Atomic and Molecular Physics
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture – 36
Quantum Mechanical treatment of Hydrogen like atom (Contd.)

So, we had, we have discuss about the Non-relativistic Spinless Schrodinger equation and we have seen the solution basically that Eigen equation.

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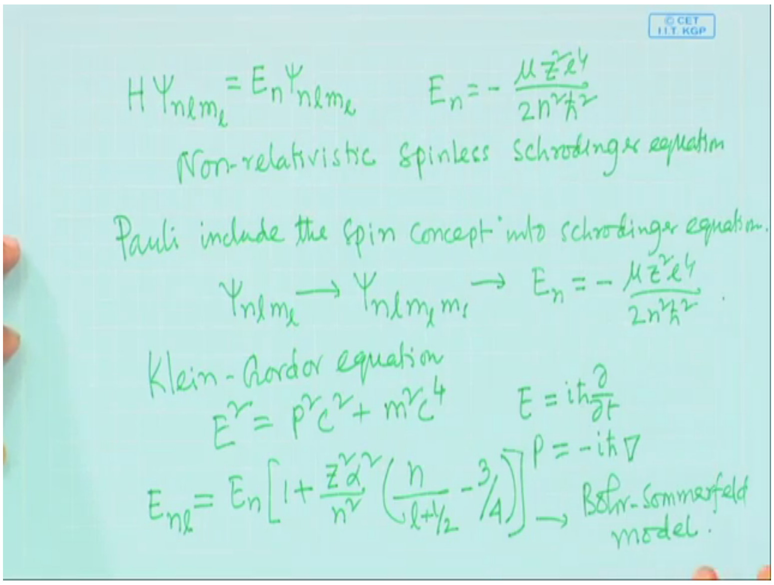

We have got that is H psi n l m l equal to E n psi n l m l. So, n we have seen the expression, n equal to minus mu Z square E to the power divided by 2 n square H cross square right. So, this is basically as I told, this is are non-relativistic, non-relativistic Spinless Schrödinger equation. So, that is the result we got, but it cannot explain the fine structure and hyperfine structure of hydrogen like atom. So, next people started to think that whether, we can include spin as well as relativistic correction, in this Schrodinger equation and that was the motivation for further study of this 1 electron system.

So, actually Pauli, Pauli include, Pauli include the spin concept into Schrodinger equation , but for that case, this psi n l m l. So, that just reminds the wave function, he got that is psi n l m l m s. So, this, but energy remains same energy that is Eigen value that remains same mu Z square e to the power 4 divided by 2 n square h cross square. So, it was. So, again it could not explain the, the fine structure and hyperfine structure. So, later on this relativistic correction, it was that Klein and Gordon. It is called Klein Gordon equation, Klein Gordon equation.

So, basically they, they took the energy expression, relativistic energy expression is basically E square equal to P square C square plus m square C to the power 4. So, then putting the Eigen, the putting the operator form E basically i h cross del by del t and P equal to minus i h cross del. So, they try to solve it and solving this Klein Gordon equation.

They got the energy expression E n l. So, l dependent they, they got the expression. So, that was basically E n 1 plus Z square alpha square by n square, then I think n by l plus half minus 3 by 4. So, so we can see that this energy expression is, is similar to this almost same, except this l plus half, it was earlier l or k that, which was got from this Bohr Sommerfeld model, Bohr Sommerfeld, Feld model right. So, it was similar to Bohr Som Sommerfeld model, so, but still it cannot explain the, it cannot explain the fine structure and hyperfine structure, hyperfine structure.

So, next the ultimate equation, which was able to explain everything about the atomic spectra for 1 electron system that was basically Dirac equation, as I mentioned this Dirac equation, this it is solving, this Dirac equation is really, is, is tough for under graduate student, but it is tough, because you are not, you have not completed the quantum mechanics course, when you will complete quantum mechanics course then it will be, it will not be that tough. So, you will be able to understand that one, but. So, just I will briefly try to discuss about the Dirac equation and it is a result to for the completeness of this discussion. So, in 1928 Dirac, 1928 Dirac discovered relativistic theory, incorporating electron spin ok.

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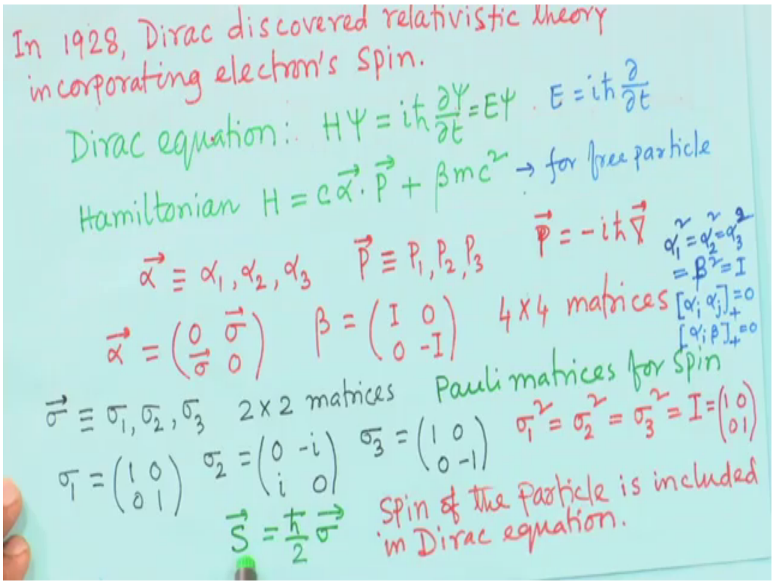

So, this Dirac equation form is this standard from is Schrodinger form basically H psi equal to E psi. So, in this i h cross del psi by del t, it is the n operator form so, but dirac took this Hamiltonian, this form is like this, this C alpha dot P plus beta m c square. This is for free particle, this Hamiltonian, Dirac Hamiltonian is for free particle. So, here alpha has three components; alpha 1 alpha 2 alpha 3. P also linear momentum, this it has three components P x P y P z, but here I have written P 1 P 2 P 3. So, and this is the operator form. And what is alpha and beta alpha; it is basically 4 by 4 matrix. So, 0 sigma, sigma 0 beta equal to I 0, 0 I. So, I is basically unitary matrix 2 by 2 matrix and sigma is called Pauli matrix, you know this, it is also 2 by 2 matrix. So, ultimately beta and alpha, this is the 4 by 4 matrix.

So, and they satisfy this property alpha 1 square equal to alpha 2 square, equal to alpha 3 square, equal to beta square equal to I unitary matrices and alpha 1 alpha 2 means alpha i alpha j, they are you know commu commutators. So, this is basically similar, anti commutatory is there. So, anti commu, commutatory is alpha, alpha i alpha j. So, alpha i alpha j minus alpha j alpha i equal to 0. So, that is the commutator, but anti commutator is basically alpha i alpha j plus alpha j alpha i equal to 0. So, then is, then it is called anti commutator. So, these are basically alpha i alpha j, alpha 1, alpha 2, alpha 3, this anti commute with each other and alpha and beta also they anti commute with each other. So, these are the properties of alpha and beta. So, so this matrix has taken are define such away. So, they should follow this, this relations and this sigma as I told, this Pauli matrix for spin. So, in this alpha beta ac actually, this spin, conc, concept is introduced ok.

So; that means, in Hamiltonian, Dirac Hamiltonian, this spin concept already is included through this Pauli matrices. So, Pauli matrices sigma 1 sigma 2 sigma 3 that is defined in this way, sigma 1 equal to 1 0 0 1 sigma 2 0 minus i i 0 sigma 3 1 0 0 minus 1 and they follow this sigma 1 square equal to sigma 2 square equal to sigma 3 square equal to i unitary matrix that is basically 1 0 0 1. So, and this sigma related with the spin. This is so spin S equal to H cross by 2 sigma. So,. So, here just, I just try to show you, tell you that this in Dirac Hamiltonian, spin is included; spin is included in Dirac Hamiltonian through alpha and beta then. So, this Dirac Hamiltonian for, for hydrogen like atom.

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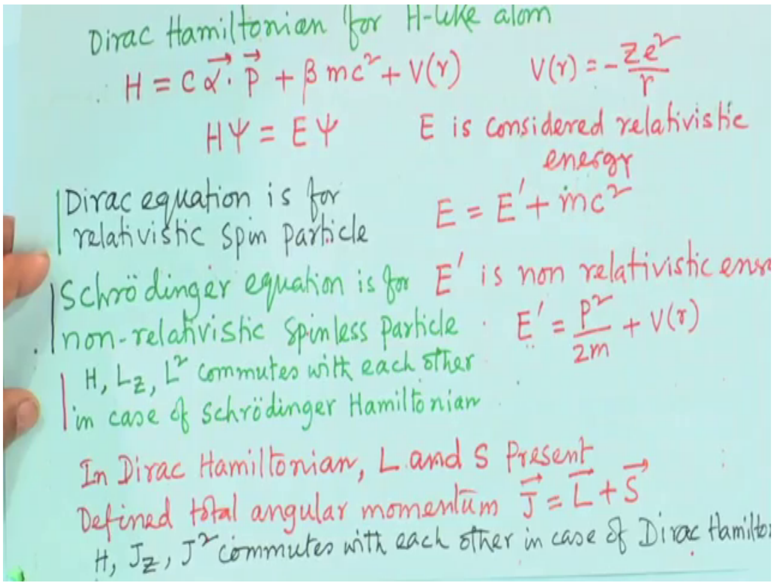

So, for free particle that was C alpha dot P plus beta m c square now, for hydrogen like atom. So, we have to include, these potential central, central fields, central potential. So, V r. So, V r equal to you know the minus Z e square by r. So, this, now, taking this Hamiltonian for hydrogen like atom, we can write this equation, Dirac equation H psi equal to E psi, where H is this and E is considered as a relativistic energy; that means, E equal to E dash plus m c square E dash is non-relativistic part and then when plus m c square. So, then becomes relativistic energy E dash equal to non-relativistic energy E, write is basically, standard in Schrodinger equation, we have considered P square by 2 m plus V r ok.

Now, now this equation then H psi equal to E psi here, already we have considered spin, through this alpha and beta as well as this energy through this energy, you have considered the realistic energy. Now, in case of in case of Schrodinger equation, there we, we solve considering the Hamiltonian, we have solve it, but we have seen that that wave function, that wave function psi n l m that is simultaneous wave function of L square and L z also not only H, it is simultaneous wave function of H L z and l square, because H L z and L square that commute with each other, if operator commute with each other. So, they, there will be simultaneous wave function, but in case of Dirac Hamiltonian, one can show that L and S L and S present, but, but this Dirac defined, the total angular momentum that is basically L is angular momentum orbital angular momentum, S is spin angular momentum.

So, Dirac defined total angular momentum J that is basically, need to sum up then L plus S and and he, he showed that this Hamiltonian Dirac, Hamiltonian H, it commutes with J z and J square, it does not commutes with L z or L square, but it commute with J z and J square ok. So, naturally in the, in natural way this form, of this form of this Hamiltonian, it is, it demands that, that L or S individually, they are not suitable for this for this Dirac equation actually, this total angular momentum is required and for that the J Dirac deals with J and J, it is J component J z and J square, this commute with this Dirac Hamiltonian.

So, in the process of solving this Dirac equation, it is clear that, that Dirac equation or Dirac Hamiltonian is, is defined is taken such a way, it is spin concept is included relativistic energy is considered as well as this Hamiltonian will commute, with total angular momentum, it is z component J z and J square.

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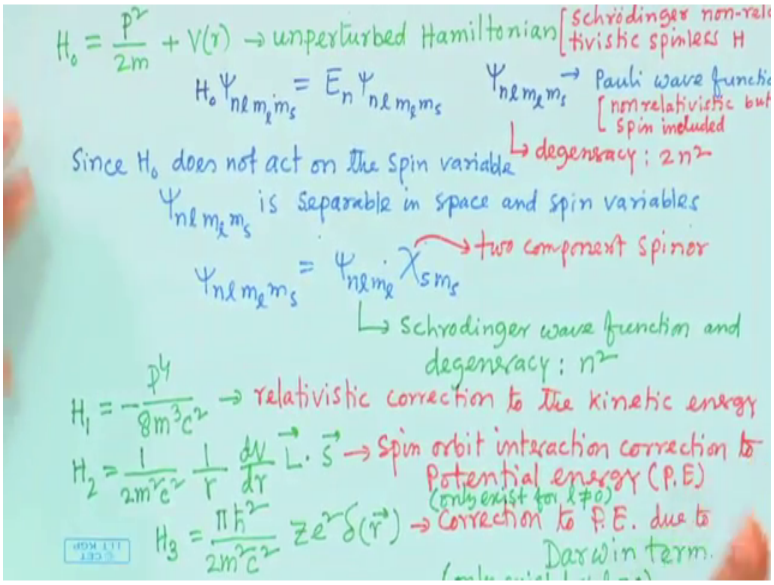

So, this. So, this of un part of. So, here now this if we take I think, I will considered this one yes, yes.

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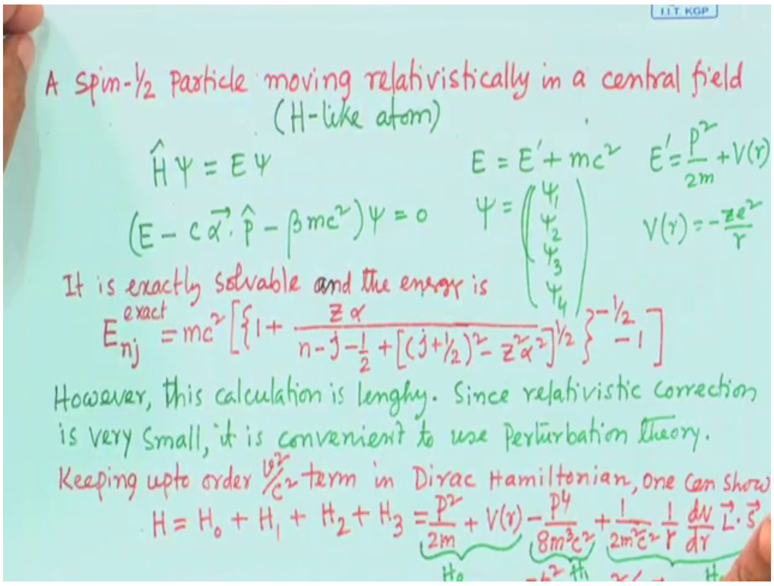

So, now what we are going to do? What we are trying to, trying to know or trying to understand or we are trying to study is spin half particle moving relativistically in a central field. So, these are our say topic that is basically, hydrogen like atom. So, for that Dirac Hamiltonian, we have taken this H psi equal to E psi E equal to E dash plus m c square, E dash relativistic, non relativistic energy and E is relativistic energy. So, E dash already I have defined ah, equal to P square by 2 m plus our this potential V r and V r, this seems alpha and beta, these are 4 by 4 matrices. So, psi also will have this four component. So, it is in matrices form, it is written in column psi 1 psi 2 psi 3 psi 4 this four component ok.

Now, this Dirac equation, we can write this way E minus C alpha dot P minus beta m c square psi equal to 0. So, this equation, this equation is exactly solvable and the energy expression, if one solve exactly. So, energy expression comes like this; however, this calculation is, is, is lengthy and if you see that relativistic correction term is very small compare to the main energy term. So, one can use in quantum mechanics, one can use this Perturbation theory. So, one has to know the Perturbation theory. So, Perturbation theory, basically what has to consider the main part and solve it and taking the wave function of that solution?

So, next that wave function will be used for the correction term, if this correction term is, is very-very small, compared to the main term. So, that is the basically in quantum mechanics called Perturbation theory. There are different method, there are approximation, there different approximation method. So, again one has to really know the quantum mechanics. So, I assume that you have not completed, completed the quantum mechanics course, but when will complete this quantum mechanics course. So, whatever I am telling you, will understand and I will just, I will just, just overlook the step, but I will just discuss the result and after completing your quantum course, you can fill up this basically gap. So, so if you if you.

So, here if you use the perturbation theory, first you have to define, which one is main term and which one is correction term. So, this Dirac Hamiltonian, if you expand it in terms of B y c and keeping term up to V square by C square in Dirac Hamiltonian. So, one can show basically H, it can be beaten H equal to H 0 plus H 1 plus H 2 plus H 3, this basically H equal to P square by 2 m plus V r minus P to the power 4 by 8 m cube c square plus 1 by 2 m square c square 1 by r d v by d r l dot s l dot s plus pi H cross square 2 m square c square Z e square delta R. So, this delta R is basically is called Dirac function, it called Dirac function. So, for delta R R equal to 0, it is 1. R is not equal to 0, it is, it is 0. So, this term in vanish. So, these, how this term has come? This is basically, this Hamiltonian, Dirac Hamiltonian one has to expand it and then, then one can get this

Dirac Hamiltonian in this form. So, there are other terms also higher terms so, but here we have written up to this V square by C square term ok.

So,. So, here you can, we can identify this H 0. Basically, we have taken this P square by 2 m plus V r. So, this is this called unperturbed, unperturbed main term and this we know this, this form already know, this term this basically Schrodinger Hamiltonian, Dirac Schrodinger Hamiltonian, this means is a non-relativistic and Spinless Hamiltonian. Now, this term minus P to the power 4 8 m square c square that we have defined taken as a H 1, H 1 and then next term.

So, what is H 1 that I will tell you what is the meaning of H 1? This correction term basically, second correction term is this one, is 1 by 2 m square c square 1 by r d v by d r l dot s. So, spin orbit here, really it will l dot s is tells of the spin orbit coupling, coupling between the orbital orbit, orbital angular momentum and the spin angular momentum. So, this term we have taken as a H 2, this is another correction term and third term is H 3, this we have defined as a H 3. So, so what are the correction? What is the meaning of H 1, H 2, H 3 that I will tell you.

So, for H 0 is as I mentioned this Unperturbed Hamiltonian, this Schrodinger, non-relativistic spin less H basically, right and, and if you ah, if you apply, you know the solution of the H 0, already from Schrodinger equation. So, it is solution is psi n l m l m s, here m s, we have taken as I mentioned this a Pauli wave function, this is the, this called Pauli wave function as I told, this Pauli included this spin in the Schrodinger equation and got the same wave function as he got that, this different wave function, but energy term is same e n, the term was same. So, this term originally this psi n l m l. So, is degeneracy was n square degeneracy was n square. Now, just is the de, de, degeneracy increased by 2 n squares, when spin term is included. So, so for, for Schrodinger equation with spin wave function is basically psi n l m l m s can be taken.

So, this the wave function for Unperturbed Hamiltonian having the energy is E n equal to minus ah, mu Z square E to the power 4 by 4 n square H cross square, this same. So, this H 0 basically, does not act on the spin variable. So, that is why this psi n l m l m s, it can be separable in space and spin variables. So, this is the Schrodinger wave function and degeneracy n square and this space part basically and this other, the one is spin part. So, this wave function has basically two part; one space part and as the spin part. So, so this can be taken as a wave function for H 0 also, because H 0 does not act on the spin part ok.

So,. So, now, H 1 correction term is basically minus P to the power 4 by 8 m cube c square. So, this correction, this is, this term is basically, it is relativistic correction to the kinetic energy, relativistic correction to the kinetic energy and H 2 term is equal to 1 by 2 m square c square 1 by r d v by d r l dot s. So, this is another correction term. This kinetics, it is basically spin orbit interaction correction to the potential energy spin orbit interaction correction to the due to this interaction energy change. So, this connection to the potential energy and this so; obviously, this correction term exist only for l is not equal to 0, because this term contains l dot s is l equal to 0.

So, there will not be spin orbit interaction. So, that is why this term is active or valid for only l equal to l is not equal to 0 for l equal to 0. This term vanish similarly, for H 3 term, another correction term. So, in this term delta R is there, this term is called basically, Darwin term, this term is called basically Darwin term and this it is, it is correction to the potential energy due to Darwin terms.

So, this term is called Darwin term and this connection only exist for l equal to 0. Why that you can understand that delta R, the Dirac, Dirac delta function, it is the delta R, it is the equal to 1, when R equal to 0 delta R equal to 0, when R is not equal to 0 ok. So, now we remember that when I have showing this, when I have showing that this form hydrogen atoms from Schrodinger equation.

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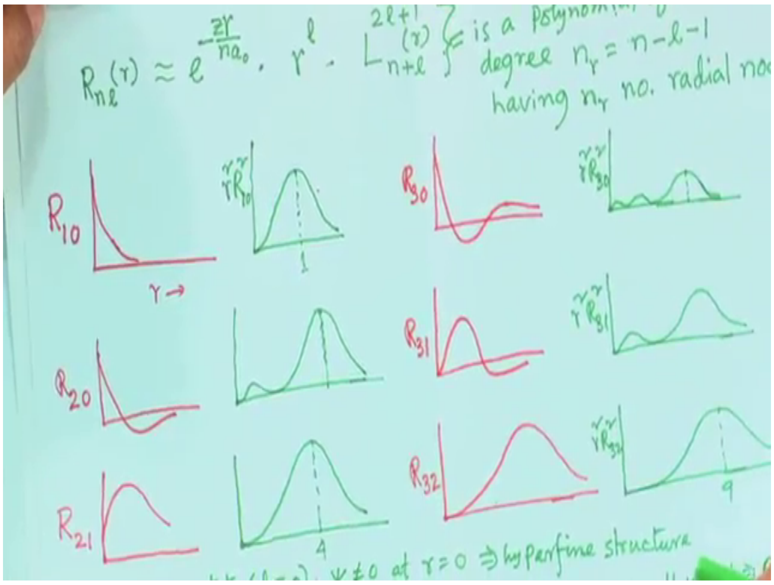

Whatever, this wave function we got. So, when we plot it, there I have shown you that when l equal to 0, whatever the n does not matter, when l equal to 0, then only psi exist or R n l exist at R equal to 0, l equal to 0, there this, this exist here, l equal to 0, 0 here. So, psi is not equal to 0 at R equal to 0 and here this in other cases. It is 0, here again 3 0 psi is not equal to 0 at R equal to 0. So, so when l equal to 0, then only wave function exist at the, at the, at R equal to 0 in other case, when l is not equal to 0, this wave function does not, is you are function is 0 at R equal to 0.

So, this is basically, this is, this has come here as a Darwin term and this term is only valid, this term is only valid for, for l equal to 0. So, Darwin term tells basically the interaction. So, wave function exist at R equal to 0 only then this term, correction terms, terms occurs. So, Darwin term is basically, this correction to potential. It is basically, it is this, this, because of the existence of the wave function, existence of the electron near to the nucleus.

So, there is interaction between nucleus and electron change of interaction of the between, between electron and nucleus, where in case of l equal to 0 or in case of R tends to 0 ok. So, this term is, is 0, when n is not equal to 0 and other term is 0, when l equal to 0 and exists when l is not equal to 0. So, these two term as if this complementary 1 is for l equal to 0 and another is for l is not equal to 0. So, one of them will, will be the correction term to the potential energy and this H 1 is basically all the time it is there and it is electric. So, electron kinetic energy.

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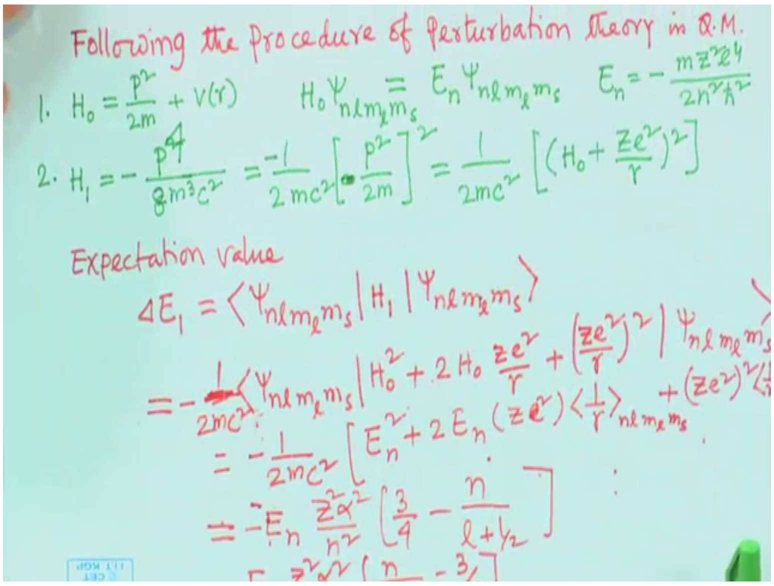

So, next, we got this form of H, we got the form of H. Now, using the perturbation theory, one can get this correction to the energy. So, as I told this unperturbed term is basically, H 0 and H 0 equal to P square by 2 m plus V r and 1 can put, 1 can. So, these waves, what is the wave function for this? So, H 0, if you apply H 0 on this wave function psi n l m l m s. So, you will get the energy n. So, energy n is this. So, here we are writing m in place of being. So, as we are considering this, in this Dirac equation m c square, we are taking m ok.

So, just I have written m. So, this is the, this is the energy, we got from the Unperturbed Hamiltonian and Unperturbed Hamiltonian is energy wave function is this n l m l m s. Now, these wave function will use for the, for, for find the expectation value of expression value of H 1, H 2, H 3. So, I think, I will, I will discuss this to find out this expectation value of correction term in next class.

Thank you for your attention.