 by H cross.

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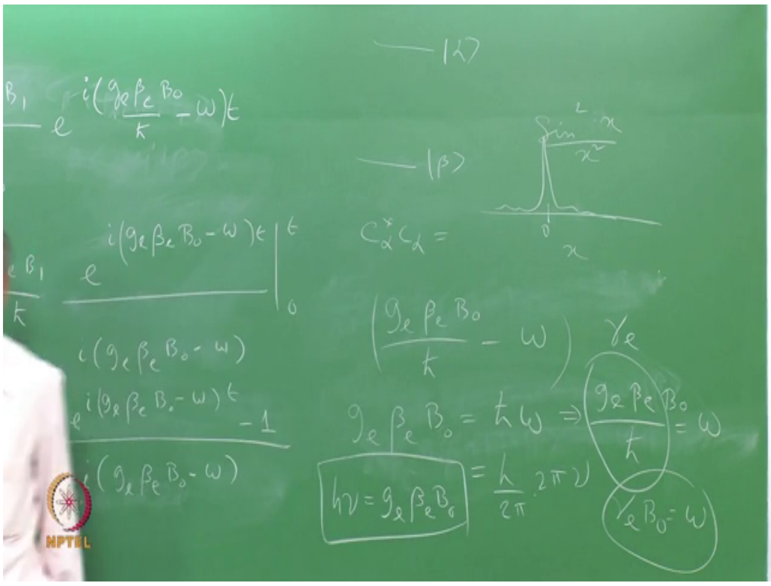

So, what you find here is that this sort of term comes there and function we have got something like sin square x type of x; x square something like that if you see the function here roughly speaking not quite the same, but the t is there, but we ignore for the time being its function of this kind. So, this is has a behavior x if you plot it, it has this behavior that is at x is equal to 0 it has very very large amplitude there is probability that the system will go from beta to alpha is very high when this are going to become 0.

Now this is interesting because this also shows that actually equal to H cross omega and this is nothing but the Larmor precession frequency in disguise where is the disguise if you write H by 2 pi and omega is 2 pi mu then this gives H mu equal to B 0 and this is nothing but the resonance condition that we have been talking all the time this also.

If you write here that g E beta E B by H cross which is actually Larmor frequency this is nothing but gamma electron gamma electron B 0 is equal to omega this is the normal frequency there. So, if you have recovered the conclusion that have derived from the classical description of magnetic resonance exactly same conclusion arrived at; but the important difference is that here we have not really brought in the concept of precession normal precession involves knowing the direction of the angular momentum or the magnetic moment in some absolute fashion that is I must know the both x, y and z components of the 3 components of the magnetic moment, then only the precession can be sort of visualized, but quantum magnetic says that is not possible we can only get one component of the angular momentum or the magnetic moment and the total magnitude of the angular momentum and that is the description that you have used here. But ultimate conclusion is just the same.

Now this can be generalized to spin which is more than half here the description was based on only S equal to half.

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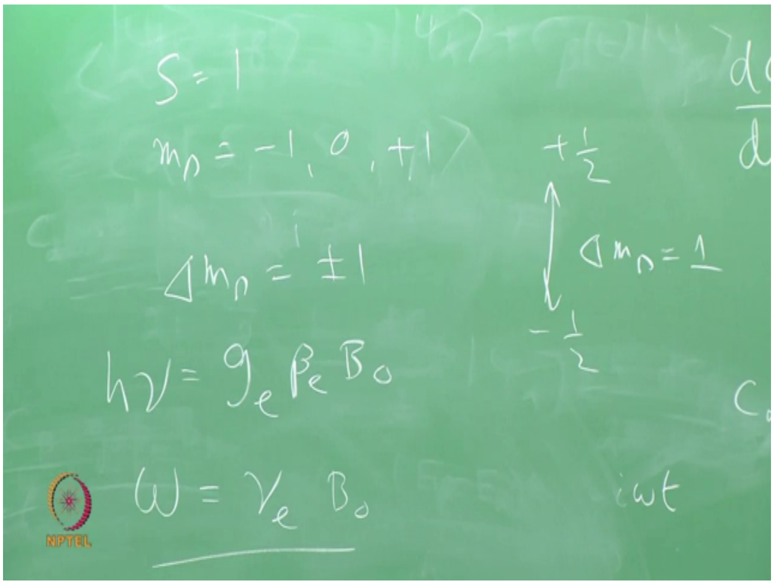

So, about 2 level system, but if we have let us say S is equal to 1, then m S will be minus 1 0 plus 1 3 level system; one can actually do exactly the similar treatment and come to the same conclusion that for delta m S will be plus minus 1 will be the allowed transition and similar resonance condition will be applicable there also there I can write H mu is equal to or so, here m S changes by 1 unit in plus minus half also the same changes 1 unit. So, everything is consistent there.

So, with this analysis, we come to the end of this quantum mechanical description of the resonance in magnetic transition. Here, we have understood that classical picture and quantum mechanical picture both give the same answer. We end here now.