Quantum Mechanics

QM in 3D

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \quad \text{with} \int |\Psi|^2\, d^3\mathbf{r} = 1}$$

For $V = V(\mathbf{r})$

$$\boxed{\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_nt/\hbar}} \quad \text{and} \quad \boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

The general solution

$$\boxed{\Psi(\mathbf{r}, t) = \sum c_n\psi_n(\mathbf{r})e^{-iE_nt/\hbar}}$$

c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$

For $V = V(r)$, i.e. central potentials

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

Separable solutions

$$\boxed{\psi(r, \theta, \phi) = R(r)Y(\theta, \phi).}$$

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

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

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

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

QM in 3D - The angular equation

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

we try separation of variables: $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi).$

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

$$\boxed{\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2 \quad \text{and} \quad \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2.}$$

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}$$

Since $\Phi(\phi + 2\pi) = \Phi(\phi).$ $\qquad m = 0, \pm 1, \pm 2, \ldots.$

The θ equation,

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

The solution is

$$\Theta(\theta) = A\, P_l^m(\cos\theta),$$

where P_l^m is the **associated Legendre function**,

$$P_l^m(x) \equiv (1 - x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x).$$

and $P_l(x)$ is the lth **Legendre polynomial**, defined by the **Rodrigues formula**:

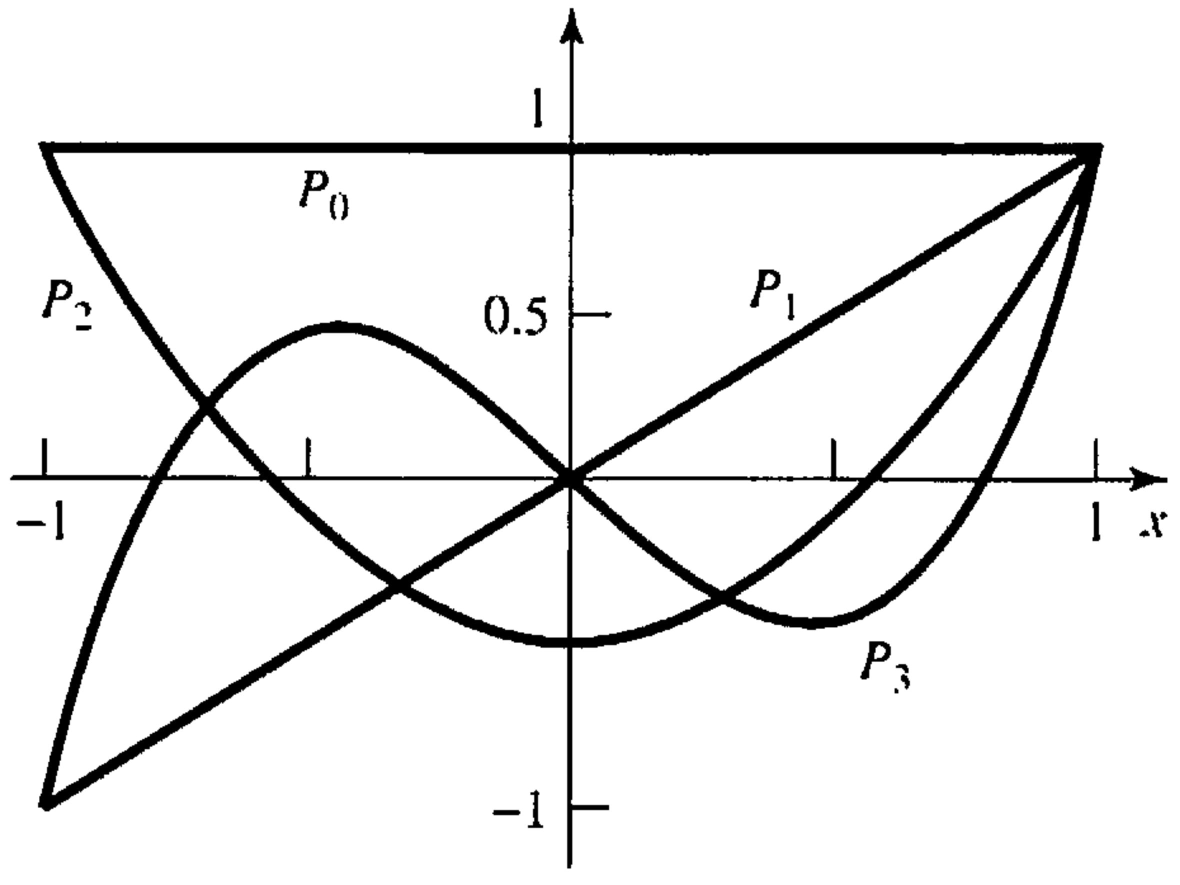
$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2 - 1)^l.$$

QM in 3D - The angular equation

Legendre polynomials

$P_0 = 1$
$P_1 = x$
$P_2 = \frac{1}{2}(3x^2 - 1)$
$P_3 = \frac{1}{2}(5x^3 - 3x)$
$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$
$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$

(a)



(b)

For example,

$$P_0(x) = 1, \quad P_1(x) = \frac{1}{2}\frac{d}{dx}(x^2 - 1) = x,$$

$$P_2(x) = \frac{1}{4 \cdot 2}\left(\frac{d}{dx}\right)^2 (x^2 - 1)^2 = \frac{1}{2}(3x^2 - 1).$$

Associated Legendre functions

$$P_2^0(x) = \frac{1}{2}(3x^2 - 1), \quad P_2^1(x) = (1 - x^2)^{1/2}\frac{d}{dx}\left[\frac{1}{2}(3x^2 - 1)\right] = 3x\sqrt{1 - x^2},$$

$$P_2^2(x) = (1 - x^2)\left(\frac{d}{dx}\right)^2\left[\frac{1}{2}(3x^2 - 1)\right] = 3(1 - x^2).$$

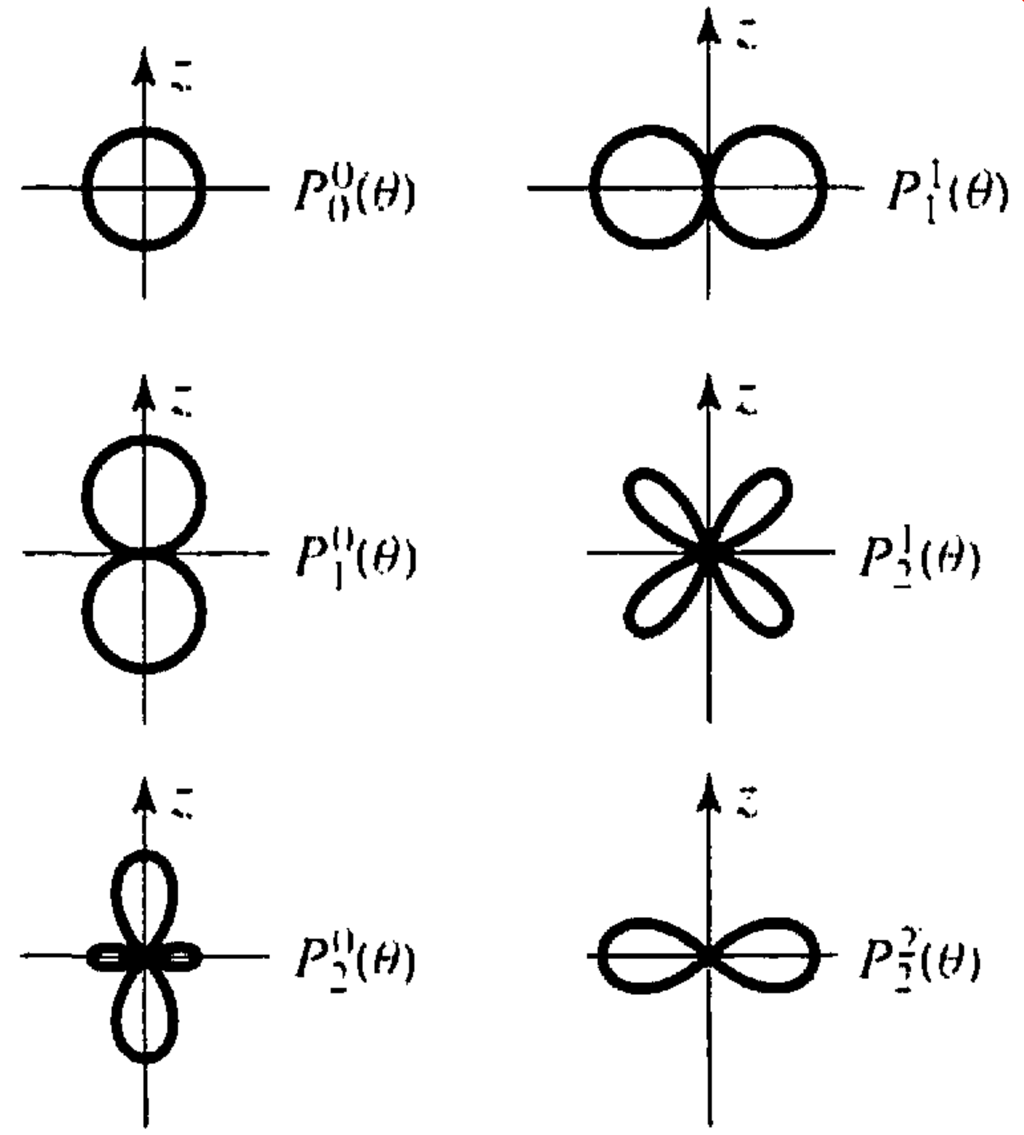
Rodrigues formula:

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2 - 1)^l.$$

Notice that l must be a nonnegative *integer*, for the Rodrigues formula to make any sense; moreover, if $|m| > l$, then $P_l^m = 0$.

$$l = 0, 1, 2, \ldots; \quad m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l.$$

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$



QM in 3D - The angular equation

The normalisation condition

$$\int |\psi|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \sin\theta \, d\theta \, d\phi = 1.$$

It is convenient to normalize R and Y separately:

$$\int_0^\infty |R|^2 r^2 \, dr = 1 \quad \text{and} \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin\theta \, d\theta \, d\phi = 1.$$

The normalized angular wave functions[8] are called **spherical harmonics**:

$$\boxed{Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} \, e^{im\phi} \, P_l^m(\cos\theta).}$$

Orthogonal

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

Azimuthal quantum number: l

Magnetic quantum number: m

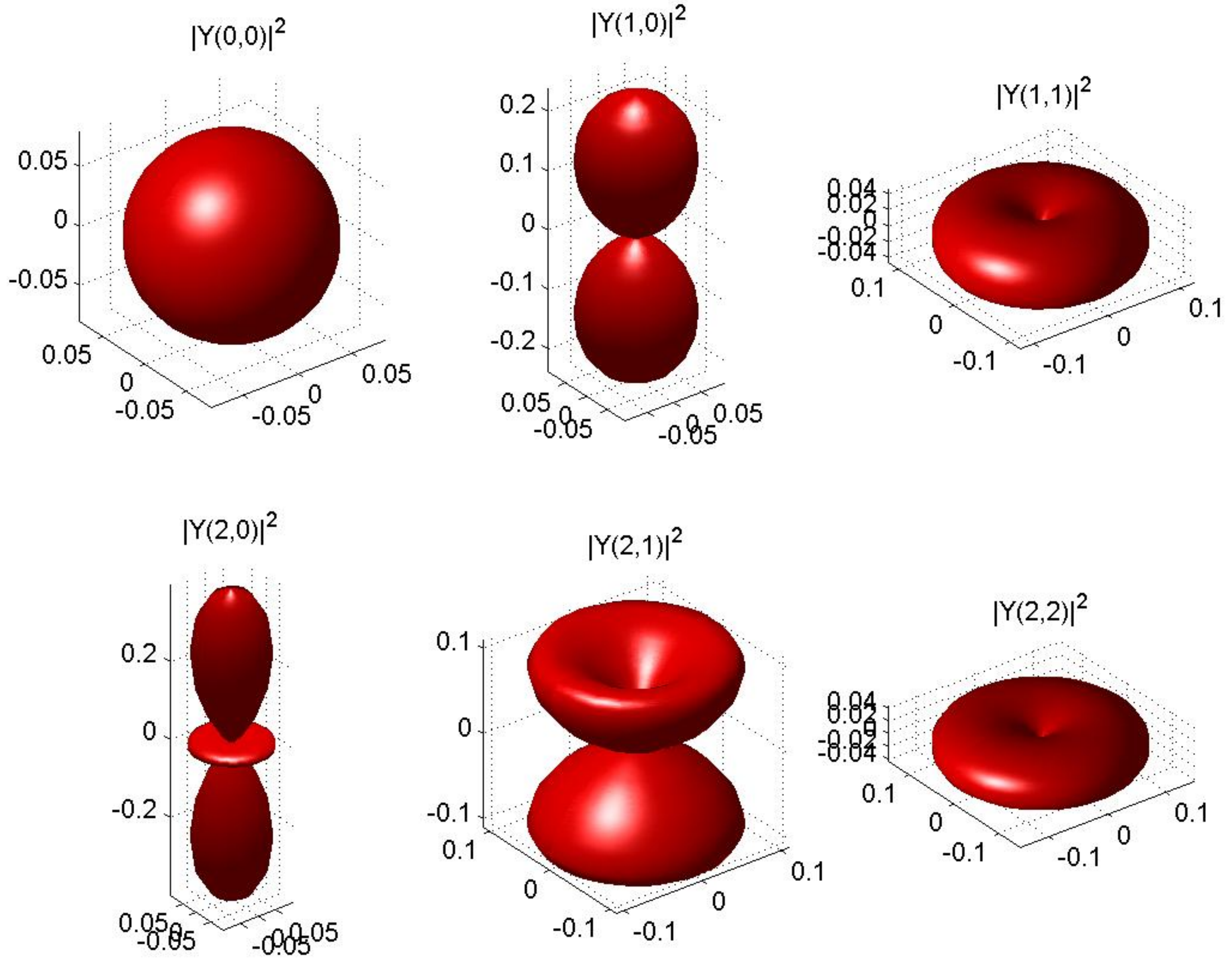
$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_2^{\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi} \qquad Y_3^{\pm1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta (5\cos^2\theta - 1) e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \qquad Y_3^{\pm2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$$

$$Y_2^{\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\phi} \qquad Y_3^{\pm3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$



QM in 3D - The radial equation

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

This equation simplifies if we change variables: Let

$$u(r) \equiv rR(r),$$

so that $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = rd^2u/dr^2$, and hence

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

We define the effective potential

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

Centrifugal term

Normalisation:

$$\int_0^\infty |u|^2\,dr = 1.$$

Infinite spherical well $V(r) = \begin{cases} 0, & \text{if } r \le a; \\ \infty, & \text{if } r > a. \end{cases}$

Inside the well $\dfrac{d^2u}{dr^2} = \left[\dfrac{l(l+1)}{r^2} - k^2\right]u, \quad k \equiv \dfrac{\sqrt{2mE}}{\hbar}.$

$l = 0$

$$\frac{d^2u}{dr^2} = -k^2u \Rightarrow u(r) = A\sin(kr) + B\cos(kr)$$

$\cos(kr)/r \to \infty$ as $r \to 0 \Rightarrow B = 0$

$u(a) = 0 \Rightarrow ka = n\pi$

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \dots).$$

$$\boxed{\psi_{n00} = \frac{1}{\sqrt{2\pi a}}\frac{\sin(n\pi r/a)}{r}}$$

QM in 3D - The Hydrogen atom

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

We are looking for bound state solutions $E < 0$ $$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u.$$ with $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}.$

Let $\rho \equiv \kappa r,$ and $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa},$ $\rightarrow$ $$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u.$$

Next we examine the asymptotic form of the solutions. As $\rho \to \infty$, the constant term in the brackets dominates, so (approximately)

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

The general solution is

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

but e^{ρ} blows up (as $\rho \to \infty$), so $B = 0$. Evidently,

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

for large ρ. On the other hand, as $\rho \to 0$ the centrifugal term dominates

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

The general solution

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

but ρ^{-l} blows up (as $\rho \to 0$), so $D = 0$. Thus

$$u(\rho) \sim C\rho^{l+1},$$

for small ρ.

Guess!

$$\boxed{u(\rho) = \rho^{l+1}e^{-\rho}v(\rho),}$$

QM in 3D - The Hydrogen atom

The radial equation

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

and

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

In terms of $v(\rho)$, then,

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

Finally, we assume the solution, $v(\rho)$, can be expressed as a power series in ρ:

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

Our problem is to determine the coefficients $(c_0, c_1, c_2, \ldots)$. Differentiating term by term:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j.$$

Differentiating again,

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

Plugging these two in our equation for $v(\rho)$ we get,

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$

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

The coefficient of ρ^j gives us

$$\boxed{c_{j+1} = \left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}c_j.}$$

QM in 3D - The Hydrogen atom

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j.$$

The radial equation

Now let's see what the coefficients look like for large j (this corresponds to large ρ, where the higher powers dominate). In this regime the recursion formula says

$$c_{j+1} \cong \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j.$$

Suppose for a moment that this were *exact*. Then

$$c_j = \frac{2^j}{j!} c_0,$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho},$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho},$$

which blows up at large ρ. The positive exponential is precisely the asymptotic behavior we *didn't* want.

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10}\ \mathrm{m} \qquad \kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{an},$$

The series must terminate!

$$c_{(j_{\max}+1)} = 0.$$

$$2(j_{\max} + l + 1) - \rho_0 = 0.$$

Defining

$$n \equiv j_{\max} + l + 1$$

(the so-called **principal quantum number**), we have

$$\rho_0 = 2n.$$

But ρ_0 determines E (Equations 4.54 and 4.55):

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

so the allowed energies are

Bohr formula

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1, 2, 3, \ldots$$

QM in 3D - The Hydrogen atom

The spatial wave functions for hydrogen are labeled by three quantum numbers (n, l, and m):

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi),$$

where

$$R_{nl}(r) = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho),$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - l - 1$ in ρ, whose coefficients are determined (up to an overall normalization factor) by the recursion formula

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

The **ground state** (that is, the state of lowest energy) is the case $n = 1$; putting in the accepted values for the physical constants, we get:

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

$$n = 1 \Rightarrow l = m = 0$$

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

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a}.$$

Normalising

$$\int_0^\infty |R_{10}|^2 r^2\, dr = \frac{|c_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2\, dr = |c_0|^2 \frac{a}{4} = 1$$

$$\boxed{\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}}$$

QM in 3D - The Hydrogen atom

For arbitrary n, the possible values of l are

$$l = 0, 1, 2, \ldots, n-1,$$

and for each l there are $(2l+1)$ possible values of m
degeneracy of the energy level E_n is

$$d(n) = \sum_{l=0}^{n-1} (2l+1) = n^2.$$

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho),$$

where

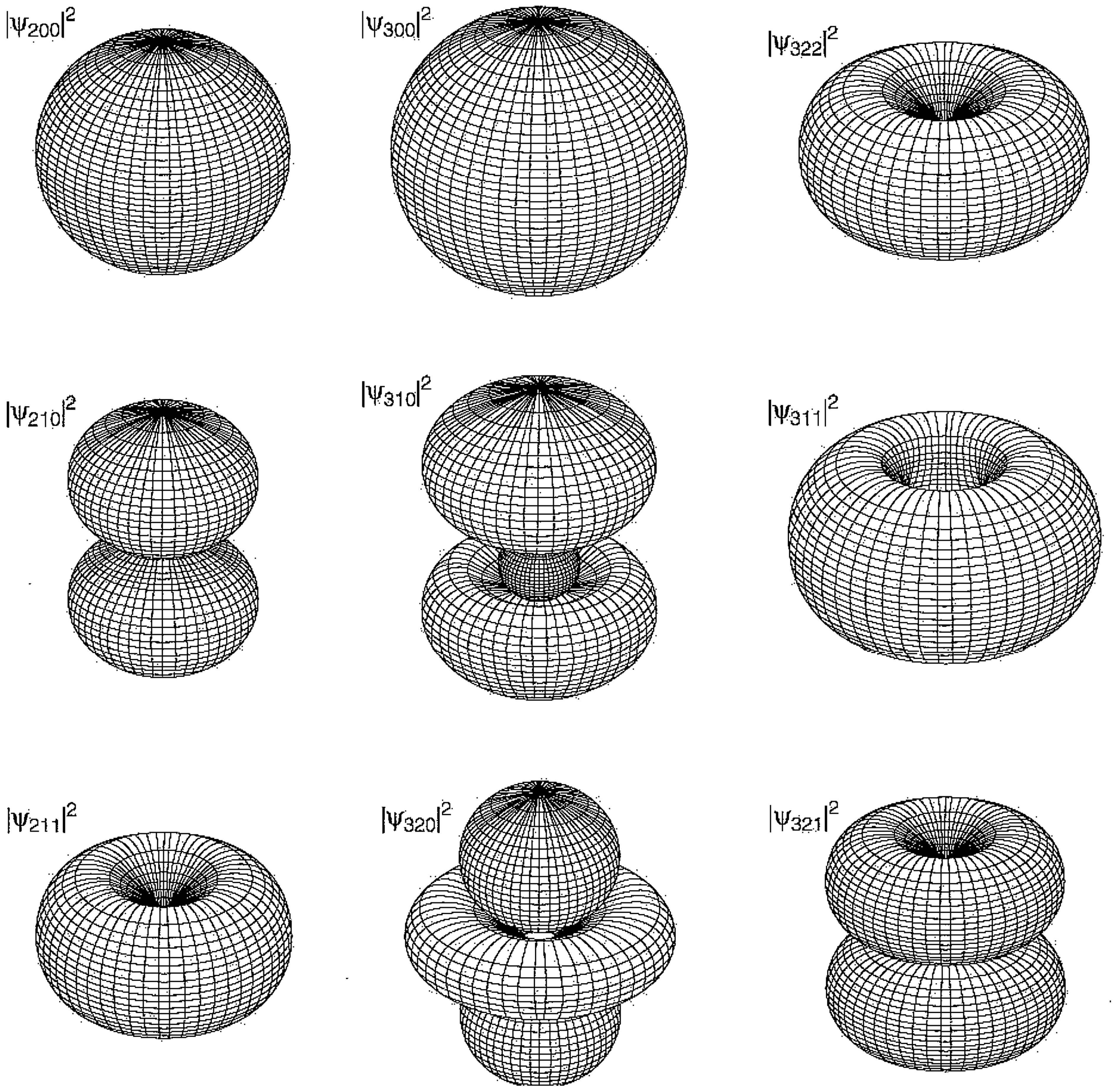
$$L_{q-p}^{p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

is the qth **Laguerre polynomial**.

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na)\right] Y_l^m(\theta, \phi).$$



QM in 3D - Angular Momentum

The operators L_x and L_y do not commute;

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z]$$
$$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z].$$
$$= yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z.$$

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y.$$

L_x, L_y and L_z are incompatible operators $\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i}\langle i\hbar L_z\rangle\right)^2 = \frac{\hbar^2}{4}\langle L_z\rangle^2,$

The square of the total angular momentum does commute with each of them.

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2,$$

$$[L^2, L_x] = [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]$$
$$= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$$
$$= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z$$
$$= 0.$$

$[L^2, L_x] = 0, \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0,$ or, more compactly, $[L^2, \mathbf{L}] = 0.$

Let's try to find simultaneous eigenstates of L^2 and L_z

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f.$$

Let's use the same old trick!

$$L_\pm \equiv L_x \pm i L_y$$

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x)$$
$$= \pm \hbar L_\pm.$$

and

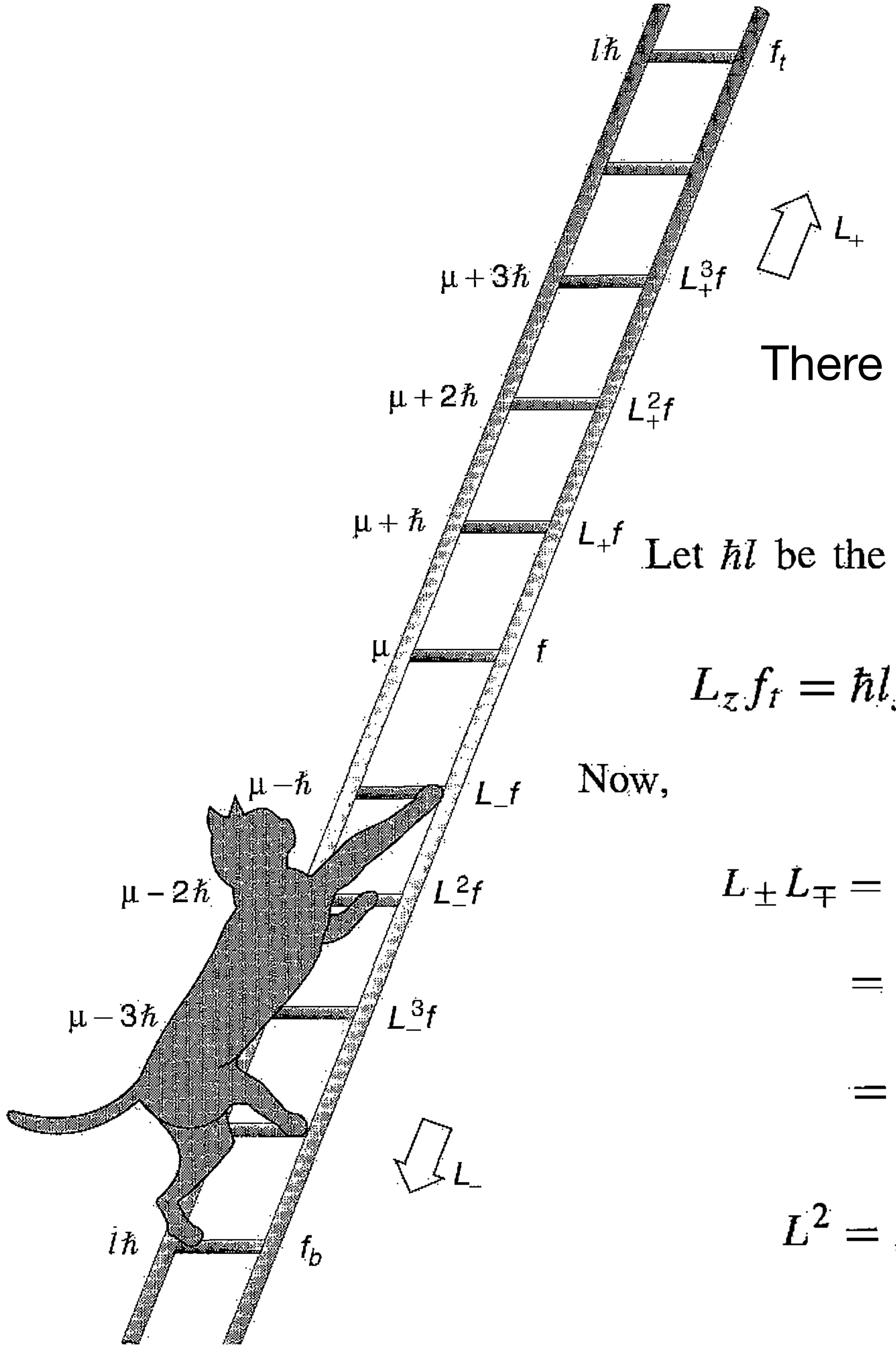
$[L^2, L_\pm] = 0.$

If f is an eigenfunction of L^2 and L_z then so is $L_\pm f$

$$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f),$$

$$L_z(L_\pm f) = (L_z L_\pm - L_\pm L_z) f + L_\pm L_z f$$
$$= \pm \hbar L_\pm f + L_\pm(\mu f)$$
$$= (\mu \pm \hbar)(L_\pm f)$$

QM in 3D - Angular Momentum



There must be a top-most rung f_t

$$L_+ f_t = 0.$$

Let $\hbar l$ be the eigenvalue of L_z at this top rung

$$L_z f_t = \hbar l f_t; \quad L^2 f_t = \lambda f_t.$$

Now,

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x)$$

$$= L^2 - L_z^2 \mp i(i\hbar L_z),$$

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z.$$

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t,$$

or, $\quad \lambda = \hbar^2 l(l+1).$

There must be a bottom-most rung f_b

Let $\hbar \bar{l}$ be the eigenvalue of L_z at this bottom rung:

$$L_z f_b = \hbar \bar{l} f_b; \quad L^2 f_b = \lambda f_b.$$

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \hbar^2 \bar{l}(\bar{l} - 1) f_b,$$

or, $\quad \lambda = \hbar^2 \bar{l}(\bar{l} - 1).$

Hence, $\quad l(l+1) = \bar{l}(\bar{l} - 1),$

$\bar{l} = l + 1$ (absurd) or, $\quad \bar{l} = -l.$

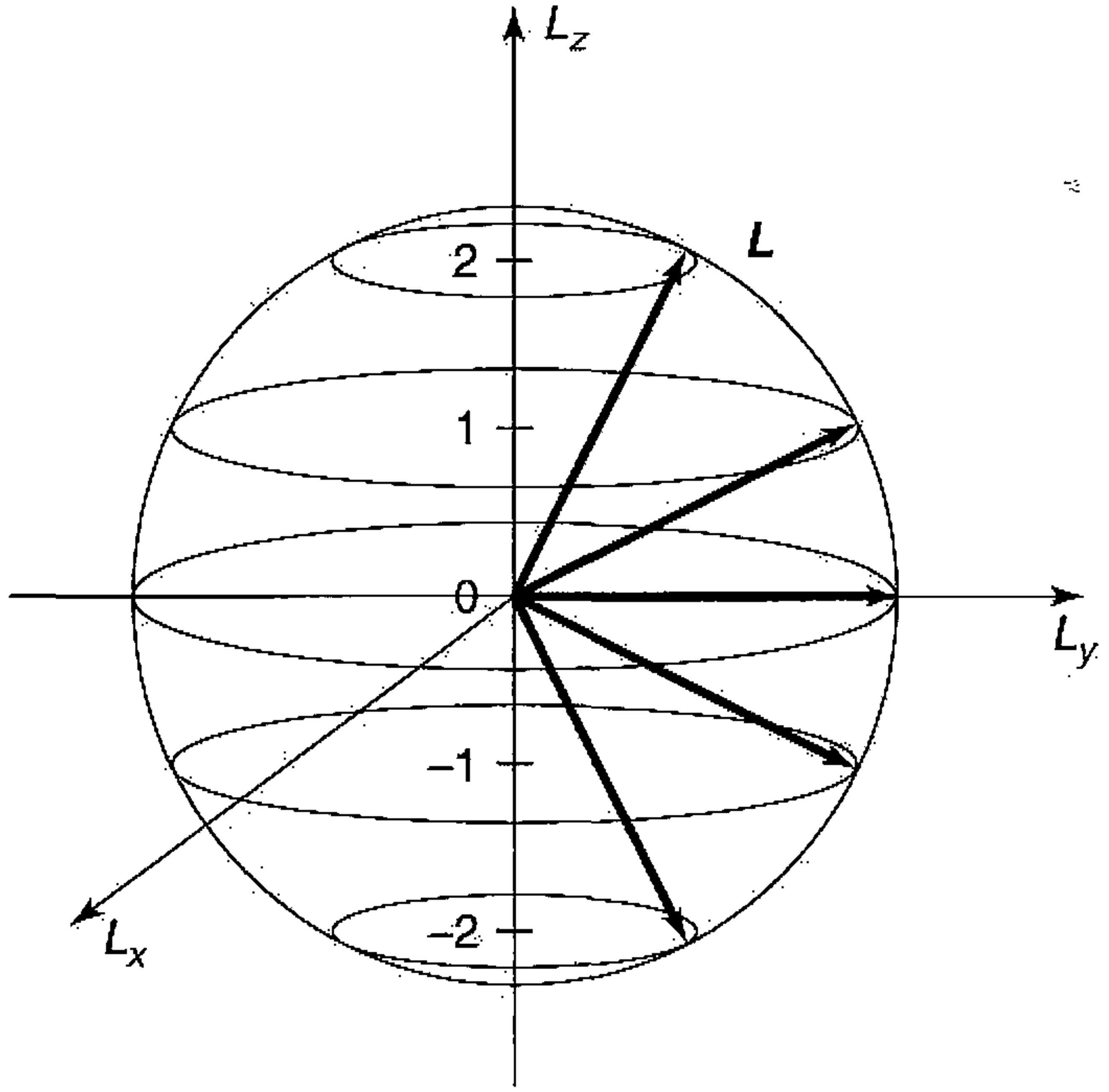
QM in 3D - Angular Momentum

The eigenvalues of L_z are $m\hbar$, where m goes from $-l$ to $+l$ in N integer steps, i.e., $l = N/2$ (an integer or a half-integer).

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m,$$

$$l = 0,\ 1/2,\ 1,\ 3/2,\ \ldots;\quad m = -l,\ -l+1,\ \ldots,\ l-1,\ l.$$

For a given value of l, there are $2l+1$ different values of m (i.e., $2l+1$ "rungs" on the "ladder").



$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi};$$

$$\mathbf{L} = \frac{\hbar}{i}\left[r(\hat{r}\times\hat{r})\frac{\partial}{\partial r} + (\hat{r}\times\hat{\theta})\frac{\partial}{\partial\theta} + (\hat{r}\times\hat{\phi})\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right].$$

But $(\hat{r}\times\hat{r}) = 0$, $(\hat{r}\times\hat{\theta}) = \hat{\phi}$, and $(\hat{r}\times\hat{\phi}) = -\hat{\theta}$ (see F

$$\mathbf{L} = \frac{\hbar}{i}\left(\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right).$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components:

$$\hat{\theta} = (\cos\theta\cos\phi)\hat{\imath} + (\cos\theta\sin\phi)\hat{\jmath} - (\sin\theta)\hat{k};$$
$$\hat{\phi} = -(\sin\phi)\hat{\imath} + (\cos\phi)\hat{\jmath}.$$

Thus

$$\mathbf{L} = \frac{\hbar}{i}\left[(-\sin\phi\,\hat{\imath} + \cos\phi\,\hat{\jmath})\frac{\partial}{\partial\theta}\right.$$
$$\left. -(\cos\theta\cos\phi\,\hat{\imath} + \cos\theta\sin\phi\,\hat{\jmath} - \sin\theta\,\hat{k})\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right].$$

QM in 3D - Angular Momentum

Evidently

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

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

and

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

We shall also need the raising and lowering operators:

$$L_\pm = L_x \pm iL_y = \frac{\hbar}{i}\left[(-\sin\phi \pm i\cos\phi)\frac{\partial}{\partial\theta} - (\cos\phi \pm i\sin\phi)\cot\theta\frac{\partial}{\partial\phi}\right].$$

But $\cos\phi \pm i\sin\phi = e^{\pm i\phi}$, so

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

$$L_+L_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi}\right),$$

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

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

But this is precisely the "angular equation"

$$L_z f_l^m = \frac{\hbar}{i}\frac{\partial}{\partial\phi} f_l^m = \hbar m f_l^m,$$

this is equiv $L^2 f = \lambda f$ and $L_z f = \mu f.$

Spherical harmonics are eigenfunctions of L^2 and L_z

$L^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle$ and $L_z|l,m\rangle = \hbar|l,m\rangle$

Earlier we were actually looking for simultaneous eigenfunctions of H, L^2 and L_z

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi. \qquad \psi \equiv |n,l,m\rangle$$

We can write the Schrödinger equation as

$$\frac{1}{2mr^2}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + L^2\right]\psi + V\psi = E\psi.$$

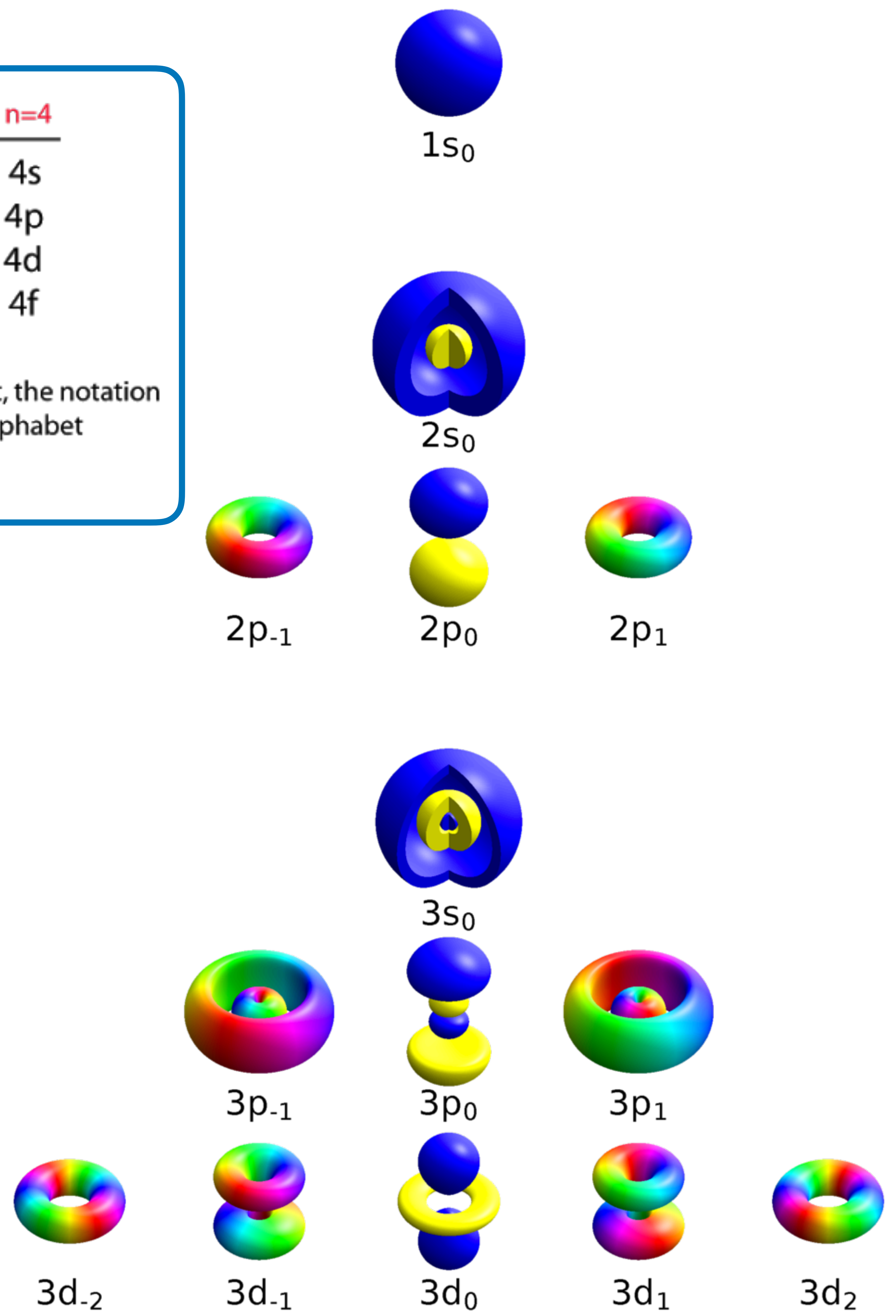
Quantum Numbers

Conserved quantities

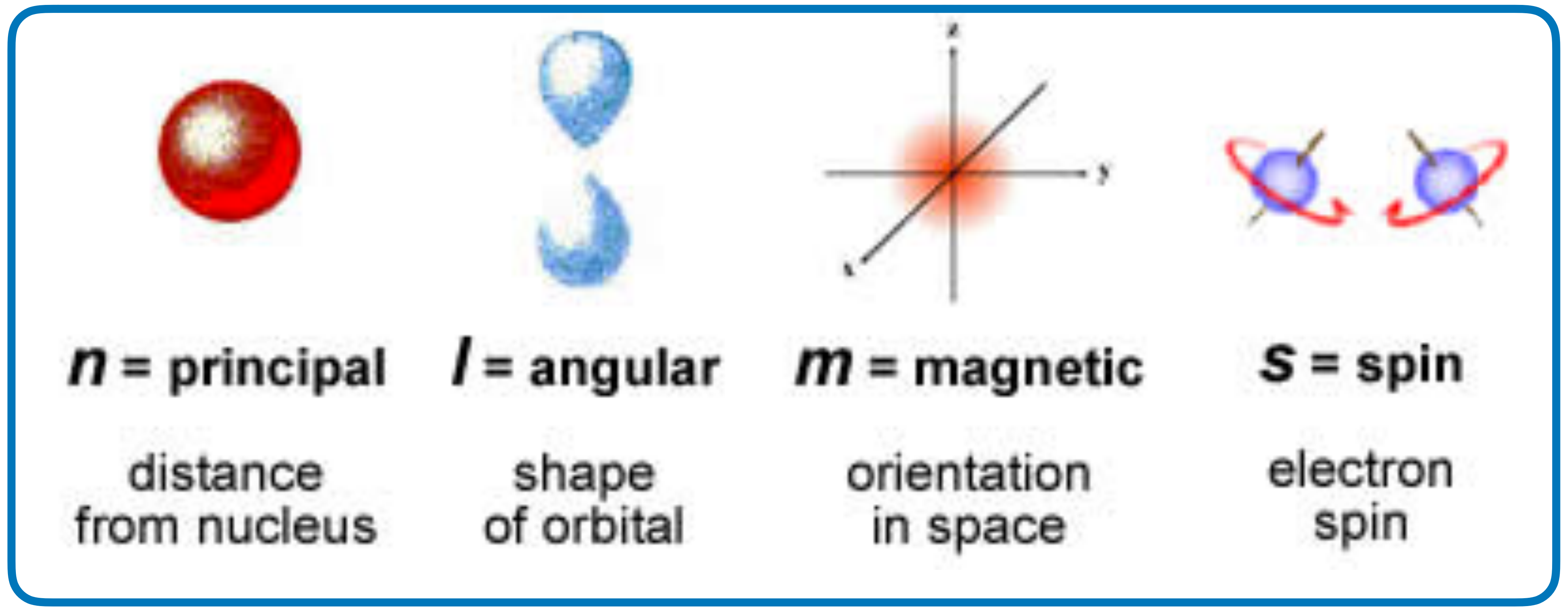
$$\psi \equiv |n, l, m\rangle$$

Eigenvalues of hermitian operators that commute with the Hamiltonian. The operators correspond to observables that can be measured together with the system's energy. A specification of all of the quantum numbers of a quantum system characterises the state of the system.

	ℓ	n=1	n=2	n=3	n=4
s - - sharp	ℓ =0	1s	2s	3s	4s
p- - principal	ℓ =1		2p	3p	4p
d- - diffuse	ℓ =2			3d	4d
f - - fundamental	ℓ =3				4f
g	ℓ =4	beyond this point, the notation just follows the alphabet			
h	ℓ =5				
...					



Address of an electron

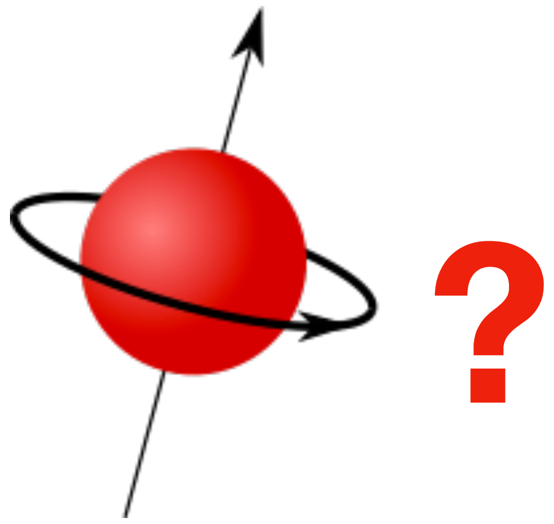


The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field.

QM in 3D - Spin

The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum,

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y.$$



$$S^2|s\,m\rangle = \hbar^2 s(s+1)|s\,m\rangle; \quad S_z|s\,m\rangle = \hbar m|s\,m\rangle;$$

$$S_\pm|s\,m\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}\;|s\,(m\pm 1)\rangle,$$

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots; \quad m = -s, -s+1, \ldots, s-1, s.$$

Spin-1/2

By far the most important case is $s = 1/2$, for this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. Moreover, once you understand spin 1/2, it is a simple matter to work out the formalism for any higher spin. There are just *two* eigenstates: $|\frac{1}{2}\,\frac{1}{2}\rangle$, which we call **spin up** (informally, $\uparrow$), and $|\frac{1}{2}\,(-\frac{1}{2})\rangle$, which we call **spin down** ($\downarrow$). Using these as basis vectors, the general state of a spin-1/2 particle can be expressed as a two-element column matrix (or **spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-,$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

representing spin up, and

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

for spin down.

$$\boxed{\mathbf{S}^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad \text{and} \quad \mathbf{S}^2\chi_- = \frac{3}{4}\hbar^2\chi_-.}$$

If we write $\mathbf{S}^2$ as a matrix with (as yet) undetermined elements,

$$\mathbf{S}^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix},$$

then the first equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\hbar^2 \\ 0 \end{pmatrix},$$

so $c = (3/4)\hbar^2$ and $e = 0$. The second equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\hbar^2 \end{pmatrix},$$

so $d = 0$ and $f = (3/4)\hbar^2$. *Conclusion:*

$$\boxed{\mathbf{S}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.}$$

QM in 3D - Spin 1/2

Similarly,

$$\mathbf{S}_z\chi_+ = \frac{\hbar}{2}\chi_+, \qquad \mathbf{S}_z\chi_- = -\frac{\hbar}{2}\chi_-,$$

from which it follows that

$$\boxed{\mathbf{S}_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.}$$

Meanwhile,

$$\mathbf{S}_+\chi_- = \hbar\chi_+, \quad \mathbf{S}_-\chi_+ = \hbar\chi_-, \quad \mathbf{S}_+\chi_+ = \mathbf{S}_-\chi_- = 0,$$

so

$$\boxed{\mathbf{S}_+ = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}, \quad \mathbf{S}_- = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}.}$$

Now $S_\pm = S_x \pm iS_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$, and hence

$$\boxed{\mathbf{S}_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad \mathbf{S}_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}.}$$

Since $\mathbf{S}_x$, $\mathbf{S}_y$, and $\mathbf{S}_z$ all carry a factor of $\hbar/2$, it is tidier to write $\boxed{\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}}$, where

$$\boxed{\sigma_x \equiv \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.}$$

Pauli Spin Matrices

The eigenspinors of $\mathbf{S}_z$ are

$$\chi_+ = \begin{pmatrix}1\\ 0\end{pmatrix}, \left(\text{eigenvalue} + \frac{\hbar}{2}\right); \quad \chi_- = \begin{pmatrix}0\\ 1\end{pmatrix}, \left(\text{eigenvalue} - \frac{\hbar}{2}\right).$$

If you measure S_z on a particle in the general state χ you could get $+\hbar/2$, with probability $|a|^2$, or $-\hbar/2$, with probability $|b|^2$.

$$|a|^2 + |b|^2 = 1$$

But what if, instead, you chose to measure S_x? What are the possible results, and what are their respective probabilities? According to the generalized statistical interpretation, we need to know the eigenvalues and eigenspinors of $\mathbf{S}_x$. The characteristic equation is

$$\boxed{\begin{vmatrix}-\lambda & \hbar/2\\ \hbar/2 & -\lambda\end{vmatrix} = 0 \Rightarrow \lambda^2 = \left(\frac{\hbar}{2}\right)^2 \Rightarrow \lambda = \pm\frac{\hbar}{2}.}$$

Not surprisingly, the possible values for S_x are the same as those for S_z. The eigenspinors are obtained in the usual way:

$$\frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \pm\frac{\hbar}{2}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} \Rightarrow \begin{pmatrix}\beta\\ \alpha\end{pmatrix} = \pm\begin{pmatrix}\alpha\\ \beta\end{pmatrix},$$

so $\beta = \pm\alpha$.

QM in 3D - Spin 1/2

Evidently the (normalized) eigenspinors of $\mathbf{S}_x$ are

$$\boxed{\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \left(\text{eigenvalue} + \frac{\hbar}{2}\right); \quad \chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} \end{pmatrix}, \left(\text{eigenvalue} - \frac{\hbar}{2}\right)}$$

As the eigenvectors of a hermitian matrix, they span the space; the generic spinor χ can be expressed as a linear combination of them:

$$\boxed{\chi = \left(\frac{a+b}{\sqrt{2}}\right)\chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}}\right)\chi_-^{(x)}.}$$

If you measure S_x, the probability of getting $+\hbar/2$ is $(1/2)|a+b|^2$, and the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$.

Example 4.2 Suppose a spin-1/2 particle is in the state

$$\chi = \frac{1}{\sqrt{6}}\begin{pmatrix} 1+i \\ 2 \end{pmatrix}.$$

What are the probabilities of getting $+\hbar/2$ and $-\hbar/2$, if you measure S_z and S_x?

Solution: Here $a = (1+i)/\sqrt{6}$ and $b = 2/\sqrt{6}$, so for S_z the probability of getting $+\hbar/2$ is $|(1+i)/\sqrt{6}|^2 = 1/3$, and the probability of getting $-\hbar/2$ is $|2/\sqrt{6}|^2 = 2/3$. For S_x the probability of getting $+\hbar/2$ is $(1/2)|(3+i)/\sqrt{6}|^2 = 5/6$, and the probability of getting $-\hbar/2$ is $(1/2)|(-1+i)/\sqrt{6}|^2 = 1/6$. Incidentally, the *expectation* value of S_x is

$$\frac{5}{6}\left(+\frac{\hbar}{2}\right) + \frac{1}{6}\left(-\frac{\hbar}{2}\right) = \frac{\hbar}{3},$$

which we could also have obtained more directly:

$$\langle S_x\rangle = \chi^\dagger \mathbf{S}_x \chi = \begin{pmatrix} \frac{(1-i)}{\sqrt{6}} & \frac{2}{\sqrt{6}} \end{pmatrix}\begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix}\begin{pmatrix} (1+i)/\sqrt{6} \\ 2/\sqrt{6} \end{pmatrix} = \frac{\hbar}{3}.$$

QM in 3D - Spin 1/2

Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, $\boldsymbol{\mu}$, is proportional to its spin angular momentum, $\mathbf{S}$:

$$\boldsymbol{\mu} = \gamma \mathbf{S};$$

the proportionality constant, γ, is called the **gyromagnetic ratio**. When a magnetic dipole is placed in a magnetic field $\mathbf{B}$, it experiences a torque, $\boldsymbol{\mu} \times \mathbf{B}$, which tends to line it up parallel to the field (just like a compass needle). The energy associated with this torque is

$$H = -\boldsymbol{\mu} \cdot \mathbf{B},$$

so the Hamiltonian of a spinning charged particle, at rest in a magnetic field $\mathbf{B}$, is

$$H = -\gamma \mathbf{B} \cdot \mathbf{S}.$$

Example 4.3 **Larmor precession:** Imagine a particle of spin 1/2 at rest in a uniform magnetic field, which points in the z-direction:

$$\mathbf{B} = B_0 \hat{k}.$$

The Hamiltonian

$$\mathsf{H} = -\gamma B_0 \mathsf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The eigenstates of H are the same as those of S_z:

$$\begin{cases} \chi_+, & \text{with energy } E_+ = -(\gamma B_0 \hbar)/2, \\ \chi_-, & \text{with energy } E_- = +(\gamma B_0 \hbar)/2. \end{cases}$$

Evidently the energy is lowest when the dipole moment is parallel to the field—just as it would be classically.

Since the Hamiltonian is time-independent, the general solution to the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = \mathsf{H}\chi,$$

can be expressed in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{pmatrix}.$$

QM in 3D - Spin 1/2

The constants a and b are determined by the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix},$$

(of course, $|a|^2 + |b|^2 = 1$). With no essential loss of generality I'll write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, where α is a fixed angle whose physical significance will appear in a moment. Thus

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}.$$

To get a feel for what is happening here, let's calculate the expectation value of **S**, as a function of time:

$$\begin{aligned}\langle S_x \rangle &= \chi(t)^\dagger \mathbf{S}_x \chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{-i\gamma B_0 t/2} & \sin(\alpha/2)e^{i\gamma B_0 t/2} \end{pmatrix} \\ &\times \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2}\sin\alpha\cos(\gamma B_0 t).\end{aligned}$$

Similarly,

$$\langle S_y \rangle = \chi(t)^\dagger \mathbf{S}_y \chi(t) = -\frac{\hbar}{2}\sin\alpha\sin(\gamma B_0 t),$$

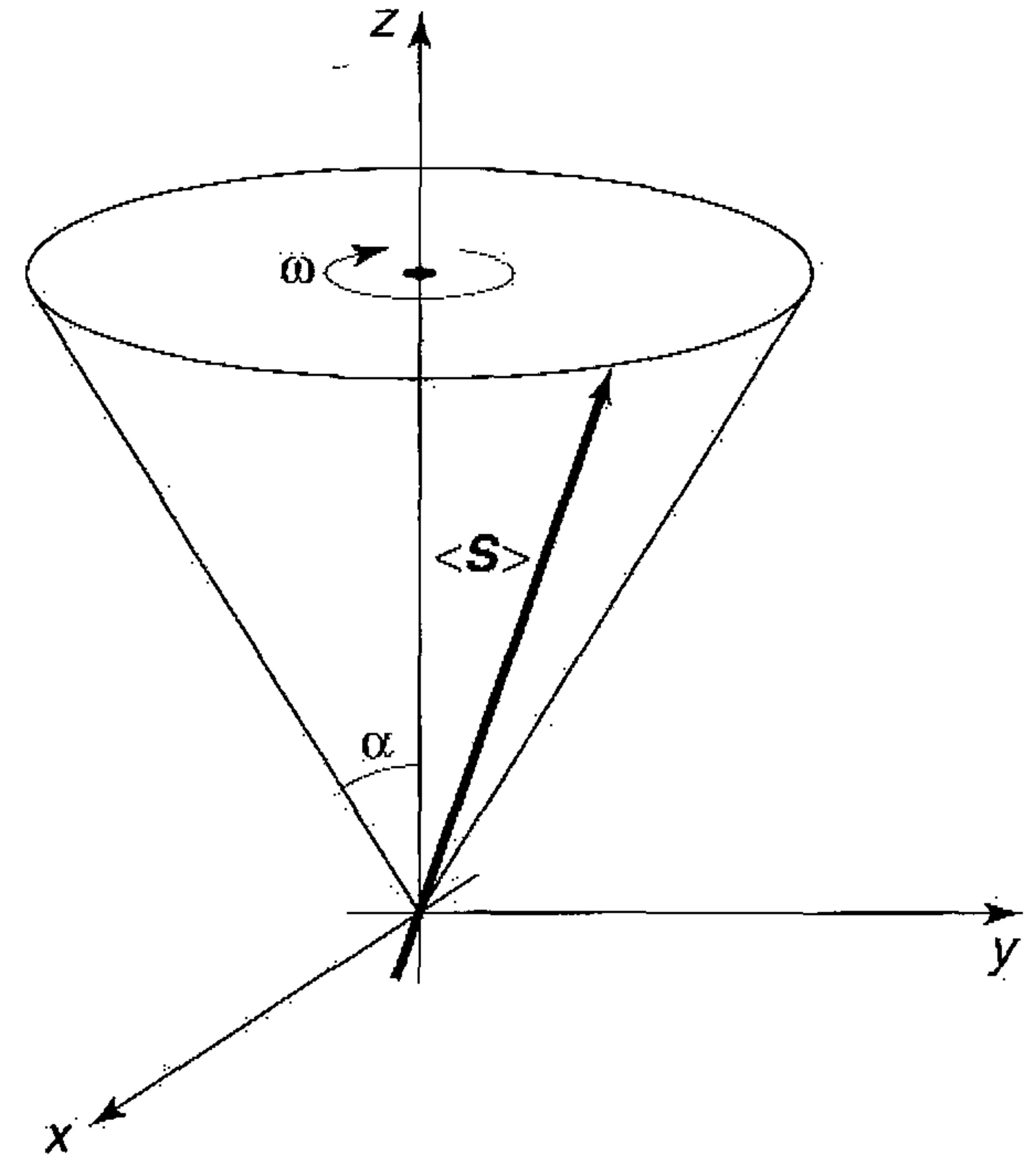
and

$$\langle S_z \rangle = \chi(t)^\dagger \mathbf{S}_z \chi(t) = \frac{\hbar}{2}\cos\alpha.$$

Evidently $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z-axis, and precesses about the field at the **Larmor frequency**

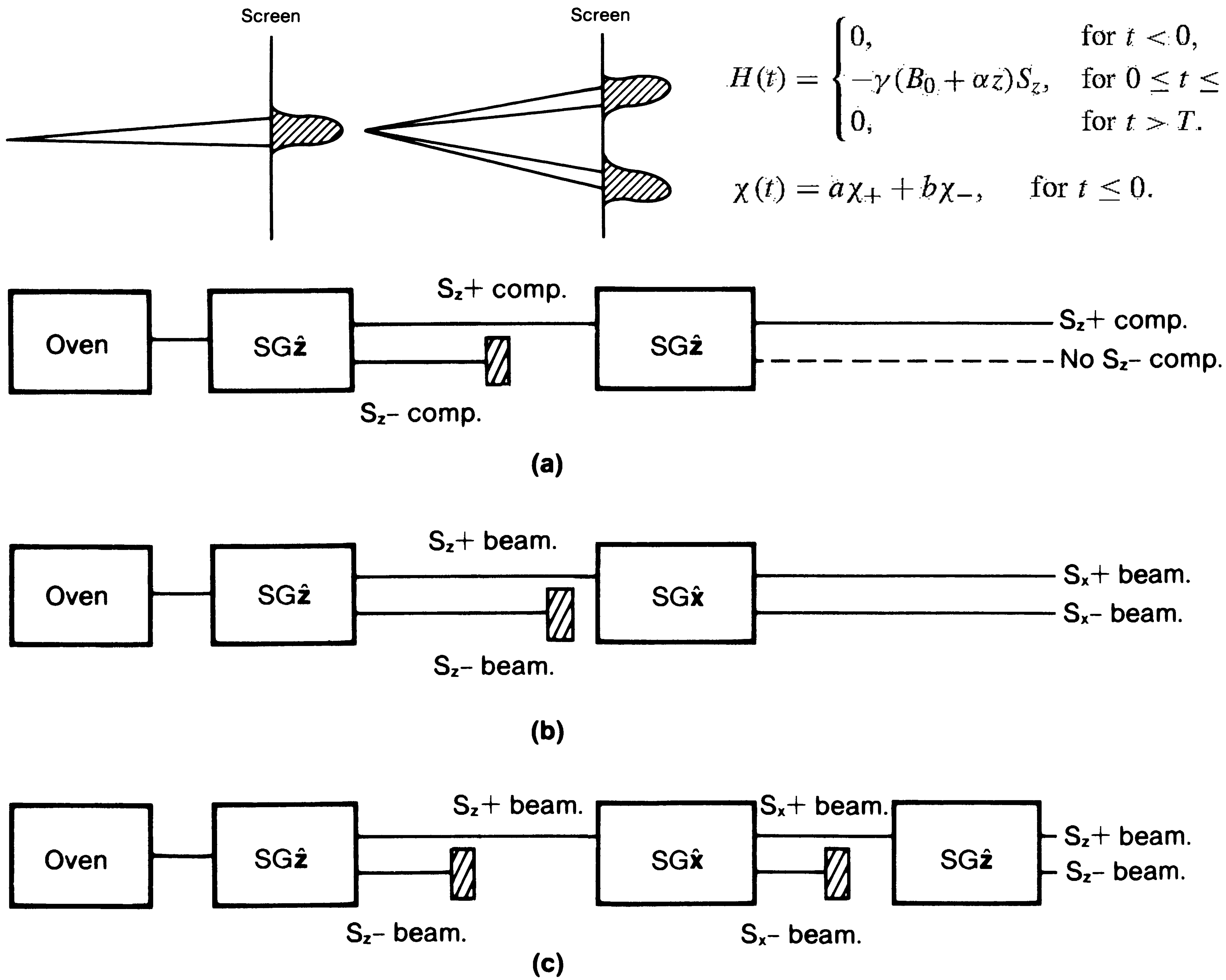
$$\omega = \gamma B_0,$$

just as it would classically



QM in 3D - Spin 1/2

Stern–Gerlach experiment



$$H(t) = \begin{cases} 0, & \text{for } t < 0, \\ -\gamma(B_0 + \alpha z)S_z, & \text{for } 0 \le t \le T, \\ 0, & \text{for } t > T. \end{cases}$$

$$\chi(t) = a\chi_+ + b\chi_-, \quad \text{for } t \le 0.$$

While the Hamiltonian acts, $\chi(t)$ evolves in the usual way:

$$\chi(t) = a\chi_+ e^{-iE_+t/\hbar} + b\chi_- e^{-iE_-t/\hbar}, \quad \text{for } 0 \le t \le T,$$

where

$$E_\pm = \mp\gamma(B_0 + \alpha z)\frac{\hbar}{2},$$

and hence it emerges in the state

$$\chi(t) = \left(ae^{i\gamma T B_0/2}\chi_+\right)e^{i(\alpha\gamma T/2)z} + \left(be^{-i\gamma T B_0/2}\chi_-\right)e^{-i(\alpha\gamma T/2)z},$$

(for $t \ge T$). The two terms now carry *momentum* in the z direction the spin-up component has momentum

$$p_z = \frac{\alpha\gamma T\hbar}{2},$$

and it moves in the plus-z direction; the spin-down component has the opposite momentum, and it moves in the minus-z direction. Thus the beam splits in two, as before.

QM in 3D

Addition of Angular Momenta

Suppose now that we have *two* spin-1/2 particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities in all:

$$\uparrow\uparrow,\ \uparrow\downarrow,\ \downarrow\uparrow,\ \downarrow\downarrow,$$

where the first arrow refers to the electron and the second to the proton. *Question:* What is the *total* angular momentum of the atom? Let

$$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}.$$

Each of these four composite states is an eigenstate of S_z—the z components simply *add:*

$$S_z\chi_1\chi_2 = (S_z^{(1)} + S_z^{(2)})\chi_1\chi_2 = (S_z^{(1)}\chi_1)\chi_2 + \chi_1(S_z^{(2)}\chi_2)$$
$$= (\hbar m_1\chi_1)\chi_2 + \chi_1(\hbar m_2\chi_2) = \hbar(m_1 + m_2)\chi_1\chi_2,$$

(note that $\mathbf{S}^{(1)}$ acts only on χ_1, and $\mathbf{S}^{(2)}$ acts only on χ_2; this notation may not be elegant, but it does the job). So m (the quantum number for the composite system) is just $m_1 + m_2$:

$$\uparrow\uparrow:\ m = 1;$$
$$\uparrow\downarrow:\ m = 0;$$
$$\downarrow\uparrow:\ m = 0;$$
$$\downarrow\downarrow:\ m = -1.$$

At first glance, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to $+s$, so it appears that $s = 1$—but there is an "extra" state with $m = 0$. One way to untangle this problem is to apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$,

$$S_-(\uparrow\uparrow) = (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow)$$
$$= (\hbar\downarrow)\uparrow + \uparrow(\hbar\downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow).$$

Evidently the three states with $s = 1$ are (in the notation $|s\,m\rangle$):

$$\boxed{\left.\begin{cases} |1\,1\rangle = \uparrow\uparrow \\ |1\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\,-1\rangle = \downarrow\downarrow \end{cases}\right\}\quad s = 1\ \text{(triplet)}.}$$

Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$\boxed{\left\{|0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)\right\}\quad s = 0\ \text{(singlet)}.}$$

I claim, then, that the combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration.

QM in 3D

Addition of Angular Momenta

$$S^2 = (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \cdot (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}.$$

$$\begin{aligned}\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\uparrow\downarrow) &= (S_x^{(1)}\uparrow)(S_x^{(2)}\downarrow) + (S_y^{(1)}\uparrow)(S_y^{(2)}\downarrow) + (S_z^{(1)}\uparrow)(S_z^{(2)}\downarrow) \\ &= \left(\frac{\hbar}{2}\downarrow\right)\left(\frac{\hbar}{2}\uparrow\right) + \left(\frac{i\hbar}{2}\downarrow\right)\left(\frac{-i\hbar}{2}\uparrow\right) + \left(\frac{\hbar}{2}\uparrow\right)\left(\frac{-\hbar}{2}\downarrow\right) \\ &= \frac{\hbar^2}{4}(2\downarrow\uparrow - \uparrow\downarrow).\end{aligned}$$

Similarly,

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\downarrow\uparrow) = \frac{\hbar^2}{4}(2\uparrow\downarrow - \downarrow\uparrow).$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|1\,0\rangle = \frac{\hbar^2}{4}\frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow + 2\uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4}|1\,0\rangle,$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|0\,0\rangle = \frac{\hbar^2}{4}\frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow - 2\uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4}|0\,0\rangle.$$

we conclude that

$$S^2|1\,0\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|1\,0\rangle = 2\hbar^2|1\,0\rangle, \qquad S^2|0\,0\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\frac{3\hbar^2}{4}\right)|0\,0\rangle = 0,$$

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: If you combine spin s_1 with spin s_2, what total spins s can you get? The answer is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$—or $(s_2 - s_1)$, if $s_2 > s_1$—in integer steps:

$$\boxed{s = (s_1 + s_2),\ (s_1 + s_2 - 1),\ (s_1 + s_2 - 2),\ \ldots,\ |s_1 - s_2|.}$$

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.) For example, if you package together a particle of spin 3/2 with a particle of spin 2, you could get a total spin of 7/2, 5/2, 3/2, or 1/2, depending on the configuration. Another example: If a hydrogen atom is in the state ψ_{nlm}, the net angular momentum of the electron (spin plus orbital) is $l + 1/2$ or $l - 1/2$; if you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is $l + 1$, l, or $l - 1$ (and l can be achieved in two distinct ways, depending on whether the electron alone is in the $l + 1/2$ configuration or the $l - 1/2$ configuration).

The combined state $|s\,m\rangle$ with total spin s and z-component m will be some linear combination of the composite states $|s_1\,m_1\rangle|s_2\,m_2\rangle$:

$$|s\,m\rangle = \sum_{m_1+m_2=m} C^{s_1 s_2 s}_{m_1 m_2 m}|s_1\,m_1\rangle|s_2\,m_2\rangle$$

(because the z components *add*, the only composite states that contribute are those for which $m_1 + m_2 = m$).

The constants $C^{s_1 s_2 s}_{m_1 m_2 m}$ are called **Clebsch-Gordan coefficients**.