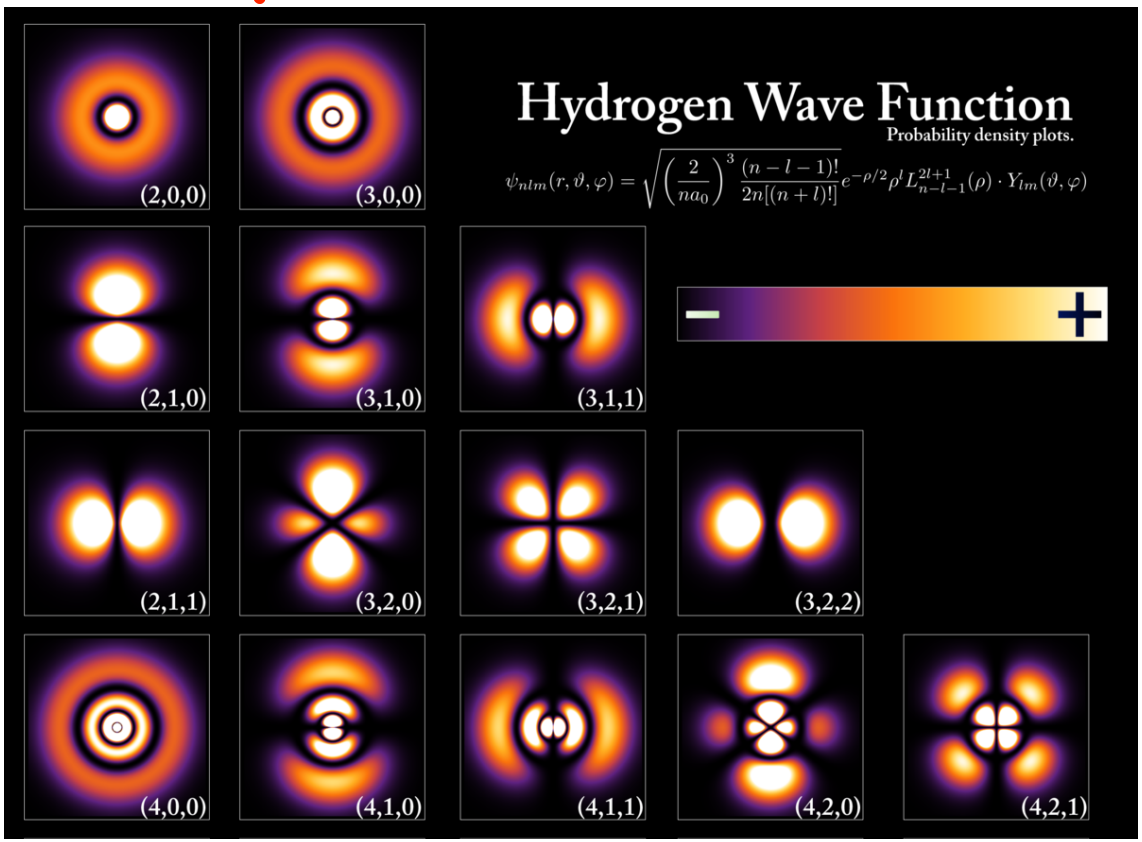
Quantum mechanics

Chapter V Quantum Mechanics in Three Spatial Dimensions



The Schrödinger equation, for a particle of mass m, in three spatial dimensions reads as

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

where H is the Hamiltonian operator, given by

$$\hat{H}=\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r}).$$

the three-dimensional momentum operator:

$$\hat{\vec{p}}=-i\hbar\vec{\nabla},\quad \vec{\nabla}=\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}.$$

Therefore, the Hamiltonian operator takes the form

$$\hat{H}=-\frac{\hbar^2}{2m}\vec{\nabla}^2+V(x,y,z),$$

where

$$\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

is the Laplacian (Laplace's operator) in Cartesian coordinates.

If the potential is time independent, the three-dimensional Schrödinger equation can also be solved by the method of separation of variables.

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

where E is the total energy. The function ϕ(r,t) satisfies the following time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\phi(\vec{r}) + V(\vec{r})\phi(\vec{r}) = E\phi(\vec{r}).$$

For the special case of a potential, V (x, y, z), that can be written in the form

$$V(\vec{r}) = V_1(x) + V_2(y) + V_3(z),$$

the three-dimensional TISE reduces to a system of one-dimensional TISE. Indeed, if we write the solution in the form

$$\phi(\vec{r}) = X(x)Y(y)Z(z),$$

therefore,

$$\left[-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + V_1(x)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + V_2(y)\right]$$

$$+ \left[-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} + V_3(z)\right] = E,$$

This is possible only if each of these terms is a constant such that their sum is equal to E. In other words,

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2}+V_1(x)=E_1,$$

$$-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2}+V_2(y)=E_2,$$

$$-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2}+V_3(z)=E_3,$$

where E_1, E_2 and E_3 are constants such that

$$E_1+E_2+E_3=E.$$

The Free Particle Solution

Consider a particle of mass m moving freely in space in the absence of any external force field.

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_1 X, \qquad X(x) = \frac{1}{\sqrt{2\pi}} e^{ik_x x},$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_2 Y, \qquad Y(y) = \frac{1}{\sqrt{2\pi}} e^{ik_y y},$$

$$-\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = E_3 Z. \qquad Z(z) = \frac{1}{\sqrt{2\pi}} e^{ik_z z},$$

where

$$k_j^2 = 2mE_j/\hbar^2, j = 1,2,3 = x,y,z \text{ and } \quad E_j = \hbar^2 k_j^2/2m.$$

As a result, the solution to the free TISE is given by

$$\psi(x,y,z) = \frac{1}{(2\pi)^{3/2}} e^{ik_1 x} e^{ik_2 y} e^{ik_3 z} = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}},$$

The total energy of the particle E is given by the sum of the energy eigenvalues E_1, E_2 and E_3:

$$E = E_1 + E_2 + E_3 = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) = \frac{\hbar^2}{2m}\vec{k}^2.$$

We note here that the energy, E, depends on the magnitude of the wave vector k but not on its direction. Hence, different orientations of k satisfying the condition

$$|\vec{k}| = \sqrt{k_1^2 + k_2^2 + k_3^2} = \text{const.},$$

The Free Particle Solution

Thus, the solution to the TISE, for this special case of zero potential, is given by

$$\psi_{\vec{k}}(\vec{r},t) = \frac{1}{(2\pi)^{3/2}} e^{ik_1 x} e^{ik_2 y} e^{ik_3 z} e^{-i\frac{E}{\hbar}t} = \frac{1}{(2\pi)^{3/2}} e^{i(\vec{k}\cdot\vec{r}-\omega t)},$$

The orthonormality condition, for the wave functions reads

$$\langle \psi_{\vec{k}'}(\vec{r},t) | \psi_{\vec{k}}(\vec{r},t) \rangle = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} d^3 r = \delta(\vec{k}-\vec{k}').$$

A free particle is represented by the following three-dimensional wave packet:

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{+\infty} A(\vec{k},t)\psi_{\vec{k}}(\vec{r},t) d^3 k = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{+\infty} A(\vec{k},t) e^{i(\vec{k}\cdot\vec{r}-\omega t)} d^3 k,$$

Consider a spinless particle confined to move in an infinite rectangular potential well given by

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0 < x < a, 0 < y < b, 0 < z < c \\ +\infty & \text{elsewhere} \end{cases}$$

The normalized solution of the three-dimensional Schrödinger equation

$$\psi_{n_1 n_2 n_3}(x,y,z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_1\pi}{a}x\right) \sin\left(\frac{n_2\pi}{b}y\right) \sin\left(\frac{n_3\pi}{c}z\right), \; n_1, n_2, n_3 = 1, 2, 3, \ldots$$

The corresponding energies are given by

$$E_{n_1 n_2 n_3} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right),$$

If a = b = c = L, the potential is called the infinite cubic well potential of side L. In this case, the wave functions are

$$\psi_{n_1 n_2 n_3}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_1\pi}{L}x\right) \sin\left(\frac{n_2\pi}{L}y\right) \sin\left(\frac{n_3\pi}{L}z\right), \; n_1, n_2, n_3 = 1,2,3,\ldots$$

and the corresponding energy eigenvalues are given by

$$E_{n_1 n_2 n_3} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right), \quad n_1, n_2, n_3 = 1,2,3,\ldots$$

Note that most of the energy levels in the cubic well potential are degenerate.

The ground state, with $n_1 = n_2 = n_3 = 1$ and energy

$$E_{111} = \frac{3\hbar^2\pi^2}{2mL^2},$$

is not degenerate.

The first excited state is characterized by three sets of quantum numbers $(n_1,n_2,n_3) = (2,1,1)$, $(n_1,n_2,n_3) = (1,2,1)$ and $(n_1,n_2,n_3) = (1,1,2)$ and its energy is given by

$$E_{211} = E_{121} = E_{112} = \frac{6\hbar^2\pi^2}{2mL^2}.$$

Since the same value energy corresponds to three distinct sets of quantum numbers n_1, n_2 and n_3, the first excited state is three-fold degenerate.

The corresponding wave functions are as follows:

$$\psi_{211}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right),$$

$$\psi_{121}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{2\pi}{L}y\right) \sin\left(\frac{\pi}{L}z\right),$$

$$\psi_{112}(x,y,z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi}{L}x\right) \sin\left(\frac{\pi}{L}y\right) \sin\left(\frac{2\pi}{L}z\right).$$

The second excited state is again characterized by three sets of quantum numbers $(n_1,n_2,n_3) = (2,2,1)$, $(n_1,n_2,n_3) = (2,1,2)$ and $(n_1,n_2,n_3) = (1,2,2)$, and it is also threefold degenerate with energy

$$E_{221} = E_{212} = E_{122} = \frac{9\hbar^2\pi^2}{2mL^2}.$$

The Energy levels and their degeneracies for the Infinite Rectangular Well Potential

$E_{n_x n_y n_z}/E_1$	$(n_x,\ n_y,\ n_z)$	g_n
3	(111)	1
6	(211), (121), (112)	3
9	(221), (212), (122)	3
11	(311), (131), (113)	3
12	(222)	1
14	(321), (312), (231), (213), (132), (123)	6

Degeneracy occurs only when there is a symmetry in the problem. For the present case of a particle in a cubic box, there is a great deal of symmetry, since all three dimensions are equivalent.

Consider a particle of mass m moving in a three-dimensional anisotropic oscillator potential

$$\hat{V}(\hat{x},\hat{y},\hat{z}) = \frac{1}{2}m\omega_x^2\hat{X}^2 + \frac{1}{2}m\omega_y^2\hat{Y}^2 + \frac{1}{2}m\omega_z^2\hat{Z}^2.$$

Its Schrödinger equation separates into three equations

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} + \frac{1}{2}m\omega_x x^2 X(x) = E_x X(x),$$

with similar equations for $Y(y)$ and $Z(z)$. The eigenenergies and wave function corresponding to the potential can be expressed as

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \left(n_x + \frac{1}{2}\right)\hbar\omega_x + \left(n_y + \frac{1}{2}\right)\hbar\omega_y + \left(n_z + \frac{1}{2}\right)\hbar\omega_z,$$

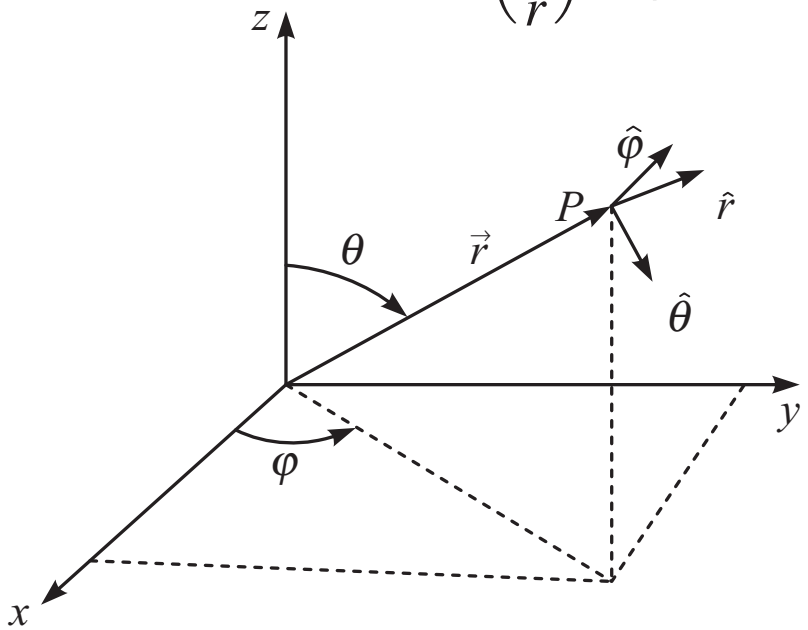
$$\psi_{n_x n_y n_z}(x,y,z) = X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z),$$

The transformation from the Cartesian system to the spherical system of coordinates is given by the following set of equations

$$x = r\sin\theta\cos\varphi, y = r\sin\theta\sin\varphi, z = r\cos\theta,$$

where

$$r = \sqrt{x^2+y^2+z^2},\ \ \theta = \cos^{-1}\left(\frac{z}{r}\right),\ \ \varphi = \tan^{-1}\left(\frac{y}{x}\right).$$



Using the transformation formulae, we obtain

$$\frac{\partial}{\partial x} = \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi},$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi},$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}.$$

The unit vectors of the spherical system of coordinates can also be calculated to be

$$\hat{r} = \left(\sin\theta\cos\varphi\hat{i} + \sin\theta\sin\varphi\hat{j} + \cos\theta\hat{k}\right),$$

$$\hat{\theta} = \left(\cos\theta\cos\varphi\hat{i} + \cos\theta\sin\varphi\hat{j} - \sin\theta\hat{k}\right),$$

$$\hat{\varphi} = \left(-\sin\varphi\hat{i} + \cos\varphi\hat{j}\right).$$

Taking these results into account, the gradient operator, can be written as

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}.$$

The Laplacian (Laplace operator), $\nabla^2 \equiv \Delta$, can now be written as

$$\vec{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \varphi^2}.$$

As a consequence, in spherical coordinates, the time-independent Schrödinger equation takes the form

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

Spherically Symmetric Potentials

If the potential is spherically symmetric, that is it is independent of the angles θ and φ and depends only on the radial distance r, the radial and angular variables in the Schrödinger equation can be separated.

$$\phi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$$

Therefore,

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V-E)\right] + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = 0.$$

The first term in this equation is just a function of r, while the second term is a function of θ and φ only.

Since the sum of these terms is zero, each of them must be equal to the same constant with opposite signs.

We take this separation constant to be l(l + 1). There, l will represent the orbital quantum number. The value of the angular momentum of the particle in a given state with quantum number l is

$$\hbar\sqrt{\ell(\ell+1)},$$

Thus, we have the system of differential equations, one each for the radial part R(r) and the angular part Y(θ, φ) of the wave function

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

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]=-\ell(\ell+1).$$

The equation about the angular part is

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}=-\ell(\ell+1)Y.$$

This can be rewritten in a more familiar form as

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\ell(\ell+1)\sin^2\theta Y+\frac{\partial^2 Y}{\partial\varphi^2}=0.$$

Separating the variables

$$Y(\theta,\varphi)=\vartheta(\theta)\Phi(\varphi),$$

Therefore,

$$\frac{1}{\vartheta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\vartheta}{\partial\theta}\right)\right]+\ell(\ell+1)\sin^2\theta+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=0.$$

Since the sum of theses terms is zero, each term must be equal to the same constant but with opposite signs. Taking this separation constant as m^2, we get

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\vartheta}{\partial\theta}\right)+\ell(\ell+1)\sin^2\theta\ \vartheta=m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2\Rightarrow\frac{d^2\Phi}{d\varphi^2}+m^2\Phi=0.$$

The solution of second equation is

$$\Phi(\varphi)=e^{im\varphi},$$

where m is a number and we have omitted the constant of integration

Since when φ advances by 2π, we return to the same point in space, we have

$$\Phi(\varphi+2\pi)=\Phi(\varphi) \quad \Rightarrow \quad e^{im(\varphi+2\pi)}=e^{im\varphi}.$$

It gives that m is an integer:

$$\exp(2i\pi m)=1, \qquad m=0,\pm1,\pm2,\pm3,....$$

The ϑ equation can be reduced to the standard form of the Legendre equation by the change of variable x = cosθ . Its solutions are

$$\vartheta(\theta)=AP_\ell^m(x), \quad x=\cos\theta,$$

where A is a constant and $P^m_l(x)$ are the associated Legendre polynomials. They are given by

$$P_\ell^m(x) = \left(1-x^2\right)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_\ell(x),$$

where $P_l(x)$ are the Legendre polynomials defined by

$$P_\ell(x) = \frac{1}{2^l l!} \frac{d^\ell}{dx^\ell} \left(x^2-1\right)^\ell,$$

with l as a non-negative integer. This formula is known as the Rodriguez formula. Therefore

$$\text{if } |m| > \ell, \text{ then } P_\ell^m(x) = 0.$$

This in turn says that for any given l, there are (2l + 1) possible values of m:

$$\ell = 0, 1, 2, \ldots; \quad m = -\ell, (-\ell+1), (-\ell+2), (-\ell+3), \ldots, -1, 0, 1, \ldots, (\ell-1), \ell.$$

So, for a given l there is a (2l + 1)-fold degeneracy with respect to the quantum number m. The normalized angular wave functions are given by

$$Y_\ell^m(\theta, \varphi) = \varepsilon \sqrt{\frac{(2\ell+1)\ (\ell-|m|)!}{4\pi\ (\ell+|m|)!}}\ P_\ell^m(\cos\theta) e^{im\varphi},$$

where

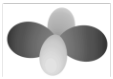
$$\varepsilon = (-1)^m \text{ for } m \geq 0 \text{ and } \varepsilon = 1 \text{ for } m < 0.$$

The functions $Y_l^m(\theta,\varphi)$ are called spherical harmonics. Its normalization condition is

$$\int_0^\pi d\theta\ \sin\theta \int_0^{2\pi} d\varphi\ |Y_\ell^m(\theta, \varphi)|^2 = 1,$$

Solution of the Angular Part

南開大學

l:		$P_\ell^m(\cos\theta)\ \cos(m\varphi)$							$P_\ell^{\lvert m\rvert}(\cos\theta)\ \sin(\lvert m\rvert\varphi)$						
0	s														
1	p														
2	d														
3	f															
4	g														
5	h														
6	i														
	m:	6	5	4	3	2	1	0	-1	-2	-3	-4	-5	-6	

The radial equation for a given l for R_l can be written as

$$\frac{d}{dr}\left(r^2\frac{dR_{n\ell}}{dr}\right)-\frac{2mr^2}{\hbar^2}(V(r)-E)R_{n\ell}=l(l+1)R_{n\ell},$$

where we have introduced an additional subscript n for the radial wave function R_l. n is called the principal quantum number. This equation can be simplified further by changing the variables:

$$u_{n\ell}(r)=rR_{n\ell}(r).$$

We have

$$\frac{dR_{n\ell}}{dr}=\frac{(du_{n\ell}/dr)}{r}-\frac{u_{n\ell}}{r^2},\quad r^2\frac{dR_{n\ell}}{dr}=r\frac{du_{n\ell}}{dr}-u_{n\ell}$$

$$\frac{d}{dr}\left(r^2\frac{dR_{n\ell}}{dr}\right)=r(d^2u_{n\ell}/dr^2).$$

Therefore,

$$\frac{d^2u_{n\ell}}{dr^2}+\frac{2m}{\hbar^2}\left[E-V(r)-\frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]u_{n\ell}(r)=0.$$

This equation for the radial function $u_{nl}(r)$ can be solved only if the potential, V (r), is prescribed.

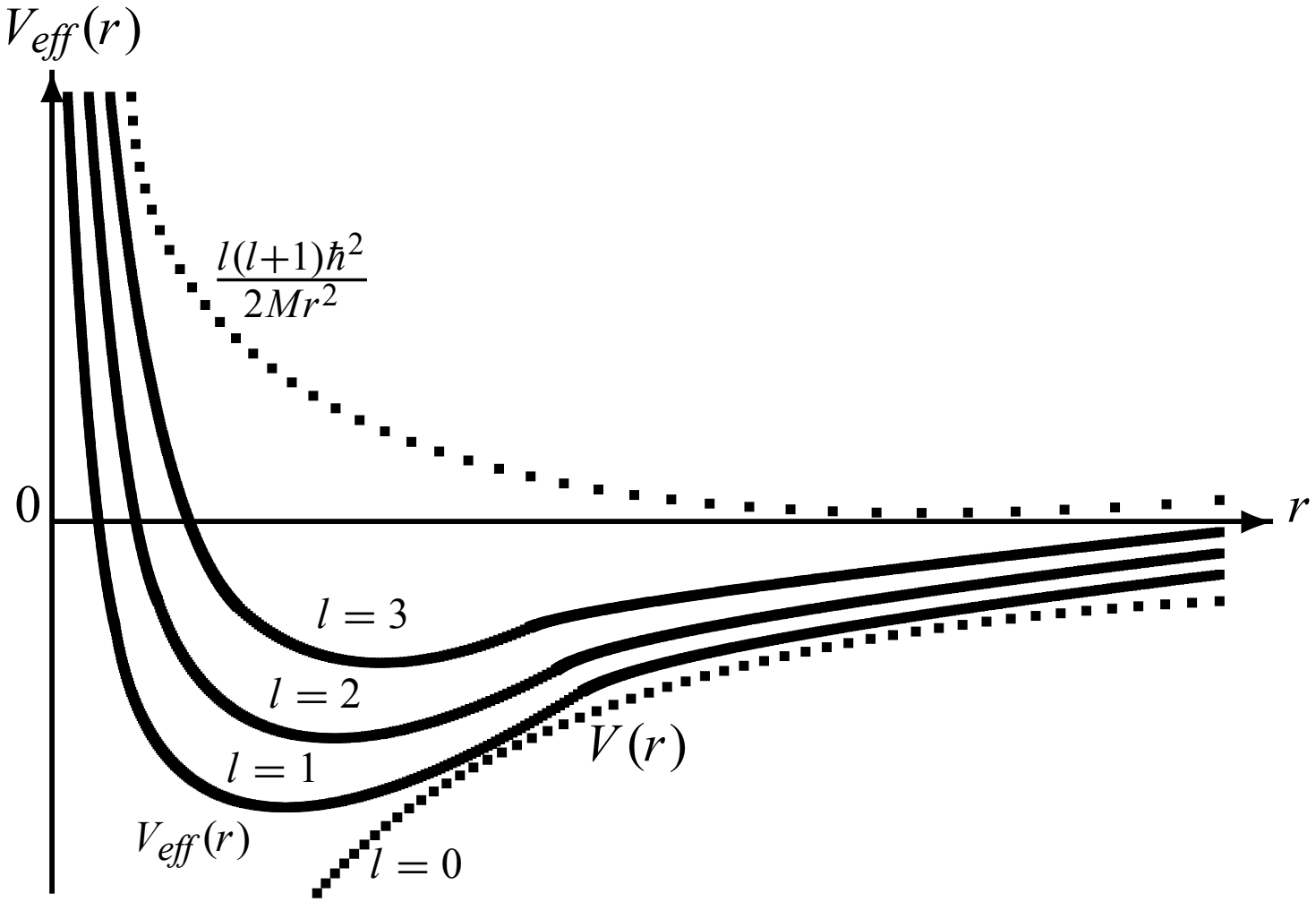
It is customary to introduce an effective potential, $V_{eff}(r)$, by

$$V_{\text{eff}}(r)=V(r)+\frac{\hbar^2\ell(\ell+1)}{2mr^2},$$

and rewrite the radial equation as

$$\frac{d^2u_{n\ell}}{dr^2}+\frac{2m}{\hbar^2}\left[E-V_{eff}(r)\right]u_{n\ell}(r)=0.$$

The effective potential



Solution of the Radial Part

This equation is similar to the one-dimensional Schrödinger equation with the difference that the effective potential V_{eff} has an extra term

$$\hbar^2 \ell(\ell+1)/2mr^2.$$

This term is called the repulsive or centrifugal potential that tries to throw the particle away from the centre.

The radial wave function, $R_{nl}(r)$, must be finite everywhere from r = 0 to r = ∞. Consequently, the function $u_{nl}(r)$ must satisfy

$$\lim_{r\to 0} u_{n\ell}(r) = \lim_{r\to 0} rR_{n\ell}(r) = 0.$$

Note that for the bound states to exist, the potential V(r), must be attractive.

Once we solve the radial wave equation for a given V (r), the full wave function will be given by

$$\phi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi).$$

The normalization condition for the total wave function reads as

$$\int_0^\infty dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi\, r^2\, |\phi_{n\ell m}(r,\theta,\phi)|^2$$

$$= \int_0^\infty r^2\, |R_{n\ell}(r)|^2\, dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi |Y_\ell^m(\theta,\varphi)|^2 = 1.$$

Solution of the Radial Part

Since the spherical harmonics are already normalized, we have

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \, \sin\theta \, |Y_\ell^m(\theta,\varphi)|^2 = 1.$$

Therefore, to have the full wave function normalized to unity, we have to simply normalize the radial wave function,

$$\int_0^{\infty} r^2 \, |R_{n\ell}(r)|^2 \, dr = 1.$$

The probability of finding the particle in the volume element

$$P_{n\ell}(r)dr = \left(\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \, |\psi_{n\ell m}(r.\theta,\varphi)|^2 \right) r^2 \, dr$$

$$= |R_{n\ell}(r)|^2 \, r^2 \, dr \int_0^{\pi} \int_0^{2\pi} (Y_\ell^m(\theta,\varphi))^* Y_\ell^m(\theta,\varphi) \, \sin\theta \, d\theta \, d\varphi$$

$$= |R_{n\ell}(r)|^2 \, r^2 \, dr.$$

Solution of the Radial Part

Since the spherical harmonics are already normalized, we have

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \, \sin\theta \, |Y_\ell^m(\theta,\varphi)|^2 = 1.$$

Therefore, to have the full wave function normalized to unity, we have to simply normalize the radial wave function,

$$\int_0^{\infty} r^2 \, |R_{n\ell}(r)|^2 \, dr = 1.$$

The probability of finding the particle in the volume element

$$P_{n\ell}(r)dr = \left(\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \, |\psi_{n\ell m}(r.\theta,\varphi)|^2 \right) r^2 \, dr$$

$$= |R_{n\ell}(r)|^2 \, r^2 \, dr \int_0^{\pi} \int_0^{2\pi} (Y_\ell^m(\theta,\varphi))^* Y_\ell^m(\theta,\varphi) \, \sin\theta \, d\theta \, d\varphi$$

$$= |R_{n\ell}(r)|^2 \, r^2 \, dr.$$

Consider a particle of mass m moving freely in space,

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

The variables separate and the solution can be represented as

$$\phi_{k\ell m}(r,\theta,\phi) = R_{k\ell}(r)Y_\ell^m(\theta,\varphi).$$

Note that in the given case of a free particle the energy, takes continuous values and hence the radial wave function is characterized by the continuous index k.

The radial wave function, $R_{kl}(r)$, satisfies

$$\frac{d}{dr}\left(r^2\frac{dR_{k\ell}}{dr}\right)+k^2r^2R_{k\ell}=\ell(\ell+1)R_{k\ell}.$$

Introducing $\rho = kr$, we have

$$\frac{d^2R_{k\ell}(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR_{k\ell}(\rho)}{d\rho}+\left(1-\frac{\ell(\ell+1)}{\rho^2}\right)R_{k\ell}(\rho)=0.$$

This is the spherical Bessel equation whose general solution, for any k, is given by

$$R_{k\ell}(\rho)=A_\ell j_\ell(\rho)+B_\ell n_\ell(\rho),\ell=0,1,2,3,...$$

where $j_l(\rho)$ and $n_l(\rho)$ are the spherical Bessel functions and the spherical Neumann functions, respectively. They are given by

$$j_\ell(\rho)=(-\rho)^\ell\left(\frac{1}{\rho^\ell}\frac{d^\ell}{d\rho^\ell}\right)\frac{\sin\rho}{\rho},n_\ell(\rho)=-(-\rho)^\ell\left(\frac{1}{\rho^\ell}\frac{d^\ell}{d\rho^\ell}\right)\frac{\cos\rho}{\rho}.$$

The asymptotic forms of these functions for $\rho \to 0$ and $\rho \to \infty$ are, respectively, given by

$$j_\ell(\rho) = \frac{2^\ell \ell!}{(2^\ell+1)!}\rho^\ell, n_\ell(\rho) = -\frac{(2\ell-1)!}{2^\ell \ell!}\frac{1}{\rho^{\ell+1}} (\rho \to 0),$$

$$j_\ell(\rho) = \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right), n_l(\rho) = -\frac{1}{\rho}\cos\left(\rho - \frac{\ell\pi}{2}\right) (\rho \to \infty).$$

Note that for $\rho \to 0$, the Neumann function blows up. As a result, we have

$$\phi_{k\ell m}(\rho,\theta,\varphi) = A_\ell j_\ell(kr) Y_\ell^m(\theta,\varphi),$$

This degeneracy corresponds to the spherical symmetry in the momentum space: all directions of k are equivalent.

The Free Particle Solution

Recall that the free particle solution in Cartesian coordinates is proportional to plane wave, which can be expanded in terms of the spherical Bessel functions as

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell m}\, j_\ell(kr)\, Y_\ell^m(\theta,\varphi),$$

where c_{lm} are arbitrary constants. Thus, the solution for a free particle in spherical coordinates is completely equivalent to the free particle solution in Cartesian coordinates.

For the particular case of propagation along the z-axis ($k \parallel z$), m = 0 and we get

$$e^{i\vec{k}\cdot\vec{r}} = e^{kr\cos\theta} = \sum_{\ell=0}^{\infty} i^\ell (2\ell+1)\, j_\ell(kr) P_\ell(\cos\theta), \longrightarrow c_{\ell m} = i^\ell (2\ell+1).$$

A particle of mass m is moving under the influence of the following potential

$$V(t) = \begin{cases} -V_0, & \text{for} \quad r < a \\ 0, & \text{for} \quad r \geq a, \end{cases}$$

In terms of the function $u_{nl}(r) = rR_{nl}(r)$, the radial equations of Schrödinger equation can then be written as

$$\frac{d^2 u_{n\ell}}{dr^2} + \left[k_1^2 - \frac{l(l+1)}{r^2} \right] u_{n\ell}(r) = 0, (0 < r < a),$$

$$\frac{d^2 u_{n\ell}}{dr^2} + \left[(ik_2)^2 - \frac{l(l+1)}{r^2} \right] u_{n\ell}(r) = 0, (r > a).$$

For the first equation, its solution is

$$R_{n\ell}^{(I)}(r) = \frac{u_{n\ell}^{(I)}(r)}{r} = A_\ell j_\ell(k_1 r).$$

The solution of second equation is

$$R_{n\ell}^{(II)}(r) = \frac{u_{n\ell}^{(II)}(r)}{r} = D_\ell h_\ell(ik_2),$$

where,

$$h_\ell(ik_2) = j_\ell(ik_2 r) + i n_\ell(ik_1 r)$$

is the Hankel function that asymptotically behaves as

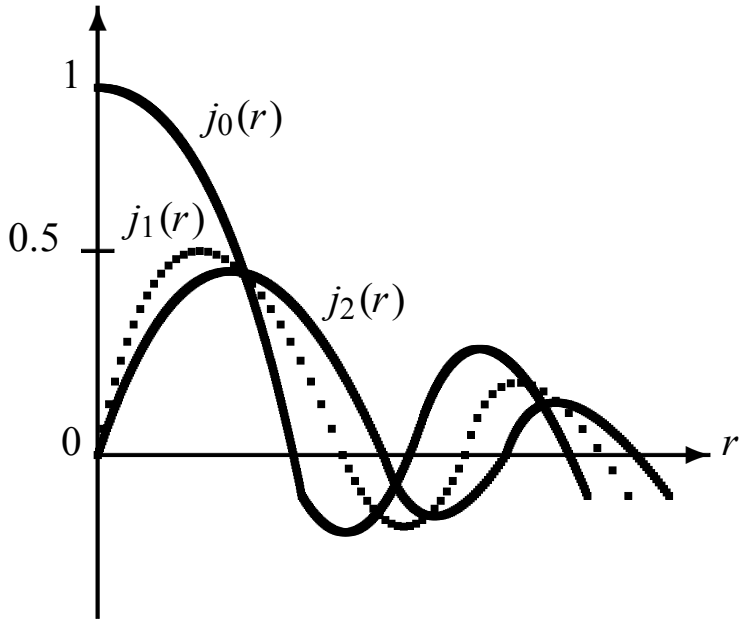
$$e^{-k_2 r}/r \text{ as } r \to +\infty.$$

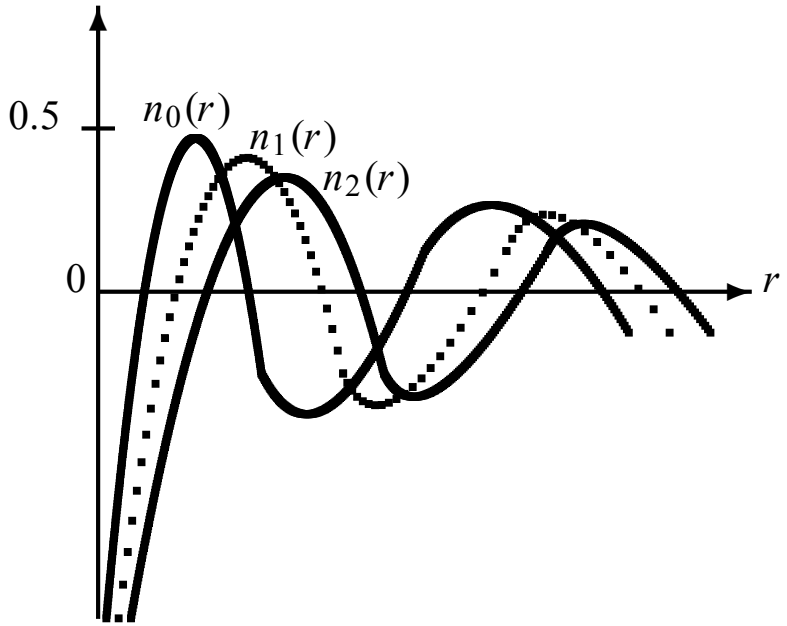
Therefore, the radial wave function of the particle for the given potential, can be written as

$$R_{n\ell}(r) = \begin{cases} A_\ell j_\ell(k_1 r), & r \le a \\ D_\ell h_\ell(ik_2 r), & r > a, \end{cases}$$

The spherical Bessel functions as

Bessel functions $j_l(r)$	Neumann functions $n_l(r)$
$j_0(r) = \frac{\sin r}{r}$	$n_0(r) = -\frac{\cos r}{r}$
$j_1(r) = \frac{\sin r}{r^2} - \frac{\cos r}{r}$	$n_1(r) = -\frac{\cos r}{r^2} - \frac{\sin r}{r}$
$j_2(r) = \left(\frac{3}{r^3} - \frac{1}{r}\right)\sin r - \frac{3\cos r}{r^2}$	$n_2(r) = -\left(\frac{3}{r^3} - \frac{1}{r}\right)\cos r - \frac{3}{r^2}\sin r$





The continuity of the wave function and its first derivative at r = a leads to the transcendental equation

$$k_1 \frac{j_\ell'(k_1 a)}{j_\ell(k_1 a)} = k_2 \frac{h_\ell'(ik_2 a)}{h_\ell(ik_2 a)},$$

for the determination of the energy eigenvalues. The solution is usually found numerically.

The constants A_l and D_l are related through

$$A_\ell j_\ell(k_1 a) = D_\ell h_\ell(ik_2 a).$$

The full bound state wave functions are given by

$$R_{n\ell}(r) = A_\ell \begin{cases} j_\ell(k_1 r) Y_\ell^m(\theta, \varphi), & r \le a \\ \frac{j_\ell(k_1 a)}{h_\ell(ik_2 a)} h_\ell(ik_2 r) Y_\ell^m(\theta, \varphi), & r > a, \end{cases}$$

A hydrogen atom consists of a proton in the nucleus and an electron orbiting around it, which is held in its orbit by the attractive Coulomb force.

Let $\vec{r}_e = (x_e, y_e, z_e)$ and $\vec{r}_p = (x_p, y_p, z_p)$ be the position vectors for the electron and the proton, respectively. Let R = (X,Y,Z) be the position vector of the centre of mass, defined by

$$\vec{R} = \frac{m_e \vec{r}_e + m_p \vec{r}_p}{m_e + m_p},$$

and let $r=(x, y, z)=r_e-r_p$ represent the relative position vector. The Schrödinger equation of Hydrogen atom is

$$i\hbar \frac{\partial \psi(\vec{r}_e, \vec{r}_p, t)}{\partial t} = \left[-\frac{\hbar^2}{2m_e} \vec{\nabla}_e^2 - \frac{\hbar^2}{2m_p} \vec{\nabla}_p^2 + V(r) \right] \psi(\vec{r}_e, \vec{r}_p, t).$$

It is easy to check that

$$\frac{1}{m_e}\vec{\nabla}_e^2+\frac{1}{m_p}\vec{\nabla}_p^2=\frac{1}{M}\vec{\nabla}_R^2+\frac{1}{\mu}\vec{\nabla}_r^2,$$

$$M=m_e+m_p,\qquad \mu=\frac{m_e m_p}{m_e+m_p},$$

where M and μ are the total and the so-called reduced mass, respectively. The Laplace's operators are given by

$$\vec{\nabla}_R^2=\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2},$$

and

$$\vec{\nabla}_r^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}.$$

We look for the stationary state solutions of the Schrödinger equation in the form

$$\psi(\vec{r}_e,\vec{r}_p,t) = \psi(\vec{r}_e,\vec{r}_p)e^{-i\frac{E_T}{\hbar}t},$$

where E_T is the total energy of the system. Taking into account that, in the SI units, the Coulomb potential between the electron and proton is given by

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0|\vec{r}_e-\vec{r}_p|},$$

therefore,

$$\left[-\frac{\hbar^2}{2m_p}\vec{\nabla}_p^2 - \frac{\hbar^2}{2m_e}\vec{\nabla}_e^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}_e-\vec{r}_p|}\right]\psi(\vec{r}_e,\vec{r}_p) = E_T\psi(\vec{r}_e,\vec{r}_p).$$

It can be rewritten in the centre of the mass system as

$$\left[-\frac{\hbar^2}{2M}\vec{\nabla}_R^2 - \frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\vec{R},\vec{r}) = E_T\psi(\vec{R},\vec{r}).$$

Since the potential depends only on the relative coordinate r, we expect the variables to separate and look for the solution in the form

$$\psi(\vec{R},\vec{r}) = \Phi(\vec{R})\phi(\vec{r}).$$

We have

$$\left[-\frac{\hbar^2}{2M}\frac{1}{\Phi(\vec{R})}\vec{\nabla}_R^2\Phi(\vec{R})\right] - \left[\frac{\hbar^2}{2\mu}\frac{1}{\phi(\vec{r})}\vec{\nabla}_r^2\phi(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0 r}\right] = E_T.$$

This leads to the following pair of equations

$$-\frac{\hbar^2}{2M}\vec{\nabla}_R^2\Phi(\vec{R}) = E_R\Phi(\vec{R}),$$

$$-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2\phi(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0 r}\phi(\vec{r}) = E_r\phi(\vec{r}),$$

where

$$E_T = E_R + E_r.$$

The first equation can be interpreted as the stationary Schrödinger equation of a free particle of mass M. Consequently, the normalized solution of this equation is written as

$$\Phi(\vec{R}) = \frac{1}{(2\pi)^{3/2}} e^{-i\vec{\kappa}\cdot\vec{R}},$$

The Coulomb potential is spherical symmetric, the second equation is convenient to be solved in spherical coordinate.

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\phi}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\varepsilon_0 r}\phi = E\phi,$$

Since the potential is spherically symmetric, the general solutions (with an arbitrary value of l) are given by

$$\phi(r,\theta,\phi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi),$$

The radial wave function $R_{nl}(r)$ satisfies

$$\frac{d}{dr}\left(r^2\frac{dR_{n\ell}(r)}{dr}\right) + \left[\lambda + \frac{2\alpha}{r}\right] r^2 R_{n\ell}(r) = \ell(\ell+1)R_{n\ell}(r),$$

where

$$\lambda = \frac{2\mu E}{\hbar^2}; \alpha = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2}.$$

Let us introduce the dimensionless independent variable

$$\rho = 2\frac{r}{r_0} = 2r\sqrt{-\lambda}. \qquad r_0 = 1/\sqrt{-\lambda}.$$

Therefore

$$\frac{d^2R_{n\ell}(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR_{n\ell}(\rho)}{d\rho}+\left(-\frac{1}{4}+\frac{\alpha}{\sqrt{-\lambda}}\frac{1}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right)R_{n\ell}(\rho)=0.$$

For $\rho \to \infty$, it reduces to

$$\frac{d^2R_{n\ell}(\rho)}{d\rho^2}-\frac{1}{4}R_{n\ell}(\rho)=0,$$

which has simple solutions $R_{nl}(r) = \exp(\pm\rho/2)$. Consequently, we look for the solution of above equation in the following form

$$R_{n\ell}(\rho)=e^{-\rho/2}u_{n\ell}(\rho),$$

where the function $u_{nl}(\rho)$ must obey the boundary conditions.

Finally, we obtain the following differential equation for the function $u_{nl}(\rho)$

$$\frac{d^2u_{n\ell}}{d\rho^2}+\left(\frac{2}{\rho}-1\right)\frac{du_{n\ell}}{d\rho}+\left[\left(\frac{\alpha}{\sqrt{-\lambda}}-1\right)\frac{1}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right]u_{n\ell}=0.$$

The form of the equation suggests that we look for the solution in the form

$$u_{n\ell}(\rho)=\rho^{\gamma}\sum_{j=0}^{\infty}c_j\rho^j,$$

where γ, c_1,c_2,c_3,... are constants to be determined. The value of γ will be determined from the requirement that the function u_{nl} is finite everywhere.

After differentiating the u_{nl}, we have

$$\sum_{j=0}^{\infty} c_j(\gamma+j)(\gamma+j-1)\rho^{\gamma+j-2} + \sum_{j=0}^{\infty} 2c_j(\gamma+j)\rho^{\gamma+j-2} - \sum_{j=0}^{\infty} c_j(\gamma+j)\rho^{\gamma+j-1}$$

$$+ \sum_{j=0}^{\infty} c_j \left[\left(\frac{\alpha}{\sqrt{-\lambda}} - 1\right)\frac{1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]\rho^{\gamma+j} = 0.$$

Or,

$$\sum_{j=0}^{\infty} c_j \left[(\gamma+j)(\gamma+j+1) - \ell(\ell+1)\right]\rho^{\gamma+j-2}$$

$$= \sum_{j=0}^{\infty} c_j \left[(\gamma+j+1) - \frac{\alpha}{\sqrt{-\lambda}}\right]\rho^{\gamma+j-1}.$$

The coefficients before identical powers of ρ, on both sides of the equation, must be equal. Therefore,

$$(\gamma(\gamma+1)-\ell(\ell+1))c_0 = 0 \Rightarrow (\gamma(\gamma+1)-\ell(\ell+1)) = 0.$$

It has two possible solutions

$$\gamma = \ell \text{ or } \gamma = -(\ell+1).$$

If we take the solution $\gamma = -(l + 1)$, then the series in would start with the term c_0/ρ^{l+1} that goes to infinity for $\rho \to 0$. Therefore, we omit it and take $\gamma = l$. As a result,

$$\sum_{j=0}^{\infty} c_j \left[(\ell+j)(\ell+j+1)-\ell(\ell+1)\right] \rho^{\ell+j-2}$$

$$= \sum_{j=0}^{\infty} c_j \left[(\ell+j+1) - \frac{\alpha}{\sqrt{-\lambda}}\right] \rho^{\ell+j-1}.$$

Since the coefficient for j = 0 on the left-hand (LHS) side of above equation is zero, the series on the LHS starts with j = 1. If we change the dummy index of summation j to j + 1, we have

$$\text{LHS} = \sum_{i=0}^{\infty} c_{j+1} \left[(\ell + j + 1)(\ell + j + 2) - \ell(\ell + 1) \right] \rho^{\ell + j - 1}.$$

Therefore,

$$\sum_{j=0}^{\infty} \left(c_{j+1} \left[(\ell + j + 1)(\ell + j + 2) - \ell(\ell + 1) \right] - c_j \left[(\ell + j + 1) - \frac{\alpha}{\sqrt{-\lambda}} \right] \right) \rho^{\ell + j - 1} = 0.$$

Recursion relation for the coefficients of the series

$$c_{j+1} = \frac{\left[(\ell + j + 1) - \frac{\alpha}{\sqrt{-\lambda}} \right]}{(\ell + j + 1)(\ell + j + 2) - \ell(\ell + 1)} c_j.$$

The ratio c_{j+1}/c_j for large values of j

$$\lim_{j\to\infty}\frac{c_{j+1}}{c_j}=\lim_{j\to\infty}\frac{\left[(\ell+j+1)-(\alpha/\sqrt{-\lambda})\right]}{(\ell+j+1)(\ell+j+2)-\ell(\ell+1)}=\frac{1}{j}.$$

On the other hand, the ratio a_{k+1}/a_k for the series

$$e^{\rho}=\sum_{k=0}^{\infty}\frac{\rho^k}{k!}a_k$$

is

$$\lim_{k\to\infty}\frac{a_{k+1}}{a_k}=\lim_{k\to\infty}\frac{k!}{(k+1)!}=\frac{1}{k+1}\sim\frac{1}{k}.$$

It must truncate at some appropriate term. This is possible only if, for some value $j = j_{max}$, the numerator in becomes zero, that is,

$$(n_r+\ell+1)-\frac{\alpha}{\sqrt{-\lambda}}=0,$$

where $n_r = j_{max}$ is the maximum value of j for which $c_{n_r+1} = 0$. The number n_r is called the radial quantum number. Introducing a new quantum number, n, by the relation

$$n = n_r + \ell + 1,$$

we get that

$$\frac{\alpha}{\sqrt{-\lambda}} = n.$$

n is called the principal quantum number. It allows us to write the recursion relation for the coefficients of the polynomial as

$$c_{j+1} = \frac{[(\ell + j + 1) - n]}{(\ell + j + 1)(\ell + j + 2) - \ell(\ell + 1)} c_j.$$

Further, we have

$$\sqrt{-\lambda} = \frac{\alpha}{n} = \frac{\mu e^2}{4\pi\varepsilon_0 n\hbar^2}.$$

Or,

$$-\frac{2\mu E}{\hbar^2} = \left(\frac{\mu e^2}{4\pi\varepsilon_0 n\hbar^2}\right)^2.$$

Therefore, the possible values of energy are

$$E_n = -\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}.$$

We see that the energy depends only on the principal quantum number n. The possible values of l, for a given n, are: l = 0, 1, 2, 3, …, n–1.

The energy states of a hydrogen atom are usually described by the triplet of quantum numbers n, l, and m, as in other cases considered earlier.

Note that all the energy states of hydrogen, except the ground state with n = 1 and l = 0, are degenerate.

For a given value of n, there are n possible values of l (0,1,2,3,...,n–1) and for every l there are 2l + 1 values of m from –l to +l. Therefore, the degeneracy g is given by

$$g = \sum_{\ell=0}^{n-1} (2\ell + 1) = 1 + 3 + 5 + \ldots + (2n-1).$$

This series is an arithmetic series with n terms and the common difference d = 2. Hence, the sum is given by

$$g=\sum_{\ell=0}^{n-1}(2\ell+1)=\frac{n}{2}[2\times 1+(n-1)\times 2]=n^2.$$

Consequently, the stationary state energies and the corresponding wave functions of the hydrogen atom are, respectively,

$$E_n=-\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2},(n=1,2,3,\ldots),$$

$$\psi_{n\ell m}(r,\theta,\varphi)=\phi_{n\ell m}(r,\theta,\varphi)e^{-\frac{i}{\hbar}E_n t}=R_{n\ell}(r)Y_\ell^m(\theta,\varphi)e^{-\frac{i}{\hbar}E_n t},$$

$$R_{n\ell}(r)=e^{-r/na_0}\left(\rho^\ell\sum_{j=0}^{n_r}c_j\rho^j\right)=e^{-r/na_0}\left(\frac{2r}{na_0}\right)^\ell\sum_{j=0}^{n_r}c_j\left(\frac{2r}{na_0}\right)^j,$$

$$c_{j+1}=\frac{[(\ell+j+1)-n]}{(\ell+j+1)(\ell+j+2)-\ell(\ell+1)}c_j,$$

Ground state: For the ground state of hydrogen, n = 1, l = 0 and m = 0. Therefore, the wave function is given by

$$\phi_{100}(r,\theta,\varphi) = \frac{2}{\sqrt{a_0^3}}\frac{1}{\sqrt{4\pi}}e^{-r/a_0} = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}.$$

First excited state: Here, n = 2 and l can take two values: 0 and 1.

$$\phi_{200}(r,\theta,\varphi) = \frac{1}{2\sqrt{a_0^3}}\frac{1}{\sqrt{4\pi}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$= \frac{1}{\sqrt{8\pi a_0^3}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}.$$

$$\phi_{21-1}(r,\theta,\varphi) = \frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta e^{-i\varphi},$$

$$\phi_{210}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi a_0^3}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta,$$

$$\phi_{211}(r,\theta,\varphi) = -\frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta e^{i\varphi}.$$

The first few radial wave functions, $R_{nl}(r)$, are presented

$$R_{10}(r) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}$$

$$R_{20}(r) = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{24a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$$

$$R_{30}(r) = \frac{2}{\sqrt{27a_0^3}} \left[1 - \frac{2r}{3a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right] e^{-r/3a_0}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6a_0^3}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30a_0^3}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$$

$$R_{40}(r) = \frac{1}{4\sqrt{a_0^3}} \left[1 - \frac{3r}{4a_0} + \frac{1}{8}\left(\frac{r}{a_0}\right)^2 - \frac{1}{192}\left(\frac{r}{a_0}\right)^3\right] e^{-r/4a_0}$$

$$R_{41}(r) = \frac{\sqrt{5}}{16\sqrt{3a_0^3}} \frac{r}{a_0} \left[1 - \frac{r}{4a_0} + \frac{1}{80}\left(\frac{r}{a_0}\right)^2\right] e^{-r/4a_0}$$

$$R_{42}(r) = \frac{1}{64\sqrt{5a_0^3}} \left(\frac{r}{a_0}\right)^2 \left[1 - \frac{r}{12a_0}\right] e^{-r/4a_0}$$

$$R_{43}(r) = \frac{1}{768\sqrt{35a_0^3}} \left(\frac{r}{a_0}\right)^3 e^{-r/4a_0}$$

n	l	Orbitals	m	g_n	E_n
1	0	s	0	1	$-e^2/(2a_0)$
2	0	s	0	4	$-e^2/(8a_0)$
	1	p	$-1, 0, 1$		
3	0	s	0	9	$-e^2/(18a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
4	0	s	0	16	$-e^2/(32a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
	3	f	$-3, -2, -1, 0, 1, 2, 3$		
5	0	s	0	25	$-e^2/(50a_0)$
	1	p	$-1, 0, 1$		
	2	d	$-2, -1, 0, 1, 2$		
	3	f	$-3, -2, -1, 0, 1, 2, 3$		
	4	g	$-4, -3, -2, -1, 0, 1, 2, 3, 4$		

Using these Laguerre polynomials, the normalized wave function of the hydrogen atom can be written as:

$$\psi_{n\ell m}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} \times \left[L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)\right] Y_{\ell}^{m}(\theta,\varphi).$$

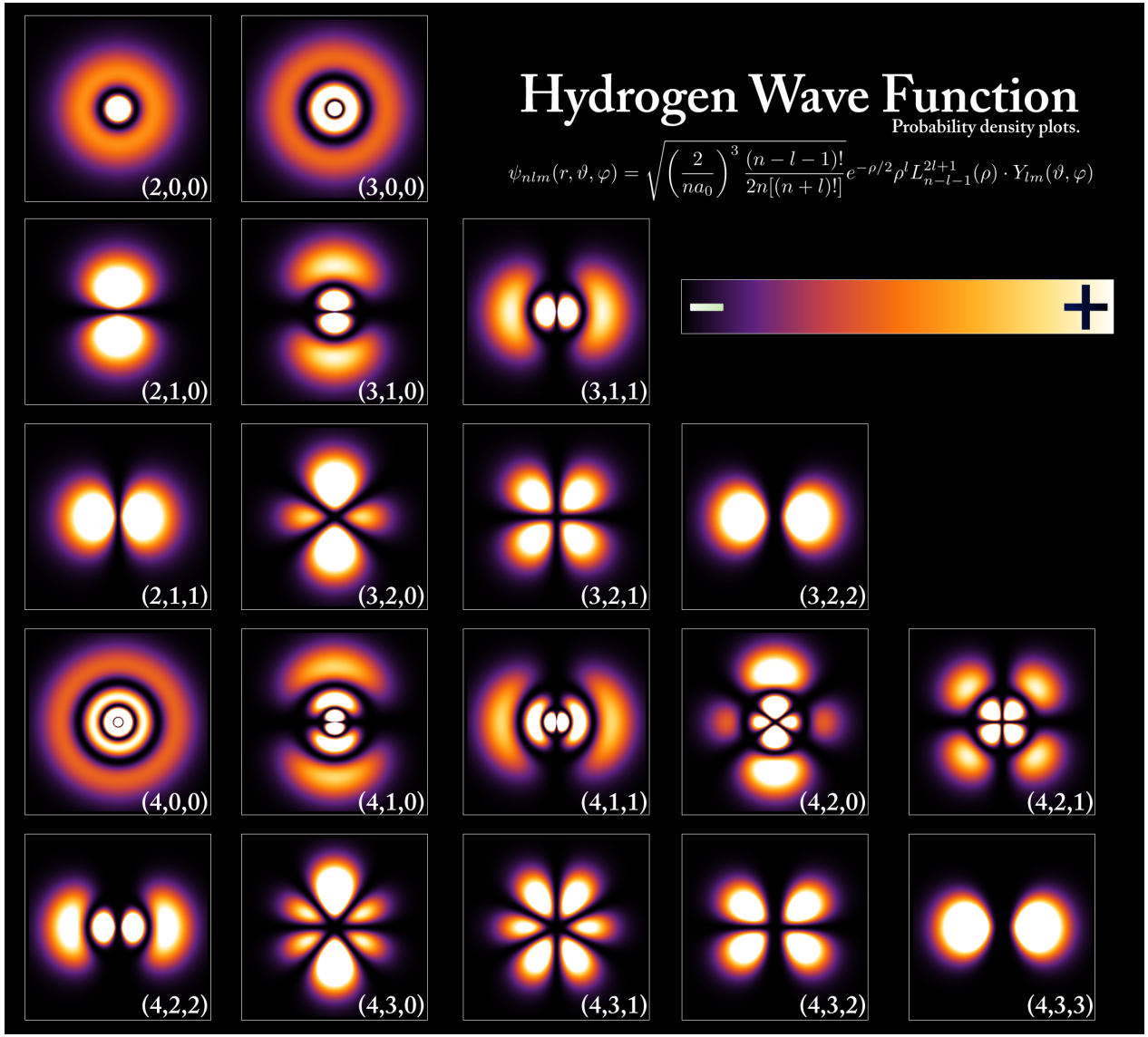
The q^{th} Laguerre polynomial is given by

$$L_q(x) = e^x \frac{d^q}{dx^q}(x^q e^{-x}).$$

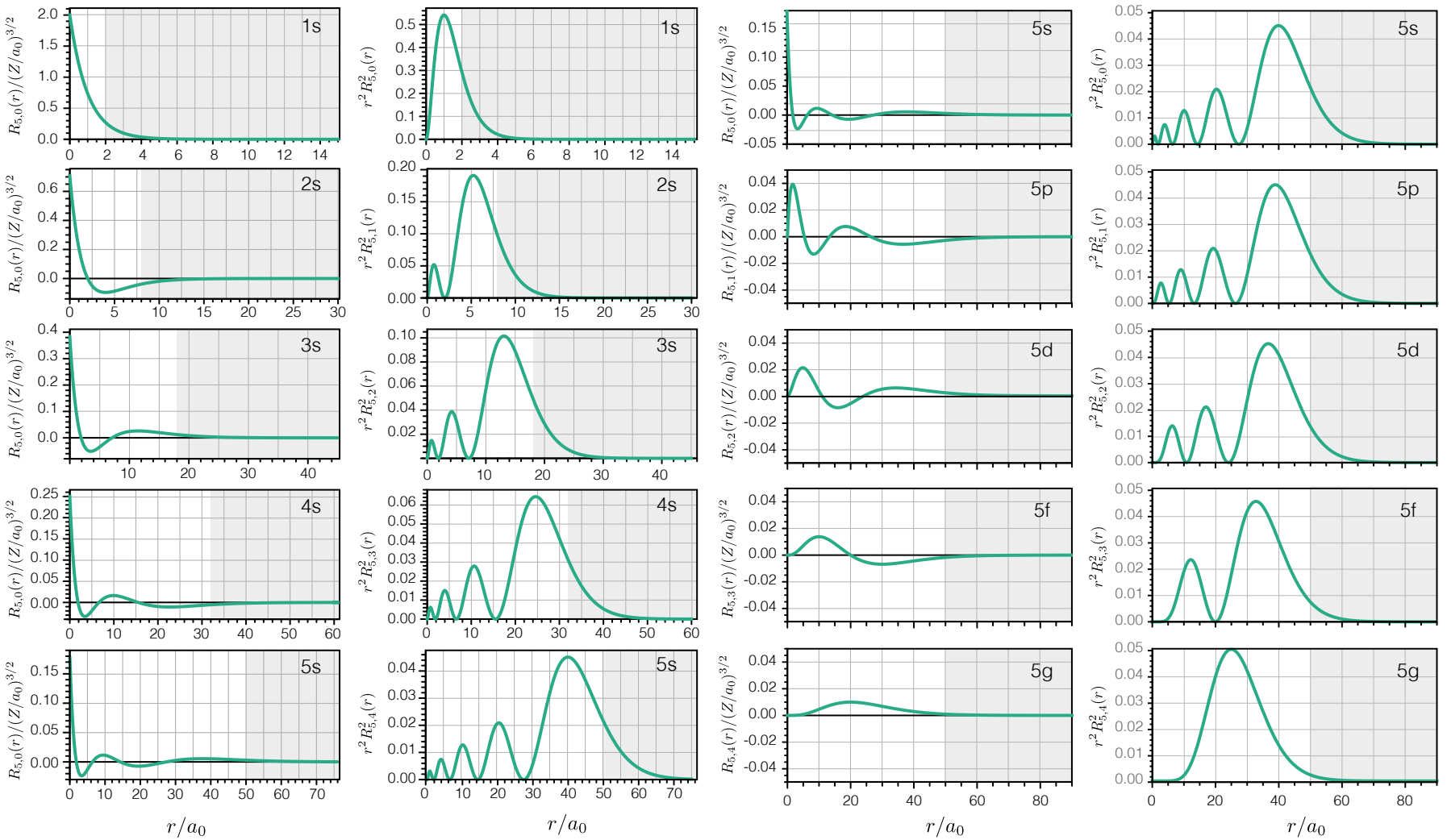
and

$$L_{q-p}^{p}(x) = (-1)^p \frac{d^p}{d\rho^p} L_q(x).$$

The Hydrogen Atom



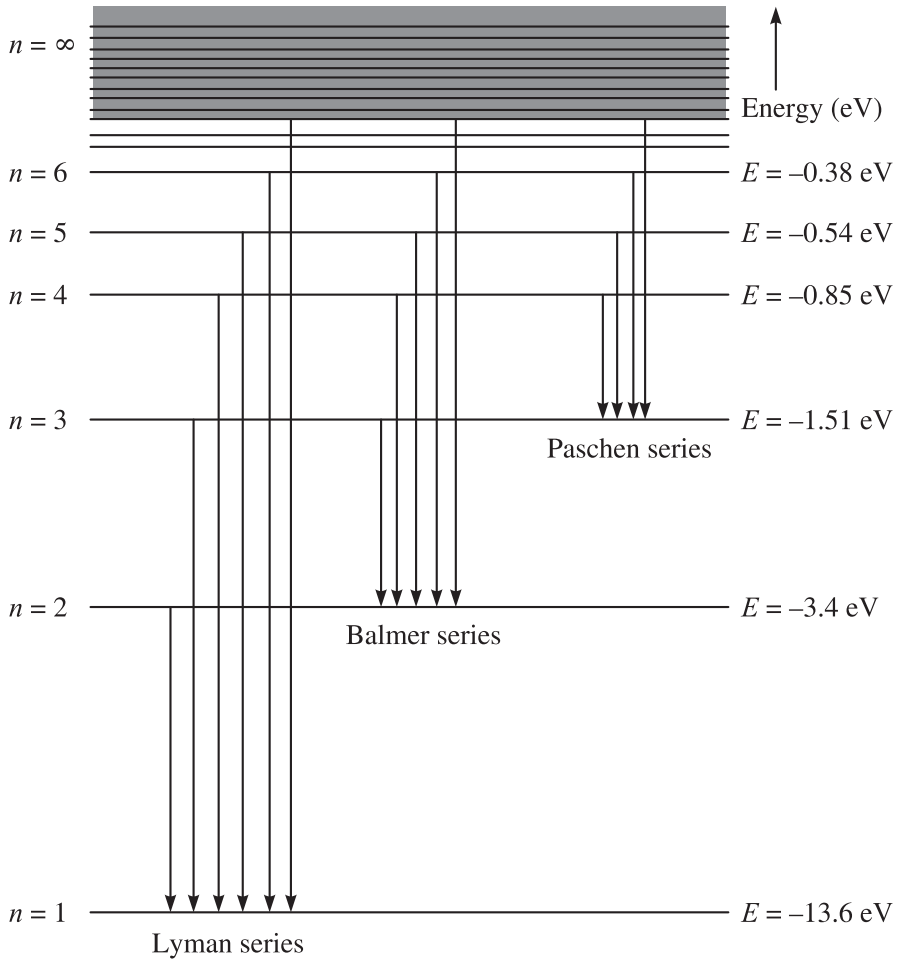
The Hydrogen Atom



$\ell =$ 0 1 2 3 4 5 6 7 8 9 10 11 12 13 ← numerical value

s p d f g h i k l m o q r t ← symbol

The spectrum of hydrogen: In principle, if the hydrogen atom is in one of the stationary states, it will reside there for ever.



The energy of the radiation, E_γ, is equal to the difference in energy of the stationary states involved in the transition:

$$E_\gamma = E_i - E_f = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right),$$

where E_f and E_i are the energy of the final and the initial stationary states, respectively, and

$$E_1 = -\frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2$$

is the energy of the ground state (n = 1). The energy of a photon is $E_\gamma = h\nu$, where h is the Planck's constant.

Consider a particle of effective mass μ moving in isotropic harmonic oscillator potential

$$V(r) = \frac{1}{2}\mu\,\omega^2\,r^2,$$

where μ is the mass, ω is the angular frequency of the oscillator and r is the radial distance from the origin.

We start with the Schrödinger equation in spherical coordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\phi}{\partial\varphi^2}\right]+\frac{1}{2}\mu\,\omega^2\,r^2\phi=E\phi.$$

The radial equation with substituting R(r) = u(r)/r is

$$\frac{d^2u}{dr^2}+\frac{2\mu}{\hbar^2}\left[E-\frac{1}{2}\mu\,\omega^2\,r^2-\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]u(r)=0.$$

For r → 0, we get

$$\frac{d^2u}{dr^2}-\frac{\ell(\ell+1)}{r^2}u(r)=0.$$

Let us look for u(r) in the form r^s. We then obtain

$$s(s-1)-\ell(\ell+1)=0,$$

which has two solutions s=–l and s=l+1.Since $u\sim r^{-l}$ blows up at r=0, it is excluded due to the standard conditions, we conclude that in the vicinity of r = 0, we should have $u\sim r^{l+1}$

We can define some new quantities

$$\alpha = \frac{\mu\omega}{2\hbar}, \quad and \quad E = \frac{\hbar\omega}{2}.$$

and the new variable

$$\rho = \sqrt{\frac{\mu\omega}{\hbar}} r.$$

The radial equation will become as

$$\frac{d^2v}{d\rho^2} + \left(\frac{2(\ell+1)}{\rho} - 2\rho\right)\frac{dv}{d\rho} + (\lambda - 2\ell - 3)\,v = 0.$$

with

$$u(\rho) = \rho^{\ell+1} e^{-\rho^2/2} v(\rho). \qquad \lambda = 2E/\hbar\omega.$$

We look for the solution in terms of an infinite series

$$v(\rho) = \sum_{p=0}^{\infty} a_p \rho^p,$$

where a_p are constant expansion coefficients. Finally, we can obtain

$$\sum_{p=0}^{\infty} \left[(p+1)(p+2)a_{p+2} + (2\ell+2)(p+2)a_{p+2} + (\lambda - 2\ell - 3 - 2p)a_p\right]\rho^p + (2\ell+2)a_1\frac{1}{\rho} = 0.$$

To hold both the terms must separately be equal to zero. This leads to $a_1 = 0$, and the recursion relation for the expansion coefficients

$$a_{p+2} = \frac{(2\ell + 2p + 3 - \lambda)}{(p+1)(p+2) + (2\ell+2)(p+2)} a_p.$$

As a result, we obtain the solution of the radial equation

$$u(\rho) = \rho^{\ell+1} e^{-\rho^2/2} v(\rho), \quad v(\rho) = \sum_p a_p \rho^p, \quad p = 0, 2, 4, \ldots.$$

For $\rho \to \infty$, the above solution diverges as $\exp(\rho^2)$ unless the infinite series is terminated at some term. Clearly, this can be achieved if

$$2\ell + 2k + 3 - \lambda = 0. \quad \Rightarrow \quad \lambda = \frac{2E}{\hbar\omega} = 2\ell + 2k + 3.$$

The above condition leads to the energy eigenvalues of the oscillator associated with a given value of l:

$$E_{k,\ell} = \hbar\omega \left(k + \ell + \frac{3}{2} \right),$$

As a result, we obtain the solution of the radial equation

$$u(\rho) = \rho^{\ell+1} e^{-\rho^2/2} v(\rho), \quad v(\rho) = \sum_p a_p \rho^p, \quad p = 0, 2, 4, \ldots.$$

For $\rho \to \infty$, the above solution diverges as $\exp(\rho^2)$ unless the infinite series is terminated at some term. Clearly, this can be achieved if

$$2\ell + 2k + 3 - \lambda = 0. \quad \Rightarrow \quad \lambda = \frac{2E}{\hbar\omega} = 2\ell + 2k + 3.$$

The above condition leads to the energy eigenvalues of the oscillator associated with a given value of l:

$$E_{k,\ell} = \hbar\omega \left(k + \ell + \frac{3}{2} \right),$$

where k is any even positive integer or zero.

If we introduce the quantum number n = k + l, the energy levels of the 3D isotropic oscillator can be written as

$$E_n = \hbar\omega\left(n+\frac{3}{2}\right),$$

Therefore, n can take any positive integer values or zero. Taking into account that for even n, l can take (n/2+1) values: 0,2,4,...,n, while for odd n, it can take [(n–1)/2+1] values: 1,3,5,...,n, the degeneracy of the energy levels is calculated to be

$$g_{n_{even}} = \sum_{\ell=0,2,4,\ldots,n}(2\ell+1) = \frac{(n+1)(n+2)}{2}, \qquad \text{for even } n,$$

$$g_{n_{odd}} = \sum_{\ell=1,3,5,\ldots,n}(2\ell+1) = \frac{(n+1)(n+2)}{2}, \qquad \text{for odd } n.$$

Ground state: The ground state corresponds to n = 0 for which l = k = 0.

$$\phi_{000} = \frac{2}{\pi^{1/4}} \left(\frac{m\omega}{\hbar}\right)^{3/4} e^{-\frac{m\omega}{2\hbar} r^2} Y_{00}(\theta, \varphi).$$

First excited state: It corresponds to n = 1. Since k has to be even, we have l = 1 and k = 0.

$$\phi_{11m} = \sqrt{\frac{8}{3\sqrt{\pi}}} \left(\frac{m\omega}{\hbar}\right)^{5/4} r e^{-\frac{m\omega}{2\hbar} r^2} Y_{1m}(\theta, \varphi), \quad m = -1, 0, 1.$$

Second excited state: It corresponds to n = 2. Since k has to be even, we have two pairs of k and l: (2,0) and (0,2).

$$\phi_{22m} = \frac{4}{\sqrt{15\sqrt{\pi}}} \left(\frac{m\omega}{\hbar}\right)^{7/4} r^2 e^{-\frac{m\omega}{2\hbar} r^2} Y_{2m}(\theta, \varphi).$$

Energy levels E_n and degeneracies g_n for an isotropic harmonic oscillator

n	E_n	Nl	m	g_n
0	$\frac{3}{2}\hbar\omega$	0 0	0	1
1	$\frac{5}{2}\hbar\omega$	0 1	$\pm 1, 0$	3
2	$\frac{7}{2}\hbar\,\omega$	1 0	0	6
		0 2	$\pm 2, \pm 1, 0$	
3	$\frac{9}{2}\hbar\omega$	1 1	$\pm 1, 0$	10
		0 3	$\pm 3, \pm 2, \pm 1, 0$	

$$g_n = \sum_{l=0,2,4,\ldots}^{n}(2l+1) = \sum_{l=0,2,4,\ldots}^{n}1 \; + \; 2\sum_{l=0,2,4,\ldots}^{n} l = \frac{1}{2}(n+2) + \frac{n(n+2)}{2} = \frac{1}{2}(n+1)(n+2).$$

1. Calculate the average distance of the electron from the nucleus in the ground state of the hydrogen atom. Also, calculate the average values of the potential and kinetic energies in the ground state of the hydrogen atom.

1. Calculate the average distance of the electron from the nucleus in the ground state of the hydrogen atom. Also, calculate the average values of the potential and kinetic energies in the ground state of the hydrogen atom.

Solution: The average value $\langle r \rangle$ of the distance of the electron from the nucleus is given by

$$\langle r \rangle = \frac{\int r|\phi(\vec{r})|^2 d\tau}{\int |\phi(\vec{r})|^2 d\tau} = \frac{1}{(\pi a_0^3)} \int_0^\infty r e^{-2r/a_0} r^2 dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta$$

$$= \frac{4\pi}{(\pi a_0^3)} \int_0^\infty e^{-2r/a_0} r^3 dr = \frac{4\pi}{\pi a_0^3} \frac{3! a_0^4}{(2)^4} = \frac{3}{2} a_0.$$

The average value of potential is

$$\langle U\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle = -\frac{e^2}{4\pi\varepsilon_0 a_0} = -\frac{e^2}{4\pi\varepsilon_0}\frac{\mu e^2}{4\pi\varepsilon_0\hbar^2} = 2\left[-\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right].$$

Since

$$\left\langle\frac{1}{r}\right\rangle = \int\frac{1}{r}|\phi(\vec{r})|^2 d\tau = \frac{1}{(\pi a_0^3)}\int_0^\infty\frac{1}{r}e^{-2r/a_0}r^2dr\int_0^{2\pi}d\varphi\int_0^\pi\sin\theta d\theta$$

$$= 4\pi\frac{1}{(\pi a_0^3)}\int_0^\infty e^{-2r/a_0}rdr = \frac{4}{a_0^3}\frac{1}{(2/a_0)^2} = \frac{1}{a_0}.$$

The average value of potential is

$$\langle T\rangle = E_1 - \langle U\rangle = -E_1 = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2.$$

2. At t=0, the wave function of a hydrogen atom is given by

$$\psi(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\phi_{300}(r,\theta,\varphi) + \frac{1}{\sqrt{3}}\phi_{311}(r,\theta,\varphi) + \frac{1}{\sqrt{6}}\phi_{322}(r,\theta,\varphi).$$

(a) What is the wave function at any t > 0? (b) If a measurement of energy is carried out in this state, what values would result and with what probabilities?

2. At t=0, the wave function of a hydrogen atom is given by

$$\psi(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\phi_{300}(r,\theta,\varphi) + \frac{1}{\sqrt{3}}\phi_{311}(r,\theta,\varphi) + \frac{1}{\sqrt{6}}\phi_{322}(r,\theta,\varphi).$$

(a) What is the wave function at any t > 0? (b) If a measurement of energy is carried out in this state, what values would result and with what probabilities?

Solution: (a) The wave function at any t > 0 would be

$$\psi(r,\theta,\varphi,t) = \left[\frac{1}{\sqrt{2}}\phi_{300}(r,\theta,\varphi) + \frac{1}{\sqrt{3}}\phi_{311}(r,\theta,\varphi) + \frac{1}{\sqrt{6}}\phi_{322}(r,\theta,\varphi)\right] e^{-\frac{i}{\hbar}E_3 t},$$

where $E_3 = E_1/9 = -13.6/9$ eV.

(b) Since the wave function is normalized and it is an eigenfunction of the Hamiltonian, the measurement of energy will give E_3 with probability 1.

3. A NaCl crystal has certain negative ion vacancies behaving like a free electron, inside a volume having dimensions of the order of a lattice constant (0.1 nm). Estimate the longest wavelength of electromagnetic radiation absorbed strongly by these electrons.

3. A NaCl crystal has certain negative ion vacancies behaving like a free electron, inside a volume having dimensions of the order of a lattice constant (0.1 nm). Estimate the longest wavelength of electromagnetic radiation absorbed strongly by these electrons.

Solution: Energy levels for a free electron confined to a cubic box having each side of length L are given

$$E = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_1^2 + n_1^2 + n_3^2\right)$$

The ground state energy is:

$$E_{111} = \frac{3\hbar^2\pi^2}{2mL^2} = \frac{3(1.054\times10^{-34})^2(3.14)^2}{2\times9.11\times10^{-31}(10^{-10})^2} = 1.8\times10^{-17}\ \text{Joules.}$$

$$E_{111} = 112.5\,\text{eV}.$$

The energy of the first excited states is:

$$E_{211} = \frac{6\hbar^2\pi^2}{2mL^2} = \frac{3\hbar^2\pi^2}{mL^2}$$

The longest wave length for transition from the ground state to the first excited state is given by:

$$\lambda = \frac{c}{\nu} = \frac{ch}{(E_{211} - E_{111})}$$

$$\lambda = \frac{3\times10^{8}\times6.626\times10^{-34}}{1.8\times10^{-17}} = 1.104\times10^{-8}\,m$$