Basic Quantum Mechanics

Prof. Ajoy Ghatak
Department of Physics
Indian Institute of Technology Delhi

Module No # 10

Time Independent Perturbation Theory

Lecture No # 03

Time Independent Perturbation Theory Fine: Structure and Zeeman Effect

The last lecture of our previous lecture, we had started with effects from relativistic consideration. The Schrödinger equation is a non-relativistic equation. We started with the relativistic mass energy relation from which we derived the relativistic equation.

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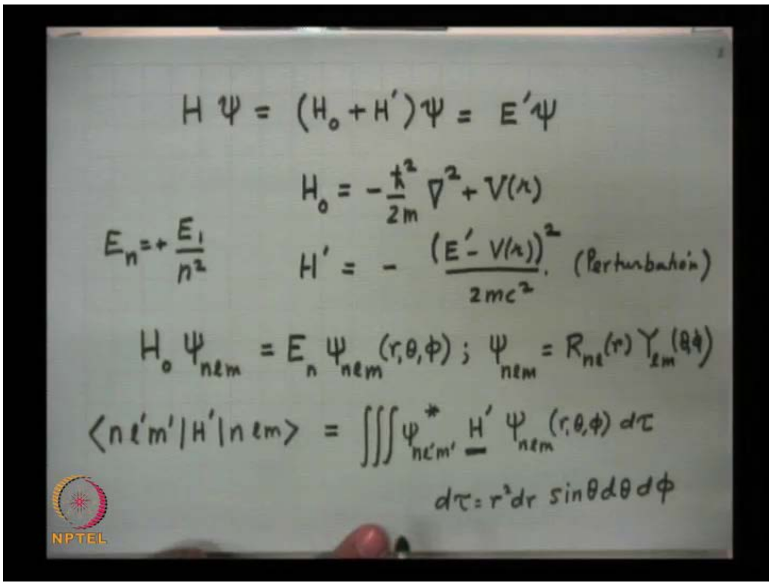

$$H\psi = (H_0 + H')\psi = E'\psi$$

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

$$E_n = +\frac{E_1}{n^2}$$

$$H' = -\frac{(E' - V(r))^2}{2mc^2} \quad \text{(Perturbation)}$$

$$H_0\psi_{n\ell m} = E_n\psi_{n\ell m}(r,\theta,\phi) \; ; \; \psi_{n\ell m} = R_{n\ell}(r)\,Y_{\ell m}(\theta\phi)$$

$$\langle n\ell' m'|H'|n\ell m\rangle = \iiint \psi^*_{n\ell' m'}\,\underline{H'}\,\psi_{n\ell m}(r,\theta,\phi)\,d\tau$$

$$d\tau = r^2 dr \sin\theta\, d\theta\, d\phi$$

And, in fact we wrote the Schrödinger, the relativistic Schrödinger equation. We wrote it in a form H is H psi is equal to H naught plus H prime psi; that is, the total Hamiltonian is written as a sum of H naught plus H prime psi is equal to E prime psi where H naught is the non-relativistic Hamiltonian. That is, this is equal to minus h cross Square by 2 m del square plus V of r.

And, for the hydrogen atom problem, I know the solution of the Eigen values, of the Eigen value equation for H naught. And, my H prime was equal to minus E prime minus Vof r by 2 m c square and the numerator was square. So, this was the Hamiltonian. And, this is the, we will take H prime as a perturbation. We will take H prime as a perturbation. As you and use the perturbation theory to calculate the effect of the term H prime on the energy Eigen values.

Now, for H naught we know the Eigen value equation. We know the solution of the Eigen value equation. In fact, H naught psi n l m is equal to E s of n psi n l m; where psi n l m is a function of r theta and phi and these wave functions are given by psi n l m functions are R n l, a function of r times the spherical harmonics, Y l m theta phi.

Now, therefore we want to use the time independent perturbation theory. This is my perturbation. So, the, we want to calculate this matrix element; n l prime m prime for the same values of n. You see, different values of n will have different energy as we all know that E n is equal to minus E 1, sorry, plus E 1 by n square. And, for the hydrogen atom E 1 is about minus 13.6 electron volts.

So, let me first calculate the matrix element H prime n l m. So, this is actually the integral, the triple integral triple integral psi n l prime m prime star H prime psi n l m r theta phi, this is as a function of r theta phi multiplied by d tau. And, that d tau is equal to, this is the volume element and we will use d tau is equal to r square d r sin theta d theta d phi. Now, in this, we must see that H prime is a function of r only. And, so we can write this integral as a product of two terms. Since this is a function of r only, we can take the r psi.

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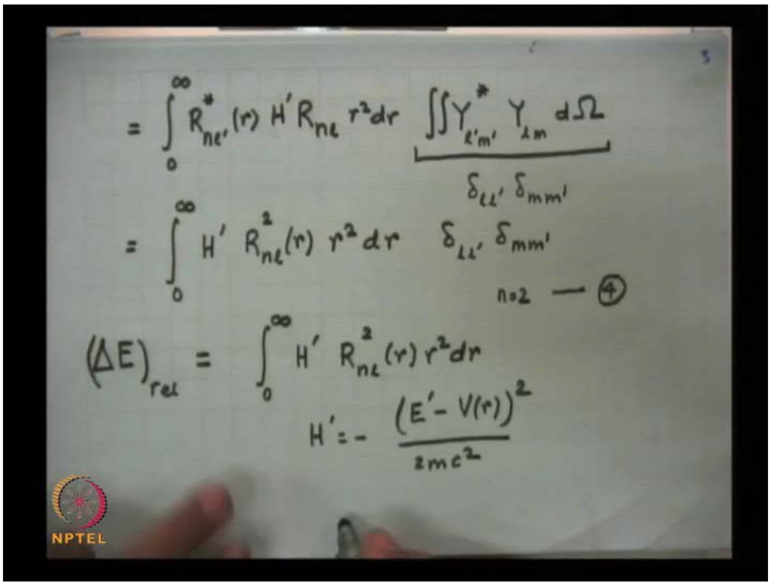

$$= \int_0^\infty R^*_{nl'}(r)\, H' R_{nl}\, r^2 dr \underbrace{\iint Y^*_{l'm'} Y_{lm}\, d\Omega}_{\delta_{ll'}\delta_{mm'}}$$

$$= \int_0^\infty H' R^2_{nl}(r)\, r^2 dr \quad \delta_{ll'}\delta_{mm'}$$

n=2 — ④

$$(\Delta E)_{rel} = \int_0^\infty H' R^2_{nl}(r)\, r^2 dr$$

$$H' = -\frac{(E' - V(r))^2}{2mc^2}$$

So, let me write it from here. The first integral will be zero to infinity zero to infinity R n l prime of r star, but these are all real function, H prime R n l r square d r multiplied by integral Y l prime m prime star Y l m sin theta d theta d phi; so that, there is a simpler way to write this. So, this is d omega, where d omega is sin theta d theta d phi. This we abbreviate as…

Now, they form orthonormal functions. So, this is equal to delta l l prime, delta m m prime. So, since H prime depends only on R coordinate, so this matrix element this matrix element becomes equal to becomes equal to zero to infinity, l must be equal to l prime, otherwise it is 0. So, this is H prime R n l of r whole square r square d r multiplied by delta l l prime delta m m prime.

So, you see, what I am trying to say is that I consider, let us suppose the n equal to 2 state, and as we had discussed in the stark effect problem, this is 4, 4 degenerate. So, among the degenerate states our wave functions are such that, any element like H prime 1 2, H prime 2 1, H prime 3 1 and so on will be 0. So, we already have a representation in which H prime is diagonal. And, so therefore, the diagonal elements will be the perturbation.

So, therefore the due to relativity effects, due to the delta E due to relativistic effects will be just the diagonal terms when l is equal to l prime and m is equal to n pi. So, this will be H prime is, so this will be just zero to infinity zero to infinity H prime R n l square of r r square d r. This will be the perturbation. And, H prime, we know that this is equal to minus E prime minus V of r whole square by 2 m c square.

So, we can write this down that, this is equal to minus 1 over 1 over 2 m c square E prime square and V of r is equal to minus z e square by r. So, this becomes E prime plus z E square by r. So, this will be minus 2 E prime. So, this will become plus, 2 E prime z E square by r plus z square e 4 by r square. So therefore, if I, since these are normalized functions; that is, what I mean by normalized function is integral of this quantity from 0 to infinity is 1.

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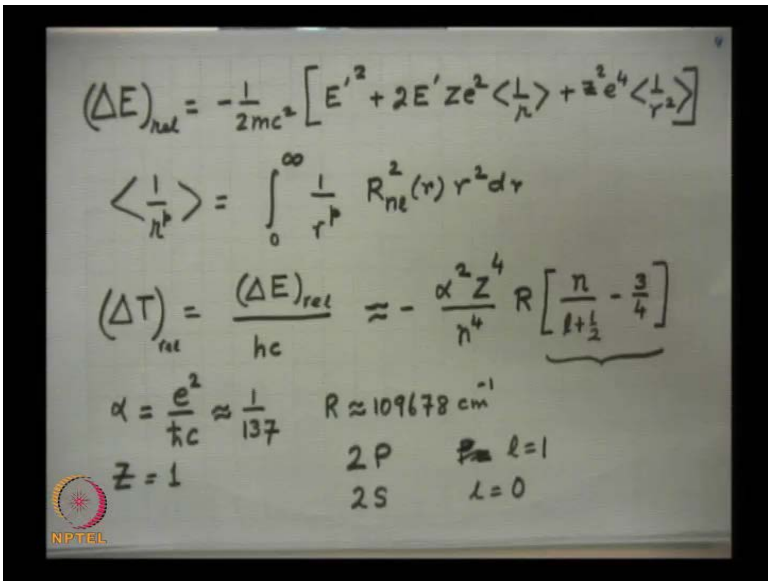

$$(\Delta E)_{rel} = -\frac{1}{2mc^2}\left[E'^2 + 2E'ze^2\left\langle\frac{1}{r}\right\rangle + z^2e^4\left\langle\frac{1}{r^2}\right\rangle\right]$$

$$\left\langle\frac{1}{r^p}\right\rangle = \int_0^\infty \frac{1}{r^p} R_{nl}^2(r)\, r^2 dr$$

$$(\Delta T)_{rel} = \frac{(\Delta E)_{rel}}{hc} \approx -\frac{\alpha^2 Z^4}{n^4} R \underbrace{\left[\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right]}$$

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \qquad R \approx 109678\ \text{cm}^{-1}$$

$Z = 1$

$2P \qquad l = 1$

$2S \qquad l = 0$

So, therefore the integral, if I carry out the integration, so this becomes this becomes equal to, let me shift it to the right, so that this will become is equal to is, so therefore, delta E relativistic, due to relativistic effects becomes equal to minus 2 m c square E prime square plus 2 E prime z E square expectation value of 1 over r plus z square e 4 expectation value of 1 over r square; where where 1 over r to the power of p is equal to 0 to infinity, 1 over r to the power of p R n l square of r r square d r.

Now, it so happens… Sometime back I had given you the formulae for obtaining R n l of r, the radial part of hydrogen atom wave functions. And, in fact using each one of them, I can calculate this integral, evaluate this integral. The integration is really very simple.

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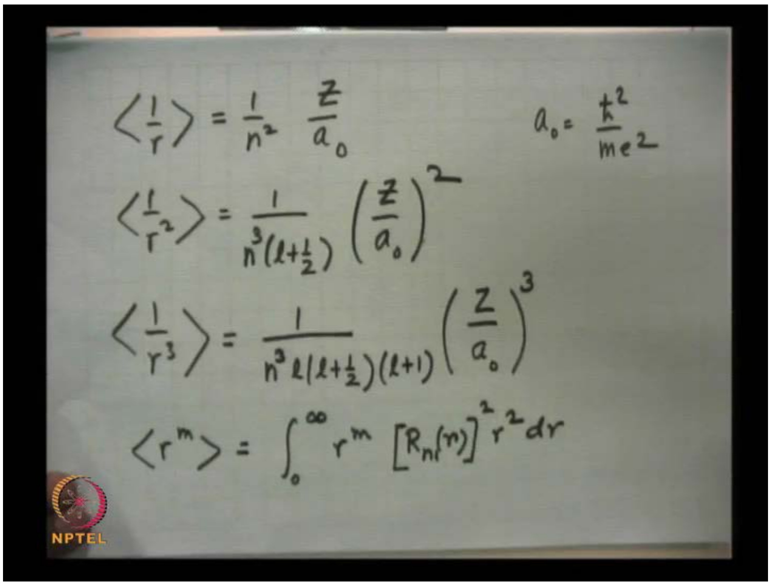

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2} \frac{Z}{a_0} \qquad a_0 = \frac{\hbar^2}{me^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{n^3(l+\frac{1}{2})} \left(\frac{Z}{a_0}\right)^2$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 l(l+\frac{1}{2})(l+1)} \left(\frac{Z}{a_0}\right)^3$$

$$\langle r^m \rangle = \int_0^\infty r^m \left[R_{nl}(r)\right]^2 r^2 dr$$

However, there are general formulae which are applied, which are available and I will just give you the result. The expectation value of 1 over r is 1 over n square z by a 0; where a 0 is the Bohr's radius. So, a 0 is equal to h cross square by m e square and has a value of about half of an angstrom. And, 1 over r square is the expectation value of 1 over r square and that is given by this expression and similarly for 1 over r cubed.

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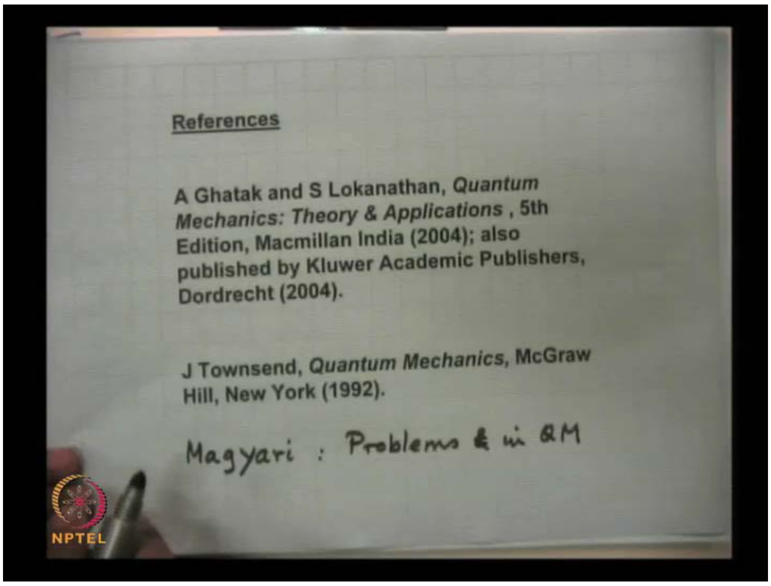

References

A Ghatak and S Lokanathan, *Quantum Mechanics: Theory & Applications*, 5th Edition, Macmillan India (2004); also published by Kluwer Academic Publishers, Dordrecht (2004).

J Townsend, *Quantum Mechanics*, McGraw Hill, New York (1992).

Magyari : Problems & in QM

These are given at many places. Including the formulae are given in this book. And, there is a book by Magyari, "Problems in Quantum Mechanics" and in which these these relations are very carefully… “Problems in Quantum Mechanics”. So, you can you can see them if you are interested in finding out the derivation of these formulae.

So, you have here, these formulae. So, if you substitute it here and carry out a very straightforward algebra, then you will obtain the following expression for the.. So, we write it in wave number units. So, in wave number units, delta T will be equal to delta E relativistic. This is the relativistic expression of the change in the energy divided by h c, delta T is in wave number units. And, if you do that, you will find that this is equal to minus alpha square z 4 by n to the power of four multiplied by R, R is the Rydberg constant and multiplied by n divided by l plus half minus 3 by 4.

So, alpha, we know alpha is equal to the fine structure constant, which is in CGS unit. It is E square by h cross c, which has a value of 1 over 137. For the hydrogen atom, z is equal to 1 and n in the denominator is the is the total quantum number. And, the R is the Rydberg, which for hydrogen atom is 109678 centimeter inverse.

So, we know all the parameters. And, for example, for the 2 P state, 2 p state P is equal to, sorry, P means l is equal to 1 and for the 2 S state, l is equal to 0. So, we find that for l equal to 1 and l equal to 0, the value of this expression a slightly different. And, we obtain a splitting of the level. This splitting is known as… due to relativistic effects. And, the final result is for the 2 P state and similarly for the other state. So, this is the relativity correction.

So, you have here n equal to 2 state. The splitting, the change is 0.213 centimeter inverse. This is very small. And, and the for l equal to 0, it is 1.1870. So, if… So, due to the relativity effects, the degeneracy is partially removed. The degeneracy is only partially removed because n equal to 2 state is 4, 4 degenerate state. But, it splits into two states; l equal to 0 state is non-degenerate, l is equal to 0 state is non degenerate and l equal to 1 state is 3, 4 degenerate because the m values takes minus 1, 0 and plus 1.

So, because of the relativity effects, the degeneracy is partially lifted. But, when you compare this splitting which is known as the fine structures splitting, so we find that the that the experiment does not agree with the theory because of the same order of magnitudes is what is there is the spin orbit interaction.

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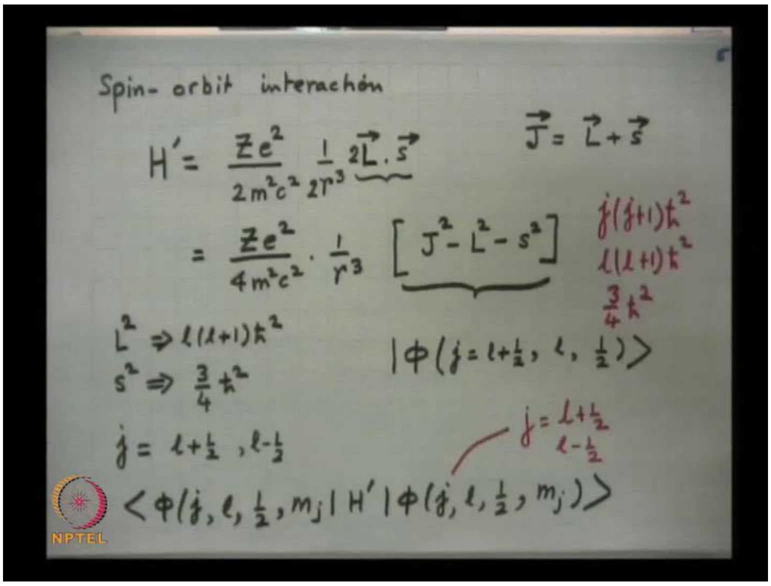

Spin- orbit interaction

$$H' = \frac{Ze^2}{2m^2c^2}\,\frac{1}{2r^3}\,\underbrace{2\vec{L}\cdot\vec{s}}_{} \qquad \vec{J} = \vec{L} + \vec{s}$$

$$= \frac{Ze^2}{4m^2c^2}\cdot\frac{1}{r^3}\underbrace{\left[J^2 - L^2 - s^2\right]}_{}$$

$j(j+1)\hbar^2$

$l(l+1)\hbar^2$

$\frac{3}{4}\hbar^2$

$L^2 \Rightarrow l(l+1)\hbar^2$

$s^2 \Rightarrow \frac{3}{4}\hbar^2$

$|\phi(j = l+\frac{1}{2}, l, \frac{1}{2})\rangle$

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

$j = l+\frac{1}{2}$

$l-\frac{1}{2}$

$\langle\phi(j, l, \frac{1}{2}, m_j|H'|\phi(j, l, \frac{1}{2}, m_j)\rangle$

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Now, so we have taken the relativity effect. We will next consider the effect due to spin orbit interaction. What is it physically? Now, you see let us consider the simplest of the atom, the hydrogen atom. Now, there in the hydrogen atom, in the Bohr model, the electron rotated around the proton. So, therefore, if I am sitting on the electron, then the proton is rotating around me; if I am sitting on the electron, then with respect to me the proton is rotating. So, it is a circulating current. So, it produces a magnetic field. Because of the circulating current, we have a magnetic field at the electron. And, since electron has a spin angular momentum or rather electron has a magnetic moment, it behaves like a tiny magnet of magnetic moment mu. So, so that magnetic moment interacts with the magnetic field of the, due to the orbital motion. And, so we have an interaction energy which is the mu dot H term, which is known as the spin orbit interaction.

Now, now before… So, therefore, if so, this was the final formula for which I would request. Using using these these expressions using these expressions, I would request all of you to to derive the expression for delta T relativistic and and show the explicit splitting of the n equal to 2 state, which will split into two state. One will be l equal to 0; the s state and the other will be l equal to 1 state.

We next consider, as I just now mentioned the spin-orbit interaction. Now, because of that we have a Hamiltonian. We have a perturbation term which is proportional to L dot

s. In fact, the perturbation term is which comes out automatically from a from the Dirac equation; 2 m square c square 1 over r cubed L dot s vector.

So, where, this is the orbital angular momentum vector and s vector is the spin angular momentum vector. So, we write this as that we multiply this by 2 and divide by 2 and we write 2 L dot s. We define the vector; the total angular momentum vector is equal to L plus s. So, we, so, we had considered the addition of angular momentum. So, 2 L dot s will be z e square by 4 m square c square 1 over r cubed, 2 L dot s will be J square minus L square minus s square.

Now our perturbation is, therefore proportional to J square minus L square minus s square. So, I must consider wave functions, which are simultaneous Eigen functions of J square, L square and s square. So, these are the phi functions that we had discussed. So here, for example, one the Eigen values of L square is equal to l into l plus 1. Eigen values of L square are l into l plus 1 h cross square and s is half. So, the Eigen values of s square is equal to 3 by 4, half into half plus 1, h cross square. So, I… So, therefore the total angular momentum value j can be either l plus half or l minus half.

So, I must choose to calculate the effect of the perturbation. I must choose the phi functions for which j will be either l plus half or l minus half and then J square l and then half j square L square and s square. So, those are the Eigen functions that we must choose. And, if we carry out this integration, calculate the calculate the matrix element that is, phi j equal to l plus half, l, half and m j. These are the wave functions, H prime and the same wave functions; phi, j, l, half, m j.

Now, you must understand that the values of j, for a given value of a values of j will be either l plus half or l minus half of only for l equal to 1, 2, 3; for l equal to 0, it will be just half. The Eigen values of J square will be j into j plus 1 h cross square; the Eigen values of s is L square will be l into l plus 1 h cross square and Eigen values of s square will be 3 by 4 h cross square.

So,. So, we use these wave functions. We can explicitly write down the form of the wave functions, as we will do slightly later. But, we do not have to do that as long as we take these wave functions. We know that this will be equal to...

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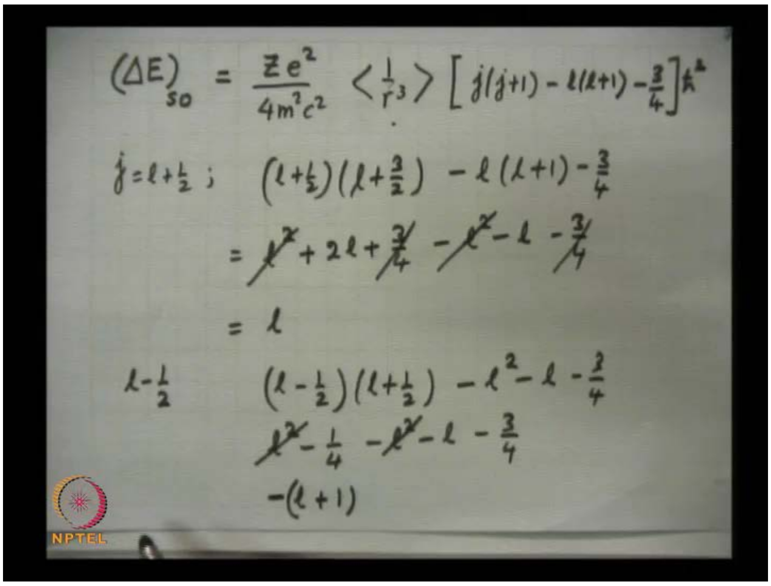

$$(\Delta E)_{so} = \frac{Ze^2}{4m^2c^2}\left\langle\frac{1}{r^3}\right\rangle\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\hbar^2$$

$$j = l + \frac{1}{2}; \quad \left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right) - l(l+1) - \frac{3}{4}$$

$$= \cancel{l^2} + 2l + \cancel{\frac{3}{4}} - \cancel{l^2} - l - \cancel{\frac{3}{4}}$$

$$= l$$

$$l - \frac{1}{2} \quad \left(l-\frac{1}{2}\right)\left(l+\frac{1}{2}\right) - l^2 - l - \frac{3}{4}$$

$$\cancel{l^2} - \frac{1}{4} - \cancel{l^2} - l - \frac{3}{4}$$

$$-(l+1)$$

So, therefore the perturbation will be equal to the delta E, the change in the energy because of the spin orbit interaction. This will be, this factor is a constant z e square by 4 m square c square the expectation value of 1 over r cubed multiplied by j into j plus 1 minus l into l plus 1 minus 3 by 4 h cross square. Ok.

So, we have already told you what is the value of 1 over r cubed. The expectation value of 1 over r cubed, that is equal to 1 over one n cubed this this rest to the power of. So, we will use this. We will substitute this here and we will use this for j is equal to l plus half and j is equal to l minus half. And, the calculation is really very very simple. For example, for j is equal to l plus half we have this expression is equal to l plus half into l plus 3 by 2 minus l into l plus 1 minus 3 by 4. So, this is equal to l square plus half plus 3 by 2 is 2 l plus 3 by 4 minus l square minus l minus 3 by 4. So, l square and l square cancels out, this cancels out. So, this becomes just l.

So, I divide, l comes there and one of these l get out. And, so we will get an expression for delta E. Similarly, for j is equal to l minus half, j is equal to L minus half this becomes l minus half l minus half plus 1 that is, l plus half minus l square minus l minus 3 by 4. So, this becomes l square minus 1 by 4 minus 1 by four is minus 1 by 4 minus l square minus l minus 3 by 4. So, l square and l square cancels out. So, this will become minus l minus 1, so minus bracket l plus 1. So, you will have a minus sign there. Here, as you can see this is a plus sign here and the other will be a minus sign here. And, the rest of the calculations are very simple.

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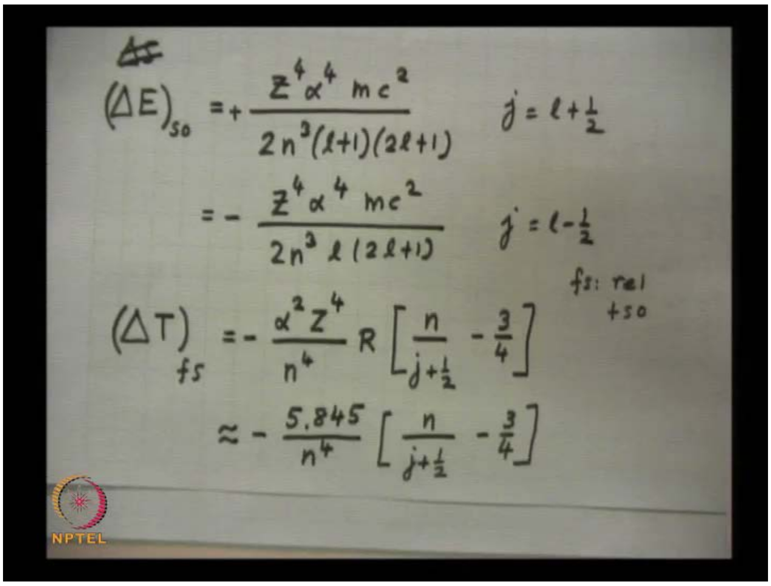

$$(\Delta E)_{so} = + \frac{Z^4 \alpha^4 mc^2}{2n^3(l+1)(2l+1)} \qquad j = l + \frac{1}{2}$$

$$= - \frac{Z^4 \alpha^4 mc^2}{2n^3 \, l \, (2l+1)} \qquad j = l - \frac{1}{2}$$

fs: rel +so

$$(\Delta T)_{fs} = - \frac{\alpha^2 Z^4}{n^4} R \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

$$\approx - \frac{5.845}{n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

And, in fact if you if you work this out if you work this out, then you will get the following simple expressions that delta E, sorry sorry, let me, delta E due to spin orbit due to spin orbit becomes z 4 alpha 4 m c square by 2 m cubed l plus 1 into 2 l plus 1, for j is equal to l plus half. And, similarly similarly an another expression for l plus l minus half. if you add this if you add this, so the second expression let me write it down. This is plus here. It is a positive and the next them as I mentioned for j equal to l minus half. This becomes z to the power of four alpha to the power of four m c square divided by 2 n cubed l into 2 l plus 1.

If you add to this, the expression for the for the relativistic correction and then used wave number units, the final result becomes delta T, the fine structure. The fine structure is the sum of the relativity effect plus the spin orbit interaction. Relativity effect plus the spin orbit interaction. So, this comes out to be very simple. You can put it combine into one formula alpha square z 4 to the divided by n to the power of four, R is the Rydberg constant, n by j plus half minus 3 by 4. z is equal to 1, for hydrogen. alpha is 1 over 137 and the Rydberg constant value, I have will...

So, for hydrogen, this comes out to be a very simple number 5.845 for hydrogen. This divided by n to the power of 4 n by j plus half. It does not really depend on the l value. It depends only on the… this is fine structure. Fine structure is relativity correction plus the spin orbit correction.

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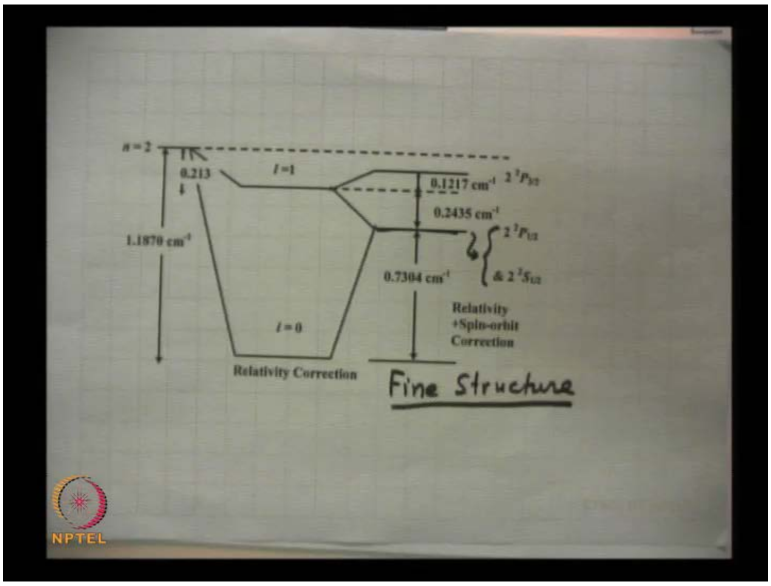

So, if I now, I had here, for example, the relativity correction is given by this. And, this is my spin orbit correction. So, on the…, I superpose this, on the relativity correction, I superpose the spin orbit correction and therefore this, 2 doublet P half. This 2 represent the total quantum number, doublet means s is equal to half and this is at the j values. j is equal to 3 by 2 and j is equal to half and this is doublet s half. Both of them have the same energy level.

So, both of them, it depends not on the l value as we see from the last expression are the last expression, this is this is the relativity plus spin orbit correction. And, so this is the fine structure of the spectral line. This is known as the fine structure. So, what is the fine structure? Fine structure is a combination of relativity effect plus spin orbit interaction. The hyperfine structure, which is even a smaller splitting, is due to the interaction. For example, in the in the simplest of the atom, hydrogen atom case, the electron has a magnetic moment; the proton has a magnetic moment. The two the two magnetic moments interact to produce an interaction term, which results in a further splitting of the spectral lines. And, that splitting is known as the hyperfine structure. That splitting is extremely small. So, you can see here, this depends; this splitting depends only on the total quantum number and not on the l values.

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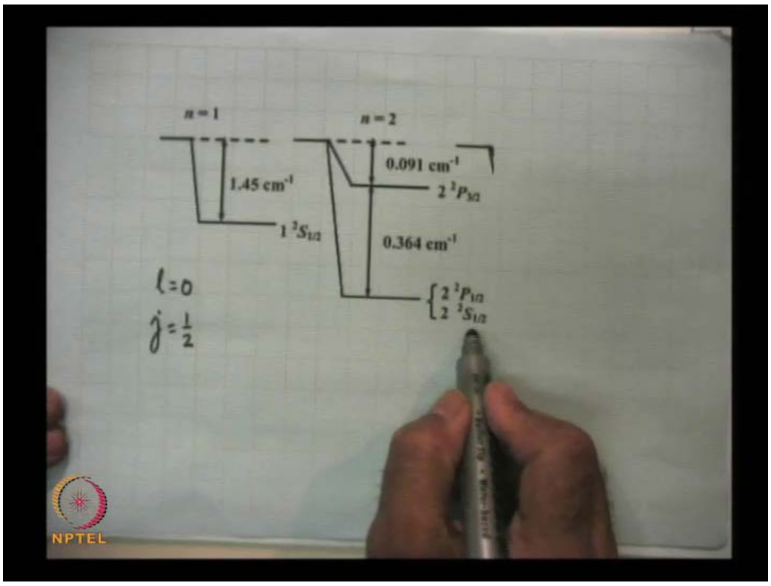

So, let me show you some of the calculations that I have. I mean, these are very simple calculations and I would request all of you to do that. These are all for the hydrogen atom. all for the hydrogen atom n is equal to 1; as you know for n is equal to 1; l is equal to zero. And, so therefore, j will be only half.

So, you have 1 that is the total quantum number doublet because S is equal to half s half. For n is equal to 2, just what I had shown the fine structure is this is 0.091 centimeter inverse. And therefore, this is the 2 doublet P 3 by 2 and P half and S half. The splitting depends only on the j value.

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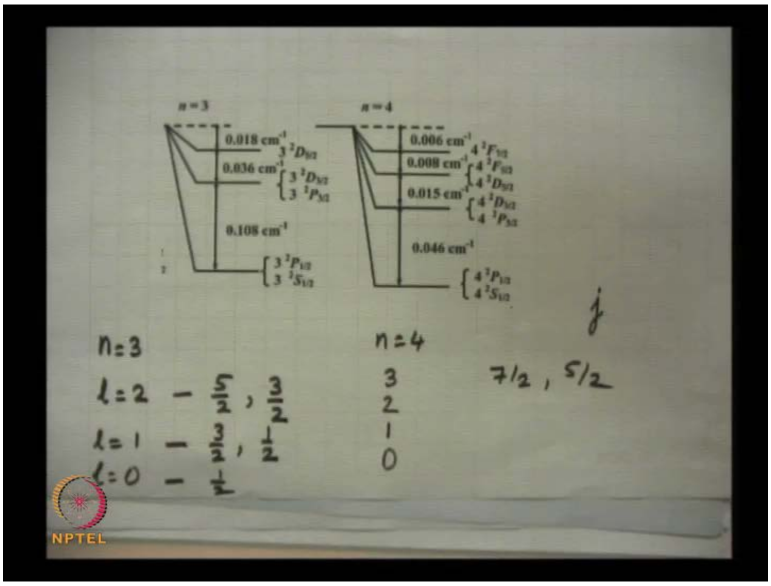

Similarly, for the n equal to 3 state, n equal to three state let me write it down l can be 2, l can be 1 and l can be 0. So, when l is 2, j can be either 5 by 2 or 3 by 2. These are the D 5 by 2 and D 3 by 2. When l is equal to 1, so this will be 1 plus half; that is, 3 by 2 and half. This is P 3 by 2 and P half. When L is equal to 0, then it is only half. So, these are the… So, n equal to 3 level splits into three levels, three states. Once again, the degeneracy is only partially lifted. And, when you have n is equal to 4, then l can take 3, 2, 1, and 0. And, you will have the j states f states corresponds to l is equal to 3. So, this can be either 7 by 2 or 5 by 2. So, it is here 7 by 2, 5 by 2. And then, then D 5 by 2, D 3 by 2, P 3 by 2, P half S R.

The splitting, the value of the splitting depends only on the j value and does not depend on the l value. And, when there is a transition from one of the lines to the other, then you have obtained the fine structures splitting of this spectral line. And, that is what we will, what we have shown here.

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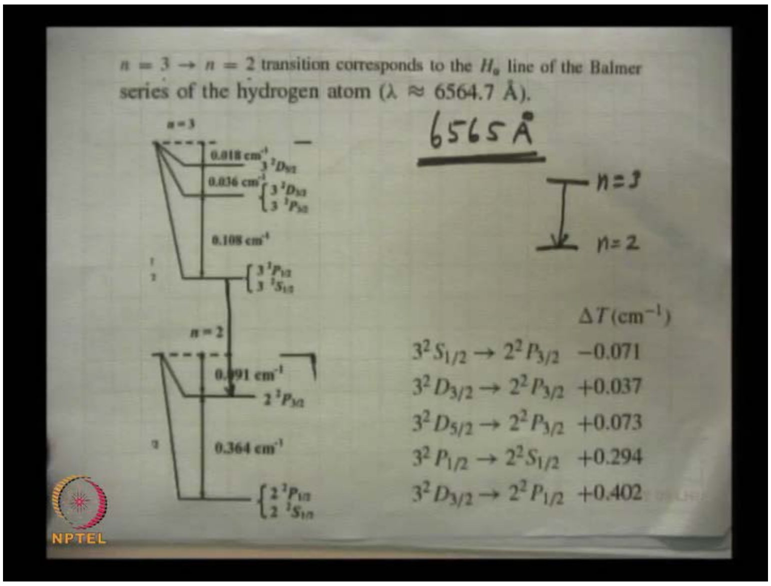

$n = 3 \rightarrow n = 2$ transition corresponds to the H_α line of the Balmer series of the hydrogen atom ($\lambda \approx 6564.7$ Å).

6565 Å

	ΔT (cm^{-1})
$3^2S_{1/2} \rightarrow 2^2P_{3/2}$	-0.071
$3^2D_{3/2} \rightarrow 2^2P_{3/2}$	$+0.037$
$3^2D_{5/2} \rightarrow 2^2P_{3/2}$	$+0.073$
$3^2P_{1/2} \rightarrow 2^2S_{1/2}$	$+0.294$
$3^2D_{3/2} \rightarrow 2^2P_{1/2}$	$+0.402$

The Balmer series: one of the lines of the Balmer series, which you have all read in your high school, is from the n equal to 3 to n equal to 2 transition. And, let us consider the n equal to 3 to n equal to 2's transition corresponds to the H alpha line of the Balmer series. And, this has a wavelength of about 6565 angstrom in the visible region.

So, the n equal to 3 level splits into three; the n equal to 2 level splits into two. And then, we, when the transition takes place, let us suppose from 3 doublet S half from this level to 2 doublet P 3 by 2. So, from this to this, the shift is 0.071. And similarly, from other levels to the other level, there is a small change in the energy. I would request all of you to calculate the shift and show that it results in five spectral lines.

That is this line. If you if you use under a very careful spectroscope, a spectroscope with a very high resolution, then the n equal to 3 to n equal to 2, this is the a H alpha line of the Balmer series, is not really a single line, it consists of five, equally five lines. This splitting of one line into several lines is known as the fine structure splitting is known as the fine structure splitting of the spectral lines.

So, I have given you the very important formula. This is, of course for single electrons that delta T fine structure is equal to so much. It depends on the total quantum number. The splitting, therefore depends on the total quantum number and also on the j value, it does not depend on the l values. And, using this, we calculated the splitting of different lines for n equal to 3, n equal to 2 and so on. And, we found out the fine structure of the spectral lines.

Now, this completes the fine structure. We have taken into account the effects due to relativity and effects due to relativity. And, there the perturbation was equal to a function of R only. But, then we considered the effect due to spin orbit interaction and we had, we considered the corresponding perturbation to the energy level resulting into splitting, which depends only on the value of j.

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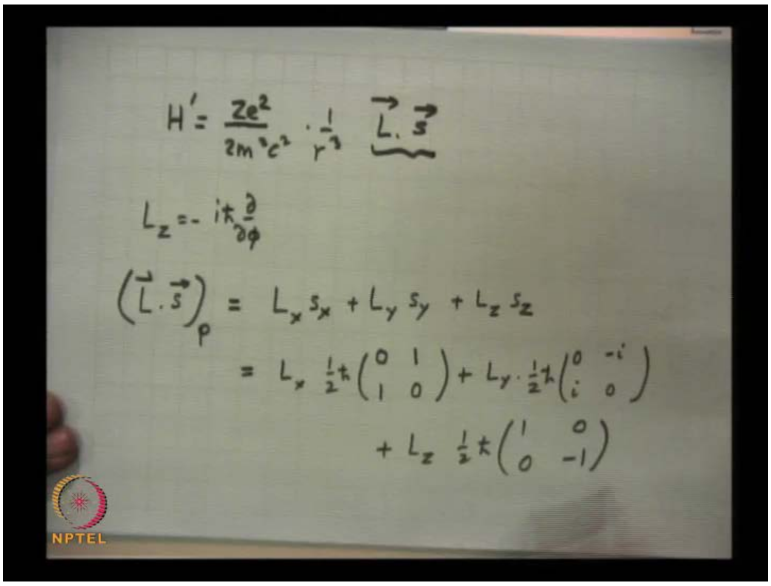

$$H' = \frac{Ze^2}{2m^2c^2} \cdot \frac{1}{r^3} \underbrace{\vec{L}.\vec{s}}$$

$$L_z = -i\hbar \frac{\partial}{\partial\phi}$$

$$(\vec{L}.\vec{s})_p = L_x s_x + L_y s_y + L_z s_z$$

$$= L_x \tfrac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + L_y \cdot \tfrac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + L_z \tfrac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Let me tell you that the perturbation term that we had taken was proportional to something like, it was actually z e square by 2 m c square 2 m square c square 1 over r cubed L dot s. So, we wrote down this as L dot s. Now, L, we know these are operators; L x, L y, L z. We had done that, for example, L z is the minus i h cross delta by del phi. And, the Eigen functions are the spherical harmonics.

What does this represents? So, for example, this represents L dot s is the Pauli representation of that is, this is what it means that L x s x plus L y s y plus L z s z. And, if you write this down, then this becomes L x, then s x is half h cross 0, 1, 1, 0 plus L y half h cross 0, minus i, 0, plus i plus L z half h cross 1, 0,0, minus 1.

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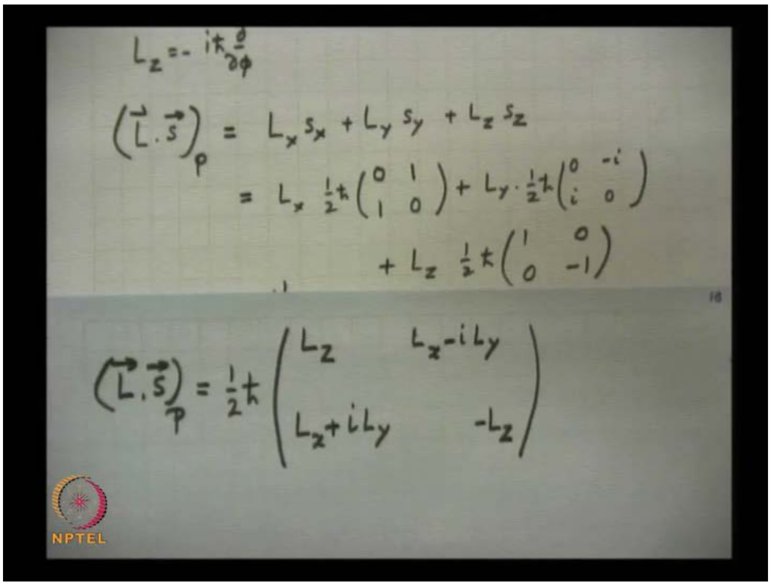

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$(\vec{L}\cdot\vec{s})_P = L_x s_x + L_y s_y + L_z s_z$$

$$= L_x \frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + L_y\cdot\frac{1}{2}\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$

$$+ L_z \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$(\vec{L}\cdot\vec{s})_P = \frac{1}{2}\hbar\begin{pmatrix}L_z & L_x - iL_y\\ L_x + iL_y & -L_z\end{pmatrix}$$

So, if you therefore, take half h cross outside, so you get L z here. So, let me write it down carefully. Let me write it down carefully. So, this becomes is equal to half h cross outside and we take a big bracket. So, this term is L z and minus L z and this term is L x minus i L y and this is L x plus i L y and minus L z. So, this matrix is known as the Pauli representation of the operator L dot s; the subscript P is the Pauli representation. So, similarly I can write this down for J square, L square and s square.

Now, we finally, discuss the… we had discussed the Zeeman splitting for singlet states. We had discussed that if we neglect the effect of the spin, the neglect the spin of the electron, then we obtain the splitting. And, if we use the selection rule that delta m is equal to plus 1 or minus 1, then we obtain r 0 then we obtain three. A level splits up into what are known as a Zeeman triplet.

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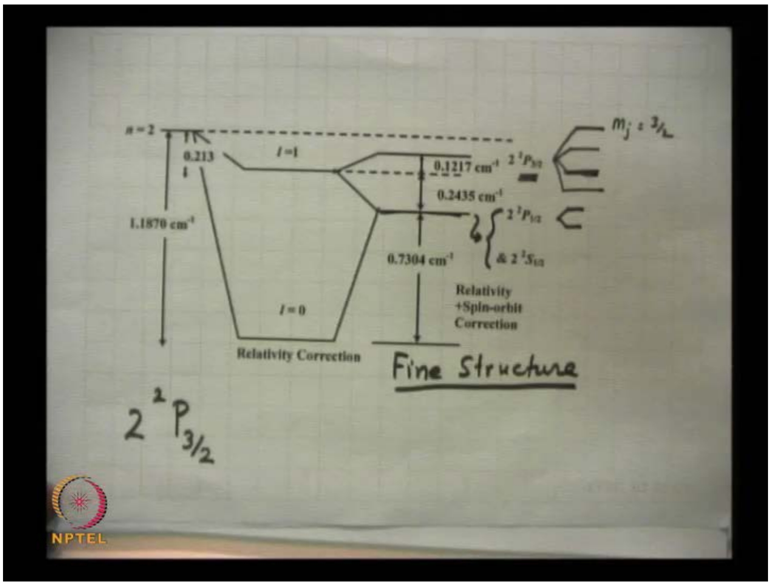

Now, if I if I look at this state, if I look at the 2 doublet P 3 by 2 state, so this 2 doublet P 3 by 2 state; l is equal to 1, s is equal to half and j is equal to 3 by 2. So, therefore, if we now apply the magnetic field, this is known as the weak field Zeeman Effect; where we have to take these wave functions and we will just now show that this will now split up into different n j values and I will show that in a minute.

And 2 doublet P half will split up into two levels. So, this corresponds to m j is equal to 3 by 2. This is the j value, j is 3 by 2. So, the z component of the total angular momentum vector j z the Eigen values will be 3 by 2, half, minus half and minus 3 by 2. So, this is known as the Zeeman splitting or anomalous Zeeman effect.

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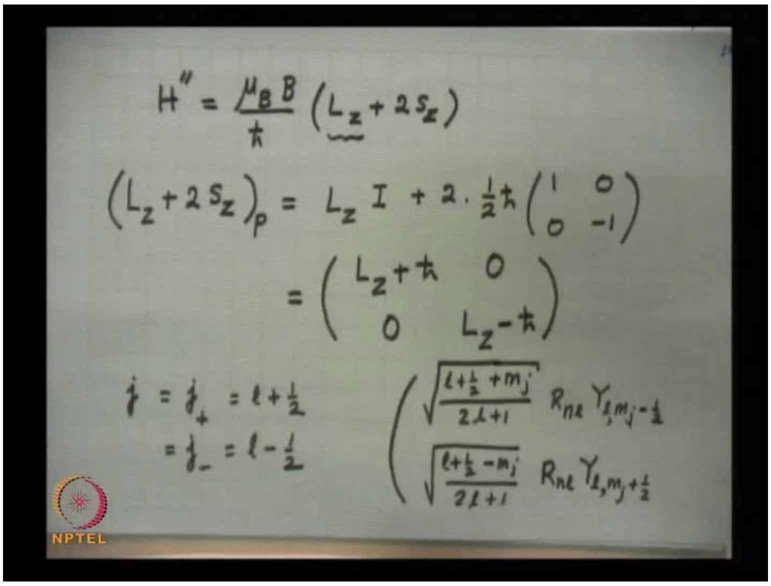

$$H'' = \frac{\mu_B B}{\hbar}\left(\underset{\sim}{L_z} + 2S_z\right)$$

$$\left(L_z + 2S_z\right)_p = L_z I + 2\cdot\frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$= \begin{pmatrix}L_z+\hbar & 0\\ 0 & L_z-\hbar\end{pmatrix}$$

$$j = j_+ = l + \frac{1}{2}$$

$$= j_- = l - \frac{1}{2}$$

$$\begin{pmatrix}\sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\, R_{nl}\, Y_{l,m_j-\frac{1}{2}}\\ \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\, R_{nl}\, Y_{l,m_j+\frac{1}{2}}\end{pmatrix}$$

Now, let me do it little more carefully. So, we have, we will take the Zeeman effect of say hydrogen like atom or a sodium atom. So, you have the perturbation due to… let me write it down as H double prime and that is equal to mu B, mu B is the Bohr magneton, mu B B by h cross L z plus 2 s z. Now, this part is due to the orbital motion. Because of the orbital motion, as I had explained earlier, it has a magnetic moment which is known as the orbital momentum, orbital angular, orbital magnetic moment and it interacts with the magnetic field B, which is assumed to be in the z direction. And then, the because of the intrinsic spin angular momentum of the electron, it has a magnetic moment. And, so therefore that interacts with the magnetic field resulting in this term.

So, what is the corresponding Pauli operator for that? So, you will have L z plus 2 s z. The Pauli operator will be L z times the unit matrix plus, 2 s z will be plus half h cross the sigma z matrix the Pauli z component of this Pauli matrix. That is, 1, 0, 0, minus 1. So, this becomes, if this is a unit matrix, so this will be L z plus h cross, 0, 0, L z minus h cross.

Now for this state, we must consider the phi functions. And, so let me consider, for example, j is equal to l plus half. So, as I had told you j can take two values; j plus j plus is equal to l plus half and j minus is equal to l minus half, of course when l is not equal to zero. When l is equal to 1, then it can take 1 plus half is 3 by 2, 1 minus half is half.

Now, corresponding to j equal to l plus half, what are the, what is the corresponding Pauli wave function? Now, this we had determined using Clebsch-Gordan coefficient; l plus half plus, I would like you to look up the 2 l plus 1 R n l Y l m j minus half and l plus half minus m j, i would like you to look up the chapter on on on Clebsch-Gordan coefficient, and where we had derived this Pauli wave functions R n l Y l m j plus half. Please see there is a comma here, there is a comma here. This is not m j minus half; it is m j plus half; m j can take 3 by 2 half etcetera. So, 3 by 2 minus half will be 1, this in Y l m, m has to be 0 or a positive or a negative integer. So, this is m j minus half and this is m j plus half.

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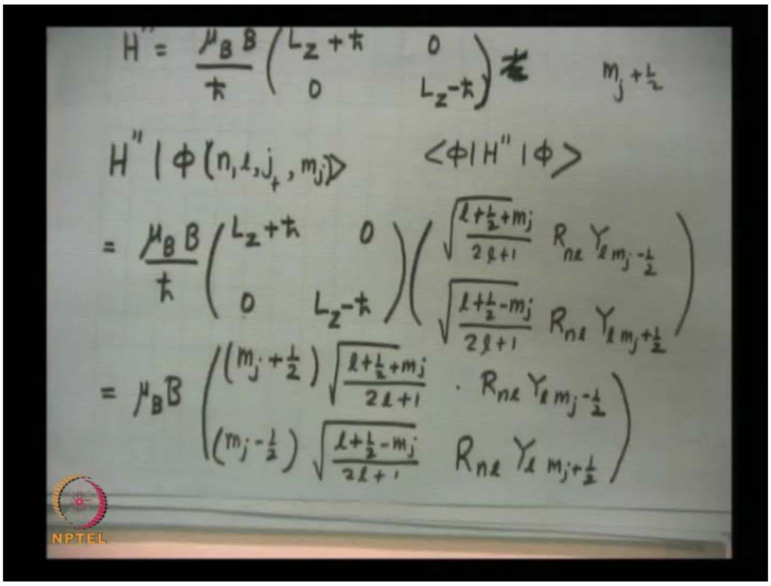

$$H'' = \frac{\mu_B B}{\hbar}\begin{pmatrix} L_z+\hbar & 0 \\ 0 & L_z-\hbar \end{pmatrix} \cancel{\hbar} \qquad m_j+\frac{1}{2}$$

$$H''\,|\phi(n,l,j_+,m_j)\rangle \qquad \langle\phi|H''|\phi\rangle$$

$$= \frac{\mu_B B}{\hbar}\begin{pmatrix} L_z+\hbar & 0 \\ 0 & L_z-\hbar \end{pmatrix}\begin{pmatrix} \sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\, R_{nl} Y_{l\,m_j-\frac{1}{2}} \\ \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\, R_{nl} Y_{l\,m_j+\frac{1}{2}} \end{pmatrix}$$

$$= \mu_B B \begin{pmatrix} (m_j+\frac{1}{2})\sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}} \cdot R_{nl} Y_{l\,m_j-\frac{1}{2}} \\ (m_j-\frac{1}{2})\sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\, R_{nl} Y_{l\,m_j+\frac{1}{2}} \end{pmatrix}$$

So, you... So, therefore, let us suppose this is my phi function. So, let me write it down H double prime is equal to mu B B by h cross L z plus 2. So, this is equal to L z plus h cross, 0, 0, L z minus h cross, multiplied by h cross. So, this is multiplied by h cross, so that h cross, no that is alright, this is L z plus...

Now, this operates. So, H double prime operates on this phi function. Let us suppose, we have phi, n, l, j plus, j plus m j; so, this will be H double prime. H this is mu B B by h cross. Please see this. L z, one just has to carefully do this. 0, 0, L z minus h cross operating on this l plus half plus m j plus divided by 2 l plus 1 R n l Y l m j minus half and then l plus half minus m j by 2 l plus 1 R n l Y l m j pus half. This is m j plus half; not j plus half. I am sure, all of you understand this.

So, if I if I if I operate this here, so we will get, please see this; L z will be m j minus half into h cross plus one. So, that is m j plus half. I hope I have done it right. And, h cross, h cross cancels out, so mu B B. And then, this is 0 times this. So, multiplied by this whole wave functions; l plus half plus m j plus 2 l plus 1 multiplied by R n l Y l m j minus half. And then, 0 times this; 0 L z minus h cross, that is m j plus half h cross minus h cross. So, therefore this is m j minus a half multiplied by l plus half.

If you do not do it yourself, you will never be able to understand. So, I would request all of you to work this out yourself. And, you will find so interesting. And, you will… everything. I am sure this is just a question of patiently. And then, bra phi the matrix element will be bra phi H double prime phi.

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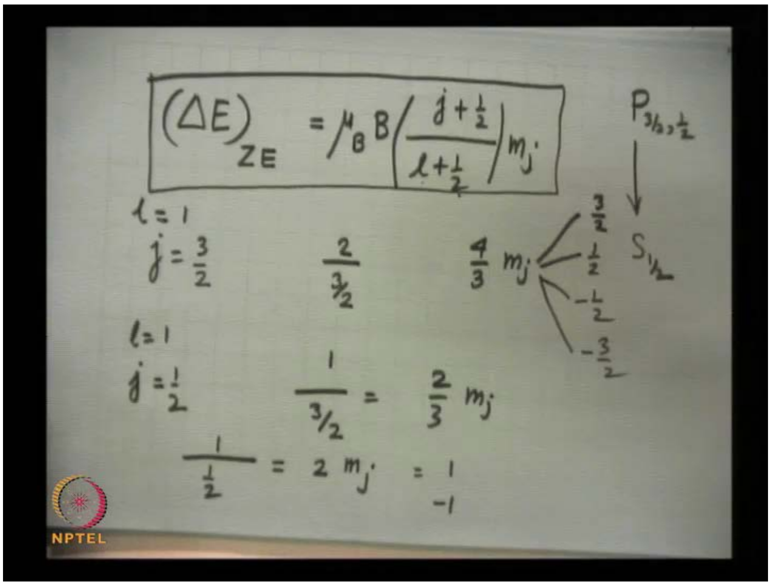

$$\boxed{(\Delta E)_{ZE} = \mu_B B\left(\frac{j+\frac{1}{2}}{l+\frac{1}{2}}\right)m_j}$$

$l=1$, $j=\frac{3}{2}$ $\quad \frac{2}{\frac{3}{2}} \quad \frac{4}{3}\, m_j$: $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$

$l=1$, $j=\frac{1}{2}$ $\quad \frac{1}{\frac{3}{2}} = \frac{2}{3}\, m_j$

$\frac{1}{\frac{1}{2}} = 2\, m_j \quad = 1, -1$

$P_{3/2,\frac{1}{2}} \rightarrow S_{1/2}$

So, you take the row coordinate of that, multiply that and carry out the integration. And, the final result is very simple. The final result; this is the delta E due to the anomalous Zeeman effect, this comes out to be… I would request all of you to work this out yourself. Comes out to be j plus half divided by l plus half m j.

So, this this splitting is, therefore proportional to… and, I had that slide somewhere. I hope I can find it. we the slide that. So, therefore j plus half divided by l plus half times m j. So, therefore let me go once more. Let me tell you that, here this is the fine structure splitting. So, here you have, for example, 3 doublet D 5 by 2. This is the j value. So, this j value is 5 by 2; the corresponding m value will be 5 by 2, 3 by 2, half, minus half, minus 3 by 2, minus 5 by 2.

So, you see. So, this is the n equal to… this is the Zeeman splitting of the D 1 and D 2 lines. Now, the D 1 and D 2 lines correspond to the 2 P state to the ground state 1 S. So, this leads to D 2 level state, lines. And, this level to, this level to this level represents the D 2 line; this level to this transition from this level to this level represents the D 1 line.

Now, please see that the j equal to 3 by 2 state splits up into four states; 3 by 2, half, this is 3 by 2, this is the z component of the total angular momentum vector, this is half, this is minus half and this is minus 3 by 2. And, the doublet P half state splits up into half and minus half. And, the splitting as I had shown is, it depends on l and also depends on j; so that, if j is equal to 3 by 2, this splitting is large. If j is equal to half, this splitting is small. I hope you understand this.

So, for these two states, this is half and this is minus half. And, let me consider this. So, for j is equal to 3 by 2 and l is equal to, let us suppose l is equal to 1. So, this term, so j is equal to 3 by 2. So, 3 by 2 plus half is 2 divided by 3 by 2. So, this is 4 by 3 m j. And, what are the possible values of m j? The possible values of m j are 3 by 2, half, minus half, minus 3 by 2. So, this line is 4 by 2 times 3 by 2, 4 by 3 times 3 by 2. So, that is. And, this is 4 by 3 times 1 by 2. So, so this splitting is three times this splitting.

And, when l becomes equal to zero or l becomes equal to 1, let us suppose and j becomes… So, l is 1 and j is equal to, let us suppose half. So, this becomes half plus half is 1 and l is 3 by 2. So, this becomes 2 by 3 m j. So, this is half of this. So, you can see this. This splitting, I have drawn to scale. This splitting is twice of that scale.

In this case, you have j is equal to half and l is equal to 0. So, if you have j is equal to half and l is equal to zero, so this will be 1 divided by half. So, this will be 2 times m j. So, you see, here the splitting is much more than here and m j can take half and minus half. So, two times 2 m j is 2 into half is 1 and 2 into minus half is minus 1. So, these are the splitting.

So, this figure. So, what I would request all of you is to use this formula to calculate the transition for the P state to the S state. And, So, P 3 by 2 and half to S half state and then this splits up. The P 3 by 2 state splits up into four levels and P half state splits up into two levels. doublet S R… leads to levels. And, this require, this results in the 6 plus, 3 plus 3, 6 plus 4 ten lines.

And, we had this this normal Zeeman Effect in which we had neglected the effect of the spin. So, it is applicable to… this actually happens for all singlet states. So, singlet D 2 state to singlet P 1 state. This is a spectrum of Cadmium and you have an equally space lines proportional to m values. And, notice that the splitting here is equal to the splitting here because this is proportional to the m value.

So, therefore we have developed the time independent perturbation theory. We first considered the examples from matrix algebra, and then we tried to put forward the care that we should take to deal with degenerate states. When we have degenerate states, then we have more than one wave function and we must try by intuition to choose those wave functions for which the perturbation H prime is diagonal.

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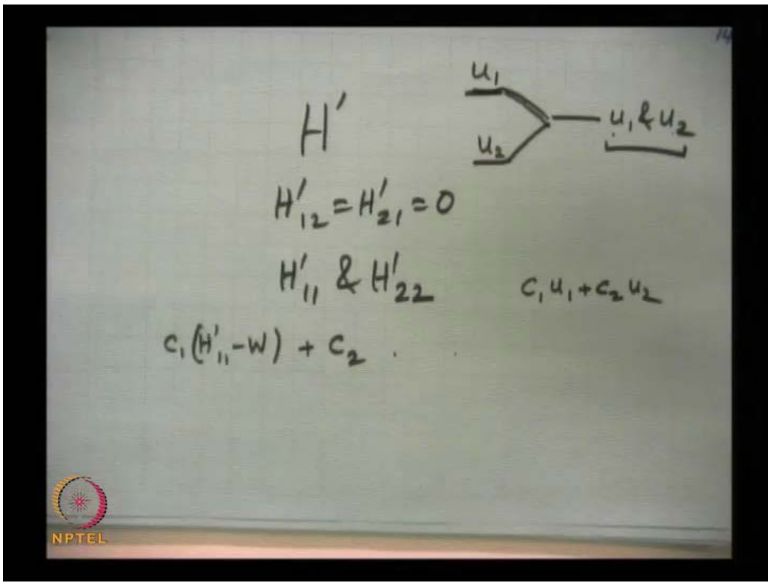

So, what I mean by; that is, that if I have a perturbation which is denoted by H prime, then and if we have two states u 1 and u 2 which correspond to a degenerating Eigen value. I must choose such a linear combination. So, is that H prime 1 2 and H prime 2 1 are 0. If I am successful to do that, then H prime 1 1 and H prime 2 2 are the perturbations. And, the corresponding Eigen functions will be… This level will split up into two states. And, the wave functions for that the zeroth order wave functions will be u 1 and u 2.

If we are unable to do that, then we choose a linear combination c 1 u 1 plus c 2 u 2 and form a set of two equations; c 1 H prime 1 1 minus w plus c 2 and so on. From the determinant equal to 0, find out the roots or values of w by setting the determinant equal to 0. And, for each value, we will find the ratio c 1 plus c 2 c 1 and c 2 c 2 by c 1. From that, we will get the wave functions of the split states; that is, if the perturbation goes to 0 what is the wave function to which it will collapse to.

So, in fact, we require these. We also consider the application of the Clebsch-Gordan coefficients by choosing appropriate wave functions, so that the wave functions that we choose are simultaneous Eigen functions of J square L square and s square. That is how we discuss the fine structure of spectral lines and then the Zeeman effect of hydrogen like atoms. Thank you.