PLENUM 12/21/2011

Particle in Central Potential, Spherical Polar Coordinates, Radial Momentum, Spherical Harmonics

Schrödinger equation of a particle of mass m in central potential $V(r)$

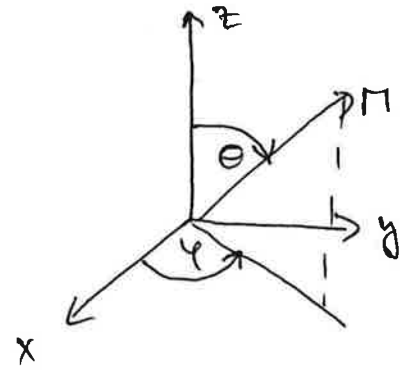
$\underline{p}$: momentum of particle

$\underline{r}$: its position

time-independent Schrödinger equation:

$$H\psi(\underline{r}) \equiv \left[-\frac{\hbar^2}{2m}\Delta + V(r)\right]\psi(\underline{r}) = E\psi(\underline{r})$$

- the Hamiltonian has spherical symmetry, we can study the problem in spherical coordinates
- we choose the z axis to be the polar axis; the cartesian coordinates (x, y, z) are given as functions of the polar coordinates (r, θ, φ)



$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$

- the expression of the potential energy as a function of polar coordinates is already given
- we want to find the expression for the kinetic energy $\frac{p^2}{2m}$, that is to express in polar coordinates the differential operator:

$$-\frac{\hbar^2}{2m}\Delta \equiv -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

- this can be done directly by means of the transformation formulae by the usual techniques of differential calculus

- BUT, in order to better grasp the physical significance of the result, we shall seek to express the kinetic energy: $\frac{p^2}{2m}$ not as function of the differential operators $\frac{\partial}{\partial r}, \frac{\partial}{\partial \theta}, \frac{\partial}{\partial \varphi}$ themselves, but as function of Hermitean operators constructed with these differential operators whose physical interpretation is more apparent
- hence, rather than using the differential operator $\frac{\partial}{\partial \varphi}$ directly, it's better to use the component of the angular momentum along the z axis, which has the explicit form:

$$L_z \equiv x p_y - y p_x \equiv \frac{\hbar}{i}\left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) = (*)$$

$$\frac{\partial x}{\partial \varphi} = -r \sin\theta \sin\varphi = -y$$

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

$$\frac{\partial z}{\partial \varphi} = 0$$

$$(*) = \frac{\hbar}{i}\left(\frac{\partial y}{\partial \varphi}\frac{\partial}{\partial y} + \frac{\partial x}{\partial \varphi}\frac{\partial}{\partial x} + \frac{\partial z}{\partial \varphi}\frac{\partial}{\partial z}\right) = \frac{\hbar}{i}\frac{\partial}{\partial \varphi}$$

[Noting that

$$\frac{\partial}{\partial \alpha} = \left(\frac{\partial r}{\partial \alpha}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial \alpha}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial \alpha}\right)\frac{\partial}{\partial \varphi}]$$

- since $V(r)$ does not depend on φ, it's clear that L_z commutes with the potential energy
- however, L_z also commutes with the kinetic energy $\frac{p^2}{2m}$ as one can easily verify by using the definition of L_z & the commutation relations: $[r_i, p_j] = i\hbar\delta_{ij}$

Exercise #1: Show that

$$[L_j, x_k] = i\hbar\, \varepsilon_{jkl}\, x_l$$

$$[L_j, p_k] = i\hbar\, \varepsilon_{jkl}\, p_l$$

& thus

$$[L_j, r^2] = [L_j, p^2] = 0$$

Proof: $L_j = \varepsilon_{jrs}\, x_r p_s$

$$[L_j, x_k] = \varepsilon_{jrs}\, [x_r p_s, x_k] =$$

$$= \varepsilon_{jrs}\left(x_r p_s x_k - x_r x_k p_s + x_r x_k p_s - x_k x_r p_s \right) =$$

$$= \varepsilon_{jrs}\, x_r \underbrace{[p_s, x_k]}_{\frac{\hbar}{i}\delta_{sk}} + \varepsilon_{jrs} \underbrace{[x_r, x_k]}_{0} p_s =$$

$$= \frac{\hbar}{i}\varepsilon_{jrk}\, x_r = i\hbar\, \varepsilon_{jkl}\, x_l \quad \square$$

$[L_j, p_k] = \ldots$ the same way as above

Consequence #1

$$[L_j, r^2] = [L_j, x_k x_k] = L_j x_k x_k - x_k L_j x_k + x_k L_j x_k$$

$$- x_k^2 L_j = [L_j, x_k]\, x_k + x_k [L_j, x_k] = 2 i\hbar\, \varepsilon_{ijk}\, x_i x_k$$

$$= -2i\hbar\, (\underline{r} \times \underline{r})_j = 0$$

Consequence #2

$$[L_j, p^2] = [L_j, p_k p_k] = [L_j, p_k] + p_k [L_j, p_k] =$$

$$= 2i\hbar\, (p \times p)_j = 0 \quad \square$$

using that $[A, B^{-1}] = -B^{-1} [A, B]\, B^{-1}$

$$\Rightarrow [L_i, \tfrac{1}{r^2}] = -\frac{1}{r^2} [L_i, r^2] \frac{1}{r^2} = 0$$

$$[L_i, r] = \frac{\hbar}{i} \varepsilon_{ijk} [x_j \partial_k, (x_e x_e)^{1/2}] =$$

$$= \frac{\hbar}{i} \varepsilon_{ijk} [x_j \partial_k (x_e x_e)^{1/2} - r x_j \partial_k] = (**)$$

$$\partial_k r = \partial_k (x_e x_e)^{1/2} = \frac{1}{2} \frac{\delta_{ke} x_e 2}{(x_e x_e)^{1/2}} = \frac{x_k}{r}$$

$$(**) = \frac{\hbar}{i} \varepsilon_{ijk} \frac{x_j x_k}{r} = \frac{\hbar}{i} \frac{(\underline{r} \times \underline{r})_i}{r} = 0$$

$$[L_i, r] = 0 \implies [L_i, \tfrac{1}{r}] = 0$$

In the same spirit as using L_z, we use the radial momentum

$$p_r \equiv \frac{\hbar}{i} \frac{1}{r} \frac{\partial}{\partial r} r = \frac{\hbar}{i} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right)$$

rather than the operator $\frac{\hbar}{i} \frac{\partial}{\partial r}$ which is not Hermitean

---

Exercise #2: Show that

$$\boxed{\frac{\underline{r}}{r} \underline{p} + \frac{\hbar}{i} \frac{1}{r} = \frac{1}{2} \left(\frac{\underline{r}}{r} \underline{p} + \underline{p} \frac{\underline{r}}{r} \right)} \equiv p_r$$

Right Hand Side =

$$= \frac{1}{2} \frac{\underline{r}}{r} \underline{p} + \frac{\hbar}{2i} \left[\frac{\partial}{\partial x} \left(\frac{x}{r} \right) + \frac{\partial}{\partial y} \left(\frac{y}{r} \right) + \frac{\partial}{\partial z} \left(\frac{z}{r} \right) \right] =$$

$$= (***)$$

$$\frac{\partial}{\partial x} \frac{x}{\sqrt{x^2+y^2+z^2}} = \frac{r - x \frac{x}{r}}{r^2}$$

$$\implies (***) = \frac{1}{2} \frac{\underline{r}}{r} \underline{p} + \frac{\hbar}{2i} \left(\frac{3r - \frac{r^2}{r}}{r^2} \right) + \frac{1}{2} \frac{\underline{r}}{r} \underline{p} =$$

$$= \boxed{\frac{\underline{r}}{r} \underline{p} + \frac{\hbar}{i} \frac{1}{r} = p_r}$$

$\square$

$$\underline{r} \cdot \underline{p} = \left(x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) \frac{\hbar}{i}$$

Claim: $x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} = r \frac{\partial}{\partial r}$

Proof:

$$r\frac{\partial}{\partial r} = r\left(\frac{\partial x}{\partial r}\frac{\partial}{\partial x} + \frac{\partial y}{\partial r}\frac{\partial}{\partial y} + \frac{\partial z}{\partial r}\frac{\partial}{\partial z}\right) =$$

$$= r\left(\sin\theta\cos\varphi\frac{\partial}{\partial x} + \sin\theta\sin\varphi\frac{\partial}{\partial y} + \cos\theta\frac{\partial}{\partial z}\right) =$$

$$= x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}$$

$$\Rightarrow \underline{r}\cdot\underline{p} = r\frac{\hbar}{i}\frac{\partial}{\partial r} = r p_r - \frac{\hbar}{i} = r p_r + i\hbar$$

Thus in fact we have

$$p_r = \frac{\hbar}{i}\left(\frac{1}{r} + \frac{\partial}{\partial r}\right) = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r \quad \square$$

Claim: p_r is Hermitean

Proof: To establish the Hermitean property of p_r, let us examine under which condition the expression $\langle\psi|p_r\psi\rangle$ (in which $\psi(\underline{r})$ is any square integrable function) is real. One must have that:

$$\langle\psi|p_r\psi\rangle = \langle p_r\psi|\psi\rangle = \langle\psi|p_r\psi\rangle^*$$

that is

$$0 = \langle\psi|p_r\psi\rangle - \langle\psi|p_r\psi\rangle^*$$

$$\equiv \int[\psi^*(p_r\psi) - (p_r\psi)^*\psi]\,d\underline{r}$$

$$= \frac{\hbar}{i}\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi\int_0^\infty\left\{\psi^*\left[\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)\psi\right]r^2 + \right.$$

$$\left. + \left[\left(\frac{\partial}{\partial r}+\frac{1}{r}\right)\psi^*\right]\psi r^2\right\}dr = \frac{\hbar}{i}\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi$$

$$\times\int_0^\infty\left[|\psi|^2 r + \psi^*(\partial_r\psi)r^2 + |\psi|^2 r + (\partial_r\psi^*)\psi r^2\right]dr$$

$$= \frac{\hbar}{i}\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi\int_0^\infty\left[2r|\psi|^2 + (\partial_r\psi^*)\psi r^2 + \right.$$

$$\left. + \psi^*(\partial_r\psi)r\right]dr = \frac{\hbar}{i}\int_0^\pi\sin\theta\,d\theta\int_0^{2\pi}d\varphi\int_0^\infty\left[\frac{\partial}{\partial r}|r\psi|^2\right]dr$$

Since $r\psi$ vanishes as $r\to\infty$, the integral with respect to r is = to its value taken at the origin

$\Rightarrow$ the operator p_r is Hermitean only if one restricts oneself to square-integrable functions subject to the condition:

$$\lim_{r\to 0} r\,\psi(r) = 0$$

Definition of the Spherical Harmonics $Y_l^m(\theta,\varphi)$

Eigenfunctions common to the operators $\underline{L}^2$ & L_z

$$\underline{L}^2\, Y_l^m = \hbar^2 l(l+1)\, Y_l^m$$

$$L_z\, Y_l^m = \hbar m\, Y_l^m$$

$(l = 0, 1, 2, \ldots, \infty\ ;\ m = -l, -l+1, \ldots, l)$

One completes their definition by adopting the conventions

a) Y_l^m are normalized to unity on the unit sphere

b) their phases are such that the recursion relations:

$$L_\pm\, Y_l^m = \left[l(l+1) - m(m\pm 1)\right]^{1/2} Y_l^{m\pm 1}$$

$$= \left[(l\mp m)(l+1\pm m)\right]^{1/2} Y_l^{m\pm 1}$$

are satisfied & $Y_l^0(0,0)$ is real & positive

Orthonormality & Closure Relations

$$\int Y_l^{m*}\, Y_{l'}^{m'}\, d\Omega \equiv \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta\; Y_l^{m*}(\theta,\varphi)\, Y_{l'}^{m'}(\theta,\varphi) =$$

$$= \delta_{mm'}\,\delta_{ll'}$$

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_l^{m*}(\theta,\varphi)\, Y_l^m(\theta,\varphi) = \frac{\delta(\theta-\theta')\,\delta(\varphi-\varphi')}{\sin\theta} \equiv \delta(\Omega-\Omega')$$

The Y_l^m form a complete set of orthonormal, square integrable functions on the unit sphere.

Recursion Relations

$$L_\pm Y_\ell^m = [\ell(\ell+1) - m(m\pm 1)]^{1/2} Y_\ell^{m\pm 1}$$
$$= [(\ell \mp m)(\ell + 1 \pm m)]^{1/2} Y_\ell^{m\pm 1}$$

$$\cos\theta\, Y_\ell^m = \left[\frac{(\ell+1+m)(\ell+1-m)}{(2\ell+1)(2\ell+3)}\right]^{1/2} Y_{\ell+1}^m + $$
$$+ \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{1/2} Y_{\ell-1}^m$$

Parity

– under space reflection $(\theta,\varphi) \to (\pi-\theta, \varphi+\pi)$

$$Y_\ell^m(\pi-\theta, \varphi+\pi) = (-)^\ell Y_\ell^m(\theta,\varphi)$$

Complex Conjugation

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

Connection with the Associated Legendre Functions $(m \geq 0)$

$$Y_\ell^m(\theta,\varphi) = (-)^m \left[\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}\right]^{1/2} P_\ell^m(\cos\theta)\, e^{im\varphi}$$

Y_ℓ^m is the product of $e^{im\varphi} \sin^{|m|}\theta$ & a polynomial of degree $(\ell - |m|)$ in $\cos\theta$ & parity $(-)^{\ell-m}$

In particular

$$m = 0: \quad Y_\ell^0 = \sqrt{\frac{2\ell+1}{4\pi}}\, P_\ell(\cos\theta)$$

$$m = \ell: \quad Y_\ell^\ell = (-1)^\ell \left[\frac{(2\ell+1)}{4\pi}\frac{(2\ell)!}{2^{2\ell}(\ell!)^2}\right]^{1/2}$$
$$\times \sin^\ell\theta\, e^{i\ell\varphi}$$

1st Few Spherical Harmonics

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \; ; \; Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \; ; \; Y_2^0 = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$$

$$Y_3^0 = \sqrt{\frac{7}{16\pi}} \left(5\cos^3\theta - 3\cos\theta\right)$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\varphi} \; ; \; Y_2^1 = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{i\varphi}$$

$$Y_3^1 = -\sqrt{\frac{21}{64\pi}} \sin\theta \left(5\cos^2\theta - 1\right) e^{i\varphi}$$

$$Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{2i\varphi} \; ; \; Y_3^2 = \sqrt{\frac{105}{32\pi}} \sin^2\theta \cos\theta \, e^{i\varphi}$$

$$Y_3^3 = -\sqrt{\frac{35}{64\pi}} \sin^3\theta \, e^{3i\varphi}$$

$\vdots$

The Spectrum of $\underline{L}^2$ & L_z

- we want to find the function $F_\ell^m(\theta, \varphi)$, that satisfies the 2 eigenvalue equations: ($\hbar = 1$ units)

(1) $\underline{L}^2 F_\ell^m(\theta, \varphi) = \ell(\ell+1) F_\ell^m(\theta, \varphi)$

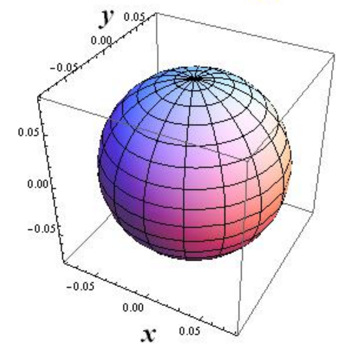
(2) $L_z F_\ell^m(\theta, \varphi) = m F_\ell^m(\theta, \varphi)$

- since $\forall$ wave function is a single-valued function of $\underline{r}$, $F_\ell^m(\theta, \varphi)$ must remain unchanged when φ is replaced with $\varphi + 2\pi$
- since $L_z = -i\frac{\partial}{\partial\varphi} \Rightarrow F_\ell^m(\theta, \varphi)$ is necessarily of the form $f_\ell^m(\theta)\, e^{im\varphi}$ with m integer
- since m is integer $\Rightarrow$ ℓ must also be integer (there's no half-integral orbital angular momentum)

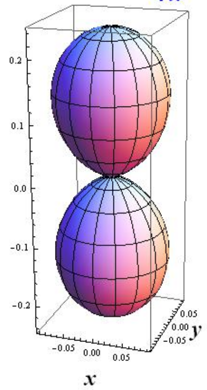
...

Source: A. Messiah, Quantum Mechanics, Dover Publication

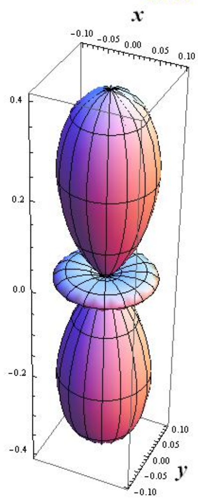
$$\{l=0, m=0, \frac{1}{4\pi}\}$$



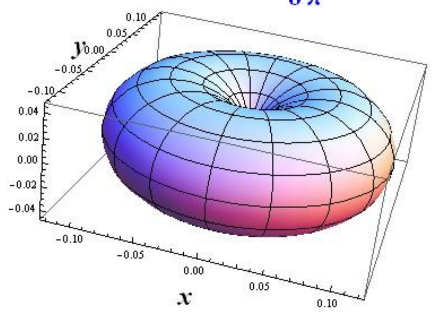
$$\{l=1, m=0, \frac{3\cos(\theta)\cos(\theta)^{*}}{4\pi}\}$$



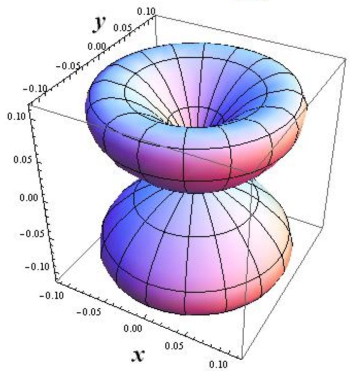
$$\{l=2, m=0, \frac{5\left(3\cos^2(\theta)-1\right)\left(3\left(\cos(\theta)^{*}\right)^2-1\right)}{16\pi}\}$$



$$\{l=1, m=1, \frac{3\, e^{i\phi - i\phi^{*}}\sin(\theta)\sin(\theta)^{*}}{8\pi}\}$$



$$\{l=2, m=1, \frac{15\, e^{i\phi - i\phi^{*}}\sin(\theta)\cos(\theta)\left(\cos(\theta)\sin(\theta)\right)^{*}}{8\pi}\}$$



$$\{l=2, m=2, \frac{15\, e^{2i\phi - 2i\phi^{*}}\sin^2(\theta)\left(\sin(\theta)^{*}\right)^2}{32\pi}\}$$