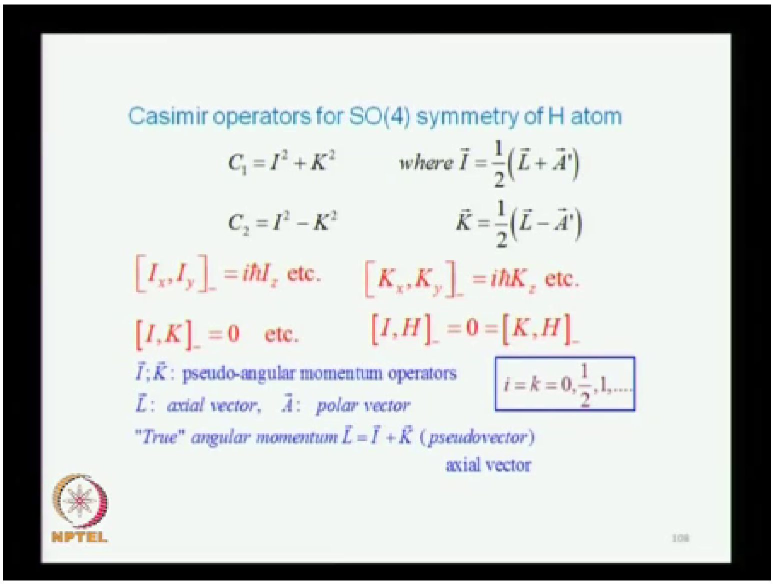
Select/Special Topics in Atomic Physics
P. C. Deshmukh
Department of Physics
Indian Institute of Technology, Madras

Lecture - 5
Wave functions of the Hydrogen Atom

Greetings, so we got the energies of the hydrogen atom without using the Schrodinger equation, we got the 1 over n square.

(Refer Slide Time: 00:27)



Casimir operators for SO(4) symmetry of H atom

$C_1 = I^2 + K^2$ where $\vec{I} = \frac{1}{2}(\vec{L} + \vec{A}')$

$C_2 = I^2 - K^2$ $\vec{K} = \frac{1}{2}(\vec{L} - \vec{A}')$

$[I_x, I_y]_- = i\hbar I_z$ etc. $[K_x, K_y]_- = i\hbar K_z$ etc.

$[I, K]_- = 0$ etc. $[I, H]_- = 0 = [K, H]_-$

$\vec{I}; \vec{K}$: pseudo-angular momentum operators

$\boxed{i = k = 0, \frac{1}{2}, 1, \ldots}$

$\vec{L}$: axial vector, $\vec{A}$: polar vector

"True" angular momentum $\vec{L} = \vec{I} + \vec{K}$ (pseudovector)

axial vector

And, we were able to do a lot more than what we could with the Schrodinger equation because the Schrodinger equation would lead us to a situation which we could not reconcile with the degeneracy that we find in the hydrogen atom right. So, the Schrodinger equation consequence could at best be dealt with, by referring to the degeneracy as accidental degeneracy.

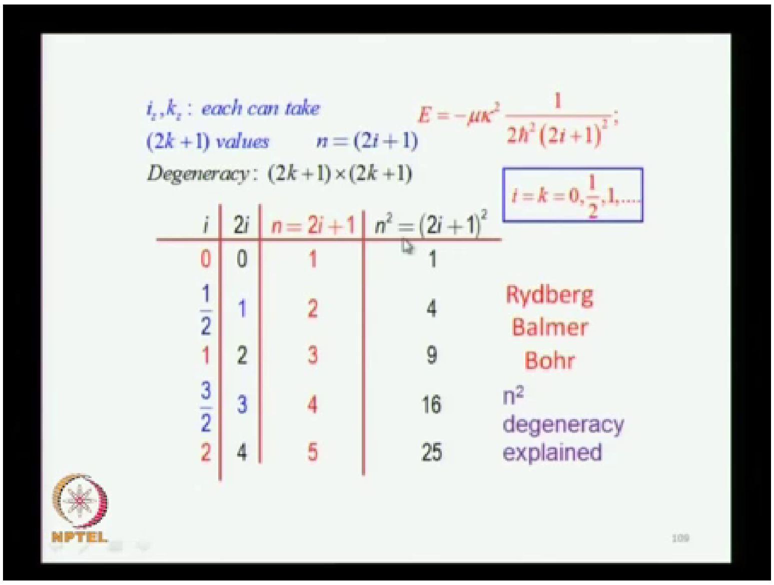
But, when you understand the symmetry of the hydrogen atom recognize that is S O 4 and symmetry in degeneracy goes together. You know what you do in perturbation theory that you apply a perturbation, and the perturbation removes the degeneracy, sometimes partially sometimes wholly that is a matter of detail we were certainly come back to at when we discuss atomic spectroscopy. But, typically a perturbation removes the degeneracy, and the presence of degeneracy suggests that there is some symmetry which you can break, as you do in the g mean fact for example, your ferromagnetic field.

So, you break the spherical symmetry right, so things are different along one direction, so symmetry and degeneracy go together. And when you recognize the complete symmetry of the hydrogen atom, which is the S O 4 you are able to explain the energy spectrum of the hydrogen atom, and also the degeneracy. Now, the casimir operator which you have on the screen C 1 and C 2 it is not such a big, you know surprise that the casimir operators are I square plus K square and I square minus K square, because we do know from rankers theorem that the number of casimir operators is equal to the ranks. So, we have something to begin with, we also know this is in response to your question vivek yesterday, you also know that from rankers theorem that a suitable bilinear construct of the generators, would give you the casimir. So, generators are the angle of momentum, and the Pauli Lenz vector operators, so you contrast the bilinear out of it.

So, you they have to come out of L square and A square and that is what you find the over here. So, you have some sort of clue to go about discovering these casimir operators, and you can get it readily, so these I and K are the pseudo angular momentum vector operators I and K are independence, so they commute with each other. And for angle of momentum algebra in some of this we are going to do in unit 2, we will ensure that these quantum numbers can be either 0 half 1 3 half and so on.

But, I have anticipated that result you have met this result earlier in some other course reassembly I have used it. But, we will establish in some details when we do unit 2, we will actually prove that angle of momentum quantum numbers can be only 0 half 1 and so on. So, these are the pseudo angle of momentum operators as I mentioned yesterday.

(Refer Slide Time: 03:45)



i_z, k_z : each can take $(2k+1)$ values $\quad n = (2i+1)$

Degeneracy: $(2k+1)\times(2k+1)$

$$E = -\mu\kappa^2 \frac{1}{2\hbar^2 (2i+1)^2};$$

$$\boxed{i = k = 0, \frac{1}{2}, 1, \ldots}$$

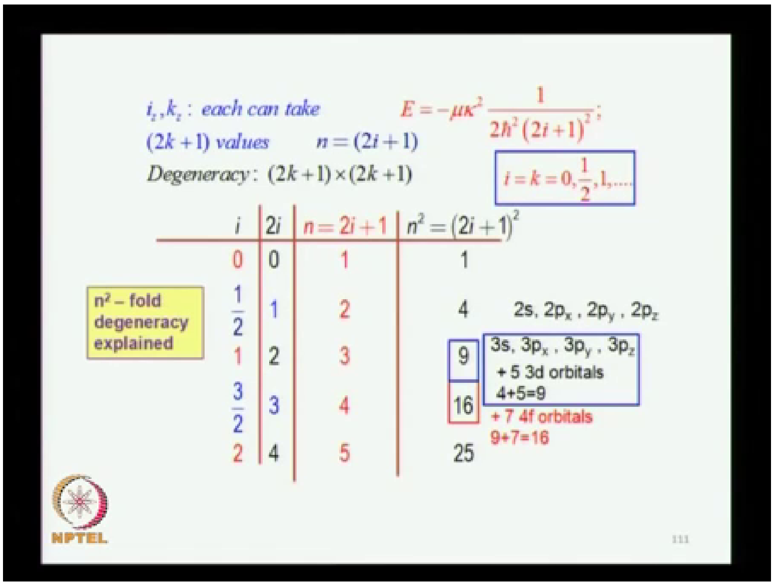
i	$2i$	$n=2i+1$	$n^2=(2i+1)^2$
0	0	1	1
$\frac{1}{2}$	1	2	4
1	2	3	9
$\frac{3}{2}$	3	4	16
2	4	5	25

Rydberg
Balmer
Bohr

n^2
degeneracy
explained

We have the degeneracy, we are which goes as n square, this is was the mystery which we wanted to explain for the hydrogen atom.

(Refer Slide Time: 03:56)



i_z, k_z : each can take $(2k+1)$ values $\quad n = (2i+1)$

Degeneracy: $(2k+1)\times(2k+1)$

$$E = -\mu\kappa^2 \frac{1}{2\hbar^2 (2i+1)^2};$$

$$\boxed{i = k = 0, \frac{1}{2}, 1, \ldots}$$

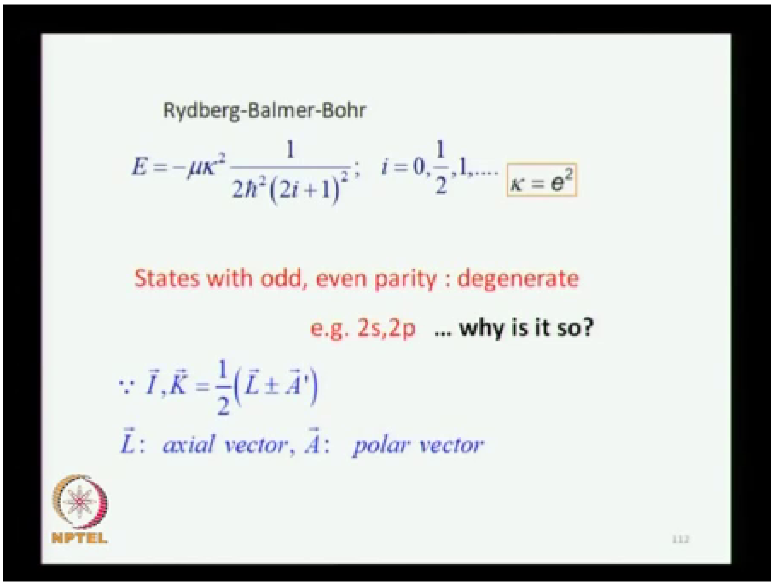
n^2 – fold degeneracy explained

i	$2i$	$n=2i+1$	$n^2=(2i+1)^2$	
0	0	1	1	
$\frac{1}{2}$	1	2	4	2s, $2p_x$, $2p_y$, $2p_z$
1	2	3	9	3s, $3p_x$, $3p_y$, $3p_z$ + 5 3d orbitals 4+5=9
$\frac{3}{2}$	3	4	16	+ 7 4f orbitals 9+7=16
2	4	5	25	

And if you see what the degenerate functions are, so for n equal to 2 you have a 4 fold degeneracy. And these of course, are the 4 linearly independent wave functions, which all belongs to the same Eigen value, this is then doubled because of spin, but without spin this is 4 fold degeneracy. So, for n equal to 2 these are the 4 for 3 you have the additional 5 orbital's which are degenerate these are the 5 orbital's with the d symmetry.

The 3D way functions there are five linearly independent functions with d symmetry, and these 5 get added to those earlier 4, which are the s n p and you get a 9 fold degeneracy, for n equal to 3, for n equal to 4 you get an additional 7 fold degeneracy coming from the 4 or 5 orbital's. So, this is how it will go and as n increases the degeneracy will increase as the square of n.

(Refer Slide Time: 05:05)



Rydberg-Balmer-Bohr

$$E = -\mu\kappa^2 \frac{1}{2\hbar^2(2i+1)^2}; \quad i = 0, \frac{1}{2}, 1, \ldots. \quad \boxed{\kappa = e^2}$$

States with odd, even parity : degenerate

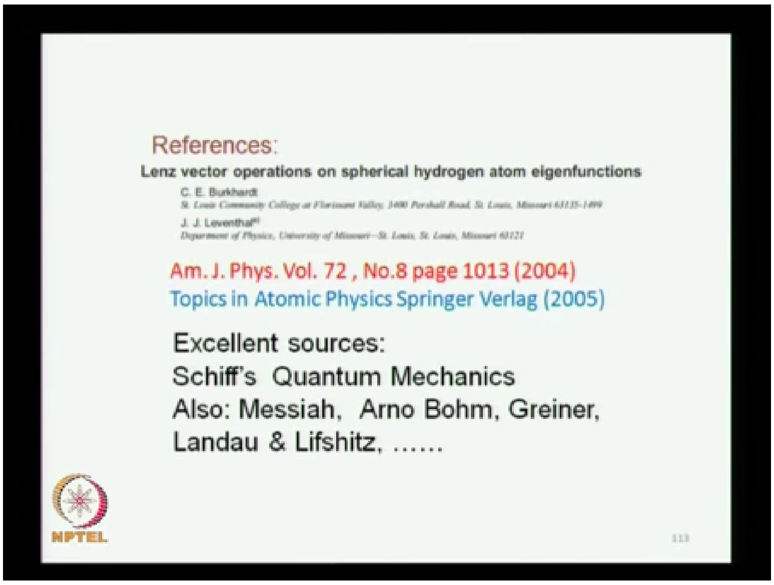
e.g. 2s,2p ... why is it so?

$$\because \vec{I}, \vec{K} = \frac{1}{2}\left(\vec{L} \pm \vec{A}'\right)$$

$\vec{L}$: axial vector, $\vec{A}$: polar vector

Now, for the Rydberg Balmer Bohar formula we put kappa equal to e square, you notice the 2 s and 2 p are degenerate, which is another surprising. Because, these wave functions have opposite parity one is g when other is odd, the parity is given by the l quantum number. And under inversion these wave functions in the parity you know, they have the parity of the l quantum number, and usually you do not have degeneracy between functions of opposite parity. In this case you have, which is rather pique your result, and this we now understand very easily because we are dealing with a mix of l and a 1 is a polar vector, the other is an axial vector that is a reason parity is not a good quantum number in this case.

(Refer Slide Time: 06:06)



References:

Lenz vector operations on spherical hydrogen atom eigenfunctions

C. E. Burkhardt

St. Louis Community College at Florissant Valley, 3400 Pershall Road, St. Louis, Missouri 63135-1499

J. J. Leventhal[a]

Department of Physics, University of Missouri—St. Louis, St. Louis, Missouri 63121

Am. J. Phys. Vol. 72 , No.8 page 1013 (2004)

Topics in Atomic Physics Springer Verlag (2005)

Excellent sources:

Schiff's Quantum Mechanics

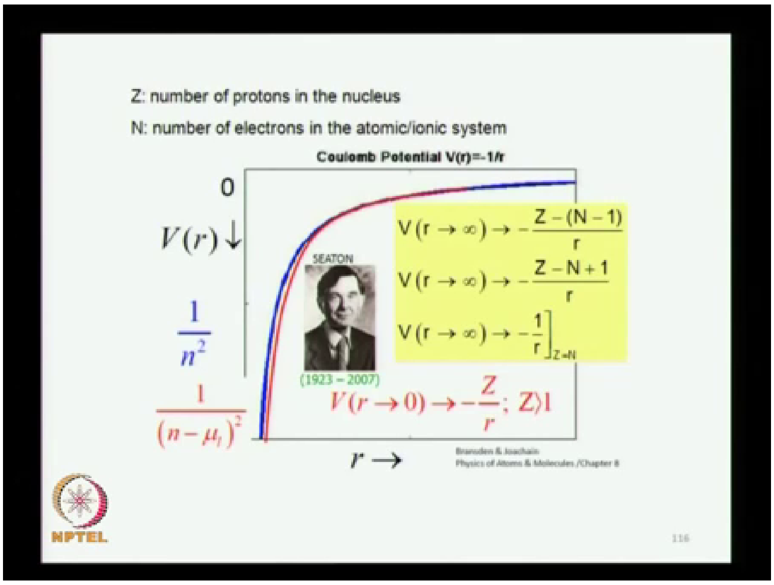
Also: Messiah, Arno Bohm, Greiner,

Landau & Lifshitz, ……

So, these are some of the references which I will like to suggest there is a very nice article by Burkhart and leventhal, which was first publish in the American general physics in 2004. And subsequently, you know they also published a book which is published by Springer verlag and this is a very nice reference for the Lenz vector properties of the hydrogen atom, this is a good reference.

But, then I will also like to suggest that the usual books in quantum mechanics Schiff's messiah Arno bohm. Now, David bohm Sandra boehm has got a book on quantum mechanics, and greiner book landau lifshitz they all have this, and you can refer to any one of these, so you what you find the main results that we have discussed in all of these sources.

(Refer Slide Time: 07:04)



Z: number of protons in the nucleus

N: number of electrons in the atomic/ionic system

Coulomb Potential V(r)=-1/r

$$V(r \to \infty) \to -\frac{Z-(N-1)}{r}$$

$$V(r \to \infty) \to -\frac{Z-N+1}{r}$$

$$V(r \to \infty) \to -\frac{1}{r}\Big]_{Z=N}$$

$$V(r \to 0) \to -\frac{Z}{r};\ Z\rangle 1$$

Bransden & Joachain
Physics of Atoms & Molecules /Chapter 8

Now, let us consider various atomic systems, an atomic when I talk in atomic system I also include an iron, which is also an atomic system. And typically in neutral atom you will have Z number of protons in the nucleus, you will have N number of electrons in the atom, in the neutral atom Z is equal to N. But, N could be less or more in negative ions N could be more than Z, and in positive ions N can be less than Z, and in highly charged ions N can lot less than Z.

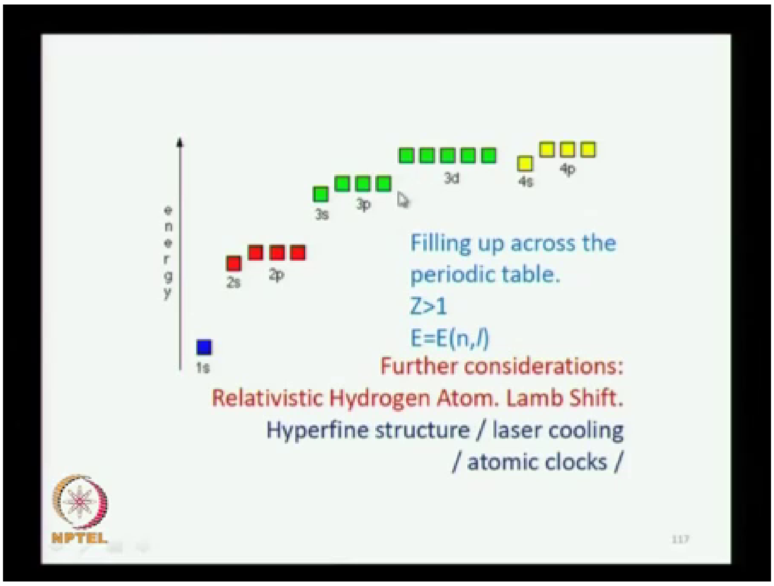
And in stiller space N do have extremely highly charged ions, you know you have ion which is strip out of it is electrons, and you are left with very few electrons with the ion nucleus. And there, so many other species of this kind and depending on the number of electrons N is either equal to Z or not equal to Z and this Z minus N could be 0, if N equal to Z. And as r tends to infinity the potential will go as 1 over r if n equal to Z, but if N is not equal to Z it will go by not just 1 over r, but by Z minus N plus 1 over r as r tends to infinity.

Whereas, as r tends to 0 the potential will go as minus z over r, so if you look at this curves here, there two lines over here, one is a blue curve which is minus 1 over r this is the typical hydrogen atom curve, you have just plotted minus 1 over r. And as r tends to infinity the red curve, which is the potential seen by the electron in an atom, which is not just a hydrogen atom. It could be, you know half more than one electron and this curve will go to 0 as minus Z over r.

So, which means that this will fall below the blue line, and that is what makes the potential in other atoms not hydrogenic strictly. So, the potential is not strictly minus 1 over r in the entire region of space, and then the S O 4 symmetry is broken for these atoms. The nature of the potential, you know it is right on top of the 1 over r only in the asymptotic infinite r tend into infinity region, but not elsewhere. So, some of these things lead to correction a 1 over N square formula needs to be corrected it because 1 over n minus mu square.

Because, the potential is different from minus 1 over r in the core as r tends to 0, you have a correction and this is sometime referred as a quantum defect. So, the mu that you see which is a correction to the principal quantum number, the energy do not go strictly as 1 over n square. But, the energies are another atoms rather than the hydrogen atom, they go as 1 over n minus mu square, where mu is called as a quantum defecter, and this was earlier introduced semi empirically. But, then you get a nicely from quantum mechanics and this was done by mics Keaton and farno and so on. So, there is a whole formalism which is known as a quantum defect theory, might that upon some of the applications that later point of in this course.

(Refer Slide Time: 10:46)

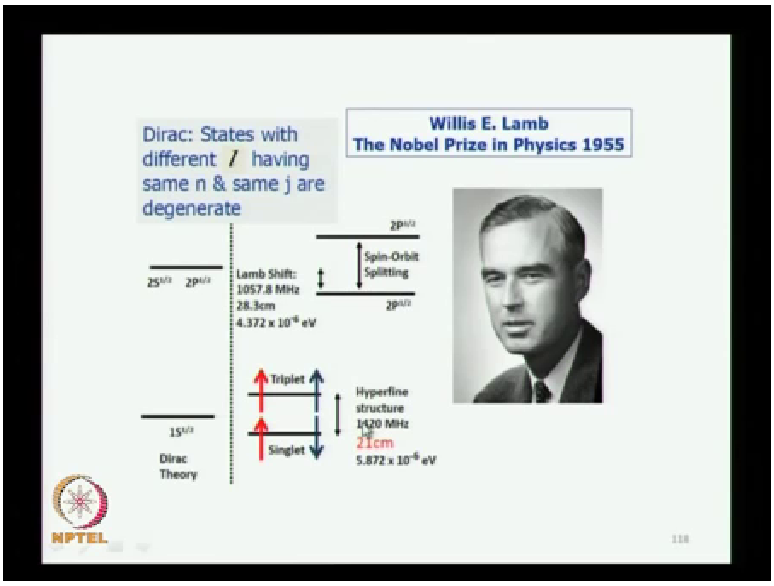


Filling up across the periodic table.
$Z>1$
$E=E(n,l)$
Further considerations:
Relativistic Hydrogen Atom. Lamb Shift.
Hyperfine structure / laser cooling
/ atomic clocks /

But, in these atoms because there is a quantum defect mu and this quantum defect depends on the l quantum number. This is what makes the energy of 2 s different from the energy of 2 p, this is what happens in sodium atom and all the other atoms. In hydrogen atom 2 s and 2 p will in the same energy 3 s 3 p 3 d will be in the same energy, but that is not the case in another atoms, in another atoms depending on the l quantum number.

So, the energy depends not just on the principal quantum number as it does for hydrogen atom, but also on the arbitral angle of momentum quantum number l for all the other atoms. Now, there are further considerations and we will just anticipate some of these things, when you do the relativistic hydrogen atom, which is what we will discuss in unit 3.

(Refer Slide Time: 11:42)



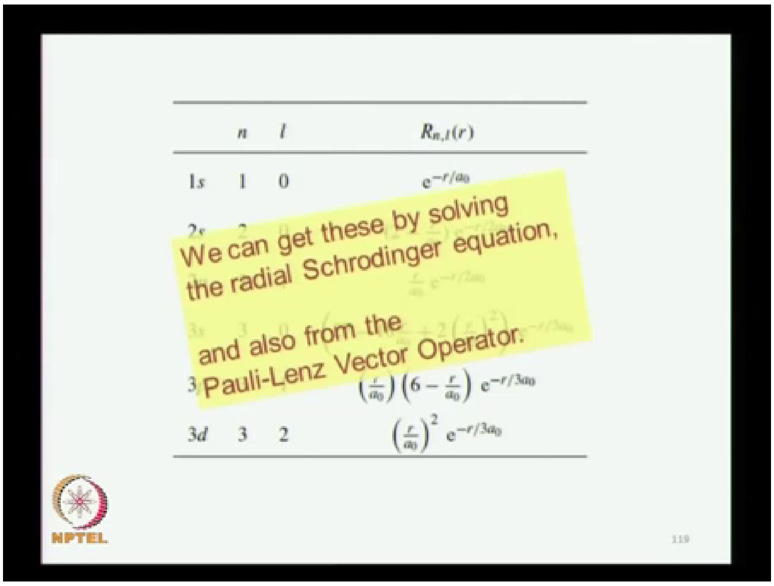
Dirac: States with different l having same n & same j are degenerate

Willis E. Lamb
The Nobel Prize in Physics 1955

You will find that states with different l, but if they have the same j quantum number they are the degenerate. But, then there is a spin orbit you know spreading because of the relativistic interaction, so these are some of the details that we will meet when we do unit 3. So, the complete story of hydrogen atom is quite rich and we have just got a vary introduction to the non relativistic hydrogen atoms spectrum, and it is degeneracy. Not only that the there is a further difference between the 2 p 1 half and 2 s 1 half this is known as a lamb shift.

And these are you know these come from you know feel theoretical correction, so the story of the hydrogen atom is really very wide and quite challenging. So, these are some of other things that you will meet, then there is the hyperfine structure which comes from coupling between the electrons span and nucleus span. So, you know depending on the level which you study the hydrogen atom, you do have a very complex spectrum, so we will talk about these things may be in a little later part of the course.

(Refer Slide Time: 12:58)



	n	l	$R_{n,l}(r)$
1s	1	0	e^{-r/a_0}
2s	2	0	$\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
[illegible]	[illegible]	[illegible]	$\frac{r}{a_0}e^{-r/2a_0}$
3s	3	0	[illegible] $+2\left(\frac{r}{a_0}\right)^2\Big) e^{-r/3a_0}$
3[illegible]	[illegible]	[illegible]	$\left(\frac{r}{a_0}\right)\left(6-\frac{r}{a_0}\right)e^{-r/3a_0}$
3d	3	2	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

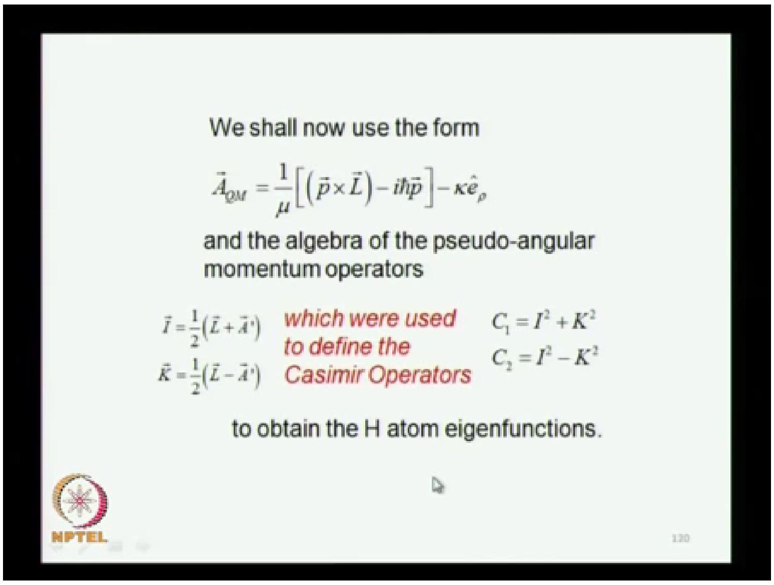
We can get these by solving the radial Schrodinger equation,

and also from the Pauli-Lenz Vector Operator.

Now, let us have a look at these wave functions and again I am not going to discuss, how you derive these solution from the Schrodinger equation. All of you have done a first course quantum mechanics, you have done the hydrogen atom you have applied the boundary conditions to the radial part, and you have actually obtain these solutions. So, I take that you are familiar with these solutions.

Now, you obtain these redial functions by solving the Schrodinger equation and applying the property boundary conditions right. So, these results are known what you are going to do now, is discover that these solutions can be obtained not just from the Schrodinger equation as you have already done in your earlier course on quantum mechanics. But, you can get these wave functions also from the Pauli Lenz vector.

(Refer Slide Time: 14:04)



We shall now use the form

$$\vec{A}_{QM} = \frac{1}{\mu}\left[\left(\vec{p}\times\vec{L}\right) - i\hbar\vec{p}\right] - \kappa\hat{e}_\rho$$

and the algebra of the pseudo-angular momentum operators

$\vec{I} = \frac{1}{2}(\vec{L}+\vec{A}')$

$\vec{K} = \frac{1}{2}(\vec{L}-\vec{A}')$

which were used to define the Casimir Operators

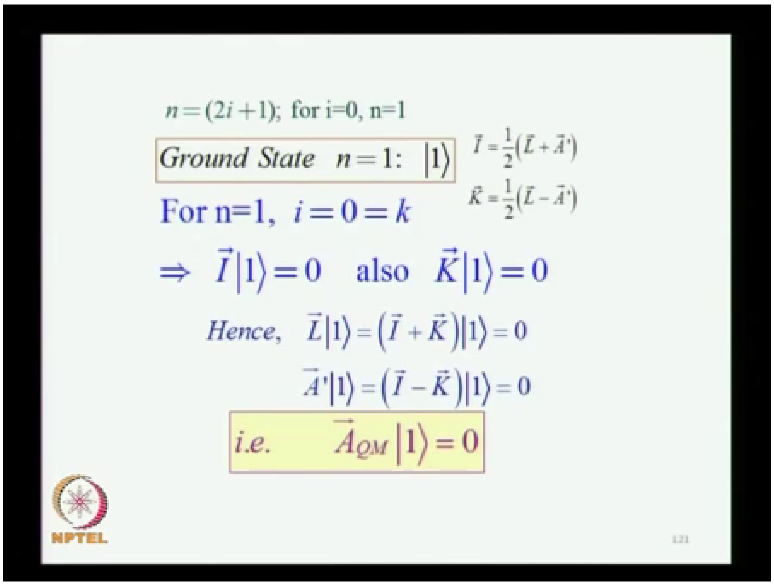
$C_1 = I^2 + K^2$

$C_2 = I^2 - K^2$

to obtain the H atom eigenfunctions.

So, we will carry the potential of the Pauli Lenz vector further, and we begin with this equivalent form of the Pauli Lenz quantum mechanical vector, and we will use this Pauli Lenz vector to get the hydrogen atomic wave function.

(Refer Slide Time: 14:14)



$n = (2i+1)$; for i=0, n=1

$\boxed{\textit{Ground State} \quad n=1: \quad |1\rangle}$

$\vec{I} = \frac{1}{2}(\vec{L}+\vec{A}')$

$\vec{K} = \frac{1}{2}(\vec{L}-\vec{A}')$

For n=1, $i = 0 = k$

$\Rightarrow \vec{I}|1\rangle = 0$ also $\vec{K}|1\rangle = 0$

Hence, $\vec{L}|1\rangle = (\vec{I}+\vec{K})|1\rangle = 0$

$\vec{A}'|1\rangle = (\vec{I}-\vec{K})|1\rangle = 0$

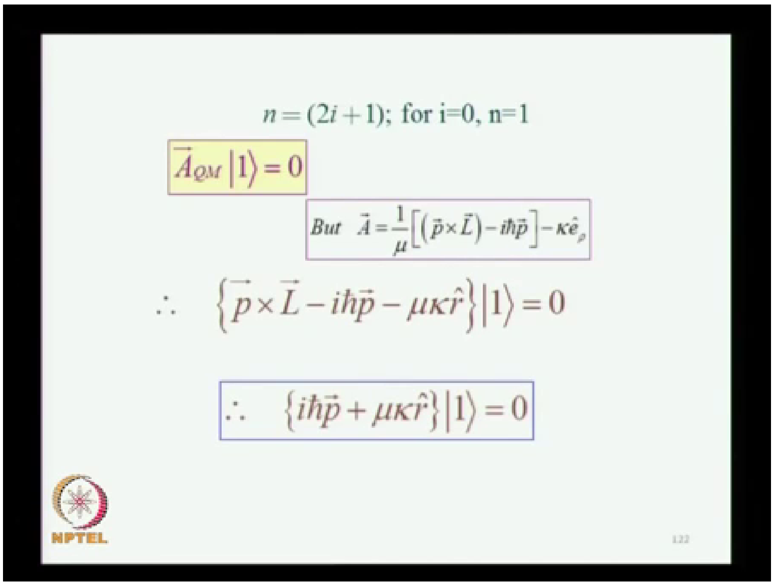
$\boxed{\text{i.e.} \quad \vec{A}_{QM}|1\rangle = 0}$

So, let see how to do that, let first of all define the ground state, the ground state has a principal quantum number n equal to 1, n we have introduced as 2 i plus 1 right. So, this corresponds to i equal to 0, and we do this book keeping by designating this vector at the Hilbert space by the principal quantum number, this is of the designation of the ground state. And we have to find what this is, we have to find this coordinate representation, we have done it from the Schrodinger equation, we will now do it from the Pauli Lenz vector.

So, given the fact that n is equal to 1 we know the corresponding value of i must be 0, and therefore, if the vector operator I would operate on this ground state, you will get 0. And the same thing would happened, if you are to operate by the other pseudo angle of momentum vector operator K, so you will get 0 out of this operation, now L and A the angle of momentum on the Pauli Lenz operators, they are made of the sum and the difference of I and K.

And since I and K is gives you 0, L operating on the ground state will give you 0 and A prime the Pauli Lenz operating on the ground state will also give you 0 it is quite straight forward. Now, A prime is proportional to the Pauli Lenz operator right, we had only defined A prime through the scaling factor if you remember, so; obviously, when the Pauli Lenz operator operates on a ground state, the result is 0. Now, this is very good because we do have an explicit form of Pauli Lenz vector operator which is this.

(Refer Slide Time: 16:22)



$$n = (2i+1);\ \text{for i=0, n=1}$$

$$\boxed{\vec{A}_{QM}\,|1\rangle = 0}$$

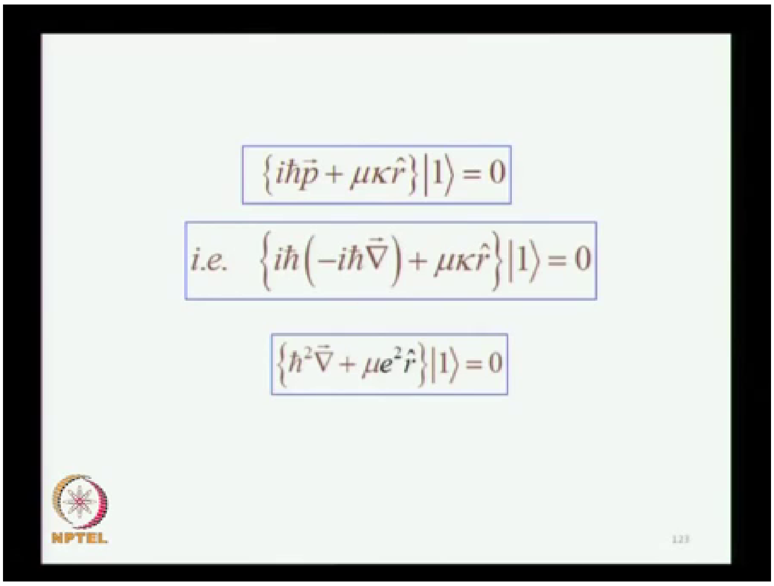
$$\boxed{But\ \ \vec{A} = \frac{1}{\mu}\left[(\vec{p}\times\vec{L}) - i\hbar\vec{p}\right] - \kappa\hat{e}_{\rho}}$$

$$\therefore\quad \left\{\vec{p}\times\vec{L} - i\hbar\vec{p} - \mu\kappa\hat{r}\right\}|1\rangle = 0$$

$$\boxed{\therefore\quad \left\{i\hbar\vec{p} + \mu\kappa\hat{r}\right\}|1\rangle = 0}$$

So, let us write this expression with the complete form of the Pauli Lenz vector operator which is this, operating on the ground state and the result is 0. The first term has got the angle of momentum operator, which is the first one which would operate on the vector, and have we already seen that when the angle of momentum operator operates on the ground state, you must get 0 we just saw it right. So, l operating on 1 on the ground state would give you 0, so out of the 3 terms that you find in the bracket. The first one would give you 0, you have only the other 2 both with the minus sign, so you can write the remaining 2 terms, which is i h cross p plus mu kappa r the unit vector r that I have change the sign. Why minus 1 into 0 still equal 0 even in the atomic physics right.

(Refer Slide Time: 17:36)



$$\boxed{\{i\hbar\vec{p} + \mu\kappa\hat{r}\}|1\rangle = 0}$$

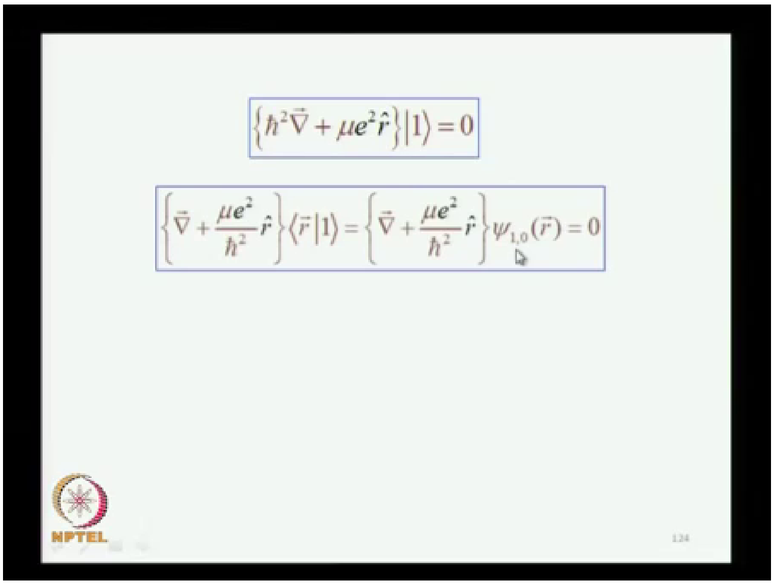
$$\boxed{i.e. \quad \{i\hbar(-i\hbar\vec{\nabla}) + \mu\kappa\hat{r}\}|1\rangle = 0}$$

$$\boxed{\{\hbar^2\vec{\nabla} + \mu e^2\hat{r}\}|1\rangle = 0}$$

So, this will what, now we know what the momentum operator is this is our expression, momentum is a gradient operator. So, plug in momentum is minus h cross gradient, and now you have a differential equation, you have a first order differential equation and it is no big problem to solve it, all of you can do it right. So, you have a first order differential equation which is h cross square gradient plus mu epsilon square operating on the ground state equal to 0.

This is; obviously, not Schrodinger equation the operator is not the Hamiltonian, it does not have a kinetic energy, it does not have a potential energy. The kinetic energy goes as the square of the gradient operator right, p square this is the first order differential equation. Schrodinger equation is a second order differential equation, this is not the Schrodinger equation, this is the first order differential equation that you are getting by exploiting the property of this Pauli Lenz vector operator.

(Refer Slide Time: 18:47)



$$\left\{\hbar^2\vec{\nabla} + \mu e^2 \hat{r}\right\}|1\rangle = 0$$

$$\left\{\vec{\nabla} + \frac{\mu e^2}{\hbar^2}\hat{r}\right\}\langle \vec{r}|1\rangle = \left\{\vec{\nabla} + \frac{\mu e^2}{\hbar^2}\hat{r}\right\}\psi_{1,0}(\vec{r}) = 0$$

And all you have to do is to solve this first order differential equation, which will give you the ground state, the coordinate representation of the state vector 1 will give to the ground state wave function psi right. And the solution is what you have seen earlier already, but you have got it from the Schrodinger equation, and we get it now without touching the Schrodinger equation. And question which I had posed to the end of our previous class, was that we get the energy Eigen values of the hydrogen atom.

And now you have seen that you get a also the wave function and in fact, if you do this if you extend this technique further, you can get not just 1 s wave function. But, all of them that involves a little extensive algebraic methods, which I will not discuss at the class, but you can go through Masaya quantum mechanics, and you will find the discussion over there. So, I am not going to discuss that, but we have shown how you can get, the ground state wave function all the other wave functions also be obtained using some other technique.

And the interesting feature is that you get the energy Eigen spectrum, the Eigen values you also get the wave functions you are able to do more with this, because you are able to explain the degeneracy of the hydrogen atom, which you could not otherwise, but you not use a Schrodinger. So, how is it that you get all the results of the quantum mechanics, without using the Schrodinger equation.

Do you recognize that you have not used the Schrodinger equation, and you do get the complete energy spectrum, the Eigen spectrum, the Eigen values, the Eigen functions and the degeneracy and everything, ((Refer Time: 20:58) answer lies in the fact that Schrodinger equation is a representation of quantum mechanics. So, whenever we ask this question as to what is it that mean by quantization. Does it mean that you replace the classical equation of the motion by the Schrodinger equation.

And the Schrodinger equation is not just h psi equal to e psi that is only the time independent part. Basically it is rate equation, it gives you the rate at which the wave function changes with time del psi by del t. So, it tells you how this state of the systems evolves with time that is the fundamental question in mechanics, how do you represent state of a system. And how does this system evolve with time, and rate equation is given by the Schrodinger equation for del psi by del t.

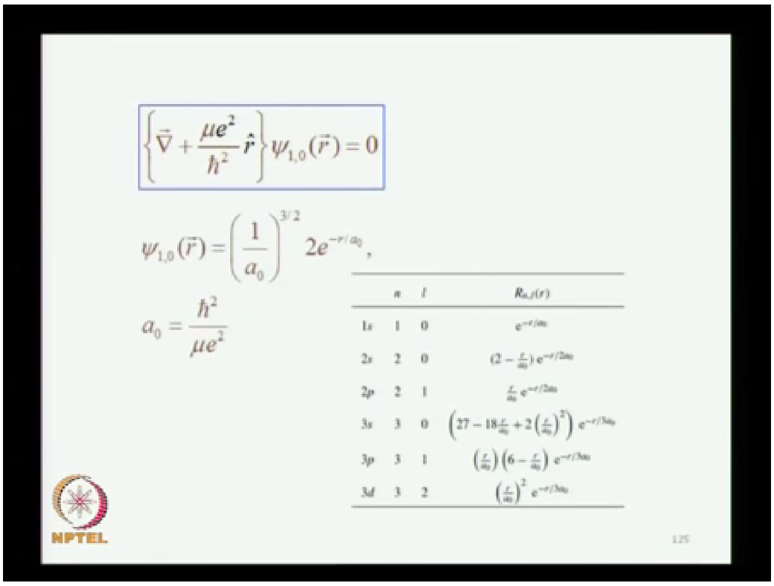
But, the heart of quantum mechanics is in the fact that you need to perform a measurement, unless you are able to carry out the measurement, you cannot relate your theory to your observations. And in classical mechanics you do it, by measuring the position and the momentum, and without this measurement you do not get the state of the system. The state of a system in classical mechanics is denoted by q and p it is a find in the free space.

So, q and p give you the state of a system in classical mechanics and this is possible because simultaneous measurement of position and momentum are not challenged in the approximation is not that they are possible, but they are challenged. They are of course, not possible because you try to do it and you meet incompatibility you try to make a measurement of position, then you do a measurement of momentum come back and measure the position, you do not recover the same answer as you did earlier.

So, repeated a measurement do not give you same results, so these operators do not commute, they do not have simultaneous Eigen state. And then you have to abandon the rate equations, which are the Hamilton's equations q dot and p dot equivalently the Lagrange equation and Newton's it is a same thing. But, essentially you are looking for rate equations, that is to how a system revolves with time, and you have to abandon the scheme and replace classical dynamic variables, by judicious operators that is quantization.

It is not just having discrete and indiscrete anything it has that is quantization, and that is something we have certainly used in our Pauli Lenz vector analysis. The essence of quantum mechanics is that, we have taken full advantage of that in our treatment of Pauli Lenz vector, which is why we are able to get all the results of quantum mechanics because they are containing in a heart of quantum mechanics which is quantization. So, we did not use a Schrodinger equation, but get the all results.

(Refer Slide Time: 24:14)



$$\boxed{\left\{\vec{\nabla} + \frac{\mu e^2}{\hbar^2}\hat{r}\right\}\psi_{1,0}(\vec{r}) = 0}$$

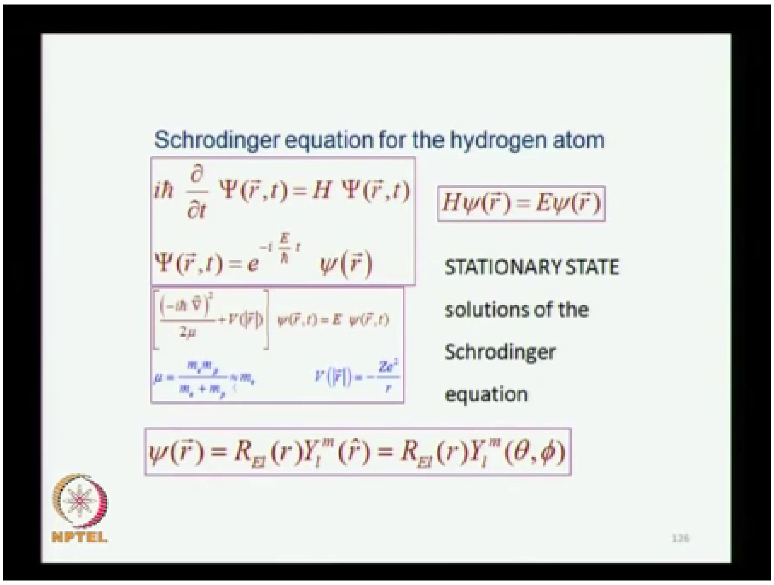
$$\psi_{1,0}(\vec{r}) = \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0},$$

$$a_0 = \frac{\hbar^2}{\mu e^2}$$

	n	l	$R_{n,l}(r)$
1s	1	0	e^{-r/a_0}
2s	2	0	$(2 - \frac{r}{a_0})\, e^{-r/2a_0}$
2p	2	1	$\frac{r}{a_0}\, e^{-r/2a_0}$
3s	3	0	$\left(27 - 18\frac{r}{a_0} + 2\left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$
3p	3	1	$\left(\frac{r}{a_0}\right)\left(6 - \frac{r}{a_0}\right) e^{-r/3a_0}$
3d	3	2	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

So, these are this is the 1 s wave function which you know goes e to the minus r, and then likewise you can do a little more, you know analysis and you can recover the entire range of radial functions of the hydrogen atom, you can get 1 s 2 s 2 p 3 s just about everything, the entire range of Eigen functions you will get using this treatment.

(Refer Slide Time: 24:45)



Schrodinger equation for the hydrogen atom

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r},t) = H\ \Psi(\vec{r},t)$$

$$\Psi(\vec{r},t) = e^{-i\frac{E}{\hbar}t}\ \psi(\vec{r})$$

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

$$\left[\frac{(-i\hbar\vec{\nabla})^2}{2\mu} + V(|\vec{r}|)\right] \psi(\vec{r},t) = E\ \psi(\vec{r},t)$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx m_e \qquad V(|\vec{r}|) = -\frac{Ze^2}{r}$$

STATIONARY STATE

solutions of the

Schrodinger

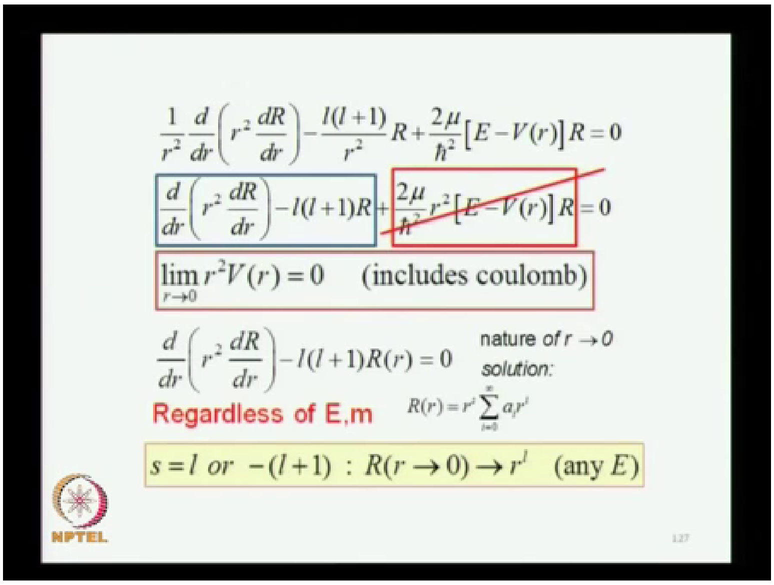
equation

$$\psi(\vec{r}) = R_{El}(r)Y_l^m(\hat{r}) = R_{El}(r)Y_l^m(\theta,\phi)$$

So, I will like to remind that the Schrodinger equation is not just h psi equal to e psi it is rather the rate equation at which the state of a system evolves with time because the whole idea is this that you want to see how a state of the quantum system, evolves with time. So, there has to be time deliberative operator which must show on that is what the Schrodinger equation is about then of course, when you have stationary state solutions you can get, the time independent differential equation.

And depending on the symmetry when there is spherical symmetry you separate the radial part in the angular part, and all of this machinery of the Schrodinger equation it is a very powerfully, you know machinery. And there is a lot that one learns out of it, and since you have already done a course in quantum mechanics, in which you have done both out of these details. I am not going to repeat any of that, but I will nevertheless touch upon a few points, just a selection of a few points of those properties which I think rather interesting in atomic physics. So, I am going to refer to the Schrodinger equation now, exploit the radial the spherical symmetry.

(Refer Slide Time: 26:07)



$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{l(l+1)}{r^2}R+\frac{2\mu}{\hbar^2}\left[E-V(r)\right]R=0$$

$$\boxed{\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-l(l+1)R}+\boxed{\cancel{\frac{2\mu}{\hbar^2}r^2\left[E-V(r)\right]R}}=0$$

$$\boxed{\lim_{r\to 0} r^2V(r)=0 \quad \text{(includes coulomb)}}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-l(l+1)R(r)=0$$

nature of $r \to 0$ solution:

Regardless of E,m

$$R(r)=r^s\sum_{l=0}^{\infty}a_l r^l$$

$$\boxed{s=l \ or \ -(l+1) \ : \ R(r\to 0)\to r^l \quad (\text{any } E)}$$

And then look at the radial differential equation, this is the one dimensional differential equation that you get, after you remove the spherical part the angular part. And I will like to discuss this for any form of the spherical potential, for which r square V goes to 0 now this includes the coulomb potential because r square V goes as 1 over r. So, r square V will go as r and r tends to 0 it goes to 0, so for any potential which goes to 0 as r tends to 0, and then look at the nature of these solutions in this limit.

Now, r square V goes to 0, so if you look at the small r behavior, and this is always nice to do when you dealing with differential equation. Does not matter whether it is in physics or any other subject, try to see what you can get in different limiting conditions. Like how does differential equation look like, in the r tending to 0 region, how does it look like in r tending to infinity region, do you get some special features. And you can get a lot of inside into the subject by doing this.

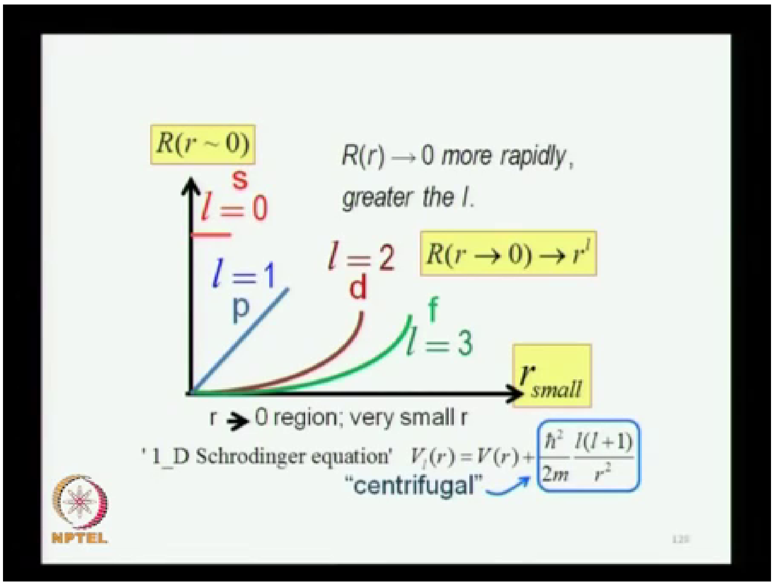
So, is r tends to 0 if you look at the last you got r square multiplying E the energy, and no matter what energy is, it could be the energy the 1 s state of the 2 s the 3 p or 15 g whatever or it could be continuum, it could be a positive energy in the continuum it does not matter. No matter what energy is r square into E will go to 0 as r tends to 0, and by our choice of the potential that r square V goes to 0 as r tends to 0. The second term over here, this one also goes to 0 which means that in your differential equation this entire thing can be struck off.

If you want to get some idea about what is the nature of the solutions in the small r region, and what is interesting is that whatever you learnt from the residual differential equation, is going to be common for all the energies. It does not matter whether you are dealing with this discrete part of this partum, with negative energies, positive energies which quantum number n equal to 1, 2, 3, 4 it does not matter, because our consideration is completely independent of the energy.

So, for this the residual differential equation consists of only the first 2 terms, and we write this differential equation here. This is a residual differential equation, which is of relevance for the small r h, this is not going to give us a complete solution for the entire domain of space from the 0 to infinity. But, it will give us some a insight into the nature of the solution in the small r h that is very important.

It of course, it is not depend on the azimuthal quantum number m either, it does not appear in anywhere, it is independent of E. And if you see kappa power series solution, then you can plug in this form of the power savory solution over here, take the first derivative take the second derivative. And immediately you are left to the condition that this radial function as r tends to 0, must go as the l'th power of r. Now, this is a very important result it has got very important consequences an atomic process in collusion in quantum collisions and so on, you will see why it is such importance.

(Refer Slide Time: 30:00)


$R(r) \to 0$ *more rapidly, greater the* l.

$R(r \to 0) \to r^l$

r ➔ 0 region; very small r

' 1_D Schrodinger equation' $V_l(r) = V(r) + \boxed{\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}$

"centrifugal"

Let us try to sketch this behavior in the small r region do not think of this line, as a line of significant length. Because, we are really looking at what we are discussing is a nature of the solution as r tends to 0, so it is in the infinitesimally small region close to r equal to 0 that you are examining the nature of the solutions. And that is what I indicate on the vertical axis that this is the redial function near the origin, and we know that the solution goes as r to the l.

So, for l equal to 0 it will be constant r to the 0 is 1, so there will be some normalization constant etcetera right. So, it will be constant as r tends to 0 for l equal to 1, which is for the p waves right l equal to 0 are s waves, for the p waves this is r to the 1, so it will be linear right for l equal to 2, you will have parabolic behavior. And for l equal to 3, it will go as r to the 3 and what you notice over here that as l increases, it goes to 0 much faster.

And this should not surprise you because if you look at the 1 dimensional radial Schrodinger equation, you have an effective potential which is made up of this part, and this term over here which is l into l plus 1 by r square. You remember this term, you got it when you separated the angular part from the redial part, this l into l plus 1 by r square term is called as a centrifugal term. Why is a centrifugal, what does the term centrifugal suggest was, centrifugal term is what you used in classical mechanics when you are dealing with pseudo forces right.

So, there is something unreal about it and what is unreal about this term is that, this is not a real physical potential. The physical potential that you have an hydrogen atom just a electromagnetic potential, which is the coulomb 1 over r right that is the physical potential. Here the effective potential is a coulomb potential plus an additional term, which is not the physics it is coming from a mathematical artifact because you have reduced the 3 dimensional problem to a 1 dimensional problem.

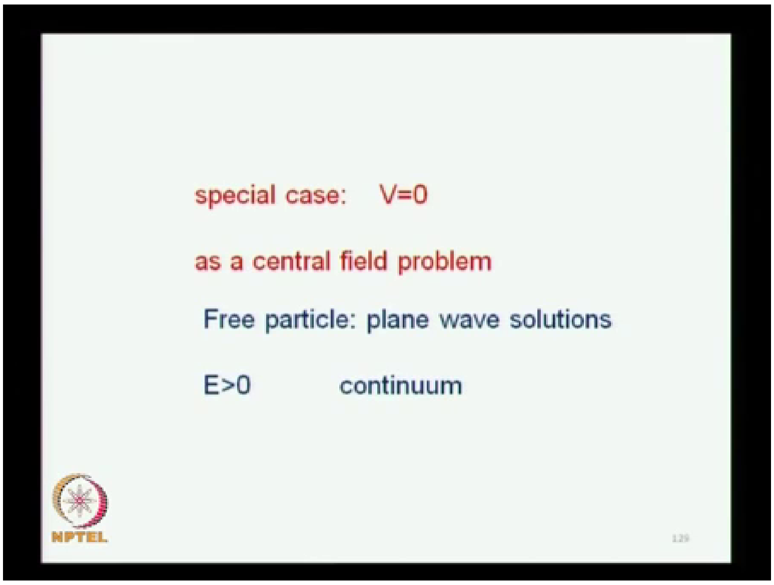
So, it is a mathematical artifact of the reduction of the 3 dimensional potential to the 1 dimensional problem that you have this term, it is not a physical potential. So, that is what makes it a pseudo potential kind of thing, so it is called as a centrifugal term because it is not really physical. The other thing it has in coming with this centrifugal term, is that what the centrifugal term does in classical mechanics when you are dealing with rotating frame of references, is to keeping on object out right.

The centrifugal force keeps on object out away that is exactly what we see over here that as l increases l into 2 l plus 1 by r plus term becomes more and more important. And the probability amplitude of the wave function, goes to 0 much faster in the small r region as l increases. So, as l equal to 0 s wave is not at all it has an amplitude at l equal to 0 because the centrifugal term is 0, but then whenever l is greater than 0 whether it is 1, 2, 3 or whatever.

The wave function is not able to reach the centre, the corresponding probability amplitude, the probability density, and the electron itself will be kept away. So, if you have a collusion experiment for example, if you got a target you bombed electrons then electrons with higher angular momentum, they would not really be able to get in the core they will be kept away. So, it has got consequences in quantum collisions, we will be discussing some of these applications later.

But, it is important to recognize that these properties come from the small r behavior of the wave function, which goes as r to the l. So, this is the centrifugal term let us now deal with the v equal to 0 case, like I mentioned that whenever you look at the differential equation, it always interesting to look at it in different limiting conditions. So, you can look at r equal to 0, r going to infinity, you can also look for a limiting behavior of the potential, v equal to 0 is also a centrifugal potential. Because, it has got the same value in every angle, no matter in which direction you look, it is always a same, which is 0, so this is an isotropic potential.

(Refer Slide Time: 35:43)



special case: V=0

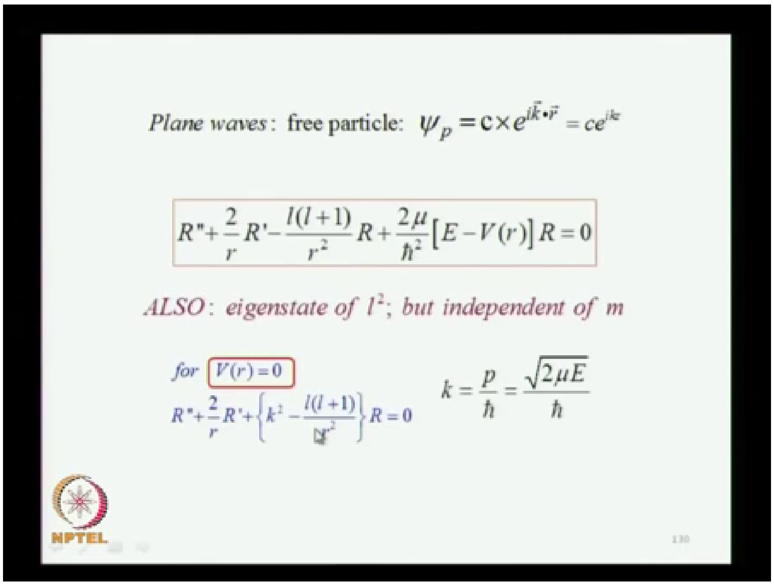
as a central field problem

Free particle: plane wave solutions

E>0 continuum

So, we consider the center field problem with a special case when V is equal to 0, when there is no potential you already know these solutions are, you have done the problem for free particle. The solution is E to the i k dot r right these are the plane waves, so you already know the solutions, you also know these are not bound particles which is why called them as free, not because you do not pay anything for it, but just because if not bound anywhere right. So, it is a free particle you know the energies are positive they belong to the continuum.

(Refer Slide Time: 36:22)



Plane waves: free particle: $\psi_p = \text{c} \times e^{i\vec{k}\bullet\vec{r}} = ce^{ikz}$

$$\boxed{R'' + \frac{2}{r}R' - \frac{l(l+1)}{r^2}R + \frac{2\mu}{\hbar^2}[E - V(r)]R = 0}$$

ALSO: *eigenstate of* l^2; *but independent of m*

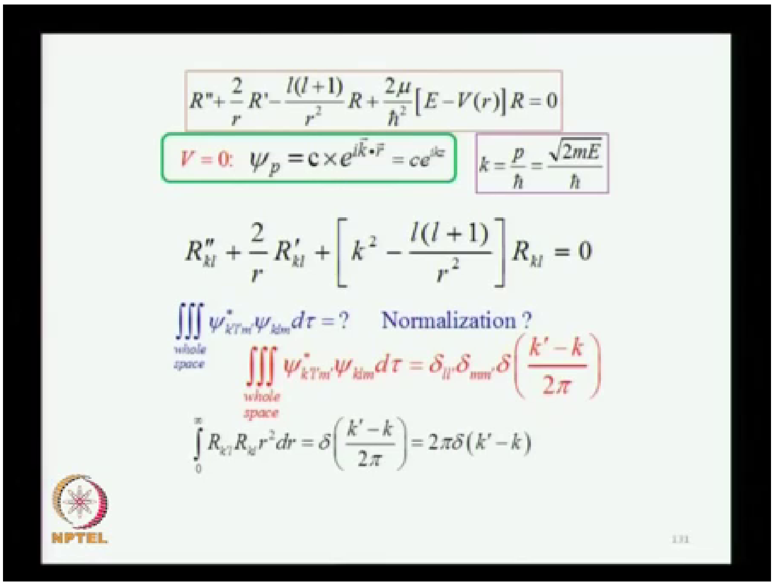
for $\boxed{V(r) = 0}$

$$R'' + \frac{2}{r}R' + \left\{k^2 - \frac{l(l+1)}{r^2}\right\}R = 0 \qquad k = \frac{p}{\hbar} = \frac{\sqrt{2\mu E}}{\hbar}$$

And the solution goes as e to the i k dot r and you can choose an axis along k, so you can get the k dot r term to be given by k z. And now, let us throw the term V, you know these are also Eigen state of l square, which is the square of angular momentum right, now put V equal to 0 in the v radial Schrodinger equation. So, V is gone you are left with 2 m e by h cross square, and you can defined the wave vector in terms of that which is p over h cross.

So, the 2 m e over h cross square is replaced by this k square in the differential equation, and now you have a differential equation in which V does not appear. And it is still a Schrodinger equation for the hydrogen atom for the special case, when you are dealing with a limiting behavior V is going to 0.

(Refer Slide Time: 37:35)



$$\boxed{R''+\frac{2}{r}R'-\frac{l(l+1)}{r^2}R+\frac{2\mu}{\hbar^2}[E-V(r)]R=0}$$

$$\boxed{V=0:\ \psi_p=c\times e^{i\vec{k}\cdot\vec{r}}=ce^{ikz}} \quad \boxed{k=\frac{p}{\hbar}=\frac{\sqrt{2mE}}{\hbar}}$$

$$R''_{kl}+\frac{2}{r}R'_{kl}+\left[k^2-\frac{l(l+1)}{r^2}\right]R_{kl}=0$$

$$\underset{\substack{\text{whole}\\\text{space}}}{\iiint}\psi^*_{k'l'm'}\psi_{klm}d\tau=?$$ Normalization ?

$$\underset{\substack{\text{whole}\\\text{space}}}{\iiint}\psi^*_{k'l'm'}\psi_{klm}d\tau=\delta_{ll'}\delta_{mm'}\delta\left(\frac{k'-k}{2\pi}\right)$$

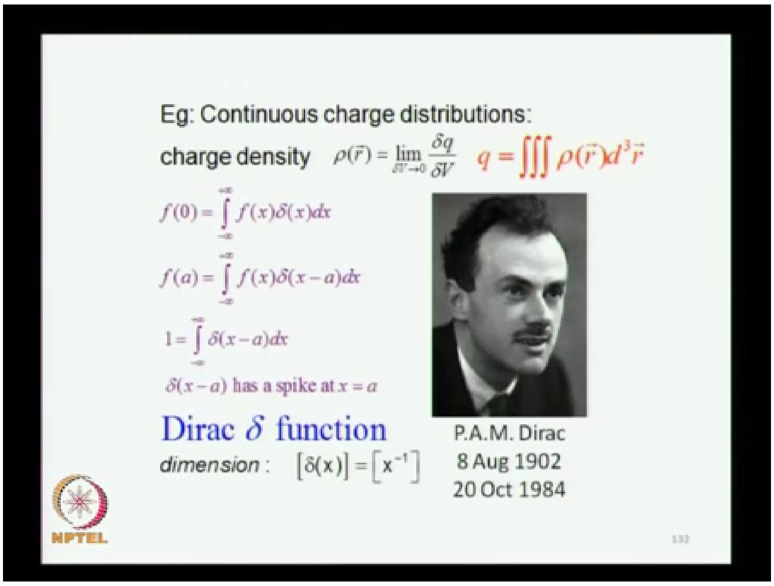
$$\int_0^\infty R_{k'l}R_{kl}r^2dr=\delta\left(\frac{k'-k}{2\pi}\right)=2\pi\delta(k'-k)$$

So, let us have a look at the nature of the solution, now what is interesting about it is how do you normalized it. Because, when you construct normalization integral, you integral it is psi over the whole space, and that is what gives you the normalization integral right. Now, what is going to happen if you have for the wave function e to the i k z, you have the e to the i k z multiplied by e to the minus i k z that gives you 1. And then you are adding the volume element of over the whole space.

So, it blows up it is just blows up, and this is not square integral this is not normalizable, so how do you normalize it. So, we have to figured out how to normalize it, and these are normalize using a technique known as a Dirac delta normalization, now you have a pearly met the delta function. And the normalization is achieved through this expression over here, that you normalized this integral by setting it equal to the orthogonality between l and l prime and m and m prime, this is coming from the orthogonality of the spherical harmonics.

So, this is not new to us that is not I am going to discuss, but the radial part will have to be normalized because the trouble is coming from the radial part of the solution. So, the radial part of the solution is normalize under k over 2 pi scale, this is called as Dirac delta normalization. And this integral 0 to infinity of the radial integral is set equal to the Dirac delta this is not the conical delta, this is the Dirac delta, and the Dirac delta is a very interesting function it has got marvelous applications, when you are dealing with continuum functions. Because, continuum functions you are always going to have deal with the quantum collision theory. So, the discrete spectra which are square integrable they are only part of quantum mechanics, but then the remaining part of the quantum mechanics, which deal with you know the continuum states, you have to normalized them using the Dirac delta functions.

(Refer Slide Time: 40:04)



Eg: Continuous charge distributions:

charge density $\rho(\vec{r}) = \lim_{\delta V \to 0} \frac{\delta q}{\delta V}$ $q = \iiint \rho(\vec{r}) d^3\vec{r}$

$f(0) = \int_{-\infty}^{+\infty} f(x)\delta(x)dx$

$f(a) = \int_{-\infty}^{+\infty} f(x)\delta(x-a)dx$

$1 = \int_{-\infty}^{+\infty} \delta(x-a)dx$

$\delta(x-a)$ has a spike at $x = a$

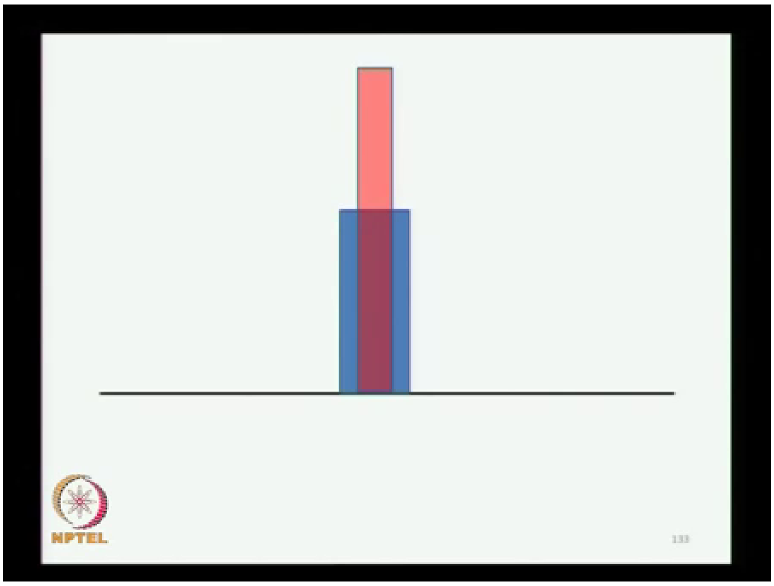
Dirac δ function

dimension : $[\delta(x)] = [x^{-1}]$

P.A.M. Dirac
8 Aug 1902
20 Oct 1984

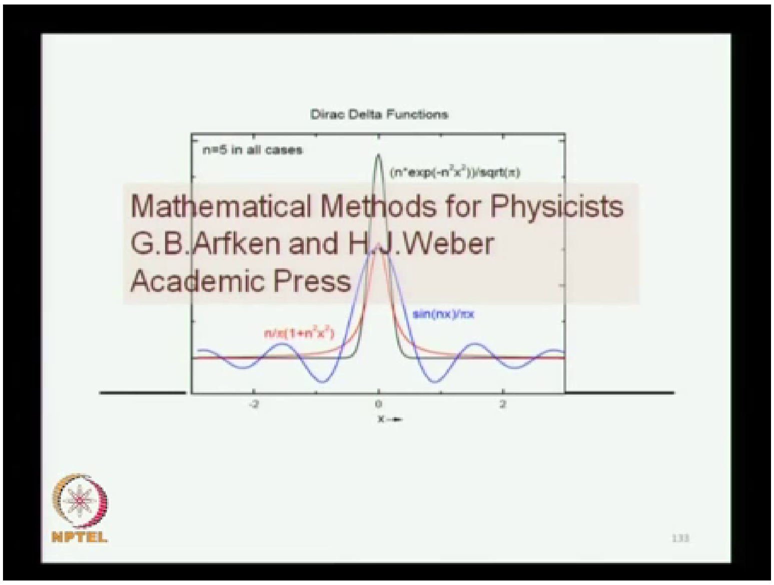
And it has some similarity with the charge density, which is charge per unit volume in the limit the volume element going to 0. When the value element is goes to 0 both the numerator and the denominator would individually vanished right, but the ratio does not and the Dirac delta functions has got properties of this kind. So, this is the definition of the Dirac delta functions, you early have met it in your mathematical physics course. And what it does is it has got a spic, when the argument of the function is 0 that is spic function, there are various representations of the Dirac delta functions. Always remember that it has got dimensions, it must have the dimension of 1 over x whatever be the argument of the delta function. So, do not ignore the dimensions of the Dirac delta.

(Refer Slide Time: 41:06)



And what it does is that, you can you know reduced the width and let the height increase of the rectangle. But, the area which is the product of one side with the other that area remains a same, and you can keep doing it and decrease a width let it becoming infinitesimally small, and let this height becomes infinitesimally large, so it does develop a spic.

(Refer Slide Time: 41:35)

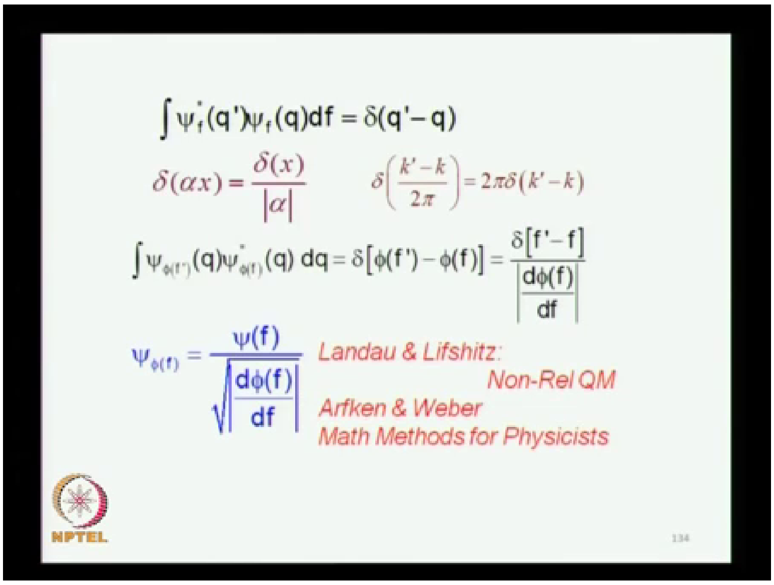


Mathematical Methods for Physicists
G.B.Arfken and H.J.Weber
Academic Press

This is not a only representation, there are many other representations of Dirac delta function, all of them have got this special feature. They are all spiced they have got a huge height in the middle, and they dies off very fast and sometime I like to call this as an exploit function. Because, it remind me a modern exporters, an expert is 1 who knows more and more about less and less right.

In the limit he knows everything about nothing, so sometime I call the Dirac delta function as expert function, but you understand why it has this behavior. And I will like to draw your attention to Arfkens book, Arfken Weber and you will find the properties of the Dirac delta and some very good exercises I strongly recommend Arfken for this.

(Refer Slide Time: 42:29)



$$\int \psi_f^*(q')\psi_f(q)df = \delta(q'-q)$$

$$\delta(\alpha x) = \frac{\delta(x)}{|\alpha|} \qquad \delta\left(\frac{k'-k}{2\pi}\right) = 2\pi\delta(k'-k)$$

$$\int \psi_{\phi(f')}(q)\psi_{\phi(f)}^*(q)\, dq = \delta[\phi(f') - \phi(f)] = \frac{\delta[f'-f]}{\left|\frac{d\phi(f)}{df}\right|}$$

$$\psi_{\phi(f)} = \frac{\psi(f)}{\sqrt{\left|\frac{d\phi(f)}{df}\right|}}$$

Landau & Lifshitz:
Non-Rel QM
Arfken & Weber
Math Methods for Physicists

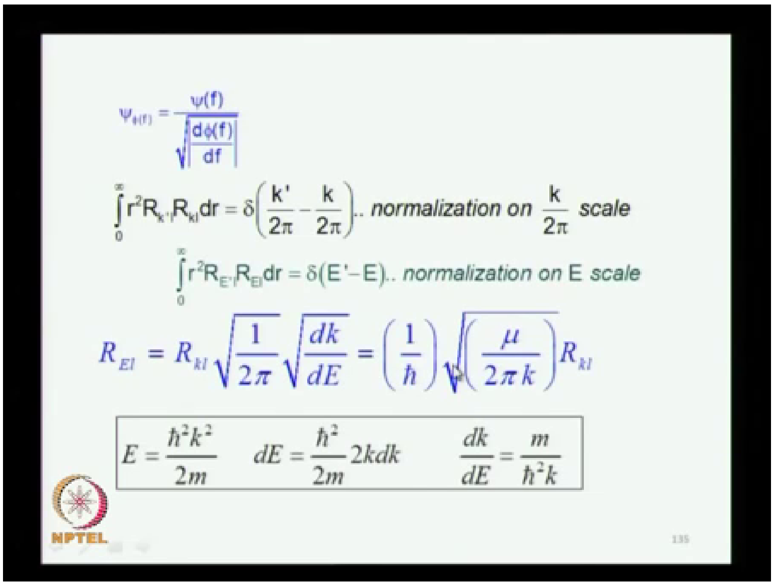
Now, you can defined this Dirac delta normalization, now notice that the dami variable here, which is being integrated out is f. And the quantum state is represented by f over here, and you integrate this out and you get the Dirac delta normalization, landau lifshitz is also very good source for this, specially for the normalization of the continuum functions. Now, if you multiply the argument by 1 factor by a scaling factor like alpha, then the Dirac delta gets scaled by 1 over modulus of alpha.

And some of these properties are parley known to you or if you look into herfkens book you will find that these are simple exercises, which are based on the properties of the Dirac delta. What it means that if you normalize this, not with reference to the state f, but you described it in terms of the function of f like phi of f, what I have in mind is the energy parameter, energy is p square over to m right. So, I can normalize the wave functions on the energy scale, I can also normalize it in p scale or the momentum scale.

The corresponding wave functions will have to be related they have to be scaled appropriately, and the scaling will come from this relation. Because, the Dirac delta for alpha x is related to delta of x by this relation over here, so if it is normalized on the phi scale rather than f scale where phi is a function of f. So, f can be your k and p is a function k e is also a function k e is p square over 2 m or it is h cross square k square over 2 m right.

So, you can write the index either it is energy or is a momentum or as k which is the wave number, and depending on which you are using you will have a Dirac delta which is now the difference of phi f prime minus phi. And this comes from the ordinary calculus that this will be delta f prime minus f divided by this modulus of this the same relation that I am writing here. So, some of these things we will have to work with when we advance this course to deal with continuum physics, with collusion quantum collision physics. So, we will come back to this, but I just thought that I will alert you to some of these properties for now.

(Refer Slide Time: 45:38)



$$\psi_{\phi(f)} = \frac{\psi(f)}{\sqrt{\left|\frac{d\phi(f)}{df}\right|}}$$

$$\int_0^\infty r^2 R_{k'l} R_{kl} dr = \delta\left(\frac{k'}{2\pi} - \frac{k}{2\pi}\right) \text{.. normalization on } \frac{k}{2\pi} \text{ scale}$$

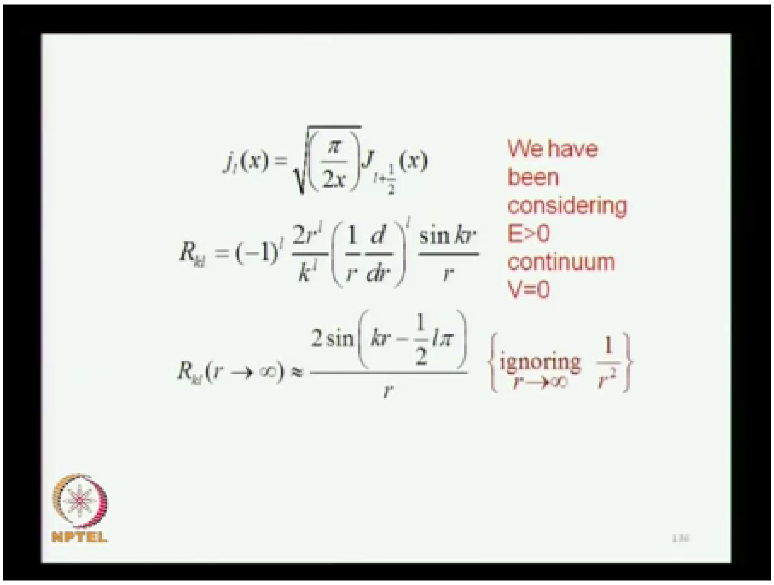
$$\int_0^\infty r^2 R_{E'l} R_{El} dr = \delta(E' - E) \text{.. normalization on E scale}$$

$$R_{El} = R_{kl}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{dk}{dE}} = \left(\frac{1}{\hbar}\right)\sqrt{\left(\frac{\mu}{2\pi k}\right)}R_{kl}$$

$$\boxed{E = \frac{\hbar^2 k^2}{2m} \quad dE = \frac{\hbar^2}{2m}2kdk \quad \frac{dk}{dE} = \frac{m}{\hbar^2 k}}$$

So, this is the normalization on the k over 2 pi scale, this is the normalization on the energy scale, and the relationship between the 2 is given by this scaling factor. So, the normalization if R E l is the redial function which is normalized on the energy scale, it is related to the redial function which is normalized on the k over 2 pi scale through this relation. This is very simple algebra, and it comes straight from the property of the Dirac delta function.

(Refer Slide Time: 46:11)



$$j_l(x) = \sqrt{\left(\frac{\pi}{2x}\right)} J_{l+\frac{1}{2}}(x)$$

$$R_{kl} = (-1)^l \frac{2r^l}{k^l}\left(\frac{1}{r}\frac{d}{dr}\right)^l \frac{\sin kr}{r}$$

$$R_{kl}(r \to \infty) \approx \frac{2\sin\left(kr - \frac{1}{2} l\pi\right)}{r} \quad \left\{\underset{r\to\infty}{\text{ignoring}} \ \frac{1}{r^2}\right\}$$

We have been considering E>0 continuum V=0

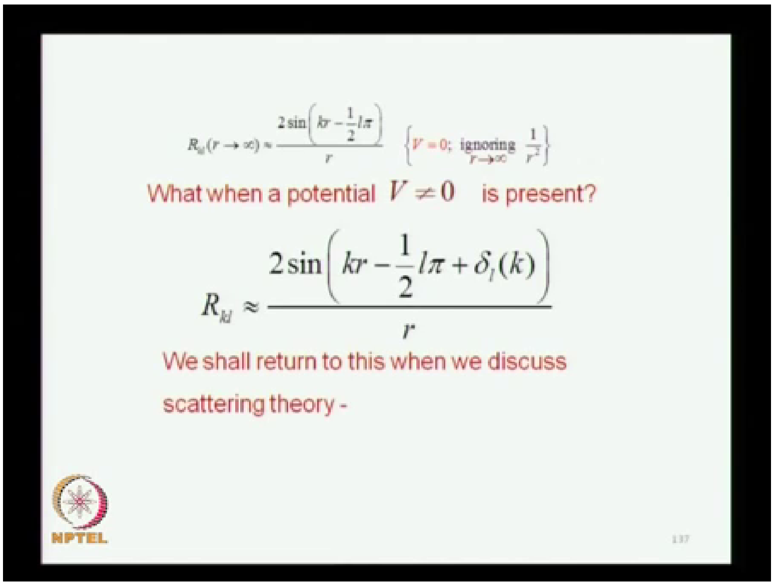
136

So, let us see what is the nature of the function in the isentropic region, the solutions we know are e to the i k k dot r. So, these are sinusoidal functions these are given by the Schrodinger basal functions, and if you look at the nature of the solution in r tending to infinity region, you have got this derivative operator operating on sin. So, for l equal to 0 this operator operating raise to a power 0 will be unity, it will be the unit operator and you have the solutions sin wave right, which is the sinusoidal wave.

As l increases, you will have the derivative operator operating on sin or sin k l over r, now what is the derivative of sin k l over r, you will get a term in 1 over r square. And another term in 1 over r, the 1 over r square term will go to 0 faster than the 1 over r as r tends to infinity right. So, you can throw the 1 over r square term take the leading term, the leading term it goes on 1 over r will be the derivative of the sine function, which is a cosine. And what is the cosine function, it is just a sine function which is fey shifted by pi by 2 right.

The cosine function is exactly the same as sin function it is only phase shifted pi by 2. So, every time you have the l quantum number go up by 1 from 0 to one to 2 to 3 to 4, every time this happens you are going to have an extra phase shift by l times pi by 2 that is the nature of the solution is r tends to infinity. Now, this is the nature of the solution for very special case of the hydrogen atom, which is v equal to 0 these are the continuum functions of free particle solutions. Now, what would happen if the potential was not 0, you stick on a potential, so there is a target it could be a hydrogen atom itself it could be any other atoms.

(Refer Slide Time: 48:33)



$$R_{kl}(r \to \infty) \approx \frac{2\sin\left(kr - \frac{1}{2}l\pi\right)}{r} \quad \left\{V = 0;\ \underset{r\to\infty}{\text{ignoring}}\ \frac{1}{r^2}\right\}$$

What when a potential $V \neq 0$ is present?

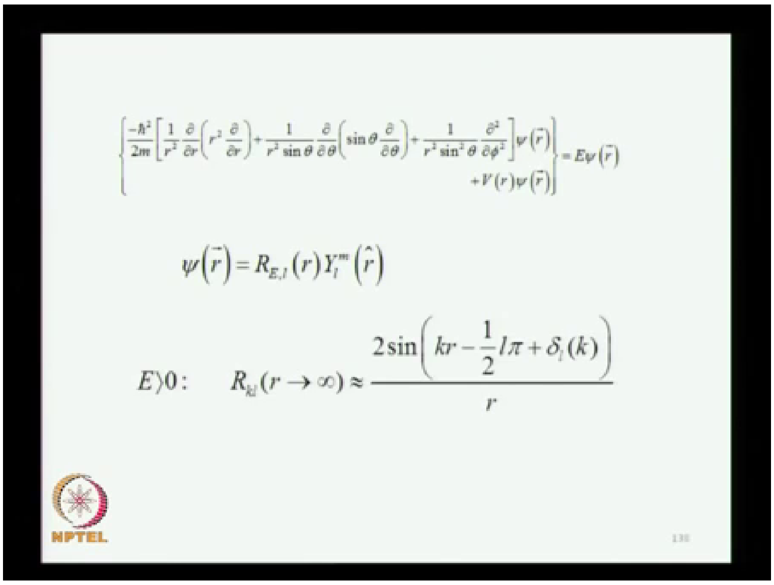
$$R_{kl} \approx \frac{2\sin\left(kr - \frac{1}{2}l\pi + \delta_l(k)\right)}{r}$$

We shall return to this when we discuss scattering theory -

Ignoring terms of the 1 over r square, then each of the solution is a sinusoidal wave whose argument is k r phase shifted by pi by 2 l times. Because, every time you got the derivative operator d by d r you are going to get phase shift of pi by 2, it was from the sine you get a cosine. When the potential is not 0 you get an additional phase shift at this phase shift is; obviously, coming because of the potential, so there is some information of the potential, which we would find this phase shift.

Now, this is a topic of some detail which we will take up later in scattering theory, and you will find that in quantum collision theory, you get a lot of information about the nature of the potential by looking at the phase shift. So, phase shift analysis is a very important tool in quantum collusion. So, this is something that we will return to other later part.

(Refer Slide Time: 49:38)



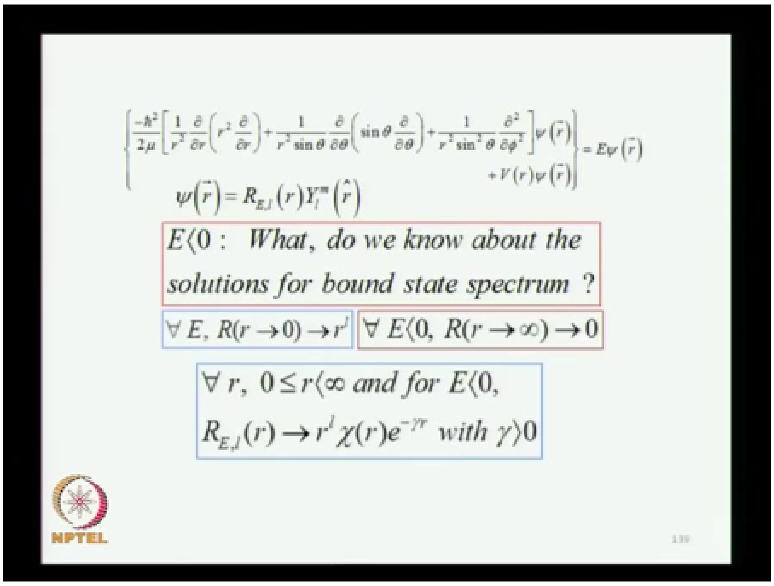
$$\left\{\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\vec{r}) + V(r)\psi(\vec{r})\right\} = E\psi(\vec{r})$$

$$\psi(\vec{r}) = R_{E,l}(r)Y_l^m(\hat{r})$$

$$E\rangle 0: \qquad R_{kl}(r\to\infty)\approx\frac{2\sin\left(kr-\frac{1}{2}l\pi+\delta_l(k)\right)}{r}$$

There are a few other properties that I would like to mention over here. So, this is a r tend to infinity the isentropic form of the solution.

(Refer Slide Time: 49:50)



$$\left\{\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\vec{r}) + V(r)\psi(\vec{r})\right\} = E\psi(\vec{r})$$

$$\psi(\vec{r}) = R_{E,l}(r)Y_l^m(\hat{r})$$

$E\langle 0$: *What, do we know about the solutions for bound state spectrum ?*

$\forall\, E,\ R(r\to 0)\to r^l$

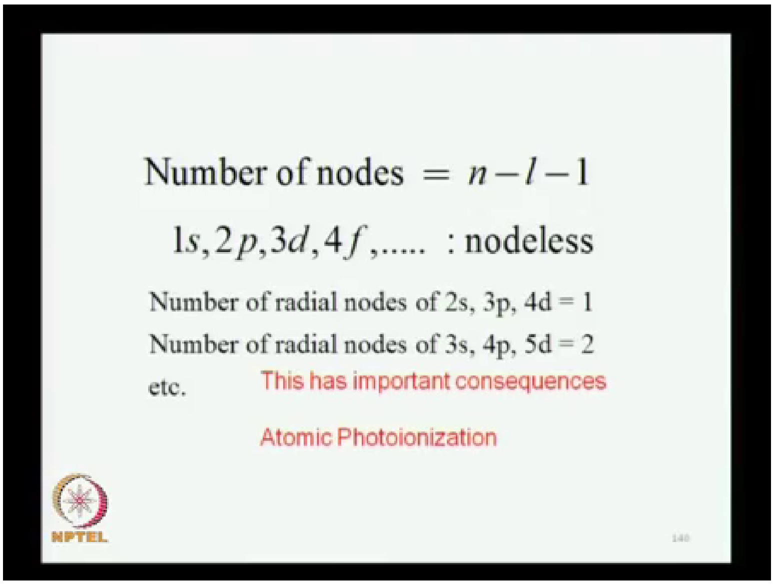
$\forall\, E\langle 0,\ R(r\to\infty)\to 0$

$\forall\, r,\ 0\le r\langle\infty$ *and for* $E\langle 0,$

$R_{E,l}(r)\to r^l\chi(r)e^{-\gamma r}$ *with* $\gamma\rangle 0$

What do we know abound bound state spectrum is that the solutions go as r to the l, as r tends to infinity, the bound state solutions go to 0 because they are bound. And then for the entire range it then goes r to the l e to the minus gamma r and some other functions chi, so you can find what must be the nature of chi, and when you do this which I have I am going to assume that you have done in your first course on in quantum mechanics.

(Refer Slide Time: 50:35)



Number of nodes $= n - l - 1$

$1s, 2p, 3d, 4f, ...$: nodeless

Number of radial nodes of 2s, 3p, 4d = 1

Number of radial nodes of 3s, 4p, 5d = 2

etc. This has important consequences

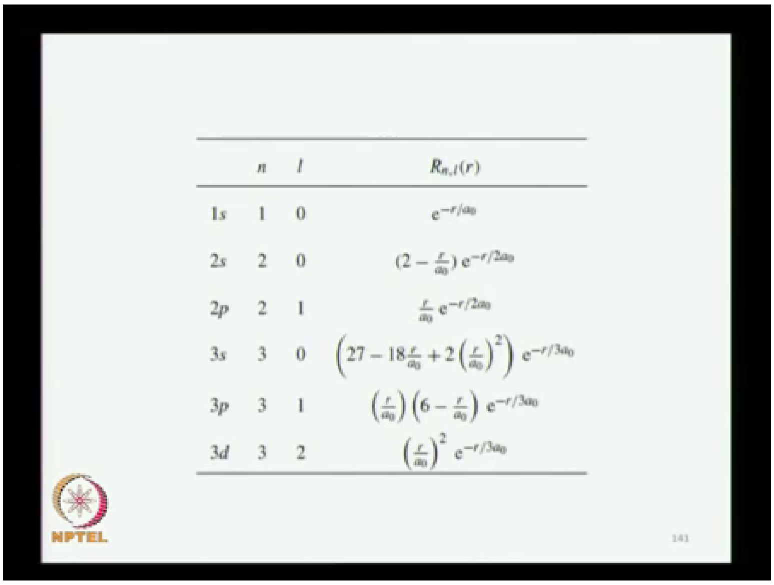
Atomic Photoionization

So, I am not going to do this algebra, but I will remind you some of other properties that the number of nodes of the redial function, when you look at this is n minus l minus 1. Those are the number of 0's that redial function will go through, and this is an important property that I will like you to register, keep track of this because it has got very important applications in spectroscopy, and quantum collisions of atomic systems. So, if you look at l equal to 0 for n equal to 1, there will be no node, 2 p will node less, 3 d will be node less right.

And the number of nodes depending on what is the difference between n and l, you will find that 2 s, 3 p, 4 d have got 1 node 3 s, 4 p 5 d will have got 1 node, have this have got 2 nodes and so on. So, without looking at the detail form of the expression, if I asked you to sketch in your notebooks, sketch the 4 d function can you do it now in the next ten seconds. The 4 d how do you do it, you know that it is a d wave therefore, l is equal to how much is it 2 s p d right l is equal to 2.

So, it goes as r is to the 2, so small r behavior is parabolic, so is r tends to 0 you will draw a parabolic curve right. As r tends to infinity you know it must go to 0, and in between 4 d will have only 1 node, so it has to be parabolic it has to go up, at cut the x axis once and only once because there is only one node and then go to 0. So, that would be the rush sketch of the 4 d, and you can do this for any redial function without knowing this detailed polynomial function explosively in front of you.

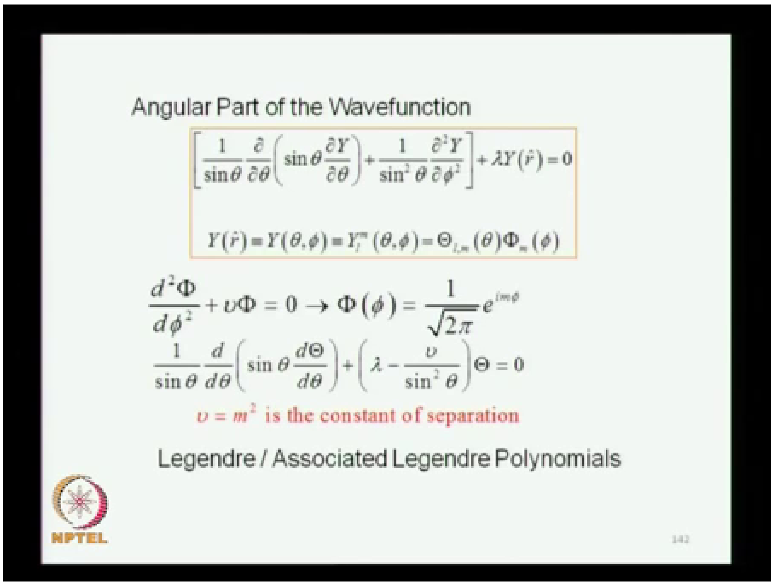
(Refer Slide Time: 52:48)



	n	l	$R_{n,l}(r)$
1s	1	0	e^{-r/a_0}
2s	2	0	$(2-\frac{r}{a_0})\,e^{-r/2a_0}$
2p	2	1	$\frac{r}{a_0}\,e^{-r/2a_0}$
3s	3	0	$\left(27-18\frac{r}{a_0}+2\left(\frac{r}{a_0}\right)^2\right)e^{-r/3a_0}$
3p	3	1	$\left(\frac{r}{a_0}\right)\left(6-\frac{r}{a_0}\right)e^{-r/3a_0}$
3d	3	2	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

So, this again has a important consequences and photo ionization and so on. So, these are the redial functions.

(Refer Slide Time: 52:51)



Angular Part of the Wavefunction

$$\boxed{\begin{gathered}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]+\lambda Y(\hat{r})=0\\ Y(\hat{r})=Y(\theta,\phi)=Y_l^m(\theta,\phi)=\Theta_{l,m}(\theta)\Phi_m(\phi)\end{gathered}}$$

$$\frac{d^2\Phi}{d\phi^2}+\upsilon\Phi=0\rightarrow\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

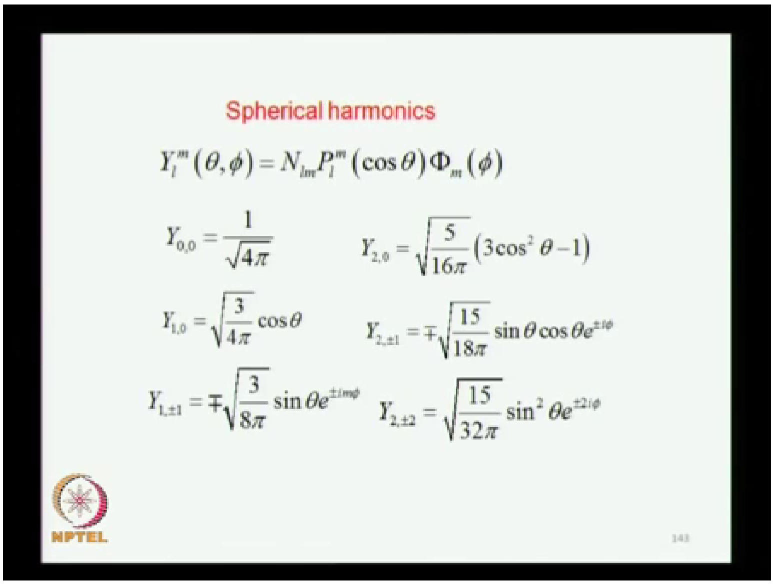
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\lambda-\frac{\upsilon}{\sin^2\theta}\right)\Theta=0$$

$\upsilon=m^2$ is the constant of separation

Legendre / Associated Legendre Polynomials

I will also like to draw your attention to the angular part, which I am not going to discuss because you have done it your quantum mechanics course. But, you know the solutions which I will run through very quickly you are familiar with the angular equations the phi equations on the theta equation.

(Refer Slide Time: 53:12)



Spherical harmonics

$$Y_l^m(\theta,\phi) = N_{lm} P_l^m(\cos\theta)\Phi_m(\phi)$$

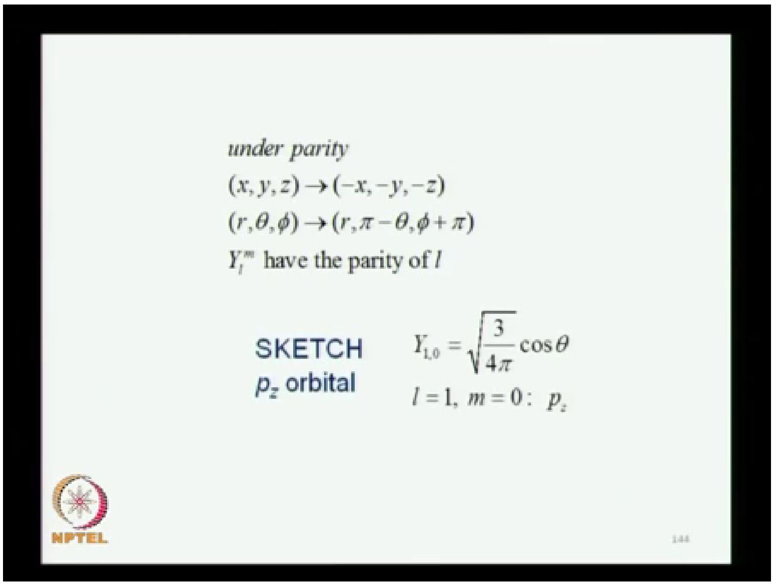
$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \qquad Y_{2,0} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{2,\pm1} = \mp\sqrt{\frac{15}{18\pi}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm im\phi} \qquad Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}$$

And I will like to ask an question over here, that you have these spherical harmonics in front of you, you have met them you have both with them.

(Refer Slide Time: 53:21)



under parity

$(x,y,z) \to (-x,-y,-z)$

$(r,\theta,\phi) \to (r,\pi-\theta,\phi+\pi)$

Y_l^m have the parity of l

SKETCH

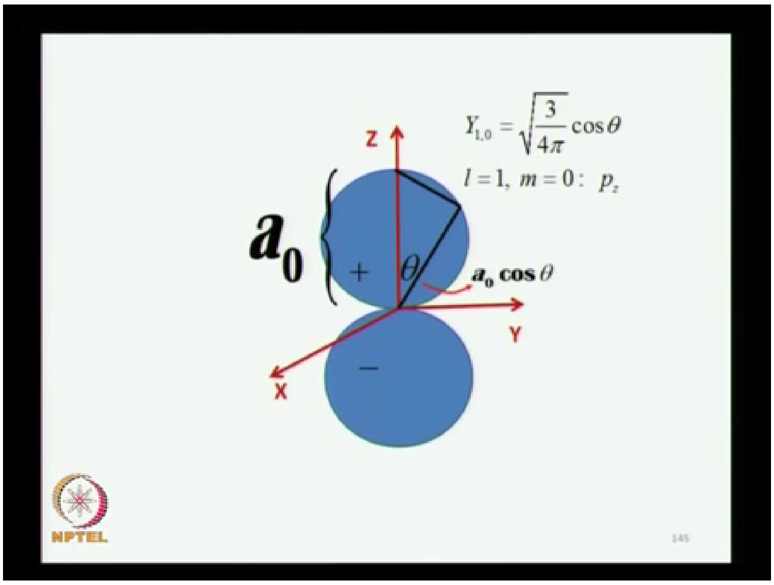
p_z orbital

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$l = 1,\ m = 0:\ p_z$

And let us take a simple case of the spherical harmonics for the p wave, the p function for l equal to 1, m equal to 0 the p z orbital, sketch it in your notebooks do it in the next ten seconds. Now, you have parley drawn these diagrams a number of times, you have seen these diagrams a number of times, and without looking at your answers I suspect that many of you do not have it right.

(Refer Slide Time: 54:07)



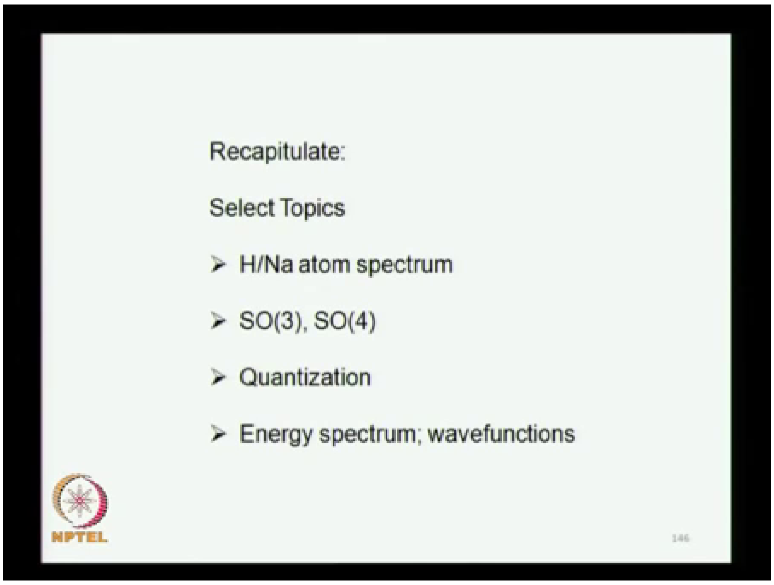
$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$l = 1,\ m = 0:\ p_z$

And the reason I suspect that is the following that this is the correct shape, and what you must notice is that you have got from this Pythagoras theorem a cosine theta term. So, this side must be exactly is 0 cos theta, which means that this upper lobe must be a perfect circle, and my suspension is that many of you have not sketch the perfect circle, you may have along lateral lobe. And if you had a long lateral lobe your sketch was wrong, you get it you realize why it must be a perfect circle, it cannot be along at a dumbbell shape thing.

Now, what you see what the pictures that you remember are not a redial functions, but the square of that, which is the probability density. The plots of the wave functions, the plots of the probability density will have to be different, so you have to keep track some of these details, I think I am running out of time this class.

(Refer Slide Time: 55:26)



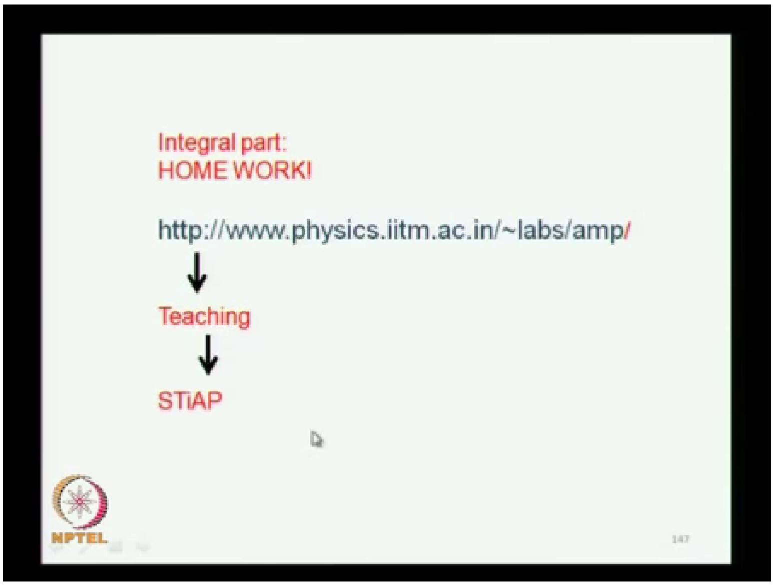
Recapitulate:

Select Topics

- H/Na atom spectrum
- SO(3), SO(4)
- Quantization
- Energy spectrum; wavefunctions

So, I am going to stop here I thought I would mentioned that essentially we had a introduction to the S O 3 and S O 4 symmetry of the hydrogen atom. We looked at the some of the property of the angular part, and some of property of the radial part which are of some consequences in atomic physics.

(Refer Slide Time: 55:39)



Integral part:
HOME WORK!

http://www.physics.iitm.ac.in/~labs/amp/

↓

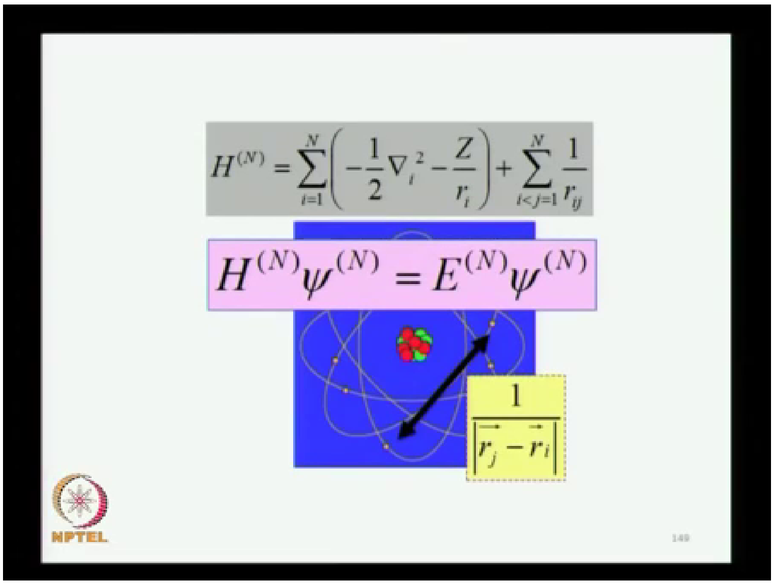
Teaching

↓

STiAP

The problems set is in integral part of this course, and you have to do the problems set number 1, which is already uploaded at this web link, and the solutions are due in a few days from now.

(Refer Slide Time: 55:56)



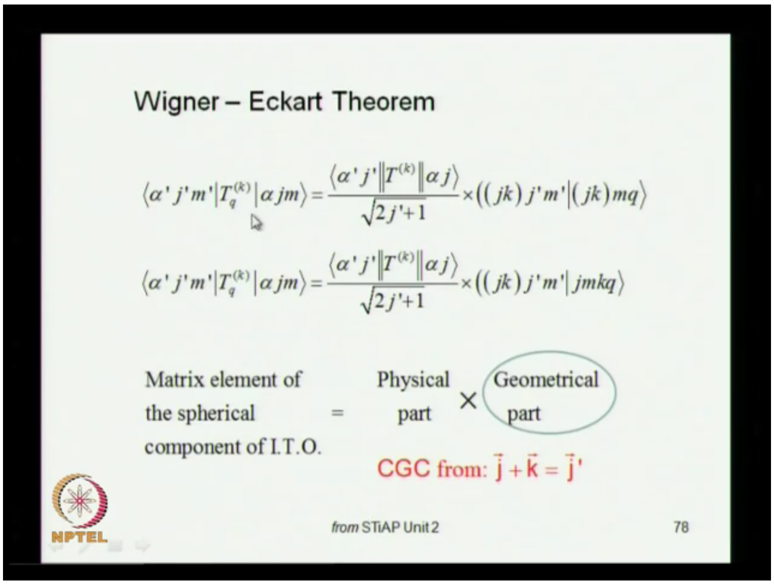
$$H^{(N)} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

$$\frac{1}{\left|\vec{r}_j - \vec{r}_i\right|}$$

And then of course, in a later part of the unit we will be talking about the quantum mechanics of many electron atoms because of in many electron atoms you got a 1 over r i j the term, the coulomb reparation between pairs of the electrons. So, you need what is known as art folk self consistent field formalism to do that, so we will get to. So, I will the stop here is there are few questions we will be happy to take, this is a preview of what you are going to meet in the unit on self consistent fields.

(Refer Slide Time: 56:33)



Wigner – Eckart Theorem

$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' \| T^{(k)} \| \alpha j \rangle}{\sqrt{2j'+1}} \times \langle (jk) j' m' | (jk) m q \rangle$$

$$\langle \alpha' j' m' | T_q^{(k)} | \alpha j m \rangle = \frac{\langle \alpha' j' \| T^{(k)} \| \alpha j \rangle}{\sqrt{2j'+1}} \times \langle (jk) j' m' | j m k q \rangle$$

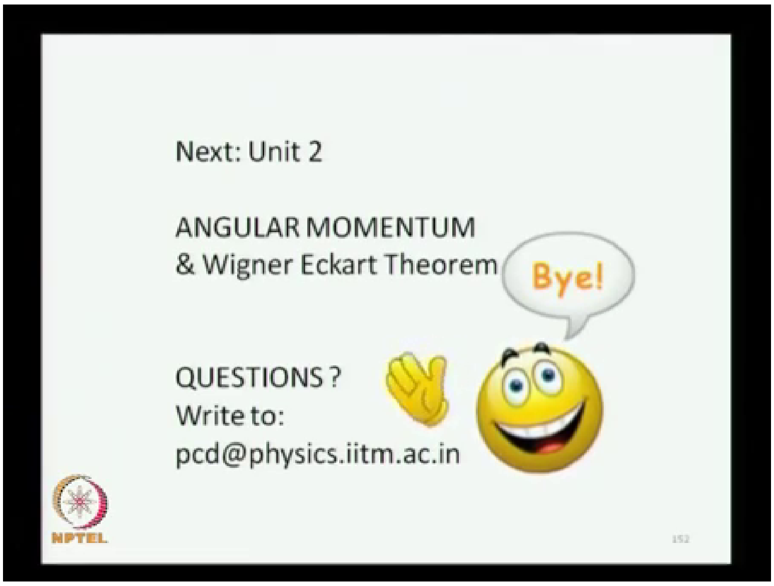
Matrix element of the spherical component of I.T.O. = Physical part × Geometrical part

CGC from: $\vec{j} + \vec{k} = \vec{j}'$

from STiAP Unit2

But, I think I would not spend any time on this because we are practically out of the time this class, I will rather takes some questions.

(Refer Slide Time: 56:49)



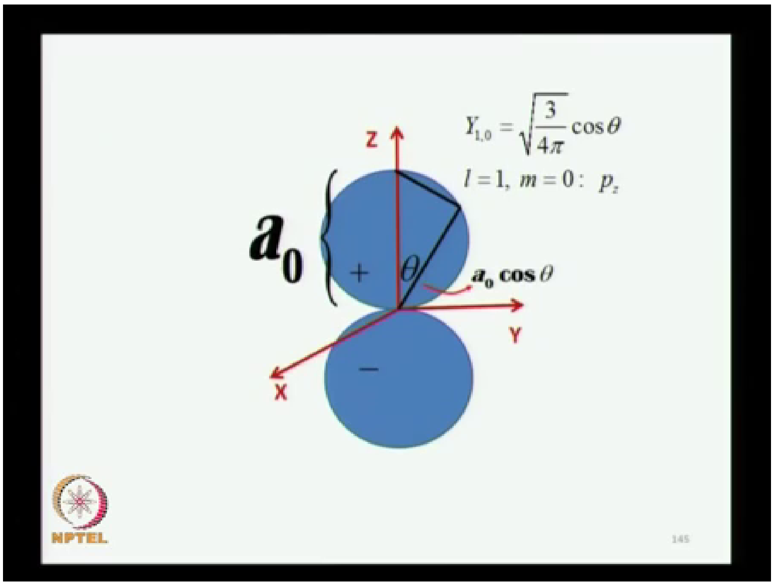
Next: Unit 2

ANGULAR MOMENTUM
& Wigner Eckart Theorem

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

And if there are no questions goodbye for now, but if there are some questions that will be nice.

(Refer Slide Time: 57:01)



$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$l = 1,\ m = 0:\ p_z$

Look at this figure, this spherical harmonic for l equal to 1 and m equal to 0 is a cosine function, which means that theta is a polar angle, it is polar angle of the spherical polar coordinate system, with reference to the z axis. It is not specially about the z axis, it is some direction in space, but having chosen that you do have a polar angle, and with reference to that polar angle the amplitude of the redial function, and the amplitude of the complete wave function will be proportional to cosine of that angle.

So, it will be most for theta equal to 0 how much it will be the theta equal to pi by 2, cosine pi by 2 is 0. So, in the horizontal plane the amplitude in the x y plane must vanish that is what you see over here, and in between it will change with theta as a function of theta, the function being the cosine of the angle right. So, there will be scaling factor and that scaling factor is cos theta, and from simple geometry which you did in your high school or even in kindergarten I do not know.

Because, you do these theorems very early these days, you know that if you have a circle the diameter subtend an angle of 90 degrees at any point on the circumference right. So, once side will go as sin theta, the other side will go as cosine theta, so this side must go as cosine theta. And if that is the nature of dependence this has to be a circle, so this diameter will subtend an angle of 90 degrees at the circumference is that clear.

So, it cannot be an long at a dumbbell it is not, not only that the cosine theta is positive for the upper lobe, and it is negative for the lower lobe right. So, you must put that sign you see in that figure, there is a plus sign on the upper lobe and there is a minus sign in the lower lobe and y must put that, but when you take the probability density that goes as chi, chi, chi right, so it goes as square of this.

And then you get the cos square theta dependence that is what gives you the along at a dumbbells, not only that when you do that there will be no plus and minus sign on the upper lobe and lower lobe because both the lobes will be positive. The square of minus 1 this plus 1 even in a atomic physics, you cannot help it right, so when you plot probability densities you have both the upper lobe and the lower lobe are with the plus sign. But, when you plot the probability amplitudes, it is a upper lobe which has got the plus sign, and the lower lobe which has got a minus sign, and both of these must be perfect circle. And of course, they have got a symmetry about z axis, so you can you know rotate this about that z axis, so you will get this spherical shape any other question.

So, thank you very much.