Atomic and Molecular Physics
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Lecture – 37
Quantum Mechanical treatment of Hydrogen like atom (Contd.)

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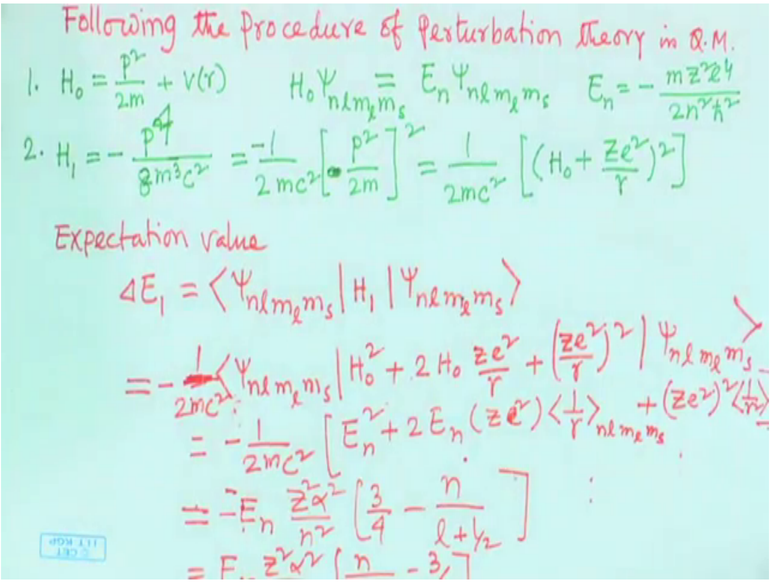

So, I will continue the discussion as I as I discussed that, we will use perturbation theory for that we have to identify we have to identify the unperturbed term in Hamiltonian. So, H 0 is basically taken as a unperturbed mean term ok, and it is wave function also already it is known from Schrodinger equation. So, this is psi n l m l m s is included is probably as I discussed that this both are valid.

So, since H 0 does that work on the spin variables? So, it does not matter this wave function whether it is psi n l m l or psi n l m l m s. So, so this the suitable wave function for alpha unperturbed Hamiltonian. So, I know wave function and also I know the energy main part in energy that is from unperturbed Hamiltonian. Now we have to using the perturbation this are the normal procedures of perturbation theory. So, without going in to details so, but you know how to find out the expectation value.

So, for H 1 term if I find out the correction in the energy from for this term; so we have to find out the expectation value. What is the possible expectation value? So, that is basically del E for H 1. So, this correction term energy is del E 1 ok. So, it 1 can find out it is the psi star H 1 psi. So, that is the procedure in quantum mechanics ok. So, this I have written in Dirac notation you know bra-ket notation, probably that I told you earlier ok.

So, in bra-ket notion this is nothing, but psi star H 1 psi. So, that has been written in Dirac notation bra-ket notation ok. So, whatever H 1 now put each 1 H 1 is basically here H 1, we can 1 can write in this form this basically P square by 2 m square ok. So, P square by 2 m from here you can you can see this H 0 plus z e square by r ok, this square terms square is there now if you put H 1 here ok, and square if you square is there. So, it will be H 0 square plus 2 H 0 z e by r plus z e square by r whole square.

Ok so, now this each this 3 term it will be operated on the on the on the psi, and you will gets you will get if it is Eigen value equation Eigen; Eigen equation, then Eigen value we will get. So, H 0 is basically if you operate on psi psi. So, it will give E n ok. So, H 0 square so, E n square a here it will give n, now you have to find out the average expectation value for 1 by r average value expectation value of 1 by r for this psi ok. And similarly other term is expectation value of 1 by r square ok, 1 by r square expectation value 1 has to find out.

So, if you find out I am not discussing in details, but it is 1 has to do few steps, and 1 has to know use the use the for this different operators operation for calculating this; so if I if I avoid this calculation, but just if I write the result. So, you will get this the result minus E n z square alpha square. Now this alpha is not this in Dirac Hamiltonian whatever alpha, and beta we use. So, this alpha is depend this is a basically used fine structure constant earlier we use this alpha for fine structure constant. So, this alpha is not same as this alpha in Dirac Hamiltonian.

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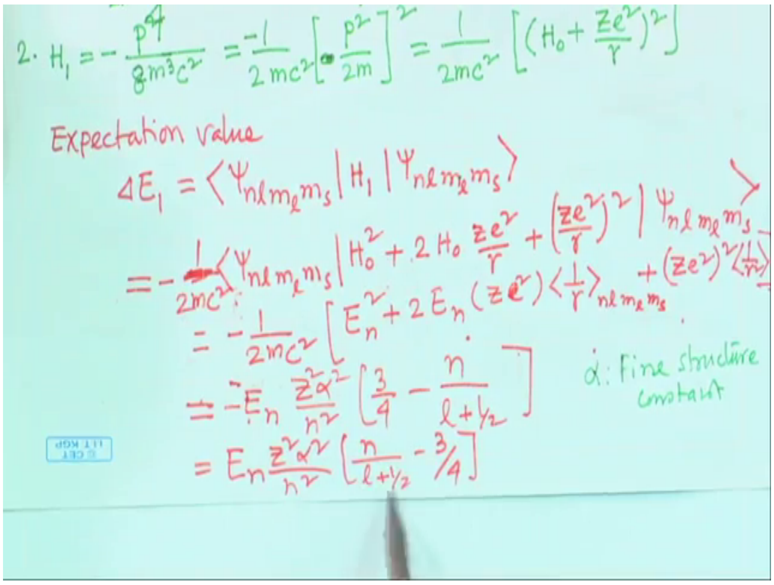

This is alpha is basically here alpha fine structure constant, fine structure constant ok. So, now so what we got del E 1 del E 1 equal to E n z square alpha square by E n square 1 n by l plus half minus 3 by 4 ok. So, this the correction term for H 1 this is the correction due to the relativistic consideration ok. So, this for H 1 similarly 1 has find out for H 2 and H 3 H 2 and H 3.

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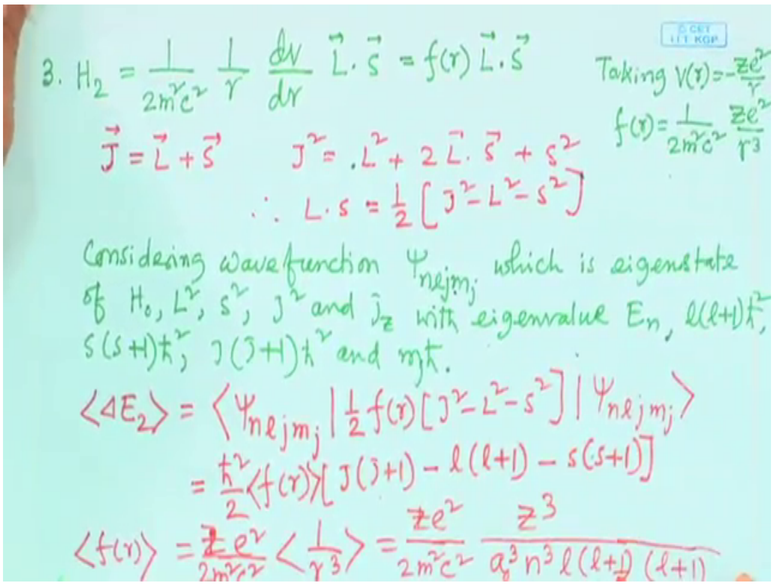

So, H 2 term you know this the L S L dot S term is there, and this other part is the function of r function of r right. So, I have written this function of r L dot S ok. So, if you take here d v by d r is there. So, your V is minus z e square z e square by r. So, if you take d v by d r and 1 by r is there here basically function of r it is 1 by r cube ok. So, now L dot S so as I discuss earlier. So, total angular momentum J is defined as a L plus S vectorial sum so, L can get J square equal to L square plus 2 L dot S plus S square. So, from here is L dot S is equal to half J square minus L square minus S square.

Now this so, so our wave function was psi n l m l m s, now that wave function for this calculation we will not use ok. So, we will use we will take we will define a wave function we will take wave function that basically psi n l j m j ok, which will be the Eigen state of H 0 L square S square J square and J z.

So, psi n l j m j in place of psi n l m l m s now m l m s, because that was m l is basically it was m l it was related with the l angular momentum l and m s it was related to the spin angular momentum s ok. Now since we are replacing this L dot S in terms of J L S. So, we have to we have to take a consider a suitable wave function which will be the simultaneous wave function simultaneous wave function of this, J square L square S square and of course, H 0. And other z component this is J z. So, that is that is the that is the psi n l j m j it is a simultaneous wave function of this operator, and it is if you operate this operator on this wave function we get the eigenvalue H 0 this is E n l square give l l plus 1 h cross square S square give S S plus 1 S h cross square J square gives J square, if we apply on this wave function it will give the eigenvalue J J plus 1 h cross square and J z will give you m J h cross.

So this the so, 1 has to take consider the suitable Eigen function or identify suitable Eigen function or wave function, and then 1 can use that wave function for calculating using the perturbation theory 1 can 1 can 1 can find out this the correction to the energy, due to this H 2 Hamiltonian Hamiltonian yes. So, so this expectation value of this H 2 1 has to find out, say again this the H 2 term H 2 term, and again psi star this H 2 psi here psi is as we have taken this n l psi n l j m j, and if you proceed then this actually this r f r function of f r. So, it is not Eigen operators for this function wave function so, 1 has find out the expectation values. So, that is what I have written in this bracket ok. So, 1 has to find out f r and here; obviously, you are getting this Eigen value J J plus 1 l l plus 1 S S plus 1 ok

Now, in function of r basically whatever this you 1 by r cube is there. So, 1 has to find out this expectation value of 1 by r cube for this wave function, and if you calculate so, alternately for this f function of r expectation function of r r will came this ok. So, now if you use this expectation value of r there is function of r. So, that if you put here if you put here.

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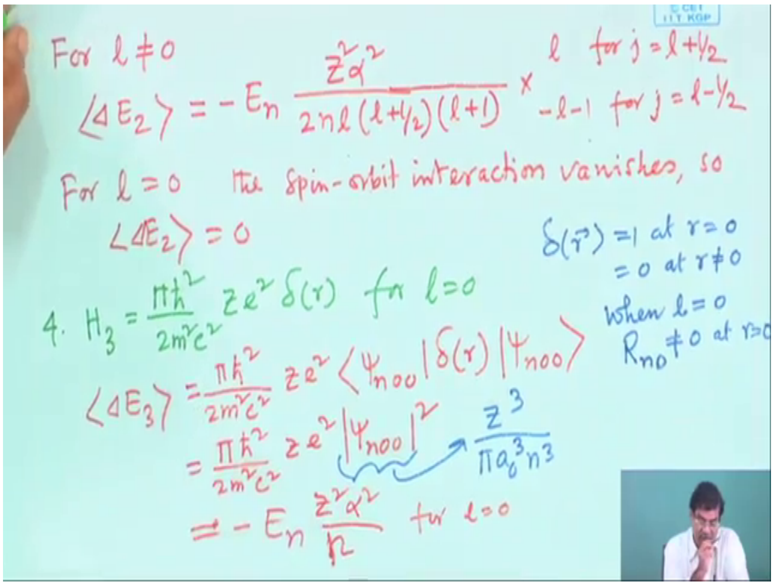

So, alternately you will get this correction term del E 2 del E 2, and as I mentioned that it is for this term is valid for l is not equal to 0 because l dot s is spin orbit coupling is there it will exist only l is not equal to 0. So, for l is not equal to 0 whatever the correction energy we got that is the correction the potential energy due to spin orbit interaction. So, del E 2 equal to minus E n z square alpha square by 2 n l l plus half l plus 1 into l when j equal to l plus half or into minus l minus 1 for j equal to l minus half s is plus half or minus half so that is why j so for.

So, depending on the j value; so either this term will be multiplied by l or minus l minus 1; so depending on the j value ok. Now this term vanish this term vanish so, l equal to 0 del dale E 2 equal to 0 when l equal to 0 and del E 2 is equal to this when l is not equal to 0 ok. So, this the second correction due to spin orbit coupling, and then come to the third correction H 3 H 3 is this, and that term this is valued for l equal 0, because this delta r delta Dirac function, it is 1 at r equal to 0 equal to 0 at r is not equal to 0 ok.

So, that I have I have shown you that only, if possible that r equal to 0 only this when l equal to 0, then only this wave function R n 0 it exist at r equal to 0 when l equal to 0 ok. So, basically this 1 has to find out this expectation value for this H 3 and so, here we have to we have to take the wave function right. So, which wave function will you choose so only psi n 0 0.

when l equal to 0; obviously, other m l will be 0 whatever m s will be 0 l s is not considered whether it is there or not does not matter, because important is l equal to 0 ok. So, only this term exist when l equal to 0, and when l is not equal to 0. So, this term will not exist. So, del E 3 will be automatically 0. So, if we evaluate this if we evaluate this. So, psi n 0 0 means R n 0 that what is the wave function that we have seen for the hydrogen atom we have seen.

So, this is basically it is this psi n 0 is basically this or square of it is this. So, we are getting del E 3 equal to minus E n z square alpha square by n for l equal to 0. So, using the perturbation theory, and then the normal accept the how to find out expectation value in quantum mechanics using this procedure 1 can get this energy term for the for the Dirac Hamiltonian Dirac equation.

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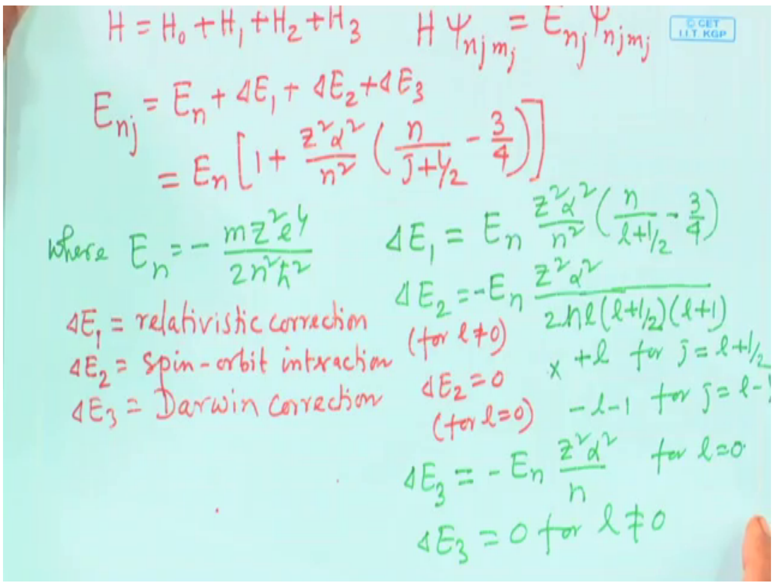

So, ultimately our Dirac equation is Dirac Hamilton is H equal to H 0 plus H 1 plus H 2 plus H 3. This the approximation upto term b square by c square, we have considered and psi n j m j is the ultimate wave function for this Hamiltonian Dirac Hamiltonian, and if you apply this Dirac Hamiltonian on this wave function we will get the energy E n j psi n j m j. So, this the Eigen value equation, and this energy E n j it basically it equal to energy comes from H 0. So, this is n and this comes from other correction term delta E 1 plus delta E 2 plus delta E 3 ok, if you add them if you add them. So, we will get basically E n j equal to E n 1 plus z square alpha square by n square into n by J plus half minus 3 by 4.

So, this expectation already I have shown you earlier ok, using the vector model in the vector model. So, we have consider l as coupling, and we have modified the energy just I mentioned so, but how it comes so, just to mention that in case of Somerfield Bohr Somerfield model whatever the energy terms we got this J in place of J it was basically l ok.

Now we just maintained if l can be replaced by J ok, when we consider the vector modal for L S coupling, and we get the total angular momentum this is J equal to l plus S. So, that is why just for similarity I wrote this energy expression, but now this energy expression has come automatically from Dirac equation.

And that is the ultimate energy expres energy expression which tells which tells about the energy levels in hydrogen like atom, and transition among the transition among this energy levels that gives the spectral lines, and that spectral lines is basically whatever it is spectral line due to fine structure or that can be explained during this, this energy expression E n j which H come automatically from the Dirac equation.

So what ultimate we got this form Dirac equation, we got the energy expression and also we got the wave function Eigen function psi n j m j so, but we are interested to deal with this energy expression, in this energy expression individual terms here, I have mentioned already I have discuss. So, so delta E 1 relativistic correction to kinetic energy, delta E 2 that spin orbit interaction correction to potential energy, and this is the Darwin correction ok, and this for potential energy this correction.

So, this for l is not equal to 0 this is the l E 2 and l equal to 0 del E 3. So, del E 2 and del E 3 is gives the complete correction term to potential energy. So, 1 active for l equal to 0 other is vanish, and other is active when l is not equal to 0, and next one Darwin term will be vanish for l is not equal to 0 ok. So, this is the solution for Dirac equation, and just I for the a sake of completeness to the discussion. So, I showed you the; I showed you the mainly result following the logic without calculating in details. So, details calculation I (Refer Time: 21:11) just because, for that you need really knowledge of quantum mechanics, advance knowledge of quantum mechanics so, but I that I left for you for future.

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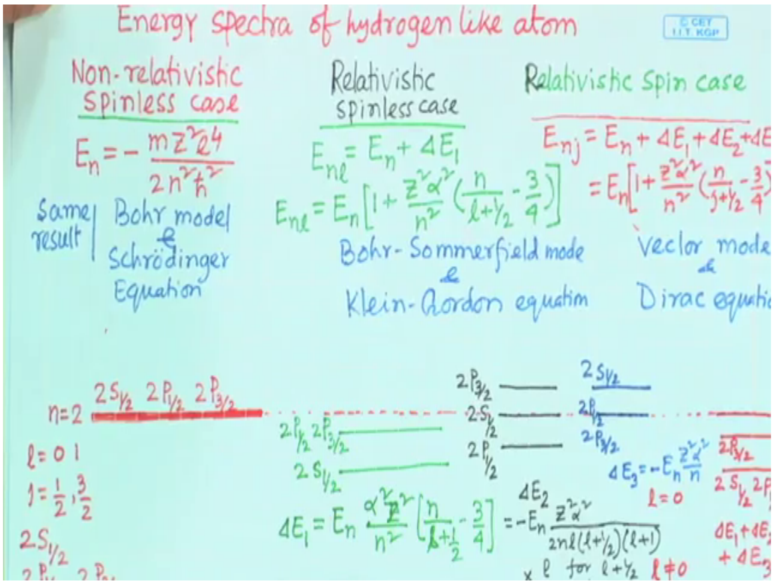

So, ultimately what we got ultimately we got this, we can energy expression is we can get energy spectra, of hydrogen like atom. So, or we have seen so, for that for non-relativistic spinless case energy is E n equal to minus m mu just I have written m z square e to the power 4 divided by 2 n square h cross square ok.

So, this same result basically is from Bohr model, and also Schrodinger's equation ok, and then next case is relativistic spinless case relativistic spinless case ok. So, E n l basically that is E n plus del E 1 ok, if you I know what is E n, and I know what is the term for del E 1 del E 1 is this and E n is there E n. So, E n plus this del E 1 so, E n if you take common 1 plus this rest of the part. So, that is what I have written here, that is what I have written here. So, 1 plus z square Alpha Square by n square n by l plus half minus 3 by 4. So, this same result as you got from Bohr Somerfield model and Klein Gordon equation.

So Klein Gordon equation it one solve relativistic equation. So, one can get the same result. So, that I have not shown. So, this relativistic, but spinless case and relativistic, and spin case ok.

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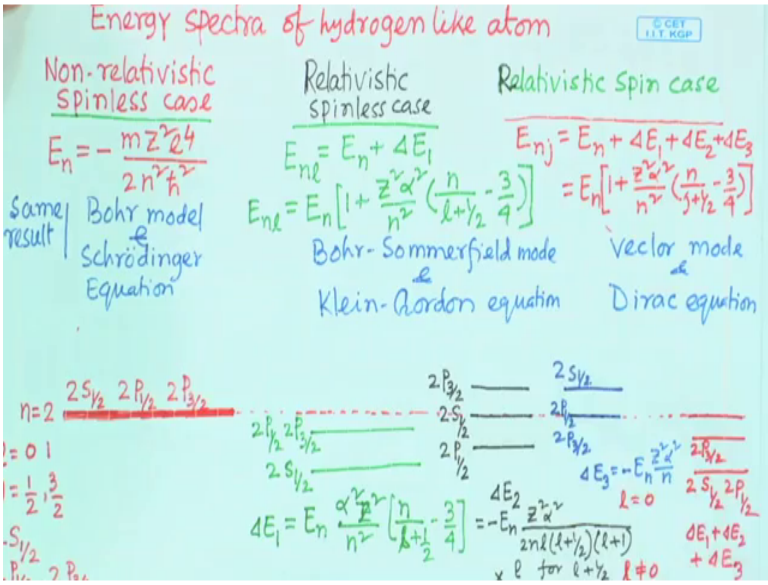

So, that is the solution of Dirac equation, and that energy expression E n j equal to 1. So, this E n plus del E 1 plus del E 2 plus del E 3 ok, if we add all of them. So, each correction term we have derived. So, now if you if you add all of them you should check it then you will get E n j equal to E n 1 plus z square alpha square by n square n by j plus half minus 3 by 4 ok.

So, this the this similar result to I told when you consider the vector model, basically the to find out the total angular momentum using the vector model J equal to V plus S ok, and this same result we got from the Dirac equation ok. Now in case of relativistic, in case of non relativistic spinless case. So, if for just if we consider n equal to 2.

So, this is the energy level, and for n equal to what are the spectroscopic term. So, n equal 2 l equal to 0 1, and then J will be half and 3 by 2 l plus half l minus half so, it is half and 3 by 3. So, this spectroscopic term you will get this n 2 n equal to 2 l equal to 0 s ok. So, j will be half so, 2 S half this is 1 spectroscopic terms state, and another l equal to 1; so P 2 P so j will be half and 3 by 2. So, j equal to so 2 P half 2 P 3. So, l equal to 2 basically as for the energy of this 3 state 3 state 2 S half 2 P half 2 P, 3 by 2 this 3 steps will have the same energy will have the same energy ok. Now if you consider the relativistic correction relativistic correction, if you include the relativistic correction. Now degeneracy will removed so, they are degenerates same energy they are so, degeneracy removed, but here in this correction term it is you can see it does not depend on J it depends on only l.

So that is why S and P it will consider s and P it will not differentiate P half and P 3 by 2. So, P half and P 3 by 2 will have the same energy, will have the same energy whereas, this S half will have the different energy. Now S half it is see this from the original energy it has come down it has come down both has come down because, this term this red line dotted line is basically this term E n ok, now additional term l when l is smaller. So, this term will be higher ok. So, it is so E n is negative. So, it will add more negative to the E n. So, it will come down more.

So, that is why half this 2 S half is here whereas, this 2 P half of 2 P 3 by 2. So, l is higher so, this term will be smaller. So, less negative so, this term it will at less negative so, but it will add some so, so it will it will come down, but it will be this value it will be smaller than the this other value for S 2 S half ok. So, that is why this the now this energy level it was degenerate for this 3 states, now this degeneracy is removed in some extent, but we are getting 2 energy level 1 is for S half and another 1 is for P half and P 3 by 2.

Now if you consider if you consider just from this original E n ok, now if you consider this other correction say just only del E 2 correction ok, d to del E 2 correction this spin orbit interaction correction. So, then in this expression you can see you can see it depends on l it depends on l, but this correction del E 2 is 0 for l equal to 0 so, S so this whatever the original energy for 2 S half. So this, it will remain the same energy 2 S half, but other P 3 by 2 and P half ok. So, 1 has gone up and 1 has come down because, here this term negative term this the negative term. Now it is multiplied with l for j plus half ok. So, when you multiply by l ok.

So, this is for l plus half means P 3 by 2 you can consider for in case of P 3 by 2 so, this is negative this is negative. So, this term this is negative ok. So, already whatever the negative energy was there so now, so, this term already negative, this term this E n it has it is there it is a negative. Now negative into this negative they have to be positive. So, some additional with negative energy some additional positive term is added. So, it will go up it will go up ok. So, that is what happening and other case when j equal to l minus half means j equal to half P half in case P half it is minus l minus 1; that means, it will be plus E n this will be plus term.

So in general this is whatever the negative energy dotted lines are there. So, some more negative part is added with it more negative part slightly added with this so, it will come down ok. So, for P 3 by 2 some small positive term was added with negative. So, it has come up is reduce the negative value and, it P half it increase the negative value ok. So, now, you see that due to this correction spin orbit interaction correction.

So, P P 3 by 2 and P half they are separated ok. So, this is due to the relativistic not relativistic spin orbit interaction correction and, other Darwin term in case of Darwin term you can see it is a it is this term is E 0 for l is not equal (Refer Time: 31:25) constant is the red dotted line, original energy for P half and P 3 by 2, but S this term has gone off why this term again it is negative this del E 3 negative ok. Now when it is negative as I told already E n this (Refer Time: 31:46) negative term.

So, now here this earlier it was plus term when it is plus more negative term is included there. Now because of this minus sign so, what about the original negative minus sign, now some positive correction term correction term is added with the negative value. So, that is why it will be less negative. So, it has gone off now 2 S half is basically separated from this P half and P 3 by 2 ok.

So, this are effect of different correction term on the spectral energy level that I have shown individually, but individually we will not see will see ultimately the total if a and this for total effect that is the energy level. So, here basically this E n j it does not depend on l. So, it depends on j ok. So, for same l value for same l value that is ya so, so only we have to see this j value of this of this term and n value. So, n is same for all n equal to 2 so, now j value we have 2 j value 1 is half and another is 3 by 2. So, this P 3 by 2 is separated from the P half and S half.

So here we has to be same when j is smaller so, this term will be higher. So, it will be more negative so this more energy than this P 3 by 2. So, this ultimate (Refer Time: 33:41) of this. Now here you can see this s half and P half these are having the same energy this are having the same energy, but Rutherford and lamb did experiment microwave experiment micro yes, I think they use this I think radio radiowave it is the longer wavelength lower frequency ok, radiowave experiment and, they found that this s half and P half is not basically having the same energy, P half is shifted upwards from the sorry S half shifted upwards from the P half.

So, they are not having the same energy they have some energy difference and, this energy difference this shift the shift of S half form P half as per the Dirac theory it should have the same energy, but in reality experiment radiowave experiment shows that they do not have the same energy this S half is basically shifted upwards from the P half; that means, they have the different energy level, but this difference is very small, and this shift as per Dirac equation they coincide, but lamb and Rutherford discovered experimentally that there is a shifting of the s half from the P half. So, this is shift this is called lamb shift and, as earlier just I mentioned here automatically it has come out that.

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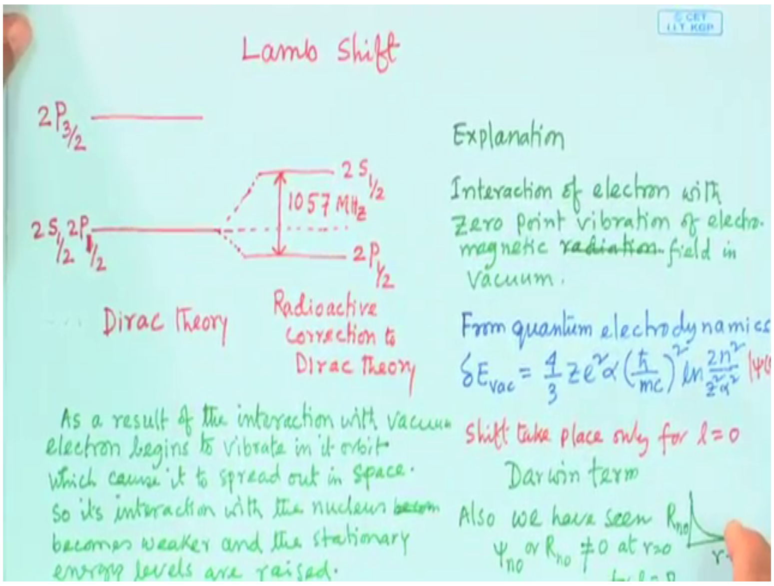

So, originally in as per the Dirac theory so, P 3 by 2 and P half S half so they have their 2 energy level. So, this is P 3 by 2 so this is a another is for S half and P half ok, but for radioactive correction to the Dirac theory that is a theoretical also calculated and, experimentally it is found.

So if we if 1 consider the radioactive correction to the Dirac theory, then it shows that this 2 S half and 2 3 half they are they have different energy, and 2 S half is shifted upwards from the 2 P half, and that shift is a basically lamb shift that shift is basically lamb shift, and this separation is very small it is the 1057 mega hertz ok. it is a very small frequency, and explanation of this is slightly difficult for you, but this is the experimental fact, but just let me let me tell you explanation.

So, this type of shift as I told that is a this comes from radioactive correction radioactive interaction ok, now explanation is that is basically this type of shift is coming due to the interaction of electron with 0 point vibration of electromagnetic field in vacuum, what does it mean, if you if you remember this simple harmonic motion harmonic oscillator. So, harmonic oscillator we tell this earlier it was n h cross kind of things. Now from this quantum mechanics it is come energy expression E n equal to n plus half h cross.

If an n equal to 0 then energy is half h cross so, this is call 0 point energy ok. So, similarly in electromagnetic field also in vacuum there should not be any electromagnetic field, there should not any electromagnetic field it is just similar to this 0 point energy of harmonic oscillator, for n equal to 0 there should not be any oscillation any energy, but it is there that is why it is called 0 point energy.

So, it has come from quantum mechanics classically you cannot think of it ok, if there is no this l equal to 0 from where this vibration will come oscillations will come, but quantum mechanics tells that no there is a there will be like t equal be 0 at 0 temperature. So, there should not be any energy vibration any movement of this oscillator or atoms in the solid, but quantum mechanics it is there. So, that is why it is called 0 point energy. So, similarly vacuum we are telling vacuum. So, from where this electromagnetic wave will come.

So, but it is possible in quantum mechanics and so, that is why it is called the 0 point vibration of electromagnetic field in vacuum, and from quantum electro dynamics classical electro quantum electro dynamic, it is shown that this energy this correction due to this radioactive radiation or electromagnetic field so, this correction in vacuum. So, it is a expression terms like this ok. So, here in this expression one can see one can see psi 0 psi 0 term ok, means l equal to 0 this term.

So, so this term only exists for l equal to 0 for other value of l is does not exist and, this basically tells about their connection to be as I mentioned this in case of there is only r equal to 0 there is existence of psi and, this psi is basically that existence of psi only for l equal to 0. So, that that here just I have shown. So, this are lamb shift is connected with that 1. So, so it is called Darwin term. So, this again this related with the Darwin term and this comes this so when so that see the importance of the wave function you know.

This not only energy expression, but wave function also important that is what I was telling that solving the Schrodinger equation, we got the same energy expression, what else we got I told that we got the wave function, this wave function also give very important information, and that is why there when we study the wave function that we have seen the variation of the wave function as a function of r and we have seen that only wave function exists at r equal 0 when l equal to 0.

And now when l equal to 0 so, Darwin term exists and then vacuum correction term exists here, whatever I am showing ok. So, and this is basically this is connected with the interaction of nucleus and the electrons. So, basically what happened this, this we can tell like this there is the as a result of the interaction with vacuum, electrons begins to vibrate in it orbit which cause it to spread out in space ok.

So, there should not be any vibration in vacuum in terms of interaction with the with the electromagnetic, but same 0 point vibration of electromagnetic field exist in vacuum. So, electron basically vibrates even if in vacuum electron beings to vibrate electron begins to vibrate electron vibrate and when electron vibrate so, when electron is stationary in orbit so fine. So, this interaction between the nucleus and electron will be whatever.

So, that will be effected when this electron is not point electron on orbit, it is a speed our say spherically speed our speed our on a on a region and that will basically affect the interaction and in principle in fact, this vibration cause it to spread out in space. So, it is interaction with the nucleus becomes weaker and, the stationary energy levels are raised. So, energy level energy depends on the potential energy v r ok. So, now how so potential energy tells about the interaction between the 2 charged interaction between the 2 charged now here electron and the nucleus.

So, potential energy it tells it is whether it is weaker or stronger so, it depends on the on the on the interaction between this between this 2 charge 1 is electron and 1 is nucleus. So, when this in place of point charge when it oscillate vibrate. So, it becomes says it spread out and, then the interaction with the nucleus is become weaker when it becomes weaker. So, it is energy value of the energy value of the energy level, it is basically it is increased means it becomes less negative. So, it become positive it goes up ok. So, that is why and it happens only for s orbit s orbit s energy level, because in case of a l equal to 0 we have seen the existence of the of the existence of the energy of the wave function.

Okay is there is of a wave function that r equal to 0. So, this only this that it tells that this s s energy level it is affected due to the interaction with the nucleus and, this interaction with the nucleus it is change, because of the because of the changing of the nature of the changing of the nature of the of the of the electron density ok. If it is stationery then fine if it is not stationery that will spread out as it is predicted that due to the 0 point oscillation, it will spread out and then this interaction will be weaker, and then (Refer Time: 46:35) will go up. So, that is why that is the nothing, but lamb shift ok.

So, this way is not very clear explanation I will able to give you, but just um because 1 has to know quantum electro mechanics to understand more in details, but this the (Refer Time: 46:57) logically I can tell you the explanation of lamb shift ok. So, I will stop here.

Thank you for your attention.