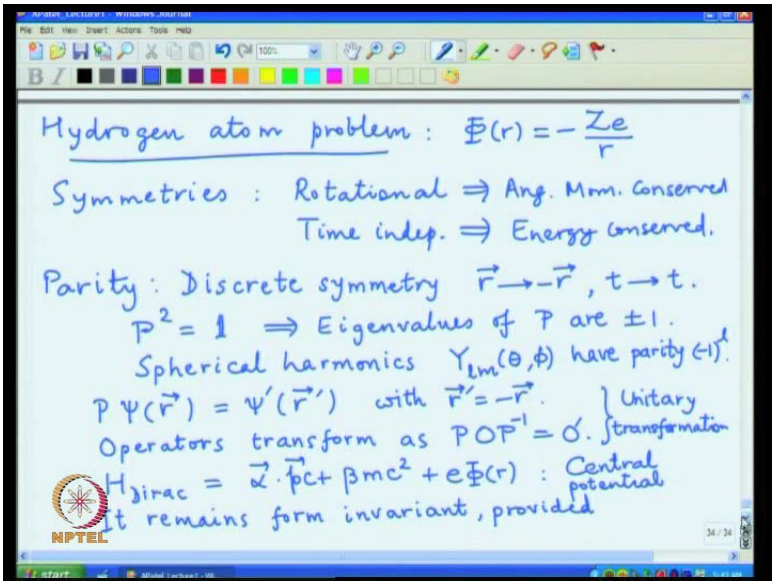
Relativistic Quantum Mechanics
Prof. Apoorva D Patel
Department of Physics
Indian Institute of Science, Bangalore

Lecture - 7
The Hydrogen atom problem, Symmetries, Parity, Separation of variables

So, today we are going to discuss the solution of the hydrogen atom problem in case of Dirac equation. Now, for any problem in quantum mechanics the solutions are easily identified in terms of a set of quantum numbers which are associated with mutually commuting operators. So, the task here is to first identify a set of mutually commuting operators which will be given specific quantum number values, and then a general solution can be expressed in terms of this quantum numbers. The quantum numbers become the Eigen values of particular operators, and the corresponding wave functions describes the various Eigen states.

Now, one of the quantum numbers in all these time independent problem is energy itself, because the Hamiltonian is a constant of motion. And so the task time is to identify all the operators which commute with the Hamiltonian, and they will give rise to the so called Eigen states which are stationary; that means they do not evolve in time. It is a easy to connect also all the operators which mutually commute with a set of symmetric transformations. Because it is a general principles that conserved quantities are associated with a symmetries which are exact for that particular problem.

(Refer Slide Time: 02:30)



And, these symmetries are well known in case of hydrogen atom. One symmetry is a time independence of the Hamiltonian which means the energy is conserved, other symmetry is a rotational symmetry which means that the angular momentum is conserved. There is a third symmetry which is discrete instead of these 2 continuous symmetries, and that is called parity. And it is generally specified in terms of coordinate transformations where the vector r goes to minus r, well time does not change.

And, clearly for a potential which depends only on the coordinator, generically referred to a central potential, parity is a symmetry of the problem. And it again has a discrete Eigen values. And the Eigen values are rather restricted for the simple reason that if I define a operator for parity p, then applying the operator twice I comeback where I started with the original system; and that means, Eigen values of p are basically plus or minus 1.

And, we have seen examples of these in a conventional mathematical physics, in particular the spherical harmonics where the radial part is completely factored out from the function and they depend only on the angular part. And generally denoted by Y l m, and the convention is used such that the parity of this objects is minus 1 raised to l. So, this is a well known in non relativistic quantum mechanics. We have to basically generalize the particular transformation in the case of Dirac equation and an extra feature comes in. And let us tackle that before going back to the hydrogen atom problem.

The Dirac equation has a wave function, and we will define a parity transformation such that p acting on some wave functions on r, gives a wave function which is psi prime, and then you coordinate r prime, and with r prime is equal to minus r. If I want to use this transformation on the wave function, and there will be a corresponding transformation on all the operators as well. So, the new operator O prime is defined as P O P inverse. And in particular, in quantum mechanics these are unitary transformations.

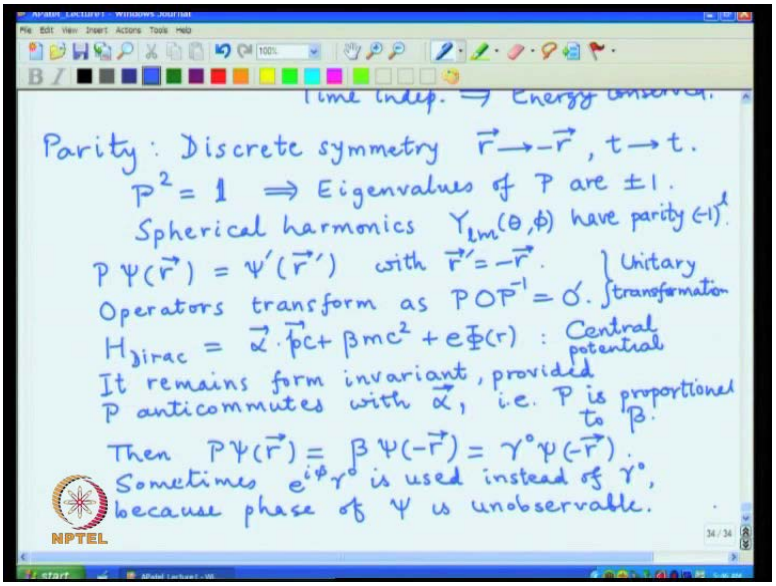
We determine the explicit form of p for Dirac equation by going back to the explicit form of the Hamiltonian, and demanding that the Hamiltonian remains form invariant when this particular transformation is applied. So, in particular, H Dirac had a structure which is alpha dot p plus beta, you can write a c here to mix everything dimensionless, plus in present of potential it will be some functions of r; this is for central potential.

Now, if we see what happens under this particular transformation, in particular we have to consider what is happens to P H P inverse when H has this explicit form. It is easily

seen that under the parity operation the term which is beta does not change because it does not involve the vector coordinate r anywhere. The term involving phi also does not change because all it has is a magnitude of r and not the direction. And so under this transformation we must have an operation which commutes with this two term of the Hamiltonian. So, the structure remains form invariant.

On the other hand, under the same transformation the sign of this vector p, which can be also written as a gradient operator changes, because r prime goes to minus r. And so the first term flips a sign, and then we need an operator p which flips the sign back to its original case if the operator anticommutes with the remaining part which is alpha, and then the Hamiltonian, the total Hamiltonian will become form invariant.

(Refer Slide Time: 09:24)



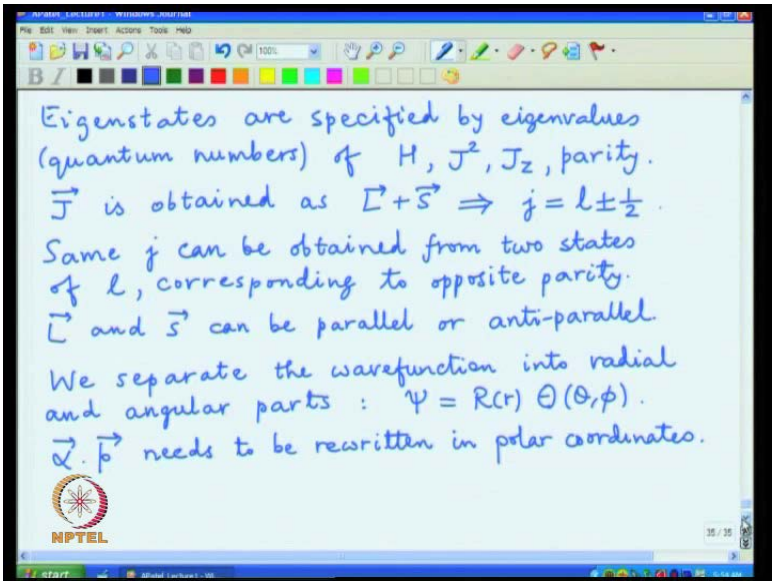
So, it remains form invariant, provided this operator anticommutes with vector alpha. And we immediately know what that answer is, that P is proportional to matrix beta, and that immediately now gives a complete specification of the parity transformation in case of Dirac equation, that P acting on psi of r is equal to beta psi of minus r. Sometimes it is also written as a matrix comma 0. It is a same as definition of beta.

And, this transformation now has both the components of the parity transformation built in. One is the change of the space time coordinate, and another is a change in the internal degrees of freedom where the matrix beta or gamma 0 acts. And it is obviously true that P square brings back the wave function to where with started with is as it necessary. And if the state is such that it is an Eigen value of the parity operator, the P times psi will also

become equal to plus or minus psi, depending on the sign of parity.

Sometimes, one writes a more general transformation which is e raised to phi gamma 0 is used for the particular operator, and reason being that because the phase of psi is unobservable. So, in case hydrogen atom problem we have a central potential, and the state should be also labeled by Eigen value of parity. And so now we are going to look for a mutually commuting set of operators which can be given Eigen values.

(Refer Slide Time: 12:48)



So, Eigenstates are specified by Eigenvalues which are can also be referred to as quantum numbers of the mutually commuting set of operators which so far we have constructed are the Hamiltonian, J square and J z. They are followed by the same logic as conventional angular momentum properties in non relativistic quantum mechanics and parity as well. It could be that there are more set of quantum numbers in addition to this, and we have to figure out if that is the case. But, at least these ones should exist.

And, there is something which we can infer from the known property of how J is a constructed. So, J is obtained as L plus S. And that from the analogy with non relativistic quantum mechanics will tell you that adding the rules of angular momenta, the Eigen values will be, J will be l plus or minus half where l is the Eigen value of orbital angular momentum, and half refers to the Eigen value of the spig.

Now, the interesting part is that one can have two possible way of constructing j when you add these 2 components of the angular momentum. So, same j can be obtained from

2 states of l, corresponding to opposite parity. Because the 2 values of l which correspond to the same j- one is j plus half, other is j minus half, they differ by 1 unit of angular momentum. It is a parity happens to be minus 1 raised to l, they will have opposite parity.

So, for every value of j we expect 2 states of parity, and they will be determined by this angular momentum. Addition, and in some sense, they mean whether the orbital and the spin part are parallel or antiparallel. They refer to this plus minus sign. And we need to quantify that behavior a little bit better. And we will have to construct an explicit operator which signifies this parallel or antiparallel addition of the angular momentums. So, L and S can be parallel or antiparallel.

We have seen already, the L and S are not separately conserved in relativistic quantum mechanics. But, it turns out that whether they are parallel or antiparallel, still makes sense. And that is because of the property that the parity turns out to be a good quantum number. And we will then be able to associate a particular quantity which designates these 2 kind of additions between L and S.

Now, before constructing an explicit operator which specifies this addition, it is useful to go back and look at the Dirac equation itself, because that operator should emerge from the structure of the Dirac equation itself. And we know that, that operator will specify whether L and S are parallel or antiparallel. So, we want general solution.

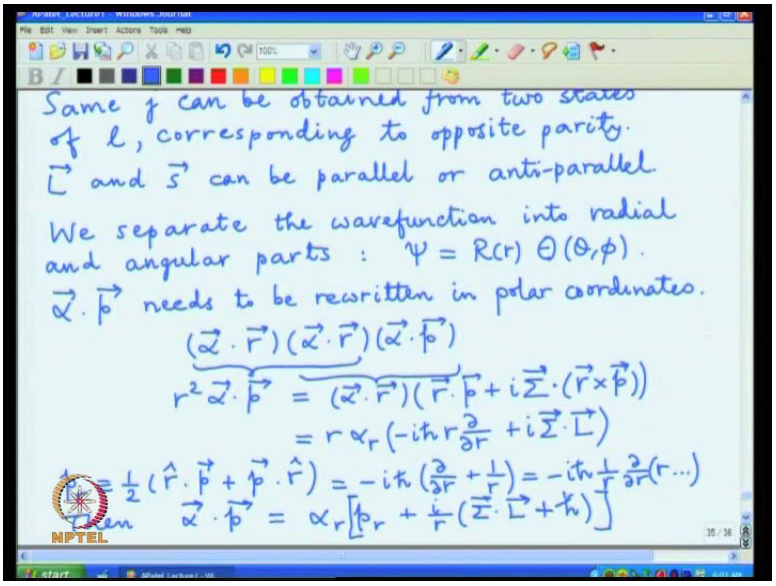
So, we separate the Dirac wave function into radial and angular parts that is dictated completely by the symmetries of the problem. And so psi will be written as some functions on radius, and some other functions on the angles. And we when separately determine the eigenvalues for the radial part, and those for the angular part.

Now, the separation of the Hamiltonian operator is trivial for the rest mass term as well as the potential because they are either constants or depend only on the radial coordinate. The angular coordinate explicitly appears only into the alpha dot p part or the corresponding gradient operator. And so we need to rewrite alpha dot p, not in terms of a Cartesian coordinates but in terms of these spherical polar coordinates where the radial and angular dependent is separated.

So, alpha dot p needs to be rewritten in polar coordinates. The earlier expressions we have seen for alpha dot p were all written in Cartesian coordinates where the things were easy. Constructing it in spherical polar coordinates requires a little bit of trickery, but it

can be done in a rather straight forward manner. And we will see the how angular momentum kind of naturally appears in this formulation.

(Refer Slide Time: 20:50)



And so to be able to do this, I want to construct a kind of triple product of these alpha matrices, and evaluate this triple product in 2 different ways. If you combine these first 2 factors, then the algebraic relations between alpha mean the product of 2 alpha matrices, the only the symmetric part contributes, and so this combination which rerise to a term which is r square alpha dot p, if I combine these 2 parts.

On the other hand, I can choose to combine the second 2 factors, and that produces a term where the first one alpha dot r remains what it is, but the second one is now the combination between r and p where both the symmetric part and the antisymmetric part contribute. And that will give r dotted with p plus i, the antisymmetric part of 2 products of alpha we have seen before gives the matrix known as sigma, the spin matrix. And then, the antisymmetry converts this r and p into a cross product. And both ways of evaluating this must equal. So, that is why this expression equals, what is on the other side.

And now we will rewrite this object by simplifying things which we already know. And alpha dot r, I will just rewrite as r times the radial component of alpha; r is just the magnitude, and the unit vector gives a radial component of alpha r. And this now can be rewritten in terms of a various derivatives. In particular, this p has a usual gradient expansion. So, this will gives minus i h cross r times del by del r, and the second part is i

sigma dotted with L.

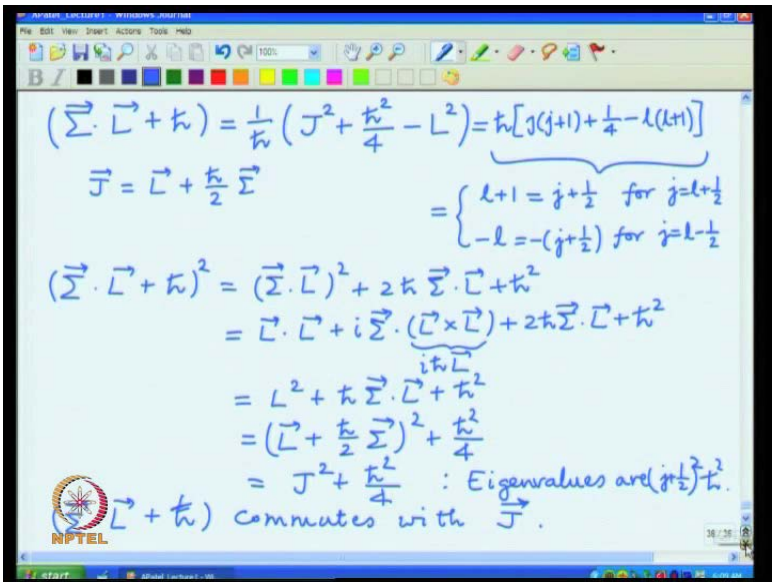
So, we have indeed now separated, alpha dot p, into a radial derivative operator, and the one which involves the angular part where the angular momentum explicitly appears. Now, it is convenient to choose a slightly different operator, then this r d by d r term, so that that operator is Hermitian. And we will define that operator p r which is not the literary that radial component of p, but it is defined as, so that it is explicitly Hermitian, its unit vector r with p.

But, to make Hermitian part, we will add the opposite order of p and r also. It is different than the radial component of the gradient, because this p acts on this r p's, as well. And one can explicitly evaluate these objects. And it comes out to be gradient plus a little bit more, and that extra term is just 1 over r. And this structure is quite common in radial coordinates involving various kinds of operators, Laplacian and gradient, etcetera. In this particular case, it can be rewritten as derivative 1 by r, d by d r r, and then whatever object it acts on. So, this is a operator p r which we constructed by hand.

And then, now we can rewrite this alpha dot p rather explicitly as various factors of r can be removed in a straight forward manner. So, it is alpha r p r plus, the alpha r is actually a common factor, so let me enclose this whole thing inside a brackets. And then, i by r sigma dotted with L, and then this little bit extra correction gives contribution which is h cross. So, this now becomes the crucial decomposition which can be used to separate radial and angular coordinates.

And, we see the pattern of spin and orbital part explicitly appearing in this operator; sigma dot L is indeed an operator, which as I said before, can tell us whether the spin is parallel to L or it is antiparallel to L. And this particular operator now we can analyze in a little more detail to figure out what its Eigen values are, and whether it can serve as a additional object for which quantum number can be specified.

(Refer Slide Time: 28:00)



So, now let us rewrite this operator in different ways- sigma dot L plus h cross. It is equal to, well L has always been written in the units of angular momentum in my notation. So, I can rewrite as a sum of L plus S, whole thing square minus L square minus S square. So, J happens to be equal to L plus h cross by 2 times sigma in this notation. And so this object can be rewritten as by squaring this equation and picking out the cross terms as sigma dot L.

And so it is J square plus h cross square by 4. The Eigen value of S square is S times S plus 1, which happens to be half multiplied by 3 half or equal to three fourth; that three fourth comes with a negative sign and combined with this h cross. It leaves behind this one fourth h cross square, and then L square is subtracted as coming from the same equation. And so now we can plug in the various Eigen values. So, this object is j times j plus 1, plus a quarter minus l times l plus 1. And this has 2 different values depending on whether j is equal to l plus half or l minus half. And so you can list them explicitly.

So, this thing has equal to l plus 1, which also is j plus half, for j is equal to l plus half. This is the state for an algebra. And then, j is equal to l minus half; this quantity is happens to be minus l, or it can be also written as minus of j plus half. So, this object indeed reduces to a sign once you pick a fixed value of j. And the sign will be either plus or minus, and the magnitude will be j plus half.

One can now see this behavior also in a little different ways, and that is to consider the square of this operator as well. So, one can look at sigma dot L plus h cross, whole thing

square. We evaluate this thing without reducing directly to the non relativistic algebra, but just completing the square of all this quantity. So, it is sigma dot L square, plus 2 h cross sigma dot L, plus h cross square.

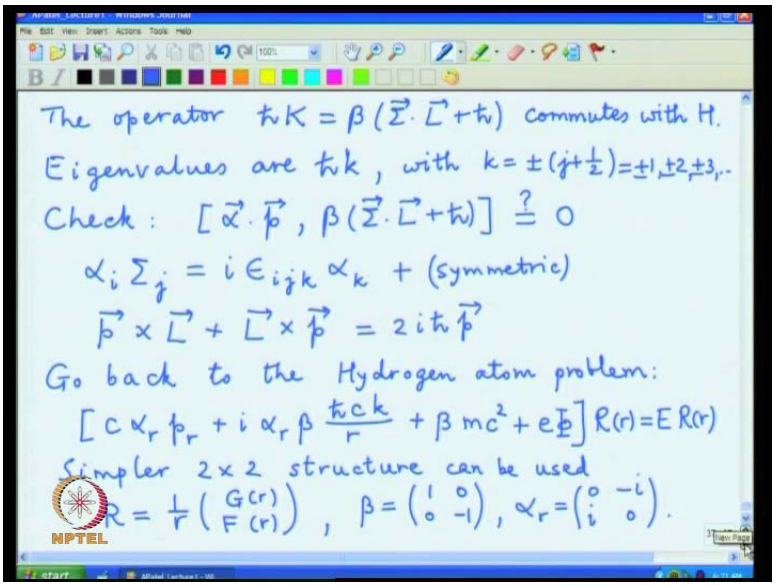
And, one can use now the algebra of these spin matrices. So, the symmetric part of this thing gives L dot L, and the antisymmetric part contributes L cross L. One should remember that this object in angular momentum algebra is not 0, unlike a classical vectors. And this, it is the anticommutator which can be rewritten as i h cross L as well. And then, one can complete addition and cancelation, if the something cancels between the second and the third term.

And, it can be now rewritten as, h cross sigma dot L, plus h cross square; which can be now rewritten as L plus h cross by 2 sigma, whole thing square, plus h cross square by 4; remember that the sigma square happens to be 3. So, this indeed is back to the expression for a angular momentum which we had, which is J square plus h cross square by 4. And now if you put the Eigen value of J square which is j times j plus 1, this can be written as a complete squares. So, the Eigen values indeed are j plus half square, times h cross square.

So, the operator does has the necessary property. Its Eigen value depends on J. It gives a particular sign when depending on whether sigma and L are parallel or antiparallel. So, it will tell us how to interpret in terms of parity conventions. And in addition to that, because of this particular structure, it is easy to see that this particular object commutes with the total angular momentum. The reason is rather trivial, h cross does not play any role in the commutation. But, sigma dot L can be return in terms of all this J square and L square.

And, we know already from study of non relativistic quantum mechanics that J will commute with J square, L square, S square, all those particular quantity, right. It can have simultaneous Eigen values, together with a Eigen values of J. The only remaining part which has to be seen is that, does this operator commute with the Hamiltonian as well. And it turns out that one has to add little more caveat to make it commute with the Hamiltonian without spoiling all the angular momentum property.

(Refer Slide Time: 35:36)



And, that caveaty is that the operator which is defined as not the same quantity, but the same object multiplied by this overall factor beta, it commutes with H. Now, beta is a diagonal matrix; and since it does not do anything with sigma or the angular momentum, sigma also happens to be a diagonal matrix. So, writing it in front or back does not matter, and it does not spoil any of the relations about angular momentum Eigen values which we just derived.

In particular coulombs, one can square K, and then beta square just happens to be equal to 1. So, the Eigen value of K square are just the same quantities which one can now label by this objects, k is equal to plus or minus j plus half. And one can now consider its all values j, the minimum value is half, and so this series starts as all positive and negative integers, but it can never take value 0.

So, this is a operator, and we want to now check it out whether the factor beta does indeed make it commute with the Hamiltonian. It is a straight forward calculation. Again, the terms in the Hamiltonian, the rest mass which has a beta operator itself it commutes with all these stuff. The potential part also commutes with all these stuff because the potential does not have any angular dependence. So, the L operator does not do anything, and it has a trivial identity structure in the internal space.

So, the only part which is necessary to check out is a commutator of these objects with the first term in the Hamiltonian which is alpha dot p. And one can easily now evaluate that what is a commutator. So, that object is alpha dotted with p, and commutator with

beta times sigma dot L, plus h cross. We want to check whether this thing indeed is 0 or not. And that now can be easily evaluated by writing these products. And 2 identities between these matrices are helpful when things are written in different order.

One of them is a product of alpha and sigma. So, that gives a general relation alpha i times sigma j; both of them have Pauli matrices buried inside it. And if you explicitly evaluate it, only the non trivial part which survives is this antisymmetric term, sigma i sigma j. It lands up on the off diagonal part. And the diagonal part does not contribute in this particular expression. In general, it can.

The other object which is necessary is alpha is going to anticommute with beta. So, once you write this expression completely, we get a term which because of the epsilon symbol here we will have a structure which is p cross product with L, plus the opposite order will have L cross p. And this 2 terms, the opposite order come because of the anticommutator, but the sign flips because of this alpha and beta anticommuting with itself.

And a cross product results from the fact that when alpha and sigma are multiplied together we get this epsilon i j k symbol, and this object can be easily evaluated from the fact that L is the star cross p. And the non trivial term arises when the gradient sitting inside this momentum operator acts on the r which is sitting inside the angular momentum. Operator in the identity is that this object results in 2 i h cross p. And once these things are put together, it is a straight forward enough exposes to see that this commutator is indeed 0; and so one can give explicit Eigen values to the Eigen states of the Hamiltonian with values of k.

So, now, we can go back. We have obtained a set of operators, determined their particular Eigen values. And the equation now is easily written down in terms of the radial part as well as the angular part. The angular part is going to be Eigen states of this sigma dot l operator, and we will treat that later. And the radial part now I can write explicitly in terms of the operator structure we have determined.

Remember, that the operator which appeared was sigma dot L plus h, and we can rewrite it as beta times k. And k has a specific Eigen value. The beta factor survives explicitly. And the potential is all there. And now we have a explicit equation for the radial part of the Hamiltonian which determines the energy of the problem, and where we have seen this E R is the operator involving derivative with respect to r, but rewritten in terms of a

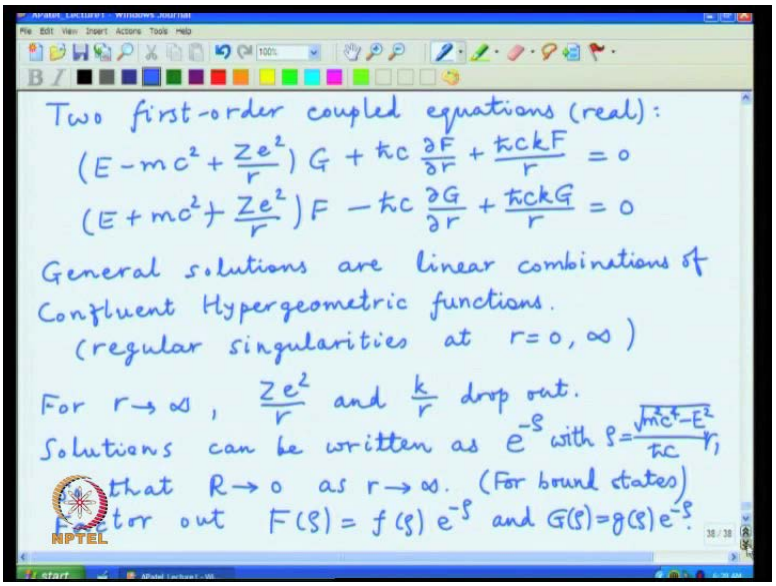
form where it is explicitly Hermitian.

So, we will solve this equation first to determine the energy Eigen values, and then we will go back to construct the angular part of the wave function. Now, to solve this object we need to pick a specific representation for these matrices alpha r and beta, and as well as some multicomponent form for the radial part. One can use the ordinary Dirac basis, but it is slightly more convenient, and save some notation to choose a alternative basis and then one can go back by a transformation to the Dirac basis.

So, instead of 4 matrices which are there in the original equation, we only have 2 matrices alpha r and beta. And one can rewrite them as 2 by 2 form instead of a 4 by 4 form. And later we will expand those 2 by 2 forms in terms of the spin components which come from the angular part of the wave function. So, simpler 2 by 2 structure can be used. And in that notation we will write this wave function as 1 over r times an upper and lower component.

The matrix beta we will not touch from its form in the Dirac case, and that will help us in separating the positive and the negative energy components or equivalently the particle and the antiparticle labels. But, alpha will choose in a clever way to make this equation look simple. And that constraint is that alpha is to be Hermitian, and it has to be anticommute with beta. And to get rid of these factors of i appearing all over the place one is inside here, then another i appears when p is written as a gradient. So, it is convenient to take alpha to be imaginary which with the anticommutation rule with beta, it is a second Pauli matrix which can be used for alpha r. And, now this equation can be written explicitly in terms of a 2 component equation or equivalently 2 coupled equations. And the convention chosen is that only real variables are left inside the explicit structures.

(Refer Slide Time: 47:30)



So, there are now 2 first order coupled equations which happen to be all with real coefficients. And their structure is by just explicitly expanding the various components. The only difference between these 2 terms comes from the fact that the upper and lower components are distinguished by the signs of the beta matrix. And that beta matrix appears with the rest mass as well as this derivative.

And, now to solve these equations, one has to bring in the whole powerful machinery of solving partial differential equations with certain kind of boundary conditions. It is a straight forward exercise in mathematical physics. And the solutions are linear combinations of what are known as confluent Hypergeometric functions. These are the well known functions, which comes from solving differential equations which have certain kind of regular singularities at specific points. So, this have so called regular singularities at the coordinates are equal to 0 and infinity.

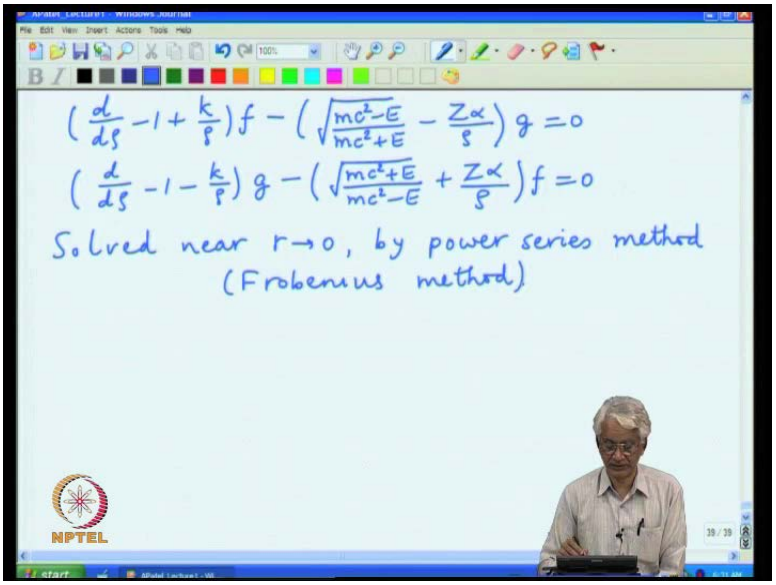
And, they are easily constructed, and also one can find explicit formula of this functions in different domains for small value of r, for large value of r, even in explicit form as a power series, etcetera. And we can write that those explicit solutions, but it is also worthwhile to just workout what these solutions are, step by step. And the method to do that- the first thing is to investigate the, this asymptotic behavior near both these points. One is r equal to 0, and the other is r equal to infinity.

It turns out that it is easy to see the behavior at r equal to infinity. From this equation, both the potential Z e square by r as well as this last term involving k over r, dropout

once we take the large r limit. And what is left is just E minus m c square and E plus m c square in this coefficient, and a gradient components is identical. And one can just substitute now F from one equation into the other, and reduces the whole thing into a second order equation with the overall coefficient is now the product of E minus m c square and E plus m c square.

So, the solutions are rather straight forward. For r going to infinity, this is Z e square by r and k by r dropout. And the solutions can be written as e raised to minus rho, with rho equal to square root of m square c raised to 4, minus e square, by h cross c. So that, r goes to 0, as r goes to infinity. So, this is the boundary condition which we impose for bound states. If the wave function vanishes at infinities, and in that case there are 2 solutions, e raised to plus rho and e raise to minus rho, and by explicit choice we have put in the exponential in decaying solution. Yes, this rho is actually scaled value of the radial coordinator, this number which comes from the coefficient of the equation multiplied by r. And now having done this separation we can simplify the equation by factoring out this explicit behavior which is F of rho is…

(Refer Slide Time: 54:53)



And then, by substituting back into this form we have a somewhat reduced equation which I can rewrite explicitly as; where I have introduced this fine structure constant to save some writing of e square over h cross c. And now these equations have a behavior which has to be consistent with the small r behavior of the wave function determined from the physical condition that the wave function should not blow up, so that it is not,

no longer integrable at, r equal to 0. And we have to keep that in mind, r equal to infinity part is separated explicitly. And this now have to be solved as near r going to 0 by what is known as a power series method; alternative name is a Frobenius method, and we will do that in the next lecture.