Select / Special Topics in Atomic Physics

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Lecture - 24
Atomic Structure
Perturbative treatment of relativistic effects…
Schrodinger's and Dirac's QM

Greetings, we will begin unit 5 today, this is going to be a small unit, just 2 classes today and tomorrow on in this unit. The reason is it is based on topics that we have done, in a certain sense it is just a matter of establishing certain connections, with between the non-relativistic Schrodinger's quantum mechanics and Dirac's quantum mechanics, which we did in unit 3. So, relativistic effect from the point of view of Schrodinger's quantum mechanics can be added as perturbations, where us from the point of you Dirac's quantum mechanics. They are intrinsic to the very statement of the problem, because that is the very foundation of Dirac's quantum mechanics. So, we will establish some connections between these

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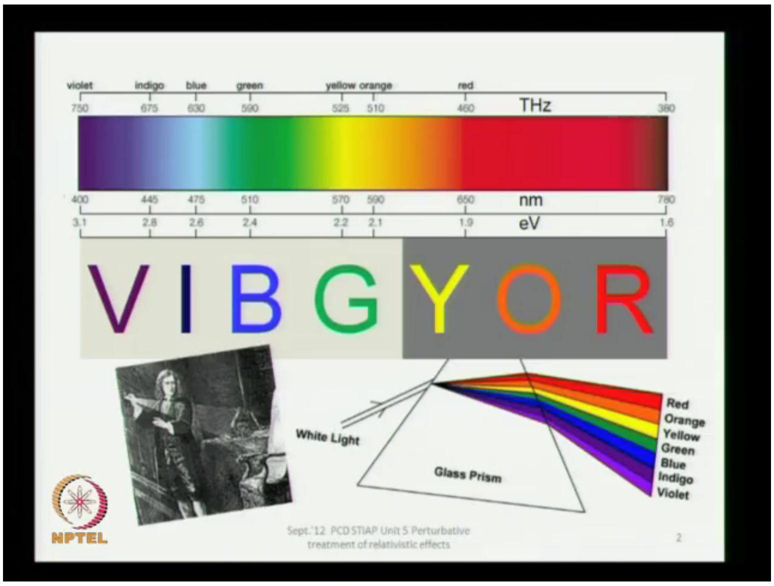

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And essentially these details are very important, because they go to the very hot of spectroscopy and atomic structure. Because, using spectroscopy you investigate atomic structure and once you know the atomic structure, you can do many other problems dynamics collisions and other things. So, essentially you are familiar with the hydrogen atom spectrum.

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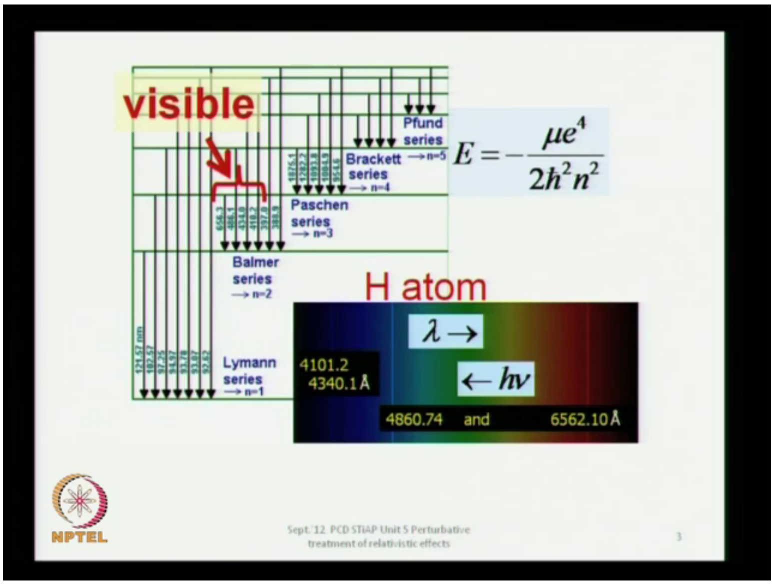

$$E = -\frac{\mu e^4}{2\hbar^2 n^2}$$

H atom

You have a visible part and an empirical study of this visible part of the spectrum, is what lead to the understanding of the 1 over n square formula, in the Rydberg Balmer empirical formula, which was later on found in Morse old quantum theory. And also in Schrodinger's quantum mechanics, which all gave the 1 over n square formula. Now, this structure is a good starting point, but then there is a long way to go and you keep making these corrections, then has to understand the atomic structure deeper. You discover that there is so much move to it than just this one over n square.

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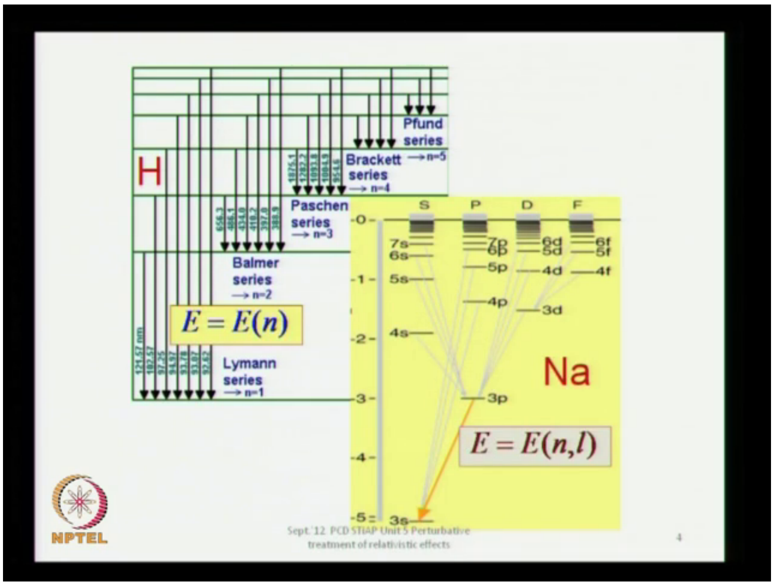

$E = E(n)$

$E = E(n,l)$

And we already found that, the sodium atom does reveal the dependence of energy on the l quantum number, but then there is what was earlier regarded as a hidden degeneracy or an accidental degeneracy, in the hydrogen atom. Because, there was no l dependence of the energy for the hydrogen atom Eigen values. And we learned that, the degeneracy in the hydrogen atom was because of the SO(4) symmitry.

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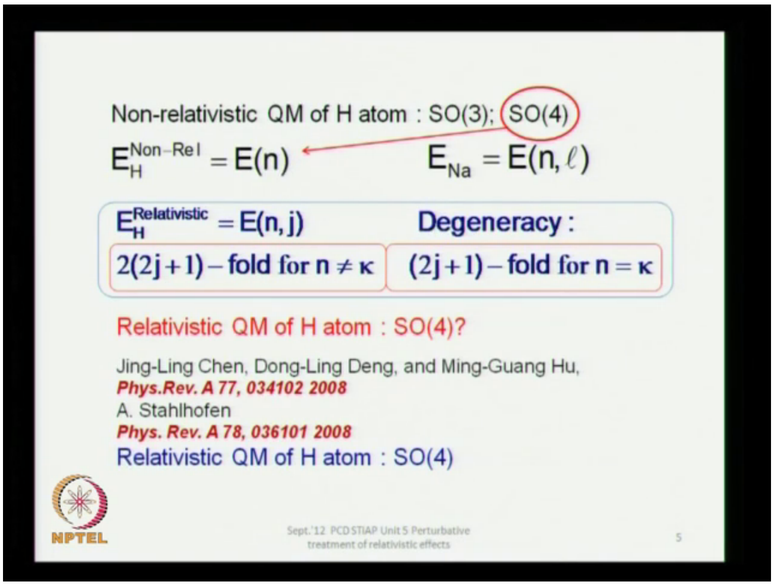

Non-relativistic QM of H atom : SO(3); $\boxed{SO(4)}$

$E_H^{Non-Rel} = E(n)$ $\qquad$ $E_{Na} = E(n, \ell)$

$E_H^{Relativistic} = E(n, j)$ $\qquad$ **Degeneracy :**

$2(2j+1)-$fold for $n \neq \kappa$ $\qquad$ $(2j+1)-$fold for $n = \kappa$

Relativistic QM of H atom : SO(4)?

Jing-Ling Chen, Dong-Ling Deng, and Ming-Guang Hu,
Phys.Rev. A 77, 034102 2008
A. Stahlhofen
Phys. Rev. A 78, 036101 2008
Relativistic QM of H atom : SO(4)

Now, let us ask this question that, when you take the relativistic energy and we have done this in unit 3, so you remember the Dirac's solution to the energy. And Dirac solution has energy which depends not just on the principle quantum number n, but also on the total angle momentum quantum number j. So, E depends on both n and j, and the degeneracy is 2 into 2 j plus 1 4, whenever n is not equal to the couple quantum number, you remember the couple quantum number in Dirac's theory.

Whereas, when n equal to couple, the degeneracy is 2 j plus 1 4, this is rather interesting observation and one would ask the question that does the relativistic hydrogen atom, what is the symmitry of the relativistic hydrogen atom, does it have SO(4) symmetry. And this is a problem of much interest and in fact, it is not very many years ago in 2008, just around 3 to 4 years ago, that there are two very interesting papers by Chen, Deng and Hu followed up by comment by Stahlhofen in which this question was addressed.

And you might want to read of these papers, it is always nice to read some original literature and these questions on whether or not the relativistic hydrogen atom have SO(4) symmitry is addressed in these papers. And it turns out that the conclusion of these papers is that, the relativistic hydrogen atom does in fact, have the SO(4) symmitry. But, this is the matter of considerable detail and I will not have the time to address this issue very much in this course.

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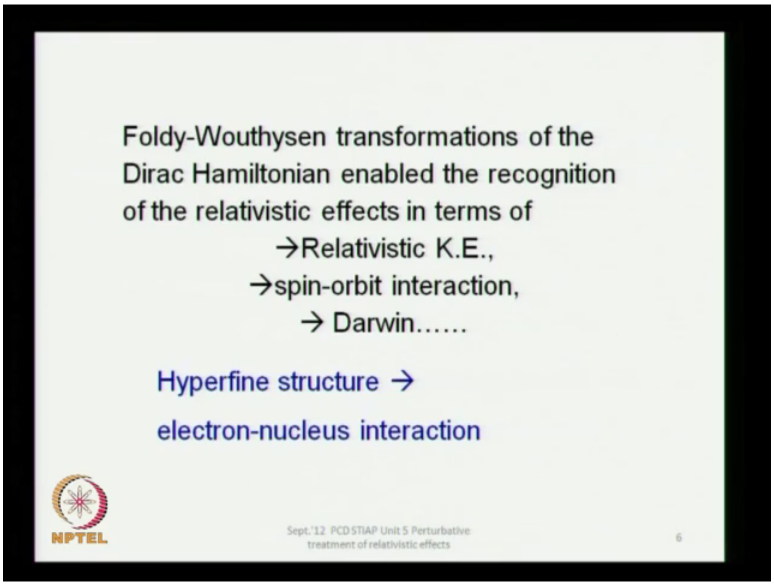

Foldy-Wouthysen transformations of the Dirac Hamiltonian enabled the recognition of the relativistic effects in terms of
→Relativistic K.E.,
→spin-orbit interaction,
→ Darwin……

Hyperfine structure →
electron-nucleus interaction

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But then we will move on to some of the other relativistic effects, and we learn from the Foldy-Wouthuysen transformations, which established the connections with terms, which were introduced earlier using perturbative methods and quantum mechanics. So, the terms like the correction due to the relativistic kinetic energy or the spin-orbit interaction or the Darwin correction and so on.

So, these connections they are not manifest in the Dirac equation they are all there, but they are not visible, but when you carry out series of Foldy-Wouthuysen transformations one, two and three. Then you are able to re-write the Hamiltonian in a form, in which these terms become manifest and in fact, they do give what we call is the fine structure of the hydrogen atom. But, that is not the end of the story, because beyond the fine structure there is the hyperfine structure, because of the electron nucleus interaction.

So, beginning with the Balmer Rydberg formula, you go through a progression of corrections and you develop deeper insight into the structure of the hydrogen atom, which is the simplest atom. But, that itself has so much, there is the wealth of physics, there is the wealth of knowledge about quantum mechanics, which is contained in the quantum mechanics of the hydrogen atom itself.

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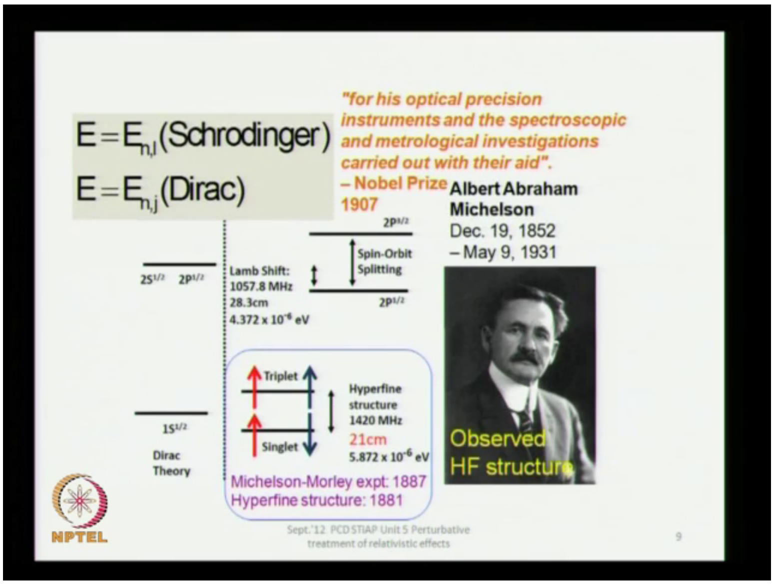

$E = E_{n,l}$ (Schrodinger)

$E = E_{n,j}$ (Dirac)

"for his optical precision instruments and the spectroscopic and metrological investigations carried out with their aid".
– Nobel Prize 1907

Albert Abraham Michelson
Dec. 19, 1852
– May 9, 1931

Observed HF structure

$2S^{1/2}$ $2P^{1/2}$

$1S^{1/2}$

Dirac Theory

Lamb Shift:
1057.8 MHz
28.3cm
4.372×10^{-6} eV

$2P^{3/2}$

Spin-Orbit Splitting

$2P^{1/2}$

Triplet

Singlet

Hyperfine structure
1420 MHz
21cm
5.872×10^{-6} eV

Michelson-Morley expt: 1887
Hyperfine structure: 1881

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So, the Schrodinger Eigen values depend only on n, Dirac Eigen values depend on n and j and then there is a further spin-orbit splitting, which we have seen, we have discussed this in the context of the Foldy-Wouthuysen transformations. The lamb shift causes the dip of the 2P 1 half level relative to the 2S 1 half level and then there is a further hyperfine structure, which come from the interaction between the electron spin and the protons spin, the nuclear spin.

So, because the proton also has got a spin half, the proton spin and the electron spin couple to give you a single state and a triplet state between these two and then these were observed first by Albert Michelson. In fact, before this hyperfine structure, he observed in 1881, this was the before famous Michelson-Morley experiment, which was done in 1887. And in fact, this was one of the major reasons that Michelson got the Nobel prize, now these are the details that one gets into in the quantum mechanics of the hydrogen atom.

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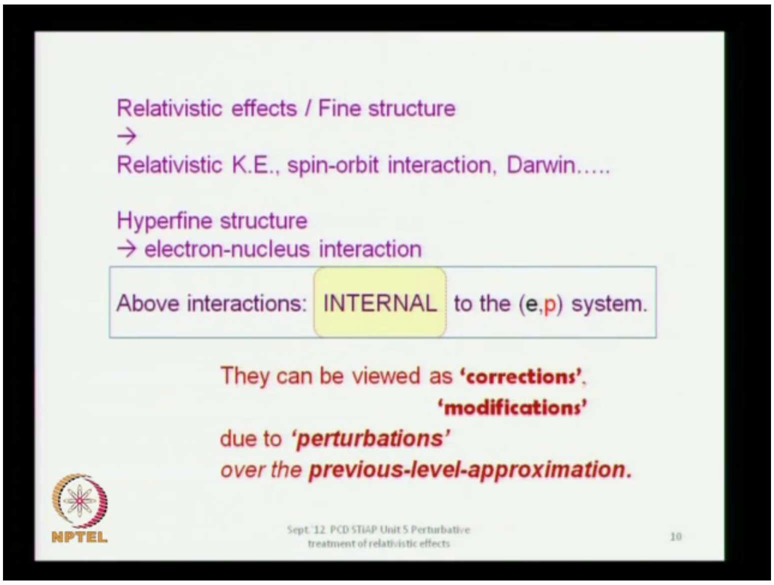

Relativistic effects / Fine structure
→
Relativistic K.E., spin-orbit interaction, Darwin…..

Hyperfine structure
→ electron-nucleus interaction

Above interactions: INTERNAL to the (e,p) system.

They can be viewed as **'corrections'**,
'modifications'
due to ***'perturbations'***
over the ***previous-level-approximation.***

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And if you look at these different corrections the like, the relativistic kinetic energy correction, the spin orbit correction or the Darwin correction, the hyperfine correction, hyperfine structure correction and so on. All of these are in built into the system, the hydrogen atom when it exists, it has got all of these interaction, these are not interactions that you can switch on and off from outside. What you can switch on and off or other perturbations that you can impose from outside, like if you put a hydrogen atom on magnetic field, you can switch of the magnetic field, you can change its strange, you can change its direction.

So, all of these external perturbations are under your control, but these internal interaction like the Darwin correction or the correction due to the relativistic kinetic energy, that is something that you have no control on. That is important even for in the electronic when the hydrogen atom addressed, it does not required the hydrogen atom to be moving at relativistic speeds. It comes essentially from the fact, that the speed of light is finite and therefore, all the consequences of the special theory of relativity have to be automatically accommodated in this key.

So, these are internal to the electronic proton system, this can be viewed as perturbations, not as perturbations which are imposed from the outside, which are switched on or off, but is perturbations over the previous level of approximation. So, you begin with the certain level of approximation and through that, you add a perturbative correction; and then you can find what the consequences of this perturbations are using perturbation theory.

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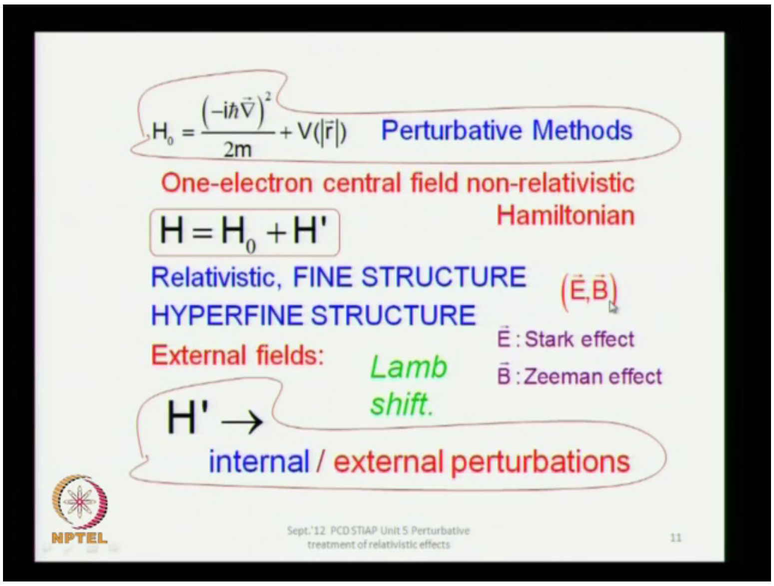

$$H_0 = \frac{(-i\hbar\vec{\nabla})^2}{2m} + V(|\vec{r}|)$$ Perturbative Methods

One-electron central field non-relativistic Hamiltonian

$$\boxed{H = H_0 + H'}$$

Relativistic, FINE STRUCTURE

HYPERFINE STRUCTURE

External fields: $(\vec{E}, \vec{B})$

$\vec{E}$: Stark effect

$\vec{B}$: Zeeman effect

Lamb shift.

$H' \rightarrow$ internal / external perturbations

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And typically the perturbations are on this non relativistic hydrogen atom, for which the unperturbed Hamiltonian is what you have over here, and you can then think of a perturbation no matter where it this comes from. It could be internal to the system like the fine structure, or the hyper fine structure or the relativistic kinetic energy term or the Darwin term. Or it can be some external perturbation, because of the electric field or magnetic field as you do in stark spectroscopy, your Zeeman spectroscopy or it could be due to feels like the lamb shift, vacuum frustration and so on. So, perturbation in general can be either internal or external to the system.

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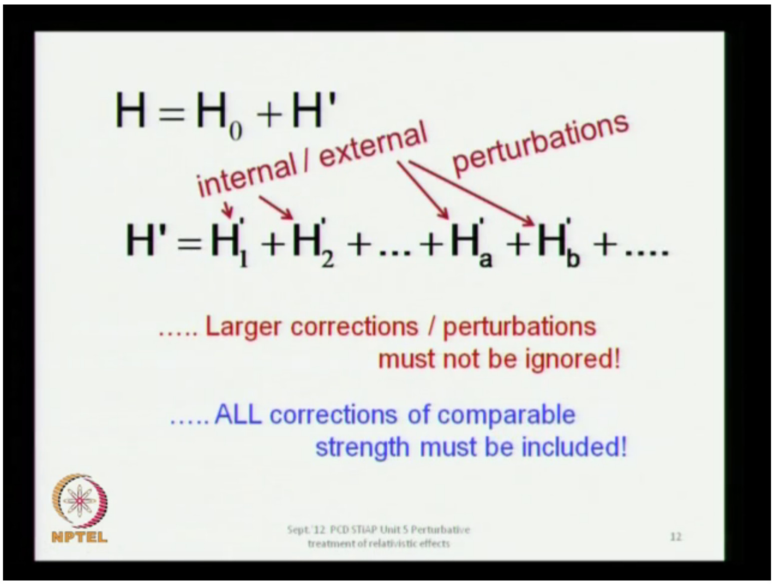

$$H = H_0 + H'$$

internal / external

perturbations

$$H' = H_1' + H_2' + \ldots + H_a' + H_b' + \ldots$$

..... Larger corrections / perturbations
must not be ignored!

..... ALL corrections of comparable
strength must be included!

And when you are using perturbation theory, it is important that you take into account all the perturbations, regardless of these perturbations been internal or external, because they will have a similar role in the structure of the Schrodinger's equation with the perturbation. Because, these come as addictive terms to the unperturbed Hamiltonian and it whenever you make these corrections always you have to be sure that, you do not ignore larger corrections.

Like H 2 prime for example, if it is correction of a certain order and there is a H 3 prime, which is larger than that, and if you choose to do perturbation theory only with the H 2 prime, but do not include H 3 prime, which is larger very make no sense. So, all perturbations, all corrections must be introduced progressively, so that the most important perturbations, the largest perturbations are first concern consider.

And further more all perturbations, all corrections whichever comparable shrine, like if H 2 prime could be an internal perturbation of the same order is H 1 prime, but H b prime is also a perturbation of the same order. Then it should also be included regardless of it being internal to the system, or something which is imposed of the system from outside. So, all perturbations of the same order should certainly be considered on an equivalent floating, regardless of these perturbations being intrinsic or imposed on the system.

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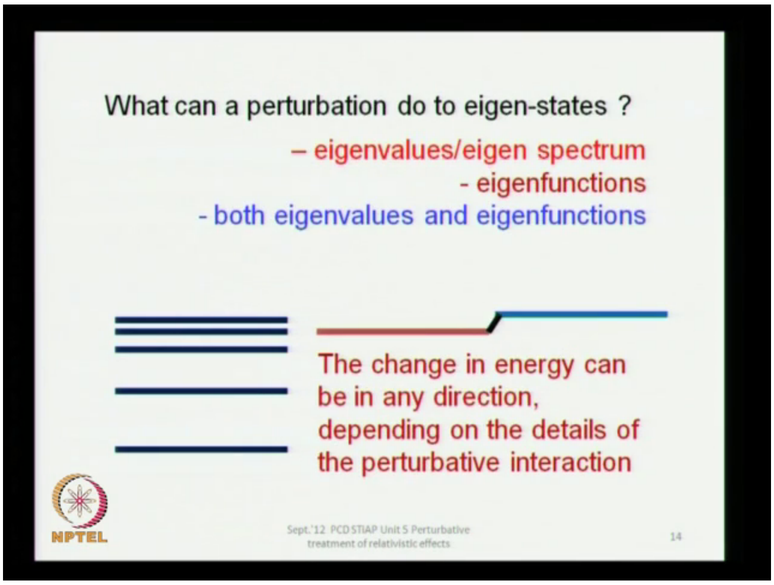

What can a perturbation do to eigen-states ?

– eigenvalues/eigen spectrum

- eigenfunctions

- both eigenvalues and eigenfunctions

The change in energy can be in any direction, depending on the details of the perturbative interaction

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So, now we need to review a little bit of perturbations theory, because we will ask this question what is it perturbation does to the Eigen-states of the system. It just exactly what will a perturbation do, does it change the Eigen value, does it changed the Eigen functions, does it changed both Eigen values and Eigen functions. And then typically what a perturbation do to a bounce state part of assistant is that, it can settle change the energy levels, whatever is the energy level we can change; it can change in one way or in can change the other way.

So, the bounce state energy is can get, most strongly bound or less strongly bound both possibilities are there, you may have degeneracy which can be removed by a perturbation, and that is a very common thing in spectroscopy. So, perturbation removes the degeneracy, it may remove the degeneracy either partially or wholly, besides the perturbation can also introduce transition and also change the occupation numbers of the states. So, perturbation can have different kind of consequences on a quantum system.

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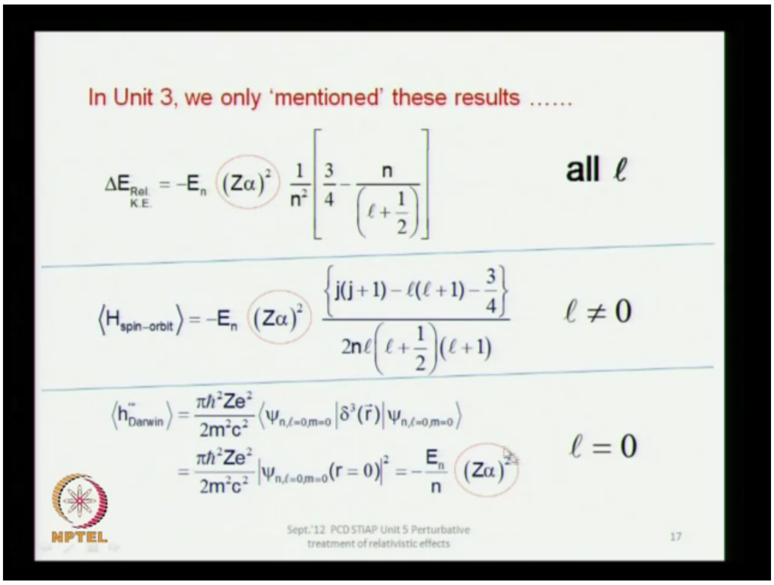

In Unit 3, we only 'mentioned' these results ……

$$\Delta E_{\substack{\text{Rel}\\ \text{K.E}}} = -E_n\,(Z\alpha)^2\,\frac{1}{n^2}\left[\frac{3}{4}-\frac{n}{\left(\ell+\frac{1}{2}\right)}\right]$$

all ℓ

$$\langle H_{\text{spin-orbit}}\rangle = -E_n\,(Z\alpha)^2\,\frac{\left\{j(j+1)-\ell(\ell+1)-\frac{3}{4}\right\}}{2n\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}$$

$\ell \neq 0$

$$\langle \ddot{h}_{\text{Darwin}}\rangle = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}\langle\psi_{n,\ell=0,m=0}|\delta^3(\vec{r})|\psi_{n,\ell=0,m=0}\rangle$$
$$= \frac{\pi\hbar^2 Ze^2}{2m^2c^2}|\psi_{n,\ell=0,m=0}(r=0)|^2 = -\frac{E_n}{n}\,(Z\alpha)^2$$

$\ell = 0$

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And what we showed in unit 3 was that, the terms which come from the Foldy-Wouthuysen transformations, if you remember the Foldy-Wouthuysen Dirac Hamiltonian, which we arrived that after the three Foldy-Wouthuysen transformations. We recognize that they were corrections due to the relativistic kinetic energy term, which were applicable for all values of the l quantum number. Then they was the spin orbit correction which was valid for l not equal to 0, when l equal to 0 it is the same.

And then there is also the Darwin correction which comes from the electron wave function amplitude at the nuclear, because of this Dirac delta function, and therefore it is relevant only for the S orbital, only when the l is equal to 0. So, we only mention these results and in today's class, we will discuss these terms in some detail and notice that, all of these corrections they are of the order of z alpha square. So, look at ((Refer Time: 15:16)) this one, this one and this one there are all of the order of z alpha square, so there are all comparable shrine.

And therefore, they must be introduced from a perturbation approach together, over here in the Foldy-Wouthuysen farm they come naturally, they come together from the Dirac equation. But, if they are to be consider perturbatively as corrections to the not relativistic Schrodinger's results, then you cannot take one of them, but you mistake all of them, because they are all of the same order.

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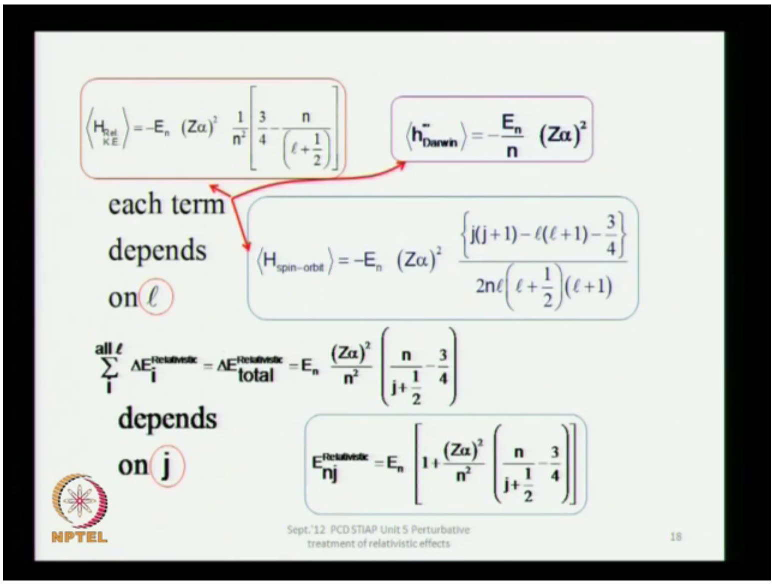

$$\left\langle H_{\substack{\text{Rel}\\ \text{K.E.}}} \right\rangle = -E_n\ (Z\alpha)^2\ \frac{1}{n^2}\left[\frac{3}{4} - \frac{n}{\left(\ell+\frac{1}{2}\right)}\right]$$

$$\left\langle h_{\text{Darwin}}^{-} \right\rangle = -\frac{E_n}{n}\ (Z\alpha)^2$$

each term depends on ℓ

$$\left\langle H_{\text{spin-orbit}} \right\rangle = -E_n\ (Z\alpha)^2\ \frac{\left\{j(j+1)-\ell(\ell+1)-\frac{3}{4}\right\}}{2n\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}$$

$$\sum_{i}^{\text{all }\ell} \Delta E_i^{\text{Relativistic}} = \Delta E_{\text{total}}^{\text{Relativistic}} = E_n\ \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)$$

depends on j

$$E_{nj}^{\text{Relativistic}} = E_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

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So, notice that each of these corrections depends on l, this is the relativistic kinetic energy correction there is an l here, that Darwin term also depends on l, because for l not equal to 0, this correction is 0. In fact, it is applicable only for l equal to 0, only for the S phase which are the only once which got an all the non-zero amplitude at the centre. And then the spin orbit correction also depends on the l quantum number. But, when you add up the three, you some over all l and this is a problem which one was included in the assignment given to you. That when you add up all of these three, you get only a j dependence, this is the very peculiar and a very interesting result.

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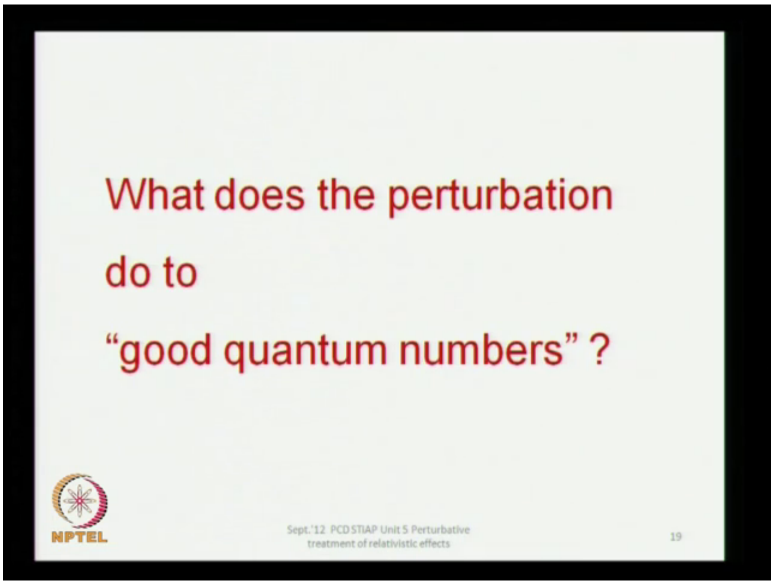

What does the perturbation do to "good quantum numbers" ?

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So, now notice that the dependence on l quantum number goes your way and then the question is what exactly does a perturbation do to good quantum numbers, what are the good quantum numbers, and how do you choose a basis at when you are doing perturbation theory. So, these are important questions and I will remind you that, the good quantum numbers are those which comes from Eigen values.

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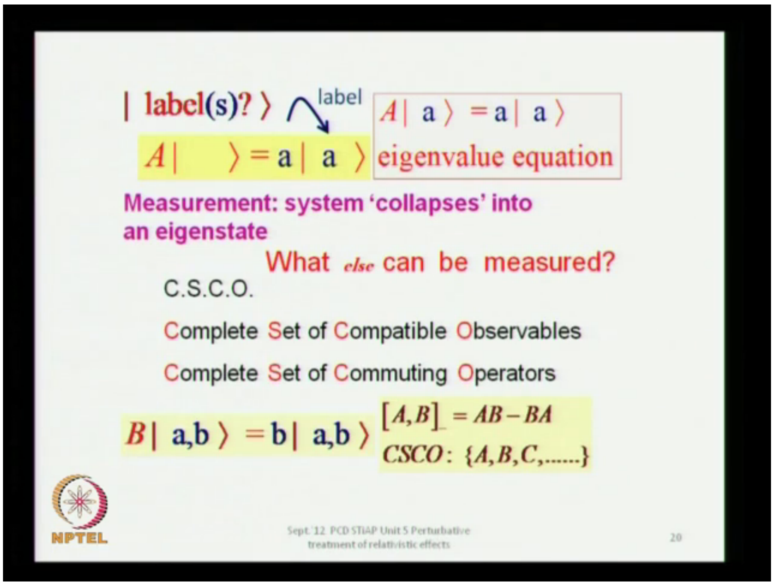

$| \text{label(s)?} \rangle$ label

$A| \quad \rangle = a| a \rangle$

$A| a \rangle = a| a \rangle$ eigenvalue equation

Measurement: system 'collapses' into an eigenstate

What *else* can be measured?

C.S.C.O.

Complete Set of Compatible Observables

Complete Set of Commuting Operators

$B| a,b \rangle = b| a,b \rangle$

$[A,B]_- = AB - BA$

$CSCO: \{A,B,C,......\}$

The operator, which operates which correspondence to a measurement of a certain property of the physical system, as a result of the, which the system collapses into an Eigen state. And if it remains in that Eigen state when you perform another measurement, so you stack a set of compatible measurements, and when you get all of them together, you get a complete set of compatible observations are equivalently a complete set of commuting operators. And the Eigen values of these complete set of commuting operators, other once which are giving you the good quantum numbers. So, this is the essential factor that we need to remember in our consideration.

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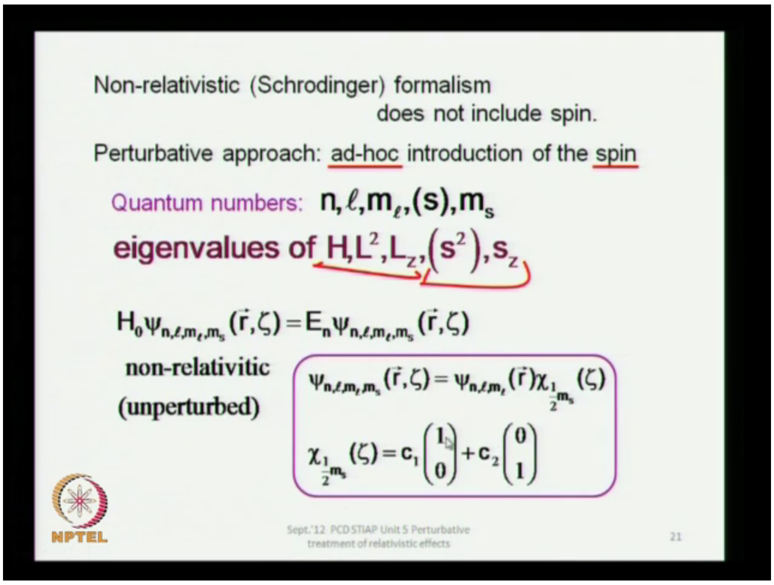

Non-relativistic (Schrodinger) formalism
does not include spin.

Perturbative approach: ad-hoc introduction of the spin

Quantum numbers: $n, \ell, m_\ell, (s), m_s$

eigenvalues of $H, L^2, L_z, (s^2), s_z$

$$H_0 \psi_{n,\ell,m_\ell,m_s}(\vec{r},\zeta) = E_n \psi_{n,\ell,m_\ell,m_s}(\vec{r},\zeta)$$

non-relativitic
(unperturbed)

$$\boxed{\begin{gathered} \psi_{n,\ell,m_\ell,m_s}(\vec{r},\zeta) = \psi_{n,\ell,m_\ell}(\vec{r})\chi_{\frac{1}{2}m_s}(\zeta) \\ \chi_{\frac{1}{2}m_s}(\zeta) = c_1\begin{pmatrix}1\\0\end{pmatrix} + c_2\begin{pmatrix}0\\1\end{pmatrix} \end{gathered}}$$

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So, now, from the point of view of non relativistic Schrodinger quantum mechanics, spin as such does not really exist, the non relativistic Schrodinger equation has no scope to accommodate spin. The only wait to do it is on a completely ad-hoc bases, when we discussed angular momentum algebra, we did point out that the definition angular momentum thus allow certain values of the j quantum number, which could be either 0, half 1, 3 half 2 and so on. So, half integer quantum numbers do have a place in the algebra of angler of momentum quantum mechanics.

That does not require any relativistic quantum mechanics, nevertheless non-relativistic quantum mechanics does not a sign, half integer quantum number to the electron spin, because electron spin as no place at all in non relativistic quantum mechanics. It can be introduced only on an ad-hoc bases, and this is how it was introduced perturbatively over the non relativistic Schrodinger equation. So, when you do that, your good quantum numbers come from these operators, come from the Eigen values of H L square L z, these are the three which give you the n, l and m l quantum numbers.

And then on an ad-hoc bases you plug-in and additional property spin, the way it was done by Hollenbeck and Gauss Smith if you wish, it comes neatly only out of the Dirac equation, only out of the relativistic quantum mechanics. But, from the point of you of perturbation of a non-relativistic quantum mechanics, it can be introduced on an ad-hoc bases. And then these four operators H L square L z and S z will give you the four quantum numbers n, l, m l and m s and you can use these to describe the quantum state of the system.

So, now your non relativistic unperturbed Schrodinger equation H 0 phi, H 0 is the unpalatable Hamiltonian, this becomes a two components wave function, the wave function excel become to component wave function. Because, you of introduced spin on an ad-hoc bases with an upstate and the downstate, so it at got it two valued functions. And this is now your unperturbed Hamiltonian, and through this you will make perturbation corrections, the two components come from the upstate and the downstate 1 0 and 0 1, if you wish with whatever coefficients.

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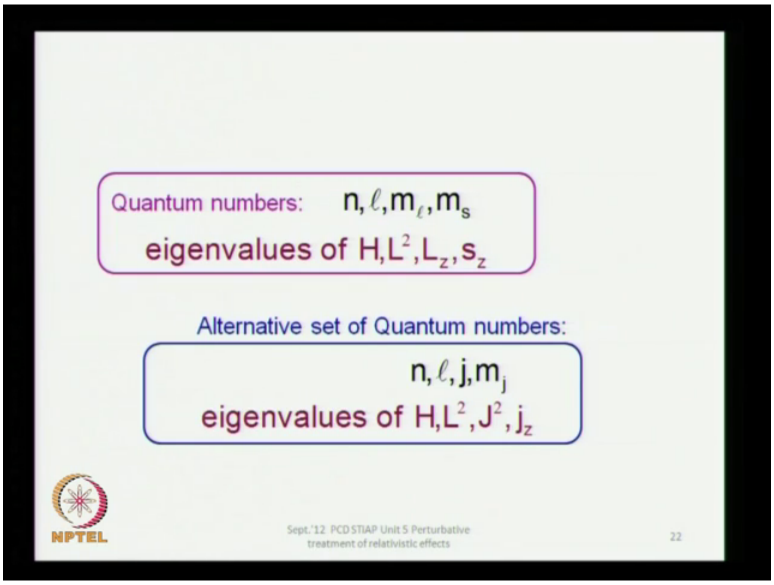

Quantum numbers: n, ℓ, m_ℓ, m_s

eigenvalues of H, L^2, L_z, s_z

Alternative set of Quantum numbers:

n, ℓ, j, m_j

eigenvalues of H, L^2, J^2, j_z

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And the alternative set of quantum number that you can use is not just n, l, m l m s, but also n, l, j, m j, so now we have to ask the question, which is the appropriate bases and this is at the heart of perturbation theory. Once you sought out these issues, one can do perturbation theory systematic, so let us consider the first order perturbation theory, in the first order perturbation theory that the correction to energy is given by the expectation value of the perturbation Hamiltonian in the unperturbed state.

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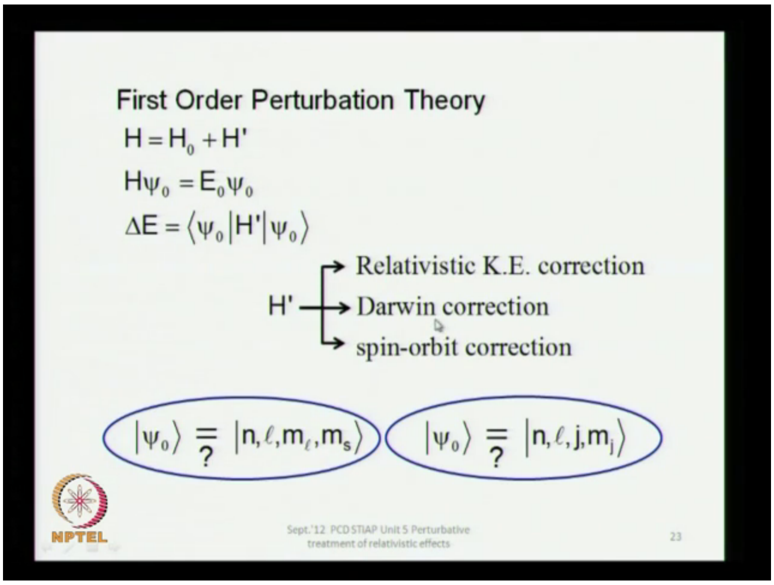

First Order Perturbation Theory

$$H = H_0 + H'$$

$$H\psi_0 = E_0\psi_0$$

$$\Delta E = \langle \psi_0 | H' | \psi_0 \rangle$$

H' → Relativistic K.E. correction

H' → Darwin correction

H' → spin-orbit correction

$$|\psi_0\rangle \overset{?}{=} |n,\ell,m_\ell,m_s\rangle \qquad |\psi_0\rangle \overset{?}{=} |n,\ell,j,m_j\rangle$$

This is the well known result which comes from perturbation theory, the question that we are addressing is what do you use for size 0, do you use n, l, m l, m s or do you use n, l, j, m j and what is it the determinants this, so these are the questions that we are going to discuss today and in tomorrow's class. The perturbations that we are considering are these H plain, this is the relativistic kinetic correction, then we have the Darwin correction, you have the spin orbit correction, these are the corrections that we need to take into account.

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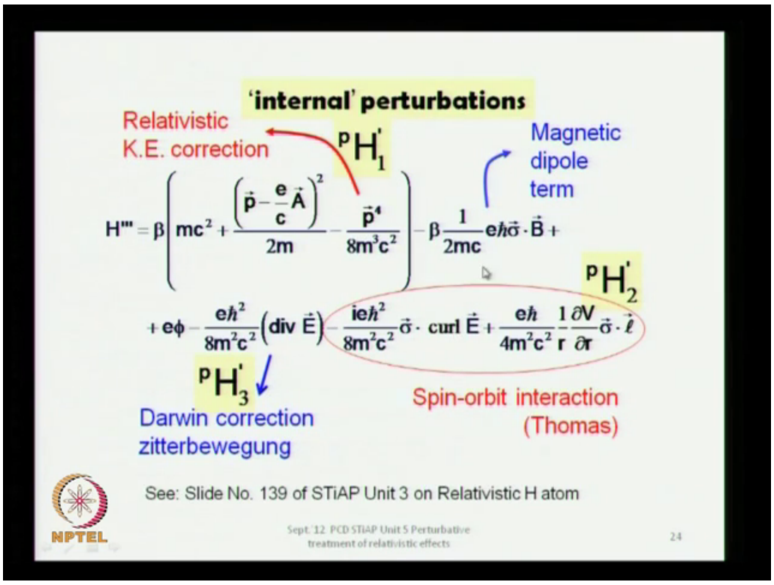

'internal' perturbations

$$H''' = \beta\left(mc^2 + \frac{\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2}{2m} - \underbrace{\frac{\vec{p}^4}{8m^3c^2}}_{{}^{p}H_1'}\right) - \beta\frac{1}{2mc}e\hbar\vec{\sigma}\cdot\vec{B} + $$

$$+ e\phi - \underbrace{\frac{e\hbar^2}{8m^2c^2}\left(\mathrm{div}\,\vec{E}\right)}_{{}^{p}H_3'} - \underbrace{\frac{ie\hbar^2}{8m^2c^2}\vec{\sigma}\cdot\mathrm{curl}\,\vec{E} + \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{\sigma}\cdot\vec{\ell}}_{{}^{p}H_2'}$$

Relativistic K.E. correction

Magnetic dipole term

Darwin correction zitterbewegung

Spin-orbit interaction (Thomas)

See: Slide No. 139 of STiAP Unit 3 on Relativistic H atom

And they have a formal place based on first principles in Dirac formalism, when you subject a to three Foldy-Wouthuysen transformations, you get the terms at you see on this screen, now over here this is coming from an external magnetic fields. So, forget about it, if you are talking only about perturbations, which are intrinsic and internal to the quantum system. So, you do not have to worry about the terms corresponding to the magnetic vector potential or this phi, for the hydrogen atom you have got central symmitry.

So, the curl of E would vanish for spherical symmitry, so this term also goes E phi is the Coulomb potential, which is the 1 over r or z e by r potential so that, so 1 that is responsible for the bound states or even the continuous states of the hydrogen atom. m c square is just a constant, without this A you have got p square over 2 m, which you go into the unperturbed Hamiltonian. So, the perturbations at you have really need to talk about are only these which are p 4, this is the p to the 4 term with the minus sign mind you, this is the relativistic kinetic energy correction.

Then the other two perturbation that you have to consider or the spin orbit perturbations, which is sigma dot l term, d V by d r square sigma dot l and then the Darwin term, so these are the three perturbative corrections that we need to discuss. So, I will refer to them as perturbations this is the first perturbation the relativistic kinetic energy term and then the spin orbit term which is the sigma dot l curl of E 0, and then the Darwin term. So, these are the three perturbations, which are intrinsic to the quantum system, that we will discuss, and see what is there consequence on the solutions to the non relativistic prediction of quantum mechanics, the Schrodinger predictions of quantum mechanics.

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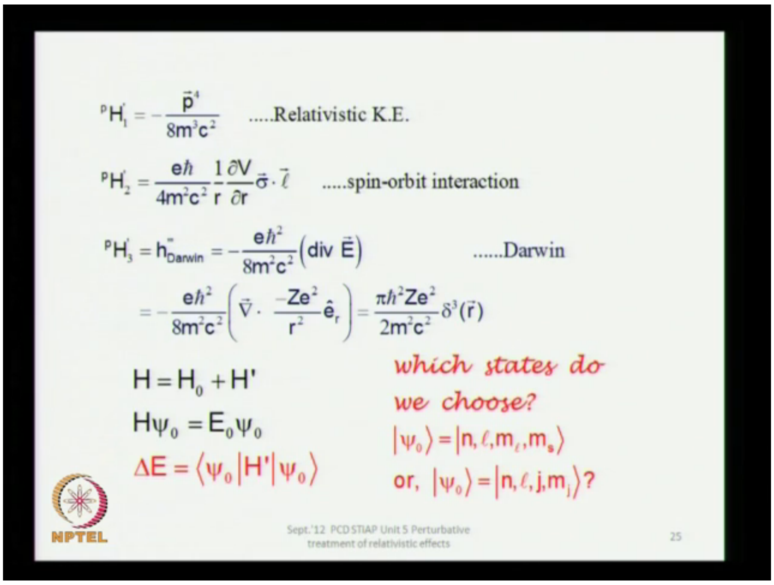

$$^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2} \quad \text{.....Relativistic K.E.}$$

$$^{P}H_2' = \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{\sigma}\cdot\vec{\ell} \quad \text{.....spin-orbit interaction}$$

$$^{P}H_3' = h_{Darwin}^{-} = -\frac{e\hbar^2}{8m^2c^2}\left(\text{div } \vec{E}\right) \quad \text{......Darwin}$$

$$= -\frac{e\hbar^2}{8m^2c^2}\left(\vec{\nabla}\cdot\frac{-Ze^2}{r^2}\hat{e}_r\right) = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}\delta^3(\vec{r})$$

$$H = H_0 + H'$$

$$H\psi_0 = E_0\psi_0$$

$$\Delta E = \langle\psi_0|H'|\psi_0\rangle$$

which states do we choose?

$|\psi_0\rangle = |n, \ell, m_\ell, m_s\rangle$

or, $|\psi_0\rangle = |n, \ell, j, m_j\rangle$?

So, now in this context, the question that we are addressing is that when you make these corrections, which states do we choose size 0 to be n, l, m l, m s or n, l, j, m j. And in your earlier course and quantum mechanics you are of learned how to make this choice, because there is the very simple and fundamental criterion that you must invoke to make this choice. That is the fundamental criterion, which must be made before you begin to use perturbations theory. And what is the choice this is, I thought it is best to court (()) from his book modern quantum mechanics.

(Refer Slide Time: 25:40)

" Remember the cardinal rule: Choose unperturbed kets that diagonalize the perturbation

-J.J.Sakurai

in 'Modern Quantum Mechanics', (1985)

He says remember the cardinal rule, choose unperturbed kets that diagonalize the perturbation, this is the cardinal rule, this is what you must do, so find out which unperturbed kets would diagonalize the perturbation and then the choice is that. So, this is the fundamental criterion, in fact goes on to say something further, but I will come back to that residual part of this remark a little later.

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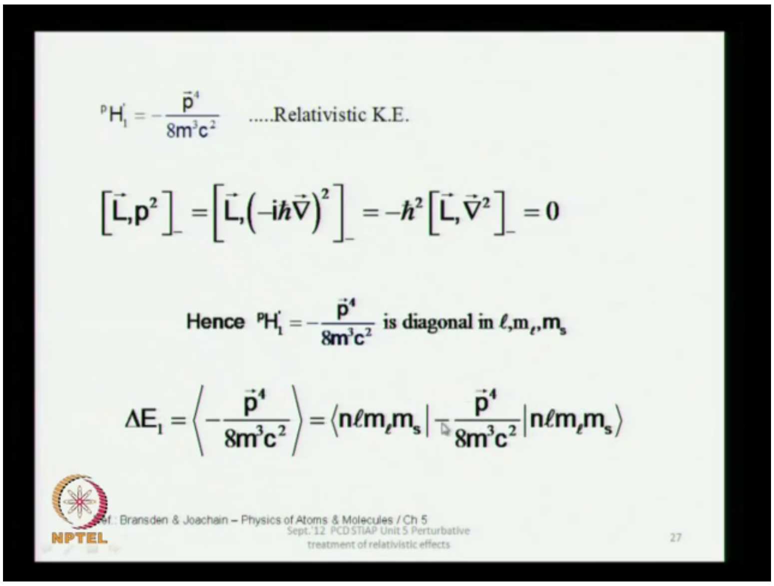

$$ {}^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2} \quad \text{.....Relativistic K.E.} $$

$$ \left[\vec{L}, p^2\right]_- = \left[\vec{L}, \left(-i\hbar\vec{\nabla}\right)^2\right]_- = -\hbar^2\left[\vec{L}, \vec{\nabla}^2\right]_- = 0 $$

Hence $ {}^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2} $ is diagonal in ℓ, m_ℓ, m_s

$$ \Delta E_1 = \left\langle -\frac{\vec{p}^4}{8m^3c^2} \right\rangle = \left\langle n\ell m_\ell m_s \right| -\frac{\vec{p}^4}{8m^3c^2} \left| n\ell m_\ell m_s \right\rangle $$

Ref.: Bransden & Joachain – Physics of Atoms & Molecules / Ch 5

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So, let us take the first correction the first correction that we want to consider is, the relativistic kinetic energy term which is p to the 4 term, now this one p to the 4 is the square of p square. So, let see what happens to p square, because p square commutes with the orbital angle of momentum quantum vector operator, and because it commutes, because l commutes with the l square. You already know that this is diagonal n, l, m l and m s, so now you know how you make your choice.

So, your n, l, m l, m s would be an appropriate bases at to go ahead and make use of first order perturbation theory correction to this, because of this term, so let us go ahead do it. So, let us take the n, l, m l, m s state plug-in perturbation, let us not forget the minus sign, it is minus p to the 4, you remember how the minus sign came it came from the Foldy-Wouthuysen transformations. So, when you do it systematically, so that was the advantage of doing the Dirac equation and the Foldy-Wouthuysen transformations prior to a discussion on this topic. So, you have the minus p to the 4 over this constant and you find the expectation value of this operator in this state n, l, m l and m s, so now this is not a very difficult task.

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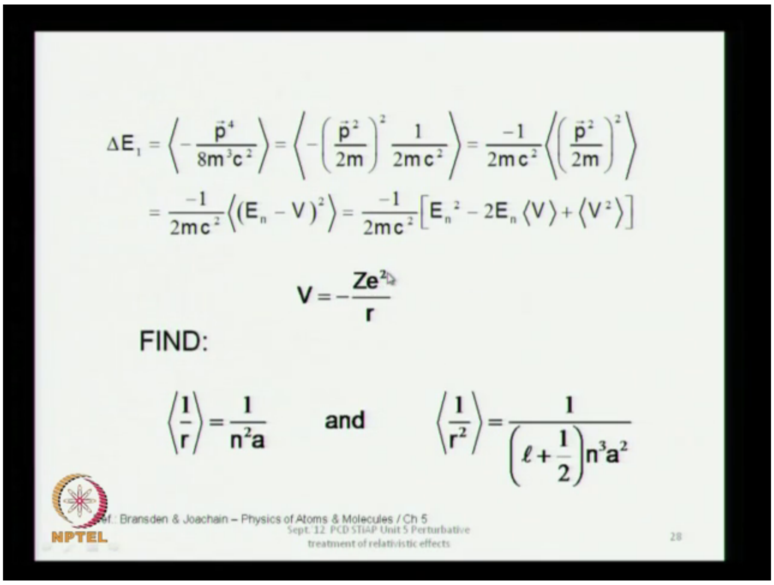

$$\Delta E_1 = \left\langle -\frac{\vec{p}^4}{8m^3c^2} \right\rangle = \left\langle -\left(\frac{\vec{p}^2}{2m}\right)^2 \frac{1}{2mc^2} \right\rangle = \frac{-1}{2mc^2} \left\langle \left(\frac{\vec{p}^2}{2m}\right)^2 \right\rangle$$

$$= \frac{-1}{2mc^2} \left\langle (E_n - V)^2 \right\rangle = \frac{-1}{2mc^2} \left[E_n^2 - 2E_n \langle V \rangle + \langle V^2 \rangle \right]$$

$$V = -\frac{Ze^2}{r}$$

FIND:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \quad \text{and} \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(\ell + \frac{1}{2}\right) n^3 a^2}$$

NPTEL

ef.: Bransden & Joachain – Physics of Atoms & Molecules / Ch 5

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So, let us see how to do that, all the constants come out nicely, here you have got p square over 2 m, which is the kinetic energy operator and square of that. So, you can get that from this E n minus V square operator and then E n of course is the constant, so twice c n and also a constant. And all you need to do is to get expectation values of V, the potential energy and V square, so if we get the expectation value of V and V square you can solve this problem readily.

Now, that is again not a very difficult task, because V is given by this 1 over r minus Z is square by r is the coulomb potential, this is the e phi term in the Dirac Hamiltonian. And then you can find 1 over r, the average value of 1 over r is 1 over n square a, this is the a is the bore radius and you can find the average value of 1 over r square. So, this is just a matter of carrying out the integrations with appropriate radial functions, the angle of parse will give you, they are normalized spherical harmonics. So, they will contribute just a multiplicative factor of 1, and essentially you have to carry out the radial integrals, to get those expectation values and the non relativistic radial functions are well known. So, you can for whichever state, you are carrying out this correction whether it is 1 S or 2 S or whatever, you can carry out this integration and get the corresponding correction for the relativistic kinetic energy term.

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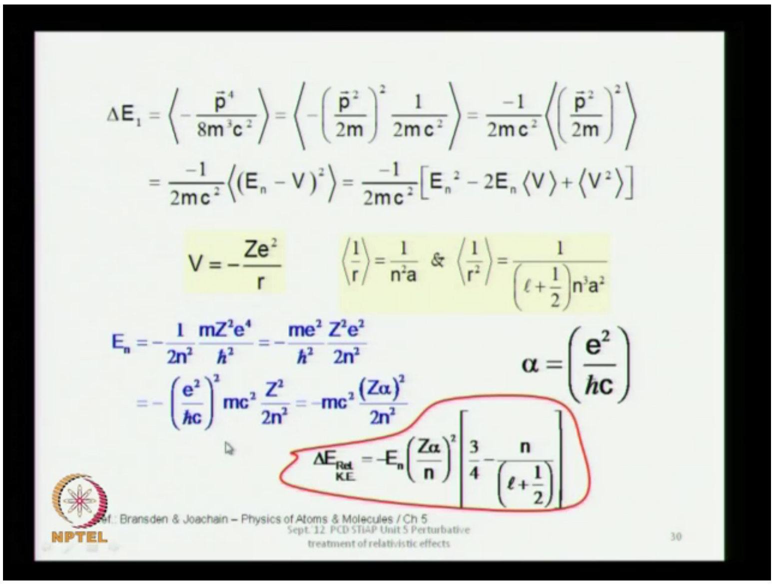

$$\Delta E_1 = \left\langle -\frac{\vec{p}^4}{8m^3c^2} \right\rangle = \left\langle -\left(\frac{\vec{p}^2}{2m}\right)^2 \frac{1}{2mc^2} \right\rangle = \frac{-1}{2mc^2}\left\langle \left(\frac{\vec{p}^2}{2m}\right)^2 \right\rangle$$

$$= \frac{-1}{2mc^2}\left\langle (E_n - V)^2 \right\rangle = \frac{-1}{2mc^2}\left[E_n^2 - 2E_n\langle V\rangle + \langle V^2\rangle\right]$$

$$V = -\frac{Ze^2}{r} \qquad \left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \;\&\; \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(\ell + \frac{1}{2}\right) n^3 a^2}$$

$$E_n = -\frac{1}{2n^2}\frac{mZ^2e^4}{\hbar^2} = -\frac{me^2}{\hbar^2}\frac{Z^2e^2}{2n^2}$$

$$= -\left(\frac{e^2}{\hbar c}\right)^2 mc^2 \frac{Z^2}{2n^2} = -mc^2\frac{(Z\alpha)^2}{2n^2} \qquad \alpha = \left(\frac{e^2}{\hbar c}\right)$$

$$\Delta E_{\substack{Rel\\KE}} = -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4} - \frac{n}{\left(\ell + \frac{1}{2}\right)}\right]$$

Ref.: Bransden & Joachain – Physics of Atoms & Molecules / Ch 5

NPTEL

So, working out these integrals is just a matter of mathematical detail and you will get for these correction for 1 over r, you get 1 over n square a, and for the square of V you get 1 over l plus half n cube a square. So, with these corrections, you get this correction delta E 1 which is given by, you put all of these three terms together add them up and then you get, an net result for the relativistic kinetic energy term, which is given by this. So, there was small minus status, which have jumped over, and essentially you can see that, this is how the relativistic kinetic energy term contributes to a change in the energy that you get from the Schrodinger equation.

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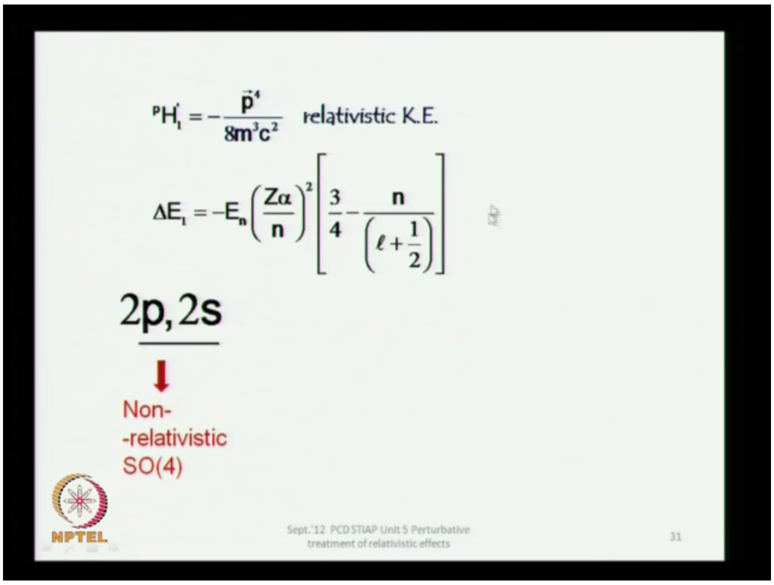

$${}^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2}$$ relativistic K.E.

$$\Delta E_1 = -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4} - \frac{n}{\left(\ell + \frac{1}{2}\right)}\right]$$

2p, 2s

Non-
-relativistic
SO(4)

NPTEL

What is the consequences of this correction, so 2 p and 2 s they are degenerate that is the consequences of the SO(4) symmitry of the hydrogen atom, there is no l dependence. But, now there is the correction which depends on l, it explicitly depends on l, so let us see what this connection does to the energy.

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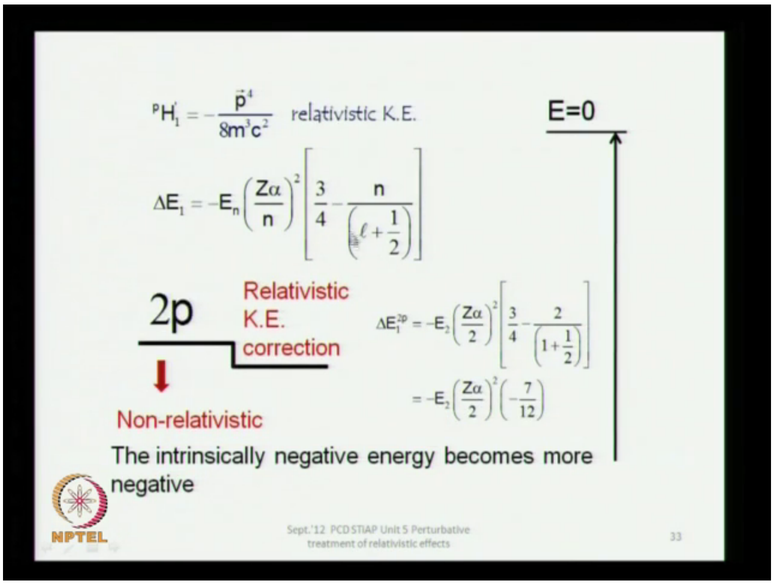

$$^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2}$$ relativistic K.E.

E=0

$$\Delta E_1 = -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4}-\frac{n}{\left(\ell+\frac{1}{2}\right)}\right]$$

2p

Relativistic K.E. correction

$$\Delta E_1^{2p} = -E_2\left(\frac{Z\alpha}{2}\right)^2\left[\frac{3}{4}-\frac{2}{\left(1+\frac{1}{2}\right)}\right]$$

$$= -E_2\left(\frac{Z\alpha}{2}\right)^2\left(-\frac{7}{12}\right)$$

Non-relativistic

The intrinsically negative energy becomes more negative

NPTEL

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So, if you put l equal to 0 and I have taken this formula and put l equal to 0 over here, so you get 3 4th minus 2 divided by half and if you carry out this simple arithmetic, you have the correction to the 2 s state, for the l equal to 0 state which is given by this factor. So, there is minus sign here, this is minus E 2 this difference this 3 4th minus of this number, which is 4. This comes with a negative sign which is the minus 3.25, so this minus sign and this minus sign will make it plus.

And the correction will have the sign of E 2, but E 2 is intrinsically negative and you are adding that to the non relativistic energy, what are you adding you are adding a negative term. So, whatever was already negative will become even more negative, so this is your energy access, this is the Rydberg series (()), this is the equal E to 0 and therefore, this relativistic kinetic energy correction causes a dip in this value from here, it is lowered by this amount.

This is the result of the relativistic kinetic energy, this is what it dons to the 2 s state, but it is difference for 2 l, 2 p, because for 2 p l is equal to 1. So, here the E 2 will be the same, but the correction will be different, because l is different for the 2 p. So, now, for 2 p you put l equal to 1, so in the denominator here instead of l plus half, you have 1 plus half and this difference is still negative, that it is the rather small number, this is minus 7 over 12, the previous number which had appear over there was like minus 3.25, so this is the small correction.

And therefore, this again these two minus sighs cancel, the correction has the sign of E 2 which is intrinsically negative, so the energy does become more tightly bound a such, but by arcs smaller amount, by a rather smaller amount, so these are the two corrections. And if you now consider a both, so 2 p as dip by a small amount, 2 s as dip by a larger amount, because of the difference in these two numbers, this is 7 over 12, this is 3.25.

So, now may I ask if the 2 s 2 p degeneracy has been removed in the hydrogen atom, would you will be appropriate to say that the hydrogen atom will not have the degeneracy with respect to the 2 s and 2 p states; because of the relativistic kinetic energy correction. But, then what did we say earlier at the beginning of the class, I showed you some pictures, I showed you the Schrodinger energy levels, then I showed you the Dirac energy levels, there are the terms.

So, these are not the only two terms, there are other terms and then when you include the other terms which may corrections of the same order of magnitude, then everything will fall in place. And this degeneracy is in fact removed, but only by the lamb shift, the relativistic kinetic energy term does not really remove this degeneracy, because whatever it does to the energies is compensator for by the corrections in the spin orbit term, the other corrections. So, when you add up all the corrections, then you have a different story and you need to wait to plug-in the lamb correction, the lamb shift to remove this degeneracy.

Now, the essential point which is highlighted over here in today’s discussion, there are couple of points, one how do you choose the unperturbed states, what is the fundamental criterion, because whenever you use perturbation theory this is the guiding principle for which I quoted from his book, and those of you who have read what have come across the quote which I mentioned. And perhaps you remember, the remaining part of his quotation is there anybody who does, it is the remaining part of the quotation, if anybody has read I can a sure that he cannot forget, he or she cannot forget that.

So, let you think about it, we are certainly going to come back and discuss the other part of quote, and for today our important lesson is to take into account all corrections, which are the same order of magnitude. If you take only one, you would be led to the wrong conclusion that the relativistic kinetic energy term. In fact, if that is a only correction you made, you would go head and conclude the 2 s and 2 p are no more degenerate, and you would expect to see in your observations in the spectrum that you will record, you will expect to see these energy is to be at different levels that of course, you do not see.

And the reason you do not see is because there are other corrections which are of the same order of magnetic, which you should also taken into account. So, there are two major learnings to take home today, one is have to choose the bases at and second to make sure that whenever you are doing perturbation theory, all corrections which are of the same order, which are of equal importance in string. Regardless of they being internal to the system or external to the system, in this case all the three are internal to the system.

But, we are going to have to remember this even when we go beyond this, because later on we will put this atom in a magnetic field, when we discuss the Zeeman effect. Or in an electric field when we discussed the stark effect, the question that will come up is, if you are going to study Zeeman effect using perturbation theory, which is the perturbation of the non relativistic Schrodinger equation for the hydrogen atom or some quantum system whatever.

Then if you are introducing corrections of a certain order using perturbative methods, have you included other corrections of the same order, and this will obviously, depend on the sprinkle the magnetic field, if you are doing Zeeman effect. For very weak magnetic fields, you may have the perturbation which is more important due to internal interactions. But, if you increase strength of the magnetic field, then the perturbation due to external fields could become more important. And then how you do perturbation theory, what is the bases at and unless you make that choice correctly you cannot really use perturbation theory, so these are the important thing I am going to stop here.

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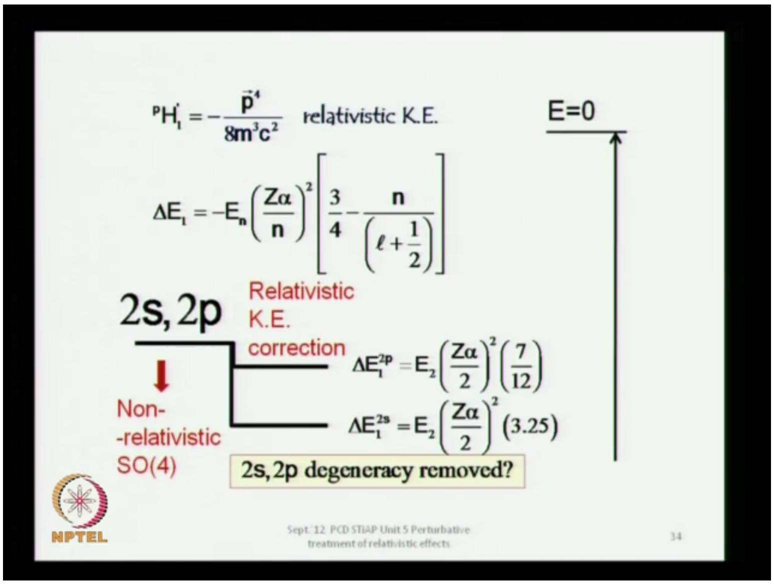

$$^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2}$$ relativistic K.E.

$$\Delta E_1 = -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4}-\frac{n}{\left(\ell+\frac{1}{2}\right)}\right]$$

E=0

2s, 2p

Relativistic K.E. correction

$$\Delta E_1^{2p} = E_2\left(\frac{Z\alpha}{2}\right)^2\left(\frac{7}{12}\right)$$

$$\Delta E_1^{2s} = E_2\left(\frac{Z\alpha}{2}\right)^2(3.25)$$

Non- -relativistic SO(4)

2s, 2p degeneracy removed?

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For today the 2 s, 2 p degeneracy is not actually removed, because of the other corrections, which I will be discussing in tomorrow's class.

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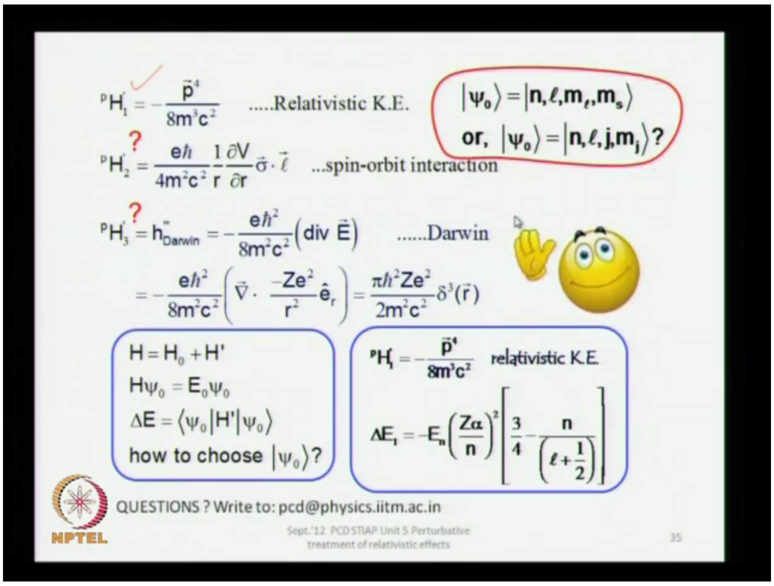

$$^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2}$$ .....Relativistic K.E.

$$^{P}H_2' = \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{\sigma}\cdot\vec{\ell}$$ ...spin-orbit interaction

$$^{P}H_3' = h_{Darwin}'' = -\frac{e\hbar^2}{8m^2c^2}(\mathrm{div}\,\vec{E})$$ ......Darwin

$$= -\frac{e\hbar^2}{8m^2c^2}\left(\vec{\nabla}\cdot\frac{-Ze^2}{r^2}\hat{e}_r\right) = \frac{\pi\hbar^2Ze^2}{2m^2c^2}\delta^3(\vec{r})$$

$|\psi_0\rangle = |n,\ell,m_\ell,m_s\rangle$

or, $|\psi_0\rangle = |n,\ell,j,m_j\rangle$?

$H = H_0 + H'$

$H\psi_0 = E_0\psi_0$

$\Delta E = \langle\psi_0|H'|\psi_0\rangle$

how to choose $|\psi_0\rangle$?

$$^{P}H_1' = -\frac{\vec{p}^4}{8m^3c^2}$$ relativistic K.E.

$$\Delta E_1 = -E_n\left(\frac{Z\alpha}{n}\right)^2\left[\frac{3}{4}-\frac{n}{\left(\ell+\frac{1}{2}\right)}\right]$$

QUESTIONS ? Write to: pcd@physics.iitm.ac.in

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And today we considered the correction due to the first perturbative correction, which is the relativistic kinetic energy correction. We also have to s do this spin orbit interaction correction in the Darwin term, and the question which is going to be raised again is, when you deal with these two perturbations, which will be an appropriate site, will you use n, l, m l, m s or would you use n, l, j, m j. So, these I will leave you with these questions and stop here for today, if the any questions I will be happy to take, no questions.

Thank you.