

Quantum Mechanics
Prof. P. Ramadevi
Department of Physics
Indian Institute of Technology – Bombay

Lecture - 35
Solutions to Other Coupled Potential Energies - II

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Hydrogen Atom

Assume proton to be heavy-
 We will try to reproduce the known results: 1s shell, 2s shell, 2p shell, ... wavefunction and their energy eigenvalues.

===== $\geq (n=1, l=0, m=0)$
 ===== $\geq (n=2, l=0)$
 ===== $\geq (n=2, l=1)$

The potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

where $r = \sqrt{x^2 + y^2 + z^2}$.

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So in the next one which is a different potential energy, it is also familiar to you it is not new to you, it is the Hydrogen Atom, right. So what do we assume in the hydrogen atom you assume proton to be very heavy. Even if it is not heavy you know what to do. What do you do? Introduce a reduce mass but let us take it to be heavy in comparison to the electron and all your chemistry way of handling is you can call that as 1s shell, 2s shell, 2p shell and so on right.

And you can also write; and here you can put the lines with the exact degeneracy, one is shell as principal quantum number $n=1$; $l=0$ but you have the red line and this one of two spin states possible so it is two-fold degenerate and so on; 2s shell is again going to have both $n=1$ and $l=0$. But why we have put 4 lines? Is that allowed, no wrong, right. Yes, or no? No. So it is not right. Everything is written as 2s, I made a mistake.

Okay, so you understand what exactly you do in your chemistry course. What this two-fold degenerate? 2s is two-fold degenerate, 2p will be 6 fold degenerate and so on. So you can; and

the potential energy is a central potential which is $1/r$ potential. Once you see this $1/r$ potential you know what coordinate system to choose. Spherical polar coordinate because then you can separate your potential energy to be only acting on the r coordinate or the potential energies are not there.

So Cartesian coordinate is not a good coordinate when you want to solve hydrogen atom problem. We mechanically put in spherical polar coordinates and solve it. The reason is that the potential energy becomes potential energy becomes dependent only on the radial coordinate so it is better to work on the r theta Phi coordinates. No point in working on XY. You can work with XYZ but then it will become more complicated.

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Choice of coordinate system: spherical polar coordinates (r, θ, ϕ) is convenient to solve the Schrodinger equation

In spherical polar coordinates, the potential energy

$$U(r, \theta, \phi) = U(r)$$

and independent of θ, ϕ coordinates. So, wavefunction is separable:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The Hamiltonian \hat{H} for the hydrogen atom is

$$\frac{-\hbar^2}{2m}\nabla^2 + \frac{-e^2}{4\pi\epsilon_0 r}$$

In spherical coordinates, $\nabla^2\psi$ will be

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

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So choice of coordinates, Spherical polar coordinates is convenient and you can choose because U of r theta phi is actually your r only; there is no theta Phi component and we can write that separable base function as a product of the radial dependent, the theta dependent and the Phi dependent. So the Hamiltonian for the hydrogen atom in three dimension you can write del squared compactly I am not writing explicitly what this Laplacian is but you know what to do and is $1/r$. So substitute r theta Phi and rewrite your Laplacian in the spherical coordinates.

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The Schrodinger equation will be

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U(r)) \psi = 0$$

We will solve the 3-d problem in two steps:


$$\psi = R(r)\Omega(\theta, \phi)$$

$$\Omega(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

Taking the first step of separable wavefunction in the Schrodinger equation and dividing by $R(r)\Omega(\theta, \phi)/r^2$ throughout

$$\frac{1}{R(r)r} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{\Omega(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Omega(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\Omega(\theta, \phi) \sin^2 \theta} \frac{\partial^2 \Omega}{\partial \phi^2} + \frac{2mr^2}{\hbar^2} (E - U(r)) \psi = 0$$

We will rewrite so that θ, ϕ dependent terms are equated to r dependent terms. Therefore.



And then what do you do you try and separate out the two equations, right. First let us write this whole solution and you can see from here there is an r dependence and theta dependence, Phi so we try and separate it out, the conventional way we did. First write Psi as R of r Omega of theta Phi and then we put Omega of theta Phi S the theta dependent in the Phi, we will do it in two steps to makes things. Incidentally, when I am typing this equation I might have made some mistakes.

If there is any mistakes please bring to my notice, I have to edit it. Okay. So this is usual conventional way we try to do, only thing is we are trying to divide by an r squared also, so that we get terms which are R of r dependent peace; Omega of theta Phi dependent piece, this is r dependent. How will you write? you will write this plus this last term to be some E1 times Psi and this to be E-E1 something like that okay.

We can write so that theta Phi dependent are equated to r dependent terms. This is a d/dr here, yeah, excellent yeah so there is no Psi, okay.

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$$\frac{1}{\Omega(\theta, \phi)} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Omega(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Omega}{\partial \phi^2} \right] = C$$



$$-\frac{1}{R(r)r} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} (E - U(r)) = C$$

We can substitute $\Omega(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ in the first equation and divide by $\Theta(\theta)\Phi(\phi)$ to get

$$\frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2} = \alpha$$

$$\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - C \sin^2 \theta = -\alpha$$

Take $\alpha = -m^2$ to make contact with magnetic quantum number m

Yeah, probably I have taking care of here. This should also be d/dr. Yeah, so as we pointed it out Psi is not there. Yes. So this is one constant which is explicitly depending only on theta and Phi there is another equation you split it up into two pieces one dependent on theta Phi and another dependent on small r. So the next question is further the first topic version we will try to rewrite it, again breaking it up into a product of theta Phi and divide by that so you have an equation which is; this is familiar. What is the solution here?

Solution is like the same problems which you will be doing, exponential. And this one will be this is a non-trivial. So having got these equations you can go back and look at special functions and see what the solutions are. So in order to make contact with the actual physics which has this magnetic quantum number we take Alpha to be -m squared and then we can solve this.

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$$\frac{1}{\Phi(\phi)} \frac{d^2\Phi}{d\phi^2} = \alpha = -m^2$$

Then a solution to the $\Phi(\phi)$ equation is simple

$$\Phi(\phi) = Ae^{im\phi}$$

Being an angular coordinate, the single-valued wavefunction forces

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$



which implies m is an integer

The θ dependent equation is $\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) - (C \sin^2\theta + m^2)\Theta(\theta) = 0$

Make a change of variable $\cos\theta = x$ and rewrite the θ equation in variable x

$$\frac{d}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left[-C - \frac{m^2}{1-x^2} \right] \Theta = 0$$

This is a differential equation for associated Legendre polynomials.

Solution will be $Ae^{im\phi}$. Equivalently you should also know that this ϕ is an Angular coordinate, ϕ goes from 0 to 2π , if suppose I put ϕ to be 4π it should be same as the 0 coordinate or 2π coordinate; that will kind of fix for me that the m cannot be fractions. m has to be integers. The single value in this of the wave function in the angle coordinates; unlike a free particle in the real line which was e^{ikx} ; the k can be anything.

Here if you put it on a circle or an angular coordinate with an identification of 0 with $2m$ times π you will be forced to choose m to be only integers. That is why the magnetic quantum numbers are integer which is consistent. So this is what I am saying. That the single valued wave function that ϕ dependent is have to satisfy this which implies m as an integer and then we get to the θ dependent equation, substituting that constant α which will be there.

And this is a equation to solve, so you can see that the θ the capital θ that wave function will be dependent on the value for m also; this equation has this m . So make a change of variable just for convenience and then to the equation is nothing but our familiar Legendre, Associated value. So this is the differential equation for Associated Legendre polynomials.

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$$\frac{d}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left[-C - \frac{m^2}{1-x^2} \right] \Theta = 0$$

associated Legendre polynomials

$$P_l^m(x) = \frac{(1-x^2)^{|m|/2}}{2^l l!} \frac{d^{l+|m|}}{dx^{l+|m|}} (x^2-1)^l$$



where

$$-C = l(l+1) \quad l \text{ are non-negative integers}$$

and

$$-l \leq m \leq l$$

Thus the θ, ϕ dependent part of the wavefunction is

$$Y_l^m(\theta, \phi) = \Theta(\theta)\Phi(\phi) = N P_l^m(x) e^{-im\phi} = Y_l^m(\theta, \phi)$$



So what are the solutions, you can compactly write the solution just like the way we wrote for Hermite Polynomial some of kind of a compact Rodrigues formula you can try to write it for a specific l , l is the Azimuthal quantum number; m is your Magnetic quantum number because you know chemistry you can try to give the meaning in the same way so that we remember them, okay.

And just play around and work out for $l=1$; $l=2$ just to get a feel of how these associated Legendre polynomials are. Okay, so I did not say what this C is for the solution; this C has to be $-C$ has to be $l(l+1)$ and they have to be non-negative integers that is also important. You may contact with the differential equations. For special functions you can compare the C to be this parallelism non-negative integer.

And your magnetic quantum number which is there in your associated Legendre functions Legendre polynomials have to be restrictive it cannot be arbitrary it has to go from $-n$ to $+n$. This is all implied by looking at just differential equation, matching it with the differential equation for special functions in the mathematics, okay. You are not doing anything here by any other method. But we will get to it in some of the fashion than we are doing it from direct formats. Okay. So what is the final θ Φ dependent part of the wave function?

You have already seen it is either $e^{im\phi}$ for the ϕ dependent piece; now we have also argued that the θ ϕ dependent piece which you can write the θ $\cos \theta$ as x as a Legendre associated Legendre polynomials. This product of $P_l^m e^{im\phi}$ as said is always called in the literature a spherical harmonics, okay. And it is denoted by a capital Y_l^m θ ϕ . Okay.

So we will come to these issues of playing with the spherical harmonics; but this is the connection the associated Legendre polynomial multiplied by $e^{im\phi}$ together is called as a spherical harmonic.

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Thus the θ, ϕ dependent part of the wavefunction is

$$\Omega(\theta, \phi) = \Theta(\theta)\Phi(\phi) = N P_l^m(x) e^{im\phi} = N Y_l^m(\theta, \phi)$$

In the literature $Y_l^m(\theta, \phi)$ are called spherical harmonics and the normalisation N is

$$N = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2}$$

We have determined angular part of the wavefunction.

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Normalization is one thing which you should work it out at least for a specific l and specific m , but it can be determine for a general lm . How do you do the normalization here? Integral of $d\theta$ alone or you have to put $d\cos \theta$? $d\cos \theta$ and $d\phi$ you have to integrate; $\cos \theta$, θ goes from 0 to π and ϕ goes from 0 to 2π and then you have to fix the normalization. Okay. What is left? The radial part, done the angular part we need to do the radial part.

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Radial Equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR'_l}{dr} \right) + \frac{2m}{\hbar^2} \left[E + \frac{\hbar^2 l(l+1)}{2m r^2} - \frac{4\pi\epsilon_0 e^2}{r} \right] R'_l = 0$$

This differential equation is satisfied by associated Laguerre polynomials

The solution is $R'_l(r) = D e^{-\rho} \rho^l L_{n+l}^{2l+1}(\rho)$ $E_n = -\frac{13.6 \text{ eV}}{n^2}$

where $l \leq n - 1$, $\rho = \frac{2r}{a_0}$, a_0 is the Bohr radius given by

$$a_0 = \frac{\hbar^2}{m e^2} 4\pi\epsilon_0$$



So we substitute that capital C which relates your Omega theta Phi, okay with; plug it in here and this is what you get for the radial part of the equation. I have inserted a small n here in anticipation. What is the anticipation? This L is dependent there; this differential equation is exactly like your; what special function, associated Laguerre polynomials. If you go and check special function polynomial for associated Laguerre polynomials. So this is the differential equation satisfied by associated Laguerre polynomials.

We are not deriving them we just matching with what is known in the differential equation context, right now. So what is the solution, solutions are given in the literature. If you remember I was trying to give you this Graham Smith orthogonalization for function spaces and I was trying to say that you should put a Weightage factor so that this; and this hydrogen atom the radial coordinate goes from 0 to infinite, right.

The square integrable functions; so do you have an e to the power of -1/2 r or a function of r calling it Rho r and the associated Laguerre polynomial. And there is a condition that n and l are not arbitrary. Your l should always be <= to <= n. <= also, less than. n should be > l. Okay. So this Rho r which I have written is just a function multiplied; it is proportional to r but there is a Bohr radius a0 attached to it. Okay.

So this is all from matching with what is said and what we know by convention; what is the Bohr radius, we can try to write the solution in a very compact fashion. These are minor things to do. But given some differential equation here to find a solution if it is familiar from the mathematics literature we just pull out the solution and rewrite all those variables accordingly. Okay. There energy may not be energy may be some constant.

But now we can try to write that energy is in terms of those. So E_n is proportional to $1/n^2$ with a negative sign. So why a negative sign? Bound state. Positive solutions are allowed or no? Positive energy or for the bound state particularly but you can have scattering state.

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$R_n^l(r) = D e^{-r/a_0} \rho^l L_{n+l}^{2l+1}(\rho)$



The normalisation constant D is

$$D = \left[\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2}$$

and associated Laguerre functions $L_{n+l}^{2l+1}(\rho)$ can be obtained using this formula:

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^k \frac{(n+l)! 2^{l+1}}{(n-l-1-k)!(2l+1+k)!k!} \rho^k$$

$R_1^0(r) = \left(\frac{1}{a_0} \right)^{3/2} 2 e^{-r/a_0}$
 $R_2^0(r) = \left(\frac{1}{2a_0} \right)^{3/2} \left[2 - \frac{r}{a_0} \right] e^{-r/2a_0}$
 $R_2^1(r) = \left(\frac{1}{2a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$

You can sit and play around for a specific n and the specific l and see whether you get the normalization. Here the normalization will be integral over $dr r^2$ should also be there. Explicitly the normalization in three dimension.

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$$\int dV \Psi^*(x, y, z) \Psi(x, y, z) = 1$$

Cartesian $\int dx dy dz$

Spherical polar $\int r^2 dr \sin \theta d\theta d\phi$

$$\Psi(r, \theta, \phi) = \Omega(\theta, \phi) R(r)$$

$$\int \sin \theta d\theta d\phi |\Omega(\theta, \phi)|^2 = 1$$

In three dimension its integral $dV \Psi^* x, y, z \Psi x, y, z$. This should be 1. dV is; in dV in Cartesian is $dx dy dz$ in Cartesian. In Spherical polar it is $dr r$ squared sine theta $d\theta d\phi$, right. So now I am trying to say that if you write your Ψ as a function of r theta ϕ as Ω theta ϕ times R of r then integral sine theta $d\theta d\phi \Omega$ of theta ϕ mod squared should be 1. What about r squared? Mod r squared will be multiplied by this piece. Okay.

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$$\int dr r^2 |R(r)|^2 = 1$$

$$\int r^2 dr \sin \theta d\theta d\phi |\Omega(\theta, \phi)|^2 |R(r)|^2 = 1$$

$$\int d\theta d\phi |\Psi(\theta, \phi, z)|^2 = 1$$

So you will have mod R of r whole squared $dr r$ squared, this has to be as 1. This purely coming from the Jacobian. When you take $x, y, z, 2r$ theta ϕ these factors are coming out according. Many of the students; in my last so many years is that they forget about these r squared when you

do the normalization. But when you go to spherical coordinates there is a non-trivial Jacobian you have remember that. Okay.

So it is squared $dr \sin \theta d\theta d\Phi$ mod $\Omega \theta \Phi$ whole squared mod R of r whole squared; this has to be 1 that is the normalization. You can split it up into r piece and $\theta \Phi$ piece. But a normalization has to be with the volume factor in that appropriate coordinate. What happens in Cylindrical coordinates? So suppose I write Ψ, ρ, Φ, z ; there will be a $dz \rho d\rho d\Phi$. Okay, you understand? You have to remember this.

Many of them forget these things and then it leads to completely your wrong physics. Okay. So let me stop here that it is an associated Legendre function and I will put this up for you and you can verify a couple of things. So the next lecture I will continue a little bit on how to get into the Stern-Gerlach experiment and then we will see what I should do the following Friday. Okay.