## Select/Special Topics in Atomic Physics Prof. P.C Deshmukh Department of Physics Indian Institute of Technology, Madras

## Lecture - 3 Hydrogen Atom; Dynamical Symmetry of the 1/r Potential

Greetings, we will continue to discuss the quantum mechanics and symmetry of the hydrogen atom.

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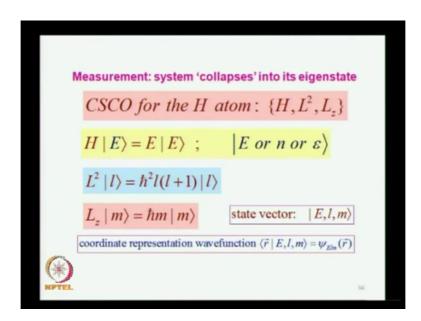
	Classical Mechanics	Quantum Mechanics
State of a System	(q,p)	)
Observables	F(q,p)	$F_{op}(q_{op},p_{op})$
Example: Energy	$E = \frac{p^2}{2m} + V(r)$	$H_{op} = \frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m} + V_{op}(r_{op})$
"Quantization" means we use the 'quantum' scheme	(q,p) NOT compatible	Develop this scheme further to connect to physical observables

We learn so far what quantization? So, we have got two schemes of doing physics, one is an approximate one, which is classical mechanics not a bad the approximation it works in many cases, nothings offside or wrong about it. But obviously it has it is limitations. And in classical mechanics you designate the states of the this system by position momentum in quantum mechanics by a states vector because these two require measurement to be carried out to find what these values are and these measurement are not compatible.

So, you have to bend that key observers are functions of position momentum in classical mechanics, where as these are operator in quantum mechanics. We have before us an example of the energy of the Hamiltonian operators. And we agreed that basically quantization, essentially means that you adopt your certain scheme of doing physics, is not like discrete energies or anything like that is not the signature. But, it is a scheme which is you find in the

right most column of this table and once you and when you adopt this scheme you have quantize the system.

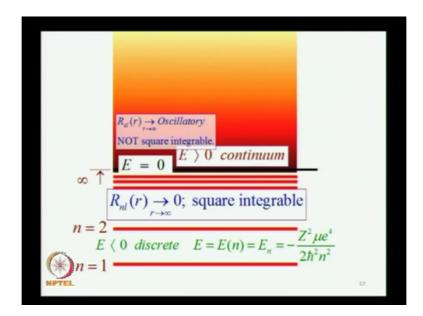
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So, the hydrogen atom we found that the Hamiltonian the energy which does not change from time to time. It is in variant with respect to time, left to itself is not going to change, which is why it gives you a constant of motion, at the measurement of energies compatible with the measurement of L square and L z one component, which I am referring to us the z component. And accordingly you get three simultaneous measurements, which are possible which are compatible each other and these measurements give you corresponding Eigen values, which go into the description of the state of the vector.

So, there is an energy quantum number there is angular momentum quantum number and there is the as metal quantum number. So, the state vector is described by E l and m or some function of e, some function of L, some function of m, but the basically the gradient are these three. The coordinate representation of from the state vector is what we call is the wave functions.

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So, far is where we have come the hydrogen atom is spectrum atoms that you have seen earlier does consist of discrete energy states, which I have been emphasizing is not the signature of the quantum mechanics, but it is a properties in off shout of quantum mechanics.

The signature is quantization which we saw in the last column, which is to have a certain scheme. Discrete energy state is the consequences of this scheme, when you apply this scheme to bound states of the hydrogen atom. But, the hydrogen atom also has got unbound states, you all know the, that the hydrogen atom in it is ground states.

The electron has got an energy of about 13.6 electron volts right. One Rydberg, what it means is that if you give energy to the hydrogen atom anything more than 13.6. The electron could be knocked out right, that is photo electric effect, how much energy can you gave suppose you will give 13.8 electron volts you pumped in 13.8. Electron volt energy into the hydrogen atom and the electron which was in its ground state; which was bound to the hydrogen atom gets knocked out right. And the total energy is conserved, total angle momentum is conserved and this excess energy which is 13.8 minus 13.6, this 0. 2 e v axis energy is carried by electron as kinetic energy fair enough.

What if you gave 13.8 1 electron volts 13.82 or 13.82356 electrons volts, you can keep it increasing that number. So, very small increments not through any discrete time, what is going to happen the electron will get naught down to the continuum, it will carry the access

energy has kinetic energy and this access energy is not discrete. This nothing discrete about it you can give 13.8, 13.81, 13.81036958.

Whatever this is nothing discrete about it and the electrons get naught out, you see these energy level. So, m equal to 1 m equal to 2 and this serious converges to the series limit which is called as rid bug series limit and beyond that is a quantum of energies and the electron goes into n Eigen states Hamiltonian of the very same Hamiltonian mind you.

The same sorting equation whose solution gives you the continuum energy states, belonging to energy values e greater than 0. So, a e equal to 0 is a Rydberg limit we need that at the discrete states. These are bounds states bound states are discrete the unbound states are not discrete. You have a got a continuum if you do any collision experiments, quantum collision experiment, you have got a target you bar in electron have its scatter and from the scatting you study the properties of the target. This is how do you atomic physics and you can fire these project tiles at any energy, these could be above the pressure. And when you do that you basically doing quantum physics and as a matter of most of the physics that people do in quantum collisions involves these continuum Eigen is states of the Hamiltonian.

It is a precisely the same sorting equation s I equal to e psi the only difference is the boundary condition. This is the differential equation that you working with and any solution depends, not just on the form of the differential equation, but on the boundary conditions. So, if you impose the boundary condition, that the electron is bound to the atom which means, that in the ((Refer Time: 07:26)) regions as were r tends to infinite you got the nucleus over here and as r tents to infinity, the probability density would vanish.

The very function amplitude would vanish, if you impose that boundary condition then you work with bounce states. When you have continuum states its electrons gets no doubt it comes out as a free electron, like e to the I k dot r and these are oscillatory, these are sinusoidal functions right. And these sinusoidal functions, it would they would go to 0 go negative come back to 0 go positive again drop back you know what sign wave does. So, it will oscillate between minus 1 and plus 1 but it will not go to 0, whereas bound state solution of the hydrogen atom like the 1 s 2 s the 2 p and all of these they all go to 0 as r tents to infinity.

So, the different between the discrete states and the continuum states is not in the differential equation that you are solving which is essentially. The same in the sorting question but in the

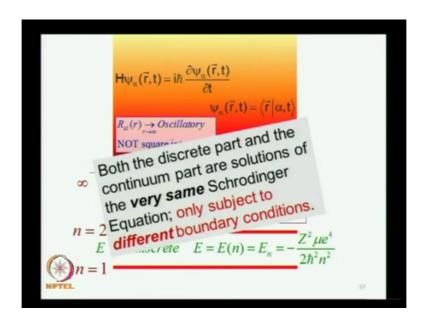
boundary conditions that you impulse, which is why the discreteness is not the signature of quantum mechanics it is the consequence of quantum mechanics When you dealing with bouncing.

The discrete states solutions are square integrable, so that you can normalize the function. The continuum functions they are oscillatory e to the I k dot r and these are not square integrable. As you can see very easily you do not even need any pen and pencil to do that because you know that the oscillatory solution is like the free electrons solution is like e to the I k dot r right.

So, when you normalize the function what do you do you construct the normalizations integral which is integral version over whole volume of psi star psi, what do you get out of psi star psi, is psi to the I k dot r. Very to the I k dot r multiplied by e to the minus I k dot r and kill each other you get unity and all you doing is integrating the volume element over a infinite space.

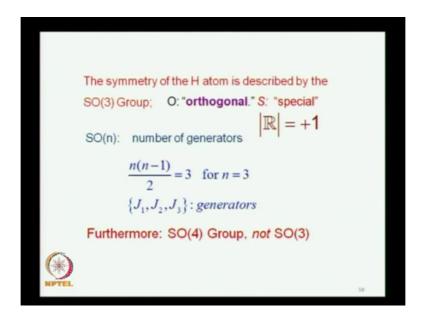
So, it blows up it is not square integral and there are other wise of normalizing the continuum functions. We will get to that a little later but the bounce state solutions are square integrable and the solutions turn out to be given by e function of integers and it goes 1 over n square. And then you have other proportionality is, the mass and the z fans ((Refer Time: 10:11)) constant and so on. You have this formulae, I am sure about this put in your first course in quantum mechanics, that is the solution of the differential equation that you get on imposing and appropriate boundary condition.

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The important thing to remember is that both the discrete part and the continuum part or solutions of the essential the same sorting the equations is the same quantum mechanics which governs. So, the signature of quantum mechanism is not the discreteness, but quantization itself, which is the scheme that you have adopted.

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The other thing that we learn, so far is that the symmetry of the hydrogen atom is represented by the S O 3 group. This is the special orthogonal group that we introduce last time, it has got three generators, which are the three components of the angular momentum. And I as will

proceed now to show then the symmetry is S O 4 rather than, S O 3, that is the topic of our discussion from this point on ward.

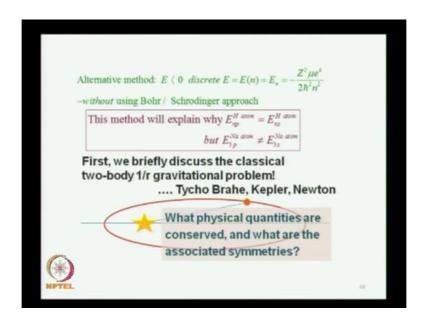
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On this approach comes from connection between symmetry and quantum mechanics and this sort of started with, Albert Einstein and you know that what laid Einstein to the special theory of relative was with his recognition of the symmetry. In the equations for the magnetic field and the electric field max equations and reconciliation of that symmetry; is what eventually laid him, to comes to terms with the finiteness of speed of light.

So, this importance of symmetry really began with the work of Einstein. This is very nicely beautifully summarized in the work of ma no either which is known as the either theorem, which I am sure you would have about heart about and some you have would not study; in some other contented and very beautifully illustrates by huge and burger. Because, he involved theatrically arguments and you know illusory by very nicely, so we are going discuss this approach in the context of the hydrogen atom now.

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What we will first do is to get, the Eigen value solution which is 1 over n square formula for the hydrogen atom without using the Bohr model and without using the Schrodinger equation that is the first thing we are going to do. And this is part of our classes of understanding the hydrogen atom and remind yourself that you learn about the 1 over n square formula from blamer, that was semi empirical formula then you learnt it from Rydberg, which was the same as Balmer formula.

But, again semi empirical one which was essential as the same formula was 1 over n square. Then you got the 1 over n square from the 1913 model of board or which was based on the set of postulates and these postulates, were belong to old quantum theory which made of use these orbits and we know that the orbiters are known as the exits.

So, you dispense about the model and then quantized the hydrogen atom set up the sorting equations solve it and you have done this in your earlier course and from the solution to the sorting equation you get the 1 over n square. So, you got 1 over n square from several different approaches.

The semi empirical approach the nails Bohr approach and the sorting quantum mechanics or equivalently. The ((Refer Time: 13:57)) quantum mechanisms completely equivalent. What we are going to now is to be 1 state 1 over formula without using any of these, but of course using quantum mechanism, because the heart of mechanics is not the sorting equation is the

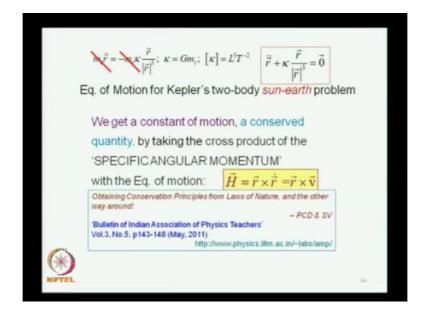
representation of quantum mechanics. The heart of quantum mechanics is quantization and that is what we have discuss already so will stay with that.

And, this approach will explain to us why for the hydrogen atom the energy of n p and n s is the same, where as it is not the case for the sodium. This was the original problem that I opposed in this course. So, we will get answer to this question is well and before we proceed, I will like to remind you of something that you would learnt in your classical mechanics course, which is the 1 over r gravitational problem. And there is the certain similarity between the 1 over r gravitational power problem and the problem of hydrogen atom because both are govern by the 1 over potential.

So, the 1 over r has got very special features in classical mechanics of the planetary model, which you know was developed by from the works of you know Tycho Brahe and Kepler and Newton. And that is very excited story by south, which I assume all of you are familiar with and I will quickly in mind you of that, because we are going to use some of those concepts.

But, not as use in classical mechanics because we will have to quantize that system. So, let me quickly remind you of this, that when you have the two body problem govern by one over r potential. The quantity is which are conserved you look for what quantity is are conserved and also for what the associated symmetry are because when you have a quantity which is conserved. There is an associated symmetry there is the connection between symmetry and conservation loss ward which is in fact, the ((Refer Time: 16:05)) right.

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So, let us consider the Kepler two body problem you have got mass times acceleration this is the equation of motion. This is the classical equation of the motion u to the equation of the motion for the gravitational two body problem, so got mass time acceleration which is given by the 1 over r square formulae this is the equation of motion. Now what you will do is look at this equation of motion I have just cancel the common mass of the earth am I left with remaining equation of motion. What I will do is take the cross product of the angler momentum with the equation of the motion.

The very simple algebra all of you have learn scalar of product. Vector product is nothing, very fancy about it and all we have going to do is to take the cross product with the equation of the motion of the angler momentum vector. And instead of angular momentum, which is r cross p and using specific angler of momentum which is r cross v.

So, it is angular momentum per unit mass, so it is not a such a big factor you can certainly use r cross p as well and all of your equation will get multiplied by the mass. So, it is only going to scale and we can always include at the end now what happen s is that when you do this, you get the coasted of motion and this is the an approach which you know I have discussed in article along with Shamala.

And, I go through this article, which discusses and I will not go to the that discussion in a detail over here. It is a very elementary idea that in physics you learn about the conservation laws right. That energy is conserved angle of momentum is conserved, linear of the momentum is conserved all of these and then you also learn there are equation motion. These are the loss of nature these are the physical loss and in your school.

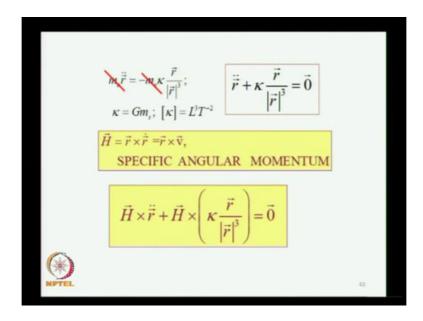
You tend to believe that you have to learn the conservation laws and you learn the laws of physics by Newton laws, Lagrange laws, Hamiltonian as laws whatever. It does not occur to us, that you can get the laws of physics from the conservation principles and vice a versa. And if you could, then you either do not need to learn one or the other because you can get them from each other or you can use them. If you knew the conservation principles to discover a law of physics which is what physics is about.

Because, at the very fundamental level what you want to do is to learn and discover the laws of nature, so you can actually, can use it is a technique. So, I will show you how you get a conservation principle by simply beginning with equation of motion. The conservation

principle I am heading toward is something that I have stated yet. It was pop out this when very simple analysis and the analysis requires you to only construct.

The gross product of the angle of momentum with the equation of motion, so it cannot be difficult right something that you will do in 5 minutes. So, you take the equation motion which is here in this rectangle box are you take the angular momentum or the specific angular momentum in this case, construct the cross product, with this.

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So, here it is H is the specific angular momentum, H cross this acceleration the first term and h cross the second term equal to 0 then null vector, that is all now you can simplified further.

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$$\vec{H} \times \vec{r} + \vec{H} \times \left(\kappa \frac{\vec{r}}{|\vec{r}|^3}\right) = \vec{0}. \vec{H} \times \vec{r} + \frac{\kappa}{|\vec{r}|^3} (\vec{r} \times \vec{v}) \times \vec{r} = \vec{0}$$

$$\vec{H} \times \vec{r} + \frac{\kappa}{|\vec{r}|^3} \{ (\vec{r} \cdot \vec{r}) \vec{v} \cdot (\vec{r} \cdot \vec{v}) \vec{r} \} = \vec{0}$$

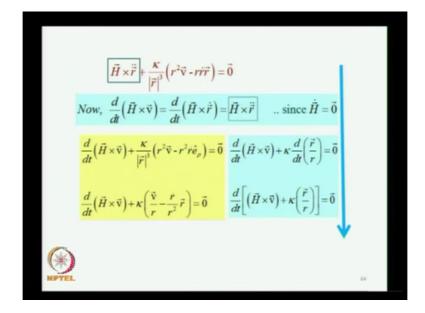
$$Use : \vec{r} \cdot \vec{v} = \vec{r} \cdot \frac{d}{dt} \{ r\hat{e}_r \} = \vec{r} \cdot \hat{e}_r \frac{dr}{dt} = r\dot{r}$$

$$\vec{H} \times \ddot{\vec{r}} + \frac{\kappa}{|\vec{r}|^3} (r^2 \vec{v} - r\dot{r}\dot{r}) = \vec{0}$$

And, I will not go through all these staff, because it very simple vector product and all you can do it. I have all the step on this page, but I will not work you through these steps this file is already available at the course web page. So, you can see it at your comfort, but you can work it out like here you see. That you got the cross product of H with this 1 over r square term and h is the specific angular momentum.

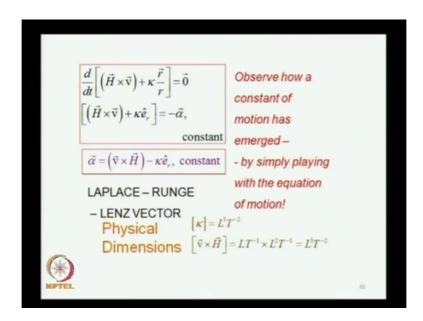
So, what you have over here is the cross product this is the vector triple products, so you can always apply, so call black role and so on and work it out. So, these are very simple you know high school level mathematics and you will plug in these steps and then the result that you would arrive at.

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Again, rearrange the terms and so on; it us very simple and I do not want to spent time doing it. I will leave it as an exercise for you, what you arrive at is this expression over here. That the time derivative of a vector which is content in this rectangle bracket must vanish, this comes from simple rearrange of terms. This is no big physics, no big mathematics exercise does the gross product of vector nothing beyond.

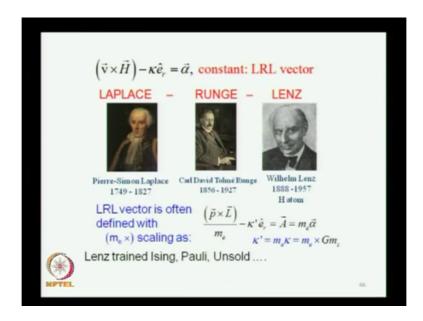
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What is it mean that the time derivative of this vector vanishes, which means that the vector is the constant of motion and this vector which is alpha or minus alpha. So, I can define alpha as minus of the vector on the left hand side this alpha is the constant of motion and you have discover the conservation law. How have we done it by doing simple vector algebra on the equation of motion, you can also get conservation of energy. Similarly that is the homework this begin with the equation motion I show that energy is conversed.

So, here you find the certain vector is conserve this vector is known as the Laplace Runge Lenz vector and we have got it in a very simple straight forward manner the physical dimensions of this capo which has appear in the 1 over r square proportionality is 1 to the 3, T to the minus 2. So, some of these things are I will like you to keep track of because these details are really important.

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So, what do we have a constant which has emerge from the equation of motion, the Lenz here is not the length of the fan periodic law, which normal is very famous, this is the different Lenz, this is the later Lenz. So, Lenz of the periodic law was a scientist of German descent. But he was a Russian and this was German in Germany and he was the student of summer felt and very distinguish scientist he trained some very distinguish physicists ISEN Polly also.

So, many of these very distinguish physicists were trained by Lenz and he work with the Laplace only vector for the quantum hydrogen atom, which is again one over protection and in classical mechanics you have learn that the Laplace along vectors conserve f and only f potential is 1 over r that is the dynamical symmetry of the Kepler problem right.

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where \vec{H} = \vec{r} \times \vec{v}

Now, take dot product \vec{\alpha} \cdot \vec{r}:

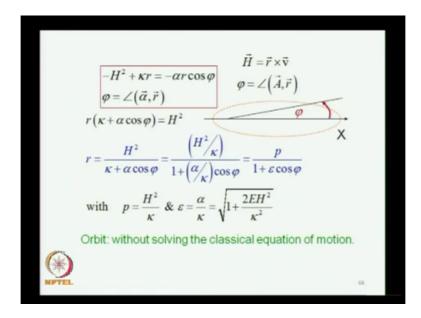
\Rightarrow Equation to the orbit / trajectory
\Rightarrow Without solving the Diff. Eq. of Motion!

(\vec{v} \times \vec{H}) \cdot \vec{r} - \kappa r = \vec{\alpha} \cdot \vec{r}
sign\ reversal: (\vec{H} \times \vec{v}) \cdot \vec{r} + \kappa r = -\vec{\alpha} \cdot \vec{r}
\vec{H} \cdot (\vec{v} \times \vec{r}) + \kappa r = -\vec{\alpha} \cdot \vec{r}
-H^2 + \kappa r = -\vec{\alpha} \cdot \vec{r} = -\alpha r \cos \varphi
\varphi = \angle(\vec{a}, \vec{r})
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So, what we also learn in classical mechanics is that given the fact the Laplace Lenz vector is conserved. If you just take the dot product of the Laplace strong Lenz vector with the position vector are alpha dot r and do some again, simple algebra just find out work with alpha dot r, so you will get the cos e theta term in side.

So, there is cos pi coming in over here rearrange the terms little bit you get a relation between r and phi, and the relation between r and phi is very simple algebra, of you to work out or you have to do is to take the dot product of alpha, with the r the details are there on this slide you cans see this ((Refer Time: 22:21)) or better still just work it out yourself.

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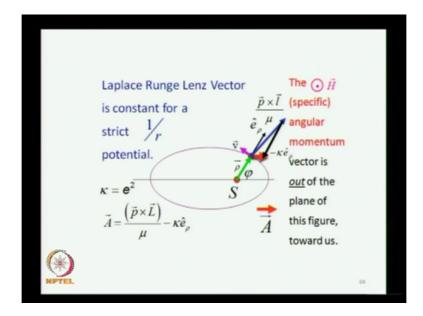


And, what you get is a relationship between r and phi which gives you essentially the equation to the r vector, what is interesting about this is the point 1 to make that you get. The equation to the orbit without solving Newton as laws whenever you get trajectory in classical mechanics or the path the locals of a point, which is moving under a force right what we do in classical mechanics is to set of the equation motion. It could be the equation Newton motion, it could be Lagrange equation or the Hamiltonians equation.

Put the initial conditions integrated that differential equation put the initial conditions and the moment you do that you get the trajectory. Here you get the trajectory without even setting. The differential equation you just get it from the consency of alpha, you know that alpha is a conserve quantity.

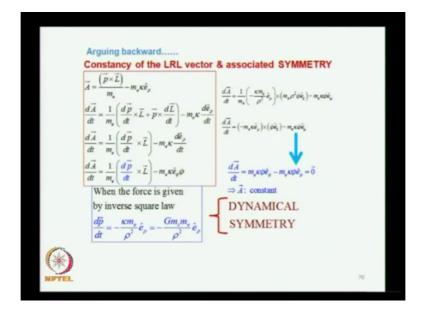
You take the dot product of alpha with r do not look at the equation motion anywhere, just take the dot product of alpha with r and what pops out is the trajectory and likewise in the quantum mechanics of the hydrogen atom where a gain you have 1 over potential. We are going to get the solutions without setting up the Bohr model or the shortening equation, but we will get the 1 over n square that as we are going to do now.

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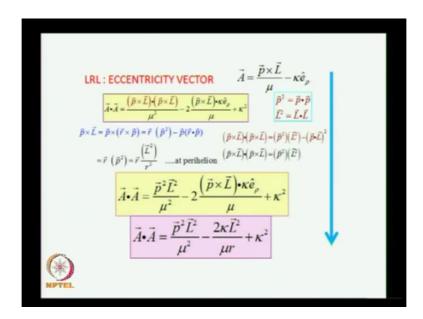
So, in classical mechanics you get the orbits without solving the classical equations or motion and this is the picture the Laplace Runge Lenz vector, for the Kepler classical problem. It is vector along the major axis and what it does is to hold the orbit face otherwise, T would bobble right and that precision is eliminated by another quantity over and above energy angle momentum must be conserved at this is coming from the nature of the potential form the nature the force which is 1 over r square, which is why it is refer to us the dynamical symmetry of the Kepler problem.

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And if you argue this backward that you have got a constant which is conserved and ask under what condition will this vector be conserve under what condition will this be constant. The condition that you will recognize is that the force much be 1 over r square. So, if you did not know the law of gravity as 1 over r square you would have deduced from this inverse argument and this cover the law of nature which is what makes a beautiful.

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So, this is the dynamical symmetry of the Kepler problem. It is also sometime refer to eccentricity vector eccentricity everybody knows because everybody has although most of us believe; that is only the others who have. And the reason you get eccentricity out of it is there is if you take the duct product of the Laplace right itself a dot a and again do simple algebras I will not work you through these steps.

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$$\vec{A} \cdot \vec{A} = \frac{\vec{p}^2 \vec{L}^2}{\mu^2} - \frac{2\kappa \vec{L}^2}{\mu r} + \kappa^2$$

$$\vec{A} \cdot \vec{A} = \frac{2\vec{L}^2}{\mu} \left( \frac{\vec{p}^2}{2\mu} - \frac{\kappa}{r} \right) + \kappa^2$$

$$\vec{A} \cdot \vec{A} = \frac{2E\vec{L}^2}{\mu} + \kappa^2 \quad \& \text{ since } \varepsilon^2 = \left( \frac{2E\vec{L}^2}{\kappa^2 \mu} + 1 \right), \text{ OM Symmetries Greiner & Muller, Springer Ex. 14.6, p. 466}$$

$$\vec{A} \cdot \vec{A} = \kappa^2 \left( \frac{2E\vec{L}^2}{\kappa^2 \mu} + 1 \right) = \kappa^2 \varepsilon^2 = (\kappa \varepsilon)^2 \quad \checkmark$$

$$\vec{A} \cdot \vec{A} = \kappa^2 \left( \frac{2E\vec{L}^2}{\kappa^2 \mu} + 1 \right) = \kappa^2 \varepsilon^2 = (\kappa \varepsilon)^2 \quad \checkmark$$

$$\vec{A} \cdot \vec{A} = \kappa^2 \left( \frac{2E\vec{L}^2}{\kappa^2 \mu} + 1 \right) = \kappa^2 \varepsilon^2 = (\kappa \varepsilon)^2 \quad \checkmark$$

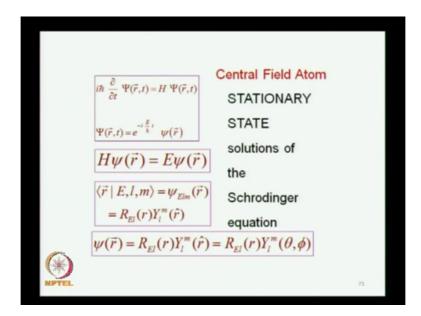
$$\vec{A} \cdot \vec{A} = \frac{2H}{\mu} \left( L^2 + \hbar^2 \right) + \kappa^2$$

So, you get a dot a and it turns out to be proportional to the square of the eccentricity. So, just work out this algebra for yourself which is one sometime call as the eccentricity vector. I would like to draw this relationship over here, which is the triangular box and 1 might thing that when you quantize. It instead of the energy you will certainly get the Hamiltonian operator instead of I square which is the square angler momentum you will get the square of the angler momentum vectors operate right.

Because, angle in momentum in quantum mechanics is a vector quantum operator all the three attributes right, but then you get an additional term over here, which is h cross square, cross square papa, square coming in happily over here, but you do get an a additional H cross square over here and the reason this happens is because you have already seen that in the Laplace long vector you got the p cross l delta and p l do not omit.

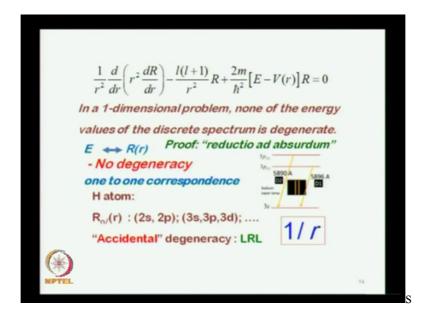
So, if you put the commendation laws correctly the basic fundamental commendation law, is just the commendation between position and momentum and that has implications on the commendation between p and l. So, when you do that you will automatically get this term. So, just make a note of this I will come back to this point as we go along, but this is something which I want to do register over here.

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So, we work with the Schrödinger equation for hydrogen atom now, which is psi I equal to e psi you look first stationary state solutions. You have got central field symmetry you separate the angular part, you have the separate radial part and all of this. You have done in first course in quantum mechanics, see you get this spherical harmonics solutions from the angular part.

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The radial part is the solution of this differential equation the 1 into 1 plus r square which is the centrifugal term, it comes from the constant of separation and I am not going to discuss all of this you have done this your first course right. So, this are very familiar equation this is the radial equation what is interesting about it is the one dimensional problem in quantum mechanics.

This is the complete one dimensional problem in quantum mechanics and there is a very well known freedom in the quantum mechanism one dimensional problems, that if you have discrete spectrum then none of the energy value is degenerate. I do not know If you have done this theorem I assume that if you have not done please prove it.

The prove is the very simple I am not going to work prove in the class, all you had is do is to use the technique of reduction you had certain assume the country and you will be laid to and obvious conduction. So, work it out for yourself otherwise, you will find it in many books in quantum mechanism. This is very elementary theorem that in the one dimensional problem there are no de generate states.

Now, let us see what it means to us in our context this is the one dimensional problem it should therefore that have any degenerate states. So, energy should not be degenerate and 1 would they for aspect that the energy of 3 p is different from the energy of 3 s there is no degenerate right. That is what 1 would aspect there is no degeneracy, it this quite consistence with this one dimensional problem and the consequences. This is what you see for the sodium atom the energy of 3 p is this the energy of your 3 s is this.

So, the electron jumps from 3 p to 3 s m s the yellow d 1 and d 2 lines right. Find what about the hydrogen atom you got the same differential equation right. This is the 1 dimensional problem in quantum mechanics, what it tell us there is no degeneracy and therefore, for the hydrogen atom also you would aspect that there is no degeneracy, but then you do know then energy of the hydrogen atom is given only by 1 over n square no matter. What the 1 S, L for any value of n goes from 0 to n minus one right and for all these different values of 1 the energy is the same it which is 1 over square.

So, whether it is 2 s and 2 p or 3 s and 3 p or 3 s, 3 p, 3 d, 4 s, 4 p, 4 d, 4 f no matter what the 1 value is the corresponding wave function are linearly independent, but they belong to the same Eigen value. This spit the fact that they are solutions or the one dimension radial equation, something wrong you cannot explain it you have a theorem in quantum mechanics.

So, fundamental theorem in quantum mechanics of one dimensions right the result are quite consistence. If you look at the sodium spectrum, but you have use for the hydrogen atom and you get the result for hydrogen atom, which is in conduction with this. It is coming from straight out of shorting equation for the hydrogen atom right. We have been all through steps separate the radial part, angular part, exploit the central symmetry get the spiracle harmonic look the radial part right.

Apply the boundary conditions get the linear independent solutions and fine they are de generate and if you cannot explain it you want to throw your hands up and say there is degenerate there is no reason for it alcohol it is the accident reasons and this is exactly what it was calls. So, the degeneracy of the hydrogen atom was called as the accidental degeneracy. But, that is skip is it not you have to able to find some reason for it, you can just say that a gas. So, happens and get up it you need to go beyond it and when you do that you do fine. That there is the additional symmetry which you had not recognize earlier that is what we are going to discuss now.

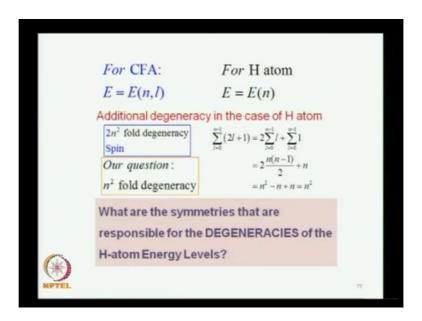
So, you aspect that there is no degeneracy you aspect that there is 1 to 1 correspondence between energy and the radial functions you know such is not that the case for the sodium atom. It is the case we do not have any problem with this spectrum of the sodium atom. Our problem is with the hydrogen atom, which we In fact expect to be simpler because it is obviously, the simpler atom that is where we have the problem. So, instead of just referring to it as a accidentally degeneracy, we will try to find out if there is some deeper reason to this.

Now, this is the consequence of the fact that the potential is 1 over r for the hydrogen atom. What about the sodium atom, is outside you had got this 3 s electron which gets excited to 3 p. The spin orbit doublet is relativistic details So, I will not touch up it right now. What is the potential seen by the 3 s electron This 3 s electron there are 11 electron in the sodium atom, 11 photons in the nuclease, 10 electrons in the core, the 3 s electron is outside right. What it sees is the filled of the 11 protons screen by 10 electron, so it see an effective potential of 1 over r. That is what makes similar to hydrogen atom it does not make it same as the hydrogen atom, because if this electron were to be in the asymptotic reason far away our tending to infinity. There it will be certainly see the 11 protons screen by 10 electrons and it will see exactly, the same as the hydrogen atom potential which s the 1 over r potential, but what if the potential seen. If it work into the core there it will not be 1 over r right.

Because, it will sense the potential due to the 11 protons and then the 10 electrons which are around it and it would be too close to seen just the 1 r potentials, 1 r potentials Is broken for the sodium at. It is not 1 over r potential it is one r only in the asymptotic region,, but not closer to r tending to 0 as r tense to 0.

The potential is no longer 1 over r in the sodium atom, for the hydrogen atom; however, it is always 1 over r all the way from 0 to infinity and this is the condition of the constant if the large lapse vector, that the potential most be strictly 1 over r in the entire reason of space. So, hydrogen atom fulfils that condition and this has therefore, something to do with the one hour our potential we will study the details that.

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The central field the approximation suggest that e should depend on n as well l. There should be no decencies that is what we find for the sodium atom,, but for the hydrogen atom we do find that there is degeneracy. There is no dependence on l and the degeneracy is actually n square 4 right.

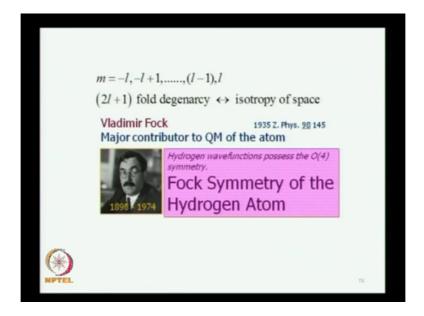
Because, I goes from 0 to n minus 1 and if you just carried out this summation all of you know how to carry out arithmetic sums. If you carry out this summation when you some over 2 l plus 1. because for each value of l you have got the m quantum number which we discuss last time which goes from minus l to plus l right.

So, get 12 plus 1 4 degeneracy, there that degeneracy we have no trouble it. that is coming from isotropy of space. Because, you can quantize the angel of momentum j square along with any 1 component which is j z and the Eigen value of j z will go as m h cross, m going from minus 1 to plus 1. So, you get a 12 plus 4 d degeneracy, that is coming from just from isotropy of space. Why isotropy because you can choose the access of quantization to be along to be a z access,, but z access can be this or this or this or this or this right, any direction is space is completely equivalent. So, there is an isentropic of the 1 over r potential which is the spherical symmetry and from this you get the 12 plus 1 4 degeneracy we are no difficulty with that.

The difficulty is from the I going from 0 to n minus 1 which sumps 1 up to n square and it is the n square 4 degeneracy that we have some difficulty. We have to solve that, actually this degeneracy if you look at the periodic table it is twice n square rather than n square because this degeneracy gets double by the 2 states of an electron spin, but that is coming from relatives quantum mechanism.

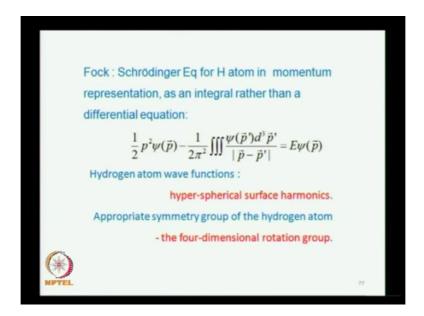
When you get to that we be able to plug it in, but we know already that it is the twice sense square the scaling by factor tool not worry it is comings from relative quantum mechanism. This n square is something that we really have to deal with. So, we will find what is origin of the n square fold degeneracy and what are the associated with symmetries for this.

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So, this is the 12 plus 4 1 degeneracy from isotropy from the space and the n square 4 degeneracy was explain by Fock. This is sometimes is called the Fock symmetry of hydrogen atom, it is an extremely important contribution in atomic physics and quantum mechanism in general.

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What fock did was to consider Hydrogen wave functions. He set up the shorting equation for the hydrogen atom in the momentum representation he set up as it a integral equation rather than as the differential equation. So, this was just matter of detailed technique that he work well and I am not going through historical development of this topic and he found that, there is an additional symmetry.

When he represented these wave function has hysterical surface harmonic he found there is the additional symmetry, which is the four dimensional rotation room rather than the three dimensional rotation. So, there was additional symmetry that discover with the sometimes call as the Fock symmetry of the hydrogen atom. (Refer Slide Time: 43:31)

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Pauli-Lenz
Quantization of the LR vector
\vec{A}_{Classical} = \frac{(\vec{p} \times \vec{L})}{\mu} - \kappa \hat{e}_{\rho}
\vec{p} \times \vec{L} \to \frac{1}{2} \left[ (\vec{p} \times \vec{L}) + (\vec{p} \times \vec{L})^{\dagger} \right] = \frac{1}{2} \left[ \vec{p} \times \vec{L} - \vec{L} \times \vec{p} \right]
\vec{A}_{QM} = \frac{1}{2\mu} \left[ \vec{p} \times \vec{L} - \vec{L} \times \vec{p} \right] - \kappa \hat{r}
W. Pauli Z. Phys. 36 336 – 363(1926)
\vec{A} \cdot \vec{L} = 0 \qquad \text{in orthogonal}
constant of motion
\vec{A}, \vec{L} : \text{quantum operators}
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What we will do is to get the solution not from the historical prospective not from the manner in Focks all these problem, but using the Laplace vector, the Laplace Regwer vector and in this contest it is sometimes called a Pauli- Lenz vector. Because, what you do is to take the classical plus Laplace Lenz vector and quantization and then develop the algebra further.

So, you take the quantum poly quantum Laplace vector this was done by poly. So, it is sometimes called poly Lenz vector what you do you when you quantization system. quantization is replacing dynamical variables and classical mechanics by corresponding operates that is quantization you want to quantize the Laplace Lenz vector sp you could replace p by the momentum operator which is minus S I gradient. We could replace l, by the angle of momentum operator, which is know what it is we define in our last class, what the angel momentum operator is we could do that and we could go head and say. We quantize,, but that is not the only thing you do in quantization that is the necessary thing not a sufficient thing the operator that you get need to be Hermitan operator.

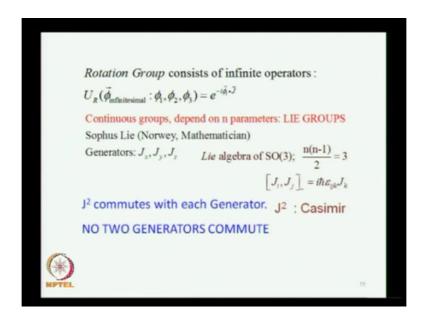
If you just replace p and 1 by corresponding operators the quantum mechanics you do not get ardbidence operators. The reason is p cross 1 is not equal to minus of 1 cross p, that would be the case for classical vector products. These are quantum vector operator right, so this is going to behave in a different way.

So, what you have to do is to simonize this operator see take p cross l minus l cross p and the quantum Laplace vector at the quantum Laplace Lenz vector or poly Lenz vector no matter.

What you call it is you symmetries this operator you take p cross 1 add to 8 the join of this operators, which is p cross 1 at joint and then you take half of this some and then quantize it that is the prescription of getting a quantum operator.

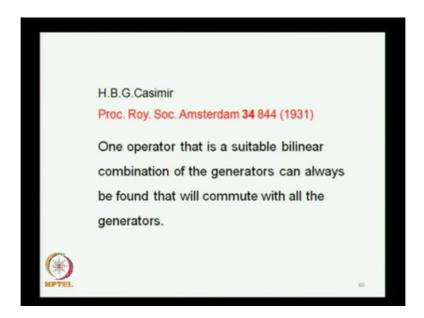
So, symmetry and now this is homework for you before the next class that you have now constructed the quantum poly Lenz vector operator, show that it commutes to the Hamiltonian show. That it is that orthogonal to the angler momentum operator remember that you now working with operators now at classical vectors. I like to repeat this that you work with vectors operators and quantum mechanism that are 3 attributes that you most carry at a restart.

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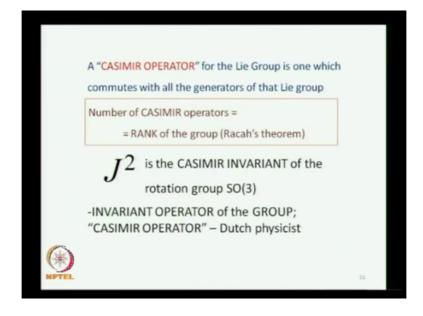
And, we have the rotation group which we first recognized the lead group the recognize and to have infinite rotation operators coming from the spherical symmetry, the generator for this were the 3 components of the angle of momentum operator j x and j y and j z. This is the S O 3 algebra and by three components of the angle momentum operator right, on the operator which commutes with every generator is j square because j square commits with j x it also commutes j y it also commutes j z that and there is only 1 operator, which commutes with all the generators and an operator which commutes with every generator is known as the Casimir. This is the Casimir operator is one which commutes with any every generator. So, the generator for the S O 3 is are the 3 components of the angular momentum and the Casimir for S O 3 is j square.

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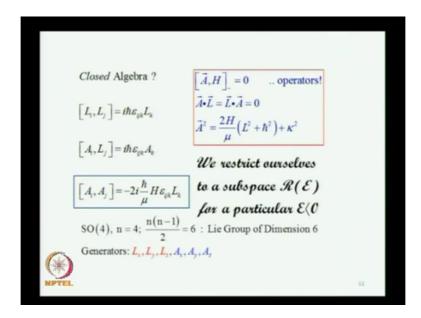
Now, there is the very famous theorem where is known as Casimir theorem what it say that 1 operator. That is the suitable bilinear combination of generators can always be found and you have an obvious example this is the bilinear combination of the generators because j square is, j square ((Refer Time: 48:22)) y square right. So, it is the bilinear combination of the generators and you find that the j square commutes with each of the generator, so this is the Casimir.

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Now, this is the Casimir for S O 3, what we able to find this is named after the Dutch physicist cashmere.

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We asked a question that between the angle of momentum operators which is 1 x and 1 y and 1 z or I will now cal them as L 1 L 2 L 3 and the three components of the poly Lenz quantum vector operator. Now you have another 3 components, components e x e y e z or I would call them as a 1 a 2 a 3.

So, that 3 components of the angle of momentum vector operator, two components of the quantum poly Lenz vector operator, you ask the question do they constitute closed algebra and you find that you take the comminator 1 y of 1 I with 1 j in you find that the result is in terms of 1 k.

So, it is closed you take the committer of a I with 1 j you find that the answer is in terms of a k. So, it belongs to the family of either a and l, so it is still closed; but if you now take the committer a I with of a j and these are all details algebra. That you are going to work out it home and not going to do more for you.

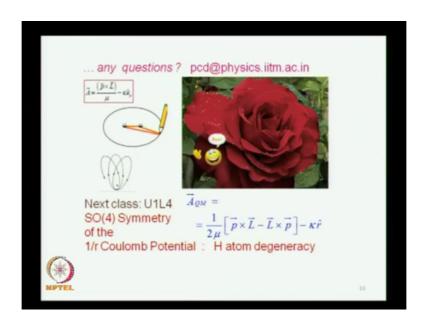
I will test you for this in exam. So, better you know how to do it, you are going to this out these committees are and you find that the committer of a I with a j turns out to be l k, which is certainly it belong to the family of l and a, but there is also the Hamiltonian coming in over here, which means that it is not quite closed, because the committer of a I with a j is in terms

not just of a and l, but there is another operator which is outside the family of a and l which is the energy operator the Hamiltonian operator. So, it is not you do not get closed algebra, however if you look into a sub space in the bounds states spectrum of the hydrogen atom, sub space of one energy in the hill.

But, space there are vectors which belongs to different energies and I take a sub space, scope out that says of the portion of the hill space, which belong to one particular round state energy and within that sub space the Hamiltonian, then it is just a number, which is the energy which is 1 over n square along with other constants right, just a number there is no longer in operator and we could work with that.

So, I guess within the subspace you have 6 generators the 3 components of angle of momentum and 3 components of the poly range vector and you have a group which is the S O 4. Because, the number of generators n into n minus 1 by 2 which is 4 into 3 by 2 which is equal to 6 even at atomic physics see you got the lie group of dimension 6 this is the S O 4 group.

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And I am going to stop here for today any question, I will happy to take and we will continue to discuss the S O 4 symmetry of the hydrogen atom in the next class any question any question yes.

Student: ((Refer Time: 52:38))

We have taken care of the all the 3 dimensions you set up the Hamiltonian the you got the Laplace and del square you expresses it r theta 5 you take all the 3 degree of freedom ((Refer Time: 53:03)) you get a separate differential equation for angle of part, whose solution are try to hard Hamilton you are taking care of that and when you do the separation once is called the conidial separation, we just add to 1 plus one we gave you to statically Evarts terms.

So, what is the constant of separation that is, the one which gives you the centrifugal term in the radial equation and if you look at just a radial equation. There is only 1 degree of freedom, which is one makes the 1 Hamiltonian and then you expect the results of the 1 dimension differential equation to be consistent with the theorems, which come from the quantum mechanics of one dimensions and that theorem is, that if you have discrete bounds states spectrum.

Then you do not have any energy value with is each other, which is except 1 to 1 correspondence between energies and wave functions. When you have many to 1 corresponds there are many linearly independent solutions which belongs to the same Eigen value that is when you have the degeneracy. So, you do not expect the degeneracy. When you do have a degeneracy in the hydrogen atom which shorting equation shorting quantum mechanics does not explain shorting goes that for. But, it does not explain and we have to admitted in to our thinking only as accidental degeneracy, there is something more to it then shorting equation. So, this more to the quantum mechanics of the hydrogen atom for the Bohr model, and more to the quantum mechanics of the hydrogen atom then the shorting equation that is all we discuss here.