

# **ELEMENTS OF MODERN PHYSICS**

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## **Lec 11: Zeeman Effect**

So we'll talk about Zeeman effect. If you remember that we have talked about Stark effect which is splitting of the spectral lines in presence of a weak electric field. Now we'll talk about Zeeman effect which is we talk in a general sense I mean not related to hydrogen atom now but then we'll talk about it later. So as a plan goes that we'll talk about Zeeman effect in an external magnetic field and of course it's a weak magnetic field that we are going to talk about and then we'll talk about normal Zeeman effect and anomalous Zeeman effect. And then we'll talk about this intrinsic magnetic field. And in that connection, we'll actually talk about hydrogen atom and splitting of levels of the hydrogen atom. In that connection, we'll talk about spin orbit coupling as well. And we'll see that we need to find a suitable basis for expressing our operators. And so there's all this traditional wisdom of writing the wave functions of the hydrogen atom for calculating the you know the correction in energy due to these this electric or I mean due to this magnetic field will now no longer remain same so the  $\psi_{n l m}$  will no longer be used as a basis for writing this problem or this Hamiltonian and we need to find a new basis and this would bring us to the total angular momentum  $J$  which is still a good quantum number in presence of a spin orbit coupling. Okay, so Zeeman effect was of course seen by Zeeman in 1896.

### **Zeeman Effect (1896)**

The splitting of spectral lines when an atom is placed in a (weak) external magnetic field was initially looked at by Faraday, and then Observed in 1896 by Zeeman.

**Normal Zeeman Effect:** The Zeeman effect that occurs for the spectral lines resulting from a transition between the spin-singlet states ( $m_s = 0$ )  
Is called normal Zeeman effect.

**Anomalous Zeeman Effect:** It occurs when the total spin of the initial state or the final state, or both is non-zero.

So it was initially being looked at by Faraday and then it was observed by Zeeman in 1896. So there are two kinds of Zeeman effect that we talk about. One is called as the normal Zeeman effect and the other is anomalous Zeeman effect. And so, the normal Zeeman effect actually occurs when the transition between the spin singlet states arise. So, what we mean by spin singlet state is that the  $m_s$  value that is the azimuthal or the magnetic quantum number rather corresponding to the spin just like angular momentum we have  $L$  and we have these quantum numbers as  $l$  and  $m$ . Now we have to write  $l$  and  $m_l$  and this is precisely for the reason that we are also going to talk about spin because spin is the one or rather the degree of freedom that's going to couple with the external magnetic field. So now we'll have to talk about  $S$  and  $m_s$  and so this is the magnetic quantum number associated with the  $S$  operator and we rename this  $m$ , which we used earlier so far, which was associated with the angular momentum, the orbital angular momentum. Now we call it as  $m_l$ . So the Zeeman effect would arise when  $m_s$  is equal to zero. And this is called as a normal Zeeman effect. So the other one is anomalous Zeeman effect, which occurs when the total spin of the initial state or the final state or both is non-zero, which means that  $m_s$  is not equal to zero and  $m_s$  is finite here. And that's called as the anomalous Zeeman effect.

In general, there is no difference between the two. There's no fundamental difference between the two, but we'll discuss each one of them. So let us see what is a normal Zeeman effect and so that corresponds to  $S$  is equal to 0 and so the spin is equal to 0 that would tell you that  $J$  which is equal to  $L$  plus  $S$  which is the total angular momentum

which is the sum of the angular the  $L$  the orbital angular momentum and the spin angular momentum this is simply equal to  $L$ . So, the energy splitting that one gets is equal to  $\Delta E$  is minus  $\mu \cdot B$ . So, this is in presence of a magnetic field. So, this is minus  $\mu \cdot B$  and suppose if you have  $B$  in the  $Z$  direction, so  $B$  in  $Z$  direction, then the dot product will only involve  $\mu_z$  and  $b$ . And so this  $\mu_z$  is nothing but equal to minus  $m_l \frac{e \hbar}{2m}$  where make a distinction between  $m_l$  is the magnetic quantum number associated with the orbital quantum orbital angular momentum And this  $m$  when it's written alone means the mass. If it helps by writing  $m$  as mass of the electron, please do that  $E_L$  or something or simply write it as  $m$ . But make sure that you know that it in the denominator, it involves the mass of the electron.

So, this is equal to nothing but minus  $m_l \mu_B$ , that is the Bohr magneton. So, your  $\Delta E$  in terms of these quantities, we have  $m_l \frac{e \hbar}{2m}$  into  $B$  and this is nothing but  $m_l \mu_B$ . So this is the  $\Delta E$  that we have. That's a splitting between the energy levels, which are, you know, because of a weak magnetic field. This one has to, you know, make a mention that  $B$  is weak. And when I say weak, what it is weak compared to, it's weak compared to any spin orbit coupling that may be there, which is going to be the second part of the discussion that we make. So the change in energy or rather the splitting in energy in a magnetic field due to these in this normal Zeeman effect where there is no  $S$ , it's only  $L$  or the orbital angular momentum. Then it involves the orbital angular momentum magnetic quantum number and then the Bohr magneton and  $B$ . And so there are, you know,  $2l + 1$  energy levels. So  $2l + 1$  energy levels. Levels because  $m_l$  actually varies from minus  $l$  to plus  $l$  through  $0$ . So this is  $0$  and  $2l + 1$  for any value of  $l$ . So there are these  $2l + 1$  levels for a given value of  $m_l$ . So one can actually show the transition between these  $l$  equal to  $2$  and  $l$  equal to  $1$  levels.

## Normal Zeeman Effect

in presence of a magnetic field.  $\vec{S} = 0$ ,  $\vec{J} = \vec{L} + \vec{S} = \vec{L}$ . B is weak.

$\Delta E = -\vec{\mu} \cdot \vec{B} = -\mu_B B$  B in z-direction

$\mu_B = -m_l \frac{e\hbar}{2m} = -m_l \mu_B$

$\Delta E = m_l \frac{e\hbar}{2m} B = m_l \mu_B B$

$(2l+1)$  energy level  $\rightarrow m_l = -l \dots 0 \dots +l$   
 $\underbrace{\hspace{10em}}_{2l+1}$

Transition between  $l=2$  and  $l=1$ .

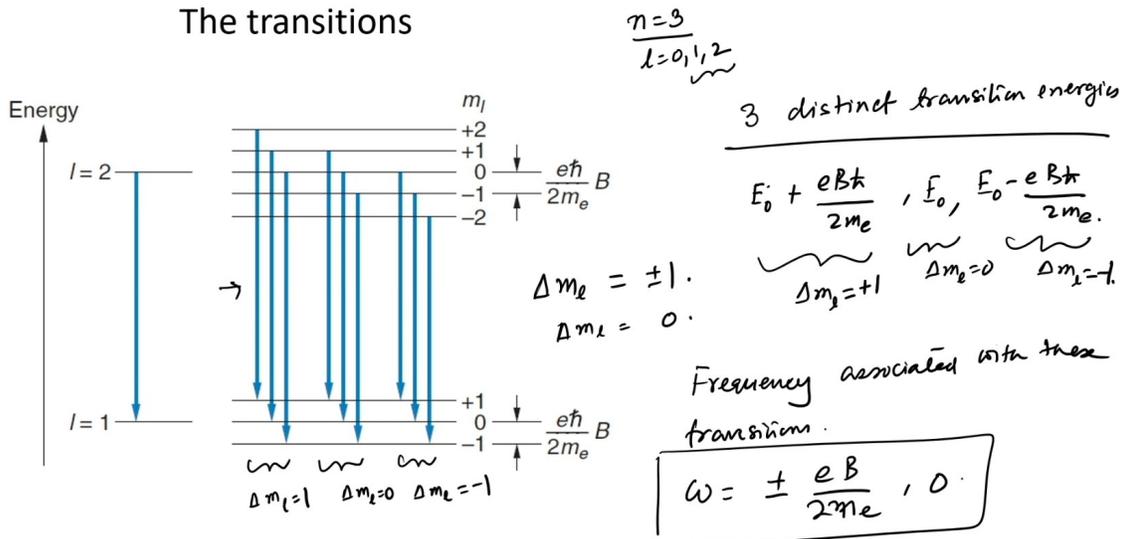
$m_l$ : magnetic quantum no.  
 $m$ : mass.  
 $= m_e$

So, we are just talking about 2 this azimuthal quantum number which is rather this orbital quantum number which is 1 and between these 1 values we are considering the transition and you see that this will cause a transition like this. So, this is m l. So, this is l equal to 2 which will have 5 levels because it is 2l plus 1 and this m l will have these values plus 2 plus 1 0 minus 1 minus 2 and each one would have sort of splitting that is given by e h cross by 2 m e. Here it's written explicitly the mass of the electron, so we can make it as e here and e here. So that would be this m l mu b b, which is this e h cross by 2 m into b. So that's the splitting that you see, and it's a uniform splitting for l equal to 1 and l equal to 2. And now these are these nine transitions that you see, which corresponds to, you know, delta m l is equal to plus minus one or the mod of delta m l equal to one. So what is meant is that you see from two it goes to one. 1 ml equal to 2 to ml equal to 1 that is this one and then from 1 to 0 and then 0 to minus 1 and then there are 1 to so there is this one is from 1 to 1 here and these are the ones for which delta ml is equal to 0.

So these are those ones because there is m l equal to plus 1 to plus 1, 0 to 0 and minus. So this is from minus 1 to minus 1 and so on. And then we have the other three. So there are nine lines that you see would arise in Zeeman effect. So if you do an experiment involving the l equal to 2 and l equal to 1 states, So suppose you talk about n equal to 3, that's the principal quantum number equal to 3. Then you have the L values that are allowed are 0, 1 and 2. And you are now looking at the transitions that could take place between these values. l equal to 1 and L equal to 2 which will have all these 9 transitions

that are possible. So, 3 with you know so, delta m l is equal to 1 and these would correspond to delta m l equal to minus 1 and so on.

So, this 0 to 1 here. So, let us call it as a minus 1 and these ones will correspond to delta m l equal to 0. So these nine transitions will be seen. And what you have is also that, you know, these the energy or the frequencies associated can be found out. So there are three distinct transition energies. And these three distinct transition energies are E0 plus, which is E0 is just your unperturbed energy, which is e B h cross by 2 m e E0. And this is E0 minus e B h cross by 2 m e E0. So, this would correspond to delta m l equal to plus 1, this corresponds to delta ML equal to 0 and this corresponds to delta m l equal to minus 1. So, what is the frequency associated with this transition? and the frequencies are nothing but this is omega equal to plus minus E b over 2 m e or 0.



So, these are the frequencies that are associated and these frequencies can be recorded in the spectroscopy measurements. So these are the transitions that one sees in normal Zeeman effect when you have S equal to 0, which means m s is equal to 0, which means J is purely equal to l And we are characterizing the states by l and m l. So the anomalous Zeeman effect, this occurs, as I said, that when the total spin is finite. So total spin corresponding to the initial state or the final state or both, they are finite. And so here, of course, your S is not equal to zero. So J is equal to L plus S will have to be now taken here. and both are finite. So, the total magnetic moment that comes here is the following mu is equal to minus g l mu B L by h cross minus g s mu B s over h cross. And here, of

course, we have  $g_l$  equal to 1. And  $g_s$  equal to 2. This is pretty close to 2. And then the total magnetic moment takes the form minus  $\mu_B$  over  $\hbar$  cross. And it's  $L$  plus  $2S$ .

This is also true for, you know, if you put  $s$  equal to 0, you can get this normal Zeeman effect. And what we can see is that we can draw a vector diagram like this. This shows these  $L$ . This is that vector inside, which is by the blue color, which is here. And then you have a  $S$  vector, which is here. And the vector sum of these two vectors is the vector  $J$ . So you can put a vector sign if you like. And then this is the magnetic moment associated with the orbital angular momentum.

This is the magnetic moment associated with the spin angular momentum. And this is that  $\mu$ , which is the vector sum of  $\mu_L$  and  $\mu_S$ , which is written here. So, in this case, you know, this  $\Delta E$ , that is the splitting between the energy levels for this spin, where the spin is, you know, finite of these initial and final states, I mean, either the initial state or the final state or that of both. Now, we have to use the quantum number corresponding to  $J$ . So, this is equal to  $g m_j e \hbar$  cross  $B$  divided by  $2 m_e$ . And this is nothing but equal to  $g m_j$  and  $\mu_B$ . So  $\mu_B$  is the Bohr magneton, which is  $e \hbar$  cross by  $2 m_e$ . And so  $g$  is called as a Landé  $g$ -factor.

and which has a form which is equal to  $g$  equal to, you know,  $1 + j(j+1) + s(s+1) - l(l+1)$  divided by  $2j(j+1)$ . That's the Landé  $g$ -factor. So, one can take an example of this doublet—the sodium doublet line splitting between these. So, this example could be sodium doublet lines involving  $2P_{1/2}$ . So that's  $L$  equal to 1 and  $2P_{1/2}$  thing.

### Anomalous Zeeman Effect

$$\vec{J} = \vec{L} + \vec{S}$$

Total magnetic moment

$$\vec{\mu} = -g_l \mu_B \frac{\vec{L}}{\hbar} - g_s \mu_B \frac{\vec{S}}{\hbar}$$

$$g_l = 1, g_s = 2$$

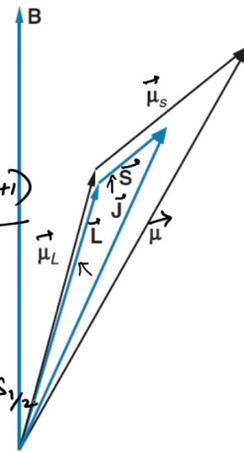
$$\vec{\mu} = -\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S})$$

$$\Delta E = g m_j \left( \frac{e \hbar B}{2 m_e} \right)$$

$$= g m_j \mu_B B$$

$g$ : Landé  $g$  factor.

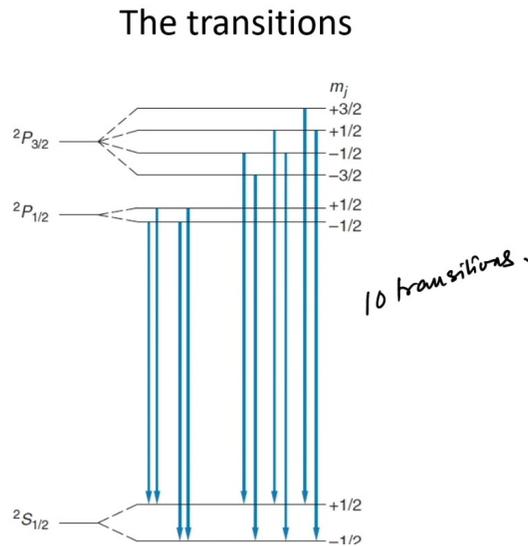
$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$



Example Na - doublet lines:

$2P_{1/2}, 2P_{3/2}$  and  $2S_{1/2}$

And then it's 2P 3 by 2 and 2S half. If you draw these lines, they look like this. These transitions that you see there, so you have a 2P 3 by 2, which has, of course, 5 and then 2P half as 2 and this 2S half that is there. So there are 10 transitions, which are shown by these vertical blue lines. And so there are 10 transitions in total.

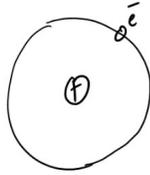


And in this particular case, we have these the energy splitting is given by this. So this is for large magnetic field. But anyway, that's not required because we're not talking about large magnetic field. So let's just keep it here itself that there are 10 transition lines and This is specifically for weak fields and something more interesting happens when you have the spin orbit coupling to be important, which is the case that we are going to discuss. And in presence of a spin orbit coupling, that acts like a magnetic field itself and will give rise to splitting even without an external magnetic field to be present.

And this spin orbit coupling is an important sort of parameter or is an important factor in deciding many of the material properties. So, we will do that and we will do that in connection with the hydrogen atom. So it's an intrinsic Zeeman effect that we are going to talk about, okay. So, you know, the basic structure of the hydrogen atom, which is the simplest one that we know that we have. a proton here and an electron here and the electron goes round in this circular orbit around the around the proton on the nucleus and you can make a simple assumption for the moment and it can be shown which I'm not going to show explicitly.

but can be shown that that approximation does not alter things in a big way. Let us just talk about the electrons moving in a rectilinear path. So there is a straight line motion of the electron instead of a circular motion. And in fact, because to take into account the circular motion, You just have a trivial factor which is sort of used here in this connection.

### Intrinsic Zeeman Effect: SO Coupling



At rest frame of the electron, there is a magnetic field to a charge (proton) in moving in its vicinity.

$$d\vec{B} = \frac{\mu_0}{4\pi} \frac{I d\vec{l} \times \vec{r}}{r^3}$$

$$I d\vec{l} = -e \vec{v}$$

$$\vec{B} = -\frac{\mu_0}{4\pi} \frac{e (\vec{v} \times \vec{r})}{r^3} \times \left( \frac{4\pi\epsilon_0}{4\pi\epsilon_0} \right) \frac{1}{\sqrt{\mu_0\epsilon_0}} = c.$$

$$\vec{E} = \frac{e \vec{r}}{4\pi\epsilon_0 r^3}$$

$$\begin{aligned} \vec{B} &= -\mu_0 \epsilon_0 \vec{v} \times \vec{E} \\ &= -\frac{1}{c^2} \vec{v} \times \vec{E} \end{aligned}$$

So we think that the electron is moving in a straight line which because of which it's like a wire of charge. And where charge is flowing, of course, where current is flowing rather. I mean, so because of that, there is a magnetic field that we produced at the location of the nucleus or at the location of the proton. So the proton will actually feel that magnetic field because of the electronic motion, because the electrons moving means their current flowing in the in the circuit or in the say along a wire. Now, if you think that in the rest frame of electron, the proton is actually moving in an orbit, and think that the proton is actually like moving in a rectilinear path, then at the position of the electron, where the electron is situated, there will be a magnetic field present there.

So, we are now looking at the rest frame of the electron. there is a magnetic field due to a charge which is nothing but coming from proton is moving in its vicinity. If that is acceptable to you. We have a way to calculate that magnetic field by a formula called as a Biot-Savart law in classical electromagnetism and which tells you that this elemental magnetic field due to a small section of the current that flows into the wire is given by mu

$\frac{0}{4\pi} I$  into  $dl$  cross  $r$ . divided by  $r$  cube, where  $r$  is the distance between the current flowing and where you want to calculate the magnetic field.

Here the current is flowing because of the proton and you want to calculate the electric field at the electron. So, this  $R$  is the distance between or difference in position between the electron and the proton. And you see what is  $dI$ ?  $dI$  is nothing but, so  $I dI$  is the current element that flows in the wire because of this motion of the proton which is a charged particle, positively charged particle. So this is that, you know, that current that flows in the small length element.

And because we are talking about a small length element and what's the corresponding magnetic field, we have written the elemental notation, that is  $dB$  here and  $dI$  here. Okay. So if you want to get the full magnetic field, that's not difficult. So this is equal to minus  $\mu_0$  by  $4\pi$ . And we have this charge. This is equal to  $v$  cross  $r$ , and this is divided by  $r$  cubed.

And what you do is that you can multiply and divide by a  $4\pi\epsilon_0$  and a  $4\pi\epsilon_0$ . Okay. And so why we have used a negative sign is that your ideal, by definition, is equal to minus  $qv$  because the current flowing and the direction of the when you multiply it by the charge, where  $q$  is the electronic charge. So  $E$  is equal to the corresponding electric field. You can find out from this relation that you have, you know, you can also find it out from Coulomb's law.

So this  $qr$  divided by  $4\pi\epsilon_0 r^3$ . Okay, so that's the electric field and that's the magnetic field. And what kind of relation do they have in between? So  $B$  is equal to minus  $\mu_0\epsilon_0$  and  $v$  cross  $E$ . And if you remember classical electromagnetism,  $\mu_0\epsilon_0 r$ .  $1$  by root over of that is equal to  $c$ . So, this is nothing but  $1$  over  $c$  squared.

So, this is  $1$  over  $c$  squared  $v$  cross  $E$ . So, that is the magnetic field that is generated at the location of the electron due to the motion of the proton. And the electric and the magnetic field, the corresponding magnetic fields are related by this equation, where  $c$  is the speed of light. All right. So, we can put this expression for  $B$  or rather  $E$ , the electric field equal to minus  $1$  by  $c$  squared. And so this is  $p$  over  $m$ , which is nothing but  $v$ . We are using the non-relativistic formula here.

So, this is equal to  $Z e$  over  $r^3$  and  $r$  vector. And where we have used  $q$  over  $4\pi\epsilon_0$  is equal to  $E$ . And so this gives you minus  $Z e$  divided by  $m c^2 r^3$ .

And  $\mathbf{p} \times \mathbf{r}$ , those are the vectors that you see here on the first line. And  $\mathbf{p} \times \mathbf{r}$  is reminding you that the angular momentum is the moment of the linear momentum, which is written as  $\mathbf{r} \times \mathbf{p}$ . Since it's  $\mathbf{p} \times \mathbf{r}$ , we'll get a minus sign. So, put together, we'll have  $-\mathbf{r}$ .

Writing this magnetic field in terms of the angular momentum of the electron is an important thing. In fact, this  $m$  is really the electronic mass that we are talking about, and this is  $l$ . So, this is an important relation for us that the magnetic field that is produced at the location of the electron, where the electron is located, situated—now we are talking about the rest frame of the electron. So, the electron is actually at rest in its rest frame or in its own frame. So, that magnetic field that is generated can be written in terms of

$\frac{m c^2}{r^3} l$  and this result is important because the spin of the electron which is  $s$  is going to couple with this  $\mathbf{b}$  and giving rise to a  $\mathbf{l} \cdot \mathbf{s}$  coupling. So let us we will use that as a perturbation term and do a perturbation theory that we have learned so far. So we have a perturbation term. Let us call that as, you know, you can call it anything, but let us call it as  $H'$  with a  $Z$ .  $Z$  means it is pertaining to the Zeeman term. So this is  $-\mu_B B$ .

That is the magnetic moment corresponding to the spin quantum number. So, it is  $\mu_B$  dot  $\mathbf{b}$  and this we have discussed just a while back that this is  $-\frac{g_s e \hbar}{2m} \mathbf{s}$  and  $\mathbf{s}$  vector and  $g_s$  is almost equal to 2 and this is called as this gyromagnetic factor and we can use this  $H'$  to be equal to, you know,  $\frac{e \hbar^2}{2m} \frac{Z}{r^3} \mathbf{l} \cdot \mathbf{s}$ , okay. So, this is  $\mu_B B$ . Sorry about that. So, this is actually  $\mu_B B$ . So, it is  $\mathbf{S} \cdot \mathbf{L}$ . And this is our a perturbation term and we have to do a perturbation theory using the hydrogen atom the states of the hydrogen atom.

$$\vec{B} = -\frac{1}{c^2} \left( \frac{\vec{p}}{m} \right) \times \frac{ze}{r^3} \vec{r} \quad \frac{ze}{4\pi\epsilon_0} = e \quad \vec{L} = \vec{r} \times \vec{p}$$

$$= -\frac{ze}{mc^2 r^3} (\vec{p} \times \vec{r}) = \frac{ze}{mc^2 r^3} \vec{L}$$

$$\vec{B} = \frac{ze}{mc^2 r^3} \vec{L}$$

Perturbation Term

$$H'_Z = -\vec{\mu}_s \cdot \vec{B}$$

$$\vec{\mu}_s = -g_s \left( \frac{e}{2m} \right) \vec{s} \quad g_s \approx 2$$

$$H'_Z = \frac{e g_s}{2m} \left( \frac{ze}{mc^2 r^3} \right) \vec{s} \cdot \vec{L}$$

But that poses a problem and we are going to, you know, talk about the problem in details. But this S dot L term makes some of the quantum numbers that we are familiar with in this notation of N L. Now, allow me to put a ML here because now there are going to be, you know, different kind of numbers. magnetic quantum numbers associated with L associated with S and maybe even associated with J. So this is no longer going to be a good basis to calculate the correction due to this intrinsic Zeeman term. And we'll have to learn how to negotiate that difficulty. All right. So if you, you know, absorb all the terms in some kind of this constant.

$$H'_Z = \alpha f(r) \vec{s} \cdot \vec{L}$$

$$\alpha \rightarrow ze, m_e, c, g_s.$$

$$f(r) \sim \frac{1}{r^3}.$$

$$s = \frac{1}{2}, m_s = +\frac{1}{2}, -\frac{1}{2}.$$

$$\chi_{s m_s} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

$$m_s = \frac{1}{2}, m_s = -\frac{1}{2}. \quad \hbar = 1.$$

$$\bar{\Psi} = \psi_{n l m_l} \otimes \chi_{s m_s}$$

$$= \psi_{n l m_l} \otimes \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$$

$$|n \ l \ m_l \ m_s\rangle \Rightarrow \text{Is it a good basis for us?}$$

So what we have is a  $Z$  prime, which is important for us, is nothing but some  $F$  of  $R$ . And we have  $L \cdot S$  or  $S \cdot L$ . It doesn't matter. I mean, you can write it because these are dot product and some other coefficient which involves all this mass, the  $g$  s, the Lande  $g$  factor and all that charge, nuclear charge and all that. I mean, the atomic number, speed of light. So,  $c$  has all of that included,  $Z e$ ,  $m_e$ , mass of electrons, which you have not written. I mean, we have written it only in terms of  $M$  and  $G$ ,  $S$ .

So, we absorb this and then of course, we know that  $f$  of  $r$  is actually  $1$  over  $r$  cube. So, this is important because when you calculate the correction, you have to consider the radial part of the hydrogenic wave function as well as the orbital, I mean the angular part as well. So, the angular part will have these kind of terms will be useful and for the radial part it's only this and the radial part is not going to have any effect on the  $l \cdot s$  term or  $s \cdot l$  term and similarly the angular part will have nothing to do with this  $f$  of  $r$  okay So, we are debating whether a  $\psi_{n l m m_l}$  now is going to be a good eigenfunction for this Zeeman term and now for that because now you have spin you have to take a product with this  $s \cdot s$  and where  $s$  is equal to half because we are talking about just electrons so  $s$  is equal to half.

So,  $M_S$ , which is a magnetic quantum number associated with the spin, this operator is equal to plus half and minus half. So, we will have a term which is and whose states are, so this  $\chi_{s m_s}$  is, can be written as a two component spinner having these values. So we can write this the wave function, the total wave function. Let's write it with a  $\psi$ .

And this is going to be like  $\psi_{n l m}$ .  $M_L$  and then we have you multiplied by  $1, 0$  spinner or a  $0, 1$  spinner depending on whether you have  $m_s$  equal to half or  $m_s$  equal to minus half. So, this is  $M_S$  equal to half. Well, when I say half, I actually put that  $\hbar$  cross is equal to  $1$ . So, remember that because  $\hbar$  cross sets the scale of the angular momentum.

So, this is  $M_S$  equal to minus half. So, we have written a wave function, but we are not sure whether the wave function is a valid wave function for this particular problem, but then at least we are able to include spin into this eigenfunction of the hydrogen atom and which now no longer becomes simply a function of  $r$  theta and phi, but it also acquires a  $2$  by  $2$  structure because of this spinner. So, we can now write this thing down in terms of  $n, l, m_l$ , and  $m_s$ . And instead of writing it as these bases, we can use this ket. This is the principal quantum number, orbital quantum number, magnetic quantum number corresponding to  $l$ , and magnetic quantum number corresponding to  $s$ . So, the question is that, is it a good basis for us?

OK. And if it's a good basis, then we don't have to worry about anything. We can simply use this basis in order to calculate this correction due to this term. But unfortunately, it turns out that it is not a good basis and we'll give you the reasons for that. So, first, let me explore point number 1.

So, let us call it 1 and explore that  $S \cdot L$  f of r, okay? F of R is  $1/R^3$ , whether that commutes with the  $L^2$  operator. Because while, you know, framing the solution for the hydrogen atom, we have, you know, fallen back on the  $L^2$  operator and the  $L_z$  operator and used their eigenfunctions to denote the  $\theta$   $\phi$  part of the, you know, the solution of the hydrogenic wave function. And so let's look at this thing and convince ourselves if this is a good operator because it has to commute. If it commutes, then they have the same set of eigenfunctions.

And so we have this as  $H Z' L^2$ . So this is nothing but  $H Z'$ . This is what we have written. OK, so a  $Z' L^2 - L^2 H Z'$ . And this is nothing but equal to  $L^2$ .

And we don't really need to worry about that f because L is purely a function of  $\theta$   $\phi$ . So wherever you want to write f, it doesn't matter. So f is only a function of r. I'm not even writing the radial dependence. So it's simply f for now. And it's  $L^2$  and  $S \cdot L$  minus f  $S \cdot L$  into  $L^2$ .

OK, so that's what we have to do. So it's basically the  $L^2$  is actually a vector operator. So this is  $L^2$ . All right. So what's the first term?

That's this term. So let's write down the first term. And the first term is nothing but this is equal to  $L^2 S \cdot L$ . This is equal to And we write it in terms of components. So this is like  $L_x L_x$ , or rather this is not  $L_x L_x$ .

This is  $L^2$ , which is  $L_x^2 + L_y^2 + L_z^2$ . And because it is a dot product, we can write it as  $S_i L_i$  sum over i, OK, where i is X, Y, and Z. All right. So this is  $L^2 S_i L_i$ . And because  $S_i$  commutes with  $L^2$ , they operate on different spaces because one is in the spin space, one is in the orbital space.

So we can write this down as  $F$  and sum over i  $S_i L_i^2 L_i$ . OK. And we can also commute these two. So we have done these two here and write this and  $L^2$ , of course, commutes with any of the  $L_x$ ,  $L_y$ , or  $L_z$ . So I can write this as  $F$  and  $S_i L_i L^2$ .

And so that's nothing but the second term. Which is here. So, this second term and the first term are the same, which means that this commutator is equal to 0, which means that this HZ prime commutes with L squared. That tells us something interesting: that L continues to be a good quantum number. All right.

$$\begin{aligned}
 & 1) \quad [\underbrace{\vec{s} \cdot \vec{L}}_{H_2}, \vec{L}^2] \\
 & H_2 \vec{L}^2 - \vec{L}^2 H_2 = \underbrace{f \vec{L}^2 \vec{s} \cdot \vec{L}} - f \vec{s} \cdot \vec{L} \vec{L}^2 \\
 & \text{1st term} \quad f \vec{L}^2 \vec{s} \cdot \vec{L} = f \sum_i \underbrace{L^2 s_i L_i} \\
 & = f \sum_i s_i \underbrace{L^2 L_i} = f \sum_i s_i L_i L^2 = \text{second term} \\
 & [H_2, \vec{L}^2] = 0 \quad \Rightarrow \quad L \text{ continues to be a good quantum no.} \\
 & \text{Share same eigenfunction}
 \end{aligned}$$

$i \in x, y, z.$

So they would share the same eigenfunction. All right. So that at least some property helps us because we need to know what the eigenfunction is or what the appropriate basis is for solving this problem. So, secondly, HZ prime does not connect—and I am going to prove that—states which have different L values. So it sort of keeps the different L values separate, and they do not couple, which means that if you're trying to calculate the matrix elements of this HZ prime operator between two L values, say L equal to two and L equal to one, then it's zero.

And how we can show that is the following. So let's write L square and L. We can write it as n, l, m, and all that. But what's important for us is just psi l. And this is l into l plus 1 h cross squared psi l. So be consistent and put h cross everywhere. You know, we have not put it in some places, but if you want, you can write it as h cross by 2 and minus h cross by 2, and so on and so forth.

OK, so here we have put it. And then now we want to calculate. So this has a definite L. It also has M and ML, and so on and so forth, but also an N, of course. But we are just interested in this L value. So now we take this psi L and calculate this commutator HZ

prime and these  $L$  square and these commutator, which is, you know, different  $L$ , which is  $L$  prime.

So, this is equal to  $\psi L H Z \text{ prime } L \text{ square } \psi L \text{ prime} - \psi L$  and you have  $L \text{ square } H Z \text{ prime } \psi L \text{ prime}$ . OK, so this is between these two states. So now this  $L \text{ square}$  will operate on this  $L \text{ prime}$  and will give me  $L \text{ prime} + 1$ . Continue writing that  $h \text{ cross square}$  and will give me  $\psi L$  and  $h z \text{ prime}$  and  $\psi L \text{ prime}$ . So  $L \text{ prime} + 1$ .

And this will give me so minus  $L$  into  $L + 1$  because this  $L \text{ square}$  is going to act on these bra  $\psi L$ . So this is  $H \text{ cross square}$  and you have a  $\psi L H Z \text{ prime}$  and there is a  $\psi L \text{ prime}$  and so on. So this can be simplified and one can write it as  $L$  into  $L + 1 L \text{ prime} + 1$ . You can take this  $h \text{ cross square}$  common as well. This minus  $l$  into  $l + 1$   $h \text{ cross square}$  and then you have a  $\psi l h z \text{ prime } \psi l \text{ prime}$ . It is equal to 0.

Now, why it is equal to 0 is that because this commute So we could have written down the 0 right from the beginning, but this is equal to 0. This commutator between the  $\psi L$  and  $\psi L \text{ prime}$  is equal to 0. Now that tells us that either, you know, this is equal to 0. or this is equal to 0.

So, this is equal to 0 when  $L$  is equal to  $L \text{ prime}$  and then this is not equal to 0 and when  $L$  is not equal to  $L \text{ prime}$  then this is not equal to 0 that the first square bracket is not equal to 0 but these expectation value of  $\psi Z \text{ prime}$  is equal to 0. So, it is either  $L$  equal to  $L \text{ prime}$  which makes this equation to be satisfied or you have this  $\psi L H Z \text{ prime } \psi L \text{ prime}$  is equal to 0. So, that tells you that  $H Z \text{ prime}$  does not connect the  $L$  quantum numbers, different  $L$  quantum numbers and that is an important thing and probably it helps. Okay.

2.  $H_2'$  does not connect states which have different  $l$  values.

$$\begin{aligned}
 L^2 |\psi_l\rangle &= l(l+1)\hbar^2 |\psi_l\rangle \\
 \langle \psi_l | \underbrace{[H_2', L^2]}_{\uparrow} | \psi_{l'} \rangle &= \langle \psi_l | H_2' L^2 | \psi_{l'} \rangle - \langle \psi_l | L^2 H_2' | \psi_{l'} \rangle \\
 &= l'(l'+1)\hbar^2 \langle \psi_l | H_2' | \psi_{l'} \rangle - \\
 &\quad - l(l+1)\hbar^2 \langle \psi_l | H_2' | \psi_{l'} \rangle \\
 &= \underbrace{[l'(l'+1)\hbar^2 - l(l+1)\hbar^2]}_{\text{either } l=l'} \underbrace{\langle \psi_l | H_2' | \psi_{l'} \rangle}_{=0} = 0.
 \end{aligned}$$

The third thing we need to check is that, you know, this HZ prime LZ is not equal to 0. And that's easy to see because these HZ prime involves LX SX plus LY SY plus LZ SZ. And it does not commute with LZ because LZ with either LX or LY is not equal to 0. So, which means that  $ml$  is not a good quantum number for this HZ prime problem, which is the Zeeman effect we are talking about. So, it is not a good quantum number, and hence you cannot use these  $ml$  or rather  $\psi_n l ml$ , which we have been using so far, even in the case of the Stark effect and so on.

So, in this ket notation,  $|n l ml ms\rangle$  is not a good basis. And when I say good, I mean whether we can calculate the matrix elements in this basis or not. And clearly, because this is not a good basis, we shouldn't be using it to calculate the energy correction due to this HZ prime term. All right. So four is that.

But there is definitely a solution to this problem. And the solution is that you use the total angular momentum, which is nothing but  $L$  plus  $S$ , as we have seen as well. OK. And we can actually use a basis involving  $J$  and  $m_j$  to get the correct basis or the proper basis to calculate the matrix elements. And how do we go ahead?

We can write this  $J \cdot J$ , which is equal to a  $J$  square, which is equal to  $L$  plus  $S$  whole square. And here we get a  $L$  square plus a  $S$  square plus a  $2L \cdot S$ . Okay. I think you can convince yourself that  $L \cdot S$  and  $S \cdot L$  are they would commute. And it means that, you know, they can be added together to get it to  $L \cdot S$ . In general, you should not use

the A plus B whole square formula to get this, you know, to expand the expression because A into B may not be equal to B into A. when A and B are arbitrary operators.

In this particular case, L acts on the coordinate space and spin acts on the spin space, so L and S would commute. All right. So J has this or rather the J square has eigenvalue, which is, you know, J into J plus 1 h cross square. L square, which is known to be a good, you know, quantity has eigenvalue L into L plus 1 h cross square. So while you actually go through this in some books, they might have dropped out this h cross or put h cross equal to 1.

So be sort of be aware that sometimes, you know, one doesn't want to carry on with this h cross and is put equal to 1. S square in a similar fashion can also be a good quantum number whose it is S into S plus 1 by h cross square. So, if you put it there, so your L dot S has can be written as it is a J square minus L square minus S square divided by 2, okay. So, this L dot S has eigenvalue which is equal to half, now this is j into j plus 1, j into j plus 1, or I put the h cross square outside, minus l into l plus 1 minus s into s plus 1.

$$3. \quad [H_2', L_z] \neq 0 \quad [L_x S_x + L_y S_y + L_z S_z, L_z] \neq 0,$$

$$[L_z, L_y] \neq 0.$$

$m_l$  is not a good quantum no.

$|n, l, m_l, m_s\rangle$  is not a good basis.

$$4. \quad \vec{J} = \vec{L} + \vec{S}$$

$$\vec{J} \cdot \vec{J} = \vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

|             |     |         |                 |   |
|-------------|-----|---------|-----------------|---|
| $\vec{J}^2$ | has | e-value | $j(j+1)\hbar^2$ | $\vec{L} \cdot \vec{S} = \frac{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}{2}$<br>$\vec{L} \cdot \vec{S}$ has eigenvalue<br>$\frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$ |
| $\vec{L}^2$ | "   | "       | $l(l+1)\hbar^2$ |   |
| $\vec{S}^2$ | "   | "       | $s(s+1)\hbar^2$ |   |

And that's the eigenvalue for this. But then we haven't talked about what exactly the state is that we are referring to. And now this J, be very careful, J can take values. This is an important thing. So, the J quantum number will take values between

L minus s to L plus s. So, m j will take values minus j to plus j through 0. So, there are 2j plus 1 values. All right. So now we are closing in identifying what the state is going to be, which are going to be eigenstates of J and L square and S square and so on. So that brings us to this fifth point that we have these J square and J z, whether they are.

you know, they are good operators for us. And if we explore the L dot S term, remember the f of r is 1 over r q, which is not entering into the discussion at all. And so this is equal to nothing but LX SX plus LY SY plus LZ SZ. And this commutator with, you know, JZ, which is nothing but SZ plus LZ, that we have to see whether it commutes in order for it to be a good eigenfunction. And if I open up this, so it's LX, SX plus LY, SY plus LZ, SZ and LZ plus, you know,

Lx Sx plus Ly Sy plus Lz Sz Sz. This needs to be seen. And the commutation between these two terms is not important here because they would commute anyway. That is what I meant. I mean, these terms you can leave because Lz Sz with Lz is definitely equal to 0.

And Lz Sz again with Sz will also definitely be equal to 0. So, what we need to check is whether Lx Sx plus Ly Sy, the first two terms, commute with Z. And the same goes for Sz that Lx Sx plus Ly Sy commutes with Sz. And so we now have four commutators which are Lx Sx Lz plus Ly Sy Lz. Plus Lx Sx Sz plus Ly Sy Sz.

*j can take values between |l-s| to |l+s|.*  
*m\_j " " " " -j to j*

$$\begin{aligned}
 5. \quad & \vec{J}^2, J_z \\
 [\vec{L} \cdot \vec{S}, J_z] &= [L_x S_x + L_y S_y + L_z S_z, S_z + L_z] \\
 &= [L_x S_x + L_y S_y + L_z S_z, L_z] + [L_z S_z + L_y S_y + L_x S_x, S_z] \\
 &= [L_x S_x + L_y S_y, L_z] + [L_x S_x + L_y S_y, S_z] \\
 &= [L_x S_x, L_z] + [L_y S_y, L_z] + [L_x S_x, S_z] + [L_y S_y, S_z]
 \end{aligned}$$

And this is simple because  $L_x L_z$  will give you a minus  $i\hbar L_y$ , so let me carry on in the next page, which is you have this  $L \cdot S$ . You're calculating  $L \cdot S$  and seeing it with  $J_z$ , and this becomes equal to  $S_x$  into minus  $i\hbar L_y$ . Remember,  $L_i L_j$  commutator or  $S_i S_j$  commutator. This is both equal to  $i\hbar \epsilon_{ijk}$ , either you have  $L_k$  or you have  $S_k$ . So, this is the first term, and then you have a term which is  $S_y$  into minus  $i\hbar L_x$ . And this minus sign is because you have broken the cyclic.

So it's  $L_x L_z$ ,  $L_z L_x$  would have been  $i\hbar$  cross  $L_y$ . But now since it's other way around, then it is minus  $i\hbar$  cross  $L_y$  and  $S_x$ , of course, commutes with that. Similarly,  $L_y L_z$  is  $i\hbar$  cross  $L_x$ . So it's  $S_y S_x$ ,  $S_x S_y$  is  $i\hbar$  cross  $L_z$ . There's no minus sign there.

So this is  $S_y$ . And then we have these the other two terms, which are  $S_x S_z$ , which is again minus  $i\hbar$  cross  $S_y L_x$ . minus  $i\hbar$  cross  $S_y L_x$  and that's coming from this bracket or we can put a need to put a square bracket anymore we just have this. And, what is the last term? That is  $L_y S_x S_z$ . So, this is equal to  $i\hbar$  cross  $S_x L_y$  plus  $i\hbar$  cross  $S_x L_y$ . And, you see that they cancel this, the first term cancels with the last one and the second one cancels with the the third one and then we have it equal to 0, which means that  $J_z$  commutes with  $H_2$  prime.

So, they will have, so  $H_2$  prime has common eigenfunctions with  $J_z$ . OK. And we have also, of course, seen that or you can check this that  $L \cdot S$  with  $J^2$  square it commutes because  $J^2$  square has terms which are  $L^2$  square, which I've already shown. In the same spirit, you can show that it commutes with  $S^2$  square. And of course, it has another term, which is  $L \cdot S$ , which would commute with  $L \cdot S$ , okay. So that tells us that now we can have a basis, which is either  $n, j, l$  and  $m, j$ , okay, so these all are valid quantum numbers.

$$[\vec{L} \cdot \vec{S}, J_z] = S_x(-i\hbar L_y) + S_y(+i\hbar L_x) \\ (-i\hbar S_y)L_x + i\hbar S_x L_y = 0.$$

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k \\ [S_i, S_j] = i\hbar \epsilon_{ijk} S_k$$

$H_z'$  has common eigenfunction with  $J_z$ .

$$[\vec{L} \cdot \vec{S}, J^2] = 0.$$

$|n j l m_j\rangle$  — valid quantum numbers.

Okay. And you can also have one, you know, corresponding to  $n j l$  and  $s$ . And because  $S$  is also a good quantum number. Now, if you have an ambiguity in basis that the term or rather the Hamiltonian or the operator that you're trying to diagonalize, can be, you know, can be diagonalized in one basis and it's also possible to diagonalize it in another basis, then these two bases will be connected by some unitary operation and these are called as a Clebsch-Gordon coefficients, okay. Anyway, that we will come later, but let's not just go ahead with  $n j, l$  and  $m_j$  basis and we have now

$n l$  or rather  $n j$ . The  $n$  is the principal quantum number, which will always be there.  $n j, l, m_j$ . And we have a  $H, Z$  prime and  $n j, l, m_j$ . This is equal to, which is what we have found out, that it is  $j(j+1) - l(l+1) - s(s+1)$ . And then it is  $n l$ . This has to be taken with  $F$  of  $R$  and  $NL$ .

Remember, these are these log-wear polynomials which are given as polynomials.  $R_{n l r}$ , okay. And this  $S$  is nothing but for our case, it's half. So this term becomes, you know, three by four. It's half into half plus one.

So what we have is the following: we have to multiply this, of course, with one over  $R$  squared. And suppose that problem is given to you. Or you don't have to solve that problem. So it's a one by  $R$  to the power  $N$  between the eigenstates of the hydrogen atom. These are known.

And suppose in this case, we do not. So let's just write it.  $f$  of  $r$ , you know,  $f$  of  $r$  goes as one over  $r$  cubed. And,  $R_{n l}$  of  $r$ , so this  $R_{n l}$  of  $r$ ,  $R_{n l}$  of  $r$ , it is supposed given, it is a  $Z$  cubed divided by  $a_0$  cubed  $N$  cubed  $L$  into  $L+1, L+1/2$ . So that's the result for this.

And now we have everything that we need. So we have these HZ prime, which is the first-order correction, Zeeman correction, because taken between the eigenstates of the hydrogenic atom, we had to work a lot to find the correct eigenstates. And that's where most of this energy went. But however, we have been able to find it at the end.

And this is equal to  $\hbar^2$  cross squared by 2. And we have a  $j$  equal to  $j$  into  $j$  plus 1 minus  $l$  into  $l$  plus 1. Minus three-fourths and multiplied by this term, okay, this term, which is nothing but this term, okay, which is  $F$  of  $r$ , the expectation value of that. And this is nothing but equal to  $\hbar^2$  squared over 2, and because  $j$  can take some values which are, in this particular case,  $j$  can take values which are  $l$  plus half and  $l$  minus half because  $s$  is equal to half. We have told this before,  $l$  minus half.

And now we have this whole thing can be written as either it's  $L$  or it's minus  $L$  minus 1. This will be there when  $J$  equals  $L$  plus half. That's the first one. And this will be there when  $J$  equals  $L$  minus half. And the whole thing will, you know, be written as.

$$\langle n j l m_j | H_2' | n j l m_j \rangle = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}] \times \langle n l | f(r) | n l \rangle$$

$\downarrow$   
 $\langle n l | f(r) | n l \rangle$   
 $\downarrow$   
 $R_{nl}(r)$

$$\langle R_{nl}(r) | f(r) | R_{nl}(r) \rangle = \frac{2^3}{a_0^3 n^3 l(l+1)(l+\frac{1}{2})}$$

$s = \frac{1}{2}$

$$\langle H_2' \rangle = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}] \langle f(r) \rangle$$

$j$  can take  
 $l + \frac{1}{2}, l - \frac{1}{2}$

$$= \frac{\hbar^2}{2} \begin{pmatrix} l \\ -l-1 \end{pmatrix} \begin{matrix} \rightarrow j = l + \frac{1}{2} \\ \rightarrow j = l - \frac{1}{2} \end{matrix}$$

So let me write down. And then, of course, this term that you have, I mean, the same term with  $F$  of  $R$ . So H Z. Prime, which is the Zeeman term, the splitting or the energy correction due to this intrinsic spin-orbit coupling or intrinsic Zeeman effect. And why it's called spin-orbit coupling is that because  $L$  is, you know, sort of tagged along with  $S$  or  $L$  is coupled to  $S$ . That's why it's called spin and orbit are coupled. And for that, we needed to find a basis, which is what we have done.

And it's  $L$  and  $L + 1$  with the sign. And now we have these  $E_0$ s. and  $Z$  squared,  $\alpha$  squared. So we write it in terms of these energy scales of the hydrogen atom, which is  $2n$ ,  $l + 1$  and  $l + \frac{1}{2}$ . And that's it.

I mean, that will be along. I mean, this gives you this  $E_0$  is given by minus  $E$  squared by  $1.2A_0$  and  $Z$  square by  $N$  square,  $Z$  is of course equal to 1 for hydrogen atom and this is called as a fine structure constant which is equal to  $E$  square by  $h$  cross  $C$ . So, this is nothing but the  $N, J$  and we have taken  $L$  and  $MJ$ . So,  $n, j, m, l$  and  $m, j, H, Z$  prime and this  $n, l, n, j, m, l, m, j$ . Sorry, what did I write?

It is  $l$ . It should be  $l$  not  $m, l$ . That is a mistake.  $m, l$  is not a good quantum number. So,  $N, J, L, M, J$ ,  $N, J, L, M, J$ . This is the first order correction number. in the Zeeman, in the sort of intrinsic Zeeman effect. Okay.

$$\langle H_Z' \rangle = \begin{pmatrix} l \\ -(l+1) \end{pmatrix} \left[ E_0 \frac{z^2 \alpha^2}{2n l (l+1) (l + \frac{1}{2})} \right]$$

$$E_0 = -\frac{e^2}{2a_0} \frac{z^2}{n^2}$$

$$\alpha = \frac{e^2}{\hbar c}$$

$\langle n, j, l, m, j | H_Z' | n, j, l, m, j \rangle$   
 $\rightarrow$  1st order correction in the intrinsic Zeeman effect.

And this is what we wanted to find. We have done that for the Stark effect inference of the electric field. Now we have done it for the magnetic field, both as an external magnetic field and for the intrinsic magnetic field, which is because these are charged particles, and the electron is actually revolving around the proton, constituting a current in the rest frame of the electron. The proton is going around it, and it constitutes a current again. And we have made an approximation that they are moving in rectilinear paths and have claimed that this approximation really doesn't have too much bearing on the results that we derived or obtained for the energy correction for the Zeeman effect.

So that concludes, you know, this Zeeman effect, and we have already done the Stark effect. These are real problems, and they have been done in experiments. People have experimentally found that these are really observable effects for the hydrogen atom. So

we'll stop here and carry on with more perturbation theory problems or approximate method problems in the next class. Thank you. Music