Chapter 9

Schrodinger Equation in Three Dimension. (Hydrogen Atom)

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z,t)+V(x,y,z,t)\psi(x,y,z,t)$$

$$=i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t)$$

$\psi(x,y,z,t)$ = wave function.

$|\psi(x,y,z,t)|^2\,dx\,dy\,dz$ = probability of finding the "electron"

in the volume element between x and $x+dx$, y and $y+dy$, z and $z+dz$ at time t

$= |\psi|^2 d^3r = |\psi|^2 dV$

In more compact notation, it can be written as

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

$$\Rightarrow \quad H\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$H=-\frac{\hbar^2}{2m}\nabla^2+V$$

For $V(\vec{r},t)=V(\vec{r})$ time independent potential, the problem can be solved by the method of seperation of variable

$$\psi(\vec{r},t)=u(\vec{r})e^{-iEt/\hbar}$$

with $u(\vec{r})$ satisfies the time-independent Schrodinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u(x,y,z)+V(x,y,z)u(x,y,z)$$

$$=E\,u(x,y,z)$$

If $V(x,y,z)=V_1(x)+V_2(y)+V_3(z)$, then

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)u(x,y,z)+(V_1(x)+V_2(y)+V_3(z))$$

$$u(x,y,z)=E\,u(x,y,z)$$

Ansatz: $u(x,y,z)=X(x)Y(y)Z(z)$

Substitute into the above equation

$$-\frac{\hbar^2}{2m}YZ\frac{d^2}{dx^2}X-\frac{\hbar^2}{2m}XZ\frac{d^2}{dy^2}Y-\frac{\hbar^2}{2m}XY\frac{d^2}{dz^2}Z$$

$$+ \; V_1(x)XYZ + V_2(y)XYZ + V_3(z)XYZ = EXYZ$$

Divide through by XYZ and rearrange

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2}{dx^2}X + V_1(x) = \frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2}{dy^2}Y + \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2}Z - V_2(y)$$

$$- V_3(z) + E$$

LHS is function of x only
RHS is function of y, z only

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

$$+\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y + \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2}Z - V_2(y) - V_3(z) + E = E_x$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y + V_2(y) = \frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2} - V_3(z) + E - E_x$$

LHS is function of y only
RHS is function of z alone

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

and $$-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2}{dz^2} + V_3(z) = E - E_x - E_y = E_z$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) + V_1(x)X(x) = E_x X(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}Y(y) + V_2(y)Y(y) = E_y X(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}Z(z) + V_3(z)Z(z) = E_z Z(z)$$

with $E = E_x + E_y + E_z$

The problem is reduced to solve three one dimensional Schrodinger equations.

Example: three dimensional infinite well problem

$$V_1(x) = \begin{cases} 0 & \text{for } 0 < x < L_1 \\ \infty & \text{for } x > L_1 , \; x < 0 \end{cases}$$

$$V_2(y) = \begin{cases} 0 & \text{for } 0 < y < L_2 \\ \infty & \text{for } y > L_2 , \; y < 0 \end{cases}$$

$$V_3(z) = \begin{cases} 0 & \text{for } 0<z<L_3 \\ \infty & \text{for } z>L_3,\ z<0 \end{cases}$$

$$\mathcal{X}(x) = A_1 \sin kx + B \cos kx \quad \text{in} \quad 0<x<L_1$$

$$\frac{\hbar^2 k^2}{2m} = E_x$$

$$= 0 \quad \text{in} \quad x<0,\ x>L_1$$

Boundary condition $\mathcal{X}(0)=0 \Rightarrow B=0$

$\mathcal{X}(L_1)=0 \Rightarrow k_n L_1 = n\pi$

$\Rightarrow k_n = \frac{n\pi}{L_1}$ $n_x =$ integers.

$\Rightarrow \mathcal{X}(x) = A_n \sin \frac{n\pi}{L_1} x$ with $n_x =$ integrals in $0<x<L_1$

Normalization $|A_n|^2 \int_0^{L_1} \sin^2 \frac{n\pi}{L_1} x \, dx = 1.$

$$A_n = \sqrt{\frac{2}{L_1}}$$

$$E_{x,n_x} = \frac{\hbar^2 n_x^2 \pi^2}{2mL_1^2}$$

The same method can be used to solve the y, z equation

$$\Rightarrow u_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{2^3}{L_1L_2L_3}} \sin \frac{n_x \pi x}{L_1} \sin \frac{n_y \pi y}{L_2} \sin \frac{n_z \pi z}{L_3}$$

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

$$E = E_{n_x} + E_{n_y} + E_{n_z} = \frac{\hbar^2\pi^2 n_x^2}{2mL_1^2} + \frac{\hbar^2\pi^2 n_y^2}{2mL_2^2} + \frac{\hbar^2\pi^2 n_z^2}{2mL_3^2}$$

Degeneracy : number diffent wave functions with same energy
↓
linear independent

Example : for the case $L_1 = L_2 = L_3 = L$

$$E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Clearly, $n_x=2,\ n_y=1,\ n_z=1$, $n_x=1,\ n_y=2,\ n_z=1$ and $n_x=1,\ n_y=1,\ n_z=2$ will have the

$\Rightarrow$ these three states are said to be degenerate.
the number of degeneracy $= 3$.

· This is an important concept that we shall encount ofter
· From this example, it can be seen the concept of degeneracy is closely related to symmetry.

Central force problem. $V(x,y,z) = V(r)$

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

Obviously, it is more convenient to use the spherical coordinate

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

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

$$+ V(r)\psi = E\psi$$

[$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$
are proved in various books on mathematical physics.
In the Appendix A]

Since $V(r)$ is a function of r only, we shall try to solve the problem using the method of seperation of variable

$\psi(r,\theta,\phi) \rightarrow$ time independent wave function

[$\psi(r,\theta,\phi,t) = \psi_E(r,\theta,\phi)e^{-iEt/\hbar}$]

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

Substitute into the time-independent Schrodinger equation

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R^2}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$+ V(r)RY = ERY$$

Divide by YR and rearrange. (multiple $-\frac{2mr^2}{\hbar^2}$)

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

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

LHS is function of r only

RHS is function of θ, ϕ

$\Rightarrow$ must be constant

For reasons that will appear in the due course, we shall choose the "seperation constant" to be $\ell(\ell+1)$

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

$\downarrow$

radial equation, depend on $V(r)$

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

$\downarrow$

angular equation, independent of $V(r)$

Multiply $Y\sin^2\theta$

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

Again, try seperation of variables

Ansatz $\quad Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

Put it into above equation, divide through by $\Theta\Phi$, and rearrange

$$\Rightarrow \frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2\theta\right]$$

$$= -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

LHS is function of θ only
RHS is function of ϕ only

$$\Rightarrow \frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2$$

$\downarrow$

θ equation

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

$\downarrow$

ϕ equation

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi$$

$$\Rightarrow \quad \Phi(\phi) = e^{im\phi}$$

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

$\downarrow$ single-valueness of the wave function

$\Rightarrow \quad e^{2\pi i m} = 1 \Rightarrow m$ must be integer.

· This is closely related to the quantization of angular momentum.

· m is known as magnetic quantum number.

Θ - equation

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0$$

Note: $m = 0, \pm 1, \pm 2, \cdots$

Change variable $\quad x = \cos\theta$

[using the chain rule

$$\frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -\sin\theta\frac{d}{dx} = -\sqrt{1-x^2}\frac{d}{dx}$$

$$\sin^2\theta = 1 - x^2 \;]$$

The above equation becomes

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

$\downarrow$

associated Legendre equation.

Physical requirement:

$\Theta(x)$ must be well-behaved at $x = \pm 1$

$\Rightarrow$ l must be integers, i.e. $l = 0, 1, 2, \cdots$

m must be from $-l$ to l, i.e.,

$m = -l, -l+1, -l+2, \cdots -1, 0, +1, \cdots l-2, l-1, l$

Θ is labelled by l, m

$\Theta(x) \propto P_l^m(x) \rightarrow$ associated Legendre polynomial.

A more general discussion of Legendre equation, Legendre polynomial is given in Appendix. B.

Radial equation depends on the $V(r)$ given, and will be discussed later.

(Orbital) Angular Momentum

$$\vec{L} = \vec{r} \times \vec{p} \rightarrow -i\hbar\, \vec{r} \times \nabla$$

In Cartesian coordinate

$$\vec{L} = \begin{vmatrix} i & j & k \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

$$L_x = y P_z - z P_y = -i\hbar\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right)$$

$$L_y = z P_x - x P_z = -i\hbar\left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right)$$

$$L_z = x P_y - y P_y = -i\hbar\left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z}\right)$$

Commutators between the angular momentum components

$$L_x L_y - L_y L_x = i\hbar L_z$$

$$L_y L_z - L_z L_y = i\hbar L_x$$

$$L_z L_x - L_x L_z = i\hbar L_y$$

Write in compact form

$$[L_i, L_j] = i\hbar\, \epsilon_{ijk} L_k$$

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } i, j, k \text{ is even permutation of } 1, 2, 3 \\ -1 & \text{if } i, j, k \text{ is odd permutation of } 1, 2, 3 \\ 0 & \text{if two or more indices are equal} \end{cases}$$

Fundamental commutator

$$[x, P_x] = [y, P_y] = [z, P_z] = i\hbar$$

$$[x, P_y] = [x, P_z] = [y, P_x] = [y, P_z] = [z, P_x] = [z, P_y] = 0$$

Theorem $[A+B, C+D]$

$$= (A+B)(C+D) - (C+D)(A+B)$$

$$= AC + BC + AD + BD - CA - DA - CB - DB$$

$$= [A,C] + [B,C] + [A,D] + [B,D]$$

Theorem $[AB, C] = A[B,C] + [A,C]B$

$$[AB,C] = ABC - ACB + ACB - CAB$$

$$= A[B,C] + [A,C]B$$

Theorem $[A, BC] = [A,B]C + B[A,C]$

$$[A,BC] = ABC - BAC + BAC - BCA$$

$$= [A,B]C + B[A,C]$$

$$[L_x, L_y] = [yP_z - zP_y, zP_x - xP_z]$$

$$= \underbrace{[yP_z, zP_x]}_{(\mathrm{I})} - \underbrace{[zP_y, zP_x]}_{(\mathrm{II})} - \underbrace{[zP_y, zP_x]}_{(\mathrm{III})} + \underbrace{[zP_y, xP_z]}_{(\mathrm{IV})}$$

$$(\mathrm{I}) = [yP_z, zP_x]$$

$$= y[P_z, zP_x] + [y, zP_x]P_z$$

$$y[P_z, zP_x] = y\left([P_z, z]P_x + z\underbrace{[P_z, P_x]}_{0}\right)$$

$$[y, zP_x]P_z = \underbrace{[y,z]}_{0}P_x P_z - z\underbrace{[y, P_x]}_{0}P_z$$

$$y[P_z, z]P_x = y(-i\hbar P_x)$$

$$= -i\hbar\, yP_x$$

(II), (III) are obviously zero

$$(\mathrm{IV}) = [z P_y, x P_z]$$
$$= z \underbrace{[P_y, x P_z]}_{=0} + \underbrace{[z, x P_z]}_{=\,\underbrace{[z, x]}_{=0} P_z P_y \,+\, x \underbrace{[z, P_z]}_{=i\hbar}} P_y$$

$$[L_x, L_y] = i\hbar (x P_y - y P_x) = i\hbar L_z$$

Use similar method, we can show

$$[L_y, L_z] = i\hbar L_x$$
$$[L_z, L_x] = i\hbar L_y$$

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2$$
$$[\vec{L}^2, L_z] = [L_x^2 + L_y^2 + L_z^2, L_z]$$
$$= [L_x^2, L_z] + [L_y^2, L_z] + \underbrace{[L_z^2, L_z]}_{=0}$$

$$[L_x^2, L_z] = \underbrace{L_x [L_x, L_z]}_{L_x(-i\hbar L_y)} + \underbrace{[L_x, L_z] L_x}_{-i\hbar L_y L_x}$$

$$[L_y^2, L_z] = L_y \underbrace{[L_y, L_z]}_{=i\hbar L_x} + \underbrace{[L_y, L_z]}_{=i\hbar L_x} L_y$$
$$i\hbar L_y L_x \qquad i\hbar L_x L_y$$

$$\Rightarrow [L^2, L_z] = 0$$

Angular Momentum in Spherical Coordinate

$$L_x = yP_z - zP_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}$$

$$= \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial \phi}$$

$$\underset{\underset{r\cos\theta}{\parallel}}{z}\frac{\partial}{\partial y} = r\cos\theta\sin\theta\sin\phi\frac{\partial}{\partial r} + \cos^2\theta\sin\phi\frac{\partial}{\partial \theta} + \frac{\cos\theta\cos\phi}{\sin\theta}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}$$

$$= \cos\theta\frac{\partial}{\partial r} + \left(-\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta} + 0$$

$$y\frac{\partial}{\partial z} = r\sin\theta\sin\phi\left[\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}\right]$$

$$= r\cos\theta\sin\theta\sin\phi\frac{\partial}{\partial r} - \sin^2\theta\sin\phi\frac{\partial}{\partial \theta}$$

Put it together

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

$$L_y = zP_x - xP_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial \theta} + \left(-\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial \phi}$$

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

$$= r\cos\theta\sin\theta\cos\phi\frac{\partial}{\partial r} + \cos^2\theta\cos\phi\frac{\partial}{\partial \theta} - \frac{\cos\theta\sin\phi}{\sin\theta}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}$$

$$= \cos\theta\frac{\partial}{\partial r} + \left(-\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta} + 0$$

$$x\frac{\partial}{\partial z} = r\sin\theta\cos\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}\right)$$

$$= r\cos\theta\sin\theta\cos\phi\frac{\partial}{\partial r} - \sin^2\theta\cos\phi\frac{\partial}{\partial\theta}$$

Put it together

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

$$L_z = xP_y - yP_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}$$

$$= \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

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

$$= r\sin^2\theta\cos\phi\sin\phi\frac{\partial}{\partial r} + \sin\theta\cos\phi\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \cos^2\phi\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$y\frac{\partial}{\partial x} = r\sin^2\theta\cos\phi\sin\phi\frac{\partial}{\partial r} + \sin\theta\cos\theta\cos\phi\sin\phi\frac{\partial}{\partial\theta} - \sin^2\phi\frac{\partial}{\partial\phi}$$

Put it together

$$L_z = -i\hbar\frac{\partial}{\partial\phi} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

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

$$\cancel{L_x^2 = -\hbar^2\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)}$$

$$\sin\phi\frac{\partial}{\partial\theta}\sin\phi\frac{\partial}{\partial\theta} = \sin^2\phi\frac{\partial^2}{\partial\theta^2}.$$

$$\cot\theta\cos\phi\frac{\partial}{\partial\phi}\left(\sin\phi\frac{\partial}{\partial\theta}\right) = \cot\theta\cos\phi\sin\phi\frac{\partial^2}{\partial\theta\partial\phi}$$

$$+ \cot\theta\cos\phi\cos\phi\frac{\partial}{\partial\theta}$$

$$\sin\phi\frac{\partial}{\partial\theta}\cot\theta\cos\phi\frac{\partial}{\partial\phi}$$

$$= \sin\phi\cos\phi\cot\theta\frac{\partial^2}{\partial\theta\partial\phi} + \sin\phi\cos\phi(-\csc^2\theta)\frac{\partial}{\partial\phi}$$

$$\cot\theta\cos\phi\frac{\partial}{\partial\phi}\cot\theta\cos\phi\frac{\partial}{\partial\phi}$$

$$= \cot^2\theta\cos\phi(-\sin\phi)\frac{\partial}{\partial\phi} + \cot^2\theta\cos^2\phi\frac{\partial^2}{\partial\phi^2}$$

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

$$L_y^2 = -\hbar^2\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$-\cos\phi\frac{\partial}{\partial\theta}\left(-\cos\phi\frac{\partial}{\partial\theta}\right) = \cos^2\phi\frac{\partial^2}{\partial\theta^2}.$$

$$\cot\theta\sin\phi\frac{\partial}{\partial\phi}\left(-\cos\phi\frac{\partial}{\partial\theta}\right) = -\cot\theta\sin\phi\cos\phi\frac{\partial^2}{\partial\theta\partial\phi}$$

$$+ \cot\theta\sin^2\phi\frac{\partial}{\partial\theta}$$

$$-\cos\phi\frac{\partial}{\partial\theta}\left(\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) = -\cos\phi\sin\phi\cot\theta\frac{\partial^2}{\partial\theta\partial\phi}$$

$$-\cos\phi(\sin\phi)(-\csc^2\theta)\frac{\partial}{\partial\phi}$$

$$\cot\theta\sin\phi\frac{\partial}{\partial\phi}\left(\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) = \cot^2\theta\sin\phi\cos\phi\frac{\partial}{\partial\phi}$$

$$+ \cot^2\theta\sin^2\phi\frac{\partial^2}{\partial\phi^2}$$

$L_x^2 + L_y^2 \quad -\hbar^2 \; [\; A \;]$

A

Coefficient of $\frac{\partial^2}{\partial\theta^2}$: $\sin^2\phi + \cos^2\phi = 1$

Coefficient of $\frac{\partial^2}{\partial\theta\partial\phi}$: $\cot\theta\cos\phi\sin\phi - \cot\theta\sin\phi\cos\phi$
$= 0$

Coefficient of $\frac{\partial}{\partial\theta}$ $\cot\theta\cos^2\phi + \cot\theta\sin^2\phi$
$= \cot\theta$

Coefficient of $\frac{\partial}{\partial\phi}$ $-\csc^2\theta\sin\phi\cos\phi - \cot^2\theta\cos\phi\sin\phi$
$+\csc^2\theta\sin\phi\cos\phi + \cot^2\theta\sin\phi\cos\phi$
$= 0$

Coefficient of $\frac{\partial^2}{\partial\phi^2}$ $\cot^2\theta\cos^2\phi + \cot^2\theta\sin^2\phi$
$= \cot^2\theta$

$$\Rightarrow \quad L_x^2 + L_y^2 = \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2}$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\Rightarrow \quad L_z^2 = -\hbar^2\frac{\partial^2}{\partial\phi^2}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\phi^2}\right]$$

$$= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]$$

$$* \quad \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} = \frac{1}{\sin\theta}\sin\theta\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin\theta}\cos\theta\frac{\partial}{\partial\theta}$$

$$= \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}$$

$$** \quad \csc^2\theta\frac{\partial^2}{\partial\phi} = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\Rightarrow \quad L^2 = L_x^2 + L_y^2 + L_z^2$$

$$= -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Angular momentum

The eigenequation associated with angular momentum reads

$$\hat{\mathbf{L}}^2 Y(\theta,\phi) = 2mr^2 E_L(r) Y(\theta,\phi) = \text{const}\cdot Y(\theta,\phi) \tag{20-1}$$

where $2mr^2E_L$ is the eigenvalue, and

$$\hat{\mathbf{L}}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\theta^2}\right) \tag{20-2}$$

Similar to the HO problem, we can proceed in two ways. We can either:

1. solve the differential equation using some Taylor expansion.
2. we can take a more abstract operator approach.

Here we will do the latter. (For the direct approach see *Gasiorowicz*, supplement *7-B*, or *F&T*.) We analyze the commutation relations for the angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{20-3}$$

Note. that since waves in orthogonal directions are independent, we have no Heisenberg uncertainty restriction on, say x and p_y, and consequently the commutator is zero, $[x,p_y]=0$.

Let us calculate the commutator between different components of $\mathbf{L}$: omit operator symbol

$$\begin{aligned}
[L_x,L_y] &= [yp_z - zp_y, zp_x - xp_z] && (20\text{-}4)\\
&= y[p_z,z]p_x + x[z,p_y]p_y && (20\text{-}5)\\
&= \frac{\hbar}{i}yp_x + i\hbar xp_y && (20\text{-}6)\\
&= i\hbar(xp_y - yp_x) && (20\text{-}7)\\
&= i\hbar L_z && (20\text{-}8)
\end{aligned}$$

$$\begin{aligned}
[L_x,L_y] &= i\hbar L_z && (20\text{-}9)\\
[L_y,L_z] &= i\hbar L_x && (20\text{-}10)\\
[L_z,L_x] &= i\hbar L_y && (20\text{-}11)
\end{aligned}$$

The fact that the different components of angular momentum do not commute means that it is not possible to find simultaneous eigenstates of, say, L_x and L_z, unless $L_z = 0$ for that state (see previous lecture).

What about $\mathbf{L}^2$?

$$[L_z, \mathbf{L}^2] = [L_z, L_x^2] + [L_z, L_y^2] \tag{20-12}$$
$$= L_x[L_z, L_x] + [L_z, L_x]L_x + L_y[L_z, L_y] + [L_z, L_y]L_y \tag{20-13}$$
$$= i\hbar L_x L_y + i\hbar L_y L_x - i\hbar L_y L_x - i\hbar L_x L_y \tag{20-14}$$
$$= 0 \tag{20-15}$$

This implies that one can find simultaneous eigenstates of $\mathbf{L}^2$ and one component of $\mathbf{L}^2$ and one component of $\mathbf{L}$, e.g., L_z, but not of all components:

Proof. (Direct proof by contradiction) For a simultaneous eigenstate $|n\rangle$ of L_x and L_y with

$$L_x|n\rangle = l_1|n\rangle, \tag{20-16}$$
$$L_y|n\rangle = l_2|n\rangle. \tag{20-17}$$

we have

$$[L_x, L_y]|n\rangle = 0 = L_z|n\rangle \tag{20-18}$$

and

$$l_2|n\rangle = L_y|n\rangle = \frac{1}{i\hbar}[L_z, L_x]|n\rangle = 0 \quad \rightarrow \quad l_2 = 0 \tag{20-19}$$

and similarly $l_1 = 0$. Only for $\mathbf{L} = 0$ can we have simultaneous eigenstates of L_x, L_y, L_z. □

In general, we can only have simultaneous eigenstates of $\mathbf{L}^2$ and L_z (or L_x or L_y, L_z by convention). Let us denote such an eigenstate by $|l, m\rangle$ with

$$L_z|l, m\rangle = m\hbar|l, m\rangle \tag{20-20}$$
$$\mathbf{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle \tag{20-21}$$

The reason for the strange definition of the quantum number l (or $\mathbf{L}^2$ eigenvalue $\hbar^2 l(l+1)$) will become apparent later. m, l are dimensionless numbers, since $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ has units of $\hbar$. We assume that the simultaneous eigenstates of $\mathbf{L}^2$ and L_z are normalized,

$$\boxed{\langle l', m'|l, m\rangle = \delta_{ll'}\delta_{mm'}} \quad \rightarrow \quad \text{orthonormality for angular momentum eigenstates} \tag{20-22}$$

Raising and lowering operators for angular momentum

It is useful to define the following non-Hermitian operators

$$\boxed{L_\pm = L_x \pm iL_y} \tag{20-23}$$

$$\boxed{L_+^\dagger = L_-} \tag{20-24}$$

$$\boxed{L_-^\dagger = L_+} \tag{20-25}$$

L_+ and L_- are Hermitian conjugate of each other (reminiscent of $\hat{a} = \frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0}$, $\hat{a}^\dagger = \frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0}$). To understand similar significance of these operators, let us analyze their commutation relations:

$$\boxed{[\mathbf{L}^2, L_\pm] = 0} \tag{20-26}$$

since $[\mathbf{L}^2, L_x] = 0$, $[\mathbf{L}^2, L_y] = 0$.

$$\begin{aligned}
[L_+, L_-] &= [L_x + iL_y, L_x - iL_y] && (20\text{-}27)\\
&= -i[L_x, L_y] + i[L_y, L_x] && (20\text{-}28)\\
&= -2i[L_x, L_y] && (20\text{-}29)\\
&= -2ii\hbar L_z && (20\text{-}30)\\
&= 2\hbar L_z && (20\text{-}31)
\end{aligned}$$

$$\boxed{[L_+, L_-] = 2\hbar L_z} \tag{20-32}$$

$$\begin{aligned}
[L_\pm, L_z] &= [L_x \pm iL_y, L_z] && (20\text{-}33)\\
&= [L_x, L_z] \pm i[L_y, L_z] && (20\text{-}34)\\
&= -i\hbar L_y \pm i(i\hbar L_x) && (20\text{-}35)\\
&= \mp\hbar L_x - i\hbar L_y && (20\text{-}36)\\
&= \mp\hbar(L_x \pm L_y) && (20\text{-}37)\\
&= \mp\hbar L_\pm && (20\text{-}38)
\end{aligned}$$

$$\boxed{[L_\pm, L_z] = \mp\hbar L_\pm} \tag{20-39}$$

We also note that

$$\begin{aligned}
L_+L_- &= (L_x + iL_y)(L_x - iL_y) && (20\text{-}40)\\
&= L_x^2 + L_y^2 - iL_xL_y + L_yL_x && (20\text{-}41)\\
&= L^2 - L_z^2 - i[L_x, L_y] && (20\text{-}42)\\
&= \mathbf{L}^2 - L_z^2 + \hbar L_z && (20\text{-}43)
\end{aligned}$$

and similarly $L_-L_+ = \mathbf{L}^2 - \mathbf{L}_z^2 - \hbar L_z$.

$$\boxed{\begin{array}{lcl} L_+L_- & = & \mathbf{L}^2 - \mathbf{L}_z^2 + \hbar L_z \\ L_-L_+ & = & \mathbf{L}^2 - \mathbf{L}_z^2 - \hbar L_z \end{array}}$$

As for the HO, we now proceed to analyze the range of allowed values for l, m: Since $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ and L_x, L_y, L_z are Hermitian operators, we have

$$\langle l,m|L_x^2|l,m\rangle = \langle L_x^\dagger(l,m)|L_x(l,m)\rangle = \langle L_x(l,m)|L_x(l,m)\rangle \geq 0, \tag{20-44}$$

similarly for y, z, and consequently $\langle l,m|\mathbf{L}^2|l,m\rangle \geq 0$ or

$$0 \leq \langle l,m|\mathbf{L}^2|l,m\rangle = \hbar^2 l(l+1)\langle l,m|l,m\rangle = \hbar^2 l(l+1). \tag{20-45}$$

Consequently, we can choose $l \geq 0$. (If $l \leq -1$, we define $l' := -(l+1)$, then $l(l+1) = -l'(l'+1)$ and $l' \geq 0$.) To understand the operators $L_\pm$, let us define a new state

$$|\psi_\pm\rangle := L_\pm|l,m\rangle, \tag{20-46}$$

and act on it with $\mathbf{L}^2$.

$$\begin{aligned} \mathbf{L}^2|\psi_\pm\rangle &= \mathbf{L}^2 L_\pm|l,m\rangle && (20\text{-}47)\\ &= L_\pm \mathbf{L}^2|l,m\rangle && (20\text{-}48)\\ &= \hbar^2 l(l+1)L_\pm|l,m\rangle && (20\text{-}49)\\ &= \hbar^2 l(l+1)|\psi_\pm\rangle, && (20\text{-}50) \end{aligned}$$

so $|\psi_\pm\rangle$ is an eigenstate of $\mathbf{L}^2$ with the same quantum number l. Also we have

$$\begin{aligned} L_z|\psi_\pm\rangle &= L_z L_\pm|l,m\rangle && (20\text{-}51)\\ &= (L_\pm L_z \pm \hbar L_\pm)|l,m\rangle && (20\text{-}52)\\ &= (m\hbar \pm \hbar)L_\pm|l,m\rangle && (20\text{-}53)\\ &= (m \pm 1)\hbar L_\pm|l,m\rangle && (20\text{-}54)\\ &= (m \pm 1)\hbar|\psi_\pm\rangle. && (20\text{-}55) \end{aligned}$$

This means that $L_\pm|l,m\rangle$ is also an eignenstate of L_z, but with an eigenvalue $(m\pm1)\hbar$ that differs from the original one by one. Since m is the quantum number associated with the z component of angular momentum, we call m **the azimuthal (or magnetic) quantum number**, while l **is the quantum number associated with total angular momentum**. L_+ (L_-) raises (lowers) the magnetic quantum number by one, while preserving the total angular momentum l.

Let us calculate the length of

$$|l, \widetilde{m \pm 1}\rangle := L_\pm|l,m\rangle, \tag{20-56}$$

the unnormalized state vector.

$$\begin{aligned}
\langle l, \widetilde{m \pm 1} | l, \widetilde{m \pm 1} \rangle &= \langle l, m | L_\mp L_\pm l, m \rangle && \text{(20-57)} \\
&= \langle l, m | \mathbf{L}^2 - L_z^2 \mp \hbar L_z | l, m \rangle && \text{(20-58)} \\
&= \hbar^2 l(l+1) - \hbar^2 m^2 \mp \hbar^2 m^2) \langle l, m | l, m \rangle && \text{(20-59)} \\
&= \hbar^2 \big(l(l+1) - m(m \pm 1) \big) && \text{(20-60)} \\
&= \hbar^2 (l \mp m)(l \pm m + 1) && \text{(20-61)}
\end{aligned}$$

Since the length squared of any vector must be non-negative, it follows that

$$l(l+1) - m(m \pm 1) \geq 0. \tag{20-62}$$

Consequently,

$$\begin{aligned}
m(m \pm 1) &= m^2 \pm m + \frac{1}{4} - \frac{1}{4} && \text{(20-63)} \\
&= \left(m \pm \frac{1}{2} \right)^2 - \frac{1}{4} && \text{(20-64)} \\
&\leq l^2 + l = \left(l + \frac{1}{2} \right)^2 - \frac{1}{4} && \text{(20-65)}
\end{aligned}$$

or

$$\left| m \pm \frac{1}{2} \right| \leq \left| + \frac{1}{2} \right| = l + \frac{1}{2} \tag{20-66}$$

since $l \geq 0$,

$$m \leq l, \text{ for } m > 0 \tag{20-67}$$

and also

$$- m \leq l, \text{ for } m \leq 0. \tag{20-68}$$

Therefore, m is bounded both from above and from below:

$$\boxed{-l \leq m \leq l}, \; l \geq 0. \tag{20-69}$$

Since $|\psi_+\rangle = L_+|l, m\rangle$ is also an eigenstate of $\mathbf{L}^2$ and L_z, but with new eigenvalue $m' = m + 1$, the bound on m is only consistent with this fact if $L_+|l, m\rangle = 0$ for some m. Consequently, with

$$\begin{aligned}
L_+|l, m\rangle &= |l, \widetilde{m + 1}\rangle && \text{(20-70)} \\
0 &= \langle l, \widetilde{m + 1} | l, \widetilde{m + 1} \rangle && \text{(20-71)} \\
&= \hbar^2 (l - m)(l + m + 1). && \text{(20-72)}
\end{aligned}$$

$$\boxed{m_{\max} = l} \tag{20-73}$$

Similarly, for
$ket\psi_- = L_-|l, m\rangle$ we have

$$\boxed{m_{\min} = -l}. \tag{20-74}$$

Thus, we have a ladder of eigenvalues spaced by one, and connected by the raising and lowering operators L_+ and L_-

$$\boxed{m = -l, -l+1, \ldots, l-1, l}, \ l \geq 0 \tag{20-75}$$

This is only possible is l is integer or half integer. It turns out that half-integer

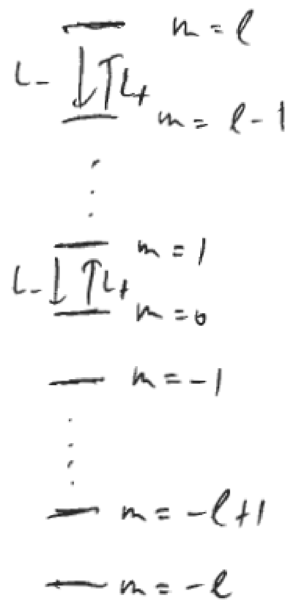


Figure I: Ladder of eigenvalues for fixed l.

values of l have no simple spatial representation, and correspond to an internal form of angular momentum called **spin** of the particle. Here we will restrict ourselves to **orbital angular momentum**, which requires l to be an **integer**.

Summary: angular momentum derivation

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{21-1}$$

$$L_x = yp_z - zp_y, \text{ etc.} \tag{21-2}$$

$$[x, p_y] = 0, \text{ etc.} \tag{21-3}$$

Angular momentum commutation relations

$$[L_x, L_y] = i\hbar L_z \tag{21-4}$$

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k \tag{21-5}$$

Levi-Civita symbol:

$$\epsilon_{ijk} = \begin{cases} +1 & \text{for even permutation of } xyz \\ -1 & \text{for odd permutation} \end{cases} \tag{21-6}$$

In general, no simultaneous eigenstates of L_x, L_y, L_z,

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2, \tag{21-7}$$

$$[\mathbf{L}^2, L_x] = [\mathbf{L}^2, L_y] = [\mathbf{L}^2, L_z] = 0, \tag{21-8}$$

simultaneous eigenstates of $\mathbf{L}^2$ and one component (L_z).

Define, without loss of generality, simultaneous eigenstates $|l, m\rangle$ of $\mathbf{L}^2$ and L_z such that

$$L_z|l, m\rangle = m\hbar|l, m\rangle \quad \rightarrow \quad m \text{ magnetic quantum number} \tag{21-9}$$

$$\mathbf{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle \quad \rightarrow \quad \begin{pmatrix} l \geq 0 \text{ quantum number of} \\ \text{total average momentum} \end{pmatrix} \tag{21-10}$$

$$\langle l', m'|l, m\rangle = \delta_{ll'}\delta_{mm'}, \quad \rightarrow \quad \text{orthonormality} \tag{21-11}$$

Raising and lowering operators

$$L_\pm = L_x \pm iL_y = L_\pm^\dagger \tag{21-12}$$

$$[\mathbf{L}^2, L_\pm] = 0 \tag{21-13}$$

Note. $L_\pm$ preserves l.

$$L_{\pm}|l,m\rangle = |l,\widetilde{m \pm 1}\rangle, \text{ from } [L_{\pm}, L_z] = \mp\hbar L_{\pm} \tag{21-14}$$

Note. $L_{\pm}$ increases (lowers) magnetic quantum number by 1.

$$\langle l,\widetilde{m \pm 1}|l,\widetilde{m \pm 1}\rangle = \langle L_{\pm}l,m|L_{\pm}l,m\rangle = \hbar^2(l \mp m)(l \pm m + 1) \tag{21-15}$$

$$\boxed{|m| \leq l} \tag{21-16}$$

Since L_+ increases m by 1 we need $L_+|l,m_{\max}\rangle = 0$ for some $m_{\max}$ or

$$\langle l,\widetilde{m_{\max} + 1}|l,\widetilde{m_{\max} + 1}\rangle = \hbar^2(l - m_{\max})(l + m_{\max} + 1) = 0 \tag{21-17}$$

$$\boxed{m_{\max} = l} \tag{21-18}$$

$$L_-|l,m_{\min}\rangle = 0, \text{ for some } m_{\min} \tag{21-19}$$

$$\langle l,\widetilde{m_{\min} - 1}|l,\widetilde{m_{\min} - 1}\rangle = \hbar^2(l + m_{\min})(l - m_{\min} + 1) = 0 \tag{21-20}$$

$$\boxed{m_{\min} = -l} \tag{21-21}$$

since $m_{\max} - m_{\min} =$ integer (integer number of application of L_+ onto $|l,m_{\min}\rangle$). We need $m_{\max} - m_{\min} = 2l =$ integer. (l integer of half-integer.)

State vector notation and wavefunctions

In the decomposition of an arbitrary state $|\psi\rangle$, in terms of energy eigenstates $|n\rangle$,

$$|\psi\rangle = \sum_n c_n|n\rangle \tag{21-22}$$

$$c_n = \langle n|\psi\rangle \tag{21-23}$$

Similarly, we can calculate the projection of the state $|\psi\rangle$ onto the state where the particle is found with certainty at x and nowhere else, i.e., onto the eigenstate $|x_0\rangle$ of the position operator with eigenvalue x_0,

$$\hat{x}|x_0\rangle = x_o|x_0\rangle \tag{21-24}$$

(In position space, these states are δ-functions.) We can expand the wavefunction in terms of the continuum of eigenstates,

$$|\psi\rangle = \int dx c(x)|x\rangle \tag{21-25}$$

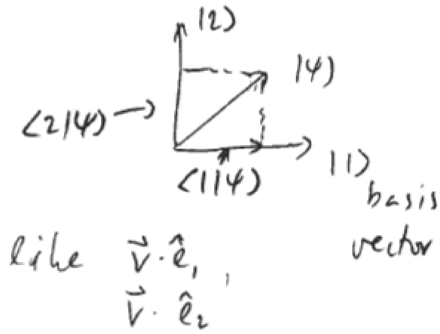


Figure I: Decomposition of a state vector into basis vectors.

where $|x\rangle$ is the position operator eigenstate with eigenvalue x, $\hat{x}|x\rangle = x|x\rangle$, and the expansion coefficients are given by,

$$c(x) = \langle x|\psi\rangle. \tag{21-26}$$

Since $c(x)dx$ is the probability to find the particle within the interval $[x, x + dx]$, we identify the expansion coefficients with the spatial wavefunction and write

$$\underbrace{|\psi\rangle}_{\text{arbitrary state}} = \int dx \quad \underbrace{\psi(x)}_{\text{scalar coefficient}} \quad \underbrace{|x\rangle}_{x \text{ eigenstate}} \quad , \tag{21-27}$$

$$\psi(x) = \langle x|\psi\rangle \quad \rightarrow \quad \begin{pmatrix} \text{projection of } |\psi\rangle \text{ vector onto} \\ \text{position eigenstate } |x\rangle \end{pmatrix}. \tag{21-28}$$

The wavefunction in position space $\psi(x)$ is the set of expansion coefficients of the state $|\psi\rangle$ in terms of position eigenstates, it is the projection of the state $|\psi\rangle$ onto the position eigenstate where the particle is localized at x. Similarly, we can expand in terms of momentum eigenstates,

$$|\psi\rangle = \int dk\tilde{\phi}(k)|k\rangle, \tag{21-29}$$

$$\tilde{\psi}(k) = \langle k|\psi\rangle. \tag{21-30}$$

The wavefunction in momentum space is the set of expansion coefficients in terms of momentum eigenstates. Similarly, we have for eigenstates of angle $|\theta, \phi\rangle$ in polar coordinates (i.e., states where the particle is found with certainty in a direction specified by θ, ϕ, and nowhere else):

$$|\psi\rangle = \int d\Omega c(\theta,\phi)|\theta,\phi\rangle \tag{21-31}$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta c(\theta,\phi)|\theta,\phi\rangle \tag{21-32}$$

$$= \int_0^{2\pi} d\phi \int_{-1}^{-1} d(\cos\theta) c(\theta,\phi)|\theta,\phi\rangle \tag{21-33}$$

with the **angular wavefunction**

$$Y(\theta,\phi) = c(\theta,\phi) = \langle\theta,\phi|\psi\rangle, \tag{21-34}$$

expansion coefficients in terms of angular eigenstates.

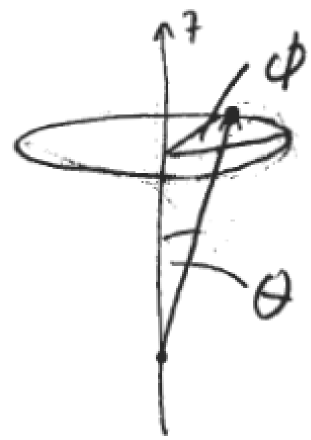


Figure II: Angles θ, ϕ in spherical coordinates.

Wavefunction of angular momentum eigenstate $|l,m\rangle$ in "angle representation"

The wavefunction corresponding to state $|l,m\rangle$ is

$$Y_{lm}(\theta,\phi) = \langle\theta,\phi|l,m\rangle \tag{21-35}$$

without proof: by expressing $L_z = xp_y + yp_x$ etc. in polar coordinates and substituting $p_i = \frac{\hbar}{i}\frac{\partial}{\partial x_i}$ we obtain the following operator expressions:

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}, \tag{21-36}$$

$$L_\pm = \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right). \tag{21-37}$$

The eigenequation for L_z becomes

$$\langle\theta,\phi|L_z|l,m\rangle = \hbar m\langle\theta,\phi|l,m\rangle \tag{21-38}$$

$$= \hbar m Y_{lm}(\theta,\phi) \tag{21-39}$$

$$\langle\theta,\phi|L_z|l,m\rangle = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\langle\theta,\phi|l,m\rangle \tag{21-40}$$

$$= \frac{\hbar}{i}\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) \tag{21-41}$$

$$\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) = imY_{lm}(\theta,\phi) \tag{21-42}$$

This differential has the solution

$$\boxed{Y_{lm}(\theta,\phi) = P_{lm}(\theta)e^{im\phi}} \tag{21-43}$$

The stretched state $m = l$ is characterized by $L_+|l, m = l\rangle = 0$ or

$$\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)Y_{ll}(\theta,\phi) = 0, \tag{21-44}$$

$$e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)P_{ll}(\theta)e^{il\phi} = 0, \tag{21-45}$$

$$\left(\frac{\partial}{\partial\theta} - l\cot\theta\right)P_{ll}(\theta)e^{(l+1)\phi} = 0, \tag{21-46}$$

$$\left(\frac{\partial}{\partial\theta} - l\cot\theta\right)P_{ll}(\theta) = 0, \tag{21-47}$$

the solution of which is $P_{ll}(\theta) = (\sin\theta)^l$. Consequently,

$$\boxed{Y_{ll}(\theta,\phi) = C_{ll}(\sin\theta)^l e^{il\phi}}. \tag{21-48}$$

As for the HO, the eigenstates for $m < l$ can be found by applying L_- to Y_{ll}:

$$\boxed{Y_{ll}(\theta,\phi) = c(\hat{L}_-)^{l-m}(\sin\theta)^l e^{il\phi}}, \tag{21-49}$$

where the operator $\hat{L}_-$ is given on p. XXI-5. These are the **spherical harmonics**, given by

$$\boxed{Y_{lm}(\theta,\phi) = (-1)^m \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{\frac{1}{2}} P_l^m(cos\theta)e^{im\phi}}, \text{ for } m \geq 0 \tag{21-50}$$

$$\boxed{Y_{l,-m}(\theta,\phi) = Y_{lm}^*}, \text{ for } m \geq 0 \tag{21-51}$$

where the $P_{lm}(\cos\theta)$ are the **associated Legendre polynomials**

$$P_l^m(u) = (-1)^{l+m}\frac{(l+m)!}{(l-m)!}\frac{(1-n^2)^{-\frac{m}{2}}}{2^l l!}\left(\frac{d}{du}\right)^{l-m}(l-u^2)^l, \text{ for } m \geq 0 \tag{21-52}$$

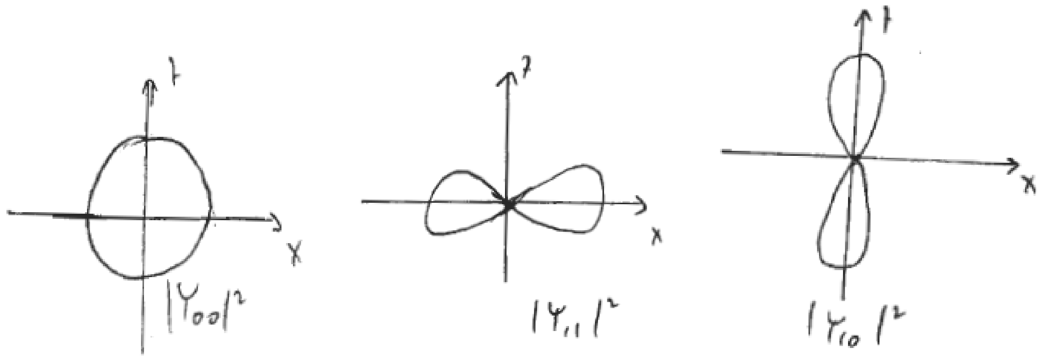
$$P_l^{-m}(u) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(u) \tag{21-53}$$

The **first spherical harmonics** are:

$$\left.Y_{00} = \frac{1}{\sqrt{4\pi}}\right\} l = 0 \tag{21-54}$$

$$\left.\begin{aligned} Y_{11} &= -\sqrt{\frac{3}{8\pi}}e^{i\phi}\sin\theta \\ Y_{10} &= \sqrt{\frac{3}{8\pi}}\cos\theta \\ Y_{1,-1} &= +\sqrt{\frac{3}{8\pi}}e^{-i\phi}\sin\theta \end{aligned}\right\} l = 1 \tag{21-55}$$

$$\left.\begin{aligned} Y_{22} &= \sqrt{\frac{15}{32\pi}}e^{2i\phi}\sin^2\theta \\ Y_{21} &= -\sqrt{\frac{15}{8\pi}}e^{i\phi}\sin\theta\cos\theta \\ Y_{20} &= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \\ Y_{2,-1} &= -\sqrt{\frac{15}{8\pi}}e^{-i\phi}\sin\theta\cos\theta \\ Y_{2,-2} &= \sqrt{\frac{15}{32\pi}}e^{-2i\phi}\sin^2\theta \end{aligned}\right\} l = 2 \tag{21-56}$$



(a) $|Y_{00}|^2$ (b) $|Y_{11}|^2$ (c) $|Y_{10}|^2$

Figure III: Distance of displayed curve from origin in given direction indicates value of $|Y_{lm}|^2$.

Geometric interpretation of quantum mechanical feature of angular momentum

Classically, we can prepare an object to have its angular momentu completely aligned along an axis, say, the z axis. Then we have classically $(L_z^2)_{\mathrm{cl}} = (\mathbf{L}^2)_{\mathrm{cl}}$, and $L_x = L_y = 0$. In **QM**, L_z and L_x do not commute, which implies a Heisenberg uncertainty between them. Quantum mechanically, the largest z component of angular momentum in that we can produce for a given total angular momentum l is $m = l$, but

$$\langle l, m = 1|\mathbf{L}^2|l, m = l\rangle = \hbar^2 l(l+1) \tag{21-57}$$
$$> \langle l, m = 1|L_z^2\rangle l, m = l \tag{21-58}$$
$$= \hbar^2 l^2 \tag{21-59}$$

Consequently, some angular momentum must be pointing in some other direction:

$$L_x^2 + L_y^2 = \mathbf{L}^2 - L_z^2 \tag{21-60}$$
$$= \hbar^2 l(l+1) - \hbar^2 l^2 \tag{21-61}$$
$$= l\hbar^2 \tag{21-62}$$
$$\neq 0 \tag{21-63}$$

So there is angular momentum $\sqrt{l}\hbar$ pointing elsewhere.

Let us analyze L_x, L_y in the stretched state $m = l$:

$$\langle L_x \rangle_{m=l} = \langle l, m | L_x | l, m \rangle \tag{21-64}$$

$$= \langle l, m | \frac{1}{2}(L_+ + L_-) | l, m \rangle \tag{21-65}$$

$$= \frac{1}{2}\big(\langle l, m | l, \widetilde{m+1} \rangle + \langle l, m | l, \widetilde{m-1} \rangle \big) \tag{21-66}$$

$$= 0 \tag{21-67}$$

since states with different quantum numbers are orthogonal. So we have $\langle L_x \rangle = \langle L_y \rangle = 0$. (Similarly for L_y.) Where, then, is the missing angular momentum?

$$\langle L_x^2 \rangle_{l=m} = \frac{1}{4} \langle l, m | (L_+ + L_-)^2 | l, m \rangle \tag{21-68}$$

$$= \frac{1}{4} \langle l, m | L_+^2 + L_+ L_- + L_- L_+ + L_-^2 \rangle l, m \tag{21-69}$$

$$= \frac{1}{4} \langle l, m | L_+ L_- + L_- L_+ \rangle l, m \tag{21-70}$$

$$= \frac{1}{4} \langle l, m | \mathbf{L}^2 - L_z^2 + \hbar L_z + \mathbf{L}^2 - L_z^2 - \hbar L_z \rangle l, m \tag{21-71}$$

$$= \frac{1}{2} \langle l, m = l | \mathbf{L}^2 - L_z^2 | l, m \rangle \tag{21-72}$$

$$= \frac{1}{2} l(l+1)\hbar^2 - l^2 \hbar^2 \tag{21-73}$$

$$= \frac{l}{2}\hbar^2 \tag{21-74}$$

and similarly for $\langle L_y^2 \rangle$:

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \frac{l}{2}\hbar^2 \tag{21-75}$$

Even though $\langle L_x \rangle = \langle L_y \rangle = 0$, some angular momentum is contained in the x- and y-components as uncertainty. Since l is constant, we can draw the following geometrical picture for angular momentum:

Note. There is nothing special about the z-direction, we could prepare, e.g., a maximally oriented state $m = l$ along x (or, in fact, any other direction) by a linear combination of $|l, m\rangle$ states,

$$|l, m = l\rangle_x = \sum_{m=-l}^{l} c_m |l, m\rangle_z \tag{21-76}$$

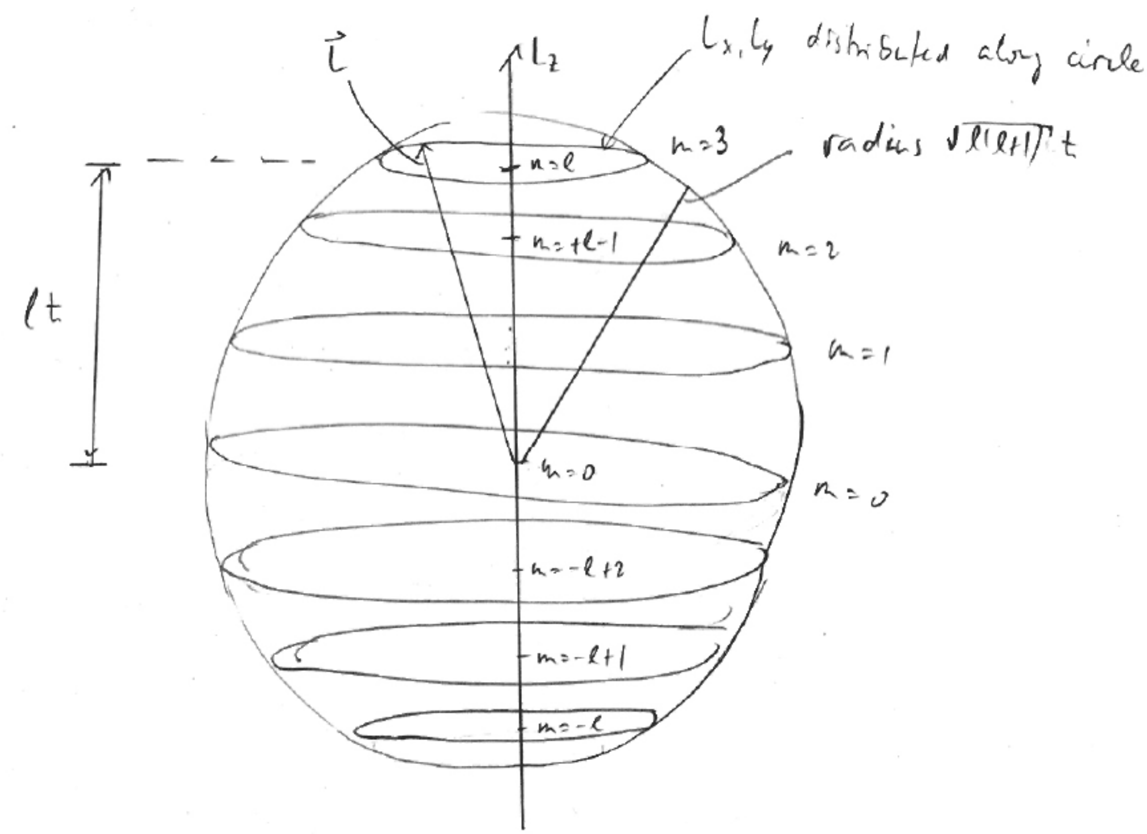


Figure IV: For given state $|l, m\rangle$, the angular momentum points somewhere along the circle that corresponds to the given m-value, but we cannot predict the direction, i.e., the L_x and L_y components.

分類：	
編號：	B-1
總號：	

Appendix B

Angular Momentum in Spherical Coordinate

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$dx = \sin\theta\cos\phi\, dr + r\cos\theta\cos\phi\, d\theta - r\sin\theta\sin\phi\, d\phi \qquad (1)$$
$$dy = \sin\theta\sin\phi\, dr + r\cos\theta\sin\phi\, d\theta + \underline{r\sin\theta\cos\phi\, d\phi} \qquad (2)$$
$$dz = \cos\theta\, dr - r\sin\theta\, d\theta \qquad (3)$$

Want to find dr $d\phi$ term has to cancel

$$\underline{\sin\theta\cos\phi}\, dx = \sin^2\theta\cos^2\phi\, dr + r\cos\theta\sin\theta\cos^2\phi\, d\theta - r\sin^2\theta\cos\phi\sin\phi\, d\phi$$
$$\sin\theta\sin\phi\, dy = \sin^2\theta\sin^2\phi\, dr + r\cos\theta\sin\theta\sin^2\phi\, d\theta + r\sin^2\theta\cos\phi\sin\phi\, d\phi$$

$d\theta$ term must cancel.

$$\sin\theta\cos\phi\, dx + \sin\theta\sin\phi\, dy = \sin^2\theta\, dr + r\cos\theta\sin\theta\, d\theta$$
$$\cos\theta\, dz = \cos^2\theta\, dr - r\cos\theta\sin\theta\, d\theta$$

$$\Rightarrow \quad dr = \sin\theta\cos\phi\, dx + \sin\theta\sin\phi\, dy + \cos\theta\, dz \qquad (A)$$

Want to find $r\,d\theta$ $d\phi$ term must cancel

$$\underline{\cos\theta\cos\phi}\, dx = \sin\theta\cos\theta\cos^2\phi\, dr + r\cos^2\theta\cos^2\phi\, d\theta - r\cos\theta\sin\theta\sin\phi\cos\phi\, d\phi$$
$$\cos\theta\sin\phi\, dy = \sin\theta\cos\theta\sin^2\phi\, dr + r\cos^2\theta\sin^2\phi\, d\theta + r\cos\theta\sin\theta\sin\phi\cos\phi\, d\phi$$

dr must cancel

$$\cos\theta\cos\phi\, dx + \cos\theta\sin\phi\, dy = \sin\theta\cos\theta\, dr + r\cos^2\theta\, d\theta$$
$$-\sin\theta\, dz = -\sin\theta\cos\theta\, dr + r\sin^2\theta\, d\theta$$

$$r\,d\theta = \cos\theta\cos\phi\, dx + \cos\theta\sin\phi\, dy - \sin\theta\, dz$$
$$\Rightarrow \quad d\theta = \frac{1}{r}(\cos\theta\cos\phi\, dx + \cos\theta\sin\phi\, dy - \sin\theta\, dz \qquad (B)$$

dr, $d\theta$ cancel

$$-\sin\phi\, dx = -\sin\theta\cos\phi\sin\phi\, dr - r\cos\theta\cos\phi\sin\phi\, d\theta + r\sin\theta\sin^2\phi\, d\phi$$
$$+\cos\phi\, dy = \sin\theta\cos\phi\sin\phi\, dr + r\cos\theta\cos\phi\sin\phi\, d\theta + r\sin\theta\cos^2\phi\, d\phi$$
$$\Rightarrow \quad -\sin\phi\, dx + \cos\phi\, dy = r\sin\theta\, d\phi$$
$$\Rightarrow \quad d\phi = \frac{1}{r\sin\theta}(-\sin\phi\, dx + \cos\phi\, dy) \qquad (C)$$

分類：
編號：B-2
總號：

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

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

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

$$= \frac{\hbar}{i}\Big(r\sin\theta\cos\phi\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$- r\sin\theta\sin\phi\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$= r\cos^2\phi\frac{\partial}{\partial\phi} + r\sin^2\phi\frac{\partial}{\partial\phi} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= \frac{\hbar}{i}\Big(r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)$$

$$- r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\Big)$$

$\frac{\partial}{\partial r}$ term cancels

$\frac{\partial}{\partial\theta}$ $\quad -\sin^2\theta\sin\phi - \cos^2\theta\sin\phi = -\sin\phi$

$\frac{\partial}{\partial\phi}$ $\quad -\cot\theta\cos\phi$

$$\Rightarrow L_x = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= \frac{\hbar}{i}\Big(r\cos\theta\left(\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$$

$$- r\sin\theta\cos\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)$$

$\frac{\partial}{\partial r}$ term cancels

$\frac{\partial}{\partial\theta}$ $\quad \cos^2\theta\cos\phi + \sin^2\theta\cos\phi = \cos\phi$

$\frac{\partial}{\partial\phi}$ $\quad -\cot\theta\sin\phi$

$$\Rightarrow L_y = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

分類:	
編號:	B-3
總號:	

$$L_\pm = L_x \pm i L_y$$

$$L_+ = \frac{\hbar}{i}\left(-\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi}\right) + i\frac{\hbar}{i}\left(\cos\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi}\right)$$

$$= \hbar\,(\cos\phi + i\sin\phi)\frac{\partial}{\partial\theta} \quad + \hbar i \cot\theta\,(\cos\phi + i\sin\phi)\frac{\partial}{\partial\phi}$$

$$= \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi}\right)$$

$$L_- = \frac{\hbar}{i}\left(-\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi}\right) - i\frac{\hbar}{i}\left(\cos\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi}\right)$$

$$= \hbar e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi}\right)$$

$$L_+ L_- = (L_x + iL_y)(L_x - iL_y)$$

$$= L_x^2 + L_y^2 - i\,[L_x, L_y]$$

$$\vec{L}^2 = L_z^2 + L_+L_- + i\,[L_x, L_y]$$

$$= L_+L_- + L_z^2 - \hbar L_z$$

分類:	
編號:	B-4
總號:	

$$L_+ L_- = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\hbar e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$= \hbar^2\Big\{ e^{i\phi}\left(\frac{\partial}{\partial\theta}\, e^{-i\phi}\left(-\frac{\partial}{\partial\theta}\right)\right) \qquad (I)$$

$$+ e^{i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi}\right) e^{-i\phi}\left(-\frac{\partial}{\partial\theta}\right) \qquad (II)$$

$$+ e^{i\phi}\frac{\partial}{\partial\theta}\, e^{-i\phi}\left(i\cot\theta\frac{\partial}{\partial\phi}\right) \qquad (III)$$

$$+ i e^{i\phi}\cot\theta\frac{\partial}{\partial\phi}\, e^{-i\phi}\, i\cot\theta\frac{\partial}{\partial\phi}\Big\} \qquad (IV)$$

$$(I) = -\frac{\partial^2}{\partial\theta^2}$$

$$(II)\ -e^{i\phi}\, i\cot\theta\frac{\partial}{\partial\phi}\left(e^{-i\phi}\frac{\partial}{\partial\theta}\right)$$

$$= -ie^{i\phi}\cot\theta\left(-i e^{-i\phi}\right)\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial^2}{\partial\theta\partial\phi}$$

$$= -\cot\theta\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial^2}{\partial\theta\partial\phi}$$

$$(III) = i\frac{\partial}{\partial\theta}\cot\theta\frac{\partial}{\partial\phi} = i\cot\theta\frac{\partial^2}{\partial\theta\partial\phi} - i\csc^2\theta\frac{\partial}{\partial\phi}$$

$$(IV) = i^2 e^{i\phi}\cot^2\theta\frac{\partial}{\partial\phi}\, e^{-i\phi}\frac{\partial}{\partial\phi}$$

$$= -e^{i\phi}\cot^2\theta\cdot e^{-i\phi}\frac{\partial^2}{\partial\phi^2} - e^{i\phi}\cot^2\theta\left(-ie^{-i\phi}\right)\frac{\partial}{\partial\phi}$$

$$= -\cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\cot^2\theta\frac{\partial}{\partial\phi}$$

$$L^2 = L_+L_- + \underset{\displaystyle -\hbar^2\frac{\partial^2}{\partial\phi^2}}{L_z^2} - \underset{\displaystyle -\frac{\hbar^2}{i}\frac{\partial}{\partial\phi}}{\hbar L_z}$$

$\hbar^2$ has taken out

$\frac{\partial^2}{\partial\theta^2}$: -1

$\frac{\partial^2}{\partial\theta\partial\phi}$: 0

$\frac{\partial}{\partial\theta}$: $-\cot\theta$

$\frac{\partial}{\partial\phi}$: 0

$\frac{\partial^2}{\partial\phi^2}$: $-(1+\cot^2\theta) = \frac{-1}{\sin^2\theta}$

$$\Rightarrow L^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Appendix C

Hermitian operator

Definition of Hermitian operator

Simple harmonic oscillator

$H\psi_n = E_n \psi_n$ $\qquad E_n = (n+\frac{1}{2})\hbar\omega$

$H = -\frac{\hbar^2}{2m} + \frac{1}{2}kx^2$

· Proof that H is Hermitian

· E_n must be real $\Leftrightarrow$ operator is Hermitian

$\int \psi_n^*(x)\,\psi_m(x) = 0$ if $n \neq m$

· ψ_n can be normalization

ψ_n is a solution (eigenfunction)
$A_n\psi_n$ is also a solution. $\Big\rangle$ H is linear operator
A_n can be chosen $\int u_n^*(x)\,u_n(x)\,dx = 1$

$\Rightarrow \{u_n\}$ form an orthormal set

$$\int_{-\infty}^{\infty} u_n^*(x)\,u_m(x)\,dx = \delta_{nm}$$

$\{u_n(x)\}$ form a complete set

$$\psi(x) = \sum_{n=1}^{\infty} c_n u_n(x)$$

$$\langle E\rangle = \int \psi^*(x) H \psi(x)\,dx = \int \sum_n c_n u_n^*(x)\; H \sum_m c_m u_m(x)\;dx$$

$$= \sum_n\sum_m c_n \int \underbrace{u_n^*(x)\,E_m\,u_m(x)\,dx}_{E_m\delta_{nm}}$$

$$= \sum |c_n|^2 E_n$$

$|c_n|^2$ = probability of finding the system described by ψ to have energy E_n

Completeness $\qquad \sum |c_n|^2 = 1$

$\psi(x) = \sum c_n u_n(x)$

$$\int u_m^*(x)\,\psi(x)\,dx = \sum_n c_n \int u_m^*(x)\,u_n(x)\,dx$$

$$= c_m$$

分類：
編號： C-2
總號：

Hydrogen Atom

Summary of the Result

- Time dependent Schrodinger Equation
- Time independent Schrodinger

$$\psi(\vec{r}, t) = \psi(\vec{r})\, e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$H\psi = E\psi$$

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

Seperation of

- $\Phi(\phi) \rightarrow$ equation

Equation $\quad \dfrac{d^2\Phi}{d\phi^2} = -m^2\Phi \qquad$ m dependence only

single valueness $\quad \underset{m}{\Phi}(\phi) = e^{im\phi} \qquad m = 0, \pm 1, \pm 2$

magnetic quantum mechanics

- $\Theta(\theta) \rightarrow$ Equation. $\qquad$ function of ℓ, m

Physical acceptable solution only for

Only $\quad \ell = 0, 1, 2, \cdots$

$m = -\ell, -\ell+1, \cdots, \ell-1, \ell$

The proof is given in the Appendix

$P_\ell^m(\theta, \phi)$

Angular part $\sim \quad A_{\ell m}\, P_\ell^m(\theta)\, e^{im\phi}$

Radial equation

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

function of ℓ, E

Change of variable

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

$$V = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

equation 4-53

(4-70)

Orbital Angular Momentum

Classically $\vec{L} = \vec{r} \times \vec{p}$

$$L_x = yP_z - zP_y, \quad L_y = zP_x - xP_z \quad \text{and} \quad L_z = xP_y - yP_x$$

The corresponding quantum operators are

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

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

L_x, L_y, L_z are linear, Hermitian operators

$$L_z = xP_y - yP_x$$

$$L^+ = P_y^+ x^+ - P_x^+ y^+ = P_y x - P_x y$$

x's and p's are Hermitian (physical observables)

$[P_y, x] = 0$ operate on $\qquad P_y x = xP_y$

$$L_z^+ = xP_y - yP_x = L_z$$

We can prove $L_y^+ = L_y$, $L_x^+ = L_x$

$\vec{L}$ is Hermitian operation.

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2$$

We can show

Use $[AB, C] = A[B, C] - [A, C]B$

$$[L_x, L_y] = [yP_z - zP_y, zP_x - xP_z]$$

$$= [yP_z, zP_x] - [zP_y, zP_x] - [yP_z, xP_z] + [zP_y, -xP_z]$$

$$= y[P_z, zP_x] + [y, zP_x]P_z - z[P_y, zP_x] - [z, zP_x]P_y$$

$$- y[P_z, xP_z] - [y, xP_z]P_z + z[P_y, -xP_z] + [z, xP_z]P_y$$

分類：	
編號：	9-10
總號：	

$[x, P_x] = i\hbar$, $[y, P_y] = i\hbar$, $[z, P_z] = i\hbar$

$[L_x, L_y] = i\hbar L_z$

and cyclic permutation.

$[\vec{L}^2, L_z] = 0$, $[\vec{L}^2, L_x] = 0$, $[\vec{L}^2, L_y] = 0$

Write L_x, L_y, L_z and $\vec{L}^2$ in spherical coordinate (See Appendix B)

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

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

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial\phi}$$

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2$$

$$= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

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

$$L_z \Phi_m = m\hbar \Phi_m$$

$$-i\hbar\frac{\partial}{\partial\phi} \Phi_m = m\hbar \Phi_m$$

$$\Phi_m = e^{im\phi}$$

↳ eigenfunction of L_z with eigenvalue $m\hbar$

Single-valueness $\Phi_m(2\pi + \phi) = \Phi_m(\phi)$

$\Rightarrow$ m must be quantizated.

$\Updownarrow$

m must be integers

$\downarrow$

the result used in Bohr model.

$[\vec{L}^2, L_z] = 0$ we can find a set of simultaneous eigenfunction of $\vec{L}^2$ and L_z

Looking at $\vec{L}^2$

$\Theta_\ell(\theta)\, e^{im\phi}$

$\downarrow$

is an eigenfunction of L_z with eigenvalue $m\hbar$

$\vec{L}^2\, \Theta_\ell(\theta)\, e^{im\phi} = \ell(\ell+1)\hbar^2\, \Theta_\ell(\theta)\, e^{im\phi}$

$\downarrow$

the equation for $\Theta_\ell(\theta)$
is exactly the angular equation
we studied in the central force
problem

$\Theta_\ell(\theta) \sim P_\ell^m(\cos\theta)$

To have acceptable solution ℓ must be integer.
With proper normalization $\Rightarrow Y_\ell^m \rightarrow$ spherical harmonics

$\vec{L}^2\, Y_\ell^m = \ell(\ell+1)\hbar^2 Y_\ell^m \qquad L_z Y_\ell^m = m\hbar Y_\ell^m$

It has acceptable solution only for ℓ, m being integers
$\ell = 0, 1, 2, 3, \cdots$
$m = -\ell, -\ell+1, -\ell+2, \cdots \ \ell-1, \ell.$

$Y_\ell^m(\theta,\phi)$ are eigenfunctions of simultaneous eigenfunction of
$\vec{L}^2$, L_z with eigenvalues $\ell(\ell+1)\hbar^2$, $m\hbar$ respectively

$\downarrow$

quantization of angular momentum.

A Measurement of the square of the angular momentum of the electron in the state $Y_{\ell m}$ will give definite value $\hbar^2\,\ell(\ell+1)$ where $\ell = 0, 1, 2, 3, \cdots$, while a measure of the z-component of the angular momentum will give the definite value $\hbar m$, where $m = \ell, (\ell-1), \cdots -(\ell-1), -\ell$.

Going to the hydrogen atom problem.

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

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

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

$$[H, \vec{L}^2] = 0$$

$$[H, L_z] = 0$$

$\psi \sim R_{El}(r)\, Y_l^m(\theta,\phi)$ is simultaneous eigenfunctions of $\vec{L}^2$, L_z

Substitute into $H\psi = E\psi$ $\Rightarrow$ radial equation $\Rightarrow R_{nl}(r)$
With proper normalization
$R_{nl}(r)\, Y_l^m(\theta,\phi)$ is simultaneous eigenfunctions of H, $\vec{L}^2$, L_z with eigenvalues E_n, $l(l+1)\hbar^2$, $m\hbar$ respectively

$\psi_{nlm}(r,\theta,\phi)$

$|R_{nl}(r)\, Y_l^m(\theta,\phi)|^2 r^2 dr \sin\theta\, d\theta\, d\phi$

$\downarrow$

probability of finding the "particle"
between r and $r+dr$
θ and $\theta+d\theta$
ϕ and $\phi+d\phi$

$\{\psi_{nlm}(r,\theta,\phi)\}$ form a orthonormal set. for $E<0$

$$\psi(\vec{r},t) = \sum C_{n,l,m}\, \psi_{nlm}(r,\theta,\phi)\, e^{-iE_n t/\hbar}$$

$C_{n,l,m}$ are determined by the initial condition
(using orthonormal properties of $\psi_{nlm}(r,\theta,\phi)$)

The Hydrogen Atom.

A hydrogen atom consists of a proton and an electron held together by the electrostatic attraction between them

$$E = \frac{\vec{P}_e^2}{2m_e} + \frac{\vec{P}_p^2}{2m_p} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

($Z=1$ for hydrogen
$Z \to$ nuclear charge for hydrogen-like atom)

$$r = |\vec{r}_e - \vec{r}_p|$$

$$\Rightarrow \quad H = -\frac{\hbar^2}{2m}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + \underset{\displaystyle -\frac{Ze^2}{4\pi\epsilon_0 r}}{\underset{\shortparallel}{V(r)}}$$

Define $\quad \vec{R} = \dfrac{m_e\vec{r}_e + m_p\vec{r}_p}{m_e+m_p} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$

$$\vec{r} = \vec{r}_e - \vec{r}_p = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\frac{\partial\psi}{\partial x_e} = \frac{\partial\psi}{\partial X}\frac{\partial X}{\partial x_e} + \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial x_e}$$

$$= \frac{m_e}{m_e+m_p}\frac{\partial\psi}{\partial X} + \frac{\partial\psi}{\partial x}$$

Similar expression for $\frac{\partial\psi}{\partial x_p}, \frac{\partial\psi}{\partial y_e}, \frac{\partial\psi}{\partial z_e}, \frac{\partial\psi}{\partial y_e}, \cdots$ can be obtained.

Define $\quad m = \dfrac{m_e m_p}{m_e+m_p} \quad \Rightarrow \quad \nabla_e = \dfrac{m}{m_p}\nabla_R + \nabla$

$m = \mu$ ↳ reduced mass

$$\nabla_p = \frac{m}{m_e}\nabla_R - \nabla$$

↳ with respect to $\vec{r}$

$$H = -\frac{\hbar^2}{2m_e}\left(\frac{m}{m_p}\nabla_R + \nabla\right)^2 - \frac{\hbar^2}{2m}\left(\frac{m}{m_e}\nabla_R - \nabla\right)^2 + V(r)$$

$$= -\frac{\hbar^2}{2m_e}\left[\frac{m^2}{m_p^2}\nabla_R^2 + \frac{m}{m_p}(\nabla_R\nabla + \nabla\nabla_R) + \nabla^2\right]$$

$$-\frac{\hbar^2}{2m_p}\left[\frac{m^2}{m_e^2}\nabla_R^2 - \frac{m}{m_e}(\nabla_R\nabla + \nabla\nabla_R) + \nabla^2\right] + V(r)$$

$$\Rightarrow \quad H = -\frac{\hbar^2}{2(m_e+m_p)}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The time independent Schrodinger equation becomes

$$\left(-\frac{\hbar^2}{2(m_e+m_p)}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(\vec{r},\vec{R}) = \phi(\vec{R})\,u(\vec{r})$$

Again carry out the seperation of variable.

Ansatz $\psi(\vec{r}, \vec{R}) = \phi(\vec{R})\, u(\vec{r})$

Substitute into above equation

$$\Rightarrow \frac{-\hbar^2}{2(m_e+m_p)} u \nabla_R^2 \phi - \frac{\hbar^2}{2m} \phi \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} u\phi = E_t u\phi$$

Divide by $u\phi$

$$-\frac{\hbar^2}{2(m_e+m_p)\phi} \nabla_R^2 \phi - \frac{\hbar^2}{2mu} \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} = E_t$$

We group together the r and the R dependent terms and equal them to the same constant

$$\frac{-\hbar^2}{2(m_e+m_p)\phi} \nabla_R^2 \phi = E_c = \frac{\hbar^2}{2mu} \nabla^2 u + \frac{Ze^2}{4\pi\epsilon_0 r} + E_t$$

Define $E = E_t - E_c$

$$\Rightarrow \quad -\frac{\hbar^2}{2(m_e+m_p)} \nabla_R^2 \phi = E_c \phi$$

↓

the solution is a plane wave describing the motion of the center of mass this part is of no interest to us

$$-\frac{\hbar^2}{2m} \nabla^2 u - \frac{Ze^2}{4\pi\epsilon_0 r} u = E u$$

↓

Schrodinger equation of a particle moving in a fixed central potential except that the electron mass have been replaced by the reduced mass

$\Rightarrow$ This seperation is sometimes referred to as the reduction of a two-body problem to a single-one-body problem. [We have carried out similar procedure in Chapter 1]

We follow "Basic Quantum Mechanics" by K. Zioch P. 73-77

$$\left[\ m = \frac{m_e m_p}{m_e + m_p} \sim m_e \quad \text{since} \quad m_p \sim 1836\, m_e \right]$$

Now we shall go back to the central force problem

Only the radial equation (μ) has to be solved

$$\frac{1}{R} \frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] - \frac{2mr^2}{\hbar^2}\left[-\frac{Ze^2}{4\pi\epsilon_0 r} - E\right] = \ell(\ell+1)$$

This is an ordinary differential equation

m appeared here is the reduced mass, <u>not</u> the magnetic quantum number.

$$\Rightarrow \frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\Big(\underbrace{-\frac{Ze^2}{4\pi\epsilon_0 r}}_{V(r)} - E\Big)R = \ell(\ell+1)R$$

this is the equation to solve.
[Equation (4.35) of Griffths]
We follow "Introduction to Quantum Mechanics"
P. 133-139

Change variable

$$u(r) = rR(r)$$

$$\Rightarrow \quad R = \frac{u}{r}, \quad \frac{dR}{dr} = \left[r\frac{du}{dr} - u\right]/r^2$$

$$\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] = r\frac{d^2u}{dr^2}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

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

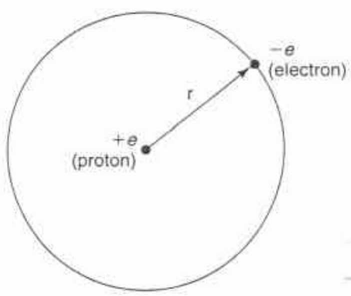
centrifugal term

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \quad \text{for hydrogen atom.}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

This is Equation (4.53)

Our problem is to solve this equation for $u(r)$ and determine the allowed electron energies E. The hydrogen atom is such an important case that I'm not going to hand you the solutions this time—we'll work them out in detail by the method we used in the analytical solution to the harmonic oscillator. (If any step in this process is unclear, you may wish to refer back to Section 2.3.2 for a more complete explanation.) Incidentally, the Coulomb potential (Equation 4.52) admits *continuum* states (with $E > 0$), describing electron-proton scattering, as well as discrete *bound* states, representing the hydrogen atom, but we shall confine our attention to the latter.



Radial equation (See Appendix F)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

For hydrogen atom $V(r) = -\dfrac{e^2}{4\pi\epsilon_0 r}$

The problem is reduced to solve

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

[Note: $u = u(r)$]

↓

this is an ordinary differential equation

We shall follow the method in solving the harmonic oscillator

$E > 0 \Rightarrow$ continous solutions describing the e-p scattering.

$E < 0 \Rightarrow$ bound states representing the hydrogen atom.

↓

we shall confine our attention to this problem.

(1) Tidy up the notation

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$$

(Note $E < 0$) κ is real

Divide the radial equation by E

$$\Rightarrow \frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2}\frac{1}{\kappa r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]u$$

It is now natural to define

$\rho = \kappa r$ and $\rho_0 = \dfrac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$ = constant

$$\Rightarrow \frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

$[u = u(\rho)]$

(2) Looking at the asymptotic solution

As $\rho \to \infty$

$$\frac{d^2u}{d\rho^2} = u$$

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

not allowed by the requirement of normalization

$$u(\rho) \sim Ae^{-\rho}$$

As $\rho \to 0$

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

Ansatz ρ^n

$$n(n-1)\rho^{n-2} = \frac{\ell(\ell+1)}{\rho^2}\rho^n$$

$$n(n-1) = \ell(\ell+1)$$

$n = -\ell$, $n = \ell+1$ (by inspection)

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

not allowed by the requirement of normalization.

$$u(\rho) = C\rho^{\ell+1}$$

(3) Peel off the asymptotic behavior

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$\frac{du}{d\rho} = \rho^{\ell} e^{-\rho} [(\ell+1-\rho)v + \rho\frac{dv}{d\rho}]$$

$$\frac{d^2u}{d\rho^2} = \rho^{\ell} e^{-\rho} \{[-2\ell-2+\rho+\frac{\ell(\ell+1)}{\rho}] + 2(\ell+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\}$$

$$\Rightarrow \rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

this is an equation for $v(\rho)$

should be well-behaved.

(4) Series expansion and recursive relation

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

The task is to find a_j

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1} = 0 + 1\cdot a_1 + 2a_2\rho^1 + \cdots$$

$\downarrow j \to j+1$

$$= \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j = 1\cdot a_1 + 2a_2\rho^1 + \cdots$$

$j=-1$ term killed by the $j+1$ factor

Same method

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1}$$

$$\Rightarrow \sum_{j=0}^{\infty} j(j+1) a_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j$$
$$-2\sum_{j=0}^{\infty} j a_j \rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty} a_j\rho^j = 0$$

Compare the coefficient

$$j(j+1)a_{j+1} + 2(l+1)(j+1)a_{j+1} - 2ja_j + [\rho_0 - 2(l+1)]a_j = 0$$

$$\Rightarrow \quad a_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)} a_j$$

$\downarrow$

recursive relation.

If $a_0 = A$ is given, then $a_1, a_2, \cdots$ can be determined by the recursive relation

Different A differ only by only an overall constant. which is eventually determined by normalization

(5) Termination of the series

Large ρ behavior is determine by the large j behavior

$$a_{j+1} \sim \frac{2j}{j(j+1)} a_j = \frac{2}{j+1}$$

$$a_{j+1} \sim \frac{2^j}{j!} A$$

$$v(\rho) = A\sum_{j=0}^{\infty}\frac{2^j}{j!}\rho^j \underset{\downarrow}{=} A e^{2\rho}$$

using the series expansion of e^x

$$\Rightarrow \quad u(\rho) = A\rho^{l+1}e^{\rho}$$

↓

diverges at $\rho\to\infty$

↓

the solution we have discarded if the series is <u>not</u> terminated

If ~~the~~ the series is terminate at j_{max}, i.e., $a_{j_{max}+1} = 0$, then

$$u(\rho) = A\rho^{l+1}e^{-\rho}(\text{polynomial of order } j_{max})$$

$$\sim e^{-\rho} \quad \text{at } \rho\to\infty$$

↓

the desired result.

(6) Condition of Termination.

$$a_{j_{max}+1} = 0$$

$$\Rightarrow \quad 2(\underbrace{j_{max}+l+1}_{n}) - \rho_0 = 0$$

↓

principal quantum number must be integer

$$2n = \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa^2} \qquad \kappa^2 = \frac{-2mE}{\hbar^2}$$

$$\Rightarrow \quad E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$

$$\Rightarrow \quad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$$

↓

Bohr formula.

The energy spectrum (first few levels only are given in Appendix E

$$\underset{\underset{2n}{\shortparallel}}{\rho_0} = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \Rightarrow \kappa = \frac{me^2}{(4\pi\epsilon_0\hbar^2)}\frac{1}{n} = \frac{1}{an}$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\cdot 10^{-10}\,m.$$

$$\rho = \frac{r}{an}$$

$\Rightarrow$ This is one of the most important result in the development of quantum mechanics

$|\psi(\vec{r})|^2 dV$ = probability in finding the "electron" in the volume element dV

In spherical coordinate

$$|\psi(r,\theta,\phi)|^2 \underbrace{r^2}_{\text{note the } r^2 \text{ factor}} dr \sin\theta \, d\theta \, d\phi$$

Normalization condition

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r,\theta,\phi)|^2 r^2 dr \sin\theta \, d\theta \, d\phi = 1$$

If $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$, we usually meet the condition by requiring

$$\int_0^\infty |R(r)|^2 r^2 dr = 1$$

$$\int_0^\pi \int_0^{2\pi} |\Theta(\theta)\Phi(\phi)|^2 \sin\theta \, d\theta \, d\phi = 1$$

For central potential

$\Theta(\theta)\Phi(\phi)$ satisfies the angular equation (independent of $V(r)$)

$$\Theta_{\ell m}(\theta)\Phi_m(\phi) = A_{\ell m} P_\ell^m(\theta) e^{im\phi}$$

Require normalization

$$\int_0^\pi \int_0^{2\pi} |A_{\ell m}|^2 |P_\ell^m(\theta) e^{im\phi}|^2 \sin\theta \, d\theta \, d\phi = 1$$

$$\downarrow$$

$$A_\ell^m(\theta,\phi) = \epsilon \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{(\ell+m)!}}$$

$\epsilon = (-1)^m$ for $m \geq 0$, and $\epsilon = 1$ for $m \leq 0$

$$\Rightarrow \underbrace{Y_\ell^m(\theta,\phi)}_{\text{spherical harmonics}} = \epsilon \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{(\ell+m)!}} P_\ell^m(\theta) e^{im\phi}$$

分類:	
編號:	7-16
總號:	

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

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

[details are given in Appendix B]

Some associated Legendre functions $P_\ell^m(x)$ and the first few spherical harmonics are listed in Appendix C.

To find $R_{E\ell}(r)$, one need to solve the radial equation (which depends on $V(r)$)

For Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \qquad E<0$$

$\downarrow$

hydrogen atom

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v_{n\ell}(\rho)$$

$\updownarrow$

E

$$v(\rho) = \sum_{j=0}^{j_{max}=n-\ell-1} a_j \rho^j \qquad \text{polynomial of degree } j_{max}$$

$$\rho = \frac{r}{n}$$

$\downarrow$ note $\rho_0 = 2n$

$$a_{j+1} = \frac{(2j+\ell+1 \ -n)}{(j+1)(j+2\ell+2)} a_j$$

$\downarrow$

the function is determined up to a constant

$\downarrow$

which is in determined by the normalization conditions

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

$\psi_{n\ell m}(r,\theta,\phi)$ is an eigenfunction of

$$H \psi_{n\ell m}(r,\theta,\phi) = E_n \psi_{n\ell m}(r,\theta,\phi)$$

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

E is a function of n only

$\downarrow$

this is only valid for Coulomb potential

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

Example:

$n=1,\ \ell=0,\ m=0$

$\psi_{100}(r,\theta,\phi) = R_{10}(r)\, Y_0^0(\theta,\phi)$

$R_{10}(r)$ only $j=0$ contributes $(a_1=0)$

$R_{10}(r) = \frac{a_0}{a_1} e^{-r/a}$

$\int |R_{10}(r)|^2 r^2\, dr = 1 \Rightarrow a_0 = \frac{2}{\sqrt{a}}$

$Y_1^1 = \frac{1}{\sqrt{4\pi}}$

$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\ eV$

Exercise: Find $\psi_{210}(r,\theta,\phi)$

$n,\quad \ell = 0, 1, \cdots n-1$
$\quad\quad m = -\ell, \cdots \ell$

E is a function of n only

$\downarrow$

states with the same n will have the same energy

$\downarrow$

degeneracy

Degeneracy of $E_n = \sum_{\ell=0}^{n-1}(2\ell+1) = n^2$

$n=2$ degeneracy $=4$ $\quad\quad$ $n=1$ degeneracy $=1$

$\downarrow$

the factor that should appear in the middle term examination.

The first few radial wave functions for hydrogen $R_{n\ell}(r)$ are given in Appendix D.

Higher $\ell \Rightarrow$ higher $\frac{\hbar^2 \ell(\ell+1)}{2mr^2}$ tends to push the wave function from the origin.

Radial equation for spherically symmetric potential

The SE in 3D in spherical coordinates is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\psi(\mathbf{r})+\frac{\mathbf{L}^2}{2mr^2}\psi(\mathbf{r})+V(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{22-1}$$

using the ansatz $\psi(\mathbf{r})=R(r)Y(\theta,\phi)$, and inserting for the angular function an eigenfunction

$$Y(\theta,\phi)=Y_{lm}(\theta,\phi)=\langle\theta,\phi|l,m\rangle, \tag{22-2}$$

we have, using $\mathbf{L}^2Y_{lm}(\theta,\phi)=\hbar^2 l(l+1)Y_{lm}(\theta,\phi)$ after dividing by Y_{lm} for the radial equation,

$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2mr^2}+V(r)\right]R_{nl}(r)=E_{nl}R_{nl}(r)}. \tag{22-3}$$

Here, we have added two subscripts n, l to the radial wavefunction $R(r)$ and the eigenenergy E because the SE for the radial part of the wavefunction depends on the total angular momentum l of the 3D wavefunction $\psi(\mathbf{r})$.

Note. The z-component of angular momentum L_z, and the corresponding magnetic quantum number m, do not appear in the radial equation.

We can define an l-dependent effective potential,

$$V_{\text{eff},l}=V(r)+\frac{\hbar^2 l(l+1)}{2mr^2}, \tag{22-4}$$

where the additional term is the centrifugal barrier for a particle with angular momentum

$$\langle\mathbf{L}^2\rangle=\hbar^2 l(l+1). \tag{22-5}$$

The radial equation can be brought into a more familiar-looking form by introducing a new function:

$$\begin{aligned} u(r)&=rR(r)\\ R(r)&=\frac{u(r)}{r}\end{aligned} \tag{22-6}$$

Then,

$$R'=\frac{u'r-u}{r^2}=\frac{u'}{r}-\frac{u}{r^2} \tag{22-7}$$

$$\frac{2}{r}R'=\frac{2u'}{r^2}-\frac{2u}{r^3} \tag{22-8}$$

$$R''=\frac{u''r-u'}{r^2}-\frac{u'r^2-u2r}{r^4}=\frac{u''}{r}-\frac{2u'}{r^2}+\frac{2u}{r^3} \tag{22-9}$$

$$\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)R(r)=R''+\frac{2}{r}R'=\frac{u''}{r} \tag{22-10}$$

and the radial equation is

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2 u}{\partial r^2} + \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]\frac{u(r)}{r} = E\frac{u(r)}{r} \tag{22-11}$$

or

$$\boxed{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]\frac{u_{nl}(r)}{r} = E_{nl}u_{nl}(r)} \tag{22-12}$$

This equation for $u(r) = rR(r)$ has the same form as the 1D SE in the effective potential

$$V_{\text{eff},l}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \tag{22-13}$$

but with slightly different boundary conditions. Therefore, $u(r)$ looks like an anti-

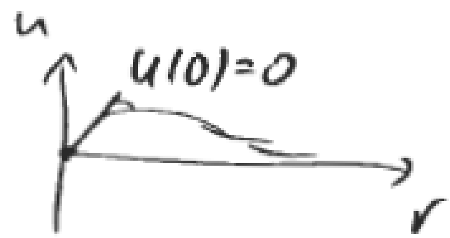


Figure I: $u(r) = rR(r)$ has the same form as the 1D SE in the effective potential $V_{\text{eff},l}(r)$, but with slightly different boundary conditions.

symmetric solution in all space. Consequences are, e.g., that since an antisymmetric

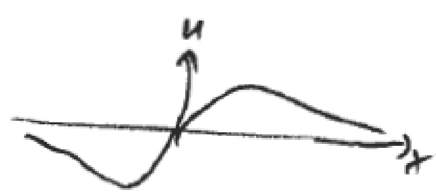


Figure II: $u(r)$ looks like an antisymmetric solution in all space.

bound state does not always exist in 1D, that a bound state does not always exist in 3D (in contrast to 1D, where a symmetric bound state always exist in a potential well). 3D wavefunctions $u(r)$ are like antisymmetric 1D wavefunctions in the effective potential

$$V_l(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{22-14}$$

Hydrogen atom

$$V(r) = -\frac{Ze^2}{4\pi\epsilon r} \quad \rightarrow \quad \text{(and the radial equation is)} \tag{22-15}$$

$$\left(-\frac{\hbar 62}{2m}\frac{\partial^2}{\partial r^2} - \frac{Ze^2}{4\pi\epsilon r} + \frac{\hbar^2 l(l+1)}{2mr^2} - E\right)u(r) = 0 \tag{22-16}$$

We introduce a dimensionless position coordinate ρ by $\rho^2 = \frac{8m|E|}{\hbar^2}r^2$, and define for $E < 0$

$$\frac{Ze^2}{r16\pi\epsilon|E|}\sqrt{\frac{8m}{\hbar^2}}\sqrt{\frac{\hbar^2}{8m}} = \frac{Ze^2}{16\pi\epsilon\hbar r}\sqrt{\frac{8m}{|E|}}\sqrt{\frac{\hbar^2}{8m|E|}} \tag{22-17}$$

$$= \frac{Ze^2}{4\pi\epsilon\hbar}\sqrt{\frac{m}{2|E|}}\frac{1}{\rho} \tag{22-18}$$

$$=: \frac{\lambda}{\rho} \tag{22-19}$$

The equation can be written as

$$\frac{\partial^2}{\partial\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)u = 0 \tag{22-20}$$

with $\rho = \sqrt{\frac{8m|E|}{\hbar^2}}r$, $\lambda = \frac{Ze^2}{4\pi\epsilon\hbar}\sqrt{\frac{m}{2|E|}} = Z\alpha\sqrt{\frac{mc^2}{2|E|}}$, where $\alpha = \frac{e^2}{4\pi\epsilon\hbar c} \approx \frac{1}{137.0...}$ is the dimensionless fine structure constant. To solve this equation, we proceed as for the HO: We write a Taylor-expansion solution after having factored out the correct asymptotic behavior.

For very large ρ we have

$$\frac{d^2}{dp^2}u = \frac{1}{4}u \tag{22-21}$$

$$u(\rho) \propto e^{-\frac{1}{2}\rho} \tag{22-22}$$

For very small ρ,

$$\frac{d^2}{dp^2}u = \frac{l(l+1)}{\rho^2}u \tag{22-23}$$

$$u(\rho) \propto \rho^{l+1} \tag{22-24}$$

Consequently, we try a **solution of the form**

$$\boxed{u(\rho) = s(\rho)\rho^{l+1}e^{-\frac{1}{2}\rho}} \tag{22-25}$$

$$u'(\rho) = \left(s'(\rho)\rho^{l+1} + s(\rho)(l+1)\rho^{l} - \frac{1}{2}s\rho^{l+1}\right)e^{-\frac{1}{2}\rho} \tag{22-26}$$

$$u''(\rho) = \big[s''\rho^{l+1} + 2(l+1)s'\rho^{l} + s(l+1)l\rho^{l-1} \tag{22-27}$$

$$- \frac{1}{2}\left(s'\rho^{l+1} + (l+1)s\rho^{l}\right) \tag{22-28}$$

$$- \frac{1}{2}\left(s'\rho^{l+1} + (l+1)s\rho^{l} - \frac{1}{2}s\rho^{l+1}\right)\big]e^{-\frac{1}{2}} \tag{22-29}$$

$$= \rho^{l+1}e^{-\frac{\rho}{2}}\left[s'' + 2(l+1)\frac{s'}{\rho} + \frac{(l+1)l}{\rho^2}s - s' - \frac{l+1}{\rho}s + \frac{1}{4}s\right] \tag{22-30}$$

$$\left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)u = \rho^{l+1}e^{-\frac{\rho}{2}}\left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)s \tag{22-31}$$

Inserting this into (**??**) leads to

$$s'' + \left(\frac{2(l+1)}{\rho} - 1\right)s' + \left(\frac{(l+1)l}{\rho^2} - \frac{l+1}{\rho} + \frac{1}{4} + \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)s = 0 \tag{22-32}$$

$$s'' + \left[\frac{2l+2}{\rho} - 1\right]s' + \frac{\lambda - l - 1}{\rho}s = 0 \tag{22-33}$$

To solve this differential equation, we write a Taylor expansion about $\rho = 0$:

$$s(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \tag{22-34}$$

$$s'' = \sum_{k=0}^{\infty} a_k k(k-1)\rho^{k-2} \tag{22-35}$$

$$= \sum_{k=0}^{\infty} a_{k+2}(k+2)(k+1)\rho^k \tag{22-36}$$

$$\left(\frac{2l+2}{\rho} - 1\right)s' = \left(\frac{2l+2}{\rho} - 1\right)\sum a_k k\rho^{k-1} \tag{22-37}$$

$$= (2l+2)\sum_{k=0}^{\infty} a_{k+2}(k+2)\rho^k - \sum a_{k+1}(k+1)\rho^k \tag{22-38}$$

$$\frac{\lambda - l - 1}{\rho}s = (\lambda - l - 1)\sum_{k=0}^{\infty} a_{k+1}\rho^k \tag{22-39}$$

which substituted into (**??**) results in

$$\sum_k \rho_k \left\{(k+2)(k+1)a_{k+2} + 2(l+1)(k+2)a_{k+2} + (\lambda - l - 1 - k - 1)a_{k+1}\right\} = 0 \tag{22-40}$$

This must vanish term by term, so we obtain a recursion relation

$$(k+2)(k+2l+3)a_{k+2} = (k+l+2-\lambda)a_{k+1} \tag{22-41}$$

or

$$\boxed{\frac{a_{k+1}}{a_k} = \frac{k+l+1-\lambda}{\big(k+1\big)\big(k+2(l+1)\big)} \quad \rightarrow \quad \begin{array}{c}\text{recursion}\\ \text{relation for}\\ \text{expansion}\\ \text{coefficients}\end{array}} \tag{22-42}$$

If the series does not break off somewhere, we will have for large k, $a_k \propto \frac{1}{k}a_{k-1}$ or $a_k \propto \frac{1}{k!}$, which gives a growth $s(\rho) \propto e^{+\rho}$, which is not acceptable for $u(\rho) = s(\rho)e^{-\frac{\rho}{2}}$. Consequently, we require the series to terminate, which implies $\lambda = k+l+1$ for some L. Let us call $n_r = k$ the integer with that property. It is cutomary to define the **principal quantum number** as

$$\boxed{n = n_r + l + 1}, \tag{22-43}$$

where $n_r \geq 0$, so $n \geq 0$, so $n \geq l+1$, n integer, and

$$\lambda_n = \frac{Ze^2}{4\pi\epsilon\hbar}\sqrt{\frac{m}{2|E_n|}} \tag{22-44}$$

$$= Z\alpha\sqrt{\frac{mc^2}{2|E_n|}} \tag{22-45}$$

$$= n \tag{22-46}$$

Consequently, the eigenenergies of the hydrogen atom are

$$\boxed{E_n = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}} \quad \rightarrow \quad \left(\begin{array}{c}\text{eigenenergies of}\\ \text{hydrogenlike atoms}\end{array}\right) \tag{22-47}$$

This is the same energy eigenspectrum as obtained from the Bohr formula.

Note. There are important differences:

- The principal quantum number $n = n_r + l + 1$ is really the sum of the radial quantum number n_r and the total angular momentum quantum number l.

- We have obtained the full radial and angular distribution of the electron, which generalizes the classical concept of an orbit.

First few radial functions

$$\rho_n^2 = \frac{8m|E_n|}{\hbar^2} r^2 \tag{22-48}$$
$$= \frac{8m}{\hbar^2}\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2} r^2 \tag{22-49}$$
$$= \frac{(2mcZ\alpha)^2}{\hbar n^2} r^2 \tag{22-50}$$
$$= \left(\frac{2Z}{a_0}\right)^2 r^2 \frac{1}{n^2} \tag{22-51}$$
$$= \frac{2Zr}{na_0} \tag{22-52}$$

with the Bohr radius

$$\boxed{a_0 = \frac{\hbar^2}{mc\alpha}} \tag{22-53}$$

Consequently, $e^{-\frac{1}{2}\rho} = e^{-\frac{Zr}{na_0}}$

1. $n_r = l = 0$, $n = m = \lambda$, $a_1 = 0$

$$u(r) = C\rho e^{-\frac{1}{2}\rho} = C_1\left(\frac{Zr}{a_0}\right)e^{-\frac{Z\alpha}{a_0}} \tag{22-54}$$
$$R(r) = \frac{u(r)}{r} = C_2 e^{-\frac{Zr}{a_0}} \tag{22-55}$$

Note. The probability to find the electron between r and $r + dr$ is given by $r^2|R(r)|^2dr = |u(r)|^2dr$.

2. (a) $n_r = 1$, $l = 0$, $n = 2 = \lambda$

$$\frac{a_1}{a_0} = -\frac{1}{1\cdot 2} = -\frac{1}{2} \tag{22-56}$$
$$u_{20}(r) = C\rho e^{-\frac{1}{2}\rho}(1 - \frac{1}{2}\rho) = C'\frac{Zr}{a_0}\left(1 - \frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}} \tag{22-57}$$
$$R_{20}(r) = C''\left(1 - \frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}} \tag{22-58}$$

(b) $n_r = 0$, $l = 1$, $n = 2 = \lambda$

$$\frac{a_1}{a_0} = 0 \quad \rightarrow \quad a_1 = 0 \tag{22-59}$$

$$u_{21}(r) = C\rho^2 e^{-\frac{1}{2}\rho} = C'\left(\frac{Zr}{a_0}\right)^2 e^{-\frac{Zr}{2a_0}} \tag{22-60}$$

$$R_{21}(r) = C''\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}} \tag{22-61}$$

$R_{20} = R_{n=2,l=0}$ and $R_{21} = R_{n=2,l=1}$ are different states that have the same eigenenergy. The occurrence of different eigenstates with the same energy, (or in general quantum number) is called **degeneracy**.

Last time

- Radial equation for given angular momentum eigenstate $Y_{lm}(\theta, \phi)$ with quantum number l

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] R_{nl}(r) = E_{nl} R(r) \tag{23-1}$$

can be written in form of 1D SE with effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \tag{23-2}$$

by defining $u(r) = rR(r)$,

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + V_{\text{eff}}(r)u(r) = Eu(r). \tag{23-3}$$

- Specialization to hydrogen atom:

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{23-4}$$

- Define dimensionless variables:

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}}r, \quad \lambda = \frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{m}{2|E|}} \tag{23-5}$$

$$u''(\rho) + \left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right)u(\rho) = 0 \tag{23-6}$$

- Asymptotic solutions:

$$u(\rho) = s(\rho)\rho^{l+1}e^{-\frac{\rho}{2}}, \text{ for } \rho \to \infty, \rho \to 0 \tag{23-7}$$

and Taylor expansion

$$s(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \tag{23-8}$$

leads to recursion relation

$$\frac{a_{k+1}}{a_k} = \frac{k + l + 1 - \lambda}{(k+1)(k + 2(l+1))}. \tag{23-9}$$

- Boundary conditions for $\rho \to \infty$ require series to terminate at some

$$k = n_r \tag{23-10}$$

$$n_r + l + 1 = \lambda, \quad \to \quad (n_r \text{ radial quantum number}) \tag{23-11}$$

- Define

$$\lambda = n = n_r + l + 1, \quad \rightarrow \quad \text{(principal quantum number)} \tag{23-12}$$

$$E_n = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2} \tag{23-13}$$

not relativistic formula, only written in simple form using

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \quad \rightarrow \quad \text{(fine structure constant)} \tag{23-14}$$

- In general, the (unnormalized) polynomial $s(\rho)$ is the associated Laguerre polynomial,

$$\boxed{s(\rho) = L^{(2l+1)}_{n-l-1}(\rho)}, \tag{23-15}$$

defined as

$$\boxed{L^{\alpha}_{n}(\rho) = \sum_{m=0}^{n}\binom{n+\alpha}{n-m}\frac{(-\rho)^m}{m!}}. \tag{23-16}$$

The 3D wavefunction is given by:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{23-17}$$

$$= \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\phi) \tag{23-18}$$

with

$$u(\rho) = s(\rho)\rho^{l+1}e^{-\frac{1}{2}\rho}, \tag{23-19}$$

normalized such that

$$1 = \int d^3\mathbf{r}|\psi_{nlm}(\mathbf{r})|^2 = \int d\Omega|Y_{nl}(\theta,\phi)|^2\int_0^\infty r^2dr|R_{nl}(r)|^2 \tag{23-20}$$

The probability to find particle within shell $[r, r+dr]$ is given by

$$\int d\Omega|Y_{nl}|^2r^2|R(r)|^2dr = |u(r)|^2\int d\Omega|Y_{nl}| \tag{23-21}$$

Degeneracy of the hydrogen spectrum

For given l_1 all magnetic quantum numbers m have the same energy, so each l is (2l + 1) degenerate. Also, for each $n = n_r + l + 1$, the radial quantum number n_r can take on the values $n_r = 0, 1, \ldots, n-1$, and the l quantum number the corresponding values $l = 0, 1, \ldots, n-1$.

So for given n, the total number of degenerate states is

$$\underbrace{1}_{(l=0)} + \underbrace{3}_{(l=1)} + \cdots + \underbrace{2(n-1)+1}_{(l=n-1)} = (n+1)^2 \tag{23-22}$$

Actually, there are twice as many states because each electron has two spin states.

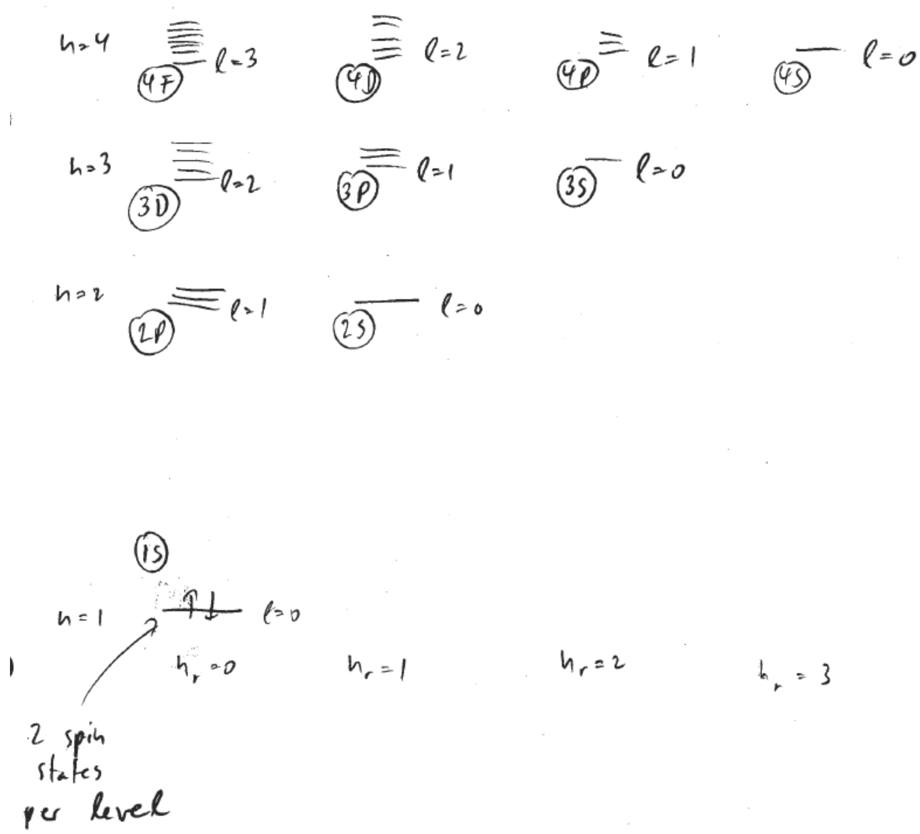


Figure I: Energy level structure of hydrogen atom.

Normalized time-independent eigenstates of hydrogen

$$\psi_{100} = \frac{2}{(a_0)^{3/2}} e^{-r/a_0} Y_{00}(\theta,\phi) \qquad 1s \qquad (23\text{-}23)$$

$$\psi_{200} = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00}(\theta,\phi) \qquad 2s \qquad (23\text{-}24)$$

$$\left.\begin{pmatrix} \psi_{211} \\ \psi_{210} \\ \psi_{21-1} \end{pmatrix} = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \begin{pmatrix} Y_{11}(\theta,\phi) \\ Y_{10}(\theta,\phi) \\ Y_{1-1}(\theta,\phi) \end{pmatrix} \right\} \qquad 2p \qquad (23\text{-}25)$$

Spectroscopic Notation		
$l = 0$	is called	s
$l = 1$	is called	p
$l = 2$	is called	d
$l = 3$	is called	f

Some useful expectation values for the hydrogen atom

Given the wavefunctions $R(r)$, we can calculate expectation values

$$\langle r^k \rangle = \int_0^\infty dr r^{2+k} |R_{nl}(r)|^2 \tag{23-26}$$

$$\langle r \rangle = \frac{a_0}{2Z}[3n^2 - l(l+1)] \tag{23-27}$$

$$\langle r^2 \rangle = \frac{a_0^2 n^2}{2Z^2}[5n^2 + 1 - 3l(l+1)] \tag{23-28}$$

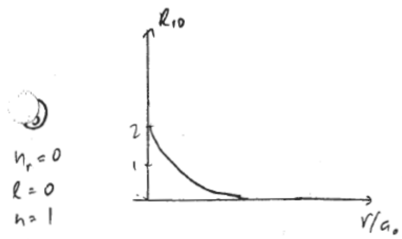
$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0 n^2} \tag{23-29}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2 n^3 \left(l + \frac{1}{2}\right)} \tag{23-30}$$

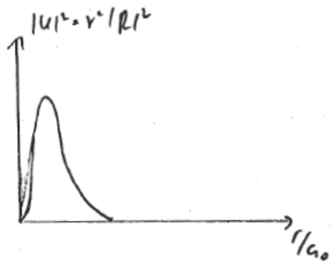
Lifting of degeneracy in hydrogen atom

Further interactions, that we have neglected so far, lift the degeneracy between s,p,d levels. For instance, from the electron's point of view, the moving proton corresponds to a current. The associated magnetic field couples to the magnetic moment associated with the spin of the electron: **spin-orbit interaction**. Furthermore, relativistic effects lead to energy shifts that depend on the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ of the electron (*8.05: addition of angular momenta*). Also, the proton has spin that has a small magnetic moment associated with it. The interaction between the proton's and the electron's magnetic moments is called the hyperfine interaction, and leads to shifts that depend on the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I} = \mathbf{L} + \mathbf{S} + \mathbf{I}$ of the atom, where $\mathbf{I}$ is the spin of the proton (nucleus). While the intrinsic angular momentum (spin) of fundamental particles is always $\hbar/2$, composite particles, such as nuclei, can have integer spin if the number of constituents is even. Therefore, when viewed as single particles, atoms can be bosons (integer spin) or fermions (half-integer spin), with dramatic consequences for quantum statistics and low-temperature behavior.

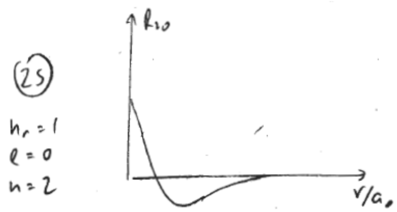
Two identical fermions must be described by a wavefunction that is antisymmetric with



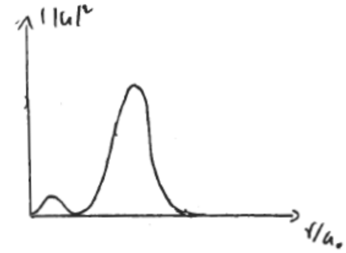
(a) $n_r = 0, l = 0, n = 1$



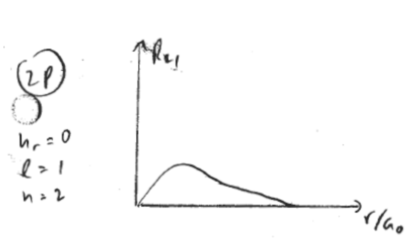
(b) $n_r = 0, l = 0, n = 1$



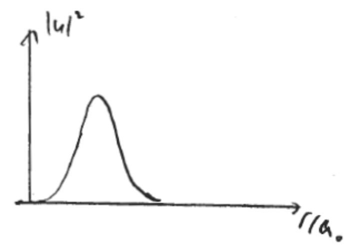
(c) $n_r = 1, l = 0, n = 2$



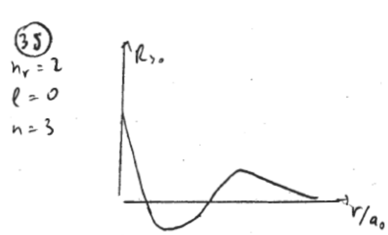
(d) $n_r = 1, l = 0, n = 2$



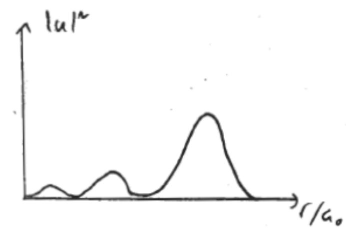
(e) $n_r = 0, l = 1, n = 2$



(f) $n_r = 0, l = 1, n = 2$



(g) $n_r = 2, l = 0, n = 3$



(h) $n_r = 2, l = 0, n = 3$

Figure II: A few radial wavefunction. Displayed on the left is the wavefunction R_{nl}, on the right the probability density $|u_{nl}|^2 = r^2|R_{nl}|^2$. n_r is the number of nodes in the radial wavefunction.

respect to particle exchange,

$$\psi_\tau(\mathbf{r}_1, \mathbf{r}_2) = -\psi_q(\mathbf{r}_2, \mathbf{r}_1) \tag{23-31}$$

$\Longrightarrow$ wavefunction vanishes for $\mathbf{r}_1 = \mathbf{r}_2 \rightarrow$ fermions avoid each other.

Bosons are described by symmetric wavefunction with repect to particle exchange

$$\psi_B(\mathbf{r}_1, \mathbf{r}_2) = +\psi_B(\mathbf{r}_2, \mathbf{r}_1) \tag{23-32}$$

$\Longrightarrow$ Bosons are more likely to be found at same position $\rightarrow$ lasers, Bose-Einstein condensation, superconductivity, classical notion of fields where amplitudes can be added.

Polarization of light

A classical light field traveling along z can be linearly polarized along x,

$$\varepsilon(z, t) = \varepsilon_0 \hat{e}_x e^{ikz - i\omega t}, \tag{23-33}$$

linearly polarized along y,

$$\varepsilon(z, t) = \varepsilon_0 \hat{e}_y e^{ikz - i\omega t}, \tag{23-34}$$

linearly polarized along a direction $\hat{e} = \cos\theta \hat{e}_x + \sin\theta \hat{e}_y$, in the xy plane,

$$\varepsilon(z, t) = \varepsilon_0 \hat{e} e^{ikz - i\omega t}, \tag{23-35}$$

circularly polarized

$$\hat{e}_{\mathrm{R}} = \frac{1}{\sqrt{2}}(\hat{e}_x + i\hat{e}_y) \tag{23-36}$$

$$\hat{e}_{\mathrm{L}} = \frac{1}{\sqrt{2}}(\hat{e}_x - i\hat{e}_y) \tag{23-37}$$

$$\varepsilon_{\mathrm{L,R}}(z, t) = \varepsilon_0 \hat{e}_{\mathrm{L,R}} e^{ikz - i\omega t} \tag{23-38}$$

or, in general, elliptically polarized

$$\hat{\varepsilon} = \cos\theta \hat{e}_x + e^{i\phi} \sin\theta \hat{e}_y \varepsilon(z, t) \qquad = \varepsilon_0 \hat{e} e^{ikz - i\omega t} \tag{23-39}$$

Any two orthogonal polarization (e.g., $(\hat{e}_x,\ \hat{e}_y)$, $(\frac{1}{\sqrt{2}}(\hat{e}_x + \hat{e}_y), \frac{1}{\sqrt{2}}(\hat{e}_x - \hat{e}_y))$, $(\hat{e}_{\mathrm{L}},\ \hat{e}_{\mathrm{R}})$, $\ldots$) form a basis. An arbitrary polarization can be expressed as a superposition of the two basis polarizations.

A linear polarizer has one strongly absorbing direction of polarization (ideally $\varepsilon \cdot \hat{e} = 0$ along that direction of polarization after the polarizer), and one weakly absorbing direction (ideally: no absorption). If we call the latter the axis of the polarizer, the light behind the polarizer is linearly polarized along that axis. No light is transmitted through two crossed polarizers unless a third polarizer is inserted between them at an intermediate angle In this case the transmitted field is

$$\varepsilon_0 \cdot (\hat{e}_x \cdot \frac{1}{\sqrt{2}}(\hat{e}_x + \hat{e}_y))\frac{1}{\sqrt{2}}(\hat{e}_x + \hat{e}_y) \cdot \hat{e}_y = \frac{1}{2}\varepsilon_0 \tag{23-40}$$

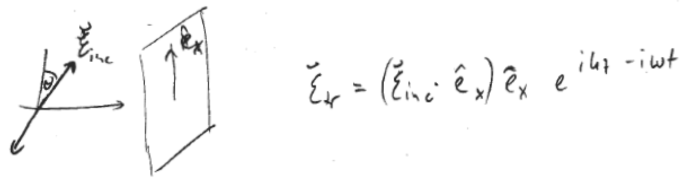


Figure III: The polarization of the transmitted light is $\varepsilon_{tr} = (\varepsilon_{\text{inc}} \cdot \hat{e}_x)\hat{e}_x e^{ikz-i\omega t}$

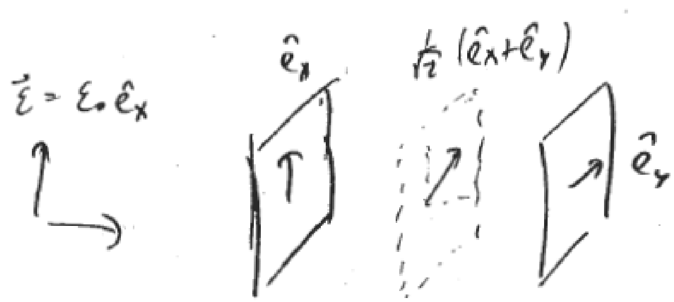


Figure IV: Light can pass two crossed polarizers if a third polarizer is inserted between them that is oriented at an angle.

and the transmitted intensity is proportional to $[\frac{1}{2}\varepsilon_o]^2$. The variation of transmitted electric field with polarizer angle, $\hat{e} = \cos\theta\hat{e}_x + \sin\theta\hat{e}_y$ for incident field along $\hat{x}$, $\varepsilon = \varepsilon_0\hat{e}_x$ is $\hat{e}_x\hat{e} = \cos\theta$, so the transmitted intensity varies as $\cos^2\theta$

Quantum mechanical description

A light beam consists of photons, if we attenuate the beam to the level where only on photon passes though the polarizer at any given time, then because photons appear only as units, the photon is either absorbed or it is not: The probability for the photon passing the polarizer is now $\cos^2\theta$ (the probabililty amplitude is θ). The polarizer "measures" the polarization state of the photon: if the photon is polarized along the polarizer axis, it is transmitted, if polarized perpindicular to the polarizer axis, the photon is absorbed.