Principles Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture - 18
Second-order Effects on EPR Spectra

Hello, today we are going to discuss second order E P R spectrum calculation, earlier we saw how to calculate spectrum up to first order, now why bother with second order calculation.

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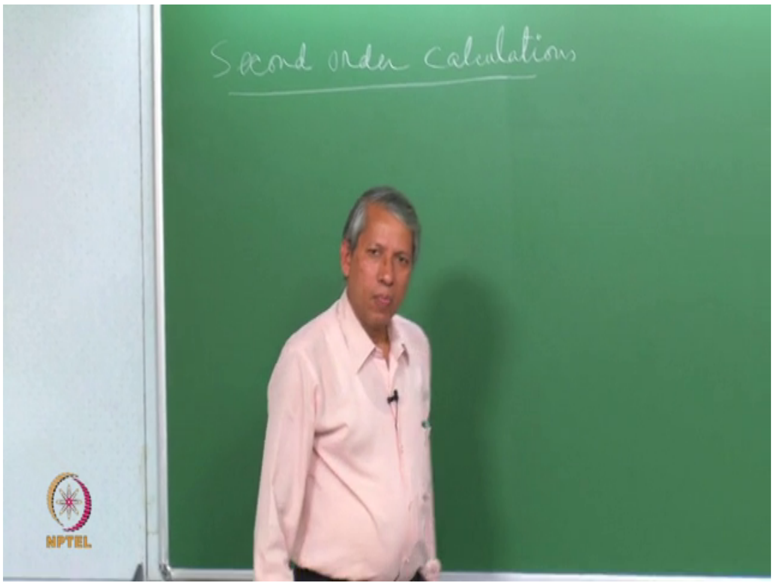

Because first order calculations gave quite good interpretation of most to the spectrum that we saw so far but, sometimes that is not sufficient.

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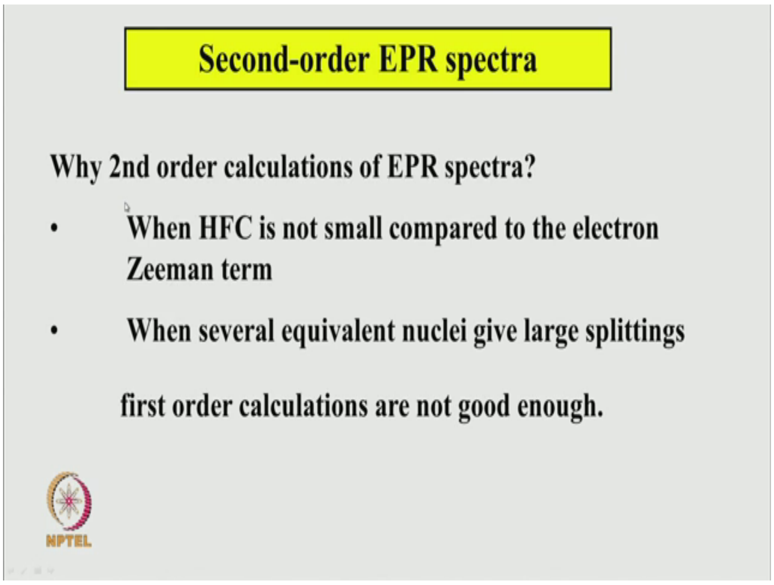

Second-order EPR spectra

Why 2nd order calculations of EPR spectra?

- When HFC is not small compared to the electron Zeeman term
- When several equivalent nuclei give large splittings

first order calculations are not good enough.

So, here the two important reasons for example, when hyperfine coupling constant is not small compared to the electron Zeeman term. Or when there are several equivalent nuclei giving large splittings in that case first order calculations are not good enough.

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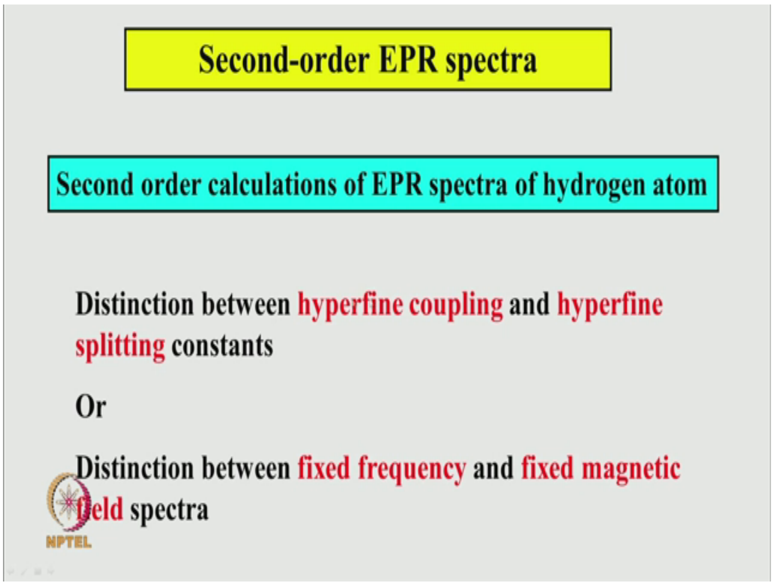

Second-order EPR spectra

Second order calculations of EPR spectra of hydrogen atom

Distinction between hyperfine coupling and hyperfine splitting constants

Or

Distinction between fixed frequency and fixed magnetic field spectra

So, when we doing the second order calculation will take hydrogen atom as an example. And then try to make a distinction between hyperfine coupling and hyperfine splitting constants, also try to make a distinction on fixed frequency experiment and fixed magnetic field experiment whether their same in all respect or not. First order spectrum that we calculated an interpret earlier gave the same value for hyperfine splitting constant or hyperfine coupling constant there was no difference, but we will see some difference may appear when we do the calculation up to second order.

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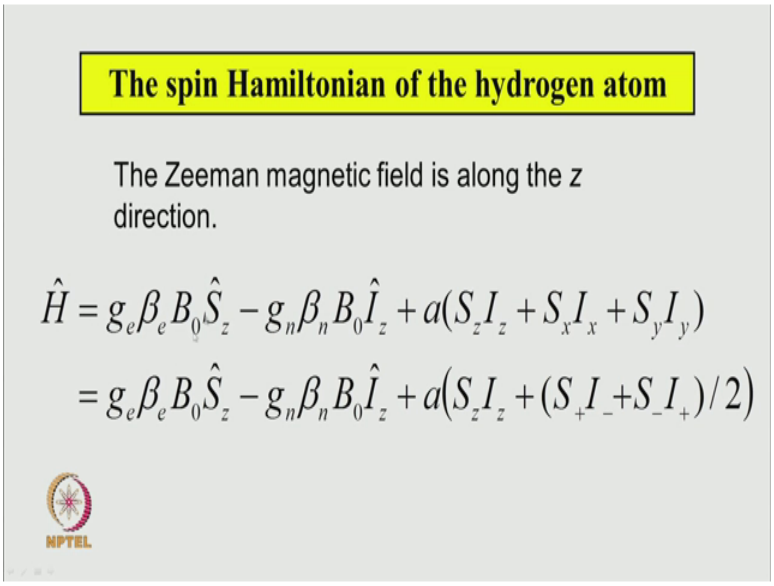

The spin Hamiltonian of the hydrogen atom

The Zeeman magnetic field is along the z direction.

$$\begin{aligned}\hat{H} &= g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + a(S_zI_z + S_xI_x + S_yI_y)\\ &= g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + a\left(S_zI_z + (S_+I_- + S_-I_+)/2\right)\end{aligned}$$

So, let us recapitulate our Hamiltonian or hydrogen atom, this is the Hamiltonian this is the electron Zeeman term, this is the nuclear Zeeman term and this is the isotropic hyperfine interaction this can be written in this fashion.

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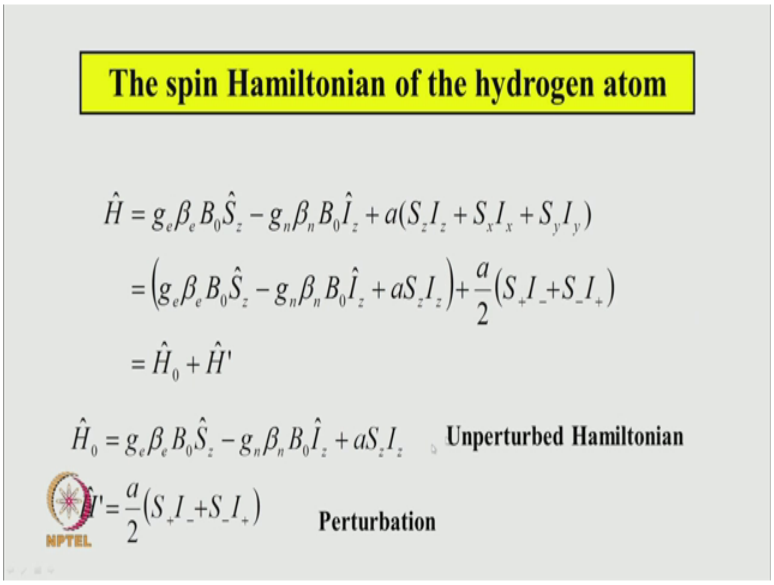

The spin Hamiltonian of the hydrogen atom

$$\begin{aligned}\hat{H} &= g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + a(S_zI_z + S_xI_x + S_yI_y)\\ &= \left(g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + aS_zI_z\right) + \frac{a}{2}\left(S_+I_- + S_-I_+\right)\\ &= \hat{H}_0 + \hat{H}'\end{aligned}$$

$\hat{H}_0 = g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + aS_zI_z$ **Unperturbed Hamiltonian**

$\hat{H}' = \frac{a}{2}\left(S_+I_- + S_-I_+\right)$ **Perturbation**

So, here we treat these part electron Zeeman, nuclear Zeeman and a S z I z as the unperturbed Hamiltonian and the other part is treated as a perturbation.

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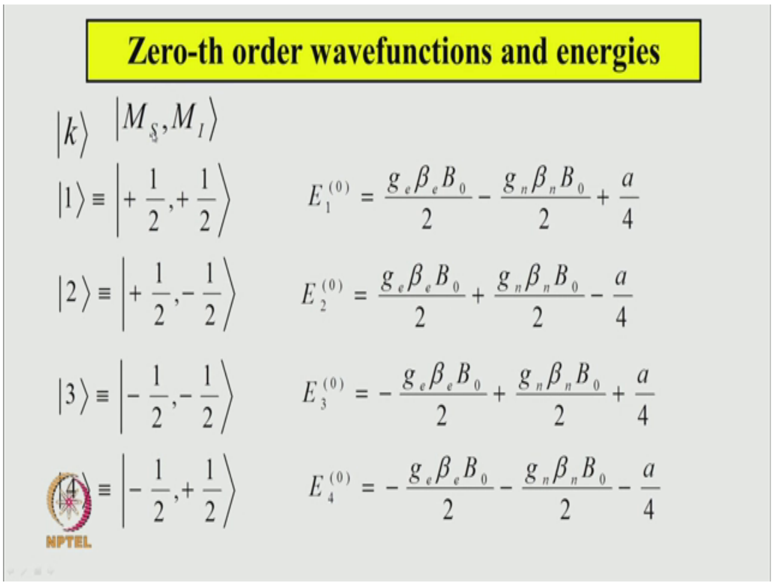

Zero-th order wavefunctions and energies

$|k\rangle \quad |M_S, M_I\rangle$

$|1\rangle \equiv \left|+\frac{1}{2},+\frac{1}{2}\right\rangle \qquad E_1^{(0)} = \frac{g_e\beta_e B_0}{2} - \frac{g_n\beta_n B_0}{2} + \frac{a}{4}$

$|2\rangle \equiv \left|+\frac{1}{2},-\frac{1}{2}\right\rangle \qquad E_2^{(0)} = \frac{g_e\beta_e B_0}{2} + \frac{g_n\beta_n B_0}{2} - \frac{a}{4}$

$|3\rangle \equiv \left|-\frac{1}{2},-\frac{1}{2}\right\rangle \qquad E_3^{(0)} = -\frac{g_e\beta_e B_0}{2} + \frac{g_n\beta_n B_0}{2} + \frac{a}{4}$

$|4\rangle \equiv \left|-\frac{1}{2},+\frac{1}{2}\right\rangle \qquad E_4^{(0)} = -\frac{g_e\beta_e B_0}{2} - \frac{g_n\beta_n B_0}{2} - \frac{a}{4}$

Zero th order wave functions are given as product a states of the electrons spin angle momentum component and nuclear spin angle of momentum component. Since each of them is half we get four states plus half plus half and this fashion, we did all this calculations earlier and zero th order wave functions are of this kinds and the zero th energy is also of this kind.

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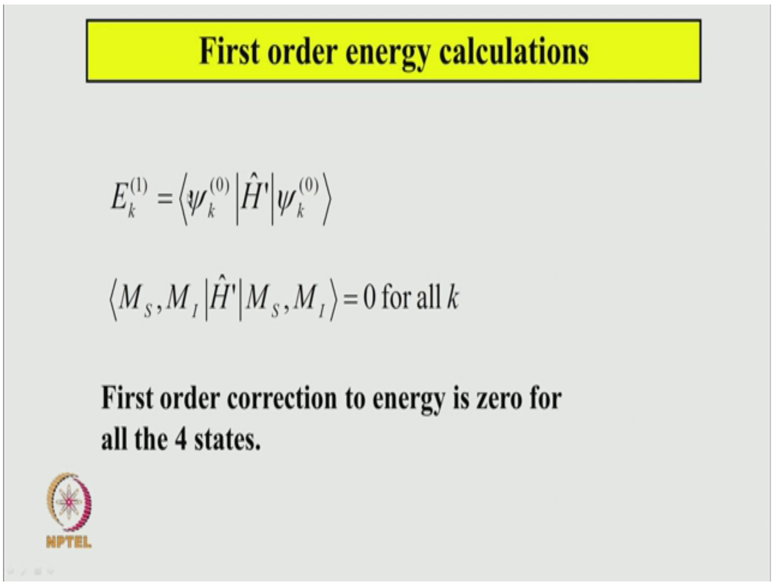

First order energy calculations

$$E_k^{(1)} = \langle \psi_k^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle$$

$$\langle M_S, M_I | \hat{H}' | M_S, M_I \rangle = 0 \text{ for all } k$$

First order correction to energy is zero for all the 4 states.

Then the first order calculation requires evaluation integral of this kind here this is the perturbation and these are the unperturbed wave function for this states here all these elements as 0 why because these are same for both of them.

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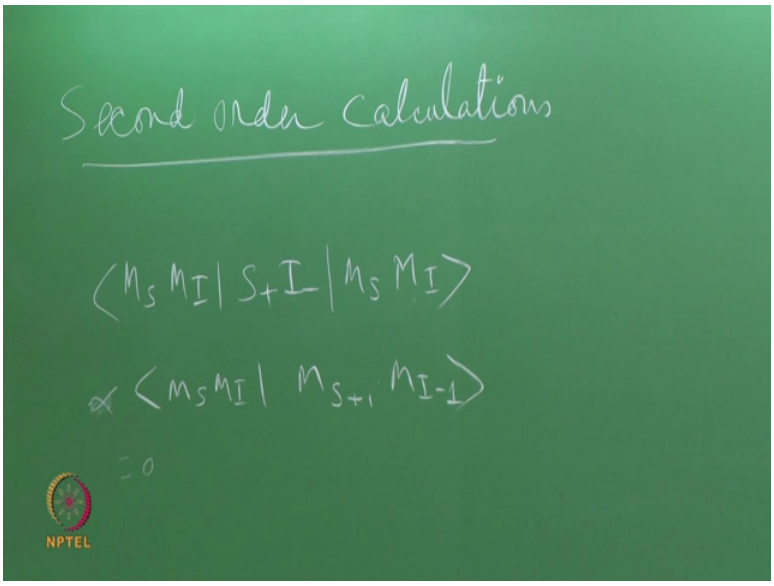

Second order Calculations

$\langle M_S M_I | S_+ I_- | M_S M_I \rangle$

$\propto \langle M_S M_I | M_{S+1} M_{I-1} \rangle$

$= 0$

Now, when this acts on this one it is going to decrease the value of M I by 1 unit, and when this acts on this one it is going to increase the value of M S by 1 unit. So, effectively this will give something, let us say M S M I times M S plus 1, M I minus 1. And because they are different because and the orthogonal is this will automatically give raise to 0. So, first order energy calculation is 0 for all the four states. So, these four states are also good wave functions up to first order energy also good up to first order.

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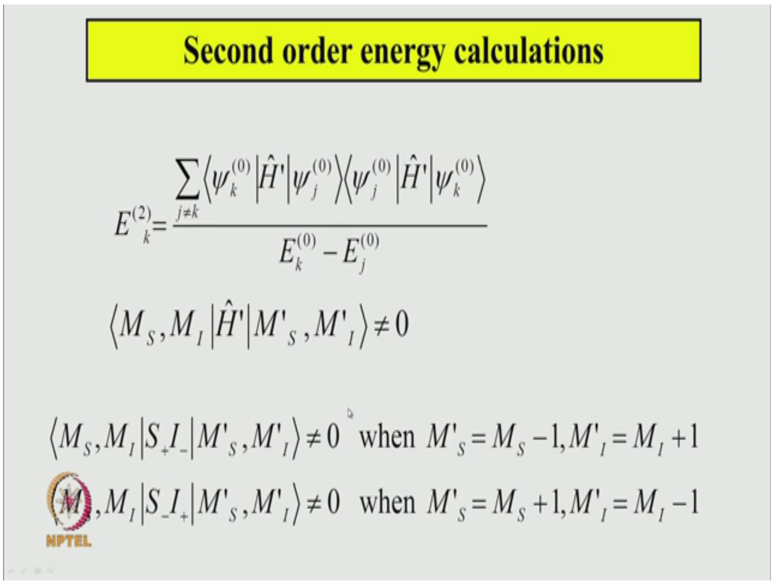

Second order energy calculations

$$E_k^{(2)} = \frac{\sum_{j\neq k} \langle \psi_k^{(0)} | \hat{H}' | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \hat{H}' | \psi_k^{(0)} \rangle}{E_k^{(0)} - E_j^{(0)}}$$

$$\langle M_S, M_I | \hat{H}' | M'_S, M'_I \rangle \neq 0$$

$\langle M_S, M_I | S_+ I_- | M'_S, M'_I \rangle \neq 0$ when $M'_S = M_S - 1, M'_I = M_I + 1$

$\langle M_S, M_I | S_- I_+ | M'_S, M'_I \rangle \neq 0$ when $M'_S = M_S + 1, M'_I = M_I - 1$

To do the second order calculation, this is the expression for the second order correction to energy here the k th state, k th is one of the four states they this energy involves this set of integral, here psi k is this k and then somewhere all possible other states which are there other than the k and this is difference of energy between the k and j state. So, for these to be non zero these integral must be non zero.

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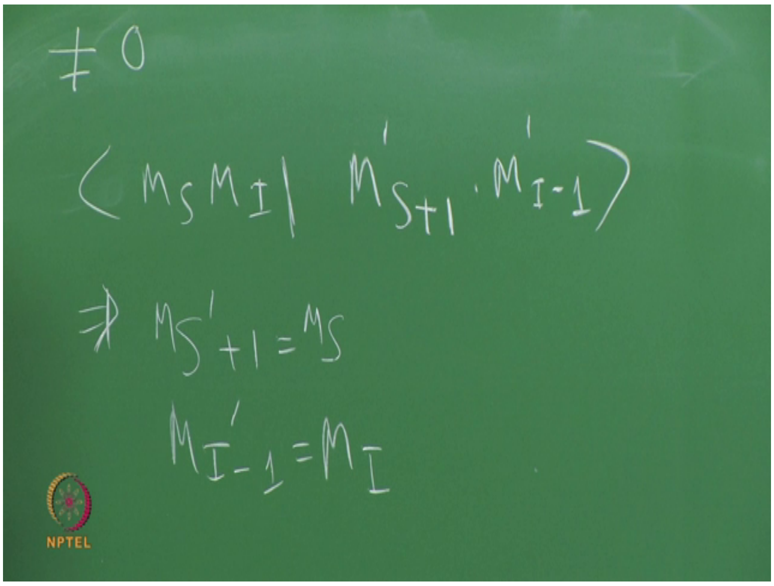

$\neq 0$

$\langle M_S M_I | M'_{S+1} \cdot M'_{I-1} \rangle$

$\Rightarrow M_S' + 1 = M_S$

$M_I' - 1 = M_I$

So, here again so if we put a prime here to indicate that they are different, these will be non zero when after raising this will be something like M prime S plus 1 and this will be

M prime minus 1, this lower seat where it is increases. So, for these to be non zero this must be same as this one. So, that is otherwise S prime plus 1 should be equal to S, M S prime plus 1 should be equal to M S. And M I prime minus 1 should be equal to M I, this kind must be satisfied for this integral to be non zero which is also written here. If you have the other one S minus I plus, then M S prime S must be equal to M S plus 1 and M prime I must be equal to M I minus 1.

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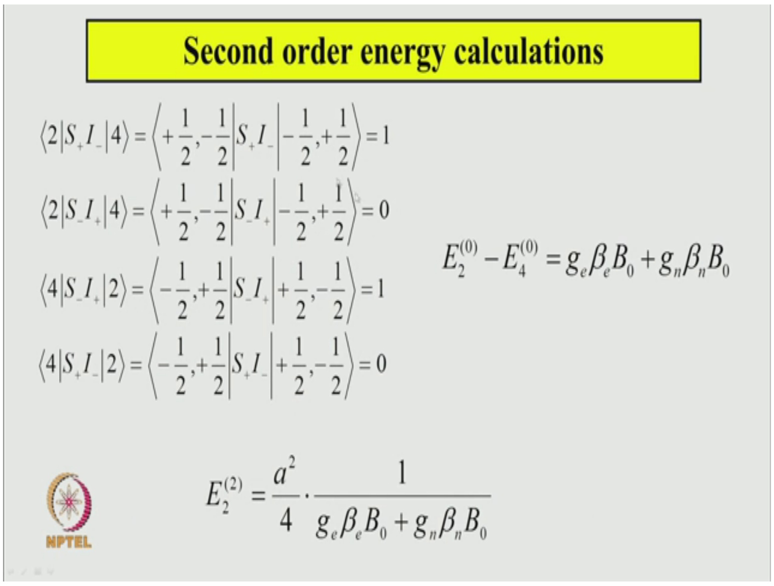

Second order energy calculations

$$\langle 2|S_+I_-|4\rangle = \left\langle +\frac{1}{2},-\frac{1}{2}\right|S_+I_-\left|-\frac{1}{2},+\frac{1}{2}\right\rangle = 1$$

$$\langle 2|S_-I_+|4\rangle = \left\langle +\frac{1}{2},-\frac{1}{2}\right|S_-I_+\left|-\frac{1}{2},+\frac{1}{2}\right\rangle = 0$$

$$\langle 4|S_-I_+|2\rangle = \left\langle -\frac{1}{2},+\frac{1}{2}\right|S_-I_+\left|+\frac{1}{2},-\frac{1}{2}\right\rangle = 1$$

$$\langle 4|S_+I_-|2\rangle = \left\langle -\frac{1}{2},+\frac{1}{2}\right|S_+I_-\left|+\frac{1}{2},-\frac{1}{2}\right\rangle = 0$$

$$E_2^{(0)} - E_4^{(0)} = g_e\beta_e B_0 + g_n\beta_n B_0$$

$$E_2^{(2)} = \frac{a^2}{4}\cdot\frac{1}{g_e\beta_e B_0 + g_n\beta_n B_0}$$

So, here not all four states will contribute to the second order calculation, state number two and four give raise to this sort of values. So, from this expression now this expression I can calculate the energy correction up to second order and that turns out to be this is the second state second order correction that turns out to be a square by 4 and this factor in the denominator this is the electron Zeeman term, this is the nuclear Zeeman term.

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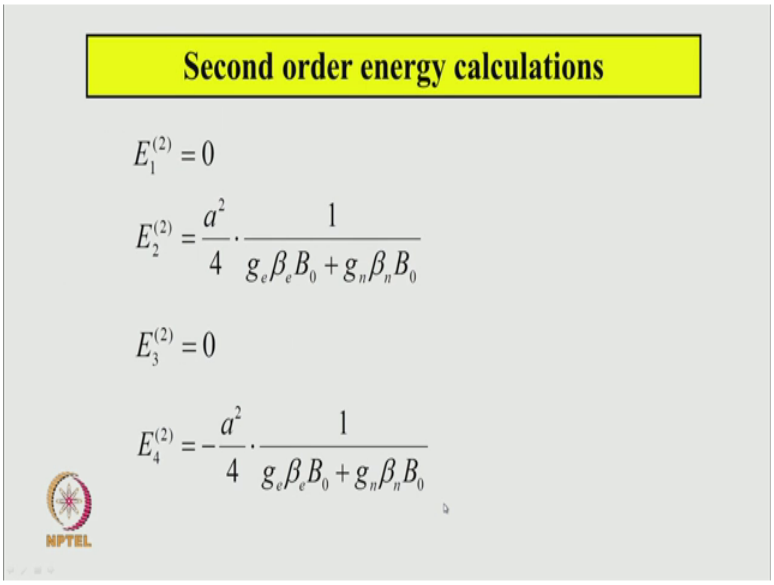

Second order energy calculations

$$E_1^{(2)} = 0$$

$$E_2^{(2)} = \frac{a^2}{4} \cdot \frac{1}{g_e\beta_e B_0 + g_n\beta_n B_0}$$

$$E_3^{(2)} = 0$$

$$E_4^{(2)} = -\frac{a^2}{4} \cdot \frac{1}{g_e\beta_e B_0 + g_n\beta_n B_0}$$

Vocalized-noise] So, that way I can calculate all the four energy corrections for the four states and you see that state 1 and 3 do not have any second order correction. An state 2 and 4 have, this as the plus value this is got minus value.

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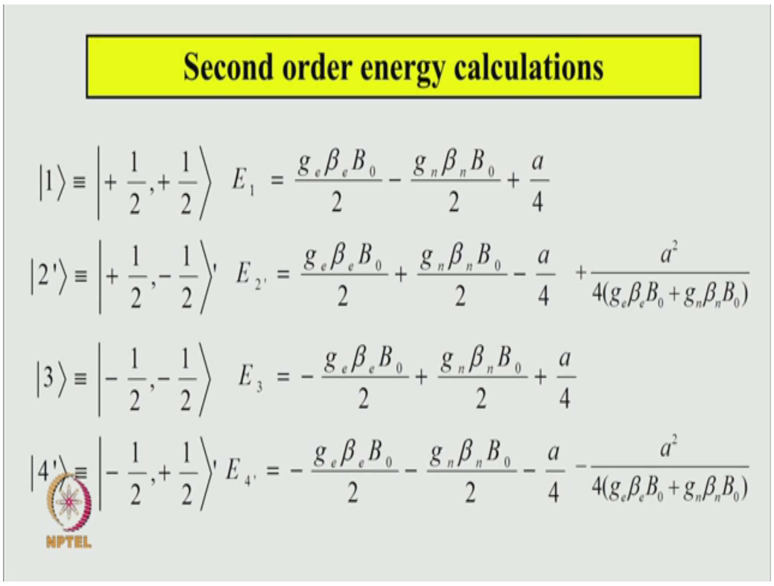

Second order energy calculations

$$|1\rangle \equiv \left|+\frac{1}{2},+\frac{1}{2}\right\rangle \quad E_1 = \frac{g_e\beta_e B_0}{2} - \frac{g_n\beta_n B_0}{2} + \frac{a}{4}$$

$$|2'\rangle \equiv \left|+\frac{1}{2},-\frac{1}{2}\right\rangle' \quad E_{2'} = \frac{g_e\beta_e B_0}{2} + \frac{g_n\beta_n B_0}{2} - \frac{a}{4} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}$$

$$|3\rangle \equiv \left|-\frac{1}{2},-\frac{1}{2}\right\rangle \quad E_3 = -\frac{g_e\beta_e B_0}{2} + \frac{g_n\beta_n B_0}{2} + \frac{a}{4}$$

$$|4'\rangle \equiv \left|-\frac{1}{2},+\frac{1}{2}\right\rangle' \quad E_{4'} = -\frac{g_e\beta_e B_0}{2} - \frac{g_n\beta_n B_0}{2} - \frac{a}{4} - \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}$$

So, with the second order calculation done I can now get the total energy up to second order. Here the state 1 does not change. So, it remains as it is similar state 3 also remains as it is, but 2 and 4 get mixed because of this cross term that we have found out here. So, this 2 and 4 I have put prime here to indicate that they are not pure state 2 or pure state 4, some admixtures is there. So, these are the energy of this 2 prime state or 4 prime state.

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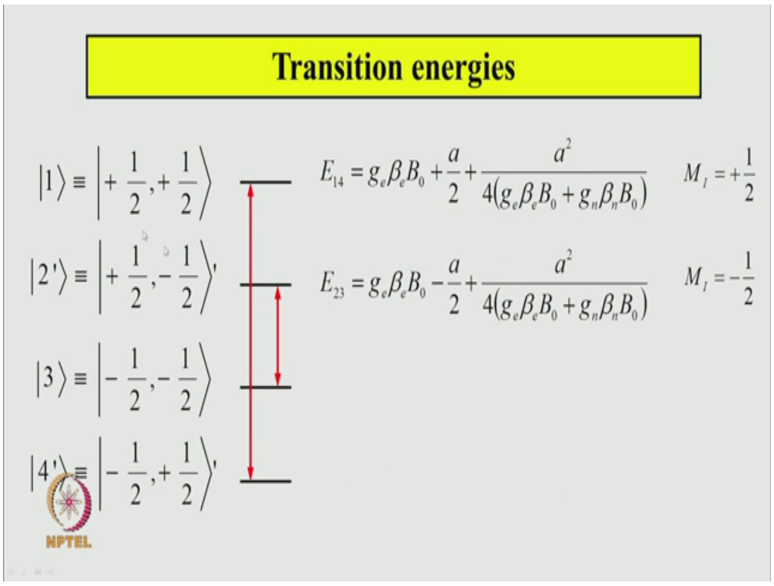

Transition energies

$|1\rangle \equiv \left|+\frac{1}{2},+\frac{1}{2}\right\rangle$

$|2'\rangle \equiv \left|+\frac{1}{2},-\frac{1}{2}\right\rangle'$

$|3\rangle \equiv \left|-\frac{1}{2},-\frac{1}{2}\right\rangle$

$|4'\rangle \equiv \left|-\frac{1}{2},+\frac{1}{2}\right\rangle'$

$E_{14} = g_e\beta_e B_0 + \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}$ $M_I = +\frac{1}{2}$

$E_{23} = g_e\beta_e B_0 - \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}$ $M_I = -\frac{1}{2}$

So, we found this 4 energy levels now we can find the transition energies, these are the transition energies were the M I does not change here also M I does not change, and this energy is given a for transition form state 1 to 4, and 2 to 3 this 2 prime to 3 this is essentially this 2 prime is very nearly equal to 2 and 4 prime is very nearly to 4.

So, this is the energy that is get here this corresponds to M I equal to plus half this corresponds to M I equal to minus half. What we see here this should look familiar there if the second order correction was not applied, energy was this similarly energy was this. So, this is same as the first order splitting the energy level is split equally by plus a by 2 minus a by 2, but now when we include the second order correction both the transition energy have increased by this amount. So, that is something different.

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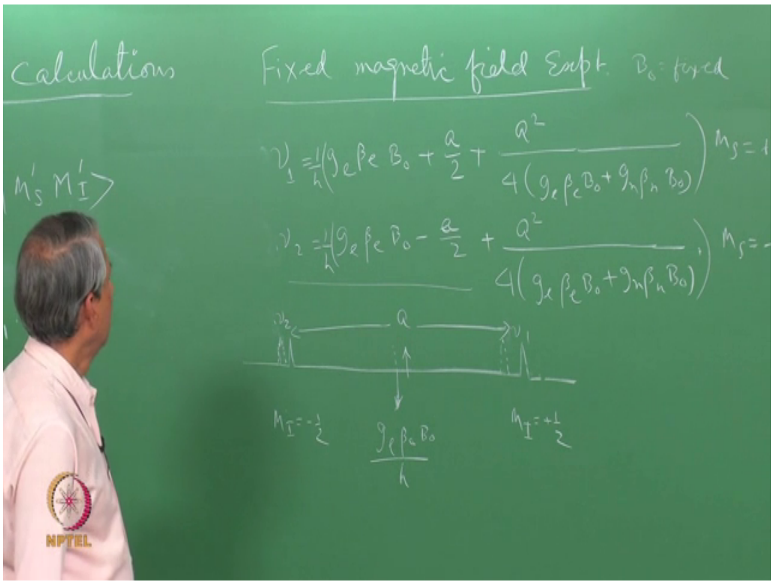

Calculations

Fixed magnetic field Expt. B_0: fixed

$M_s' M_I'\rangle$

$$\nu_1 = \frac{1}{h}\left(g_e\beta_e B_0 + \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}\right) M_S =$$

$$\nu_2 = \frac{1}{h}\left(g_e\beta_e B_0 - \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)}\right) M_S =$$

Now we do the experiment now, let us say fixed magnetic field experiment and after as we will see the fixed micro frequency experiment and see how the spectrum looks like. In this condition the magnetic field is kept fixed then the frequency required to cause the transition for the first one we say this will be given as, this would be the first transition where M S is equal to plus half and second one similar corresponds to this cause M S equal to minus half.

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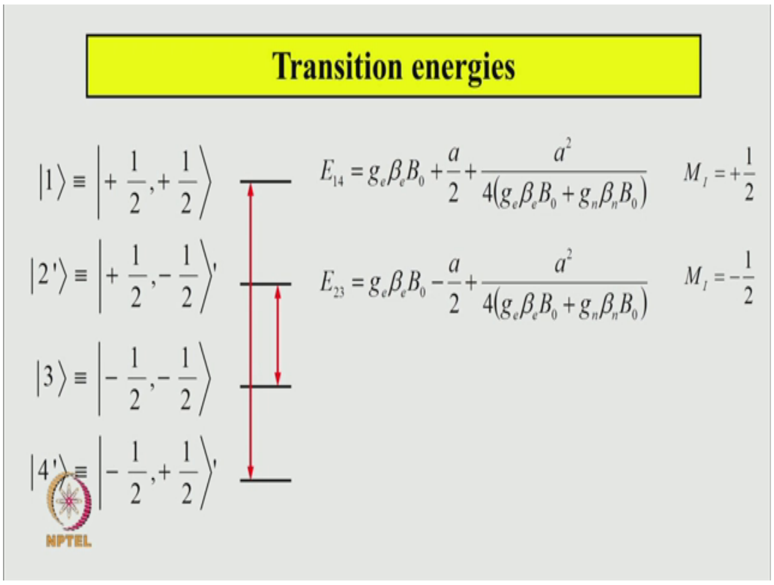

Transition energies

$|1\rangle \equiv \left|+\frac{1}{2},+\frac{1}{2}\right\rangle$

$|2'\rangle \equiv \left|+\frac{1}{2},-\frac{1}{2}\right\rangle'$

$|3\rangle \equiv \left|-\frac{1}{2},-\frac{1}{2}\right\rangle$

$|4'\rangle \equiv \left|-\frac{1}{2},+\frac{1}{2}\right\rangle'$

$$E_{14} = g_e\beta_e B_0 + \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)} \qquad M_I = +\frac{1}{2}$$

$$E_{23} = g_e\beta_e B_0 - \frac{a}{2} + \frac{a^2}{4(g_e\beta_e B_0 + g_n\beta_n B_0)} \qquad M_I = -\frac{1}{2}$$

So, this spectrum will look like some like this way, this B 0 is kept constant fixed. So, this frequency is higher than this one. So, this energies a higher for this lower for this one with come in minus sign. So, together the particular frequency now, I divide this whole thing by 1 by h, similarly divide this by 1 by h. So, this gives me that is a nu 1 and nu 2. So this corresponds to M I equal to plus half this corresponds to M I equal to minus half.

Now, where is this centre of this now if this was absent the centre would be just average of this and this. So, some where here. So, this would be g e beta e B 0 by h, now the way this obvious now these lines are shifted with respect to centre by this amount. So, again if this was absent I would got the first total spectrum, and then so the spectra would have been dotted line here; also shifted that some if so, this way the spectrum model appeared now both the lines are shifted to the higher frequencies.

So, the centre of the spectrum has now moved towards higher side. So, the actual g value is here, but the wait appear center of the spectrum now appear somewhere here now. So, this is the important outcome of this analysis is that if one blindly looks at the middle of the spectrum and then calculate the g value for this magnetic field the answer will be wrong, the actual g value is here both the lines have shifted up and that can be understood from this sort of analysis now.

The next point is that the difference between these and these if we take the weight appears which different between these and these, then this of course cancels so this gap is still equal to a, which is the hyperfine coupling constant. So, this experiment gives the value of the hyperfine coupling constant though it will not give you the g value correctly unless you account for this correction and find out exactly the correct place of the magnetic field to calculate the g value.

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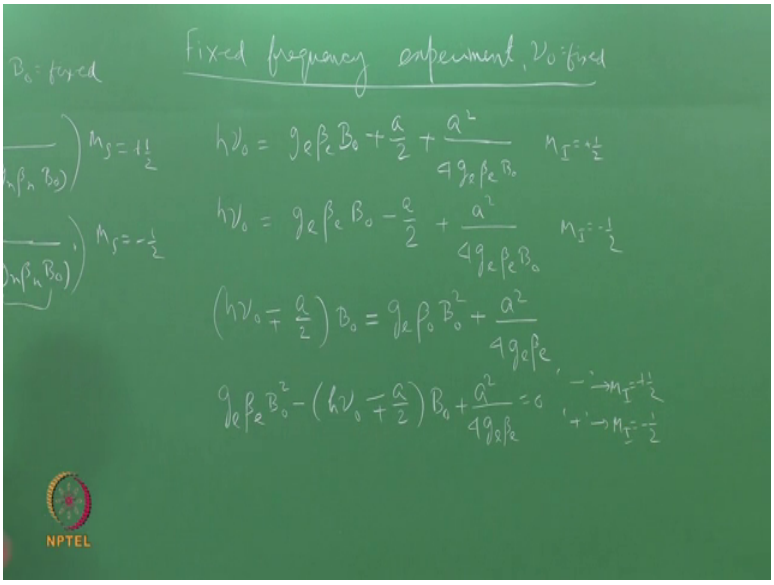

B_0 : fixed

$m_S = +\frac{1}{2}$

$m_S = -\frac{1}{2}$

Fixed frequency experiment, ν_0 : fixed

$$h\nu_0 = g_e\beta_e B_0 + \frac{a}{2} + \frac{a^2}{4g_e\beta_e B_0} \quad m_I = +\frac{1}{2}$$

$$h\nu_0 = g_e\beta_e B_0 - \frac{a}{2} + \frac{a^2}{4g_e\beta_e B_0} \quad m_I = -\frac{1}{2}$$

$$\left(h\nu_0 \mp \frac{a}{2}\right)B_0 = g_e\beta_0 B_0^2 + \frac{a^2}{4g_e\beta_e}$$

$$g_e\beta_e B_0^2 - \left(h\nu_0 \mp \frac{a}{2}\right)B_0 + \frac{a^2}{4g_e\beta_e} = 0$$

'−' → $m_I = +\frac{1}{2}$

'+' → $m_I = -\frac{1}{2}$

Now let us do a fixed frequency experiment, let us say nu 0 is kept fixed . So, here in this energy expression I keep the frequency fixed on both sides and find out for which value of nu 0 I will get a transition. So, if nu 0 is a frequency is kept fixed then the energy is h nu 0 and that will be equal to, here let us ignore this a nuclear Zeeman term unnecessarily because just making the equation looking ugly, but one could return them one requires it, though it is safety ignored because this term is about 2000 times smaller than this one.

So, unless one is interested very precise measurement one might as well to ignore this. So, for the second transition, minus half so here this is constant I want to find out the value of B 0 for this line and also B 0 for this line, which the rearrange the equation then a that will look like this. So, the only difference is here plus minus I am combining these together to write one single equation, this could be further rearrange it to give raise to a quadratic equation and B 0.

Here again the minus sign corresponds to M I equal to plus half and plus sign corresponds to M I equal to minus half. So, this is the quadratic equation in B 0. So, I can solve it and get the value of the magnetic field for a given value of nu 0, now of course you know the quadratic equation gives two roots, here will one of them roots will give physically meaning full value realistic values.

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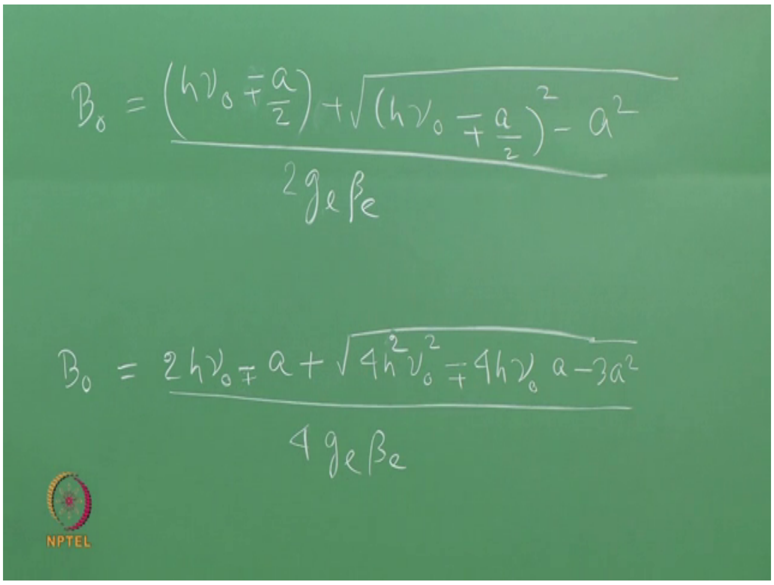

$$B_0 = \frac{\left(h\nu_0 \mp \frac{a}{2}\right) + \sqrt{\left(h\nu_0 \mp \frac{a}{2}\right)^2 - a^2}}{2g_e\beta_e}$$

$$B_0 = \frac{2h\nu_0 \mp a + \sqrt{4h^2\nu_0^2 \mp 4h\nu_0 a - 3a^2}}{4g_e\beta_e}$$

So, let me write that. Here I have taken only the positive square root of this one; this could be simplified by the rearranging the term and it will look like this. So, this appear corresponds to one root, this corresponds to the other root this two possible transition that I can get. So, this equation is exact. So, if I put the values now for a given frequency and let us say known value of the this hyperfine coupling constant we can get the two correspond magnetic fields.

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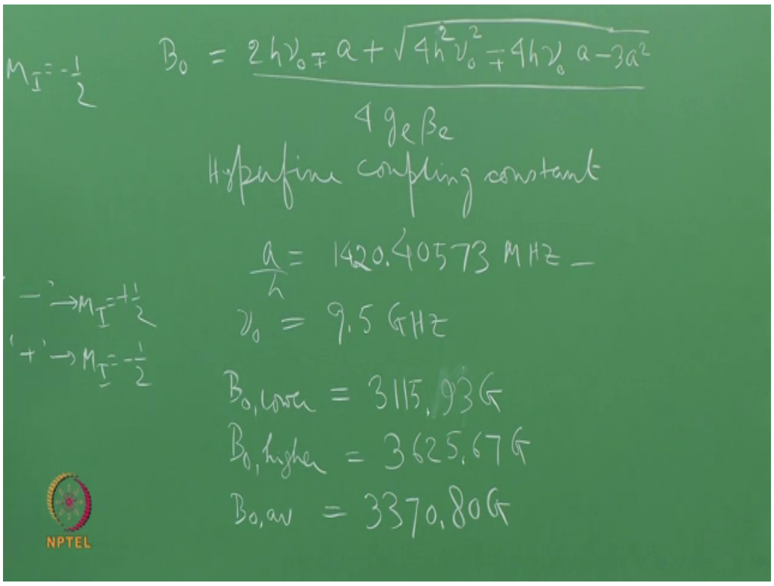

$M_I = -\frac{1}{2}$

$$B_0 = \frac{2h\nu_0 \mp a + \sqrt{4h^2\nu_0^2 \mp 4h\nu_0 a - 3a^2}}{4g_e\beta_e}$$

Hyperfine coupling constant

$\frac{a}{h} = 1420.40573$ MHz

$\nu_0 = 9.5$ GHz

'$-$' $\rightarrow M_I = +\frac{1}{2}$

'$+$' $\rightarrow M_I = -\frac{1}{2}$

$B_{0,\text{lower}} = 3115.93$ G

$B_{0,\text{higher}} = 3625.67$ G

$B_{0,\text{av}} = 3370.80$ G

So, since the values are known let us see what numbers we get the, a in frequency unit is 2 0 mega hertz frequency unit. So, in otherwise a by h is the frequency of this hyperfine coupling constant. So, if we put a let us say some typical frequency for the E P R experiment of the x band, say 9.5 giga hertz then we can calculate the corresponding magnetic field for the two transitions. They turn out to be B 0 lower line corresponds to 3115.93 gauss, and B 0 higher corresponds to 3625.67 gauss.

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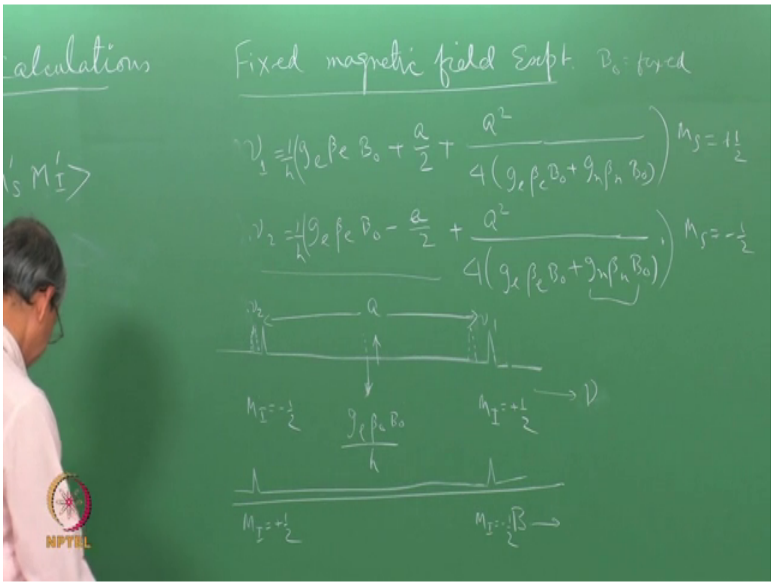

So, we get a spectrum which in a sense similar to this, but let me draw it here now, this was done is a function of frequency, now is the experiment is a function of magnetic field. So, get a spectrum will looks like this one is here now this now this corresponds to M I equal to plus half this corresponds to minus half, now where will be the g value. So, if we simply take them average of these two positions and B average B 0 is equal average that turns out to be 3380 gauss, but this is see this is not the resonance position for the g value, because both the lines are now move towards the lower side.

So, here knowing that for this, I forgot to mention that g value for this is given as 22 yeah with this g value one can calculate the magnetic field. So, that g value will correspond to this magnetic field which is this is the value that will calculate come out to be if you use this micro frequency and this g value that is a way suppose to be. So, you see the difference now, the average value is lower than the place for at which I must calculate the g value. So, here in other words here the lines are shifted towards the higher frequency, here the actual g value would be somewhere, let us say here this lines both of them have gone down words.

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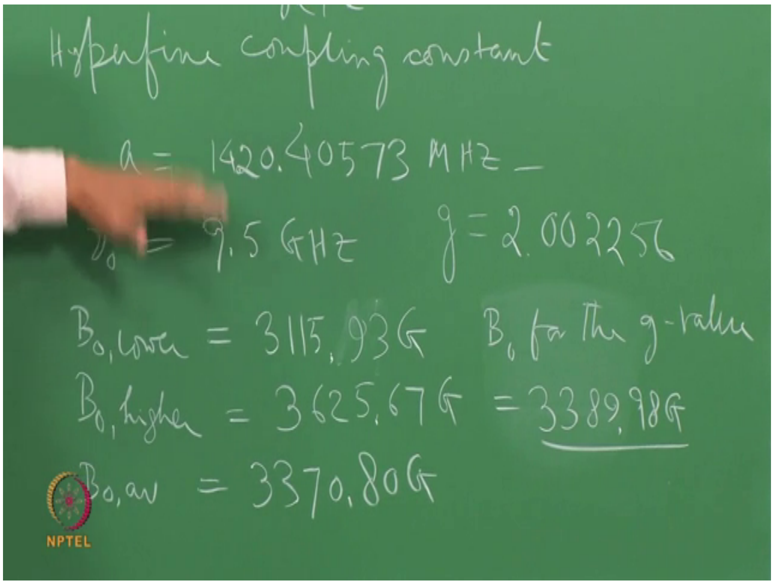

Hyperfine coupling constant

$a = 1420.40573\ \mathrm{MHz}$

$\nu_0 = 9.5\ \mathrm{GHz}$ $g = 2.002256$

$B_{0,\mathrm{lower}} = 3115.93\ \mathrm{G}$ B_0 for the g-value

$B_{0,\mathrm{higher}} = 3625.67\ \mathrm{G}$ $= \underline{3389.98\ \mathrm{G}}$

$B_{0,\mathrm{av}} = 3370.80\ \mathrm{G}$

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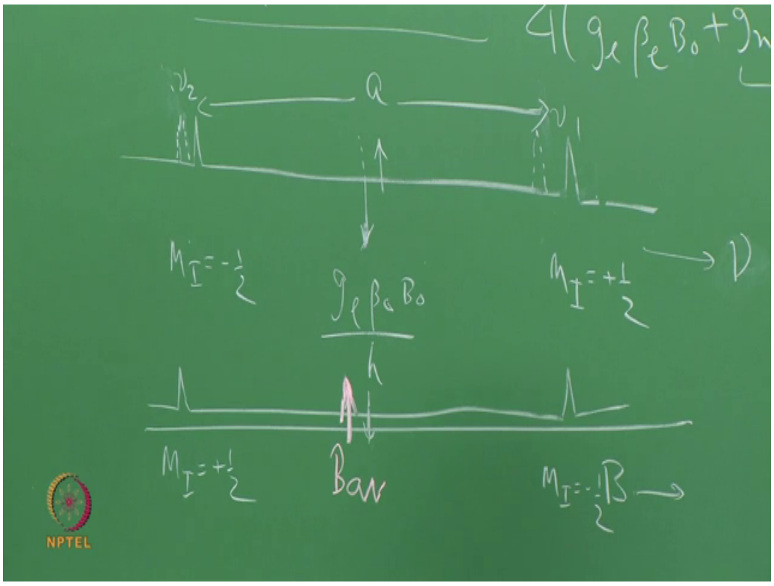

So, if it is the average value of this average may be here B average. So, if you calculate the g value at this at the centre of this thing. I will again get higher g value the true g value is somewhere here both the lines got shifted down words. Now to see a little more about this complicated equation let us start a simple way little bit by taking the approximate value of this square root because here this numbers come out, but they do not quite through much light in what is going on inside this one.

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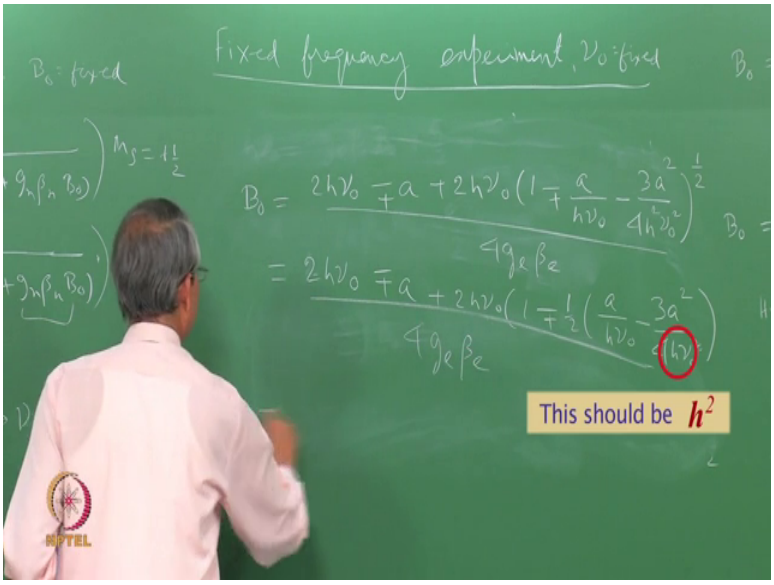

So, just simplify it such that we understand at least qualitatively what we saying here is correct. So, this one I can to, I can take this common and then write this way square root here. So, then as a the approximate approximation of this square root I can write it in this fashion. So, there is bottom is 4 g e b e. So, half and further simplification can give raise to this expression which I am writing straight away.

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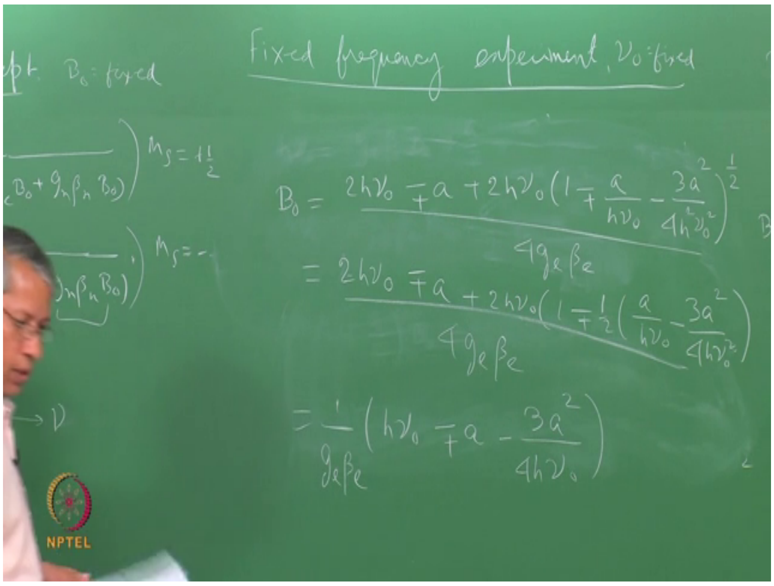

So, here now it is shows that the magnetic field that appears here with respect to this h nu 0 by g beta I that true centre of the spectrum and from there minus a and plus a that is the there is the splitting, but both of them now have gone towards the lower side for this much amount. So, that is what we are saying that the implication of this exact equation there, because this is approximation this cannot be treated for a exact calculation we must use these whenever it does is. So, all the two lines have gone down.

So, second point is that the wave again this difference of the two line position has such that they are not same as the hyperfine coupling constant. Hyperfine coupling constant this if you convert magnetic field this will turn out to be 86 gauss, now here if it is the difference of these two the difference turned out to be right side by side.

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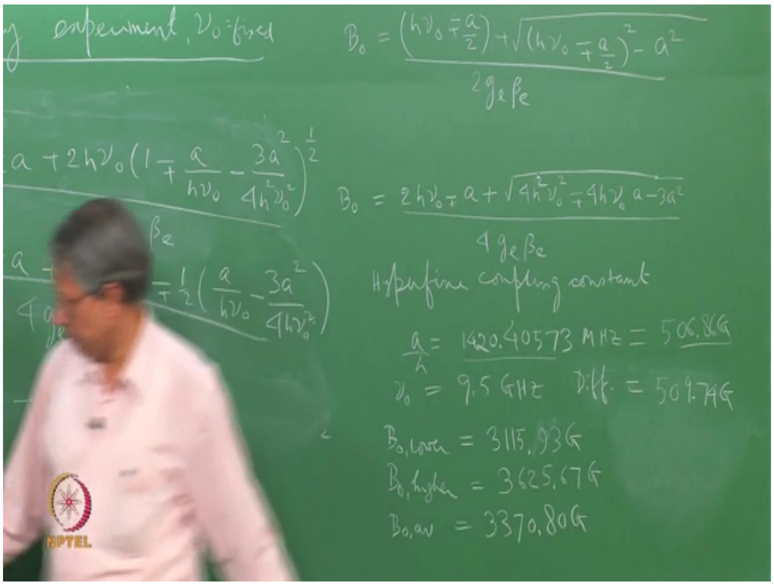

The difference a line position that turns out to be 74 gauss. So, this is the observed splitting in the spectrum given by this experiment when we do that the impairment experiment here. And this is the intrinsically the splitting because of the hyperfine interaction is 506 gauss, what we see here is 509 gauss.

So, this is where one makes the distinction between electron nuclear hyperfine coupling is the strength of interaction in energy unit either here or this one and this is the electron nuclear hyperfine splitting constant this one got this frequency unit, but this is a measured quantity that appears in spectrum in the form of splitting of lines. So, one must really mention what it what it is that is one is reporting. In the first order spectrum these two things do not make any difference they are the same, but once we apply second order correction this difference is possible and one can see that here it is definitely measurable quantity, this is the second important consequence of the second order calculation. First important consequence was that the g value will be absolutely wrong if we simply blindly take the center of the spectrum to with the correct place for calculating to the g value second one is this.

Now, this hydrogen atom the case is very special because this coupling constant is really large, that is no surprising because hydrogen atom the electron is actually in one as arbitral and that is the also the main and the principal requirement for form a contract interaction. So, this interaction is very strong and we get such large splitting, most of the E P R signal or getting molecules and typical hyperfine coupling constant that one sees, usually this is not of much significant a importance. So, one tends to ignore these, but there are cases other than hydrogen atom at this can become important. One is that there could be more than one nuclei couple to the electron and each of them contributes you know hyperfine coupling constant such that overall the effect is large.

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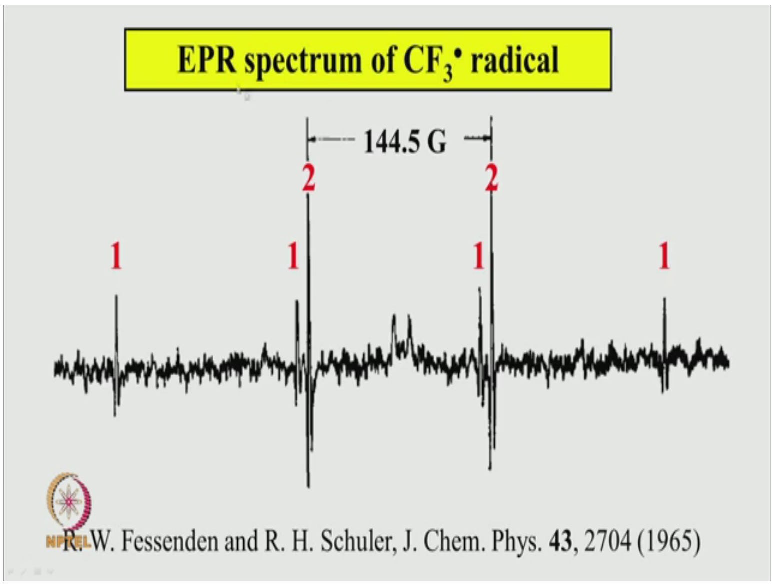

EPR spectrum of $CF_3^\bullet$ radical

R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **43**, 2704 (1965)

So, if I have set of equivalent nuclei they are couple together same simultaneous to the electron and then second order corrections might be necessary so here is an example, this E P R spectrum of the C F 3 radical. So, (Refer Time: 32:20) it has nuclear spin of half. So, one we expect that these three equivalent (Refer Time: 32:28) in should give a spectrum of this 1 is to 3 is to 3 is to 1, but what it gives is this that this what was suppose be the intensity 3 is now split into two lines, one is intensity of unit 1 this is 2 1 and 2. So, this line is split here also we are splitting constant is reasonably large.

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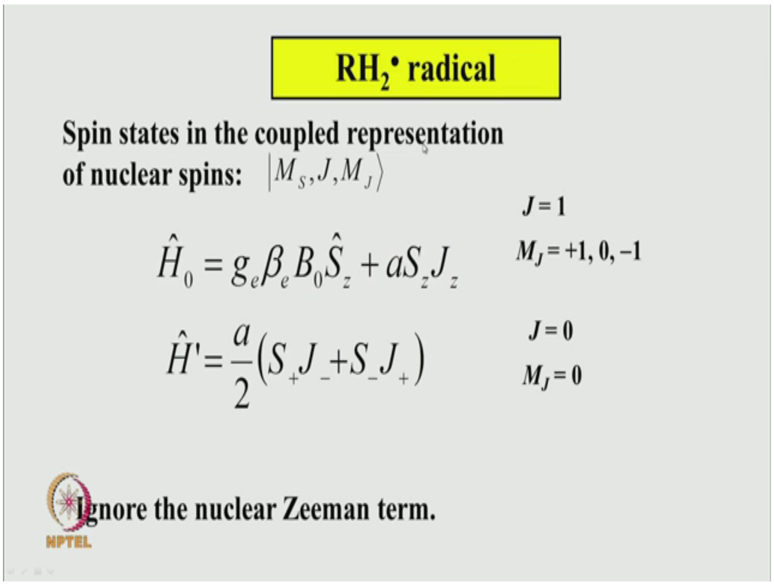

$RH_2^{\bullet}$ radical

Spin states in the coupled representation of nuclear spins: $|M_S, J, M_J\rangle$

$$\hat{H}_0 = g_e\beta_e B_0 \hat{S}_z + aS_z J_z$$

$$\hat{H}' = \frac{a}{2}\left(S_+ J_- + S_- J_+\right)$$

$J = 1$

$M_J = +1, 0, -1$

$J = 0$

$M_J = 0$

Ignore the nuclear Zeeman term.

So, to understand that let us take a simpler radical system somethingly RH 2 radical. So, 2 spin half system, which are equivalent and coupling to the electron. So, here we will write the Hamiltonian again this fashion were we coupled the first nuclear spin states to get a total nuclear angle of momentum and it is component and then that will couple to the electron spin that is the idea. So, here again for simplicity we ignore the nuclear Zeeman term without serious consequence any how that is very small. So, the hyperfine in term we know look like a S Z J Z, J is the component of the total nuclear spin quantum number. So, when there are two nuclear spin total J can be 1 or 0. So, these are corresponding components 1, 0 minus 1 this is for 0.

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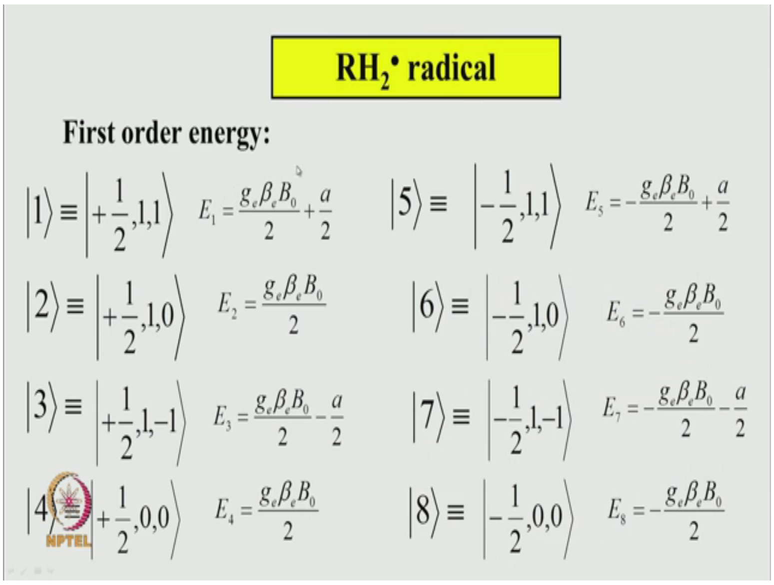

RH$_2^\bullet$ radical

First order energy:

$|1\rangle \equiv \left|+\frac{1}{2},1,1\right\rangle$ $E_1 = \frac{g_e\beta_e B_0}{2} + \frac{a}{2}$

$|2\rangle \equiv \left|+\frac{1}{2},1,0\right\rangle$ $E_2 = \frac{g_e\beta_e B_0}{2}$

$|3\rangle \equiv \left|+\frac{1}{2},1,-1\right\rangle$ $E_3 = \frac{g_e\beta_e B_0}{2} - \frac{a}{2}$

$|4\rangle \equiv \left|+\frac{1}{2},0,0\right\rangle$ $E_4 = \frac{g_e\beta_e B_0}{2}$

$|5\rangle \equiv \left|-\frac{1}{2},1,1\right\rangle$ $E_5 = -\frac{g_e\beta_e B_0}{2} + \frac{a}{2}$

$|6\rangle \equiv \left|-\frac{1}{2},1,0\right\rangle$ $E_6 = -\frac{g_e\beta_e B_0}{2}$

$|7\rangle \equiv \left|-\frac{1}{2},1,-1\right\rangle$ $E_7 = -\frac{g_e\beta_e B_0}{2} - \frac{a}{2}$

$|8\rangle \equiv \left|-\frac{1}{2},0,0\right\rangle$ $E_8 = -\frac{g_e\beta_e B_0}{2}$

So now we have 8 possible states they are represented by the electron spin component and nuclear total angle of momentum component J and M J. So, that we get 8 states plus half for electron and 1 0 minus 1 0 for the nuclear spin and similarly again for minus half component will electron I get on another state of 4.

Now, you follow similar type of calculation that have you done for this hydrogen atom exactly similar. So, first order energy calculation appears to be this same for all the 8 levels. So, first order spectrum is obtained by following this selection rule delta M J is 0 delta M is plus minus 1 and this give the spectrum is fashion 1 is to 2 is to 1 what we of course, expect for this type of radical. Now when we do the second order calculation these are the states which gives non zero value of the integral and the value is given here. And then the second order calculation energy also are in this fashion this state 2 3 5 and 6 they have non zero value of second order corrections to energy, and 2 and 3 are positive correction, and 5 and 6 are negative correction.

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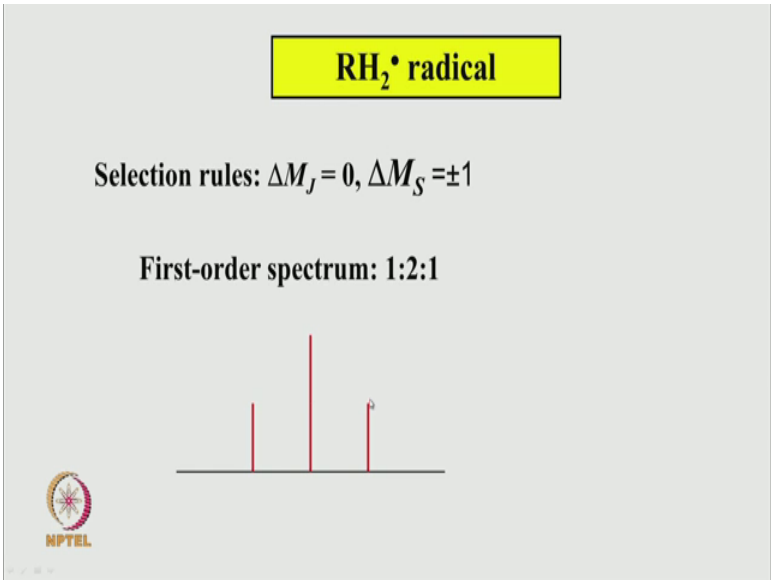

$RH_2^{\bullet}$ radical

Selection rules: $\Delta M_J = 0, \Delta M_S = \pm 1$

First-order spectrum: 1:2:1

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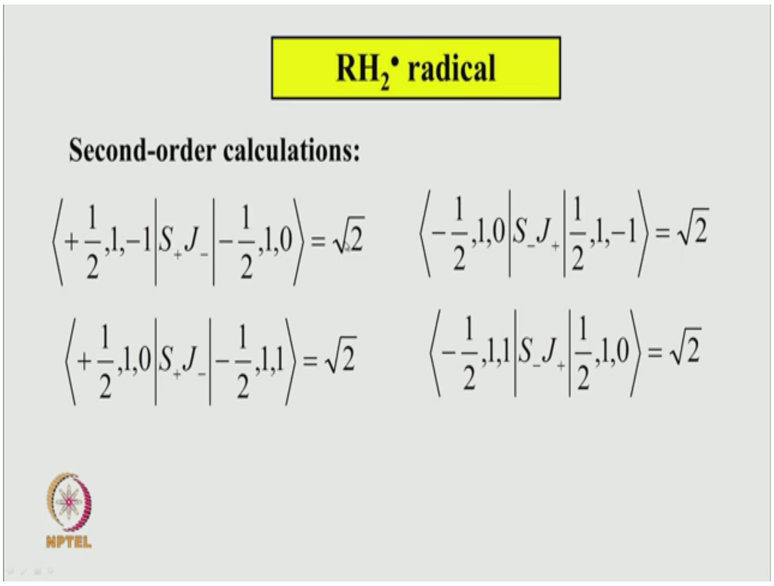

$RH_2^{\bullet}$ radical

Second-order calculations:

$$\left\langle +\frac{1}{2},1,-1 \middle| S_+J_- \middle| -\frac{1}{2},1,0 \right\rangle = \sqrt{2} \qquad \left\langle -\frac{1}{2},1,0 \middle| S_-J_+ \middle| \frac{1}{2},1,-1 \right\rangle = \sqrt{2}$$

$$\left\langle +\frac{1}{2},1,0 \middle| S_+J_- \middle| -\frac{1}{2},1,1 \right\rangle = \sqrt{2} \qquad \left\langle -\frac{1}{2},1,1 \middle| S_-J_+ \middle| \frac{1}{2},1,0 \right\rangle = \sqrt{2}$$

So, then is in that one can find out the position of that resonance magnetic field and that is the way it will look like. So, here the first order spectrum gave 1 is to 2 is to 1 line position. And then if you apply the second order corrections using this sort of energy then this three lines will shift towards lower magnetic field and this intensity 2 is split into 2. So, of 1 is to 1 and the spectrum will appear in this fashion. So, this of course depends on the value of the coupling constant and the magnetic field B 0. If B 0 is very large this correction is small and this will not be seen there will not only the coupling constant, but also at what magnetic field experiment is done.

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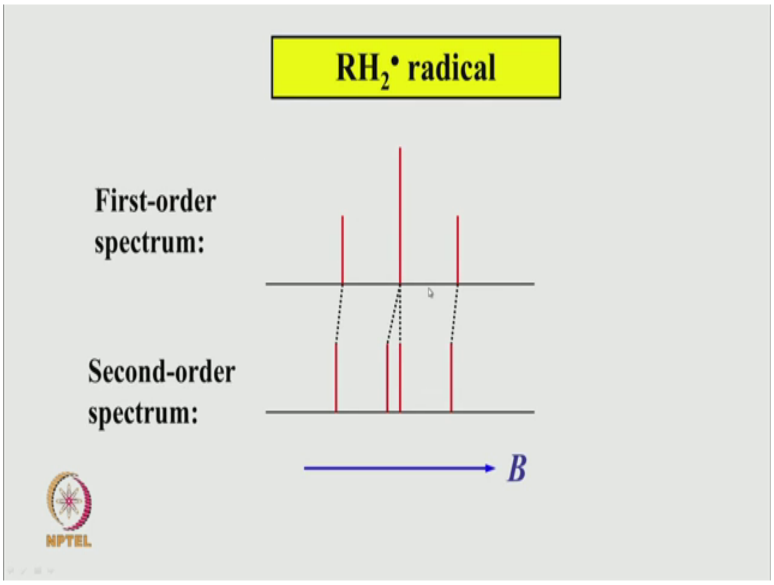

RH$_2^\bullet$ radical

First-order spectrum:

Second-order spectrum:

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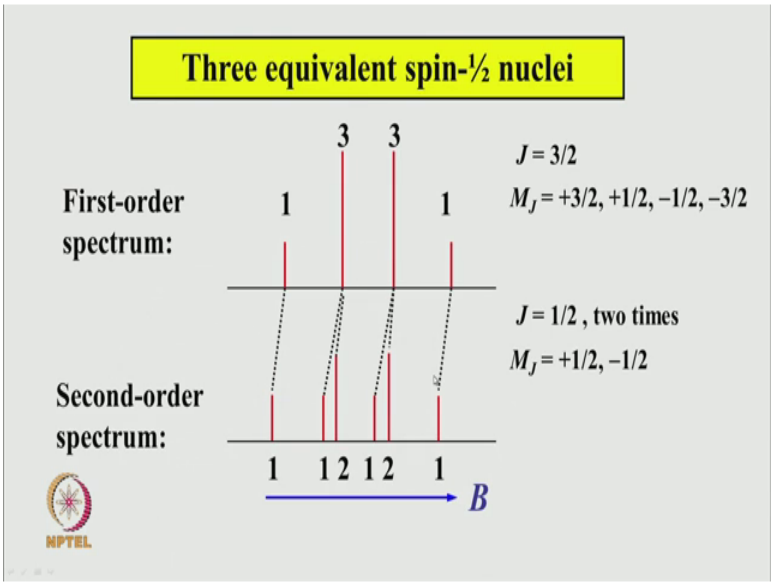

Three equivalent spin-½ nuclei

First-order spectrum:

Second-order spectrum:

$J = 3/2$

$M_J = +3/2, +1/2, -1/2, -3/2$

$J = 1/2$, two times

$M_J = +1/2, -1/2$

So, if one works at low frequency appear spectra meter this effect might become more prominent. The same way if one does the calculation for three equivalent spin half nuclei then the total nuclear spin will combine in this fashion to give raise to total J equal to 3 by 2 and total J equal to 1 by 2, it left 2 times each of them the M J values are given here. So exactly same calculation what we are done here, then we calculated and their energy will be split such way that all the lines will so shift towards the lower magnetic field and in particular these intensity of three units, will split into one intensity one unit one is another intensity of 2 units, all of the will shift down words it. So, here again the calculation of g value will requires special consideration because the center the spectrum does not correspond to the true magnetic field.

So, this is exactly what was what are here C F 3 radical. Now the example there I showed second order coupling and the splittings, it is possible that one may not see those splittings all the time nevertheless they are there if the hyperfine coupling constant is extremely large, or there are many equivalent nuclei which are couple together to produce a large splitting.

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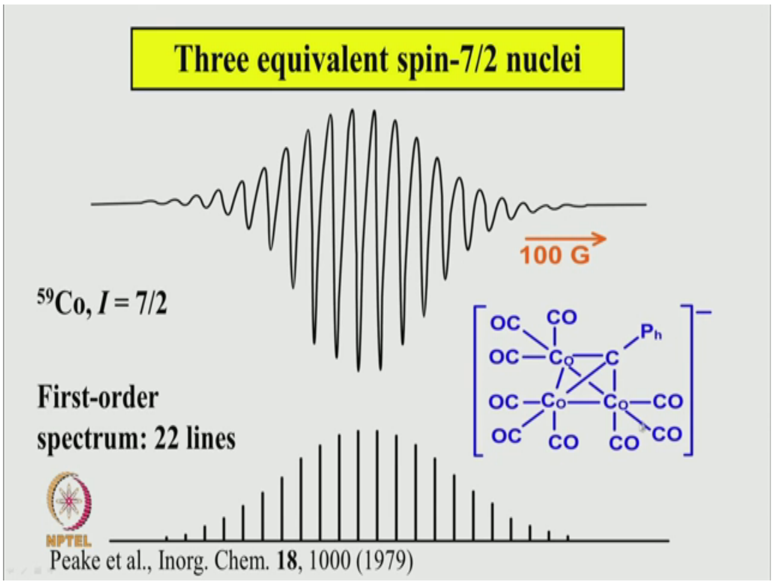

Three equivalent spin-7/2 nuclei

^{59}Co, *I* = 7/2

First-order spectrum: 22 lines

Peake et al., Inorg. Chem. **18**, 1000 (1979)

So, here is an example for this type of metal complex it is a tri nuclear cobalt complex arranging this fashion, all three cobalts are equivalent and they E P R spectrum is shown here. So, cobalt 59 I should have I equal to 7 by 2. So, that will give total I will be 21 by 2, either rows there will be 22 lines and if one compute the first line spectrum they will do intensity among this 22 lines will look like this.

So, in the since there are 22 lines though one may not see the extreme end, all the 20 lines are seen and they reasonably reproduce this relative intensities, but nevertheless look at this line shape is narrow here and brought there each of them narrow towards the bottom and brought at the top why is that whatever you discussed. So, for it is just cannot none of them explain this sort of line shape. So, here the explanation was that the second order coupling constants or second order splitting constants are actually playing a role here it is so happened that they are not resolved.

So, look at that the three cobalt nuclei each of them have 7 by 2 nuclear spin and splitting constant if you measure from the scale which is typically may be 25 30 gauss which is not very large, but because. So, many of them of there the effect can be noticeable. So, this calculation was done of second order and this the way the result is.

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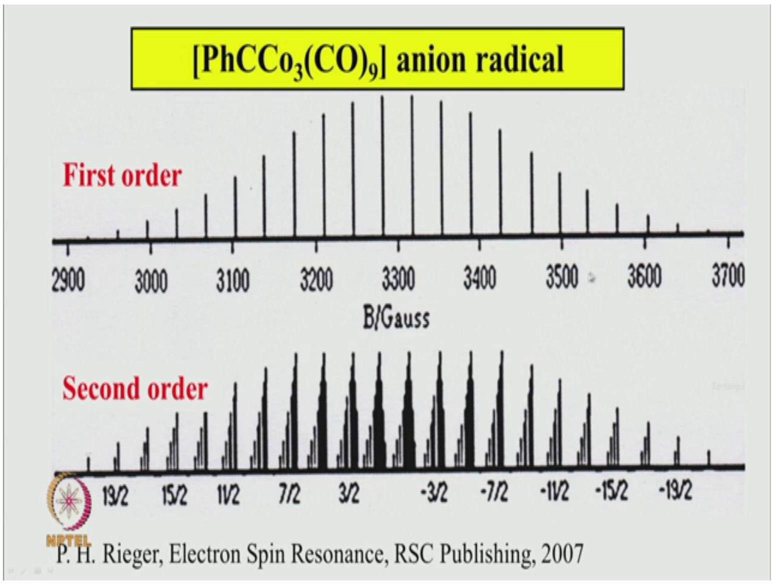

$[PhCCo_3(CO)_9]$ anion radical

P. H. Rieger, Electron Spin Resonance, RSC Publishing, 2007

So, the first order spectrum predicts they (Refer Time: 39:30) intensity of this sort of values. Now if you include second order calculation then many of this degenerate transitions become non degenerate now this is how the appear here bunch of them are appearing everywhere and all of them were shifted towards u r magnetic field

So, the reason behind this unusual line shape, we saw that second order interactions are important if the hyperfine coupling constant is large or there are more than one equivalent nuclei present there, which are also contributing to large over all splitting then these second order calculation unnecessary for an accurate measurement of the g values and hyperfine coupling constant, even to reproduce the unusual line shape of a spectrum were these splittings are not resolved that is all.