In 3- dimensional problems, Schrödinger equation is closely similar to that for one-dimensional system. The wave equation, the boundary conditions imposed on the wavefunctions and the physical interpretation of the wavefunctions for the general system are closely related to those of one-dimensional System. The only changes being those consequences to the increase the number of dimensions of configuration spaces

In this case, schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,z) + V(x,y,z)\Psi = E\Psi(x,y,z) \qquad (1)$$

However, in the case where there is no relation between x, y and z, this equation can be solved by separation of variables.

Examples

1- Free particles

In this case schrödinger equation becomes

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2}{\partial z^2}\Psi = -\frac{2m}{\hbar^2}E\Psi \qquad (2)$$

The method of separation of variables assumes that we can write

$$\Psi(x,y,z) = X(x)\,Y(y)\,Z(z) \qquad (3)$$

where X, Y and Z are functions only in x, y and z, respectively

Let us write

$$K^2 = \frac{2m}{\hbar^2}(E_x + E_y + E_z) = K_x^2 + K_y^2 + K_z^2 \qquad (4)$$

So

$$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + (K_x^2 + K_y^2 + K_z^2)XYZ = 0 \qquad (5)$$

Dividing by XYZ

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} + K_x^2 + K_y^2 + K_z^2 = 0$$

Now, Since the sum of all terms is equal to a constant, we are led to the conclusion that $\frac{1}{X}\frac{d^2X}{dx^2}$ is independent of x as well as y and z, and is therefore itself equal to a constant

Thus $$\frac{1}{X}\frac{d^2X}{dx^2} = -K_x^2$$

This is a simple equation to be solved

$$X = A_x \exp iK_x x + B_x \exp -iK_x x$$

also for y and z.

2. Particle in a box.

Let us consider a particle constrained to stay inside of a cubic box with sides each of length L. We can represent this system by saying that the potential function $V(x,y,z)$ is given by

$$V(x,y,z) = \begin{cases} 0 & 0 < \frac{x}{y}_{z} < L \\ \infty & \text{outside the box} \end{cases}$$

In this case, following the same argument in the case of free particle, we have

$$X = A_x \cos K_x x + B_x \sin K_x x$$

also for y and z

at $x = 0$, $X = 0$ $\rightarrow A_x = 0$

$$X = B_x \sin K_x x$$

at $x = L$ $\quad X = 0$ $\quad \sin K_x L = 0$; $K_x = \frac{n_x \pi}{L}$

$$X = B_x \sin \frac{n_x \pi}{L} x$$

B_x Can be determined from the normalization condition

$$\int_0^L |X(x)|^2 dx = 1 = B_x^2 \int_0^L \sin^2 \frac{n_x \pi x}{L} dx = \frac{L}{2} B_x^2$$

or $B_x = \sqrt{\frac{2}{L}}$ $\qquad X = \sqrt{\frac{2}{L}} \sin \frac{n_x \pi x}{L}$

Also $\qquad Y = \sqrt{\frac{2}{L}} \sin \frac{n_y \pi}{L} y \qquad Z = \sqrt{\frac{2}{L}} \sin \frac{n_z \pi}{L} z$

So

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin \frac{n_x \pi}{L} x \sin \frac{n_y \pi}{L} y \sin \frac{n_z \pi}{L} z$$

and

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

where n_x, n_y and $n_z > 1$ are called quantum numbers. The complete time-dependent wavefunction may be written as

$$\psi_{n_x, n_y, n_z}(x, y, z, t) = \psi_{n_x, n_y, n_z}(x, y, z, t=0)\, e^{-\frac{i E_{n_x, n_y, n_z}}{\hbar} t}$$

In this case, most of the energy levels are degenerate, the lowest level with quantum numbers (1, 1, 1) is nondegenerate with energy

$$E_{1,1,1} = \frac{3}{2} \frac{\pi^2 \hbar^2}{mL^2}$$

The next level with quantum no (211, 121, 112) and energy $\frac{3}{2} \frac{\pi^2 \hbar^2}{mL^2}$ and the corresponding 3-possible wavefunctions are given by

$$\psi_{211} = \sqrt{\frac{8}{L^3}} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L}$$

$$\psi_{121} = \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L} \sin \frac{\pi z}{L}$$

$$\psi_{112} = \sqrt{\frac{8}{L^3}} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{2\pi z}{L}$$

These wavefunctions have different spatial distribution but, they all have the same energy. This energy level is said to be 3-fold degenerate. On the other hand, if the box is rectangular of dimensions a, b and c, with no integral relationship, then each eigenvalue has only a single wavefunction and the energy levels are non degenerate.

Three - Dimensional Harmonic Oscillator

A 3-dimensional Harmonic oscillator consists of a particle bound to origin by a force having components $-K_x x$, $-K_y y$ and $-K_z z$ along x, y and z-axes respectively

As in one-dimensional case

$$K_x = 4\pi^2 m \nu_x^2$$

$$K_y = 4\pi^2 m \nu_y^2$$

and $$K_z = 4\pi^2 m \nu_z$$

ν_x, ν_y and ν_z being the frequencies of x, y and z components of the oscillation

The potential energy of the system

$$V = \frac{1}{2}\left(K_x x^2 + K_y y^2 + K_z z^2\right)$$

and schrödinger equation becomes

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}\left(K_x x^2 + K_y y^2 + K_z z^2\right)\right)\psi = 0$$

using the separation of variables method, ie setting

$\psi(x, y, z) = X(x)\, Y(y)\, Z(z)$ and

$E = E_x + E_y + E_z$, we get

$$\left\{\frac{1}{X}\frac{d^2X}{dx^2} - \left(\frac{2\pi m \nu_x x}{\hbar}\right)^2\right\} + [Y] + [Z]$$

$$+ \frac{2m}{\hbar^2}\left(E_x + [Y] + [Z]\right) = 0$$

[ ] means the same quantity but with y and z.

Each bracket depends on its own variable, so each bracket = zero.

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$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\left(E_x - (2\pi m \nu_x x)^2\right) X = 0$$

Also for Y and Z.
Each of the above 3. equations is the same as that of one-dimensional harmonic oscillator. Thus the components of energy values are

$$E_x = (n_x + \tfrac{1}{2})\hbar\omega_x \qquad \omega_x = 2\pi\nu_x$$

also for y and z.

Thus the eigenvalues of the 3-dimensional H. oscillators are

$$E = E_x + E_y + E_z = \left\{(n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z\right\}$$

The wavefunctions are given by

$$X(x) = \frac{\alpha_x}{\left[2^{n_x}\, n_x!\, \sqrt{\pi}\right]^{1/2}} \exp -\frac{q_x^2}{2} \; H_{n_x}(q_x)$$

also for Y and Z

where $q_x = \alpha_x x = \left(\frac{m k_x}{\hbar^2}\right)^{1/2} x$

and the complete wavefunction is given by

$$\psi(x, y, z) = \frac{\alpha_x \alpha_y \alpha_z}{\left[2^{n_x+n_y+n_z}\, n_x!\, n_y!\, n_z!\, \pi^{3/2}\right]^{1/2}} \exp -\tfrac{1}{2}\left(q_x^2 + q_y^2 + q_z^2\right).$$

$$H_{n_x}(q_x)\; H_{n_y}(q_y)\; H_{n_z}(q_z)$$

and in this case λ_x, λ_y and λ_z are restricted to the values $\lambda_x = 2n_x + 1$ $\lambda_y = 2n_y + 1$,

$$\lambda_z = 2n_z + 1$$

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Spherically Symmetric Harmonic Oscillator

Here we shall consider a particular case of the 3-dimensional H.O. already discussed before, where

$$\nu_x = \nu_y = \nu_z = \nu_0$$

The acting force on this system can be written as

$$F = -Kr$$

and K is the force constant and

$$K = 4\pi^2 \nu_0^2 m$$

so that the potential energy function of the oscillator will be

$$V = -\int F \cdot dr = \frac{1}{2} Kr^2$$
$$= \frac{1}{2} K (x^2 + y^2 + z^2)$$

In this case Schrödinger equation will be

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} K (x^2 + y^2 + z^2) \right) \psi = 0$$

with

$$\alpha^2 = \sqrt{\frac{mK}{\hbar^2}} \qquad \lambda = 2E \sqrt{\frac{m}{\hbar^2 K}}$$

Schrödinger equation becomes

$$\nabla^2 \psi + \left[\lambda - (q_x^2 + q_y^2 + q_z^2) \right] \psi = 0$$

with

$\lambda = \lambda_x + \lambda_y + \lambda_z$, we have

$$\frac{d^2 \Theta_x}{dq_x^2} + (\lambda_x - q_x^2) \Theta_x(x) = 0$$

also for y and z

Each represents one-dimensional harmonic oscillator, for which the eigenfunction and the eigenvalues are

$$Q_x(q_x) = \frac{1}{(2^{n_x} n_x! \sqrt{\pi})^{\frac{1}{2}}} e^{-q_x^2/2} H_{n_x}(q_x)$$

and also for $Q_y(q_y)$ and $Q_z(q_z)$

and

$\lambda_x = 2n_x + 1$ also for y and z.

Thus the complete normalized wavefunction is given by

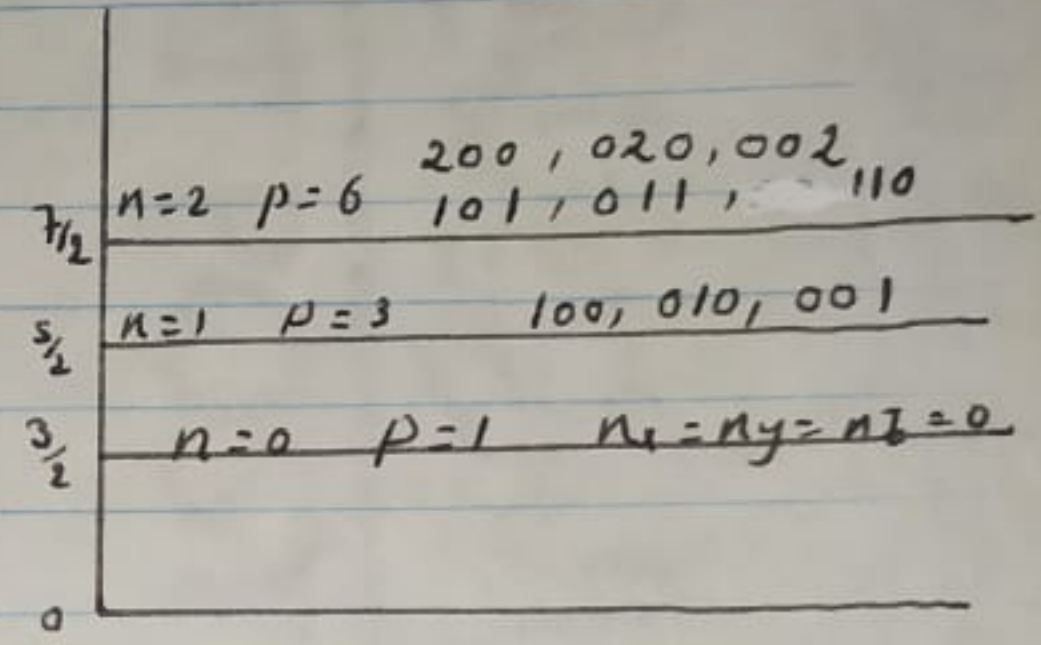
$$\psi = \frac{1}{[2^n n_x! n_y! n_z! \pi^{3/2}]^{\frac{1}{2}}} e^{-\frac{1}{2}(q_x^2 + q_y^2 + q_z^2)} H_{n_x}(q_x) H_{n_y}(q_y) H_{n_z}(q_z)$$

The eigenvalues are given by

$$E_n = (n + \tfrac{3}{2}) \hbar\omega$$

$n = n_x + n_y + n_z$.

is called the total quantum number. As the energy of the system depends only on the total quantum number, all the energy levels, except the lowest one are degenerate with the quantum weight



$$p = \tfrac{1}{2}(n+1)(n+2)$$

To calculate the degree of degeneracy for given n, we note that, if n_x is fixed, the number of combinations of n_y and n_z would be

$(0, n-n_x), (1, n-n_x-1), (2, n-n_x-2), \ldots \quad (n-n_x, 0)$

Thus there will be $(n-n_x+1)$ states

Now n_x can also vary from $0 \to n_j$, thus the degree of degeneracy would be

$$(n+1) + n + (n-1) + \cdots + 1$$

$$= \frac{n+1}{2}[1+n+1] = \frac{1}{2}(n+1)(n+2)$$

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MOTION IN A SPHERICALLY SYMMETRIC FIELDS.

One of the most important example of the 3- dimensional problems is the motion of a particle in a potential which depends only on the magnitude of the distance from a fixed point

i.e $$V(\vec{r}) = V(r) \qquad (1)$$

Schrödinger equation of such a potential is

$$\nabla^2 \Psi + \frac{2m}{\hbar^2}(E - V(r))\Psi = 0 \qquad (2)$$

In spherical polar coordinates we have

$$\nabla^2 \Psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \Psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \Psi}{\partial \phi^2} \qquad (3)$$

Note In any coordinates System (Cartesian- Cylindrical- Spherical)

$$\nabla^2 = \frac{1}{Q_1 Q_2 Q_3}\left\{\frac{\partial}{\partial q_1}\left(\frac{Q_2 Q_3}{Q_1}\frac{\partial}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{Q_1 Q_3}{Q_2}\frac{\partial}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{Q_1 Q_2}{Q_3}\frac{\partial}{\partial q_3}\right)\right\}$$

Coordinates	Q_1	Q_2	Q_3	q_1	q_2	q_3
Cartesian	1	1	1	x	y	z
Cylindrical	1	ρ	1	ρ	ϕ	z
Spherical	1	r	$r\sin\theta$	r	θ	ϕ

We denote the operator

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \quad \text{by} \quad \Lambda(\theta,\phi)$$

we note from eqn.s (2) and (3) that, as long as the potential is Spherically Symmetric, the angular part of the Hamiltonian is fixed. We therefore expect the angular dependence

of the wavefunctions for such problems to be the same in all cases.

now we write

$$\Psi(r, \theta, \phi) = R(r)\, Y(\theta, \phi) \qquad (4)$$

Substituting in equation (2), we have

$$\left\{ \frac{1}{r} \frac{d^2}{dr^2}(rR) + \frac{2m}{\hbar^2}(E - V(r))R \right\} Y(\theta,\phi) + \frac{R}{r^2} \wedge Y(\theta,\phi) = 0 \qquad 5$$

Dividing by RY

$$r^2 \left\{ \frac{1}{rR} \frac{d^2}{dr^2}(rR) + \frac{2m}{\hbar^2 R}(E - V)R \right\} = - \frac{\wedge Y(\theta,\phi)}{Y(\theta,\phi)} = \lambda \qquad 5$$

where we have set the terms equal to a constant λ because the left side of eqn. (6) depends only on r, while the other terms depend only on θ and ϕ.

Set $r R(r) = u(r)$ $\qquad R = \frac{u(r)}{r}$

$$r^2 \left\{ \frac{d^2}{dr^2} u(r) + \frac{2m}{\hbar^2}(E - V(r))u(r) \right\} = \lambda u(r)$$

OR

$$\frac{d^2}{dr^2} u(r) + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\lambda \hbar^2}{2mr^2}\right) u(r) = 0 \qquad (8)$$

and

$$\wedge Y(\theta,\phi) = -\lambda Y(\theta,\phi) \qquad (9)$$

i.e the angular part of eqn. (9) is independent of the potential.

Note:

The operator $\wedge$ is related to the orbital angular momentum. To show this, let us remember the angular momentum operator in cartesian and spherical polar coordinates

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = -i\hbar\left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi}\right) \qquad (10)$$

↓ set $\phi = \phi - \pi/2$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = -i\hbar\left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi}\right) \qquad (11)$$

$$L_z = -ik\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -ik\frac{\partial}{\partial \phi}$$

**

$$L_x^2 + L_y^2 + L_z^2 = -k^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} = -k^2\Lambda \qquad 13$$

For convenience we introduce the operators

$$L_+ = L_x + iL_y = -ik\left\{ie^{i\phi}\frac{\partial}{\partial\theta} - \cot\theta\, e^{i\phi}\frac{\partial}{\partial\phi}\right\} \qquad 14$$

$$L_- = L_x - iL_y = -ik\left\{-ie^{-i\phi}\frac{\partial}{\partial\theta} - \cot\theta\, e^{-i\phi}\frac{\partial}{\partial\phi}\right\} \qquad 14'$$

Thus the solution of equation (9) is just the problem of determining the eigenvalues of the angular momentum operator.

Writing $$Y(\theta,\phi) = \Theta(\theta)\cdot\Phi(\phi) \qquad 15$$

we have, after separation of variables in equation (9),

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{\sin^2\theta}{\Theta(\theta)}\left\{\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\Theta\right\} = m^2 \qquad 16$$

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$$x = r\sin\theta\cos\phi \qquad r = \sqrt{x^2+y^2+z^2}$$

$$y = r\sin\theta\sin\phi \qquad \theta = \cos^{-1}\frac{z}{r}$$

$$z = r\cos\theta \qquad \phi = \tan^{-1}\frac{y}{x}$$

and

$$\frac{\partial}{\partial q_i} = \frac{\partial}{\partial r}\cdot\frac{\partial r}{\partial q_i} + \frac{\partial}{\partial\theta}\cdot\frac{\partial\theta}{\partial q_i} + \frac{\partial}{\partial\phi}\cdot\frac{\partial\phi}{\partial q_i}$$

$i = 1, 2, 3$

$q_1 = x,\ q_2 = y,\ q_3 = z$

$0 \le \theta \le \pi \qquad 0 \le \phi \le 2\pi \qquad 0 \le r \le \infty$

The volume integral

$$\iiint f(x,y,z)\,dx\,dy\,dz = \iiint g(r,\theta,\phi)\left|\frac{\partial(x,y,z)}{\partial(r,\theta,\phi)}\right| dr\,d\theta\,d\phi$$

↑ Jacobian.

we have set each side equals to a positive constant m^2 so that the solution of Φ will be periodic in ϕ.

So

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \rightarrow \Phi = A e^{im\phi} \quad m: 0, \pm 1, \ldots$$

Since $\int_0^{2\pi} \Phi^* \Phi \, d\phi = 1 \rightarrow \int_0^{2\pi} A^2 \, d\phi = 1 \quad A = \frac{1}{\sqrt{2\pi}}$

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$m = 0, \pm 1, \ldots$ comes from the periodicity of the function as follows

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

So

$$1 = e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m$$

$$\cos 2\pi m = 1 \rightarrow 2\pi m = 2\pi n \Rightarrow m = n.$$

$n: 0, \pm 1, \ldots$

From equation (16)

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \lambda\Theta - \frac{m^2}{\sin^2\theta}\Theta = 0 \qquad 19$$

Set $\cos\theta = \mu$ and $F(\mu) = \Theta(\theta)$ we obtain

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{dF}{d\mu}\right] + \left[\lambda - \frac{m^2}{1-\mu^2}\right]F(\mu) = 0 \qquad 20$$

For $m=0$, this equation is reduced to Legendre equation

$$(1-\mu^2)\frac{d^2P}{d\mu^2} - 2\mu\frac{dP}{d\mu} + \lambda P = 0 \qquad (21)$$

If we try to solve this equation using power series method, namely

$$P(\mu) = \sum_{r=0}^{\infty} a_r \mu^{r+s}$$ you can put $s=0$

we have from 21

$$\sum a_r (s+r)(s+r-1)\mu^{s+r-2} - \sum a_r (s+r)(s+r-1)\mu^{s+r} -$$

$$-2\sum a_r (s+r)\mu^{s+r} + \lambda \sum a_r \mu^{s+r} = 0 \qquad (22)$$

The indicial equation is

$$s(s-1) = 0,$$

which has the roots $s = 0, 1$,
and $s = 0$ provides all the necessary independent solutions.
The corresponding recurrence relation is

$$a_{r+2} = \frac{r(r+1) - \lambda}{(r+1)(r+2)} a_r \xrightarrow[r\to\infty]{} a_r \qquad (23)$$

Thus if the series does not terminate, it will diverge for values of $\mu = \pm 1$. However, if we assume it could terminate at $r = \ell$, say, we get

$$\lambda = r(r+1) = \ell(\ell+1) \qquad \ell = 0, 1 \ldots \qquad (24)$$

and the series will stop at $a_\ell \mu^\ell$ and the resulting polynomial is the Legendre polynomial. $P_\ell(\mu)$. The first few legendre polynomial are

$$P_0(\mu) = 1$$

$$P_1(\mu) = \mu \qquad P_2(\mu) = \frac{1}{2}(3\mu^2 - 1)$$

A concise expression for $P_\ell(\mu)$ is given by

$$P_\ell(\mu) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\mu^\ell} (\mu^2 - 1)^\ell \qquad \ell = 0, 1, \ldots$$

and has the following orthonormalization property

$$\int_{-1}^{1} P_\ell(\mu) P_m(\mu) \, d\mu = \frac{2}{2\ell+1} \delta_{\ell m}$$

Thus, the solution of equation (19), <u>for $m = 0$</u>, is given by

$$\Theta(\theta) = P_\ell(\cos\theta) \qquad (26)$$

In order to obtain the solution of equation (20) for $m \neq 0$

we note that if we differentiate (21) m-times, we obtain

$$(1-\mu^2)\frac{d^2}{d\mu^2}P^{(m)} - 2(m+1)\frac{d}{d\mu}P^m + (\lambda - m(m+1))P^{(m)} = 0 \qquad 27$$

where

$$P^{(m)} = \frac{d^m}{d\mu^m}P \qquad m>0$$

we use Leibniz's theorem for the m^{th} derivative of a product of two functions

$$\frac{d^m}{dx^m}(f(x)g(x)) = \sum_{k=0}^{m}\binom{m}{k}\frac{d^k}{dx^k}f(x)\frac{d^{m-k}}{dx^{m-k}}g(x).$$

In our case $f(\mu) = 1-\mu^2$, $g(\mu) = \frac{d^2}{d\mu^2}P$

For the first term in (21)

$$\binom{m}{0}f(\mu)\frac{d^m}{\partial\mu^m}g(\mu) + \binom{m}{1}\frac{d}{d\mu}f(\mu)\cdot\frac{d^{m-1}}{d\mu^{m-1}}g(\mu) + \binom{m}{2}\frac{d^2}{d\mu^2}f\frac{d^{m-2}}{d\mu^{m-2}}g(\mu)$$

For the second term $f(\mu) = \mu$, $g(\mu) = \frac{dP}{d\mu}$

$$\binom{m}{0}f(\mu)\frac{d^m}{\partial\mu^m}g(\mu) + \binom{m}{1}\frac{d}{d\mu}f(\mu)\cdot\frac{d^{m-1}}{d\mu^{m-1}}g(\mu)$$

So we get

$$(1-\mu^2)\frac{d^{m+2}}{\partial\mu^{m+2}}P + \frac{m!}{1!(m-1)!}(-2\mu)\frac{\partial^{m+1}}{\partial\mu^{m+1}}P + \frac{m!}{2!(m-2)!}(-2)\frac{d^mP}{d\mu^m}$$

$$-2\mu\frac{d^{m+1}}{d\mu^{m+1}}P - 2m\frac{d^m}{d\mu^m}P + \lambda\frac{d^m}{\partial\mu^m}P = 0$$

or

Setting $P^{(m)} = \frac{d^m}{\partial\mu^m}P$, we get

$$(1-\mu^2)\frac{d^2P^m}{d\mu^2} - 2\mu(m+1)\frac{d}{d\mu}P^m + \left[\lambda - 2m - m^2 + m\right]P^m$$

or

$$(1-\mu^2)\frac{d^2}{d\mu^2}P^m - 2(m+1)\mu\frac{d}{d\mu}P^m + \left\{\lambda - m(m+1)\right\}P^m = 0$$

which is eqn. (27)

Further in eqn. (20), if we make the substitution

$$F(\mu) = (1-\mu^2)^{m/2} G(\mu),$$

Then we will find that $G(\mu)$ satisfies the same equation as $P^m(\mu)$. Thus for $m \neq 0$, the solution of equation (20) is the associated Legendre polynomial

$$P_\ell^m(\mu) = (1-\mu^2)^{m/2} \frac{d^m}{d\mu^m} P_\ell(\mu) \qquad 28$$

which has the following orthogonality properties

$$\int_{-1}^{1} P_\ell^{(m)} P_{\ell'}^{(m)} \, d\mu = \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \delta_{\ell,\ell'}$$

Note that P_ℓ^m, equation (28) is defined only for non negative integers $m \leq \ell$. It is convenient to introduce the spherical harmonics

$$Y_{\ell m}(\theta,\phi) = (-1)^m \left\{ \frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!} \right\}^{1/2} P_\ell^m(\cos\theta)\, e^{im\phi} \quad m>0 \qquad 29$$

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$$Y_{\ell m}(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$
$$= A\, P_\ell^m(\cos\theta)\, e^{im\phi}$$

A is the normalization constant can be determined as follows

$$A^2 \int_0^\pi \sin\theta \, d\theta \, P_\ell^{m^2} P_\ell^m \int_0^{2\pi} e^{im\phi} e^{-im\phi} \, \partial\phi = 1$$

$$2\pi A^2 \int_0^\pi P_\ell^{*m} P_\ell^m \sin\theta \, d\theta = 1$$

$$2\pi A^2 \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} = 1$$

$$\Rightarrow A = \left\{ \frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!} \right\}^{1/2}$$

It is prefered to write $A = (-1)^m \left\{ \frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!} \right\}^{1/2}$ (Spherical harmonic)

$$Y_{\ell,-m} = (-1)^m Y_{\ell,m}^*$$

$\ell = 0, 1, \ldots$ $\qquad m = -\ell, -\ell+1, \ldots, 0, \ldots \ell-1, \ell$

Note $\int_0^{\pi}\int_0^{2\pi} Y_{\ell m}^{*} Y_{\ell' m'} \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}$

From eqn. (13) and (9) we obtain the eigenvalues of L^2

$$L^2 Y_{\ell m}(\theta, \phi) = -\hbar^2 \Lambda Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m} \qquad 31$$

Also from equation (12) and (29), we have

$$L_z Y_{\ell m}(\theta, \phi) = m\hbar \, Y_{\ell m}(\theta, \phi) \qquad 32.$$

The number m is called the magnetic quantum number, since the splitting of levels in a uniform magnetic field depends on m. Thus $Y_{\ell m}(\theta, \phi)$ are simultaneous eigenfunctions of L^2 and L_z. It is easy to show that they are not eigenfunctions of L_x and L_y. In fact, it is impossible to construct eigenfunctions of any but L^2 and one of the 3-components of $\vec{L}$. This follows from the fact that L_x, L_y and L_z do not commute.

Returning to equation (8) and replacing λ by $\ell(\ell+1)$, we may consider the radial motion to be similar to the one-dimensional motion of a particle in a potential

$$\dot{V}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \qquad 33$$

Now, a classical particle that has angular momentum L about the axis through the origin perpendicular to the plane of the orbit has the angular velocity $\omega = \frac{L}{mr^2}$ where r is the radial distance from the origin. The centripetal force

$$\frac{mv^2}{r} = m\omega^2 r = mr\frac{L^2}{m^2r^4} = \frac{L^2}{mr^3} \qquad L = mvr, \; v = \omega r$$

$\ell(\ell+1)\hbar^2$

is required to keep the particle in its orbit. The centripetal force is supplied by the potential energy and hence adds to the potential an additional term

$$V_{add} = -\int F_{cen} \cdot dr = -\int \frac{L^2}{mr^3} dr = \frac{L^2}{2mr^2}.$$

If we replace L^2 by $\ell(\ell+1)\hbar^2$ then

$$V_{add} = \frac{\ell(\ell+1)\hbar^2}{2mr^2}$$

which is the second term in (33)

Hydrogen Atom

Since the potential experienced by the electron in a hydrogen atom possesses a spherical symmetry, the angular part of the wavefunction is already determined. However, strictly the proton in the hydrogen atom can not be regarded as fixed to that one must reduce the two-body problem to a one body problem. This can be done as follows:
Hamiltonian in this case is given by

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\underline{r}_1 - \underline{r}_2|)$$

$$= -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|\underline{r}_1 - \underline{r}_2|) \qquad (1)$$

The subscripts 1 and 2 refer to electron and proton respectively. Schrödinger eqn. is

$$\left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|r_1 - r_2|)\right]\psi(r_1, r_2) = E\,\psi(\underline{r}_1, r_2) \qquad (2)$$

It can easily be shown that if we try to separate the variables by assuming

$$\psi(r_1, r_2) = \psi_1(r_1)\,\psi_2(r_2),$$

the variables will not separate (due to $V(|\underline{r}_1 - r_2|)$).
However if we introduce the center of gravity coordinates

$$\bar{R} = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \qquad 3$$

and the relative coordinates $\vec{r} = \bar{r}_1 - \bar{r}_2$ (4)
of the two particles, then the schrödinger equation becomes

(1)

$$\left[-\frac{\hbar^2}{2(m_1+m_2)}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(|\vec{r}|)\right]\Psi(R,r)$$

$$= E\,\Psi(R,r) \qquad (5)$$

where $\bar{R} = X\,\underline{i} + Y\,\underline{j} + Z\,\underline{k}$ $\quad \bar{E}_r + ER$

$r = x\,\underline{i} + y\,\underline{j} + z\,\underline{k}$

$\mu = \dfrac{m_1 m_2}{m_1+m_2}$ is the reduced mass.

Since the potential does not depend on R at all, we write

$$\Psi(\underline{R},\underline{r}) = \Psi(\underline{r})\,\Phi(R)$$

and the Schrödinger equation is now separable giving the following equation for Φ

$$-\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right]\Phi(R) = E_R\,\Phi \qquad (7)$$

$M = m_1+m_2$

The solution of this equation is

$$\Phi = A\exp\left(\frac{i\underline{P}.\underline{R}}{\hbar}\right) \qquad E_R = \frac{\hbar^2 P^2}{2M} \qquad 8$$

(Equation (7) represents a particle of mass M moving in potential = 0 ; free particle)

Eqn. (8) describes simply, the motion of the H_2-atom as a whole.

On the other hand, $\Psi(r)$ describes the internal motion of the atom and satisfies the equation

$$\frac{\hbar^2}{2m}\nabla_r^2\Psi + (E_r - V(r))\,\Psi(r) = 0 \qquad 9$$

where Er (relative energy) = $E - E_R$. 10

Equation (9) is, of course, the same as that for a one-body motion in a potential V(r) with the changes that the mass is the reduced mass and the coordinates are the relative coordinates.

In the H_2 - atom problem, we are interested in the relative motion and therefore we can consider the center of mass is at rest.

Now

$$\psi(r) = R(r)\, Y_{\ell,m}(\theta,\phi) = \frac{u(r)}{r} Y_{\ell,m}(\theta,\phi) \quad (11)$$

Thus setting $\lambda = \ell(\ell+1)$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{r} - \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right]R(r) = 0 \quad (12)$$

From which it is clear that $R(r)$ does not depend on the magnetic quantum number m. In equation (12) we have set

$$V(r) = -\frac{Ze^2}{r} \quad 13$$

and the nuclear charge is assumed to be Ze so that the treatment will hold for hydrogen - like systems as well.

We introduce the dimensionless variable

$$\rho = \alpha r$$

so that equation (12) becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left\{\frac{2\mu E}{\hbar^2\alpha^2} + \frac{2\mu}{\hbar^2}\frac{Ze^2}{\alpha\rho} - \frac{\ell(\ell+1)}{\rho^2}\right\}R(\rho) = 0 \quad 14$$

we choose $\alpha^2 = \frac{8\mu}{\hbar^2}|E| = -\frac{8\mu}{\hbar^2}E$ 15

(since we are interesting for energy levels corresponding to bound state ; therefore $E<0$)

and set

$$\lambda = \frac{2\mu Ze^2}{\hbar^2\alpha} = \frac{Ze^2}{\hbar^2}\left(\frac{\mu}{2|E|}\right)^{1/2}$$

Thus eqn. (14) becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\right]\underline{R(\rho)} = 0 \quad 16$$

(3)

As we did in harmonic oscillator problem, we first look for solutions valid for $\rho \to \infty$. It can be shown that for solutions:

$$R(\rho) \sim \rho^n \exp \pm \frac{1}{2}\rho$$

satisfies equation (16) for large values of ρ. This suggests that we look for a solution of the form

$$R(\rho) = F(\rho)\, e^{-\frac{1}{2}\rho}$$

On substitution we obtain

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] F(\rho) = 0 \qquad 18$$

We now try a series solution of the form

$$F(\rho) = \sum_p a_p \rho^{s+p} \qquad 19$$

Substituting this into equation (18) and equating the coefficient of lowest power of ρ, we obtain

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

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

For $s = -(\ell+1)$, $F(\rho)$ would diverge for $\rho \to 0$; thus we should reject the solution $s = -(\ell+1)$. We also obtain the following recurrence relation

$$a_{p+1} / a_p = \frac{p + \ell + 1 - \lambda}{(p+1)(p+2\ell+2)} \qquad 20$$

For large values of p, $a_{p+1}/a_p \sim \frac{1}{p}$. This is also the ratio of terms in the expansion of $\exp \rho$. Thus if the series (19) does not terminate then $F(\rho)$ will behave as $\exp \frac{1}{2}\rho$ for $\rho \to \infty$ and will diverge. We can make the series terminate by requiring that

$$\lambda = n = n' + \ell + 1 \qquad 21$$

and $a_{n'+1} = a_{n'+2} = \ldots = 0$

Since n' and ℓ can be positive integer or zero, n can have the values $1, 2, 3, \ldots$. The number n is

is called the total quantum number

Using equations (15) and (21) we obtain

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad n = 1, 2, \ldots \qquad 22$$

Equation (22) gives the energy levels of the hydrogen atom. Before the development of quantum mechanics, it was known from experimental studies of the hydrogen atom spectrum, that the energy levels are given by

$$E_n = -E_R \frac{1}{n^2} \qquad n = 1, 2, \ldots \qquad 23$$

and from observation E_R was found to be 13.6 eV. Bohr then devised a model which gave equation (23) and predicted E_R should be $me^4/2\hbar^2$

The corresponding eigenfunctions are related to the associated Legendre polynomials. The complete solution is

$$\psi_{n,l,m}(\vec{r}) = R_{nl}(r)\, Y_{l,m}(\theta, \phi) \qquad 24$$

and the first few $R_{n,l}$ are given by

$$R_{10} = \left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-Zr/a_0}$$

$$R_{20} = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} \qquad 25$$

where

$a_0 = \frac{\hbar^2}{\mu e^2}$ is known as Bohr radius

The normalization constants are such that

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1 \qquad 26$$

For the ground state, the wavefunction is spherically symmetric

$$\psi_{100} = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} 2 \exp -\frac{r}{a_0} \qquad (Z=1)$$

Thus $P(r)\,dr$ represents the probability of finding the electron in the shell between r and $r+dr$, then

$$P(r) = \frac{4r^2}{a_0^3} e^{-2r/a_0} \qquad \left[\int_0^\infty P(r)\,dr = 1\right]$$

Thus $P(r) = 0$ at $r=0$ and $r=\infty$ and is maximum at $r = a_0$, implying that the position of the electron is not certain, but we can say that the probability for finding the electron at a certain distance is largest if the distance is at Bohr radius; this is consistent with the uncertainty principle.

From equation (22), we see that the energy depends only on the total quantum number n. Since for each n we have values of l ranging from 0 to $n-1$ and of m from $-l$ to l; there are

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \qquad \text{states } \psi_{n,lm}$$

belonging to a particular energy. The degeneracy with respect to m is due to spherical symmetry. But the l degeneracy is peculiar to the Coulomb field and is removed for alkali atoms for which the valence electron experiences a potential somewhat different from Coulomb potential.

* i $n' = n-l-1$ is called the radial quantum number
ii The wavefunction corresponding to distnict set of values for n, l, m are independent.
iii principal quantum no $n = 1, 2, \ldots$ K, L, M, ..
iv Azimuthal quantum no $l = 0, 1, \ldots n-1$ S, P, D, ..
v orbital magnetic q. numbers $m = -l, -l+1, \ldots, 0, \ldots l-1, l$

To prove equation (5)

In classical mechanics, the energy of a system consisting of two interacting particle is

$$E = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + U(r)$$

where

m_1 and m_2 are the masses of particles, P_1 and P_2 are their momenta, $U(r)$ is the energy of interaction and r is the distance between the particles. Accordingly, the Hamiltonian of the system has the form

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + U(r)$$

$\nabla_{1,2}^2$ is the second partial derivatives with respect to the coordinates of the first and the second particle.

let us replace $\vec{r_1}$ and $\vec{r_2}$ by $\vec{r}$ (the mutual arrangement of the particles) and the position vector $\vec{r_c}$ of the center of mass of the system, where

$$\bar{r} = \bar{r_2} - \bar{r_1} \quad , \quad \bar{r_c} = \frac{m_1\bar{r_1} + m_2\bar{r_2}}{m_1 + m_2}$$

i.e.

$$x = x_2 - x_1 \qquad x_c = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial x}\cdot\frac{\partial x}{\partial x_1} + \frac{\partial}{\partial x_c}\cdot\frac{\partial x_c}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{m_1}{m_1+m_2}\frac{\partial}{\partial x_c}$$

$$\frac{\partial^2}{\partial x_1} = \left(-\frac{\partial}{\partial x} + \frac{m_1}{m_1+m_2}\frac{\partial}{\partial x_c}\right)^2$$

$$= \frac{\partial^2}{\partial x^2} - \frac{2m_1}{m_1+m_2}\frac{\partial^2}{\partial x\,\partial x_c} + \frac{m_1^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial x_c^2}$$

Similarly

$$\frac{\partial}{\partial x_2} = \frac{\partial}{\partial x}\cdot\frac{\partial x}{\partial x_2} + \frac{\partial}{\partial x_c}\frac{\partial x_c}{\partial x_2} = \frac{\partial}{\partial x} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial x_c}$$

$$\frac{\partial^2}{\partial x_2^2} = \left(\frac{\partial}{\partial x} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial x_c}\right)\left(\frac{\partial}{\partial x} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial x_c}\right)$$

$$= \frac{\partial^2}{\partial x^2} + \frac{2m_2}{(m_1+m_2)}\frac{\partial^2}{\partial x_c \partial x_i} + \frac{m_2^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial x_c^2}$$

Thus $$\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2} = \left(\frac{1}{m_1}+\frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} + \frac{1}{m_1+m_2}\frac{\partial^2}{\partial x_c^2}$$

$$= \frac{1}{\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{M}\frac{\partial^2}{\partial x_c^2}$$

$$H = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_c^2 + U(r)$$

i.e The Hamiltonian breaks up into two Hamiltonians

a) One contains the total mass of the system and the position vector of the center of mass

b) the other contains the reduced mass and the vector of the mutual arrangement.