

UC4

Quantum Mechanics in 3D

UC4 contents:

- Schrodinger Equation in Spherical Coordinates
- Coulomb potential and quantum description of the Hydrogen atom
- Angular momentum and spin
- Larmor precession and the Stern- Gerlach experiment

Schrödinger equation in 3D

The generalization to three dimensions is straightforward. Schrödinger's equation says

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi;$$

the Hamiltonian operator \hat{H} is obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V$$

by the standard prescription (applied now to y and z , as well as x):

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}, \quad p_y \rightarrow -i\hbar \frac{\partial}{\partial y}, \quad p_z \rightarrow -i\hbar \frac{\partial}{\partial z},$$

or

$$\mathbf{p} \rightarrow -i\hbar \nabla,$$

Schrödinger equation in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi,$$

where

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

is the **Laplacian**, in cartesian coordinates.

The potential energy V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$ and t . The probability of finding the particle in the infinitesimal volume $d^3\mathbf{r} = dx dy dz$ is $|\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$, and the normalization condition reads

$$\int |\Psi|^2 d^3\mathbf{r} = 1,$$

with the integral taken over all space.

Schrödinger equation in 3D

If V is independent of time, there will be a complete set of stationary states,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-i E_n t / \hbar},$$

where the spatial wave function ψ_n satisfies the *time-independent* Schrödinger equation:

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

The general solution to the *(time-dependent)* Schrödinger equation is

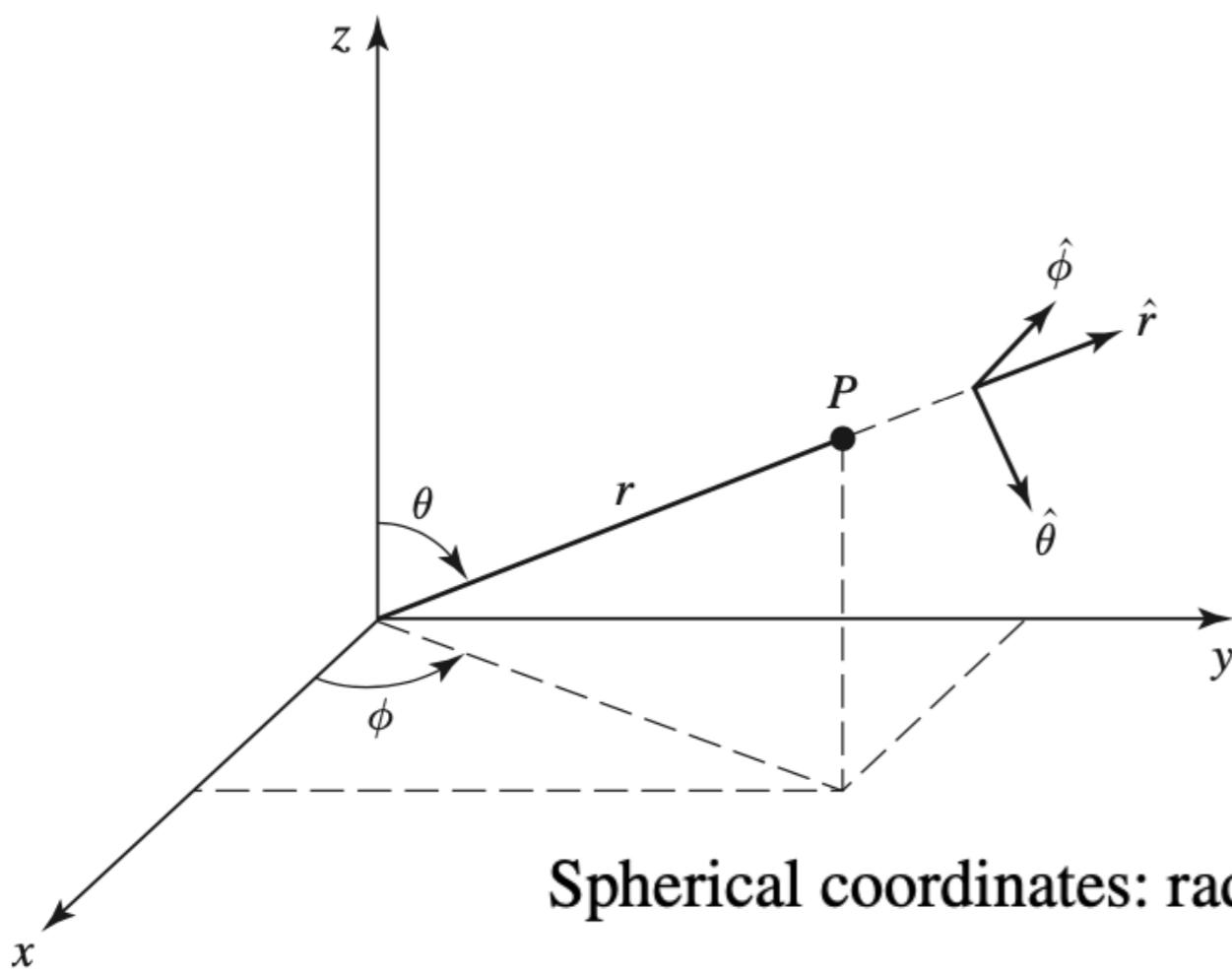
$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-i E_n t / \hbar}, \quad (4.9)$$

with the constants c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$, in the usual way. (If the potential admits continuum states, then the sum in Equation 4.9 becomes an integral.)

Schrödinger equation in spherical coordinates:

Most of the applications we will encounter involve **central potentials**, for which V is a function only of the distance from the origin, $V(\mathbf{r}) \rightarrow V(r)$. In that case it is natural to adopt **spherical coordinates**, (r, θ, ϕ) (Figure 4.1). In spherical coordinates the Laplacian takes the form¹

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



Spherical coordinates: radius r , polar angle θ , and azimuthal angle ϕ .

Schrödinger equation in spherical coordinates:

In spherical coordinates, then, the time-independent Schrödinger equation reads

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

Variable separation:

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

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

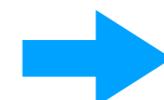
Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

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

Schrödinger equation in spherical coordinates:

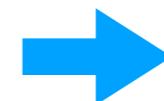
$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial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

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



The Radial Equation

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



The Angular Equation

The Angular Equation

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

Multiplying by: $Y \sin^2 \theta$,

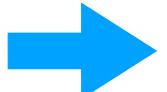
$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell (\ell + 1) \sin^2 \theta Y.$$

Separation of variables: $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$.

Dividing by: $\Theta \Phi$

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

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



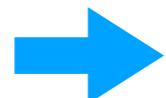
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2.$$

Solution for Φ :

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

where m can be positive or negative.

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



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

$$\exp[im(\phi + 2\pi)] = \exp(im\phi), \text{ or } \exp(2\pi im) = 1.$$

m must be an integer: $m = 0, \pm 1, \pm 2, \dots$

Solution for Θ :

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

The solution reads:

$$\Theta(\theta) = A P_\ell^m(\cos \theta)$$

where P_ℓ^m is the **associated Legendre function**, defined by:

$$P_\ell^m(x) \equiv (-1)^m \left(1 - x^2\right)^{m/2} \left(\frac{d}{dx}\right)^m P_\ell(x), \quad \text{for } m \geq 0$$

and $P_\ell(x)$ is the ℓ^{th} **Legendre polynomial**, defined by the **Rodrigues formula**:

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

Solution for Θ :

For negative values of m :

$$P_\ell^{-m}(x) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(x).$$

$P_\ell(x)$ is a polynomial (of degree ℓ) in x , and is even or odd according to the parity of ℓ .

$P_\ell^m(x)$ is not, in general, a polynomial — if m is odd it carries a factor of $(1-x^2)^{0.5}$

ℓ must be a non-negative *integer*.

If $m > \ell$, $P_\ell^m = 0$. For any given ℓ , then, there are $(2\ell + 1)$ possible values of m :

$\ell = 0, 1, 2, \dots$



$m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$

Solution for Θ :

For negative values of m :

$$P_\ell^{-m}(x) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(x).$$

First Legendre polynomials:

$$P_0 = 1$$

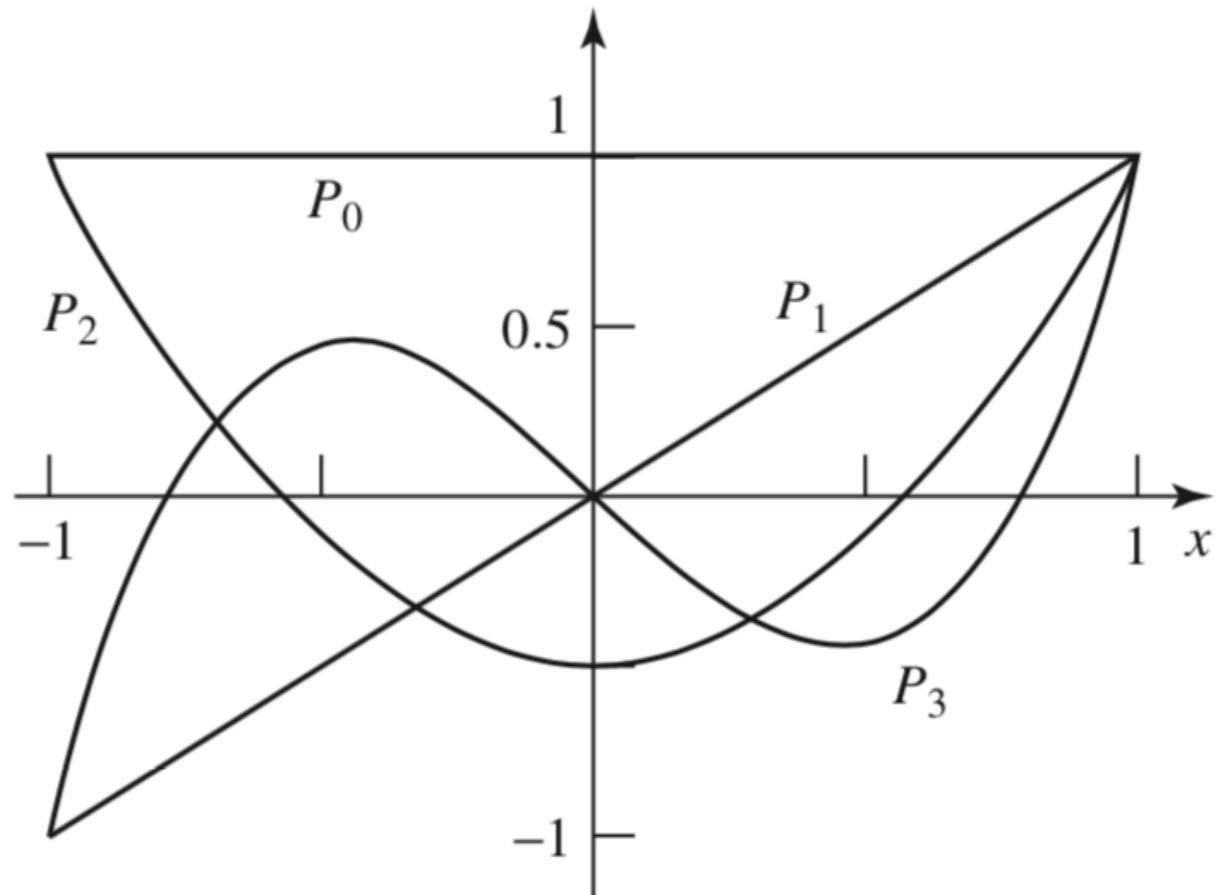
$$P_1 = x$$

$$P_2 = \frac{1}{2}(3x^2 - 1)$$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



Solution for Θ :

We need $P_\ell^m(\cos \theta)$, and $(1 - \cos^2 \theta)^{0.5} = \sin \theta$, so $P_\ell^m(\cos \theta)$ is always a polynomial in $\cos \theta$, multiplied — if m is odd — by $\sin \theta$.

$$P_0^0 = 1$$

$$P_2^0 = \frac{1}{2}(3 \cos^2 \theta - 1)$$

$$P_1^1 = -\sin \theta$$

$$P_3^3 = -15 \sin \theta (1 - \cos^2 \theta)$$

$$P_1^0 = \cos \theta$$

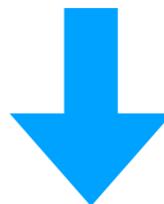
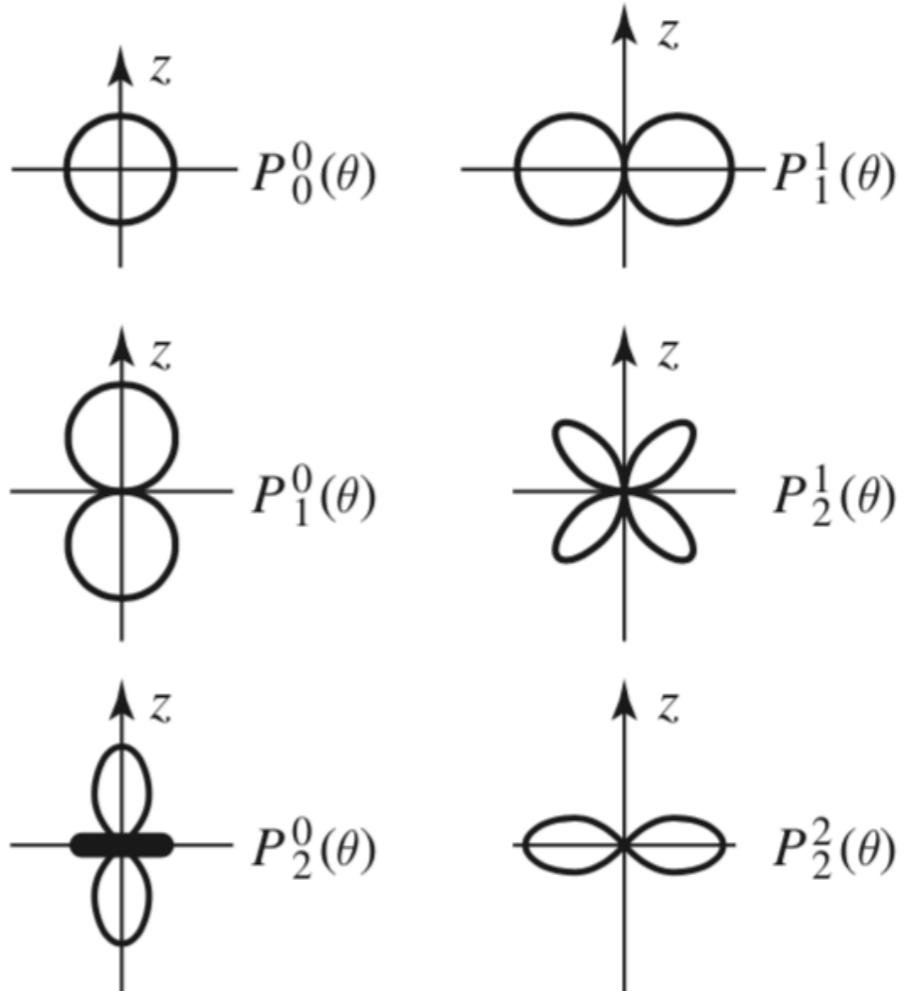
$$P_3^2 = 15 \sin^2 \theta \cos \theta$$

$$P_2^2 = 3 \sin^2 \theta$$

$$P_3^1 = -\frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$$

$$P_2^1 = -3 \sin \theta \cos \theta$$

$$P_3^0 = \frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$$



graphs of $r = |P_\ell^m(\cos \theta)|$ (in these plots r tells you the magnitude of the function in the direction θ ; each figure should be rotated about the z axis).

Normalisation condition: solution for Θ :

The volume element in spherical coordinates:

$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi = r^2 \, dr \, d\Omega, \quad \text{where} \quad d\Omega \equiv \sin \theta \, d\theta \, d\phi,$$

Normalisation condition:

$$\int |\Psi|^2 \, d^3\mathbf{r} = 1, \quad \rightarrow \quad \int |\psi|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \, d\Omega = 1.$$

It is convenient to normalise R and Y separately:

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

$$\int_0^\pi \int_0^{2\pi} |Y|^2 \sin \theta \, d\theta \, d\phi = 1.$$

Normalisation condition: solution for Θ :

The normalised angular wave functions are called **spherical harmonics**:

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

They are orthogonal:

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

Spherical Harmonics:

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

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

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

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

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$$

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

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$$

$$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$$

The Radial Equation

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

The angular part of the wave function, $Y(\theta, \phi)$, is the same for *all* spherically symmetric potentials.

The actual *shape* of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$.

Variable change:

$$R = u/r,$$

$u(r) \equiv rR(r) \quad \rightarrow \quad dR/dr = [r(du/dr) - u]/r^2,$

$$(d/dr)[r^2(dR/dr)] = rd^2u/dr^2,$$

We get the **radial equation**:

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

The Radial Equation

We get the **radial equation**:

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

It is *identical in form* to the one-dimensional Schrödinger, where:

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

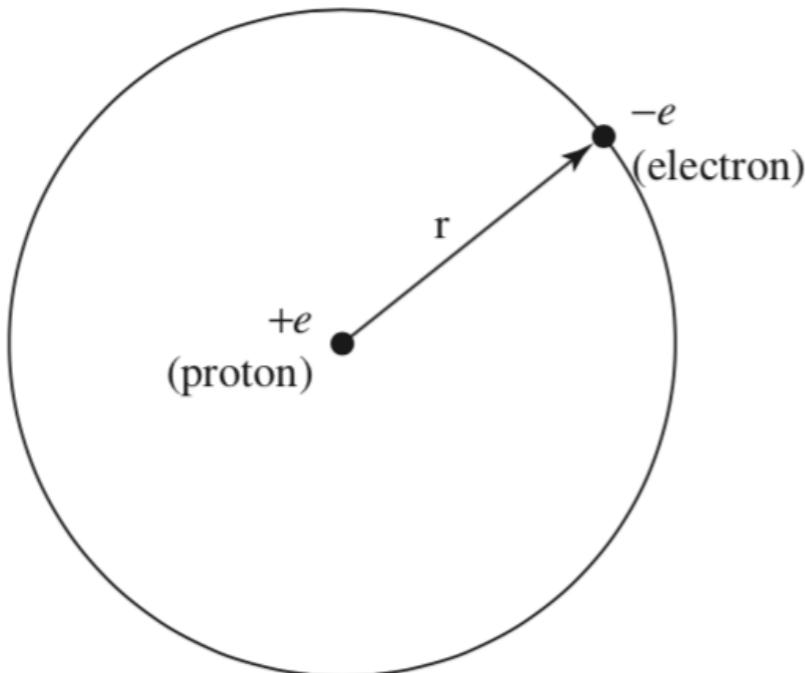
is the **effective potential**, which contains a **centrifugal term**: $(\hbar^2/2m) [\ell(\ell+1)/r^2]$

It tends to throw the particle outward (away from the origin), just like the centrifugal (pseudo-)force in classical mechanics.

The normalisation conditions is: $\int_0^\infty |u|^2 dr = 1.$

which is potential $V(r)$ specific.

The hydrogen atom



The hydrogen atom consists of proton of charge e , together with a much lighter electron charge $-e$.

$$m_p = 1.67 \times 10^{-27} \text{ kg}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$

$$e = 1.60 \times 10^{-19} \text{ C}$$

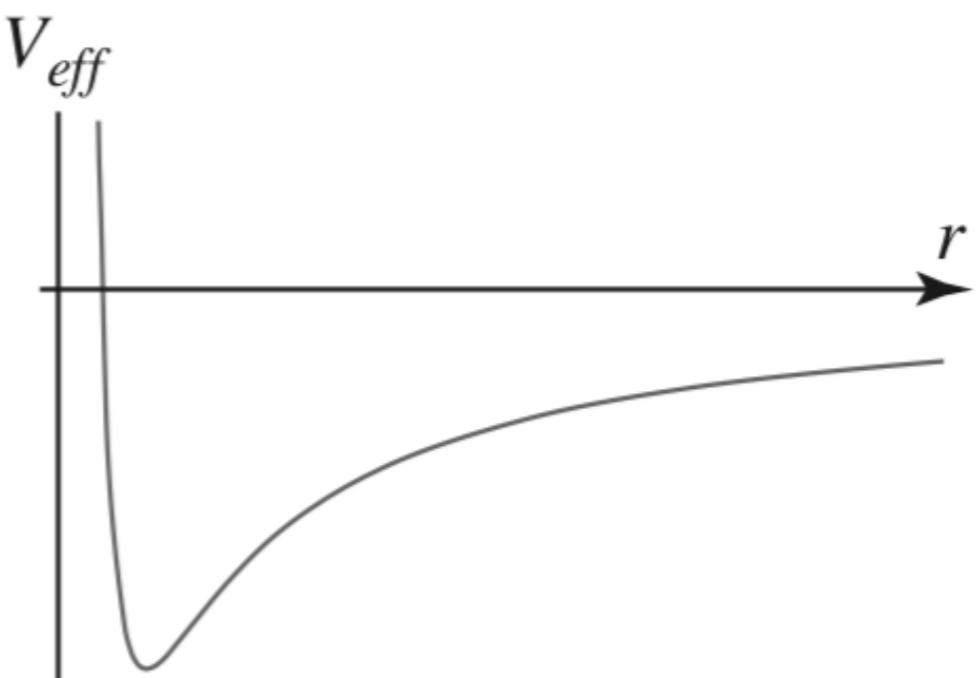
From Coulomb's law: $F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$ the potential in SI units is: $V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$

And the radial equation becomes:

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

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

Effective potential (V_{eff})



The hydrogen atom

We need to solve this equation for $u(r)$, and determine the allowed energies.

The Coulomb potential admits:

- Scattering states ($E > 0$) -> electron-proton scattering
- Bound states ($E < 0$) -> hydrogen atom

The Radial Wave Function

We are interested in finding bound states ($E < 0$) of:

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

Let's divide this equation by E and define: $\kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar}$



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

The hydrogen atom

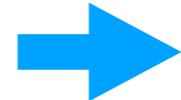
The Radial Wave Function

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

We introduce:

$$\rho \equiv \kappa r,$$

$$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa},$$



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

Let's analyse the asymptotic behaviour of this equation.

$$\rho \rightarrow \infty$$



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



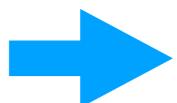
$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

blows up



$$u(\rho) \sim Ae^{-\rho} \quad (\text{for large } \rho)$$

$$\rho \rightarrow 0$$

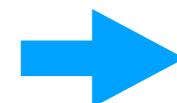


$$\frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$



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

blows up



$$u(\rho) \sim C\rho^{\ell+1} \quad (\text{for small } \rho)$$

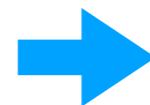
The hydrogen atom

The Radial Wave Function

We introduce the new function $v(\rho)$:

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

(for large ρ)



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

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

(for small ρ)

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

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

Therefore:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell + 1)}{\rho^2} \right] u \quad \rightarrow \quad \rho \frac{d^2v}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1)] v = 0$$

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

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

The hydrogen atom

The Radial Wave Function

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

We assume the solution, $v(\rho)$, can be expressed as a power series in ρ , for which we need to determine the coefficients (c_0, c_1, c_2, \dots).

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

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

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

Replacing into the radial equation above, we get:

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

→ $j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0$

The hydrogen atom

The Radial Wave Function

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

→ $j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0$

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

This recursion formula determines the coefficients, and hence the function $v(\rho)$.

For large j (this corresponds to large ρ , where the higher powers dominate):

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j \quad \rightarrow \quad c_j \approx \frac{2^j}{j!} c_0$$

If this were the exact result, it blows up at large ρ (so it is not normalisable):

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho} \quad \rightarrow \quad u(\rho) = c_0 \rho^{l+1} e^\rho$$

The hydrogen atom

The Radial Wave Function: the Bohr radius

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho} \quad \rightarrow \quad u(\rho) = c_0 \rho^{l+1} e^\rho.$$

Thus, the series must terminate: $c_{N-1} \neq 0$ but $c_N = 0$

$$c_{j+1} = \left\{ \frac{2(j + \ell + 1) - \rho_0}{(j + 1)(j + 2\ell + 2)} \right\} c_j \quad \rightarrow \quad 2(N + \ell) - \rho_0 = 0.$$

which makes $v(\rho)$ a polynomial of order $(N - 1)$, with (therefore) $N - 1$ roots, and hence the radial wave function has $N - 1$ nodes.

Let's define: $n \equiv N + \ell$. $\rightarrow \rho_0 = 2n$

Remember: $\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}$,



$$\kappa = \left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an}$$



$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

This is the so-called **Bohr radius**.

The hydrogen atom

The Radial Wave Function: the Bohr formula

Remember: $\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}, \quad \kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar}$

$$\rightarrow E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m_e e^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$



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

This is the **Bohr formula**

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

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

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

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

$n \equiv$ principal quantum number
 $\ell \equiv$ azimuthal quantum number
 $m \equiv$ magnetic quantum number

and $v(\rho)$ is a polynomial of degree $n - \ell - 1$ in ρ , whose coefficients are determined (up to an overall normalisation factor) by the recursion formula:

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

The hydrogen atom

Energy levels

Bohr formula:

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

The **ground state** (that is, the state of lowest energy) is the case $n = 1$:

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

The **binding energy** of hydrogen (the amount of energy we would have to impart to the electron in its ground state in order to ionise the atom) is 13.6 eV.

$$n \equiv N + \ell,$$

Remember:

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

Thus, $\ell = 0$ and $m = 0$:

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



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

The hydrogen atom

Energy levels for hydrogen

For arbitrary n , the possible values of ℓ are:

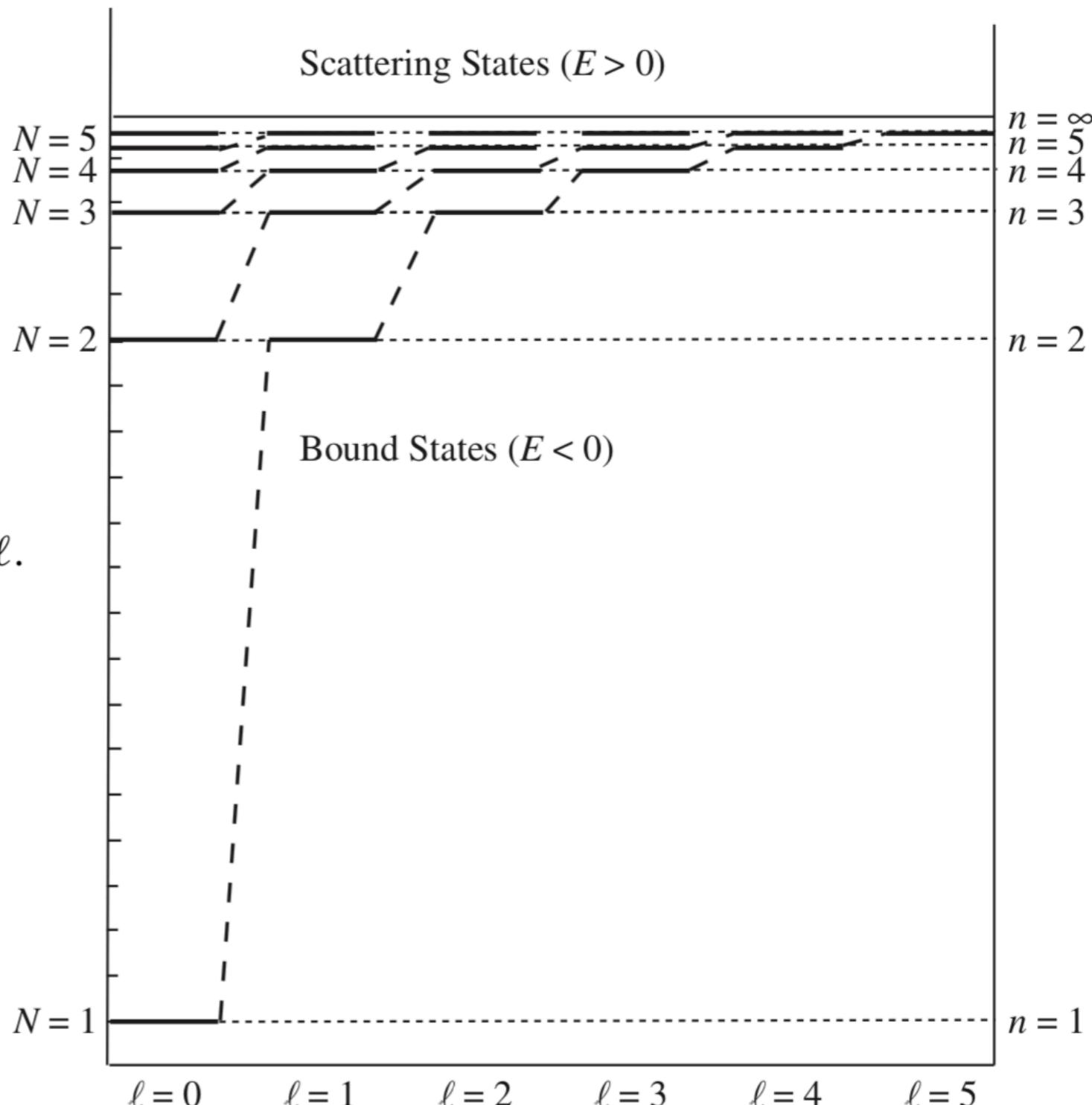
$$\ell = 0, 1, 2, \dots, n - 1$$

For each ℓ there are $(2\ell + 1)$ possible values of m .

$$m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

The total degeneracy of the energy level E_n is:

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



The hydrogen atom

Radial wave function of hydrogen

The polynomial $v(p)$ is a function well known to applied mathematicians; apart from normalisation, it can be written as:

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

where:

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

is an **associated Laguerre polynomial**, and:

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

is the **q th Laguerre polynomial**.

The hydrogen atom

Laguerre polynomials

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

Associated Laguerre polynomials

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

$$L_q^p(x) = \frac{x^{-p} e^x}{q!} \left(\frac{d}{dx} \right)^q (e^{-x} x^{p+q})$$

$L_0(x) = 1$		
$L_1(x) = -x + 1$		
$L_2(x) = \frac{1}{2}x^2 - 2x + 1$		
$L_3(x) = -\frac{1}{6}x^3 + \frac{3}{2}x^2 - 3x + 1$		
$L_4(x) = \frac{1}{24}x^4 - \frac{2}{3}x^3 + 3x^2 - 4x + 1$		
$L_5(x) = -\frac{1}{120}x^5 + \frac{5}{24}x^4 - \frac{5}{3}x^3 + 5x^2 - 5x + 1$		
$L_6(x) = \frac{1}{720}x^6 - \frac{1}{20}x^5 + \frac{5}{8}x^4 - \frac{10}{3}x^3 + \frac{15}{2}x^2 - 6x + 1$		

$L_0^0(x) = 1$	$L_0^2(x) = 1$
$L_1^0(x) = -x + 1$	$L_1^2(x) = -x + 3$
$L_2^0(x) = \frac{1}{2}x^2 - 2x + 1$	$L_2^2(x) = \frac{1}{2}x^2 - 4x + 6$
$L_0^1(x) = 1$	$L_0^3(x) = 1$
$L_1^1(x) = -x + 2$	$L_1^3(x) = -x + 4$
$L_2^1(x) = \frac{1}{2}x^2 - 3x + 3$	$L_2^3(x) = \frac{1}{2}x^2 - 5x + 10$

The hydrogen atom

Radial wave functions for hydrogen:

$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

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

$$R_{21} = \frac{1}{2\sqrt{6}} a^{-3/2} \left(\frac{r}{a} \right) \exp(-r/2a)$$

$$R_{30} = \frac{2}{3\sqrt{3}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a} \right)^2 \right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$$

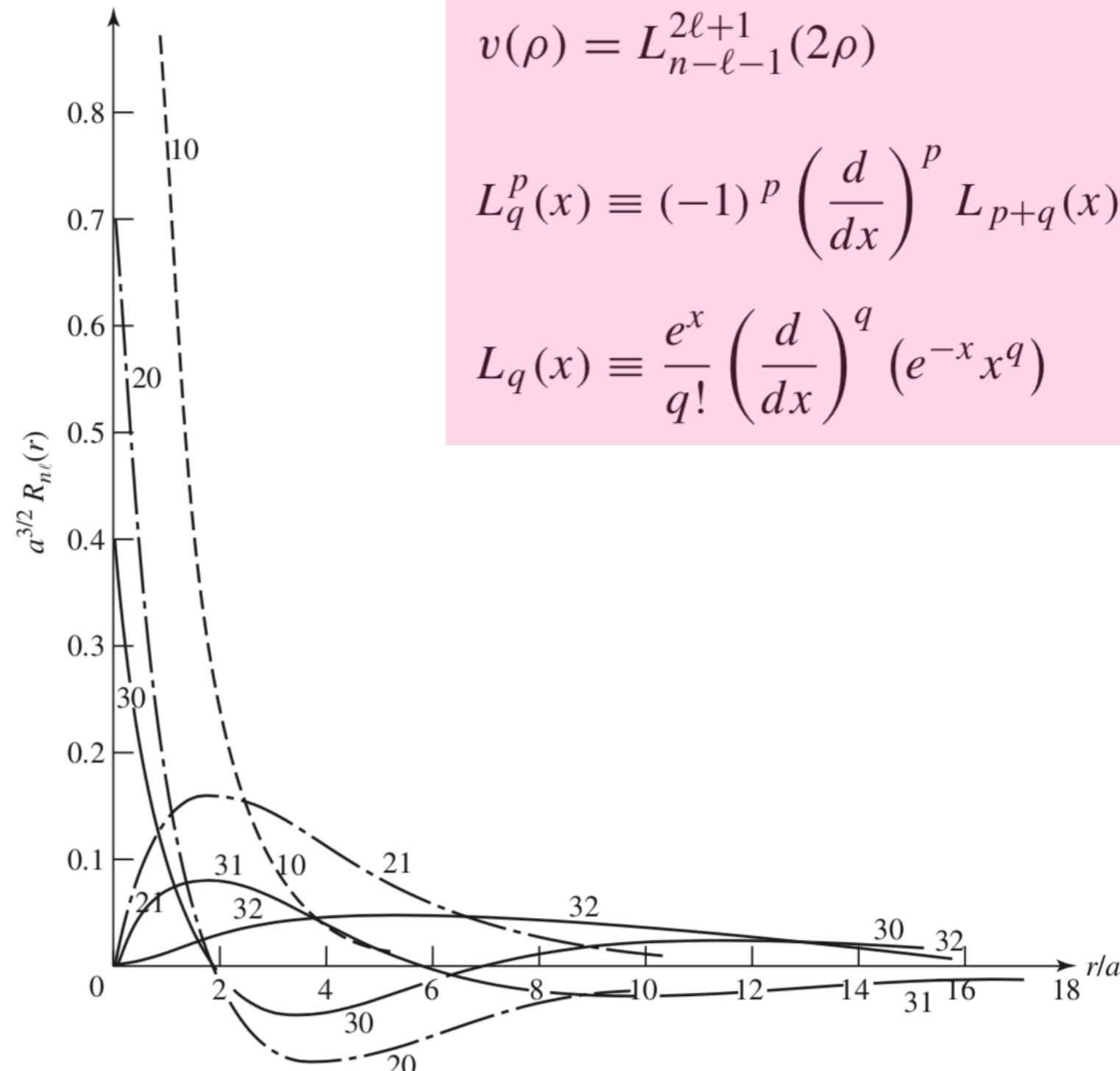
$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4}a^{-3/2} \left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8} \left(\frac{r}{a}\right)^2 - \frac{1}{192} \left(\frac{r}{a}\right)^3 \right) \exp(-r/4a)$$

$$R_{41} = \frac{5}{16\sqrt{15}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a} \right)^2 \right) \left(\frac{r}{a} \right) \exp(-r/4a)$$

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

$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a}\right)^3 \exp(-r/4a)$$



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

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

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

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

The hydrogen atom

Normalised hydrogen wave functions:

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

The stationary states of the hydrogen atom are labeled by three quantum numbers: n , ℓ , and m .

The wave functions are mutually orthogonal:

$$\int \psi_{n\ell m}^* \psi_{n'\ell' m'} r^2 dr d\Omega = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}.$$

This follows from the orthogonality of the spherical harmonics:

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

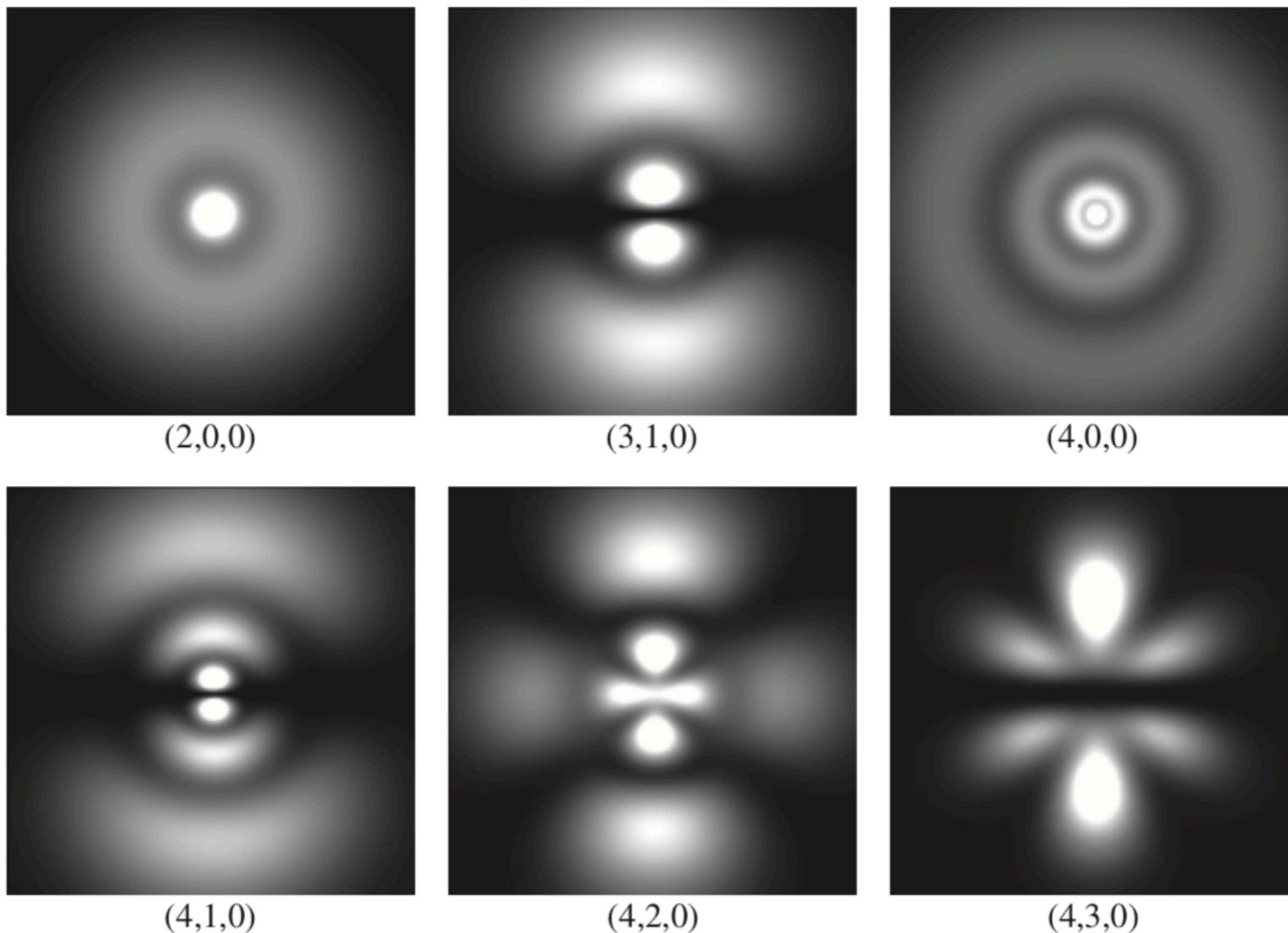
and (for $n \neq n'$) from the fact that they are eigenfunctions of \hat{H} with distinct eigenvalues.

The hydrogen atom

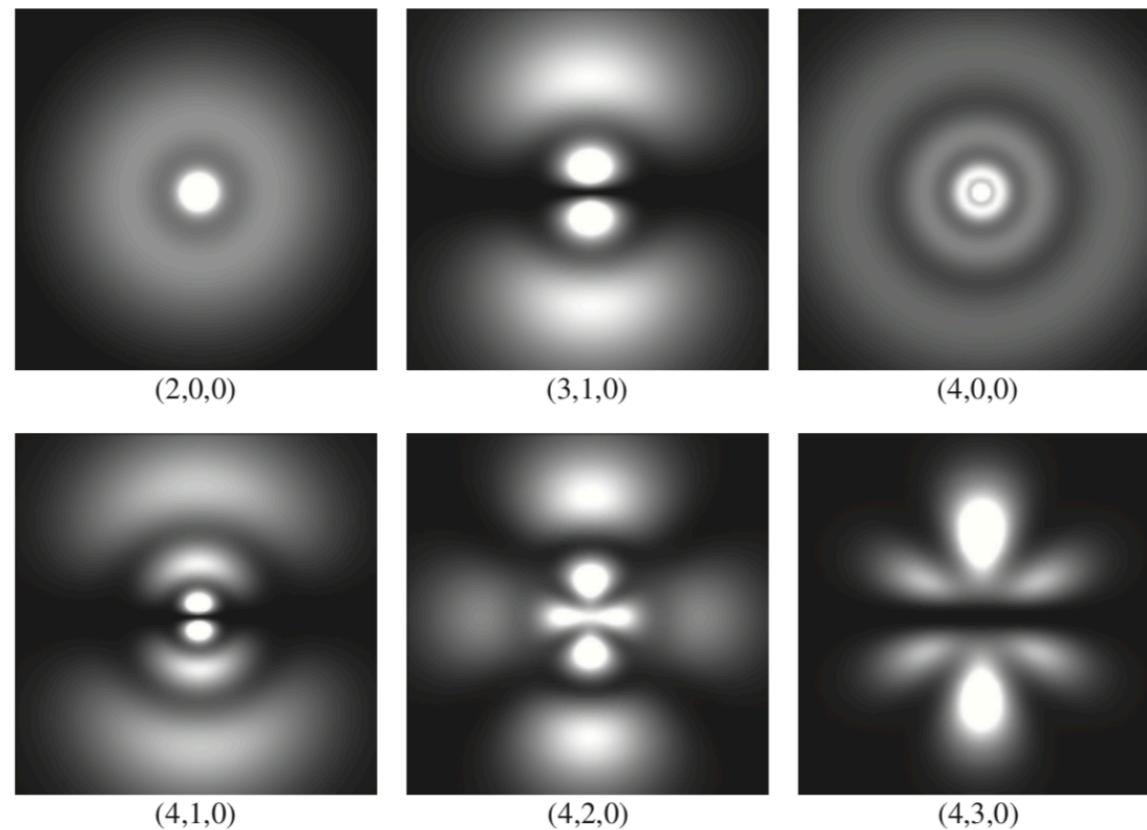
Normalised hydrogen wave functions:

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

They can be visualised via **density plots**, in which the brightness of the cloud is proportional to $|\Psi|^2$



The hydrogen atom



The quantum numbers n , ℓ , and m can be identified from the nodes of the wave function.

The number of radial nodes is given by $N - 1$ (for hydrogen this is $n - \ell - 1$).

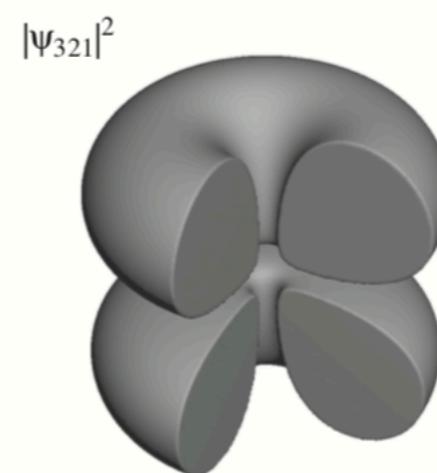
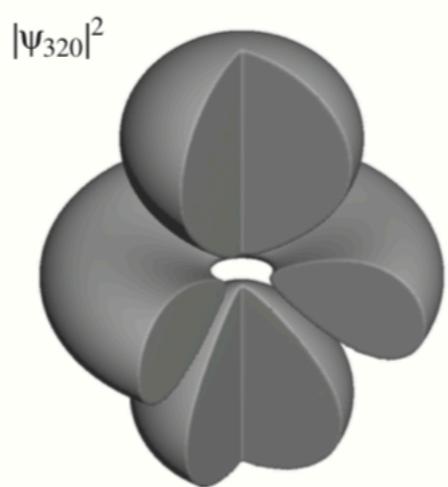
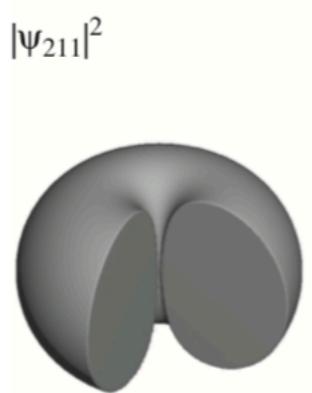
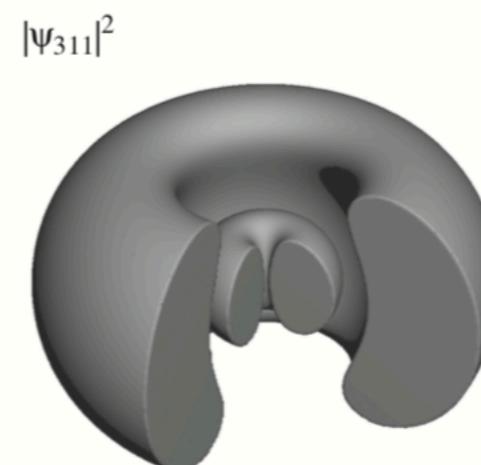
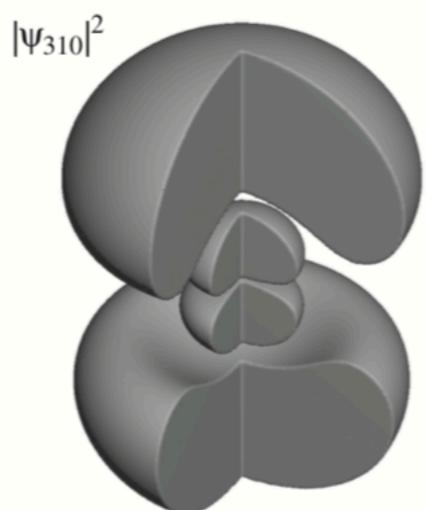
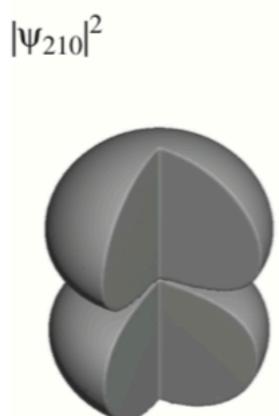
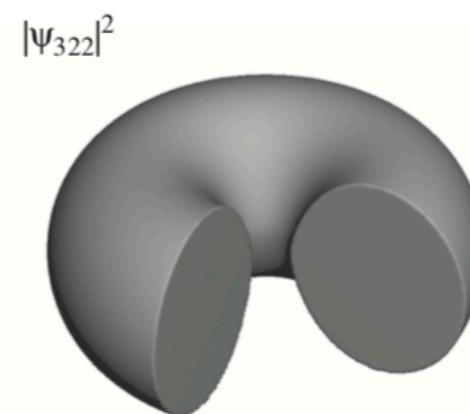
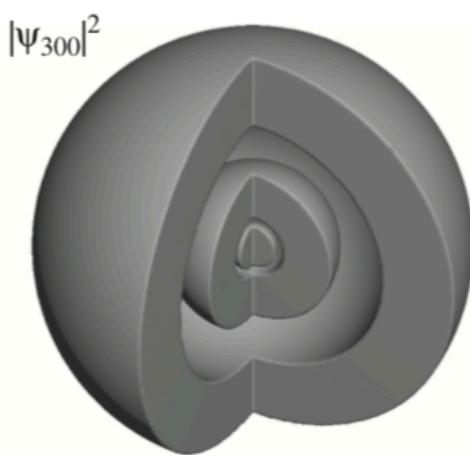
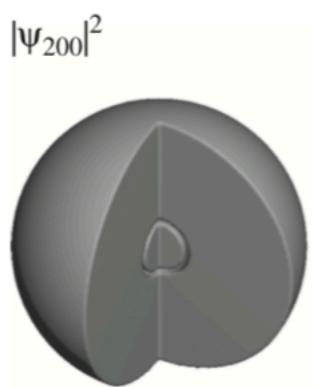
For each radial node the wave function vanishes on a sphere.

m counts the number of nodes of the real (or imaginary) part of the wave function in the ϕ direction. These nodes are planes containing the z axis on which the real or imaginary part of ψ vanishes.

$\ell - m$ gives the number of nodes in the θ direction. These are cones about the z axis on which ψ vanishes.

The hydrogen atom

Or via **surfaces of constant probability density**:



The hydrogen atom

The spectrum of Hydrogen:

If we put a hydrogen atom into some stationary state Ψ_{nlm} , it should stay there forever.

If we *tickle* it slightly (by collision with another atom, say, or by shining light on it), the atom may undergo a **transition** to some other stationary state:

- by *absorbing* energy, and moving up to a higher-energy state, or
- by *giving off* energy (typically in the form of electromagnetic radiation), and moving down.

Such perturbations are *always* present.

Transitions (**quantum jumps**) are constantly occurring.

A container of hydrogen gives off light (**photons**), whose energy corresponds to the *difference* in energy between the initial and final states:

$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

The hydrogen atom

The spectrum of Hydrogen:

$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

According to the **Planck formula**: $E_\gamma = h\nu$. and we know: $\lambda = c/\nu$,

$$\frac{1}{\lambda} = \mathcal{R} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Rydberg formula

where:

$$\mathcal{R} \equiv \frac{m_e}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

is known as the **Rydberg constant** (Bohr calculated it!).

The spectrum of Hydrogen:

Lyman series: transitions to the ground state ($n_f = 1$) lie in the ultraviolet.

Balmer series: transitions to the first excited state ($n_f = 2$) lie in the optical.

Paschen series: transitions to the second excited state ($n_f = 3$) lie in the infrared.

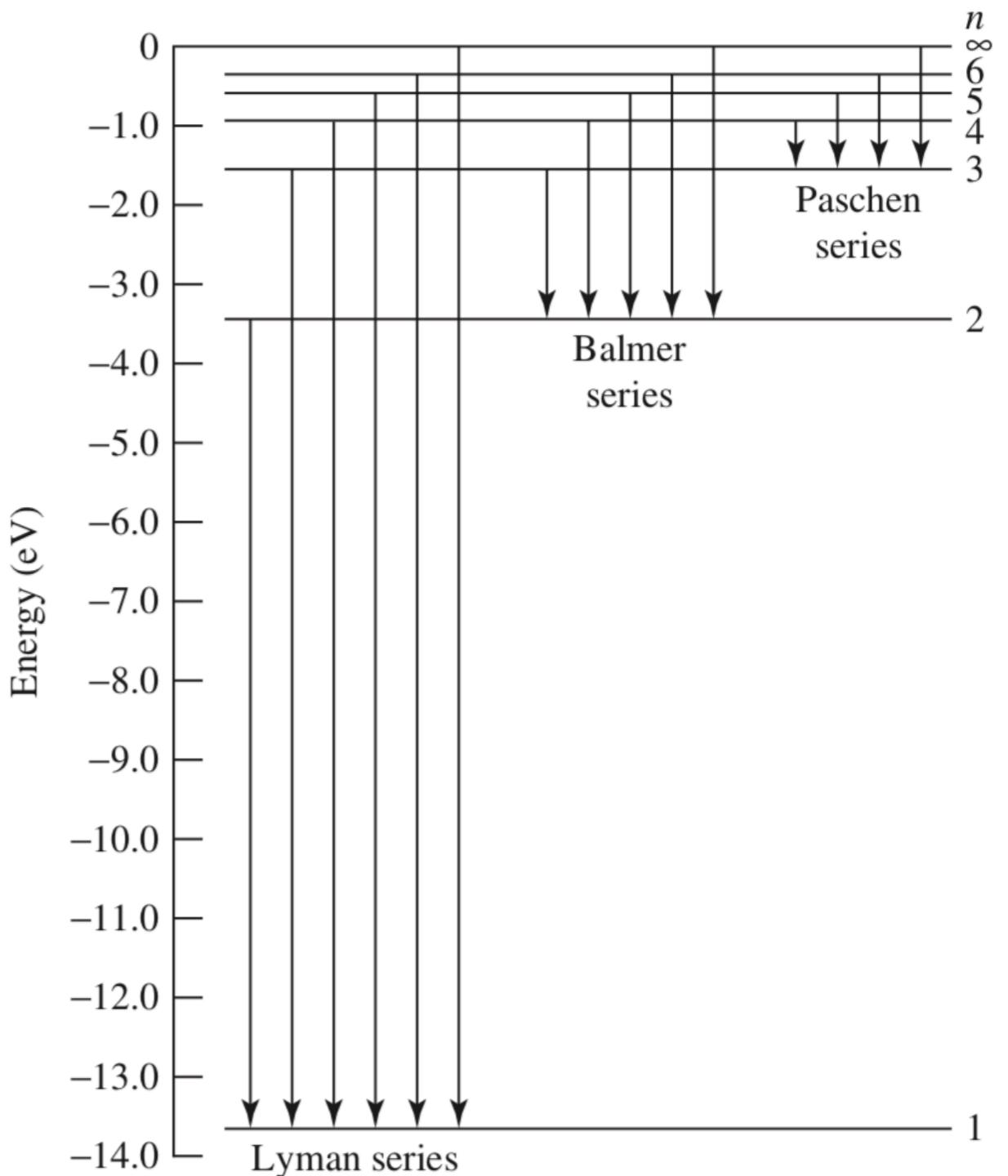
$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

At room temperature, most hydrogen atoms are in the ground state.

To obtain the emission spectrum we must populate the excited states.

This is done by passing an electric spark through the gas.



Problem 4.1

(a) Work out all of the **canonical commutation relations** for components of the operators **r** and **p**: $[x, y]$, $[x, p_y]$, $[x, p_x]$, $[p_y, p_z]$, and so on. *Answer:*

$$[r_i, p_j] = -[p_i, r_j] = i\hbar\delta_{ij}, \quad [r_i, r_j] = [p_i, p_j] = 0, \quad (4.10)$$

where the indices stand for x , y , or z , and $r_x = x$, $r_y = y$, and $r_z = z$.

The hydrogen atom

Angular momentum:

The principal quantum number (n) determines the energy of the state:

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

ℓ and m are related to the orbital angular momentum:

In the classical theory of central forces, energy and angular momentum are the fundamental conserved quantities. The angular momentum of a particle (with respect to the origin) is given by:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

The corresponding quantum operators are obtained by the standard prescription:

$$p_x \rightarrow -i\hbar\partial/\partial x, \quad p_y \rightarrow -i\hbar\partial/\partial y, \quad p_z \rightarrow -i\hbar\partial/\partial z.$$

We need to obtain the eigenvalues and the eigenfunctions of the angular momentum operators.

The hydrogen atom

Angular momentum: Eigenvalues

The operators L_x and L_y do not commute:

$$\begin{aligned}[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z].\end{aligned}$$

x with p_x , y with p_y , and z with p_z fail to commute:

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

We can get the others by cyclic permutation of the indices ($x \rightarrow y, y \rightarrow z, z \rightarrow x$):

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

These are the **fundamental commutation relations for angular momentum**.

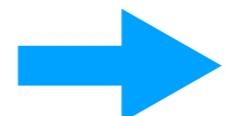
Notice that L_x , L_y , and L_z are *incompatible* observables.

The hydrogen atom

Angular momentum: Eigenvalues

According to the generalised uncertainty principle:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2.$$



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

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

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|.$$

There are no states that are simultaneously eigenfunctions of L_x and L_y .

The *square* of the *total* angular momentum: $L^2 \equiv L_x^2 + L_y^2 + L_z^2$,

does commute with L_x :

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_y (-i\hbar L_z) + (-i\hbar L_z) L_y + L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= 0. \end{aligned}$$

Problem 3.14

(a) Prove the following commutator identities:

$$[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}], \quad (3.64)$$

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}. \quad (3.65)$$

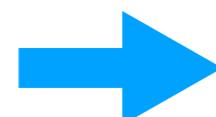
The hydrogen atom

Angular momentum: Eigenvalues

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_y (-i\hbar L_z) + (-i\hbar L_z) L_y + L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= 0. \end{aligned}$$

L^2 also commutes with L_y and L_z :

$$[L^2, L_x] = 0, \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0,$$

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

We can hope to find simultaneous eigenstates of L^2 and (say) L_z :

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

The hydrogen atom

Angular momentum: Ladder operator technique

Let: $L_{\pm} \equiv L_x \pm iL_y$.

Its commutator with L_z is:

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

→ $[L_z, L_{\pm}] = \pm\hbar L_{\pm}$.

Remember: $[L^2, \mathbf{L}] = 0$. → $[L^2, L_{\pm}] = 0$.

Then, f is a common eigenfunction:

$$[L^2, L_{\pm}] = 0. \rightarrow L^2 (L_{\pm} f) = L_{\pm} (L^2 f) = L_{\pm} (\lambda f) = \lambda (L_{\pm} f),$$

Therefore, $L_{\pm} f$ is also an eigenfunction of L^2 with the same eigenvalue λ .

The hydrogen atom

Angular momentum: Ladder operator technique

$L_{\pm}f$ is also an eigenfunction of L^2 with the same eigenvalue λ .

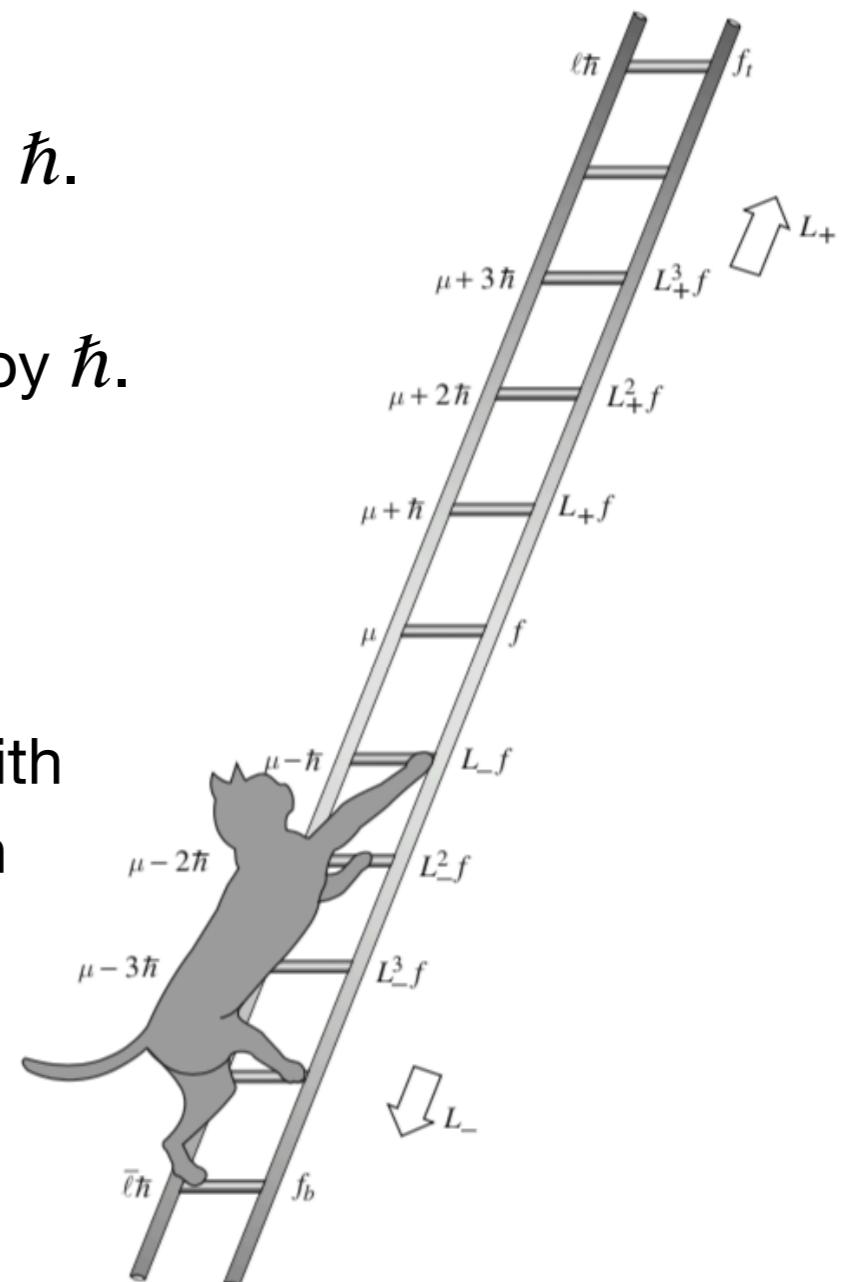
$$[L_z, L_{\pm}] = \pm \hbar L_{\pm} \quad \rightarrow \quad L_z(L_{\pm}f) = (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f = \pm \hbar L_{\pm}f + L_{\pm}(\mu f) \\ = (\mu \pm \hbar)(L_{\pm}f),$$

so $L_{\pm}f$ is an eigenfunction of L_z with the new eigenvalue $\mu \pm \hbar$.

L_+ is the **raising operator**: it *increases* the eigenvalue of L_z by \hbar .

L_- is the **lowering operator**: it *lowers* the eigenvalue by \hbar .

For a given value of λ , then, we obtain a “ladder” of states, with each “rung” separated from its neighbours by one unit of \hbar in the eigenvalue of L_z .



The hydrogen atom

Angular momentum: Ladder operator technique

There must exist a “top rung”, f_t , such that: $L_+ f_t = 0$.

Let $\hbar\ell$ be the eigenvalue of L_z at the top rung: $L_z f_t = \hbar\ell f_t$; $L^2 f_t = \lambda f_t$.

Now,

$$\begin{aligned} L_{\pm} L_{\mp} &= (L_x \pm i L_y)(L_x \mp i L_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) \\ &= L^2 - L_z^2 \mp i(i\hbar L_z), \end{aligned}$$

We have:

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

Thus:

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

$$\rightarrow \lambda = \hbar^2 \ell (\ell + 1).$$

This tells us the eigenvalue of L^2 in terms of the *maximum* eigenvalue of L_z .

The hydrogen atom

Angular momentum: Ladder operator technique

There must also exist a “bottom rung”, f_b , such that: $L_- f_b = 0$.

Let $\hbar\bar{\ell}$ be the eigenvalue of L_z at the bottom rung: $L_z f_b = \hbar\bar{\ell} f_b$; $L^2 f_b = \lambda f_b$.

Remember: $L^2 = L_+ L_- + L_z^2 \mp \hbar L_z$.

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

→ $\lambda = \hbar^2 \bar{\ell} (\bar{\ell} - 1)$

Comparing with: $\lambda = \hbar^2 \ell (\ell + 1)$

$$\ell (\ell + 1) = \bar{\ell} (\bar{\ell} - 1) \rightarrow \begin{array}{ll} \bar{\ell} = \ell + 1 & \times \\ \bar{\ell} = -\ell. & \checkmark \end{array}$$

So the eigenvalues of L_z are $m \boxed{?}$, where m goes from $-\ell$ to $+\ell$, in N integer steps.

It follows that $\ell = -\ell + N$, and hence $\ell = N/2$, so ℓ must be an integer or a half-integer.

The hydrogen atom

Angular momentum: Eigenvalues

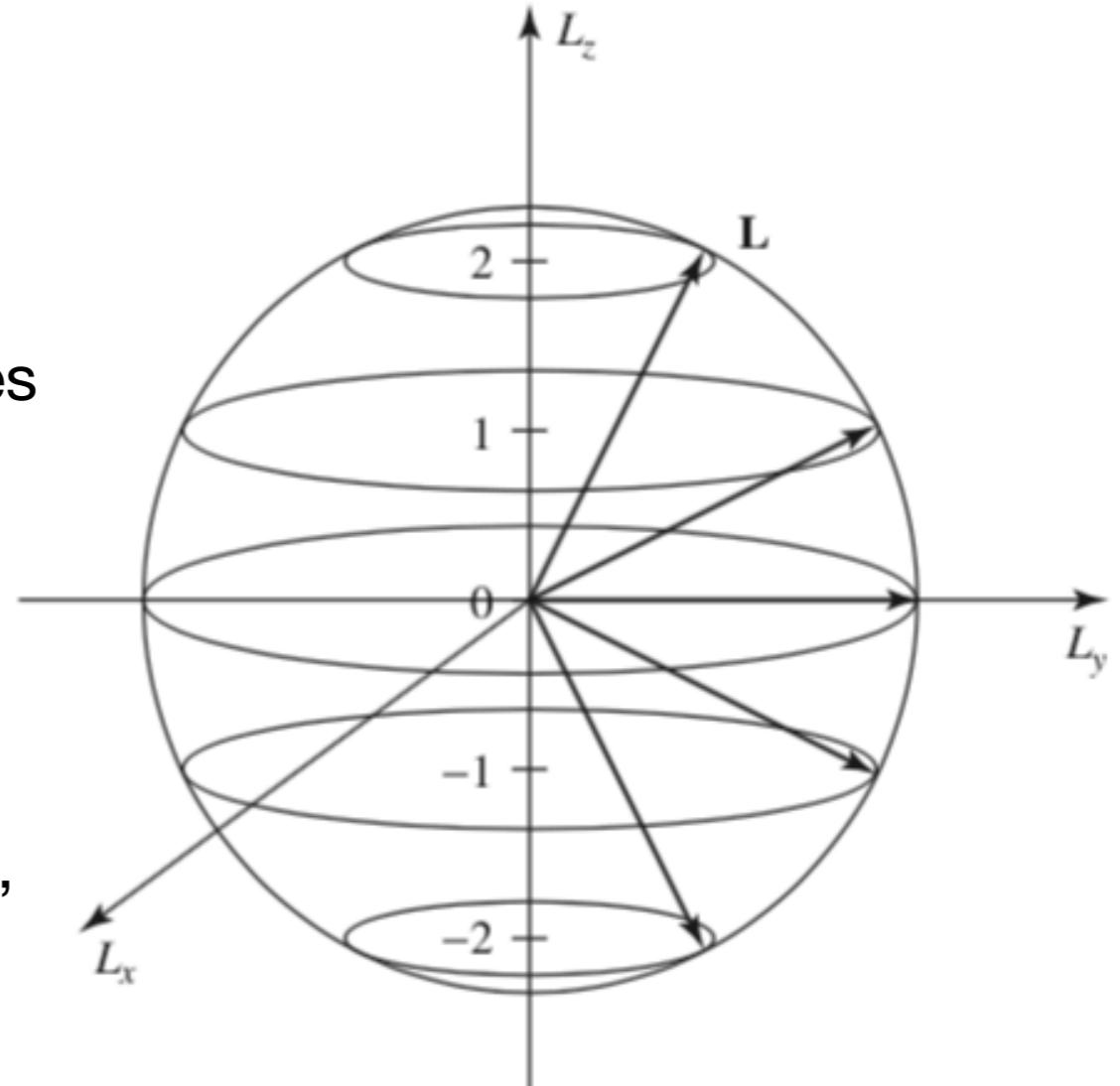
The eigenfunctions are characterised by the numbers ℓ and m :

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

where: $\ell = 0, 1/2, 1, 3/2, \dots;$

$m = -\ell, -\ell + 1, \dots, \ell - 1, \ell.$

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



Arrows are possible angular momenta (in units of \hbar), they all have the same length.

Their z components are the allowed values of m (-2, -1, 0, 1, 2).

Angular momentum states (for $\ell = 2$).

The hydrogen atom

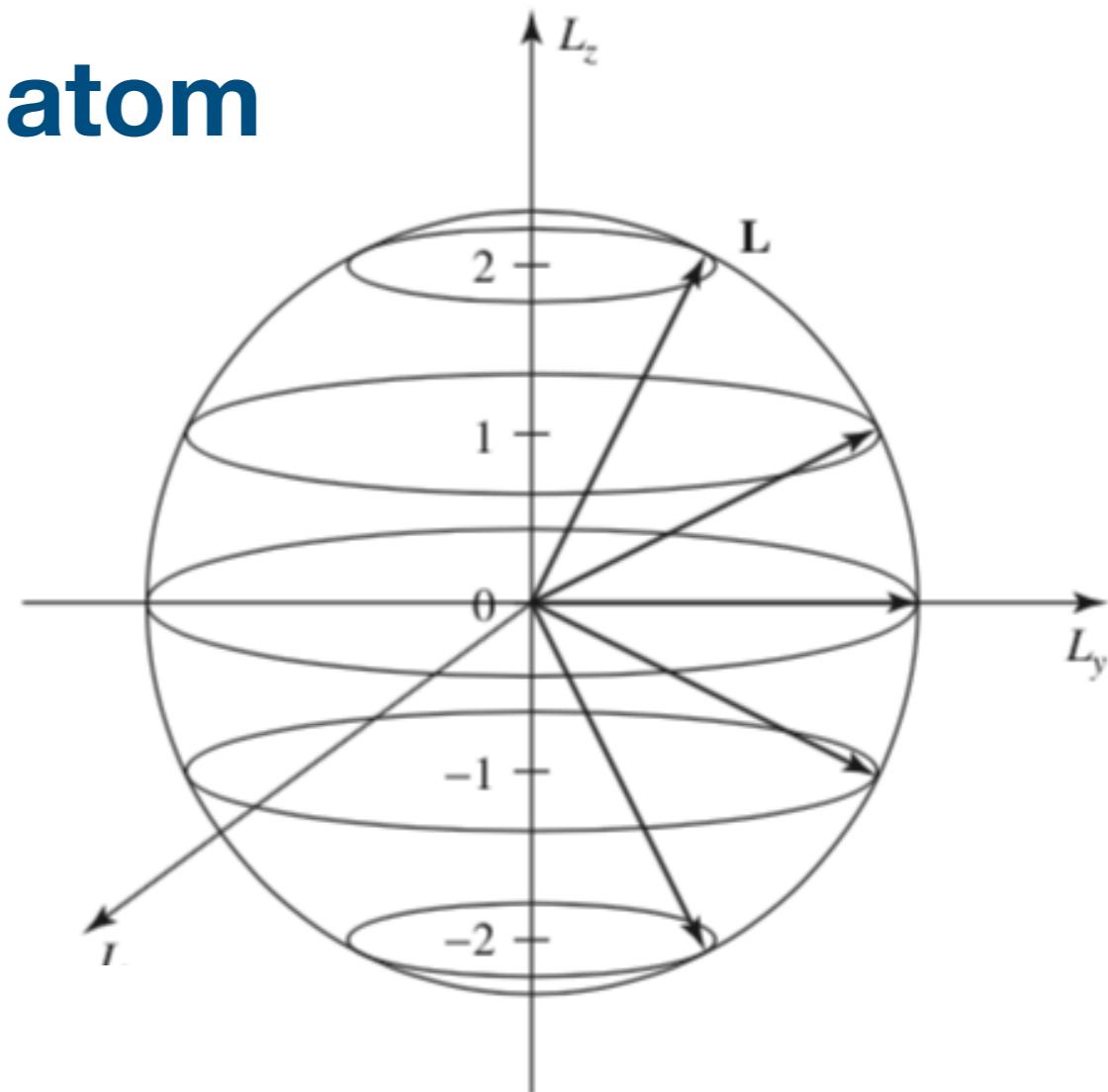
Angular momentum: Eigenvalues

Arrows are possible angular momenta (in units of \hbar),
they all have the same length: $\sqrt{\ell(\ell + 1)}$

Their z components are the allowed values of m
(-2, -1, 0, 1, 2).

The magnitude of the vectors (the radius of the sphere) is *greater* than the maximum z component:

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



Angular momentum states (for $\ell = 2$).

The uncertainty principle implies that we cannot know all three components of L .

Actually, there aren't three components — a particle simply cannot *have* a determinate angular momentum vector.

If L_z has a well-defined value, then L_x and L_y do *not*.

The hydrogen atom

Angular momentum: Eigenfunctions

We will see that $f_\ell^m = Y_\ell^m$, i.e. the eigenfunctions of L^2 and L_z are the spherical harmonics.

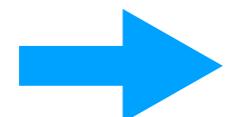
Let's rewrite L_x , L_y , and L_z in spherical coordinates: $\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla)$,

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

Since: $\mathbf{r} = r\hat{r}$,

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

Here: $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$


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

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

$$\hat{\theta} = (\cos \theta \cos \phi) \hat{i} + (\cos \theta \sin \phi) \hat{j} - (\sin \theta) \hat{k};$$

$$\hat{\phi} = -(\sin \phi) \hat{i} + (\cos \phi) \hat{j}.$$

The hydrogen atom

Angular momentum: Eigenfunctions

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

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

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

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

We also need the raising and lowering operators:

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

And: $\cos\phi \pm i\sin\phi = e^{\pm i\phi},$

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

The hydrogen atom

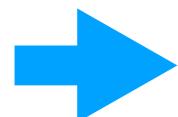
Angular momentum: Eigenfunctions



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

In particular:

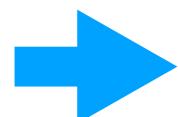
$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \cot^2\theta \frac{\partial^2}{\partial\phi^2} + i \frac{\partial}{\partial\phi} \right),$$



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

We are now in a position to determine $f_{\ell}^m(\theta, \phi)$.

It's an eigenfunction of L^2 , with eigenvalue $\hbar^2\ell(\ell + 1)$.



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

But this is precisely the “angular equation”:

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

The hydrogen atom

Angular momentum: Eigenfunctions

And it's also an eigenfunction of L_z , with the eigenvalue $m\boxed{?}$:

$$L_z f_\ell^m = -i\hbar \frac{\partial}{\partial \phi} f_\ell^m = \hbar m f_\ell^m,$$

which is equivalent to the azimuthal equation:

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

We have already solved this system of equations!

The result (appropriately normalised) is the spherical harmonic, $Y_\ell^m(\theta, \phi)$.

Conclusion:

Spherical harmonics *are* the eigenfunctions of L^2 and L_z . When we solved the Schrödinger equation by separation of variables, we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 , and L_z :

$$H\psi = E\psi, \quad L^2\psi = \hbar^2\ell(\ell+1)\psi, \quad L_z\psi = \hbar m\psi.$$

The hydrogen atom

Angular momentum: Eigenfunctions

We can rewrite Schrödinger's equation as follows:

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

The *algebraic* theory of angular momentum permits ℓ (and hence also m) to take on *half*-integer values:

$$\ell = 0, 1/2, 1, 3/2, \dots; \quad m = -\ell, -\ell + 1, \dots, \ell - 1, \ell.$$

Separation of variables yielded eigenfunctions only for *integer* values.

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

Are the half-integer solutions spurious?

No, they are of profound importance, as we shall see in the following sections.

The hydrogen atom

Spin:

In ***classical mechanics***, a rigid object admits two kinds of angular momentum:
orbital ($\mathbf{L} = \mathbf{r} \times \mathbf{p}$), associated with motion *of* the center of mass, and
spin ($\mathbf{S} = I \omega$), associated with motion *about* the center of mass.

In ***quantum mechanics***, the distinction is absolutely fundamental.

Orbital angular momentum, associated (in the case of hydrogen) with the motion of the electron around the nucleus (and described by the spherical harmonics).

Spin, which has nothing to do with motion in space (and not described by any function of the position variables r, θ, ϕ) but which is somewhat analogous to classical spin.

The electron (as far as we know) is a structureless point, and its spin angular momentum cannot be decomposed into orbital angular momenta of constituent parts.

Suffice it to say that elementary particles carry **intrinsic** angular momentum (**\mathbf{S}**) in addition to their “extrinsic” angular momentum (**\mathbf{L}**).

The hydrogen atom

Spin:

Fundamental commutation relations:

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

It follows (as before) that the eigenvectors of S^2 and S_z satisfy:

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

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

where $S_{\pm} \equiv S_x \pm i S_y$. The eigenvectors are not spherical harmonics (they're not functions of θ and ϕ at all), and there is no reason to exclude the half-integer values of s and m :

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

The hydrogen atom

Spin:

Every elementary particle has a *specific and immutable* value of s , which we call **the spin** of that particular species:

- π mesons have spin 0
- electrons have spin $1/2$
- photons have spin 1
- Δ baryons have spin $3/2$
- gravitons have spin 2; and so on.

By contrast, the *orbital* angular momentum quantum number l (e.g. for an electron in a hydrogen atom) can take on any (integer) value, and will change from one to another when the system is perturbed.

s is *fixed* for any given particle, so the theory of spin is comparatively simple.

The hydrogen atom

Spin 1/2:

$s = 1/2$ is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons.

There are just *two* eigenstates: $|s m\rangle$:

1. **spin up** (informally, \uparrow): $\left| \frac{1}{2} \frac{1}{2} \right\rangle$

2. **spin down** (informally, \downarrow): $\left| \frac{1}{2} \left(-\frac{1}{2} \right) \right\rangle$

Using these as basis vectors, the general state of a spin-1/2 particle can be represented by a two-element column matrix (or **spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-, \quad \text{where:} \quad \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

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

The hydrogen atom

Spin 1/2:

The spin operators become matrices: $S^2|s m\rangle = \hbar^2 s(s+1) |s m\rangle$; $S_z|s m\rangle = \hbar m |s m\rangle$;

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

If we write S^2 as a matrix with undetermined elements:

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

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad \rightarrow \quad \begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\hbar^2 \\ 0 \end{pmatrix}, \quad c = (3/4)\hbar^2 \text{ and } e = 0.$$

$$S^2\chi_- = \frac{3}{4}\hbar^2\chi_- \quad \rightarrow \quad \begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\hbar^2 \end{pmatrix}, \quad d = 0 \text{ and } f = (3/4)\hbar^2.$$

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

The hydrogen atom

Spin 1/2:

Similarly:

$$S_z \chi_+ = \frac{\hbar}{2} \chi_+, \quad S_z \chi_- = -\frac{\hbar}{2} \chi_-,$$

For which:

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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

→ $S_+ \chi_- = \hbar \chi_+, \quad S_- \chi_+ = \hbar \chi_-, \quad S_+ \chi_+ = S_- \chi_- = 0,$

→ $S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$

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

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

The hydrogen atom

Spin 1/2 (Pauli spin matrices).

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

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

These are the famous **Pauli spin matrices**.

S_x , S_y , S_z , and S^2 are all *hermitian* matrices (as they *should* be, since they represent observables).

On the other hand, S_+ and S_- are *not* hermitian—evidently they are not observable.

The eigenspinors of S_z are:

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

The hydrogen atom

Spin 1/2 (Pauli spin matrices).

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

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 $|b|^2$. Since these are the *only* possibilities:

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

(i.e. the spinor must be *normalised*: $\chi^\dagger \chi = 1$.

But what if, instead, we chose to measure S_x ? What are the possible results and probabilities?

We need to know the eigenvalues and eigenspinors of S_x .

The characteristic equation is:

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

The hydrogen atom

Spin 1/2 (Pauli spin matrices).

We need to know the eigenvalues and eigenspinors of S_x .

The characteristic equation is:

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

The possible values for S_x are the same as those for S_z . The eigenspinors are obtained via:

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

The (normalised) eigenspinors of S_x are:

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

The hydrogen atom

Spin 1/2 (Pauli spin matrices).

The (normalised) eigenspinors of S_x are:

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

The generic spinor χ can be expressed as a linear combination of them:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad \chi = \left(\frac{a+b}{\sqrt{2}} \right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}} \right) \chi_-^{(x)}$$

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 $(1/2)|a-b|^2$.

The hydrogen atom

Spin 1/2 (implications):

For a particle in the state x_+ , what is the z-component of a particle's spin angular momentum?

We can answer unambiguously: $+\hbar/2$.

What is the x-component of that particle's spin angular momentum?

If you measure S_x , the chances are fifty-fifty of getting either $+\hbar/2$ or $-\hbar/2$.

It simply *does not have* a particular x-component of spin.

The hydrogen atom

Electron in a Magnetic Field

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

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

The proportionality constant, γ , is called the **gyromagnetic ratio**.

The gyromagnetic ratio of an object whose charge and mass are identically distributed is $q/2m$, where q is the charge and m is the mass.

For reasons that are fully explained only in relativistic quantum theory, the gyromagnetic ratio of the electron is (almost) exactly *twice* the classical value: $\gamma = -e/m$.

When a magnetic dipole is placed in a magnetic field \mathbf{B} , it experiences a torque, $\mu \times \mathbf{B}$, which tends to line it up parallel to the field (just like a compass needle).

The hydrogen atom

Electron in a Magnetic Field

The energy associated with this torque is:

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

so the Hamiltonian matrix for a spinning charged particle, at rest in a magnetic field \mathbf{B} , is:

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

where \mathbf{S} is the appropriate spin matrix:

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

The hydrogen atom

Addition of Angular Momenta

Suppose now that we have *two* particles, with spins s_1 and s_2 .

$$s_1 \quad \xrightarrow{\hspace{1cm}} \quad |s_1 m_1\rangle$$

$$s_2 \quad \xrightarrow{\hspace{1cm}} \quad |s_2 m_2\rangle$$

we denote the composite state by:

$$|s_1 s_2 m_1 m_2\rangle$$

$$S^{(1)2} |s_1 s_2 m_1 m_2\rangle = s_1 (s_1 + 1) \hbar^2 |s_1 s_2 m_1 m_2\rangle,$$

$$S^{(2)2} |s_1 s_2 m_1 m_2\rangle = s_2 (s_2 + 1) \hbar^2 |s_1 s_2 m_1 m_2\rangle,$$

$$S_z^{(1)} |s_1 s_2 m_1 m_2\rangle = m_1 \hbar |s_1 s_2 m_1 m_2\rangle,$$

$$S_z^{(2)} |s_1 s_2 m_1 m_2\rangle = m_2 \hbar |s_1 s_2 m_1 m_2\rangle.$$

What is the *total* angular momentum of the system?

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

The hydrogen atom

Addition of Angular Momenta

What is the *total* angular momentum of the system?

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

What is the net spin, s , of the combination, and what is the z component, m ?

The z component is easy:

$$\begin{aligned} S_z |s_1 s_2 m_1 m_2\rangle &= S_z^{(1)} |s_1 s_2 m_1 m_2\rangle + S_z^{(2)} |s_1 s_2 m_1 m_2\rangle, \\ &= \hbar(m_1 + m_2) |s_1 s_2 m_1 m_2\rangle = \hbar m |s_1 s_2 m_1 m_2\rangle \end{aligned}$$

Thus: $m = m_1 + m_2$

The net spin, s , is much more subtle. If you combine spin s_1 with spin s_2 , what total spins s can we 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:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|.$$

The hydrogen atom

Addition of Angular Momenta

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.

Example 1: 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.

Example 2: If a hydrogen atom is in the state ψ_{nlm} , the net angular momentum of the electron (spin plus orbital) is $\ell + 1/2$ or $\ell - 1/2$.

If you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is $\ell + 1$, ℓ , or $\ell - 1$ (and ℓ can be achieved in two distinct ways, depending on whether the electron alone is in the $\ell + 1/2$ configuration or the $\ell - 1/2$ configuration).

The hydrogen atom

Addition of Angular Momenta

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

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1 s_2 m_1 m_2\rangle$$

Because the z components add, the only composite states that contribute are those for which:

$$m_1 + m_2 = m$$

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

Example 1: The shaded column of the 2×1

$$|30\rangle = \frac{1}{\sqrt{5}} |21\rangle |1-1\rangle + \sqrt{\frac{3}{5}} |20\rangle |10\rangle + \frac{1}{\sqrt{5}} |2-1\rangle |11\rangle$$

If two particles (of spin 2 and spin 1) are at rest in a box, and the *total* spin is 3, and its z component is 0, then a measurement of $S_z^{(1)}$ could return the value \hbar (with probability 1/5), or 0 (with probability 3/5), or $-\hbar$ (with probability 1/5). Notice that the probabilities add up to 1 (the sum of the squares of any column on the Clebsch–Gordan table is 1).

The hydrogen atom

Clebsch-Gordan coefficients $C_{m_1 m_2 m}^{s_1 s_2 s}$

Table 4.8: Clebsch–Gordan coefficients. (A square root sign is understood for every entry; the minus sign, if present, goes outside the radical.)

$1/2 \times 1/2$	$\begin{matrix} 1 \\ +1 \end{matrix}$	$\begin{matrix} 1 & 0 \\ 0 & 0 \end{matrix}$
$+1/2 +1/2$	1	$\begin{matrix} 1/2 & 1/2 & 1 \\ -1/2 & +1/2 & -1 \\ -1/2 & -1/2 & 1 \end{matrix}$
$+1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 1/2 & -1/2 \\ 1/2 & -1/2 \end{matrix}$
$-1/2 +1/2$	$\begin{matrix} 1/2 \\ +1/2 \end{matrix}$	$\begin{matrix} 1/2 & -1/2 \\ -1/2 & -1/2 \end{matrix}$
$-1/2 -1/2$	$\begin{matrix} 1 \\ 1 \end{matrix}$	

$1 \times 1/2$	$\begin{matrix} 3/2 \\ +3/2 \end{matrix}$	$\begin{matrix} 3/2 & 1/2 \\ +1/2 & +1/2 \end{matrix}$
$+1 +1/2$	1	$\begin{matrix} 1/3 & 2/3 & 3/2 & 1/2 \\ 2/3 & -1/3 & -1/2 & -1/2 \end{matrix}$
$+1$	$\begin{matrix} 1/2 \\ 0 \end{matrix}$	$\begin{matrix} 0 & -1/2 \\ -1 & +1/2 \end{matrix}$
0	$\begin{matrix} +1/2 \\ +1/2 \end{matrix}$	$\begin{matrix} 2/3 & 1/3 & 3/2 \\ 1/3 & -2/3 & -3/2 \end{matrix}$
$+1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} -1 & -1/2 \\ 1 & 1 \end{matrix}$

2×1	$\begin{matrix} 3 \\ +3 \end{matrix}$	$\begin{matrix} 3 & 2 \\ +2 & +2 \end{matrix}$
$+2 +1$	1	$\begin{matrix} 1/3 & 2/3 & 3 & 2 & 1 \\ 2/3 & -1/3 & +1 & +1 & +1 \end{matrix}$
$+2$	$\begin{matrix} 0 \\ +1 \end{matrix}$	$\begin{matrix} 1/3 & 2/3 \\ 2/3 & -1/3 \end{matrix}$
$+1$	$\begin{matrix} +1 \\ +1 \end{matrix}$	$\begin{matrix} +2 & -1 \\ +1 & 0 \end{matrix}$
$+1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 1/15 & 1/3 & 3/5 \\ 8/15 & 1/6 & -3/10 \\ 6/15 & -1/2 & 1/10 \end{matrix}$

1×1	$\begin{matrix} 2 \\ +2 \end{matrix}$	$\begin{matrix} 2 & 1 \\ +1 & +1 \end{matrix}$
$+1 +1$	1	$\begin{matrix} 1/2 & 1/2 & 2 & 1 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 \end{matrix}$
$+1$	$\begin{matrix} 0 \\ +1 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & 1/6 & 1/2 & 1/3 \\ 1/2 & -1/2 & 2/3 & 0 & -1/3 \end{matrix}$
0	$\begin{matrix} +1 \\ +1 \end{matrix}$	$\begin{matrix} +1 & -1 \\ 0 & 0 \end{matrix}$
$+1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 1/6 & 1/2 & 2/3 & 1/2 & 1/3 \\ 2/3 & 0 & -1/6 & -3/10 & -1/3 \\ 1/6 & -1/2 & 1/6 & -1/2 & 1/3 \end{matrix}$

$+1 -1$	$\begin{matrix} 1/2 \\ 0 \end{matrix}$	$\begin{matrix} 2 & 1 \\ -1 & -1 \end{matrix}$
0	$\begin{matrix} 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 & -1 \\ -1 & 0 \end{matrix}$
$-1 +1$	$\begin{matrix} 1/2 \\ 1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & 0 & -1 \\ -1/2 & -1/2 & 1 & 1 \end{matrix}$
$-1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & -1 & 1 \\ -1/2 & -1/2 & -1 & 1 \end{matrix}$
$-1/2 +1/2$	$\begin{matrix} 1/2 \\ +1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & 1 & -1 \\ 1/2 & -1/2 & 1 & -1 \end{matrix}$

$-1 -1$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 2 & 1 \\ -1 & -1 \end{matrix}$
0	$\begin{matrix} 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 & -1 \\ -1 & 0 \end{matrix}$
$-1/2 +1/2$	$\begin{matrix} 1/2 \\ +1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & 0 & -1 \\ -1/2 & -1/2 & 1 & 1 \end{matrix}$
$-1/2 -1/2$	$\begin{matrix} 1/2 \\ -1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & -1 & 1 \\ -1/2 & -1/2 & -1 & 1 \end{matrix}$
$-1/2 +1/2$	$\begin{matrix} 1/2 \\ +1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 & 1 & -1 \\ 1/2 & -1/2 & 1 & -1 \end{matrix}$

$2 \times 1/2$	$\begin{matrix} 5/2 \\ +5/2 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ 3/2 & +3/2 \end{matrix}$
$+2 1/2$	1	$\begin{matrix} 1/5 & 4/5 \\ 4/5 & -1/5 \end{matrix}$
$+2 -1/2$	$\begin{matrix} 1/5 \\ 4/5 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ +1/2 & +1/2 \end{matrix}$
$+1 +1/2$	$\begin{matrix} 4/5 \\ -1/5 \end{matrix}$	$\begin{matrix} +1 & -1/2 \\ 0 & +1/2 \end{matrix}$
$+1 -1/2$	$\begin{matrix} 2/5 \\ 3/5 \end{matrix}$	$\begin{matrix} 2/5 & 3/5 \\ 3/5 & -2/5 \end{matrix}$
$0 +1/2$	$\begin{matrix} 3/5 \\ -2/5 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ -1/2 & -1/2 \end{matrix}$
$-1 +1/2$	$\begin{matrix} 2/5 \\ 2/5 \end{matrix}$	$\begin{matrix} 3/5 & 2/5 \\ 2/5 & -3/5 \end{matrix}$
$-1 -1/2$	$\begin{matrix} 3/5 \\ -2/5 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ -3/2 & -3/2 \end{matrix}$
$-2 +1/2$	$\begin{matrix} 2/5 \\ -3/5 \end{matrix}$	$\begin{matrix} 4/5 & 1/5 \\ 1/5 & -4/5 \end{matrix}$
$-2 -1/2$	$\begin{matrix} 2/5 \\ -3/5 \end{matrix}$	$\begin{matrix} 5/2 & 5/2 \\ -5/2 & -5/2 \end{matrix}$

$3/2 \times 1/2$	$\begin{matrix} 2 \\ +2 \end{matrix}$	$\begin{matrix} 2 & 1 \\ +1 & +1 \end{matrix}$
$+3/2 +1$	1	$\begin{matrix} 1/4 & 3/4 \\ 3/4 & -1/4 \end{matrix}$
$+3/2 0$	$\begin{matrix} 1/4 \\ 3/4 \end{matrix}$	$\begin{matrix} 2 & 1 \\ 0 & 0 \end{matrix}$
$+1/2 +1$	$\begin{matrix} 3/4 \\ -1/4 \end{matrix}$	$\begin{matrix} +1/2 & -1/2 \\ -1/2 & +1/2 \end{matrix}$
$+1/2 -1/2$	$\begin{matrix} 1/2 \\ 1/2 \end{matrix}$	$\begin{matrix} 1/2 & 1/2 \\ 1/2 & -1/2 \end{matrix}$
$-1/2 +1/2$	$\begin{matrix} 1/2 \\ -3/2 \end{matrix}$	$\begin{matrix} 2 & 1 \\ 1/4 & -3/4 \end{matrix}$
$-1/2 -1/2$	$\begin{matrix} 1/2 \\ -3/2 \end{matrix}$	$\begin{matrix} 2 & 1 \\ -3/2 & -1/2 \end{matrix}$

$3/2 \times 1$	$\begin{matrix} 5/2 \\ +5/2 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ 3/2 & +3/2 \end{matrix}$
$+3/2 +1$	1	$\begin{matrix} 2/5 & 3/5 \\ 3/5 & -2/5 \end{matrix}$
$+3/2 0$	$\begin{matrix} 2/5 \\ 3/5 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ +1/2 & +1/2 \end{matrix}$
$+1/2 +1$	$\begin{matrix} 3/5 \\ -2/5 \end{matrix}$	$\begin{matrix} +3/2 & -1 \\ 3/10 & -8/15 \end{matrix}$
$+3/2 -1$	$\begin{matrix} 1/10 \\ 3/10 \end{matrix}$	$\begin{matrix} 1/10 & 2/5 & 1/2 \\ 3/10 & 1/15 & -1/3 \\ -1/2 & -1/2 & -1/2 \end{matrix}$
$+1/2 0$	$\begin{matrix} 3/10 \\ 1/10 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 & 1/2 \\ -1/2 & -1/2 & -1/2 \end{matrix}$
$-1/2 +1$	$\begin{matrix} 3/10 \\ 1/10 \end{matrix}$	$\begin{matrix} 3/10 & 8/15 & 1/6 \\ 3/5 & -1/15 & -1/3 \\ 1/10 & -2/5 & 1/2 \end{matrix}$
$-3/2 +1$	$\begin{matrix} 3/10 \\ 1/10 \end{matrix}$	$\begin{matrix} 5/2 & 3/2 \\ -3/2 & -3/2 \end{matrix}$
$-1/2 -1$	$\begin{matrix} 3/10 \\ -3/2 \end{matrix}$	$\begin{matrix} 3/10 & 2/5 & 5/2 \\ 3/5 & -3/5 & -5/2 \\ -1/2 & 0 & 1 \end{matrix}$
$-3/2 0$	$\begin{matrix} 3/10 \\ 2/5 \end{matrix}$	$\begin{matrix} 3/10 & 2/5 & 5/2 \\ 3/5 & -3/5 & -5/2 \\ -3/2 & 0 & 1 \end{matrix}$
$-3/2 -1$	$\begin{matrix} 3/10 \\ -3/2 \end{matrix}$	$\begin{matrix} 3/10 & 2/5 & 5/2 \\ -3/2 & -3/2 & -5/2 \\ -3/2 & -1 & 1 \end{matrix}$

ELECTROMAGNETIC INTERACTIONS

Minimal Coupling

In classical electrodynamics the force on a particle of charge q moving with velocity \mathbf{v} through electric and magnetic fields \mathbf{E} and \mathbf{B} is given by the **Lorentz force law**:

$$\mathbf{F} = q (\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

This force cannot be expressed as the gradient of a scalar potential energy function, and therefore the Schrödinger equation in its original form cannot accommodate it. But in the more sophisticated form there is no problem:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

The classical Hamiltonian for a particle of charge q and momentum \mathbf{p} , in the presence of electromagnetic fields is

$$H = \frac{1}{2m} (\mathbf{p} - q\mathbf{A})^2 + q\varphi,$$

where \mathbf{A} is the vector potential and φ is the scalar potential:

$$\mathbf{E} = -\nabla\varphi - \partial\mathbf{A}/\partial t, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

ELECTROMAGNETIC INTERACTIONS

Minimal Coupling

Making the standard substitution $\mathbf{p} \rightarrow -i\hbar\nabla$, we obtain the Hamiltonian operator

$$\hat{H} = \frac{1}{2m} (-i\hbar\nabla - q\mathbf{A})^2 + q\varphi,$$

and the Schrödinger equation becomes:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\frac{1}{2m} (-i\hbar\nabla - q\mathbf{A})^2 + q\varphi \right] \Psi.$$

This is the quantum implementation of the Lorentz force law; it is sometimes called the **minimal coupling rule**.