

QM applications in 3D

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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:

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

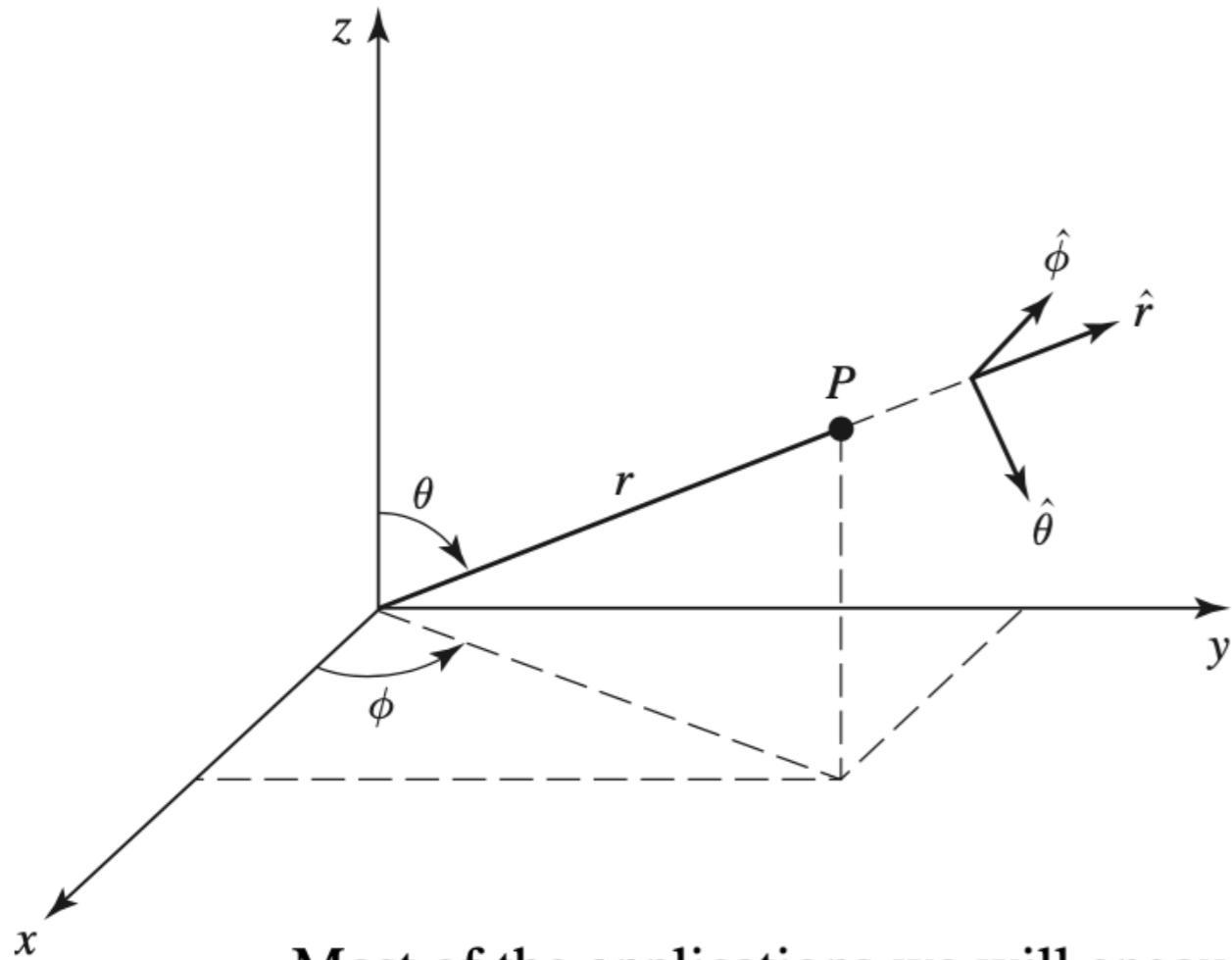
The general solution to the *(time-dependent)* Schrödinger equation is

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

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:

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



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

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

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:

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

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

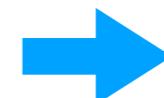
Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

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

Schrödinger equation in spherical coordinates:

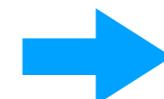
$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial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

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



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: $Y \sin^2 \theta$,

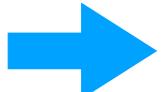
$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell (\ell + 1) \sin^2 \theta Y.$$

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

Dividing by: $\Theta \Phi$

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

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



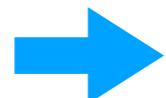
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2.$$

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:

$$P_0 = 1$$

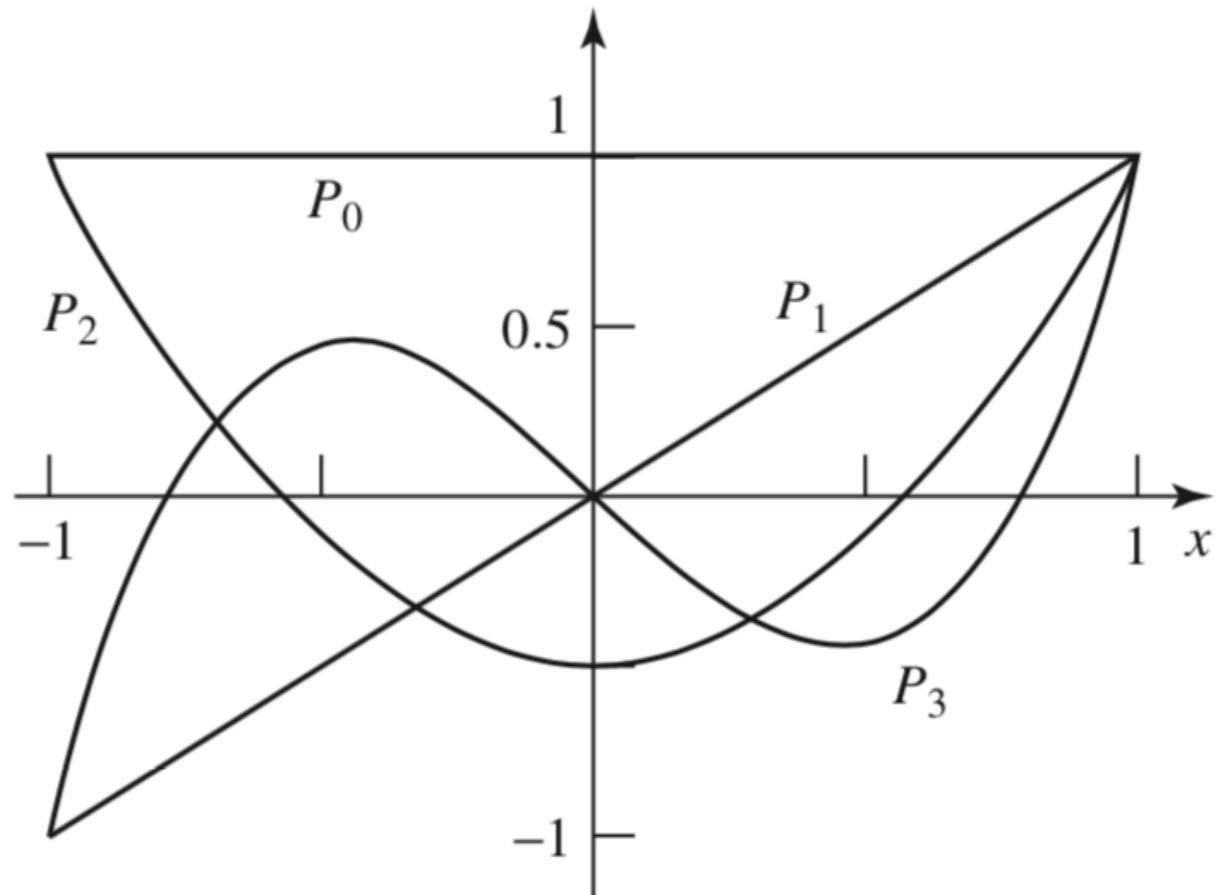
$$P_1 = x$$

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

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

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

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



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 $\sin \theta$.

$$P_0^0 = 1$$

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

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

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

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

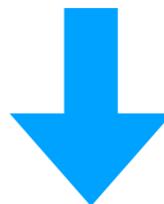
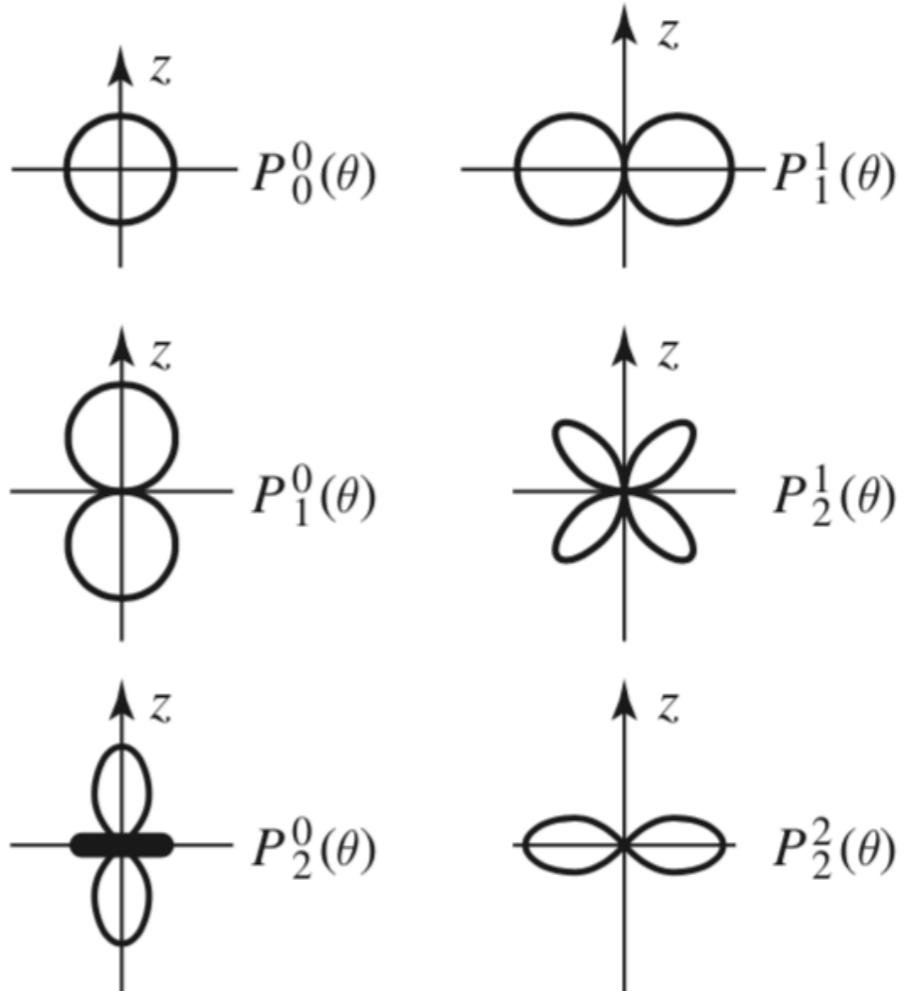
$$P_3^2 = 15 \sin^2 \theta \cos \theta$$

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

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

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

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



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:

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

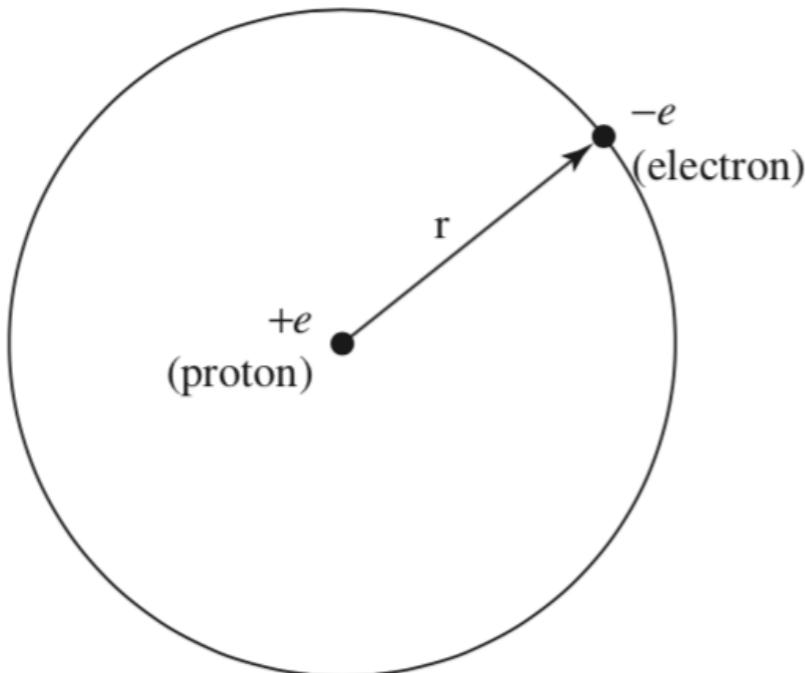
is the **effective potential**, which contains a **centrifugal term**: $(\hbar^2/2m) [\ell(\ell+1)/r^2]$

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 $-e$.

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

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

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

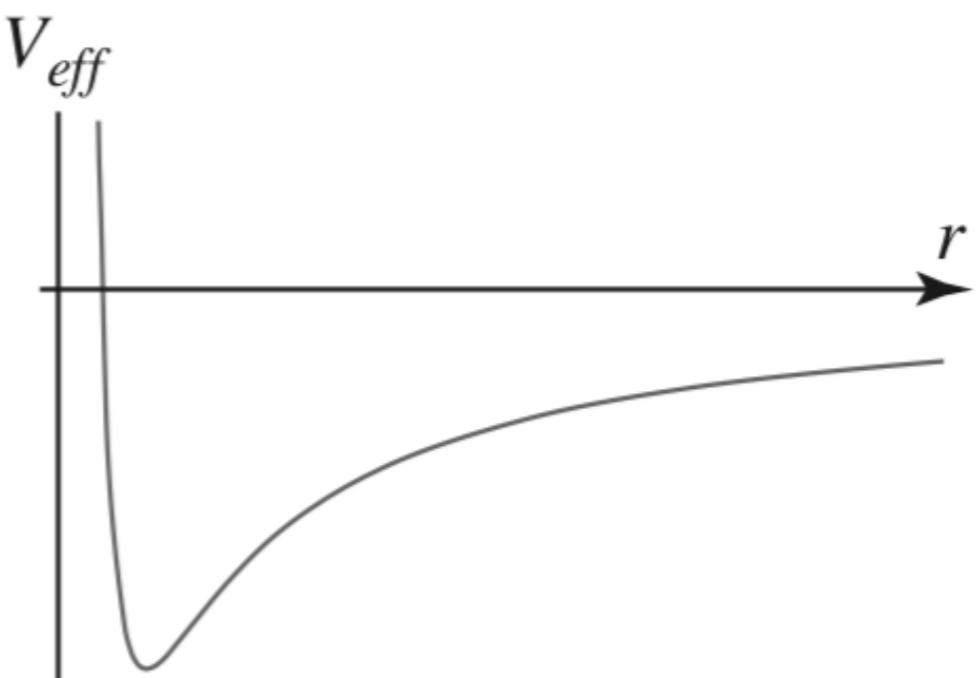
From Coulomb's law: $F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$ the potential in SI units is: $V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$

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

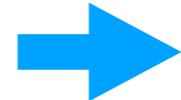
The Radial Wave Function

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

We introduce:

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

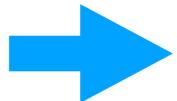
$$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa},$$



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

Let's analyse the asymptotic behaviour of this equation.

$$\rho \rightarrow \infty$$

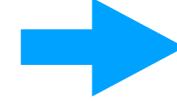


$$\frac{d^2 u}{d\rho^2} = u$$



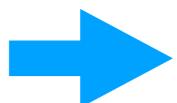
$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

blows up



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

$$\rho \rightarrow 0$$

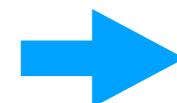


$$\frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$



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

blows up



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

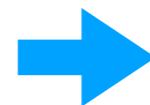
The hydrogen atom

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

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

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 , 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:

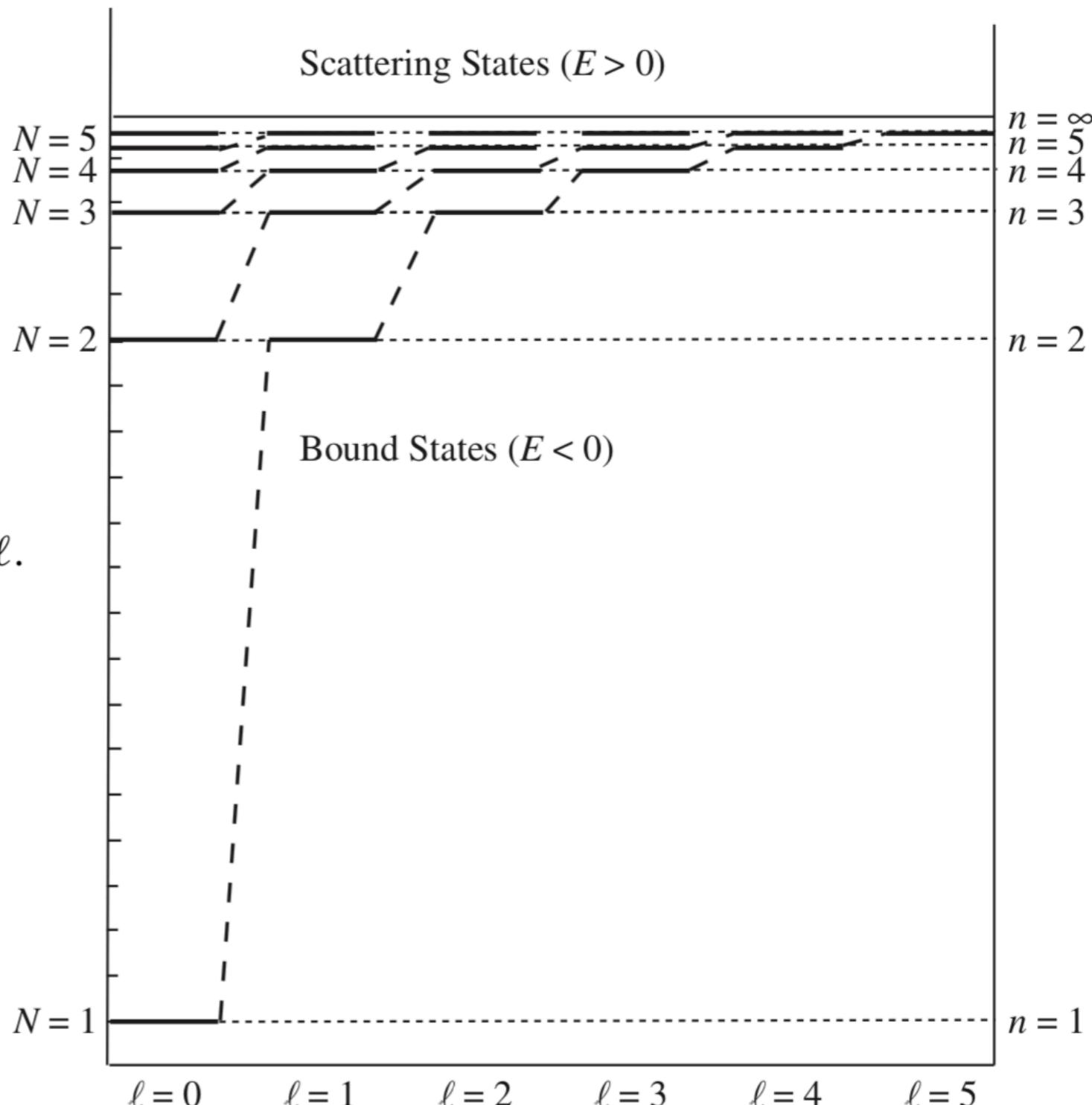
$$\ell = 0, 1, 2, \dots, n - 1$$

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

Energy levels for hydrogen

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

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

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:

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

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

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

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

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

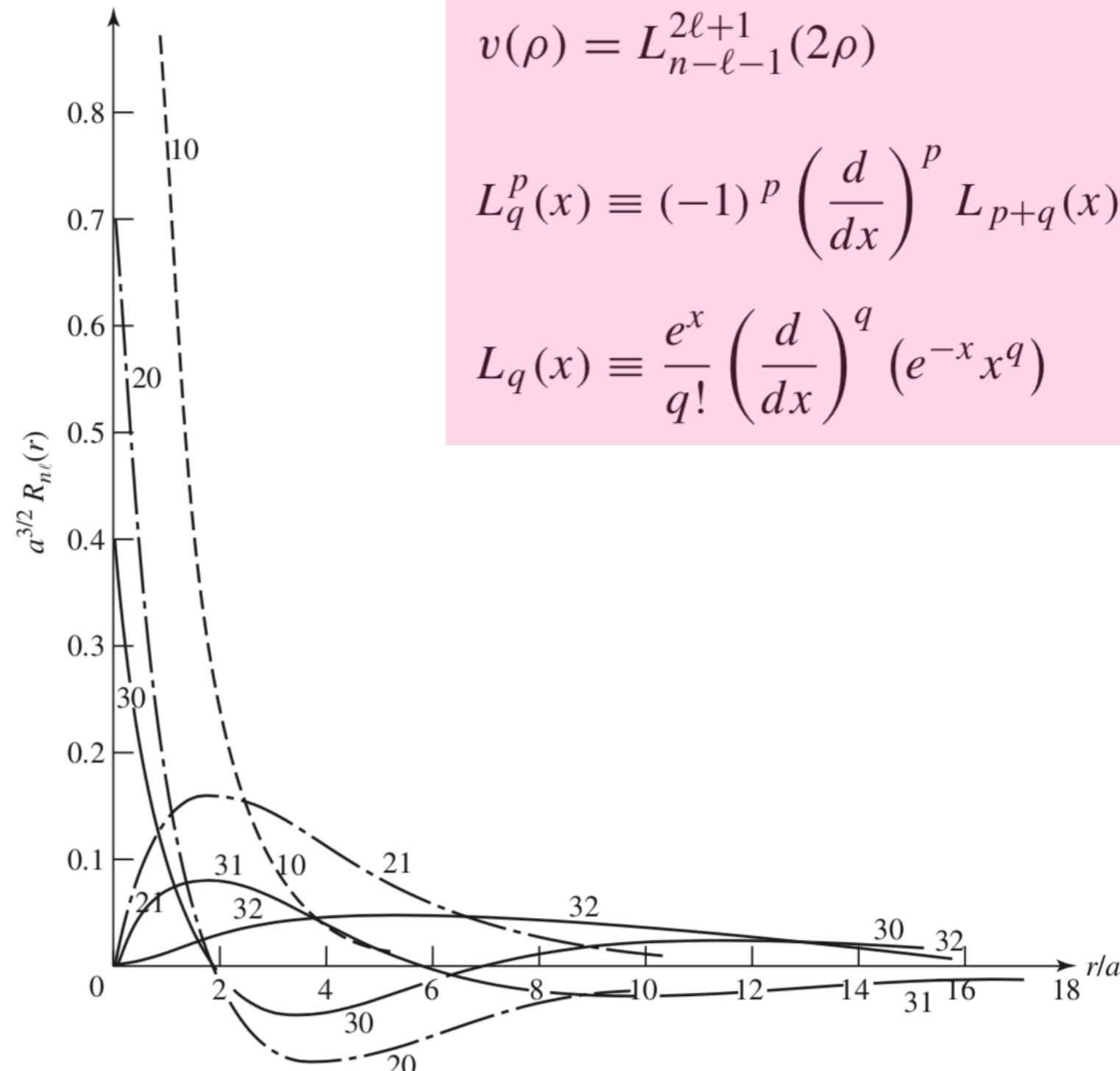
$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$$

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

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

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

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



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

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

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

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

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:

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

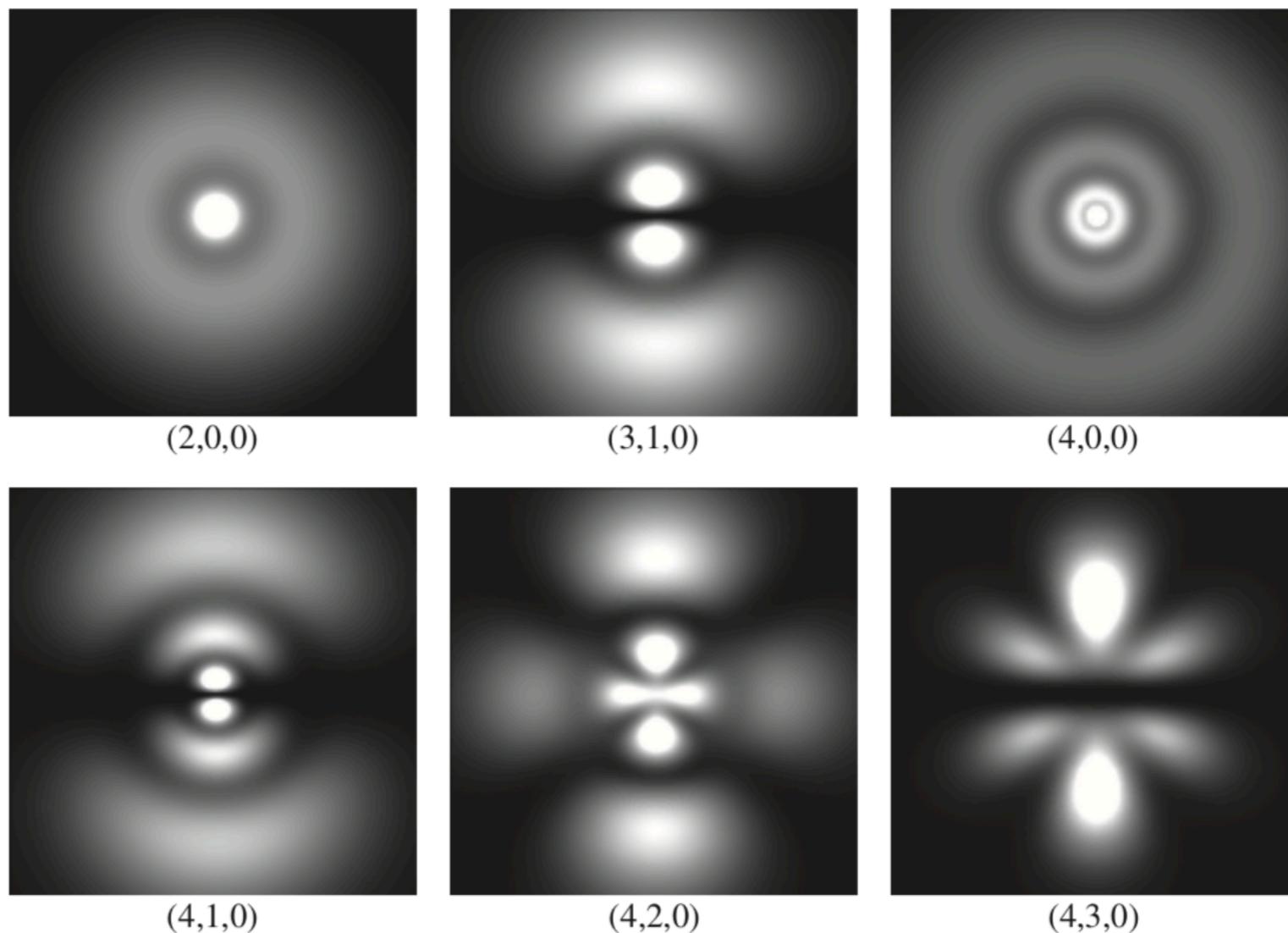
and (for $n \neq n'$) from the fact that they are eigenfunctions of \hat{H} with distinct eigenvalues.

The hydrogen atom

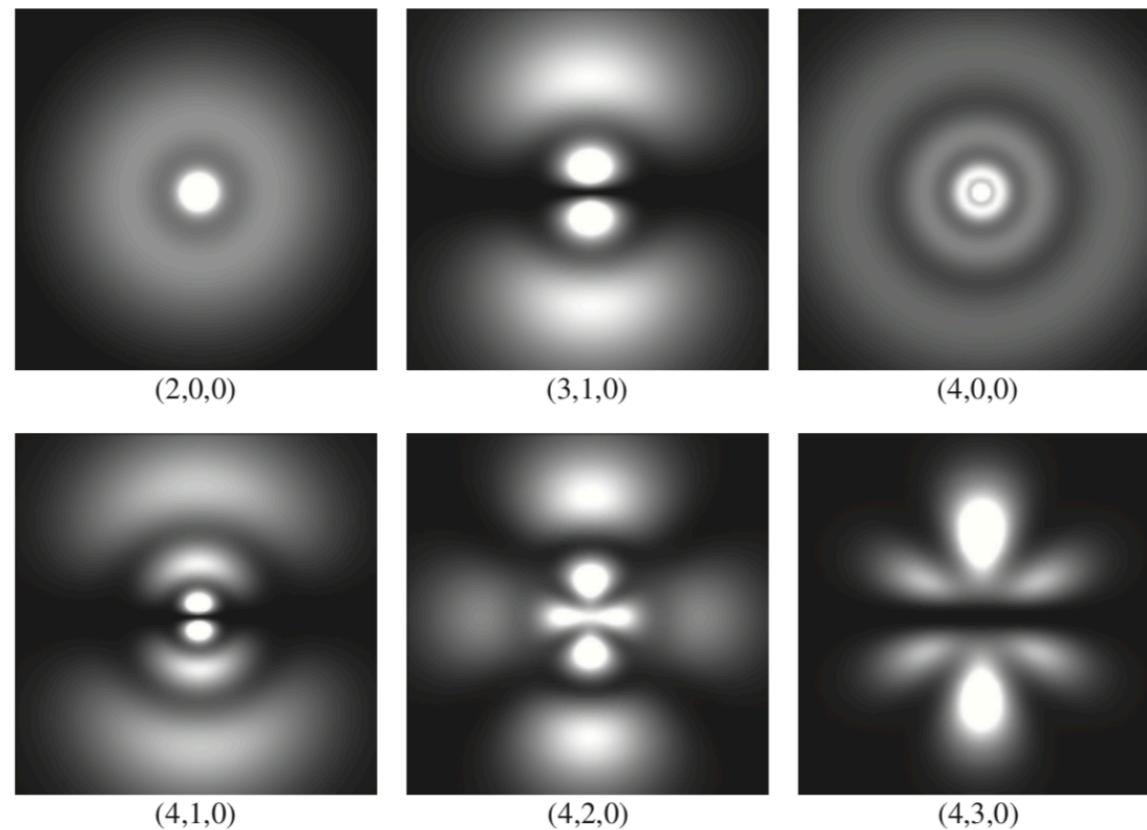
Normalised hydrogen wave functions:

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

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 $n - \ell - 1$).

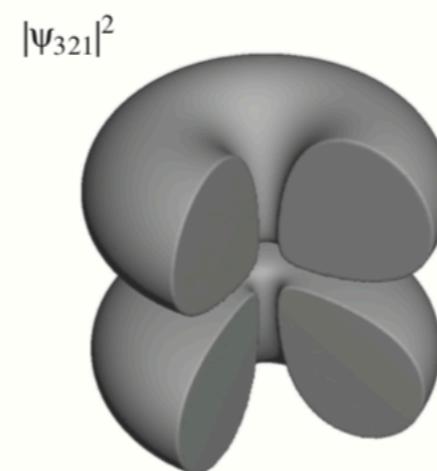
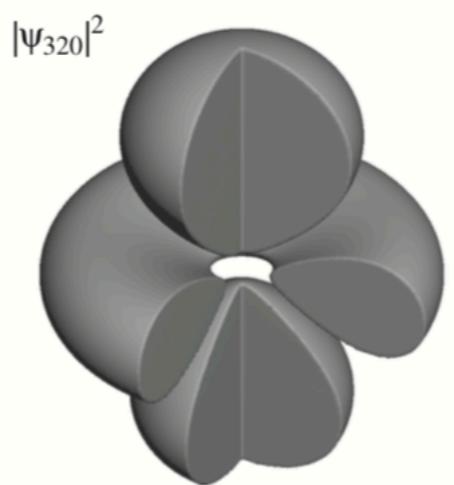
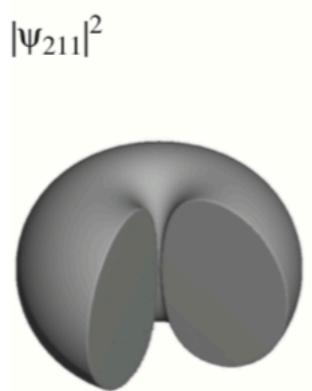
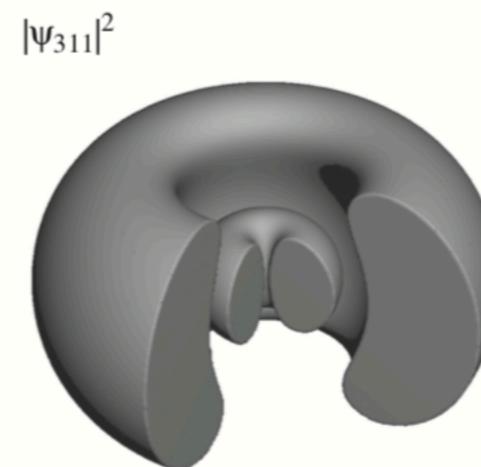
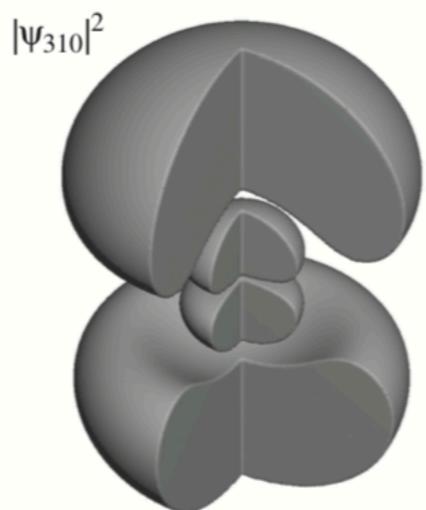
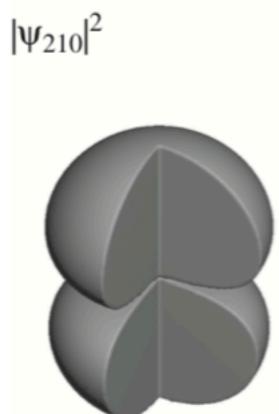
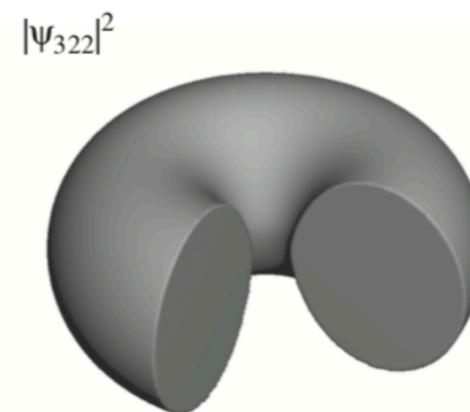
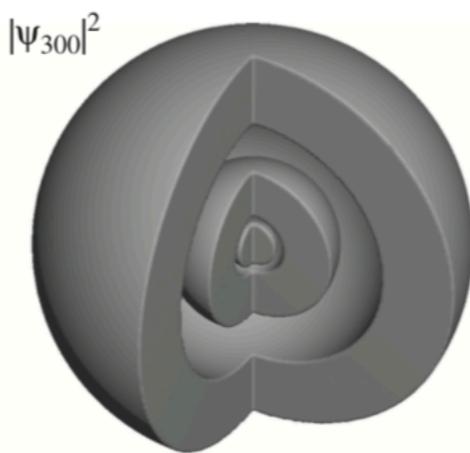
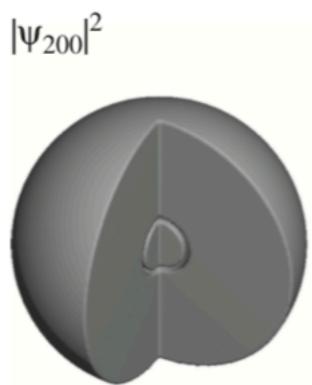
For each radial node the wave function vanishes on a sphere.

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.

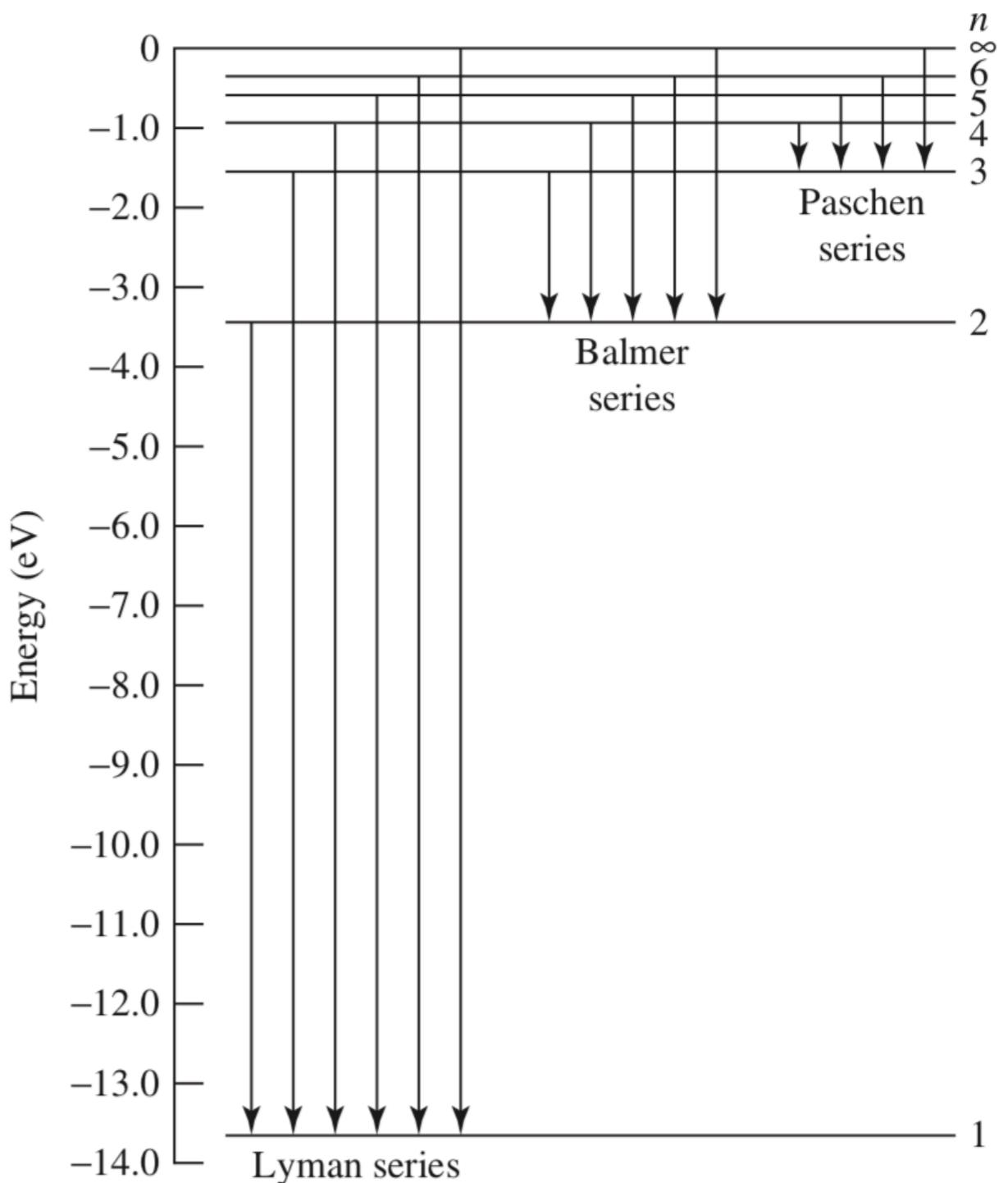
$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

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

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.



End