

Basic Quantum Mechanics
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Module No # 10
Time Independent Perturbation Theory
Lecture No # 02
Time Independent Perturbation Theory (Contd.)

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$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + 1$$

$$H' = \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix} \quad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$H'_{11} = H'_{12} = \dots = \epsilon$$

$$c_1 (H'_{11} - W^{(0)}) + c_2 H'_{12} = 0 \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$c_1 H'_{21} + c_2 (H'_{22} - W^{(0)}) = 0$$

$$c_1 + c_2 = 0 \quad W^{(0)} = 0, 2\epsilon$$

$$c_2 = -c_1$$

In our last lecture, we had considered the hermitian matrix H naught which had 2, 4 degeneracy. We applied a perturbation; we framed the secular determinant and found out the first order perturbation to the Eigen values. The matrix that we had started out with H naught was equal to 1 0 0 1, which has Eigen value plus 1 and it is a 2, 4 degeneracy. And then, we said that, let this perturbation be very simple perturbation epsilon, epsilon, epsilon, and epsilon. And, we choose the base states as ket 1 is equal to 1 0 and ket 2 is equal to 0 1.

So, my, all the matrix element H prime 1 1, H prime 1 2, H prime 2 1, H prime 2 2; they are all equal to epsilon. So, we set up the secular equation and we found that $c_1 H$ prime

1 1, the equation is $H'_{11} - W_1 + c_2 H'_{12}$ is equal to 0 and then $c_1 H'_{21} + c_2 H'_{22}$.

If you understand this part clearly, then everything will become clearer. So, all these matrix elements are epsilon. And, we found that the values of W_1 was either 0 or 2 epsilon. So, let me consider 0 first. So, W_1 is 0. So, we have c_1 epsilon plus c_2 epsilon is 0. So, c_1 plus c_2 is equal to 0.

Even this equation will give me the same thing. W_1 is 0, this is, this is epsilon, this is epsilon c_1 plus c_2 is equal to 0. So, therefore c_2 is equal to minus c_1 . So, my Eigen state that corresponding to the level, the Eigen values splits and the Eigen function is 1 minus 1 divided by under root of 2. Under root of 2 is just to normalize it. You can put minus 1 and 1 also. That is also...

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$$-\epsilon C_1 + C_2 \epsilon = 0 \quad C_1 = C_2$$

$$|4\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \& \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \& |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$H'_{11} = \langle 1 | H' | 1 \rangle = \frac{1}{2} \begin{pmatrix} 1 & 1 \end{pmatrix} \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 2\epsilon$$

Now, we take them 2 epsilon, W_1 is equal to 2 epsilon. So, we have if W_1 is equal to 2 epsilon, so H'_{11} is epsilon, epsilon minus 2 epsilon is minus epsilon. So, minus epsilon c_1 plus c_2 epsilon, this is equal to 0. So, epsilon epsilon cancels out. Sorry, c_1 . So, c_1 becomes equal to c_2 . So, my Eigen ket becomes, so it is $c_1 u_1$ plus $c_2 u_2$. So, this one c_1 is equal to c_2 . So, my Eigen ket becomes 1 1 under root...

So, therefore you have, the degenerate state had only one Eigen value 1 plus 1. When you apply the perturbation, it splits into two states; one the perturbation is 0 and the

second is 2 epsilon. So, this splitting is 2 epsilon. This wave function is, say ket 3. Ket 3 is equal to 1 minus 1 divided by root 2. And, this wave function, say ket 4. This is equal to 1 over root 2, 1 1.

So, this is a 2, 4 degenerate state. It splits into two states. Let me find out the exact. The one more thing that I want to mention that, we could have equally well started with these Eigen kets. Let us suppose, instead of 1 0 and 0 1, we had started with this kets; that is, we had assumed that 1 was equal to under root of 2 1 1 and 2 is equal to 1 over root 2 1 minus 1.

Now notice that, what is H prime 1 1? H prime 1 1 is equal to? So, this is 1 H prime 1. So, this is equal to half 1, the bra 1 will be 1 1; epsilon, epsilon, epsilon, epsilon; 1 1. So, this will be epsilon plus epsilon, 2 epsilon here and 2 epsilon here. So, you, simple analysis will show that this will be equal to 2 epsilon. It will come out to be 4 epsilon.

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$$H'_{12} = \langle 1 | H' | 2 \rangle = \frac{1}{2} (1 \ 1) \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$= 0$$

$$H'_{12} = H'_{21} = 0 \quad H'_{22} = 0$$

$$H' = \begin{pmatrix} 2\epsilon & 0 \\ 0 & 0 \end{pmatrix}$$

Then, let me calculate the other Eigen values. The other matrix elements; H prime 1 2, H prime 1 2 will be bracket 1 H prime 2. And therefore, this will be 1 by 2; 1, 1; epsilon, epsilon, epsilon, epsilon and 1 minus 1.

Now, please see, epsilon minus epsilon; that is 0. And, epsilon minus epsilon that is 0. So, this becomes 0. In fact, in fact all other matrix elements are 0. So that, H prime 1 2 is equal to H prime 2 1 is equal to 0 and H prime 2 2 also happens to be 0.

So, if you write down the H prime matrix, then it will be 2 epsilon, 0, 0, and 0. It is a diagonal matrix. And, the Eigen values are 2 epsilon and 0. And, the off diagonal elements are 0. So, we now have a representation in which we are chosen our base states such that, H prime is a diagonal matrix. And, so therefore, if we choose initially those wave functions for which H prime is a diagonal matrix, then the diagonal elements will be the Eigen values, will be the perturbation. And, this also follows from if you, if you recollect that we had started with this. And then, we said that we multiplied by, we wrote down psi n 1 as $E_m 1 u_m$. Then, we multiplied by u_k^* and had obtained this equation.

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The slide shows the following handwritten equations:

$$\sum_m a_m E_m \delta_{km} + H'_{kn} = W_n \delta_{kn} + E_n \sum_m a_m \delta_{km} \quad m \neq k$$

$$H'_{kn} \equiv \int u_k^* H' u_n d\tau = \langle k | H' | n \rangle$$

$$a_k^{(0)} E_k + H'_{kn} = W_n \delta_{kn} + E_n a_k^{(0)}$$

For $k \neq n$:

$$E_k = E_n$$

$$H'_{kn} = 0$$

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Now, if you just look at this equation, then, first we had considered k is equal to n , but let me consider the case when k is not equal to n , but E_k is equal to E_n . That is, I am considering multiplication between those states for which the energies are equal, but the wave functions are different. So, E_k is equal to E_n . So, this term gets cancelled with this term and then it will become $W_n 1$. So, therefore k is not equal to n . So, this term is 0.

So, my H'_{kn} must necessarily be 0. That means... And then, if I had chosen that representation in which my H' matrix is diagonal, then the diagonal elements will represent the perturbation to this state.

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$$H' = \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix} \quad H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$H = \begin{pmatrix} 1+\epsilon & \epsilon \\ \epsilon & 1+\epsilon \end{pmatrix} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\begin{vmatrix} 1+\epsilon-\lambda & \epsilon \\ \epsilon & 1+\epsilon-\lambda \end{vmatrix} = 0 \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$(1+\epsilon-\lambda)^2 = \epsilon^2$$

$$\lambda - (1+\epsilon) = \pm \epsilon$$

$$\lambda = 1+\epsilon \pm \epsilon$$

$$= 1+2\epsilon$$

$$= 1$$

We will illustrate this again if you have not followed through another example. Now, before I continue further, let me also mention that the total matrix H is given by epsilon, sorry, this is, sorry, H naught plus H' . So, H' prime was equal to H' . This thing and H naught was equal to 1 0 0 1. So, the total matrix was equal to 1 plus epsilon, epsilon, epsilon, 1 plus epsilon. And therefore, the Eigen values are obtained by 1 plus epsilon minus lambda, epsilon, epsilon, 1 plus epsilon minus lambda. This is equal to 0.

So, you have 1 plus epsilon minus lambda whole square is equal to epsilon square. So, you can write down lambda minus 1 plus epsilon is equal to plus minus epsilon. So, you will have, if I take it to that side, so you will get lambda is equal to 1 plus epsilon plus minus epsilon. So, you have here two Eigen values. One is for the upper state. This 1 plus 2 epsilon and the other is just one.

So, these are the rigorously correct Eigen values for H . And, if you find out the corresponding Eigen kets, then **there it will be** $\frac{1}{\sqrt{2}}$ 1 1 under the root 2 and $\frac{1}{\sqrt{2}}$ 1 minus 1. We also say that by introducing this perturbation, the degeneracy has got lifted.

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stark effect

$$u_1 = R_{20} Y_{00} = \frac{1}{\sqrt{4\pi}} R_{20}(r)$$

$$u_2 = R_{21} Y_{10} = \sqrt{\frac{3}{4\pi}} R_{21}(r) \cos \theta$$

$$u_3 = R_{21} Y_{11} = -\sqrt{\frac{3}{8\pi}} R_{21} \sin \theta e^{i\phi} E_1 \quad n=1 \text{ --- } u_0$$

$$u_4 = R_{21} Y_{1,-1} = +\sqrt{\frac{3}{8\pi}} R_{21}(r) \sin \theta e^{-i\phi}$$

R_{nl}

$n=2 \quad l=1 \text{ --- } (4)$
 $l=0$

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Now, let me consider another example, a very important example and that is the example of the **stark** effect. Now, we have here, **we have here** let us consider the hydrogen atom problem. And, we represent the ground state by u_0 . The first excited state, this is n is equal to 1, the ground state has an energy equal to E_1 , which we know **has** to be minus 13.6 electron volts. It is a minus number. And this, the n is equal to two state is 4, 4 degenerate. So, n is equal to 2, then you have l is equal to 1 or l is equal to 0.

When n is equal to 1, you will have n equal to plus 1 0 minus 1. So, this will have 4, 4 degeneracy **4, 4 degeneracy**. So, you will have, you will have four wave functions; u_1 and that is, first let me consider that l is equal to 0. So, $R_{20} Y_{00}$; n is equal to 2, l is equal to 1, l is equal to 0.

When l is equal to 0, n must be 0. So, Y_{00} is nothing but under root of 4 pi. So, this is 1 over 4 pi R_{20} of r . Then u_2 will be R_{21} and **when** l is 1, this is R_{nl} **R_{nl}** . l is 1, so **Y_n** can be 0 and this will be under root of 3 by 4 pi, Y_{10} we have derived R_{21} of r cos theta. And then, we have another wave function $R_{21} Y_{11}$ and that is equal to minus under root of 3 by 8 pi R_{21} of r sin theta. And, since this is 1, so this is e to the power of $i\phi$ and u_4 is equal to, this is the **stark** effect problem that we will be considering; **stark** effect in hydrogen atom, $R_{21} Y_{1,-1}$. So, m is equal to minus 1, so sin to the power of 1; that is sin theta, but this will be plus under root of 3 by 8 pi R_{21} of r sin theta e to the power of minus $i\phi$.

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Handwritten equations on a slide:

$$\begin{aligned} \psi_{200} u_1 &= R_{20} Y_{00} = \frac{1}{\sqrt{4\pi}} R_{20}(r); & n=2, l=1 \\ \psi_{210} u_2 &= R_{21} Y_{10} = \sqrt{\frac{3}{4\pi}} R_{21}(r) \cos \theta; & \psi_{n\ell m} \\ \psi_{211} u_3 &= R_{21} Y_{11} = -\sqrt{\frac{3}{8\pi}} R_{21}(r) \sin \theta e^{i\phi}; & \psi \\ \psi_{21-1} u_4 &= R_{21} Y_{1-1} = \sqrt{\frac{3}{8\pi}} R_{21}(r) \sin \theta e^{-i\phi}; \end{aligned}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}} \frac{1}{a_0^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} = R_{20}(\lambda)$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}} \frac{1}{a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$

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So, these are the four wave functions that I have typed out. So u_1 , this is the n equal to 2 **n equal to two**. So, we will have l equal to 1. So, if you write down $\psi_{n\ell m}$, so you will have, this is **this is** the first is ψ_{200} , this is ψ_{210} , this is ψ_{211} and this is ψ_{21-1} . And, R_{20} of r and R_{21} of r are known functions. These are the radial functions, which we had expressed in terms of the confluent hyper geometric functions.

So, these are the wave functions that we have chosen for the **for the** degenerate state. And of course, for since there is a 4, 4 degenerate state, any linear combination of them will be also, will also be a wave function.

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The image shows a handwritten derivation on a grid background. At the top left, two position vectors \vec{r}_1 and \vec{r}_2 are shown. To their right, the dipole moment is defined as $\vec{P} = q(\vec{r}_2 - \vec{r}_1)$. Below this, the relative vector is given as $\vec{r} = \vec{r}_1 - \vec{r}_2$. The electric field \vec{E} is shown, and the perturbation Hamiltonian is derived as $H' = -\vec{P} \cdot \vec{E}$. This is then simplified to $H' = qEz$ and finally to $H' = qEr \cos \theta$, which is boxed. To the right of the boxed equation, the basis states u_1, u_2, u_3, u_4 are listed. At the bottom, the matrix elements H'_{ij} are shown, with H'_{11} circled and labeled (16).

Now, let me put the hydrogen atom in an electric field. Now hydrogen atom, let us suppose hydrogen atom consists of an electron and a proton. Let the electron position coordinate is r_1 and the proton position coordinate is... So, it has a dipole moment is equal to q , where q is the... And, r_2 is the position vector of the proton minus r_1 .

So, if I write down the relative vector of the electron with respect to this is r . This is the relative coordinate that we had introduced while solving the hydrogen atom problem. So, this will be minus q r dot. This is the dipole moment of the hydrogen atom. And, in the presence of the electric field, the perturbation is minus P dot the electric field, I am **I am** using a script notation, so that we use the notation capital E for the energy. So, this is the electric field.

So, let us suppose, the electric field is in the z direction. So, E is equal to the magnitude of E in the z direction. So, the z direction will be therefore $q E z$. This is the perturbation. And, this z in spherical polar coordinates is **just $r \cos \theta$** . So, this is my perturbation.

In the presence of an electric field, this is the perturbation. In the presence of magnetic field, there will be another expression for H' . We will consider relativistic correction and spin orbit correction. In each case, the Hamiltonian will be different. For the Stark effect problem, the H' is given by this.

So, now I have a 4, 4 degenerate state. u_1, u_2, u_3 and u_4 . So, the recipe is, we found out first all the matrix elements H'_{ij} ; that is, $H'_{11}, H'_{12}, H'_{21}, H'_{13}, H'_{14}, H'_{44}$. So, **when we just**, sixteen such elements that we have to calculate.

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$$H'_{ij} = \langle i | H' | j \rangle \quad \begin{matrix} i = 1, \dots, 4 \\ j = 1, \dots, 4 \end{matrix}$$

(16)

$$u_3 = -\sqrt{\frac{3}{8\pi}} R_{21}(r) \sin\theta e^{i\phi}$$

$$u_1 = \frac{1}{\sqrt{4\pi}} R_{20}(r)$$

$$H' = qEr \cos\theta$$

$$H'_{13} = \langle 1 | H' | 3 \rangle = \int u_1^* H' u_3 d\tau$$

$$= -\frac{1}{\sqrt{4\pi}} \sqrt{\frac{3}{8\pi}} \cdot \int_0^\infty R_{20} R_{21} r \cdot r^2 dr \int \sin^2\theta \cos\theta d\theta$$

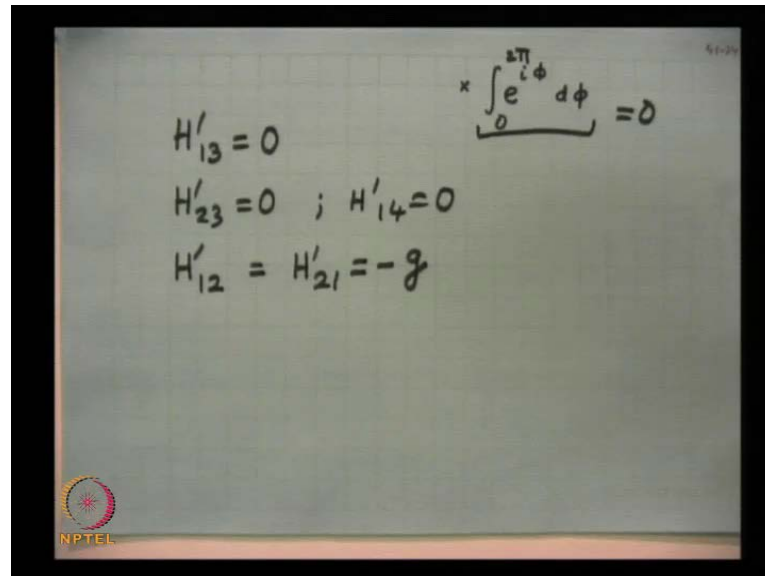
So, we first calculate H'_{ij} , where H' and i goes from 1 to 4 and j goes from 1 to 4. So, we will have a total of sixteen matrix elements. And, let me, it is a **book force** calculation. So, let me first calculate this matrix element. So, my u_3 , u_3 is say minus under root of 3 by 8 pi, let me write it down R_{21} of $r \sin\theta e^{i\phi}$. And, u_1 is, let us suppose $1/\sqrt{4\pi} R_{20}$ of r . This is, this is **psi 2 n l 1 n l m** and this is **psi 2 0 0** and my H' is equal to $qEr \cos\theta$.

So, let me calculate, say H'_{31} or 13 , does not matter. So, this is **bra 1 H prime ket 3**; that is, this is a short hand form for writing that $u_1^* H' u_3 d\tau$. So, u_1^* is, let me write it down. So, H' is $qEr \cos\theta$. So, let me write down what is u_1 . So, $1/\sqrt{4\pi}$, u_3 will be minus under root of 3 by 8 pi. You have to patiently write it.

And then, first the R integral; so, R integral will be $R_{20} R_{21}$ times r square times r here, that is r and then the volume element will consider r square dr from 0 to infinity. The theta integral will be **will be** $\sin\theta$ and the volume element consist of r square dr

sin theta d theta d phi. So, this is d tau. So, I have taken r square d r. So, sin theta d theta multiplied by sin theta. So, sin square theta cos theta d theta

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Handwritten equations on a whiteboard:

$$H'_{13} = 0$$

$$H'_{23} = 0 ; H'_{14} = 0$$

$$H'_{12} = H'_{21} = -g$$

Integral equation:

$$\int_0^{2\pi} e^{i\phi} d\phi = 0$$

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And then, the phi integral will be, that is the most important. It will be e to the power of i phi multiplied by e to the power of i phi u 1 e to the power of i phi d phi from 0 to 2 pi. This limit will be from 0 to 2 pi. Now, because of this, **this** will be 0. So, we will have, H prime 1 3 will come out to be 0. Similarly, if you calculate H prime 2 3 that will be 0, H prime 1 4 that will be 0. The only two non-vanishing matrix element will be H prime 1 2 is equal to H prime 2 1 is equal to a constant quantity which I denote by g.

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$$\begin{aligned}
 H'_{23} &= \iiint u_2^* H' u_3 d\tau \quad d\tau = r^2 dr \sin\theta d\theta d\phi \\
 &= \iiint \left[\sqrt{\frac{3}{4\pi}} R_{21}(r) \cos\theta \right] [q e^{i\phi} \cos\theta] \\
 &\quad \times \left[-\sqrt{\frac{3}{8\pi}} R_{21}(r) \sin\theta e^{i\phi} \right] r^2 dr \sin\theta d\theta d\phi \\
 &= 0
 \end{aligned}$$

$\int_0^{2\pi} e^{i\phi} d\phi = 0$

So, you see, let me **let me** tell you once again that for example, in this I have calculated H'_{23} . So, H'_{23} is $u_2^* H' u_3 d\tau$ and what is $d\tau$? This $d\tau$ is, $d\tau$ is $r^2 dr \sin\theta d\theta d\phi$. And, this is actually a triple integral **triple integral** as I have shown here.

So, the R ... So, u_2 will be u_2^* , the **R** and theta part is this. **r** theta phi, **the** this is the perturbation. This is u_3 multiplied by $r^2 dr \sin\theta d\phi$. Because of this term $e^{i\phi} d\phi$, this integral from 0 to 2π is just 1. I am **sorry**, this is just 0. I am just sorry, this is 0. So, the total integral comes out to be 0.

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$$\begin{aligned}
 H'_{12} &= \int u_1^* H' u_2 d\tau \quad Y_{00} = \frac{1}{\sqrt{4\pi}} \\
 &= \frac{\sqrt{3}(qE)}{4\pi} \int_0^\infty \frac{1}{\sqrt{2}} \frac{1}{2\sqrt{6}a_0^3} \frac{1}{a_0} r^2 \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} r^2 dr \\
 &\quad \times \int_0^\infty \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi \quad 2\pi \\
 &= -3qEa_0 = -g \quad a_0 = \frac{\hbar^2}{\mu e^2} \\
 H'_{12} &= H'_{21} = -g; \quad g = 3qEa_0
 \end{aligned}$$

Similarly, however the only non-vanishing integral is H'_{12} . So, you calculate this is multiplication of **I said**.... So, both of them is Y_{00} and this is also Y_{00} . So, Y_{00} will be, the angular part will be Y_{00} . So, that is $1/\sqrt{4\pi}$ and this integral will be just, you have to calculate this. **This** integral will be 2π and there is a **r** cos theta term which is because of the perturbation and it will come out like this. So, that comes out to be g .

So, only non-vanishing is, one has to spend some time in **...force** calculating these on the only two non-vanishing matrix elements will be H'_{21} is equal to minus g , where g is equal to $3qE$, E is the strength of the electric field and a_0 is the ...radius. a_0 is $\hbar^2/\mu e^2$.

So, once again I have a 4, 4 degenerate state and these are the four Eigen functions; u_1 , u_2 , u_3 , u_4 . And, R_{20} and R_{21} are given by. So, we could have chosen any linear combination of them also. Now, we have this perturbation H' , which is equal to H' which is equal to $qEr \cos\theta$.

So, we **have** this and then we calculate it **laboriously** all the matrix elements. And, we found that all the matrix elements are 0 excepting for H'_{12} and H'_{21} . So, therefore if I write this down, so you may remember that we have to, we have to write down this equation.

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$$\begin{aligned}
 c_1 (H'_{11} - W_2^{(1)}) + c_2 H'_{12} + c_3 H'_{13} + c_4 H'_{14} &= 0 \\
 c_1 H'_{21} + c_2 (H'_{22} - W_2^{(1)}) + c_3 H'_{23} + c_4 H'_{24} &= 0 \\
 c_1 H'_{31} + c_2 H'_{32} + c_3 (H'_{33} - W_2^{(1)}) + c_4 H'_{34} &= 0 \\
 c_1 H'_{41} + c_2 H'_{42} + c_3 H'_{43} + c_4 (H'_{44} - W_2^{(1)}) &= 0
 \end{aligned}$$

$$\begin{vmatrix}
 H'_{11} - W_2^{(1)} & H'_{12} & H'_{13} & H'_{14} \\
 H'_{21} & H'_{22} - W_2^{(1)} & H'_{23} & H'_{24} \\
 H'_{31} & H'_{32} & H'_{33} - W_2^{(1)} & H'_{34} \\
 H'_{41} & H'_{42} & H'_{43} & H'_{44} - W_2^{(1)}
 \end{vmatrix} = 0$$

We said that if it is a 3, 4 degenerate state, you will have a set of three equations; if you have a 2, 4 degeneracy, you will have a set of two equations; if you have a set of 3, 4 degenerate state, you will have a set of three equations; if you have a 4, 4 degenerate state, you will have a set of four equations.

Now, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0, this term is 0. So, only... So, in general we **had** to, if all of them are non-zero, this is the determinant that we have to solve. But, **let me do it yeah yeah** let me do it, let me take the values of the different matrix elements.

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$$H'_{12} = H'_{21} = -g$$

$$\begin{bmatrix} -c_1 W_2^{(1)} & -c_2 g \\ -g c_1 & -c_2 W_2^{(1)} \end{bmatrix} = 0$$

$$\begin{bmatrix} c_3 (-W_2^{(1)}) \\ c_4 (-W_2^{(1)}) \end{bmatrix} = 0$$

$$W_2^{(1)2} = g^2 \Rightarrow W_2^{(1)} = \pm g$$

$W_2^{(1)} = 0$ then c_3 & c_4 can be arbitrary

So, we will have H'_{12} and H'_{21} . H'_{12} is equal to H'_{21} is equal to minus g . So, please see this. My objective is to calculate the perturbation. So, please see, these four equations simplify to c_1 minus sign $W_2^{(1)}$ is the first term, minus $c_2 g$ plus 0 plus 0. So, this is equal to 0. The second term is c_1 minus g minus $c_2 W_2^{(1)}$, this is equal to 0. Then, c_3 multiplied by minus $W_2^{(1)}$, this is equal to 0 and similarly c_4 is also like that.

Actually, we will have a determinant like this; four by four determinant. But, it simplifies because these **are** two are coupled and these two are not coupled. But, we can say these two equations tell us that, either c_3 is 0 or $W_2^{(1)}$ is 0.

So, the first 2 equations tells us that $W_2^{(1)2}$ is equal to g^2 . So, the perturbation is $W_2^{(1)}$ is equal to plus minus g . The second tells us that if $W_2^{(1)}$ is anything else other than 0, then c_3 must be 0, c_4 must be 0. But, if I chose $W_2^{(1)}$ is equal to 0, **then c_3** then c_3 and c_4 can be arbitrary.

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Handwritten mathematical derivation on a whiteboard:

$$\begin{aligned}
 c_1 W_2^{(1)} + c_2 g &= 0 \\
 c_1 g + c_2 W_2^{(1)} &= 0 \\
 W_2^{(1)2} &= g^2 \quad W_2^{(1)} = \pm g \\
 \\
 W_2^{(1)} = +g &\Rightarrow \begin{aligned} c_2 &= -c_1 \\ c_3, c_4 &= 0 \end{aligned} \quad \frac{u_1 - u_2}{\sqrt{2}} \\
 W_2^{(1)} = -g &\Rightarrow \begin{aligned} c_1 &= c_2 \\ c_3, c_4 &= 0 \end{aligned} \quad \frac{u_1 + u_2}{\sqrt{2}} \\
 W_2^{(1)} = 0 &\quad c_3 \text{ \& \& } c_4
 \end{aligned}$$

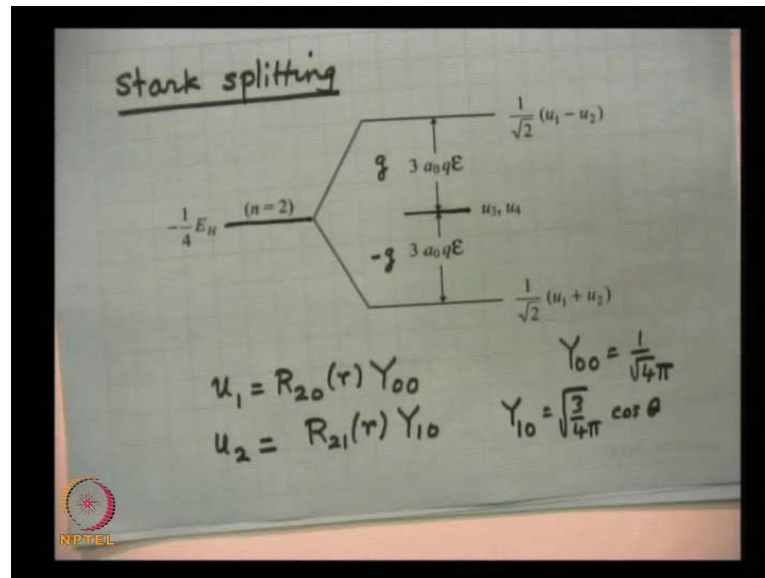
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Now, first let me write down the first two equations. So, if I **take the** take the minus sign out, so we get $c_1 W_2^{(1)} + c_2 g = 0$, $c_1 g + c_2 W_2^{(1)} = 0$. So, the determinant must be zero. So, therefore $W_2^{(1)2}$ will be equal to g^2 and then $W_2^{(1)}$ is equal to plus minus g .

For plus g ; so, for $W_2^{(1)}$ equal to plus g , we will have c_2 will be equal to minus c_1 and my wave function will be $u_1 - u_2$ by root 2. And, for $W_2^{(1)}$ equal to minus g , c_1 is equal to c_2 . I think I am right. This is $u_1 + u_2$ is divided by root 2. Root 2 factor is just for normalization.

Now, the other two equations, these 2 equations tells us $W_2^{(1)}$ is 0. If $W_2^{(1)}$ is 0, then c_1 must be 0, c_2 must be zero. So, $W_2^{(1)}$ is plus g , then c_3, c_4 must be 0. c_3, c_4 must be 0 and the four roots are, therefore $W_2^{(1)}$ is equal to 0, then c_3 and c_4 can be arbitrary.

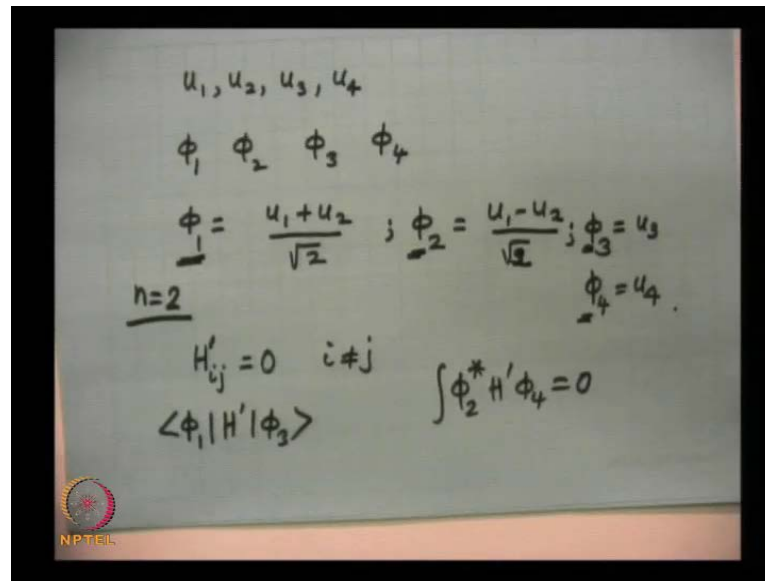
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So, therefore we obtain the following. That, this is the n equal to 2 state. This is plus g and this is minus g . So, the n equal to 2 state, of course I am neglecting spin. Splits into three states; the first, this u_3 and u_4 , the first order perturbation is 0. And, so for this the degeneracy is not lifted. But, for the other, **the** there is, this two states which split the function are u_1 plus u_2 by root 2 and u_1 minus u_2 by root 2. And, the question arises as we had mentioned that, what is u_1 and **what is** what are u_1 and u_2 ? We had mentioned that u_1 is $R_{20} Y_{00}$, $R_{21} Y_{10}$.

So, u_1 as you recall was R_{20} of $R Y_{00}$ of θ and ϕ . And, Y_{00} , as you remember is just $1/\sqrt{4\pi}$. This is spherical harmonic. And, u_2 is equal to R_{21} of r and Y_{10} and what is Y_{10} ? That is just $\sqrt{3/4\pi} \cos \theta$. So, they both correspond to n equal to 0 states. So, this is, this splitting of the n equal to 2 state is known as the stark splitting **stark splitting**.

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$$u_1, u_2, u_3, u_4$$

$$\phi_1, \phi_2, \phi_3, \phi_4$$

$$\phi_1 = \frac{u_1 + u_2}{\sqrt{2}}; \phi_2 = \frac{u_1 - u_2}{\sqrt{2}}; \phi_3 = u_3$$

$$\phi_4 = u_4$$

$$n=2$$

$$H'_{ij} = 0 \quad i \neq j$$

$$\langle \phi_1 | H' | \phi_3 \rangle$$

$$\int \phi_2^* H' \phi_4 = 0$$

Now, I leave it as an exercise for you that, instead of **instead of** u_1, u_2, u_3, u_4 , you start with these wave functions; $\phi_1, \phi_2, \phi_3, \phi_4$. Where, ϕ_1 is equal to u_1 plus u_2 by root 2; ϕ_2 is equal to u_1 minus u_2 by root 2; ϕ_3 is equal to u_3 and ϕ_4 is equal to u_4 .

If we start because these are also well behaved Eigen functions, orthonormal Eigen functions, **sorry**, this is square root of 2; orthonormal Eigen functions corresponding to the n equal to 2 states. These are the four linearly independent orthonormal set of functions.

I leave it as an exercise for you to show that H'_{ij} is equal to 0, if i is not equal to j ; that is, if we choose ϕ_1, ϕ_2, ϕ_3 and ϕ_4 as the base vectors, then any matrix element like ϕ_1, H' , ϕ_3 or say integral $\phi_2^* H' \phi_4$, anyone, that is 0. Only the diagonal terms survive.

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$$\begin{aligned} \int \phi_1^* H' \phi_1 d\tau &= -g \\ \int \phi_2^* H' \phi_2 d\tau &= +g \\ \int \phi_3^* H' \phi_3 d\tau &= 0 \\ \int \phi_4^* H' \phi_4 d\tau &= 0 \end{aligned}$$

$$H' = qEz = qEr \cos \theta$$

$$\begin{vmatrix} -g - W^{(1)} & 0 & 0 & 0 \\ 0 & +g - W^{(1)} & 0 & 0 \\ 0 & 0 & -W^{(1)} & 0 \\ 0 & 0 & 0 & -W^{(1)} \end{vmatrix} = 0$$

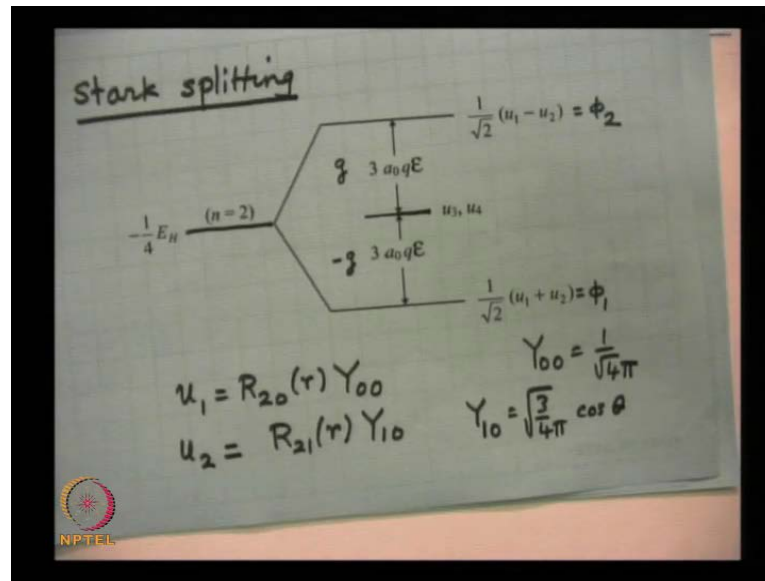
$$W^{(1)} = -g, +g, 0, 0$$

And, you will find that the two terms that will survive will be **will be**, say **phi 1** phi 1 star H prime phi 1 d tau, this will be come out to be minus g. And, phi 2 star H prime phi 2 d tau, this will be plus g. Phi 3 star H prime phi 3 d tau, this will be 0 and phi 4 star, sorry, H prime phi 4 d tau is equal to 0.

So, we have **an** all other matrix element. So, we, all other matrix element are 0. And, of course I have H prime is equal to q E z; that is, equal to q E r cos theta. So, we will have... So, only the diagonal terms will be there and my secular matrix will be minus g minus W 1, 0, 0, 0. This will be 0, then 0, plus g minus W 1, 0, 0 and then 0, 0, minus W 1, 0, 0, 0, 0, minus W 1. And, the Eigen values, the perturbation therefore will be, W 1 will be minus g, plus g, 0 and 0.

So, we then, if we start out with a representation in which H prime is diagonal, if we start out **with a** with those set of unit vectors in which H prime is diagonal, then, when it is... and the diagonal elements will represent the perturbation.

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So, in this particular case, the diagonal, **those are** this is ϕ_1 we had chosen and this is ϕ_2 . We then, consider another simple problem and that is **and that is, that** a hydrogen atom will neglect spin. For hydrogen atom, we cannot neglect spin. But, let us suppose we neglect spin. And, we assume a magnetic field in the z direction, now if I apply a magnetic field in the z direction, then **then** the perturbation will be the, you see for the hydrogen atom, you have here a proton and an electron is **a in the Bohr's** model you can assume that it is rotating in a circular orbit. So, if I am sitting on the electron, the proton is rotating at this thing. So, because of the orbital motion, there is a magnetic moment, there is a magnetic field and there is a magnetic moment which interacts with the magnetic field.

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

$$\vec{B} = B \hat{z}$$

$$H' = \frac{qB}{2m} L_z$$

$$H' = \frac{\mu_B B}{\hbar} L_z$$

$$\mu_B = \frac{q\hbar}{2m}$$

$$= 9.274 \times 10^{-24} \text{ J/T}$$

$$H_0 \psi_{nlm} = E_n \psi_{nlm}$$

$$\psi_{nlm} = R_{nl} Y_{lm}$$

$$L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

$$L_z Y_{lm} = m\hbar Y_{lm}$$

And, and the perturbation is equal to minus the magnetic moment times, the magnetic moment due to the orbital motion of the electron multiplied by B. And, this comes out to be plus q B by 2 m; m is the mass of the electron multiplied by L z.

I am assuming that, that the B field is in the z direction. So, this we usually write it as mu B B by h cross L z and what is mu B? mu B is equal to q h cross by 2 m is known as the Bohr magneton. And, the value is 9.274 into 10 to the power of minus 24 joules per tesla.

So, I consider the orbital motion of the electron, I neglect that the electron itself has a magnetic moment because of the orbital motion of the electron, it has a, it sees the, it sees a magnetic moment because of the orbital motion. And therefore, there is an interaction energy with the, when a magnetic field is applied and that interaction energy is given by this. So, mu B is a constant, B is a constant and of course, h cross is a constant.

Now, the, I have a magnetic a field, static magnetic field which is applied in the z direction. Now, the in the hydrogen atom problem, you have H naught psi n l m is equal to E s of n psi n l m. And therefore, psi n l m, as we all know is R n l Y l m. And, you recall that, Y l m are known as the spherical harmonics. The spherical harmonics are simultaneous Eigen functions of L square. This is equal to l into l plus 1 h cross square Y l m. And, L z Y l m, this spherical harmonics are also simultaneous Eigen functions of L z; m h cross Y l m. So, the hydrogen atom wave functions are Eigen functions of the

operator L_z . So, when L_z or H' operates on this, so please see. That $L_z Y_{lm}$ is equal to $m \hbar$ times Y_{lm} .

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$$H' = \frac{\mu_B B}{\hbar} L_z$$

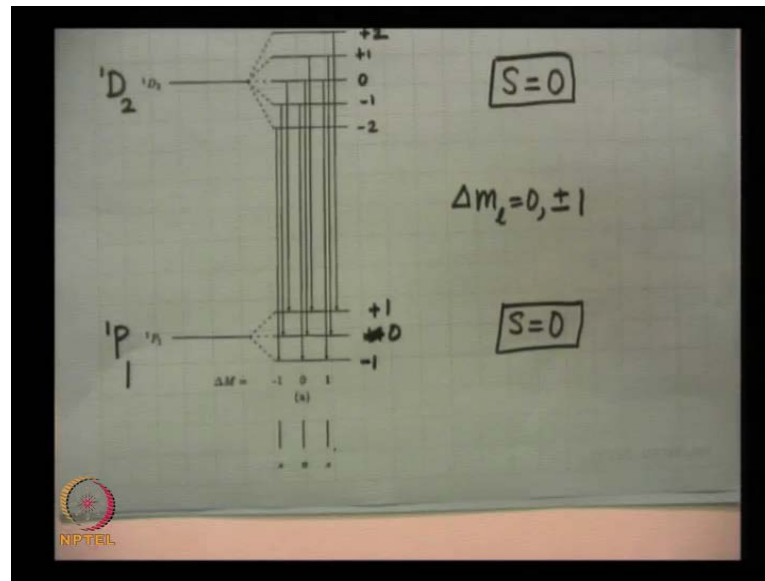
$$H' \psi_{nlm} = \frac{\mu_B B}{\hbar} m \hbar \psi_{nlm}$$

$$\int \psi_{n'l'm'}^* H' \psi_{nlm} d\tau = (\mu_B B m) \delta_{ll'} \delta_{mm'}$$

So, H' prime, what is H' prime? As I said that, this is equal to $\mu_B B$ by \hbar cross because just of the orbital motion L_z is the z component of the orbital angular momentum. So, H' prime ψ_{nlm} is equal to $L_z \psi_{nlm}$. So, therefore, this will be $\mu_B B \hbar$ cross times $m \hbar$ cross ψ_{nlm} . And, if I now multiply by $\psi_{n'l'm'}^*$, same value of n , but different value of l prime and m prime. And, I integrate H' prime $\psi_{nlm} d\tau$, which is a three dimensional integral. So, this will be \hbar cross **m** . So, $\mu_B B$ times m . And, this is $\psi_{n'l'm'}^* \psi_{nlm}$ **$\delta_{ll'} \delta_{mm'}$** . So, n l m are equal because **because** two different values of n will correspond to different energy. This is n is equal to 1, n is equal to 2 and n is equal to 3 and so on.

So, this will be $\delta_{ll'} \delta_{mm'}$. So, we already... because the magnetic field is assumed to be in the z direction, we already have a representation in which H' prime is diagonal because any **of** diagonal elements are zero. So, therefore, this will represent the perturbation. And, this is known as the normal zeeman effect. And, any value of l will make it split into **into** different values of **m** . Unfortunately, this theory is not applicable to hydrogen atom because we have to take into account the effect of spin and the spin orbit interaction and other thing.

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However, if I have a single state like in Cadmium, then s is equal to 0. So, this is the singlet D 2 state **this is the singlet D2 state**. So, l is 2, singlet means s is equal to 0. So, we neglect there is the spin is 0. And, so therefore, because l is 2, so m will be minus 2, minus 1, 0, **minus 2 minus 1**, 0, plus 1 and plus 2. This is the normal Zeeman splitting **normal Zeeman splitting**. And this, if I assume a transition to singlet p 1, here s is again 0 and l is 1. So, m can take values minus 1, plus 1, sorry, minus 1, 0 and plus 1. And, the selection rules are, that is transition takes place when change in m_l is 0 or plus minus 1. And, as you can see from the figure, the splitting is the same here, as well as here. And therefore, it results in a **Lorentz triplet**. This is what is known as **Lorentz normal**, **Lorentz triplet**. There are three lines.

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

$$\vec{B} = B\hat{z}$$

$$H' = \frac{qB}{2m} L_z$$

$$H' = \frac{\mu_B B}{\hbar} L_z$$

$$H_0 \psi_{n\ell m} = E_n \psi_{n\ell m}$$

$$\psi_{n\ell m} = R_{n\ell} Y_{\ell m}$$

$$\mu_B = \frac{q\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T}$$

$$L^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}$$

$$L_z Y_{\ell m} = m\hbar Y_{\ell m}$$

So, therefore if I am able, if I am able to neglect the spin term, then the interaction occurs only with the orbital motion. If the spin term is 0, then my Hamiltonian is proportional to L_z . And, fortunately we had a representation, which is an Eigen function of L_z . and, so therefore, we have a representation in which H' is diagonal. And, so therefore, diagonal elements represent the perturbation. And, in this case, the diagonal elements are I wrote down, so this is $m\hbar$ cross, the diagonal elements are L_z . Therefore, $m\mu_B$ times B . So, it is proportional to m . and therefore, this **this** splits, the splitting is proportional to... So, this corresponds to m equal to plus 2 and this corresponds to m is equal to minus 2. And, this leads to what is a **normal Zeeman triplet**.

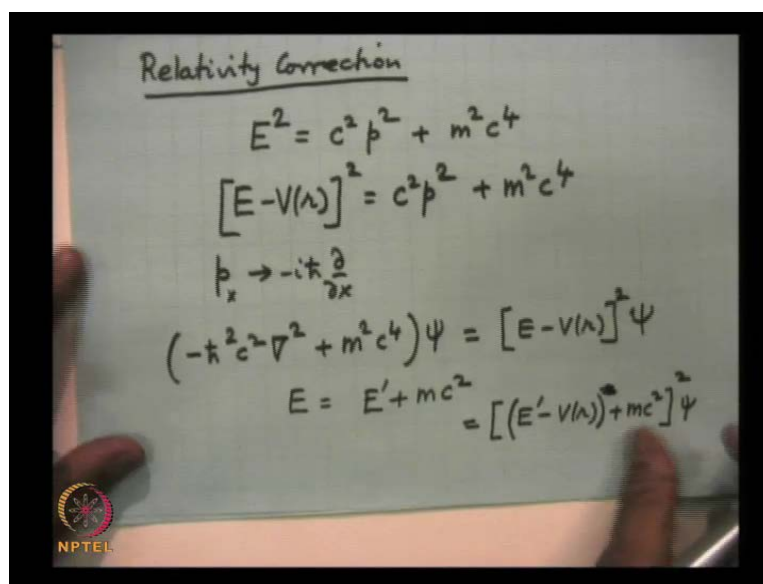
If you ask me the question that what would have happened if I had applied a magnetic field in the x direction? Of course, there is nothing secret about the z direction, then what would have happened is these are Eigen kets of L_z . If you, if you assume that this to be **L_x** , then $Y_{\ell m}$ are not Eigen kets of L_x . You would have obtained non diagonal elements, but the final results would have come out the same, the final splitting would come out the same. And, the Eigen kets that we would have obtained would have been Eigen functions of the operator L_x , so that $Y_{\ell m}$ are the Eigen kets of L^2 and L_z , but if you take linear combinations of them, then you can form Eigen kets of L^2 and L_x or of L^2 and L_y .

And, so therefore, if I had, if I assumed the magnetic field to be in the x direction, then calculations would of course become very cumbersome. We would have to calculate matrix elements, but the final result; this actual splitting would have come out to be the same.

So, I have told you two very important examples; one is the Stark's splitting of the n equal to two state of the hydrogen atom and the **Zeeman splitting** corresponding to the Zeeman splitting, when we neglect the spin of the electron.

Now, we will just introduce what is known as the relativistic correction and then we will conclude today's lecture. And then, we will solve for the fine structure of the hydrogen atom in my next lecture.

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Relativity Correction

$$E^2 = c^2 p^2 + m^2 c^4$$

$$[E - V(r)]^2 = c^2 p^2 + m^2 c^4$$

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$$

$$(-\hbar^2 c^2 \nabla^2 + m^2 c^4) \psi = [E - V(r)]^2 \psi$$

$$E = E' + mc^2 = [(E' - V(r)) + mc^2]^2 \psi$$

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So, as you know, we will discuss the relativity corrections. Corrections due to relativistic.... You have the Einstein's equation; E square is equal to c square p square plus m square c 4, where m is the rest mass of the electron.

In the presence of a potential energy, you will have E minus V of r whole square is equal to c square p square plus m square c 4. So, I write the corresponding relativistic Schrödinger equation. I represent p_x, p_y, p_z , by the p_x by minus $i\hbar$ cross delta by delta x and so on. So, this will become minus \hbar cross square c square ∇ square plus m square c 4 ψ is equal to $[E - V(r)]^2 \psi$. I write E as equal to E'

prime plus $m c^2$. So, my **right** hand side becomes E' prime minus V of r , I put that within brackets, plus $m c^2$ psi, **sorry, sorry**. So, I square this and obtain the following expression.

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The image shows a chalkboard with the following handwritten equations:

$$(-\hbar^2 c^2 \nabla^2 + m^2 c^4) \psi = [E' - V(r)]^2 \psi + m^2 c^4 \psi$$

$$+ 2 m c^2 (E' - V(r)) \psi$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi - \frac{[E' - V]^2}{2 m c^2} \psi - (E' - V) \psi = 0$$

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

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

$$H' = -\frac{(E' - V)^2}{2 m c^2}$$

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So, we will get for the left hand side, minus \hbar cross square c square del square plus m square c^4 psi is equal to E' prime minus V of r whole square times ψ plus m square c^4 psi plus $2 m c^2$ E' prime minus V of r psi. And, just square this expression. This term, cancels out with this term. And, I obtained **I obtain** this particular equation. I divide the whole equation by $2 m c^2$. So, I will obtain \hbar cross square by $2 m$ del square psi. I divide the whole equation by $2 m c^2$ and then I bring it to this side. So, minus E' prime minus V of r whole Square by $2 m c^2$ psi minus **minus** E' prime minus V of r psi is equal to 0.

So, I rewrite this. Take the E' prime on the other side. So, I can write this as H_0 plus H' psi is equal to E' prime psi; where H_0 is minus \hbar cross square by $2 m$ del square, minus minus plus, that is H_0 and H' is this whole term. That is, E' prime minus V by $2 m c^2$ whole square with a minus sign.

Of this, I know the solutions. So, I will take this as an unperturbed Hamiltonian. And, in my next lecture, I will consider this as the perturbation and calculate the effect of this correction term. This correction term is to take care of effects of relativity. And, **this**

correction are known as the relativistic correction. And, we will discuss this in the last, in the next lecture. Thank you.