

# 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 generalisation 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

Thus:

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

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  $\Psi$  are now functions of  $\mathbf{r} = (x, y, z)$  and  $t$ . The probability of finding the particle in the infinitesimal volume  $d^3r = dx dy dz$  is  $|\Psi(\mathbf{r}, t)|^2 d^3r$ , and the normalisation 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  $\psi_n$  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:

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

With the  $c_n$  constants determined by the initial wave function,  $\Psi(\mathbf{r}, 0)$ , in the usual way.

Notice that if the potential admits continuum states, then the sum becomes an integral.

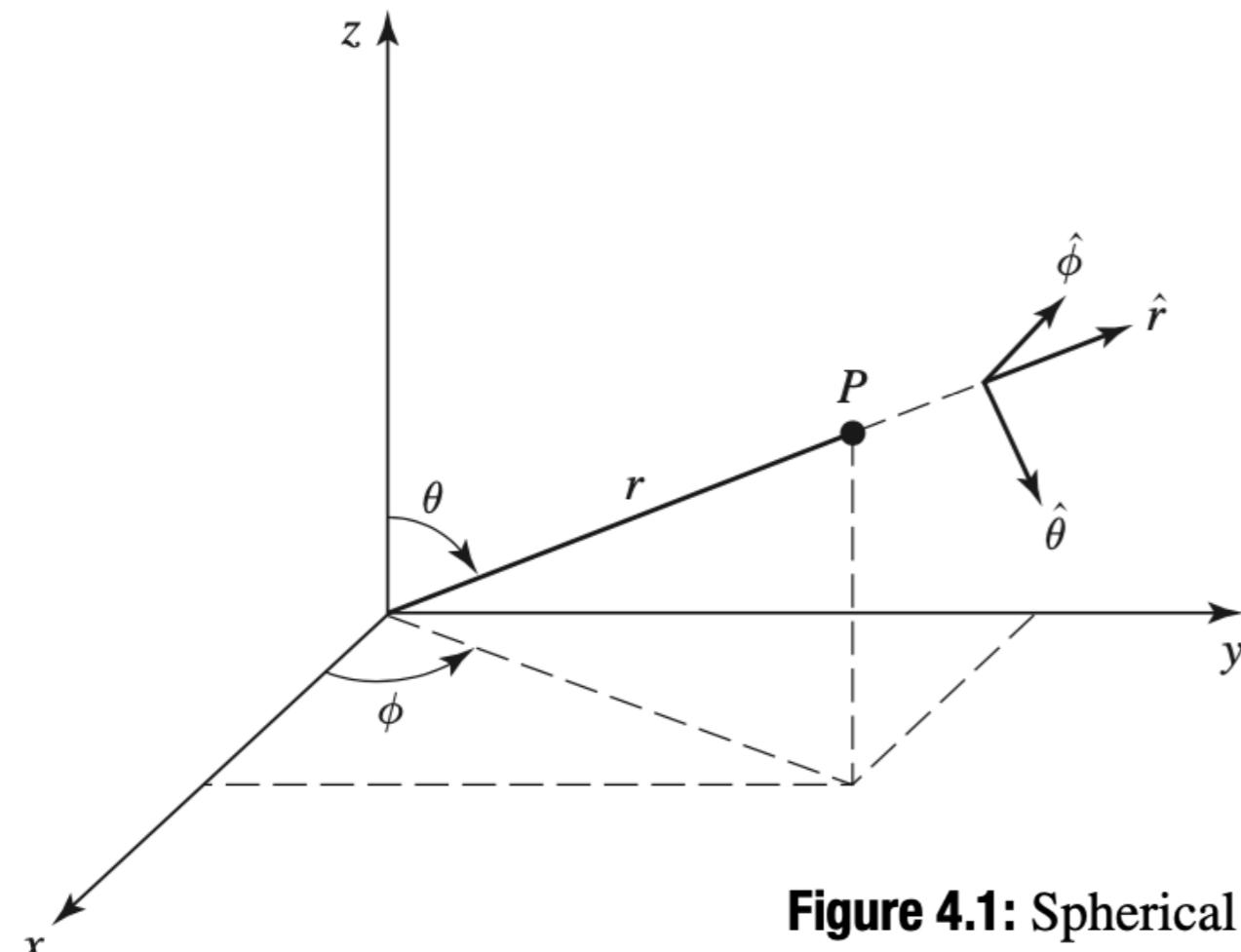
# Schrödinger equation in spherical coordinates:

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**,  $(r, \theta, \phi)$  (Figure 4.1).

In spherical coordinates the Laplacian takes the form:

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



**Figure 4.1:** Spherical coordinates: radius  $r$ , polar angle  $\theta$ , and azimuthal angle  $\phi$ .

# 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:

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

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

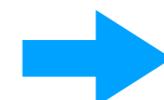
Dividing by  $RY$  and multiplying by  $-2mr^2/\hbar^2$ :

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

# Schrödinger equation in spherical coordinates:

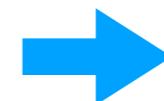
$$\left\{ \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial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

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



**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:  $Y \sin^2 \theta$ ,

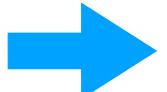
$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell (\ell + 1) \sin^2 \theta Y.$$

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

Dividing by:  $\Theta \Phi$

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

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



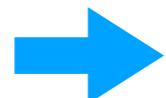
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2.$$

## Solution for $\Phi$ :

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

where  $m$  can be positive or negative.

when  $\Phi$  advances by  $2\pi$ , 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 $\Theta$ :

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

The solution reads:

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

where  $P_\ell^m$  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  $\ell^{\text{th}}$  **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 $\Theta$ :

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  $\ell$ ) in  $x$ , and is even or odd according to the parity of  $\ell$ .

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

$\ell$  must be a non-negative *integer*.

If  $m > \ell$ ,  $P_\ell^m(x) = 0$ .

For any given  $\ell$ , 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 $\Theta$ :

For negative values of  $m$ :

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

## First Legendre polynomials:

$$P_0 = 1$$

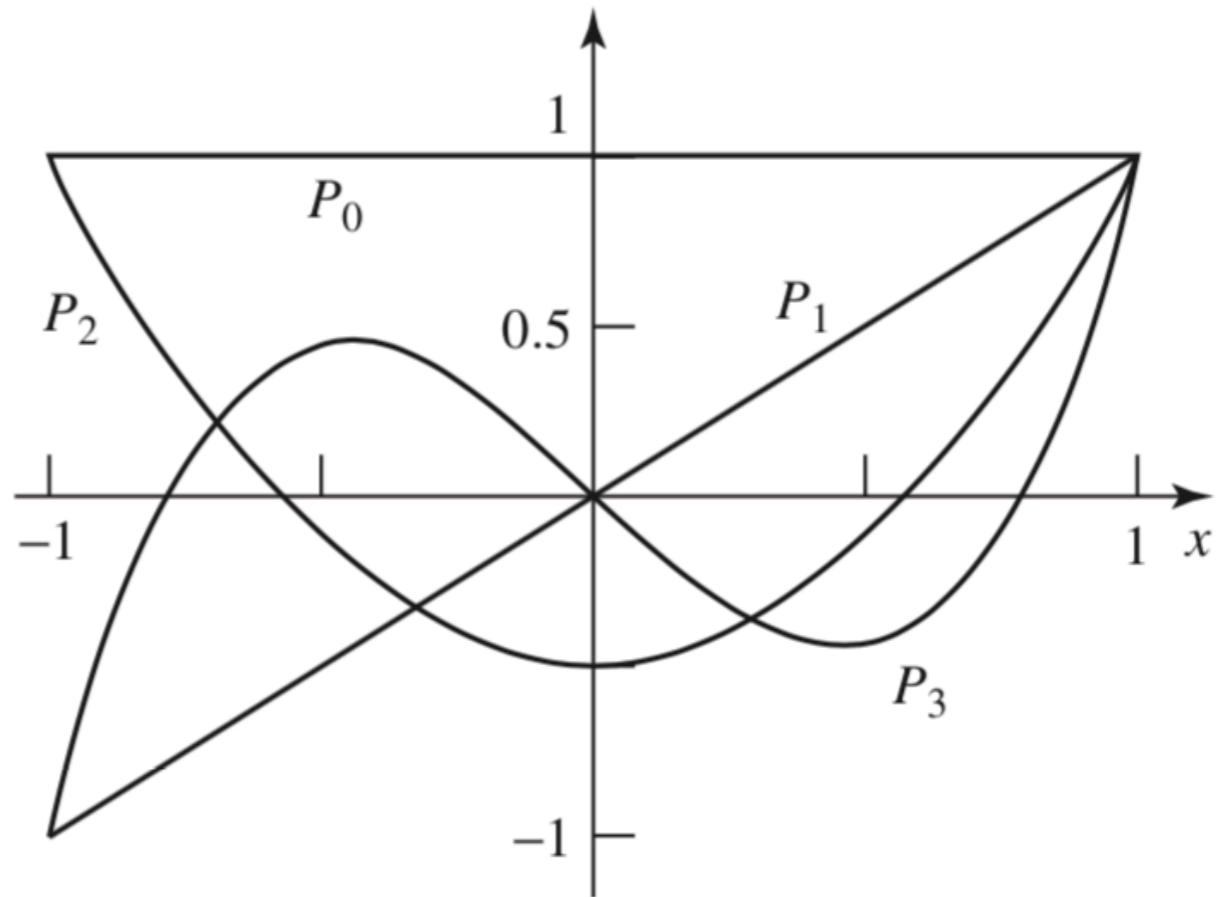
$$P_1 = x$$

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

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

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

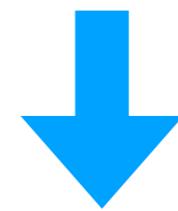
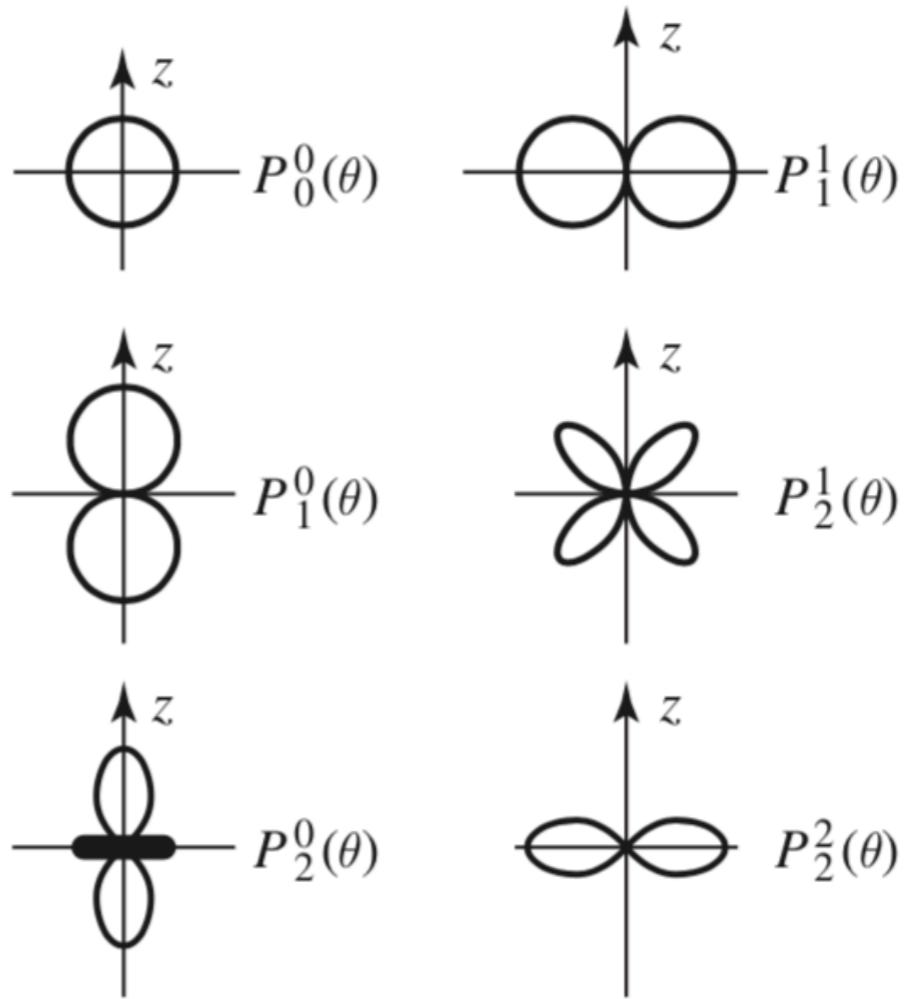
$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



# Solution for $\Theta$ :

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  $\theta$ ; each figure should be rotated about the  $z$  axis).

## Normalisation condition: solution for $\Theta$ :

The volume element in spherical coordinates:

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

and  $\Omega$  is the solid angle.

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:

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

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

# Normalisation condition: solution for $\Theta$ :

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:

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

## 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**:

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

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

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

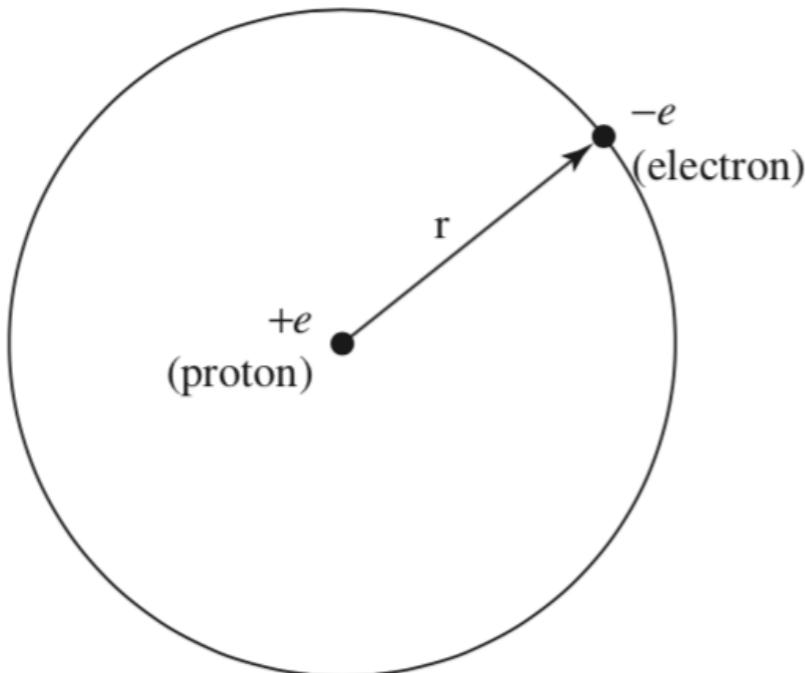
is the **effective potential**, which contains a **centrifugal term**:  $(\hbar^2/2m) [\ell (\ell + 1) / r^2]$

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  $-e$ .

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

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

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

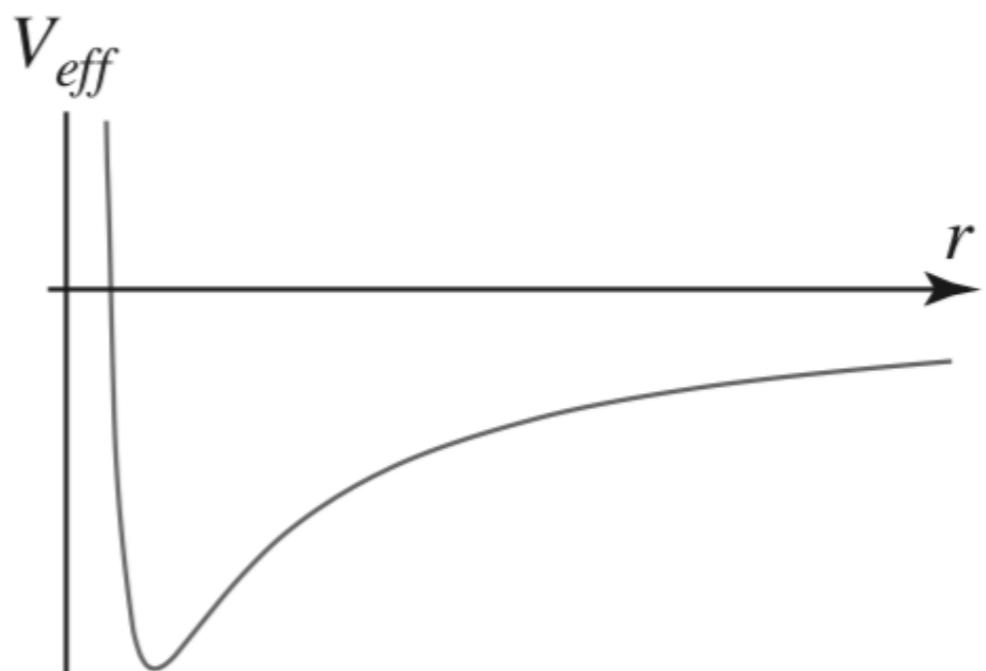
From Coulomb's law:  $F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$  the potential in SI units is:  $V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$

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

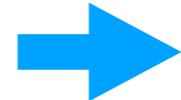
## The Radial Wave Function

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

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.

$$\rho \rightarrow \infty$$



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



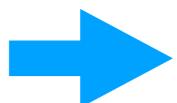
$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

blows up



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

$$\rho \rightarrow 0$$

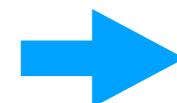


$$\frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$



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

blows up



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

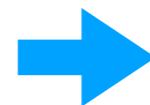
# The hydrogen atom

## The Radial Wave Function

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

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

(for large  $\rho$ )



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

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

(for small  $\rho$ )

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

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

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  $\rho$ :

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

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

$$\rightarrow \kappa = \left( \frac{m_e e^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an} \quad \rightarrow \quad a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

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 ( $n$ ,  $\ell$ , 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  $\rho$ , 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  $\ell$  are:

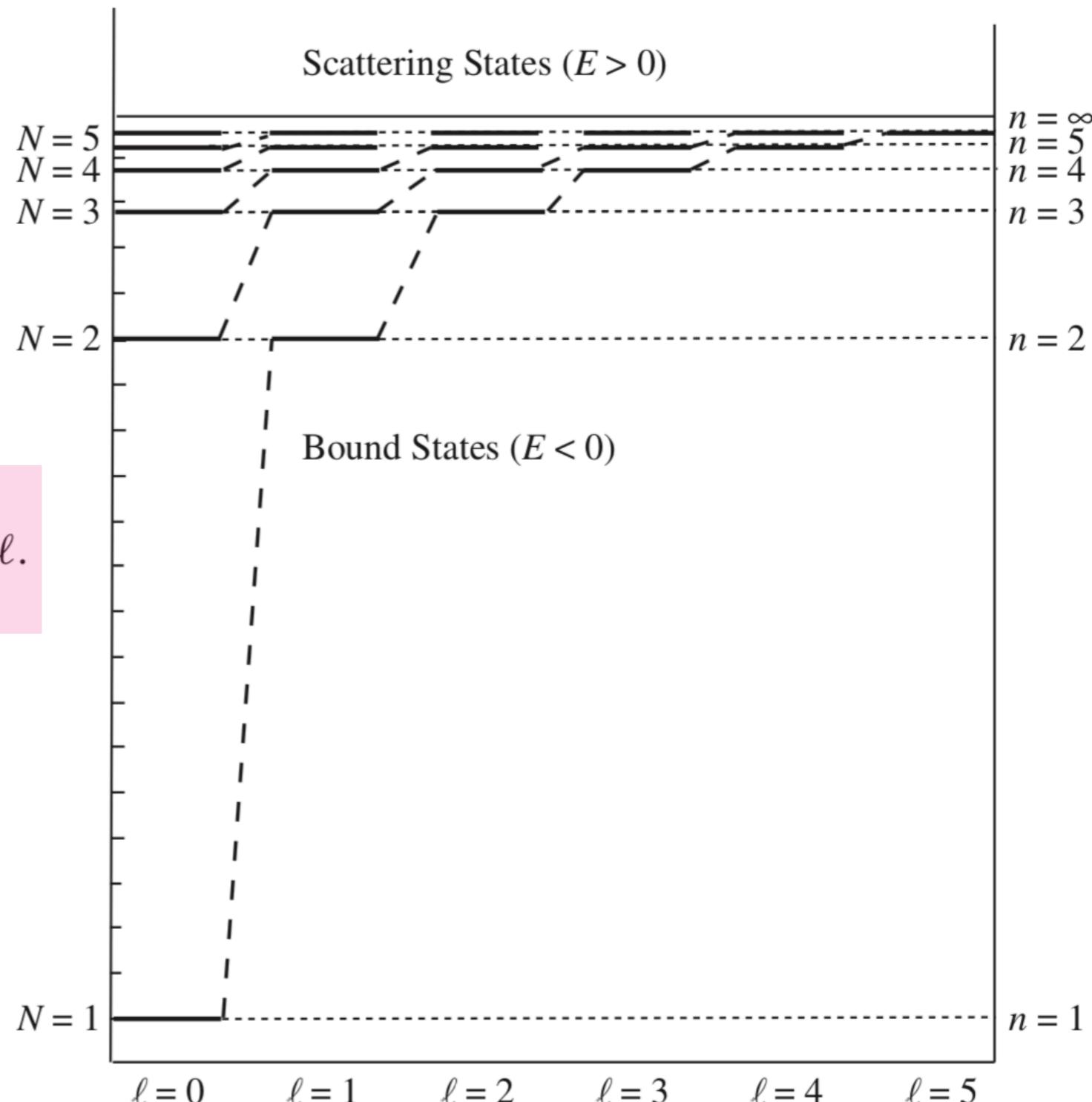
$$\ell = 0, 1, 2, \dots, n - 1$$

For each  $\ell$  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:

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

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

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

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

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

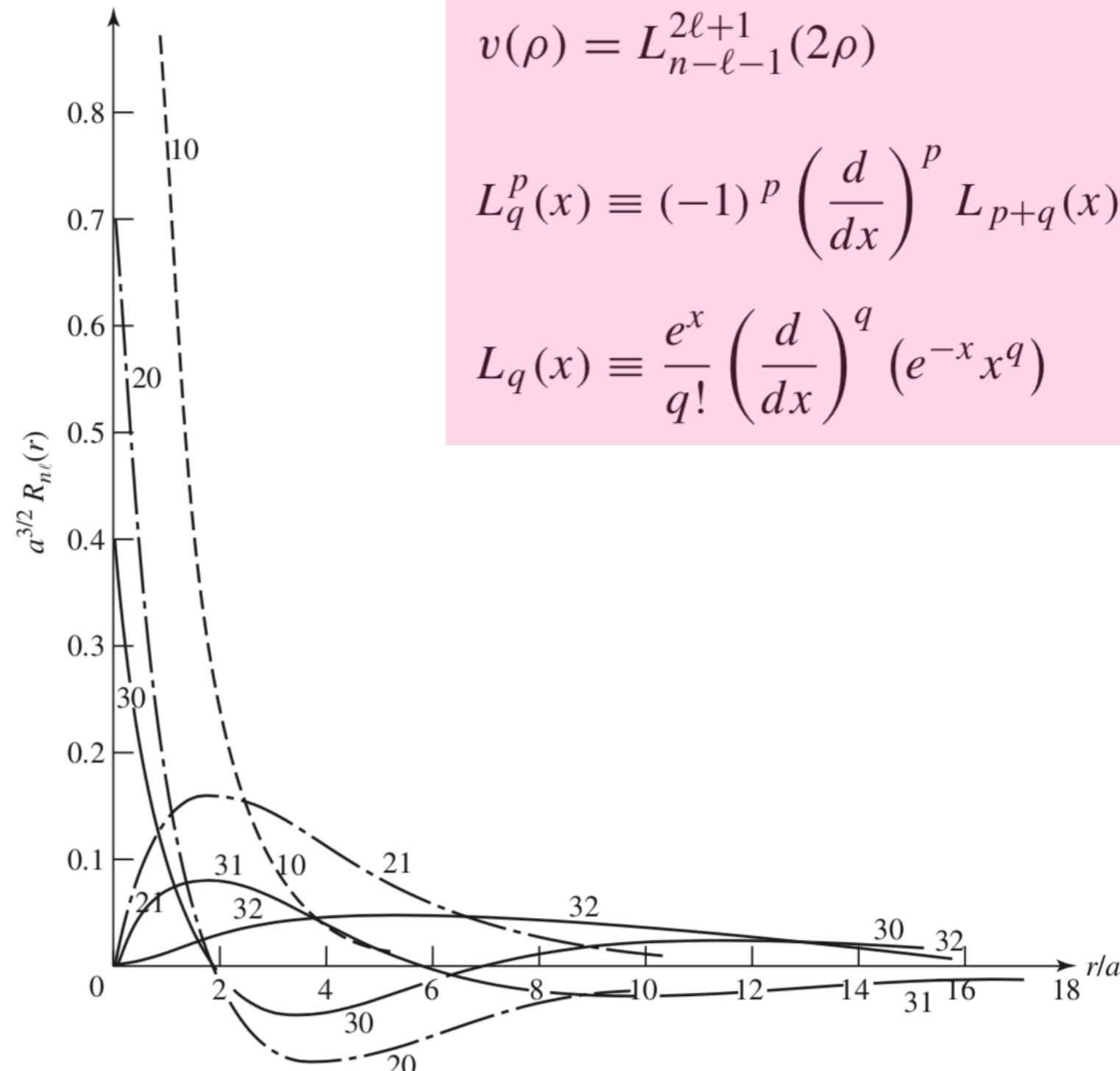
$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

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

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

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

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



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

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

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

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

# 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:  $n$ ,  $\ell$ , 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:

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

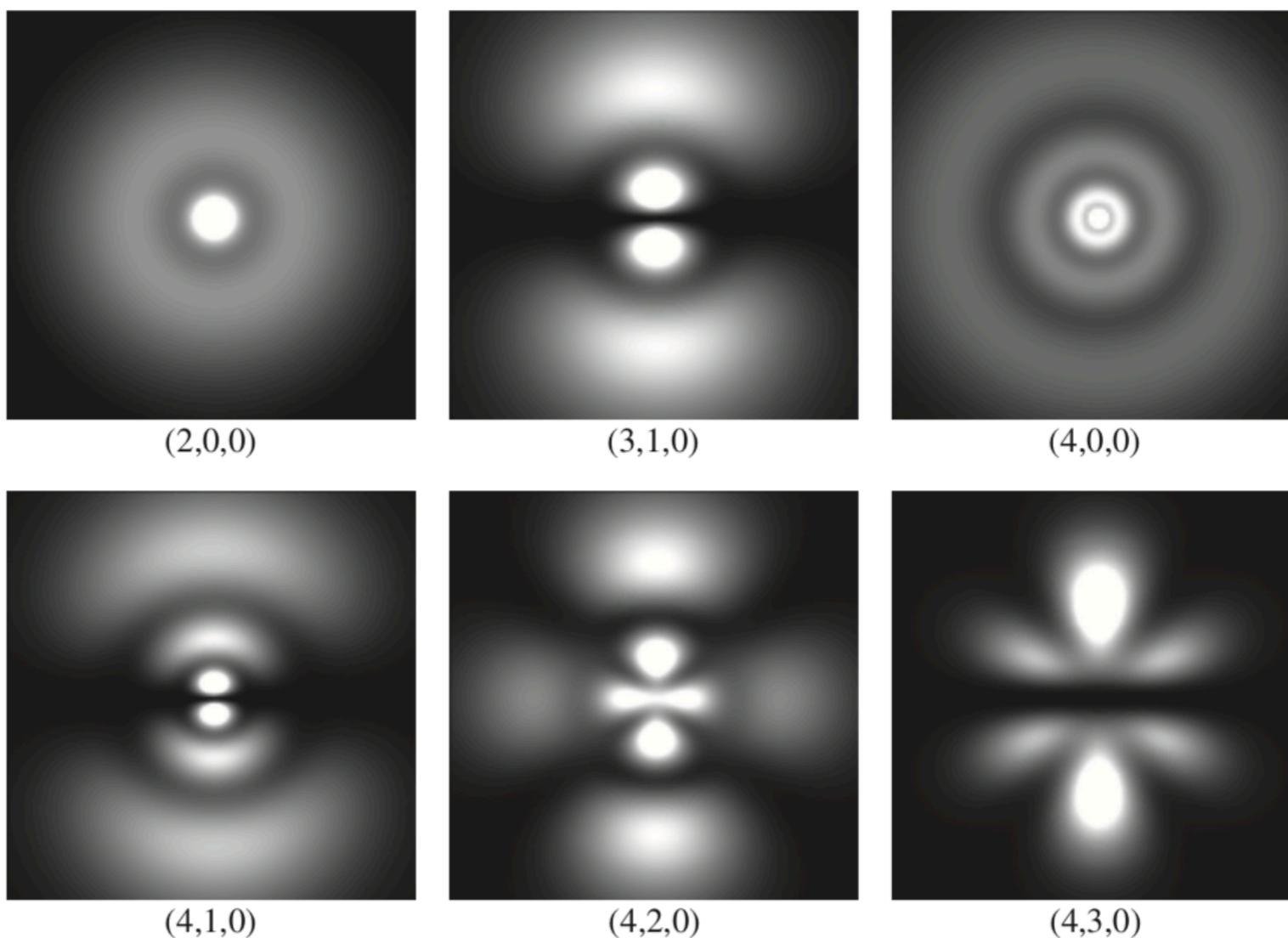
and (for  $n \neq n'$ ) from the fact that they are eigenfunctions of  $\hat{H}$  with distinct eigenvalues.

# The hydrogen atom

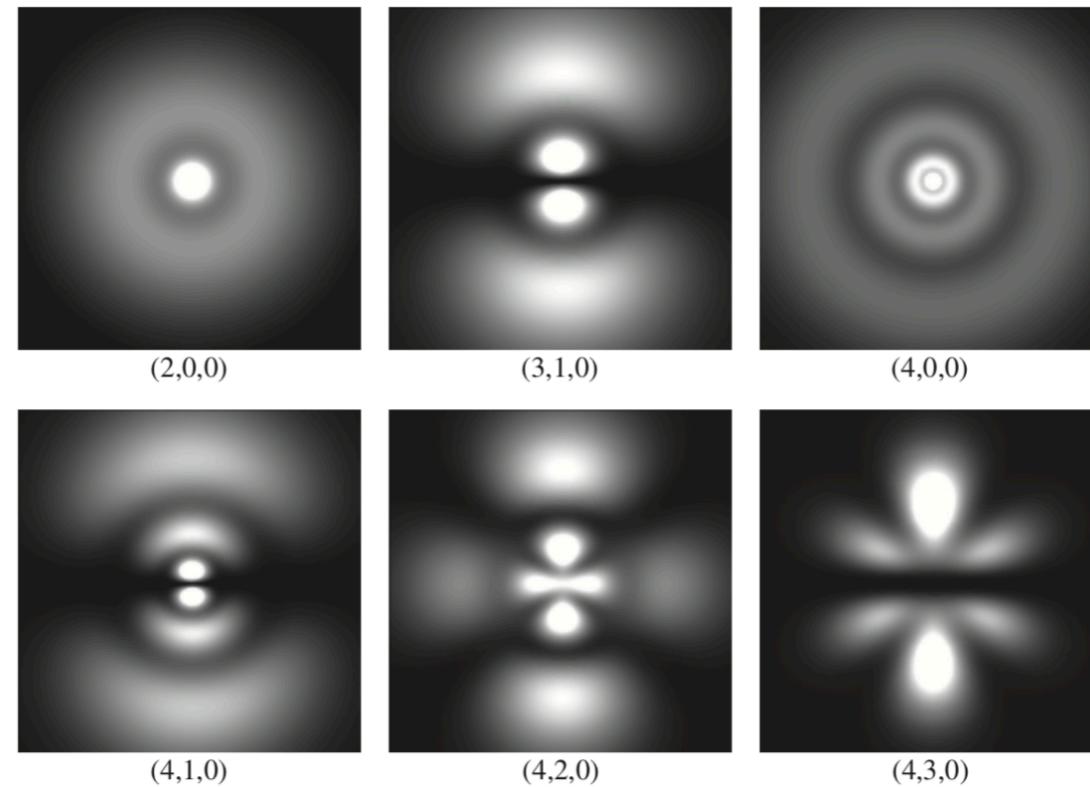
## Normalised hydrogen wave functions:

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

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  $n$ ,  $\ell$ , 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  $n - \ell - 1$ ).

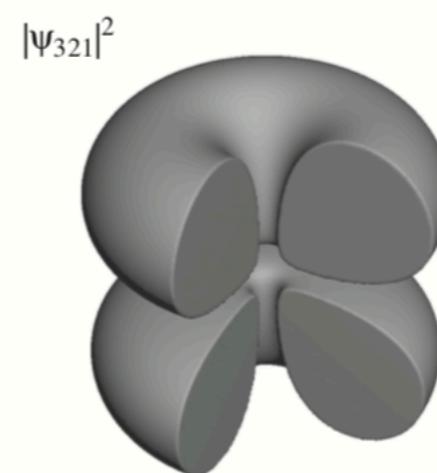
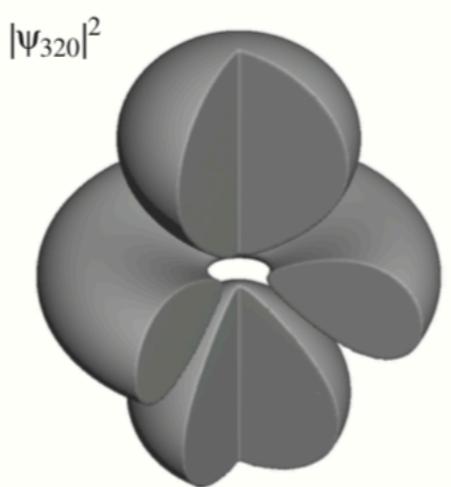
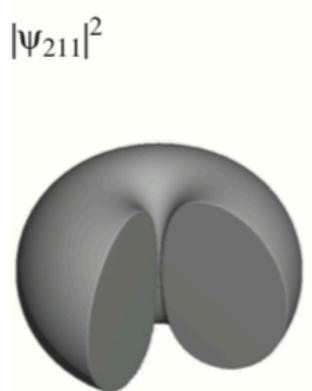
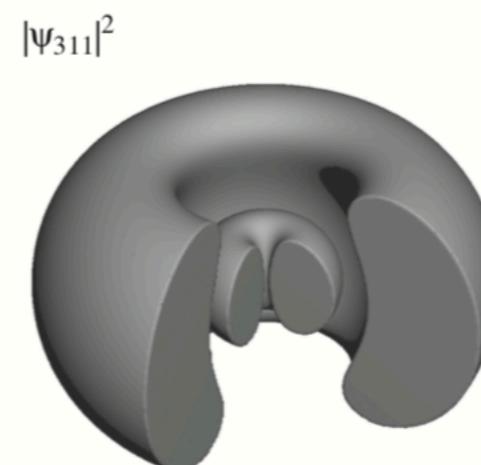
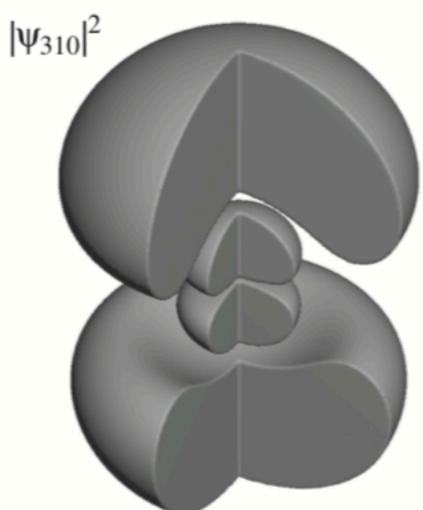
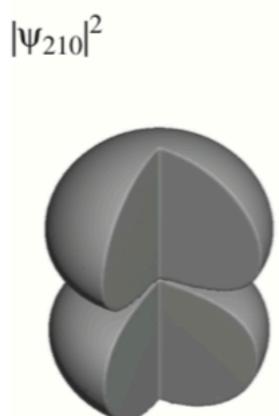
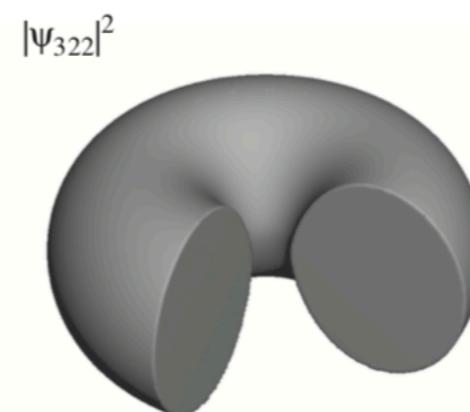
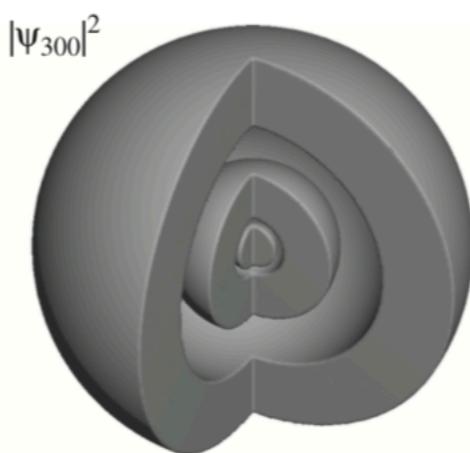
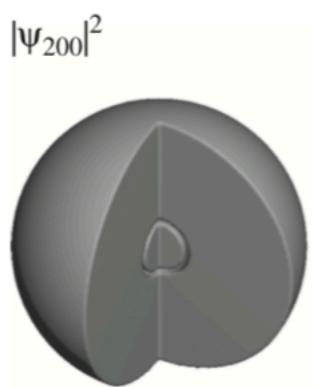
For each radial node the wave function vanishes on a sphere.

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

$\ell - m$  gives the number of nodes in the  $\theta$  direction. These are cones about the z axis on which  $\psi$  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  $\psi_{nlm}$ , 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.

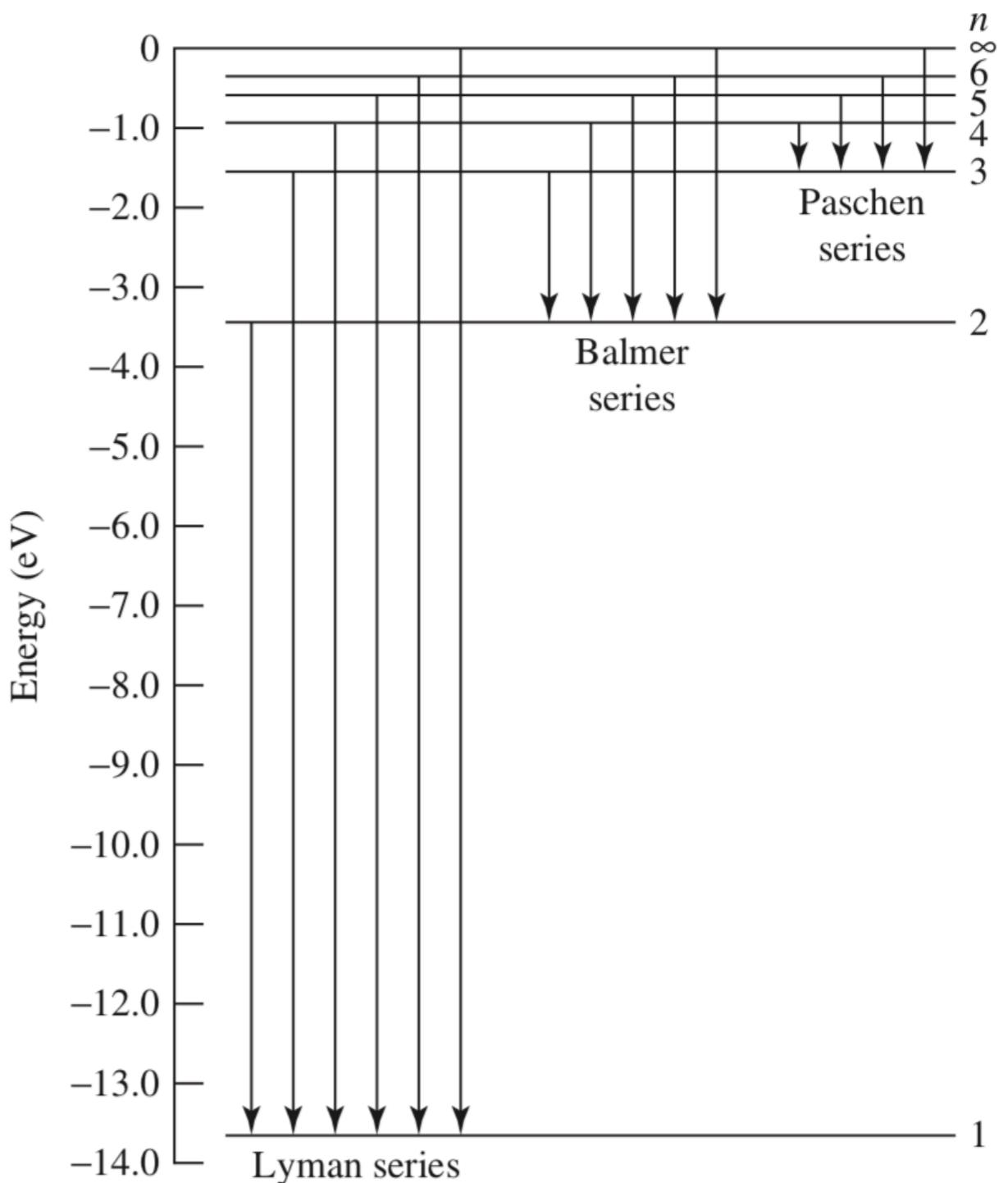
$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

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

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 3.14**

(a) Prove the following commutator identities:

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

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

### 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:

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

### **$\ell$ 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  $L_x$ :

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

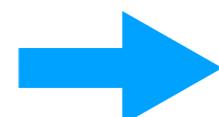
# The hydrogen atom

## 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  $\lambda$ .

# The hydrogen atom

## Angular momentum: Ladder operator technique

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

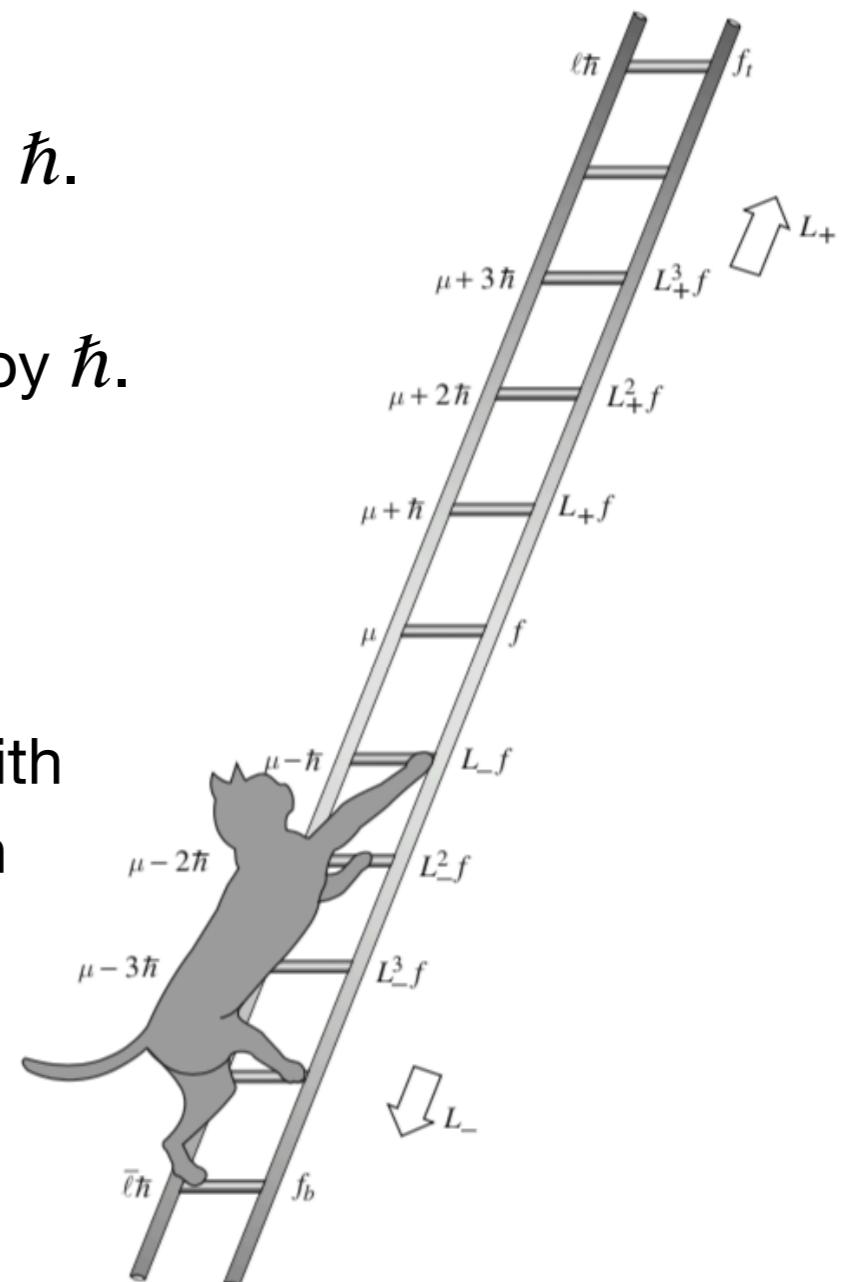
$$[L_z, L_{\pm}] = \pm \hbar L_{\pm} \quad \rightarrow \quad L_z(L_{\pm}f) = (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f = \pm \hbar L_{\pm}f + L_{\pm}(\mu f) \\ = (\mu \pm \hbar)(L_{\pm}f),$$

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  $\lambda$ , 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,

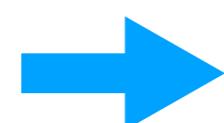
$$\begin{aligned} L_{\pm} L_{\mp} &= (L_x \pm i L_y)(L_x \mp i L_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) \\ &= L^2 - L_z^2 \mp i(i\hbar L_z), \end{aligned}$$

We have:

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

Thus:

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



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

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  $\hbar m$ , where  $m$  goes from  $-\ell$  to  $+\ell$ , in  $N$  integer steps.

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

# The hydrogen atom

## Angular momentum: Eigenvalues

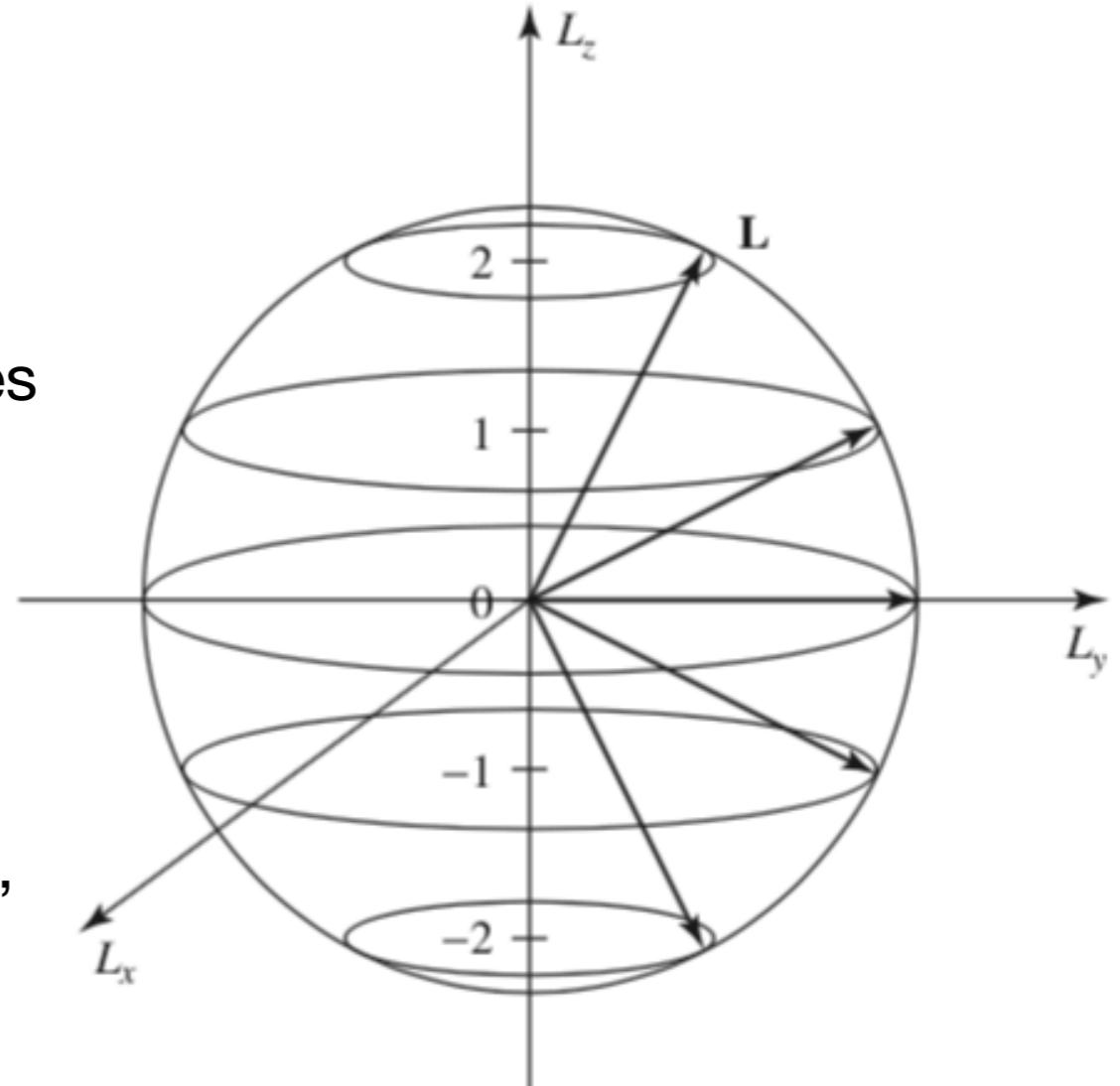
The eigenfunctions are characterised by the numbers  $\ell$  and  $m$ :

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

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

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

For a given value of  $\ell$ , 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

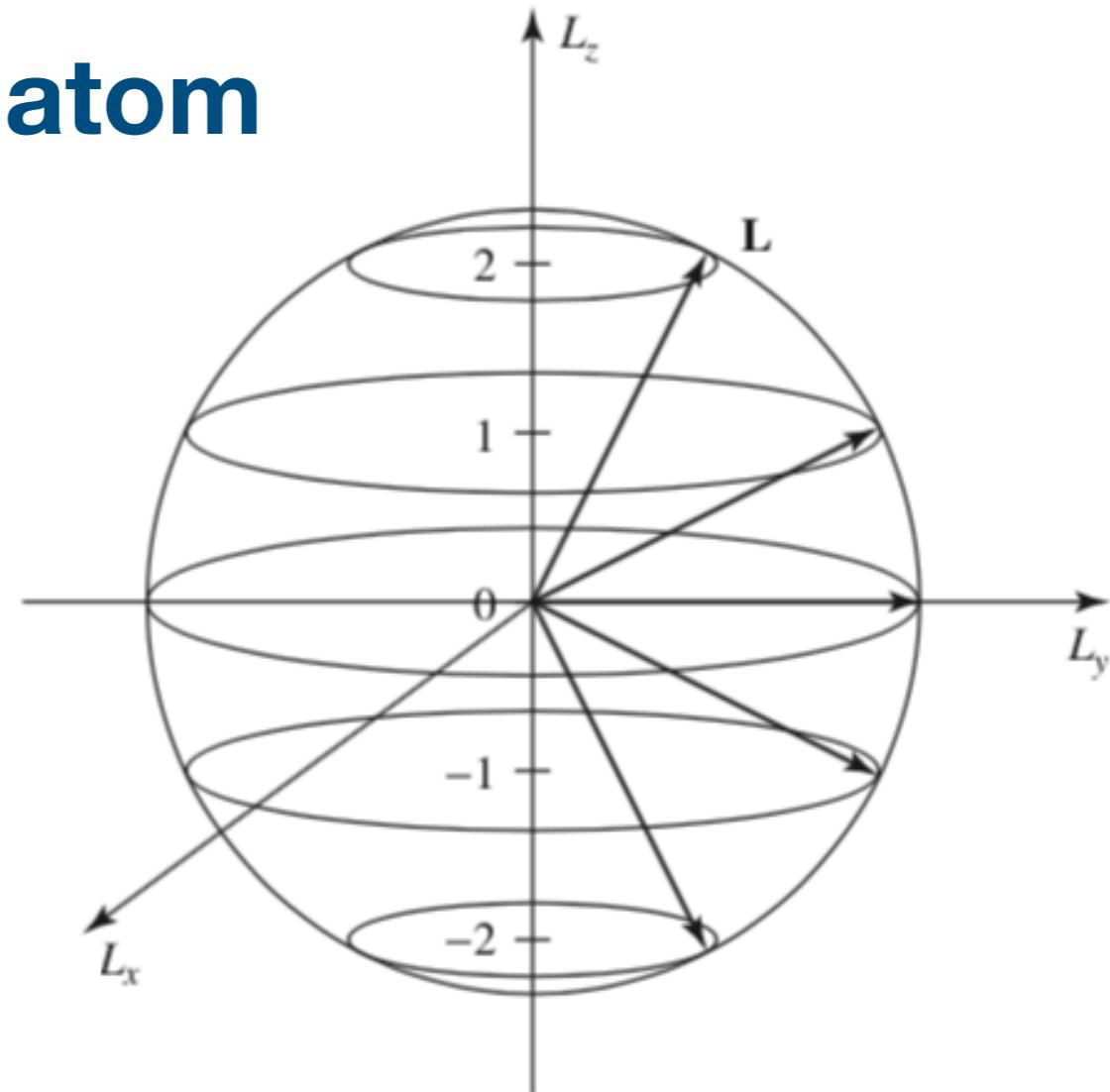
## Angular momentum: Eigenvalues

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.

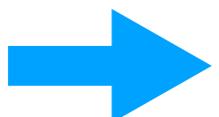
Let's rewrite  $L_x$ ,  $L_y$ , and  $L_z$  in spherical coordinates:  $\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla)$ ,

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

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 is 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  $\hbar m$ :

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

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  $\ell$  (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 next.**

# 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** ( $S = I\omega$ ), 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  $r, \theta, \phi$ ) 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 ( $S$ ) in addition to their “extrinsic” angular momentum ( $L$ ).**

# 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  $S_{\pm} \equiv S_x \pm iS_y$ . **The eigenvectors are not spherical harmonics (they're not functions of  $\theta$  and  $\phi$  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:

- $\pi$  mesons have spin 0
- electrons have spin 1/2
- photons have spin 1
- $\Delta$  baryons have spin 3/2
- gravitons have spin 2; and so on.

By contrast, **the orbital angular momentum quantum number  $\ell$  (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**):

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

where:

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

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

# The hydrogen atom

## Spin 1/2:

The spin operators become matrices:

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

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

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  $\chi$ , 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:

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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  $\chi$  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:  $+\frac{\hbar}{2}$  is  $\frac{1}{2}|a+b|^2$ ,

and the probability of getting:  $-\frac{\hbar}{2}$  is  $\frac{1}{2}|a-b|^2$

# 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 we 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

## 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  $\psi_{nlm}$ , the net angular momentum of the electron (spin plus orbital) is  $\ell + \frac{1}{2}$  or  $\ell - \frac{1}{2}$

If you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is  $\ell + 1$  or  $\ell - 1$ .

Notice that  $\ell$  can be achieved in two distinct ways, depending on whether the electron alone is in the  $\ell + \frac{1}{2}$  configuration or the  $\ell - \frac{1}{2}$  configuration.

# The hydrogen atom

## Addition of Angular Momenta

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

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

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  $2 \times 1$

$$|3 0\rangle = \frac{1}{\sqrt{5}} |2 1\rangle |1 -1\rangle + \sqrt{\frac{3}{5}} |2 0\rangle |1 0\rangle + \frac{1}{\sqrt{5}} |2 -1\rangle |1 1\rangle$$

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

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

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

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

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

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

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

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

# Electron in a Magnetic Field

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

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

The proportionality constant,  $\gamma$ , is called the **gyromagnetic ratio**.

The gyromagnetic ratio of an object whose charge and mass are identically distributed is  $\frac{g_s q}{2m}$ , where  $g_s$  is the spin g-factor,  $q$  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:  $\gamma = -\frac{e}{m}$

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).

# 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:

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

in the case of spin 1/2.

# Electron in a Magnetic Field

## 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 is:

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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

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

# Larmor precession

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:

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

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

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

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

# Larmor precession

With no essential loss of generality we can write  $a = \cos(\alpha/2)$  and  $b = \sin(\alpha/2)$ , where  $\alpha$  is a fixed angle whose physical significance will appear in a moment.

Thus :

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

Let's calculate the expectation value of  $\mathbf{S}$ , as a function of time:

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

# Larmor precession

$$\langle S_x \rangle = \chi(t)^\dagger S_x \chi(t) = \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t).$$

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

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

Thus,  $\langle \mathbf{S} \rangle$  is tilted at a constant angle  $\alpha$  to the  $z$  axis, and precesses about the field at the Larmor frequency:

$$\omega = \gamma B_0$$

just as it would classically. The Ehrenfest theorem guarantees that  $\langle \mathbf{S} \rangle$  evolves according to the classical laws.

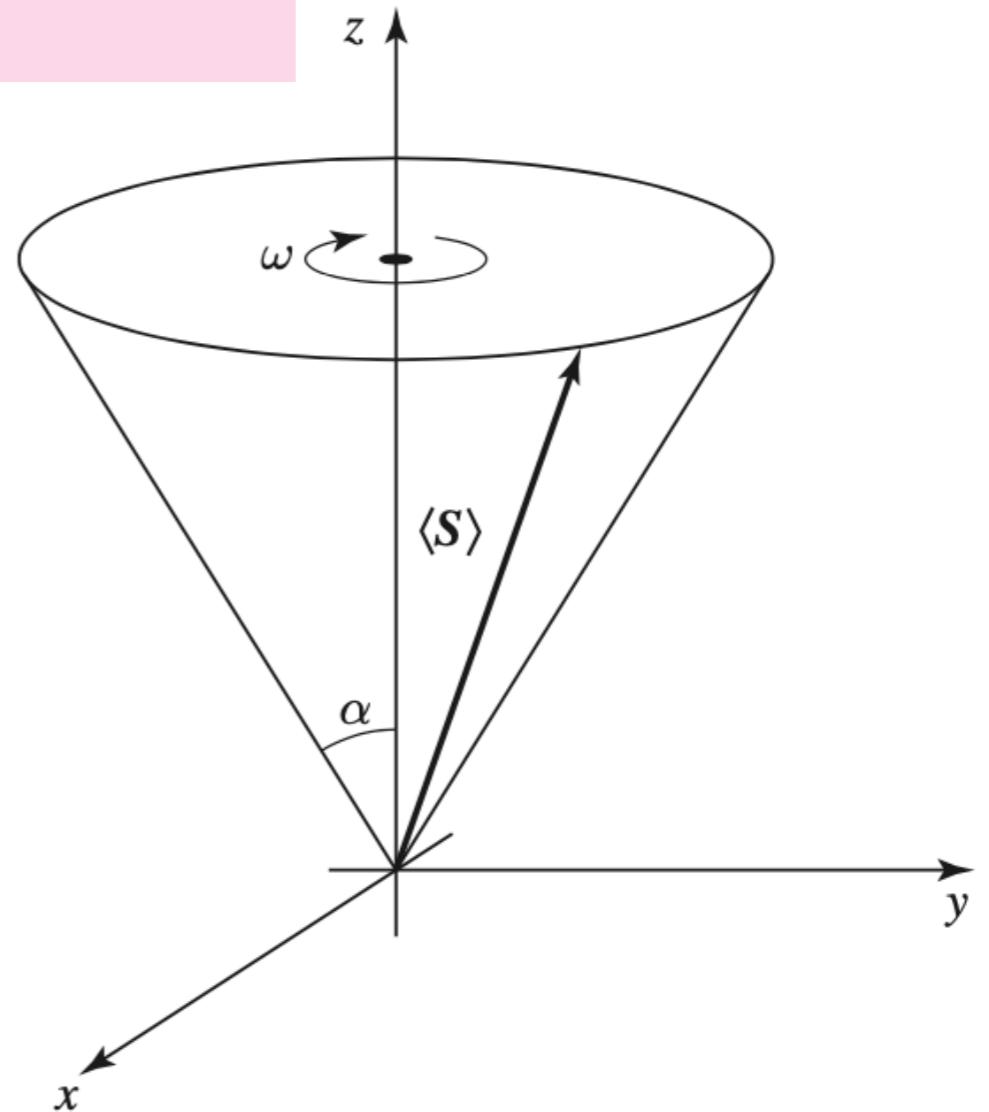


Figure 4.14: Precession of  $\langle \mathbf{S} \rangle$  in a uniform magnetic field.

# Stern-Gerlach experiment

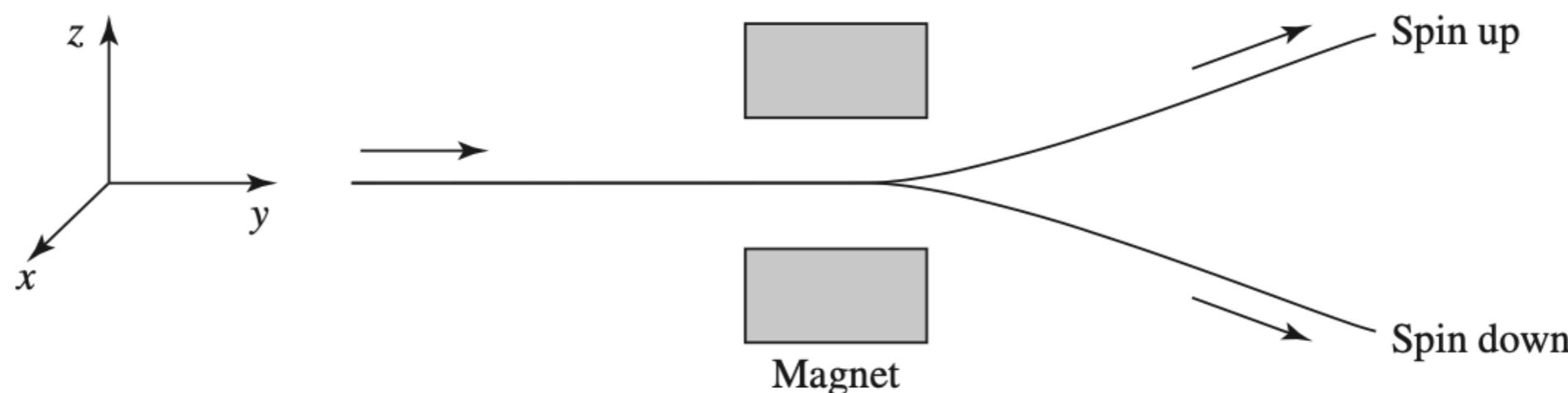
In an *inhomogeneous* magnetic field, there is not only a *torque*, but also a *force*, on a magnetic dipole:

$$\mathbf{F} = \nabla (\mu \cdot \mathbf{B})$$

This force can be used to separate out particles with a particular spin orientation. Imagine a beam of heavy neutral atoms, traveling in the  $y$  direction, which passes through a region of static but inhomogeneous magnetic field (Figure 4.15)—say

$$\mathbf{B}(x, y, z) = -\alpha x \hat{i} + (B_0 + \alpha z) \hat{k},$$

where  $B_0$  is a strong uniform field and the constant  $\alpha$  describes a small deviation from homogeneity.



**Figure 4.15:** The Stern-Gerlach apparatus.

# Stern-Gerlach experiment

The force on these atoms is:

$$\mathbf{F} = \gamma\alpha \left( -S_x \hat{i} + S_z \hat{k} \right).$$

**But because of the Larmor precession about  $B_0$ ,  $S_x$  oscillates rapidly, and averages to zero; the net force is in the z direction:**

$$F_z = \gamma\alpha S_z$$

and the beam is deflected up or down, in proportion to the z component of the spin angular momentum.

*Classically we'd expect a smear (because  $S_z$  would not be quantised), but in fact the beam splits into  $2s + 1$  separate streams, demonstrating the quantisation of angular momentum.*

In silver atoms all the inner electrons are paired, in such a way that their angular momenta cancel. The net spin is simply that of the outermost— unpaired—electron, so in this case  $s = \frac{1}{2}$ , and the beam splits in two.)

# Stern-Gerlach experiment

The Stern–Gerlach experiment has played an important role in the philosophy of QM, where it serves both as the prototype for the preparation of a quantum state and as an illuminating model for a certain kind of quantum measurement.

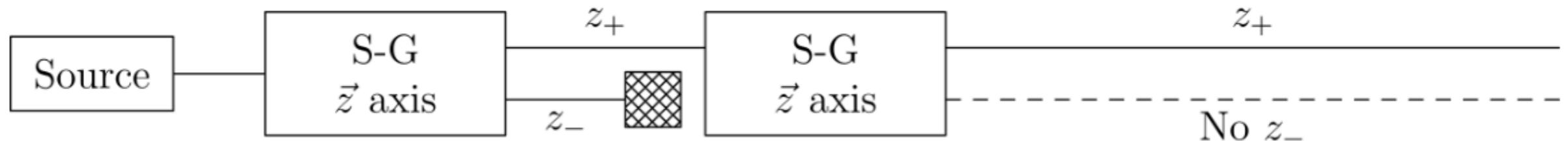
We tend casually to assume that the *initial* state of a system is *known* (the Schrödinger equation tells us how it subsequently evolves)—but it is natural to wonder **how we get a system into a particular state in the first place.**

If we want to prepare a beam of atoms in a given spin configuration, **we pass an unpolarised beam through a Stern–Gerlach magnet, and select the outgoing stream we are interested in** (closing off the others with suitable baffles and shutters).

Conversely, if we want to *measure* the z component of an atom's spin, we send it through a Stern–Gerlach apparatus, and record which bin it lands in. This may not be the most *practical* way to do the job, but it is *conceptually* very clean, and hence a useful context in which to explore the problems of state preparation and measurement.

# Stern-Gerlach experiments

?



## Experiment 1:

When a second, identical, S-G apparatus is placed at the exit of the first apparatus, **only  $z_+$  is seen** in the output of the second apparatus.

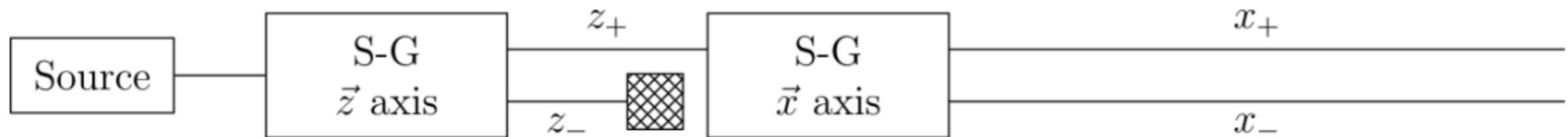
This result is expected since all neutrons at this point are expected to have  $z_+$  spin, as only the  $z_+$  beam from the first apparatus entered the second apparatus

Source:

[https://en.wikipedia.org/wiki/Stern%20-%20Gerlach\\_experiment](https://en.wikipedia.org/wiki/Stern%20-%20Gerlach_experiment)

# Stern-Gerlach experiments

?



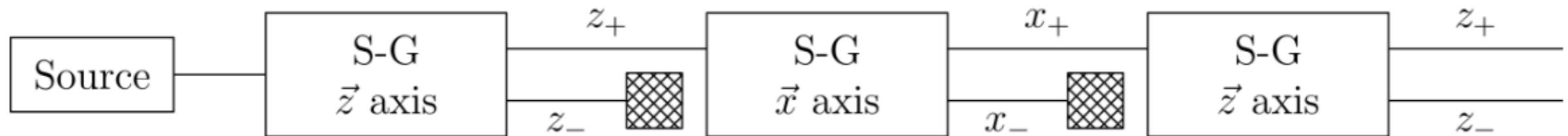
## Experiment 2:

The middle system shows what happens when a different S-G apparatus is placed at the exit of the  $z_+$  beam resulting of the first apparatus, the second apparatus measuring the deflection of the beams on the  $x$  axis instead of the  $z$  axis.

**The second apparatus produces  $x_+$  and  $x_-$  outputs.** Now classically we would expect to have one beam with the  $x$  characteristic oriented + and the  $z$  characteristic oriented +, and another with the  $x$  characteristic oriented - and the  $z$  characteristic oriented +.

# Stern-Gerlach experiments

?



## Experiment 3:

The output of the third apparatus which measures the deflection on the z axis again shows an **output of z-** as well as z+.

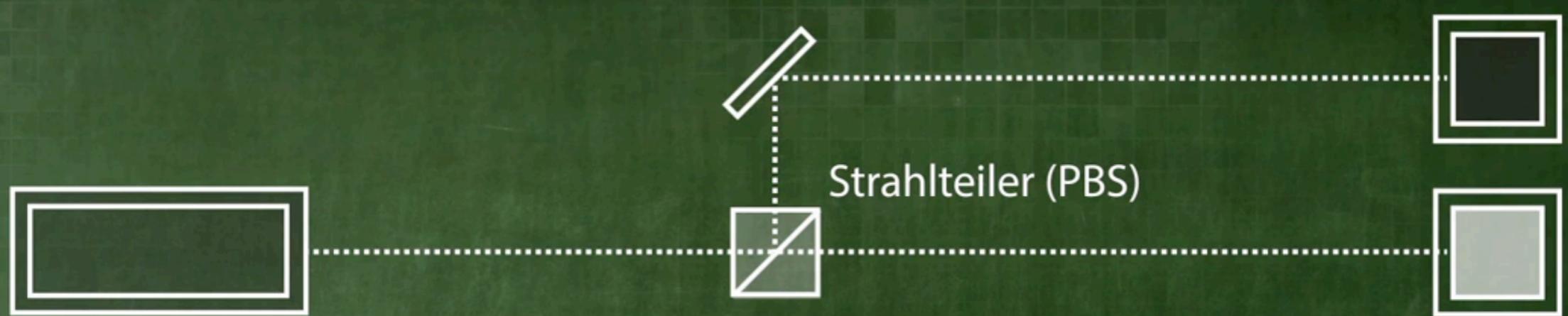
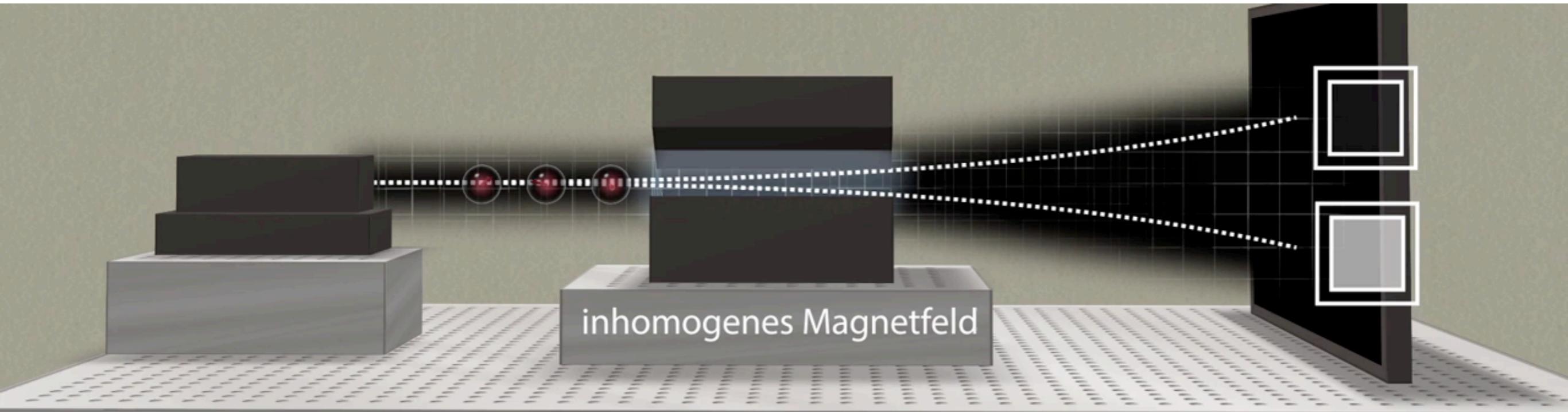
Given that the input to the second S-G apparatus consisted **only of z+**, it can be inferred that a S-G apparatus must be altering the states of the particles that pass through it.

## This experiment can be interpreted to exhibit the uncertainty principle:

Since the angular momentum cannot be measured on two perpendicular directions at the same time, **the measurement of the angular momentum on the x direction destroys the previous determination of the angular momentum in the z direction.**

That's why the third apparatus measures renewed z+ and z- beams like the x measurement really made a clean slate of the z+ output.

# Stern-Gerlach experiment



**U1 08 | Polarisation von Photonen**