The Schrödinger equation in three dimensions.

* In one dimension, the Schrödinger equation is:
  
  \[ i \hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \psi + U(x) \psi \]

  The term \(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}\) corresponds to the classical kinetic energy \(K = \frac{p^2}{2m}\) in one dimension.

* In three dimensions, \(K = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)\) and the Schrödinger equation becomes:
  
  \[ i \hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \psi(x,y,z,t) + U(x,y,z) \psi(x,y,z,t) \]

  With the usual notation \(\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\), this becomes

  \[ i \hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + U \psi. \]

* In one dimension, the squared magnitude of the wave function is the probability density of finding the particle at a given \(x\):
  \[ \frac{\partial P}{\partial x} = |\psi(x,t)|^2. \]

  In three dimensions, it is the same but the probability density is given per unit volume instead of per unit length:

  \[ \frac{\partial P}{\partial V}(x,y,z,t) = |\psi(x,y,z,t)|^2. \]
Just as we did in one dimension we can write a three dimensional time independent Schrödinger equation by factorising space \( \Psi(x,y,z) \) & time \( \phi(t) = e^{-i\frac{Et}{\hbar}} \).

dependence \( \Psi(x,y,z,t) = \Psi(x,y,z) \phi(t) \).

\& the time independent Schrödinger equation reads

\[-\frac{\hbar^2}{2m} \nabla \Psi(x,y,z) = U(x,y,z) \Psi(x,y,z) = \mathbf{E} \Psi(x,y,z)\]

In one dimension we have seen that boundary conditions give rise to a quantum number. In three dimensions, boundary conditions have to be applied along all three directions (for bound systems) and three quantum numbers can be expected to appear.

3) The three dimensional infinite well.

4) Solving the Schrödinger equation

\[ U(r) = 0 \text{ if } 0 < x < L_x \]
\[ 0 < y < L_y \]
\[ 0 < z < L_z \]

\[ U(r) = \infty \text{ otherwise.} \]

* Outside the region where \( U(r) = 0 \), we have \( \Psi(r) = 0 \)

* We look for a solution of the form

\[ \Psi(r) = \Psi(x,y,z) = F(x) G(y) H(z) \]
* Applying the Schrödinger equation, we get
\[-\frac{\hbar^2}{2m} \left[ G(y)H(z) \frac{\partial^2 F(x)}{\partial x^2} + F(x)H(z) \frac{\partial^2 G(y)}{\partial y^2} + F(x)E(y) \frac{\partial^2 H(z)}{\partial z^2} \right] = E F(x) G(y) H(z)\]

which can be rewritten as:
\[\frac{1}{F(x)} \frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)} \frac{\partial^2 G(y)}{\partial y^2} + \frac{1}{H(z)} \frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}.

* So each term must be a constant & we have
\[\frac{\partial^2 F(x)}{\partial x^2} = C_x F(x) \quad \text{& equivalent for y & z.}\]

& the solution is \(F(x) = A_x \sin \frac{m_x \pi x}{L_x}\) & equivalent for y & z.

* The solutions to the time independent Schrödinger equation are
\[\psi_{n_x n_y n_z}(x, y, z) = A_x \sin \frac{m_x \pi x}{L_x} \sin \frac{m_y \pi y}{L_y} \sin \frac{m_z \pi z}{L_z}\]

with \(E_{n_x n_y n_z} = \left(\frac{m_x^2}{L_x^2} + \frac{m_y^2}{L_y^2} + \frac{m_z^2}{L_z^2}\right) \frac{\pi^2 \hbar^2}{2m}\).

* Take the example where \(L_x = 1A\), \(L_y = 2A\), \(L_z = 3A\).

The ground state is \(E_{111} = \left(\frac{1^2 + 1^2 + 1^2}{5^2} \right) \frac{\pi^2 \hbar^2}{10^{-10} 2m} = \frac{49 \pi^2 \hbar^2}{10^{-10} \times 72 \text{ m}}\).

The first excited state is \(E_{112} = \left(1 + 1 + \frac{2^2}{3^2} \right) \frac{\pi^2 \hbar^2}{2 \times 10^{-10} \text{ m}} = \frac{61 \pi^2 \hbar^2}{72 \times 10^{-10} \text{ m}}\).

The second excited state is \(E_{113} = \left(1 + 1 + \frac{3^2}{3^2} \right) \frac{\pi^2 \hbar^2}{2 \times 10^{-10} \text{ m}} = \frac{81 \pi^2 \hbar^2}{72 \times 10^{-10} \text{ m}}\).

The third excited state is \(E_{223} = \frac{10 \times \pi^2 \hbar^2}{72 \times 10^{-10} \text{ m}}\).

The fourth excited state is \(E_{124} = \frac{10 \pi^2 \hbar^2}{72 \times 10^{-10} \text{ m}}\).
2) Degeneracy.

* Different states may have the same energy - we then talk about the degeneracy of an energy level. A p-fold degenerate energy level corresponds to p states with that same energy.

* Example: Suppose \( L_x = L_y = L_z = L \). The energy becomes \( E_{n_x n_y n_z} = \left( n_x^2 + n_y^2 + n_z^2 \right) \frac{\hbar^2}{2mL^2} \). For each combination \((n_x, n_y, n_z)\) we can write \( E_{n_x n_y n_z} = \frac{\hbar^2}{2mL^2} \cdots \):

\[
\begin{align*}
(1,1,1) & \rightarrow 3 & \text{not degenerate} \\
(2,1,1), (1,2,1), (1,1,2) & \rightarrow 6 & 3\text{-fold degenerate} \\
(1,2,2), (2,1,2), (2,2,1) & \rightarrow 9 & 3\text{-fold} \\
(3,1,1), (1,3,1), (1,1,3) & \rightarrow 11 & 3\text{-fold} \\
(2,2,2) & \rightarrow 12 & \text{not degenerate} \\
(1,2,3), (2,3,1), (3,1,2), (2,1,3), (1,3,2), (3,2,1) & \rightarrow 14 & 6\text{-fold}.
\end{align*}
\]

* Degeneracy generally results from symmetry. In the cubic limit well we have \( E_{211} = E_{121} = E_{112} \). Now if the cube is squeezed along the \( x \) direction all the levels would rise but \( E_{211} \) would rise more and we would have \( E_{211} > E_{121} = E_{112} \). This is known as the splitting of energy levels.

\[ \begin{array}{ccc}
211 & 121 & 112 \\
\hline
111 & 111 & 111
\end{array} \]

\[ L_x = L_y = L_z = L \quad L_x < L_y = Lz = L \]
c) The Schrödinger equation in spherical coordinates.

1) Spherical coordinates.

* Spherical coordinates \((r, \theta, \phi)\) are represented on the figure.

\(r > 0; 0 \leq \theta \leq \pi; 0 \leq \phi < 2\pi\)

* Conversion from rectangular \((x, y, z)\) to spherical \((r, \theta, \phi)\)

\[
\begin{align*}
    r &= \sqrt{x^2 + y^2 + z^2} \\
    \theta &= \cos^{-1} \left( \frac{z}{\sqrt{x^2 + y^2 + z^2}} \right) \\
    \phi &= \tan^{-1} \left( \frac{y}{x} \right)
\end{align*}
\]

* Conversion from spherical to rectangular

\[
\begin{align*}
    x &= r \sin \theta \cos \phi \\
    y &= r \sin \theta \sin \phi \\
    z &= r \cos \theta
\end{align*}
\]

2) Integration & differentiation in spherical coordinates.

* A small displacement \(d\vec{r}\) can be written

\[
    d\vec{r} = d\left(r \hat{r}\right) = dr \hat{r} + r \hat{r} \times \hat{r} = dr \hat{r} + r \left( \frac{\partial \hat{r}}{\partial r} dr + \frac{\partial \hat{r}}{\partial \theta} d\theta + \frac{\partial \hat{r}}{\partial \phi} d\phi \right)
\]

\[
    = dr \hat{r} + r \hat{r} \times \hat{\theta} + r \sin \theta \hat{\phi}.
\]

* We have already seen & used that a small element of volume \(dV\) is

\[
    dV = r^2 \sin \theta \ dr \ d\theta \ d\phi.
\]
Consider now a function \( f \) of \((\mathbf{r}, \theta, \phi)\). When the point where \( f \) is evaluated changes by a small amount \( \Delta \mathbf{r} \), the change of \( f \) can be written as

\[
\Delta f = \frac{\partial f}{\partial \mathbf{r}_n} \Delta \mathbf{r}_n + \frac{\partial f}{\partial \mathbf{r}_\theta} \Delta \theta + \frac{\partial f}{\partial \mathbf{r}_\phi} \Delta \phi = \nabla f \cdot \Delta \mathbf{r}
\]

where \( \nabla f \) is the gradient of \( f \). (In rectangular coordinates,

\[
\nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)
\]

So we have \( \frac{\partial f}{\partial \mathbf{r}_n} \Delta \mathbf{r}_n + \frac{\partial f}{\partial \mathbf{r}_\theta} \Delta \theta + \frac{\partial f}{\partial \mathbf{r}_\phi} \Delta \phi = (\nabla f)_n \Delta \mathbf{r}_n + (\nabla f)_\theta \Delta \theta + (\nabla f)_\phi \Delta \phi \). Since this should hold for any choice of \( \Delta \mathbf{r}_n, \Delta \theta \) and \( \Delta \phi \), so we can identify

\[
(\nabla f)_n = \frac{\partial f}{\partial \mathbf{r}_n}, \quad (\nabla f)_\theta = \frac{1}{r} \frac{\partial f}{\partial \theta}, \quad \text{and} \quad (\nabla f)_\phi = \frac{1}{r \sin \theta} \frac{\partial f}{\partial \phi}
\]

Given with this one can prove that

\[
\text{div} \ \nabla \mathbf{A} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 A_r \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( A_\theta \sin \theta \right) + \frac{1}{r \sin \theta} \frac{\partial A_\phi}{\partial \phi}
\]

and

\[
\nabla \cdot \mathbf{A} = \frac{\hat{r}}{r \sin \theta} \left[ \frac{\partial}{\partial \theta} \left( A_\theta \sin \theta \right) - \frac{\partial A_r}{\partial \theta} \right]
\]

\[
+ \frac{\hat{\theta}}{r \sin \theta} \left[ \frac{\partial}{\partial \phi} \left( A_\phi \right) - \sin \theta \frac{\partial A_r}{\partial \phi} \right]
\]

\[
+ \frac{\hat{\phi}}{r} \left[ \frac{1}{\sin \theta} \left( r A_\theta \right) - \frac{\partial A_r}{\partial \phi} \right]
\]

Laplacian \( \nabla^2 f = \nabla \cdot (\nabla f) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right)
\]

\[
+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2}
\]
With this we can write the Schrödinger equation in its time independent form as:

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

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

With \( V \) a function of \( r \) only, we look for solutions that can be written as \( \psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \).

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

Dividing by \( R Y \) and multiplying by \( -\frac{2m \hbar^2}{\hbar^2} \) we obtain:

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

The left hand side depends only on \( r \) while the right hand side depends only on \( \theta \) & \( \phi \) so both sides must equal a constant which we call \( l(l+1) \), a notation to be later justified.

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

\[ \frac{1}{Y} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = -l(l+1). \]
4) The angular equation

4.1 The angular equation can be written:

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

& once more we try separation of variables \( Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \)

which gives (after dividing by \( \Theta(\theta) \Phi(\phi) \))

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

**Only function of \( \theta \)**

**Only function of \( \phi \).**

\[ \Rightarrow \text{Both terms are constant} \]

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

\[ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -M^2. \]

4.2 The equation in \( \phi \) implies \( \Phi(\phi) = e^{i\mu \phi} \)

where \( \mu \) changes by \( 2\pi \) we return to the same point so we must have \( \Phi(\phi + 2\pi) = \Phi(\phi) \) so \( e^{i\mu \phi + 2\pi} = 1 \)

which implies \( \mu = 0, \pm 1, \pm 2, \pm 3, \ldots \)

4.3 The equation in \( \theta \) is not as simple. The solution can be shown to be \( \Theta(\theta) = A P_{\ell}^{\mu} (\cos \theta) \)

where \( P_{\ell}^{\mu} \) is the associated Legendre function \( P_{\ell}^{\mu} (x) = \frac{(1-x^2)^{\mu/2}}{2^\mu \Gamma(\mu+1)} (\frac{d}{dx})^\mu P_{\ell} (x) \) where \( P_{\ell} (x) \) is the Legendre polynomial of degree \( \ell \geq 0 \)

\( P_0 = 1; \quad P_1 = \theta; \quad P_2 = \frac{1}{2} (3\theta^2 - 1); \quad P_3 = \frac{1}{2} (5\theta^3 - 3\theta) \)

\& see that if \( \mu > \ell \) \( P_{\ell}^{\mu} (x) = 0 \) so for a given \( \ell \) there are \( 2\ell + 1 \) possible values of \( \mu \): \( -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell \).
\[ A \text{ is a normalization constant } \int_0^{2\pi} \int_0^\pi |y|^2 \sin \theta \ d\theta \ d\phi = 1. \]

\[ \rho = (\frac{1}{4\pi})^{1/2} \quad Y_0^0 = (\frac{3}{4\pi})^{1/2} \quad Y_1^0 = + (\frac{3}{8\pi})^{1/2} \sin \theta \ e^{\pm i\phi} \]

\[ Y_2^0 = (\frac{5}{16\pi}) (3 \cos 2\theta - 1) \quad Y_2^1 = + (\frac{15}{8\pi}) \sin \theta \ \cos \theta \ e^{\pm i\phi} \]

\[ Y_2^{-1} = (\frac{15}{32\pi}) \sin^2 \theta \ e^{\pm 2i\phi} \]

and all these functions which are known as spherical harmonics constitute a complete or orthonormal basis.

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

We will look at the general aspect of these functions once we will have solved the radial equation for the hydrogen atom.

Before going to the special case of the hydrogen atom let's look at \( \Phi_{\ell m} = e^{im\phi} \) the real part of which is represented radially on the following figures.

\[ \implies Re(\Phi_{\ell m}) = 0 \]

Thinking again about Bohr's model with de Broglie's hypothesis

\[ 2\pi r = m_e \lambda = m_e \frac{h}{m_e c} \Rightarrow m_e = 2\pi n m_e \lambda \]

or \( m_e \chi = m_r \nu \), \( \nu = \frac{e}{m_e c} \) the \( z \) component of the angular
Momentum. The quantum number \( m \) in determining the value of \( L_z \) for which \( \phi_{m_z}(p) \) are eigenfunctions of eigenvalue \( m \hbar \) with \( m = 0, \pm 1, \pm 2, \ldots, \pm l \).

It can be shown that \( l \) specifies the magnitude of the angular momentum \( |L| = \sqrt{l(l+1)} \hbar \) for that reason \( l \) is known as the orbital quantum number.

One expects some relationship between \( L \) & \( L_z \). We just saw:

\[
L_z = m \hbar \quad m = 0, \pm 1, \pm 2, \ldots, \pm l
\]

\[
L = \sqrt{l(l+1)} \hbar \quad l = 0, 1, 2, \ldots
\]

- \( L_z \) is a component of \( L \) & we can see that \( L_z < L \)
- but it seems we cannot have \( L_z = L \) - The thing is that the various components of the angular momentum do not commute so there is an uncertainty relation between them - The angular momentum cannot be known absolutely.

For \( L = L_z \) to be true would require \( z = 0 \) & \( \phi_z = 0 \) which we have seen to be impossible earlier. The magnitude & one component of the angular momentum can however be known simultaneously (they commute).

Example \( l = 2 \) \( |L| = \sqrt{6} \hbar \)
5) The radial equation & the hydrogen atom.

We found the radial equation as
\[
\frac{d}{dr} \left( r^2 \frac{dr}{dr} \right) - \frac{2m}{\hbar^2} \left( V(r) - E \right) r = l(l+1) r
\]
which can be greatly simplified by introducing \( u(r) = r \phi \). 

So \( R = \frac{u}{r} \), \( \frac{dR}{dr} = \left( r \frac{du}{dr} - u \right) r \) and \( \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = r \frac{d^2 u}{dr^2} \).

So we have \( -\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = E u \),

which is just the Schrödinger equation in one dimension where the potential is replaced with an effective potential

\[ V_{eff} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \]

where the extra term accounts for the centrifugal effect: \( \frac{\hbar^2 l(l+1)}{2m r^2} = \frac{L^2}{2I} \)

In the case of the hydrogen atom \( V(r) = -\frac{e^2}{4\pi \epsilon_0 r} \).

After manipulating the Schrödinger equation, expressing its solutions as a power series & requiring the solution to be of integrable square, the allowed energies happen to be just what we found with Bohr's model:

\[ E_n = -\frac{m e^2}{8 \hbar^2 (4\pi \epsilon_0)^2} \frac{1}{n^2} = \frac{E_1}{n^2} \] with \( n = 1, 2, \ldots \).

with \( E_1 = -13.6 \) eV.

and the \( R \) is given by:

\[ R_{nl} = \left( \frac{\hbar}{m a} \right)^3 \left( n - \frac{1}{2} \right)^3 e^{-\frac{\hbar}{m a} \left( \frac{2n}{\hbar} \right)^{2l+1}} \left( \frac{2n}{\hbar} \right)^{l} L_{n-l-1} \left( \frac{2n}{\hbar} \right) \]

where \( L_q \) is an associated Laguerre polynomial & \( l = 0, 1, 2, \ldots, n-1 \).

\[
L_0 = 1 \\
L_1 = -2 + 1 \\
L_2 = -4x + 2
\]

\[
L_0 = 2 \\
L_1 = -6x + 8 \\
L_2 = 12x^2 - 96x + 144
\]

\[
L_0 = 1 \\
L_1 = -2x + 4 \\
L_2 = 3x^2 - 18x + 18
\]

What is important here is that \( l = 0, 1, 2, \ldots, n-1 \).
Remember \( \Psi_{nem} = R_{Re} \cdot Y_{m} \). The \( \Psi_{nem} \) constitute an orthogonal basis. All of these functions with the same index correspond to the same energy \( E_n \). It is a peculiarity of the Coulomb potential that the energy \( E_n \) does not depend on \( \ell \).

The degeneracy is \( g = n^2 \).

\[
\begin{array}{ccc}
\ell = 0 & m = 0 & (1) \ g = 1 & 1s \\
\ell = 1 & m = 0 \pm 1 & (3) \ 2p \\
\ell = 2 & m = 0 \pm 2 \pm 2 & (5) \ 3d \\
\ell = 3 & m = 0 \pm 3 \pm 3 & (7) \ 4f \\
\end{array}
\]

This structure of the states of the hydrogen atom provides a clear understanding of the periodic table of elements but before doing this we’ll need to look into the quantum description of several particles in a potential well. Before we do that, we should describe the solutions \( \Psi_{nem} = R_{Re} \cdot Y_{m} \) of the Schrödinger equation.

*Note: \( \ell = 4 \leftrightarrow g \) & \( \ell = 5 \leftrightarrow h \).
6) The hydrogen electron whereabouts

\[ \frac{dP}{dv} = 14 \rho_n \rho_m = |R_{nm}|^2 \frac{1}{4\pi \rho_n^2} \frac{1}{4\pi \rho_m^2} \text{ in the volume probability density (in m}^{-3}) \]

\[ R_{nm} \] being the solution of the Schrödinger equation for an effective potential, it respects the rule according to which the number of nodes corresponds to the \( p \)th excited state considered.

\[ \text{When } l = 0, \ R_{nm}(r) \text{ is maximal at } r = 0 \]

\[ \text{When } l > 0, \ R_{nm}(r) = 0 \text{ and } R_{nm}(r) \text{ extends to increasing values of } r \text{ with increasing } l \]

\[ \text{Values of } r \text{ where } R_{nm}(r) = 0 \text{ define spheres at the surface of which the electron can not be found.} \]

\[ \text{It should be noted that the chance probability of finding the electron between distances } r_1 \text{ and } r_2 \text{ is } P(r_1, r_2) = \int_{r_1}^{r_2} R_{nm}^2(r) r^2 \, dr \]

So the radial probability density is \( \frac{dP}{dr} = R_{nm}^2(r) r^2 \)

& when \( l = 0 \), the most likely place where to find the electron is not inside the nucleus.

The distance probability density is shown in the graph next page.

**FIGURE 4.4: Graphs of the first few hydrogen radial wave functions, \( R_{nm}(r) \).**

*Figure from "Introduction to Quantum Mechanics" by David J. Griffiths*
The full 3-dimensional description is obtained as the product $\Psi_{\ell m} = \Phi_{\ell m} \cdot \Phi_{nm}$, as illustrated on the figure next page.

- For $\ell = 0$, the kinetic energy is "radial" only, and $\Phi_{n\ell 00}$ is symmetric.

- For $\ell = 1$, the kinetic energy can be along the $z$ axis ($m_\ell = 0$) or within the $(x,y)$ plane ($m_\ell = \pm 1$).

- For a fixed $\ell$, increasing $n$ increases the energy without changing the "angular" energy. So for a fixed $\ell$ increasing $n$ increases the number of radial nodes. In the same way increasing $\ell$ for a fixed $n$ reduces the number of radial nodes.

Figure 7.17 Radial probabilities and energies in the hydrogen atom. (Note: Each higher $n$ adds an $\ell$ value and a corresponding radial function.)

For a given $n$, lower $\ell$ is smaller rotational energy and larger radial.

With more radial antinodes - a more elliptical orbit. The $3s$ has three radial antinodes.

Higher $\ell$ is like a circular orbit at a single radius. The $3d$ has only one antinode.

$U(r) = -\frac{1}{r}$

Figure from "Modern Physics" by Randy Harris.
Figure 7.15 Electron probability densities in the hydrogen atom, through \( n = 3 \).

\[
|\psi(r, \theta, \phi)|^2 = R^2(r) \Theta^2(\theta)
\]

1s

\( (n, \ell, m_\ell) = (1, 0, 0) \)

2s

\( (2, 0, 0) \)  \( (2, 1, 0) \)  \( (2, 1, \pm 1) \)

3s

\( (3, 0, 0) \)

3p

\( (3, 1, 0) \)  \( (3, 1, \pm 1) \)

3d

\( (3, 2, 0) \)  \( (3, 2, \pm 1) \)  \( (3, 2, \pm 2) \)

\[ \Psi_{1s}^-(n_1+) = \Psi_i^-(n_1+) + \Psi_f^-(n_1+) \]

\[ = \psi_i(n) e^{-iE_i t/\hbar} + \psi_f(n) e^{-iE_f t/\hbar} \]

\( \Psi_{1s}^+ \) is the wave function for the atom in its ground state, \( \psi_i(n) \) is the wave function for the electron in the initial state, and \( \psi_f(n) \) is the wave function for the electron in the final state.

The power radiated by an oscillating electric dipole \( \mathbf{p} = q \mathbf{v} \) is

\[ P = \frac{\hbar}{12} e \mathbf{e} \cdot \mathbf{\mathbf{v}}^2 \int dV \left| \sum_{\text{trans}} \psi_{i}^* \psi_{f} \right|^2 \]

The sum terms \( \psi_i^* \psi_f \) and \( \psi_f^* \psi_i \) are "oscillating" at the right frequency to emit a photon of energy \( |E_i - E_f| \) but, in order to contribute to the electric dipole, these terms need to be odd with \( \ell \) which implies \( \ell_f \) and \( \ell_i \) to have different parity. Which implies \( \ell_f - \ell_i \) to be odd.
2) Adding Spin & Atomic Physics

1) Angular momentum & Magnetic dipole moment

* When discussing the hydrogen atom, we commented on the fact that angular momentum is quantized.

* The electron being electrically charged, if its angular momentum is quantized, the magnetic moment of its orbit should be quantized too.

* In the classical picture on the right, \( I = e / r \) (with \( r \) the orbital period) is the current associated with the motion of the electron.

* A current loop of intensity \( I \) & area \( A \) has a magnetic dipole moment \( \mathbf{m} = I \mathbf{A} = \frac{e}{I} \pi r^2 = \frac{e}{2 \pi I} \pi r^2 \)

* \( \mathbf{m} = \frac{e}{2} \mathbf{r} \times \mathbf{I} = \frac{e}{2m} \mathbf{r} \mathbf{I} \times \mathbf{I} = -\frac{e}{2m} \mathbf{L} \)

* A magnetic dipole \( \mathbf{m} \) in a magnetic field is under the influence of a torque \( \mathbf{T} = \mathbf{m} \times \mathbf{B} \) which causes the angular momentum to precess like a top. \( \mathbf{L} = \frac{d\mathbf{L}}{dt} \).

* The precession rate is the Larmor frequency

\[
\left| \frac{d\mathbf{L}}{dt} \right| = \left| \frac{e}{2m_e} \mathbf{L} \times \mathbf{B} \right| = \frac{e}{2m_e} L B \sin \theta
\]

\( L \sin \theta \frac{d\phi}{dt} = \frac{e}{2m_e} L B \sin \theta \) & \( \frac{d\phi}{dt} = \frac{eB}{2m_e} \).

* The \( z \) component of \( \mathbf{m} \) (along the magnetic field) is constant while the \( x \) & \( y \) components keep changing.
The magnetic field direction sets a special axis \( \hat{z} \) along which the angular momentum (and thus the magnetic moment) is quantized. As we have seen, \( L_z = m_e \hbar \).

2) The Stern & Gerlach experiment

* In 1922 Otto Stern & Walther Gerlach investigated the intrinsic angular momentum of atoms and particle with an experiment which now bears their names.
* A magnetic dipole \( \vec{\mu} \) in a magnetic field \( \vec{B} \) has a potential energy \( U = -\vec{\mu} \cdot \vec{B} \).

* Such a way, when the magnetic field is non-uniform, it is subject to a force \( \vec{F} = -\nabla (-\vec{\mu} \cdot \vec{B}) \).

* For a configuration as on the figure

\[
F = m_3 \frac{\partial B_3}{\partial z} \hat{z}
\]

\[
F = \left(-\frac{e}{2m_e}L_3\right) \frac{\partial B_3}{\partial z} \hat{z}
\]

\[
F = \left(-\frac{e}{2m_e} \frac{m_e \hbar}{2}\right) \frac{\partial B_3}{\partial z} \hat{z} \quad \text{with } m_e = -e, \ldots, +e
\]

which explains why \( m_e \) is referred to as the magnetic quantum number.

* Hydrogen atoms in state \( \ell = 1 \) should be projected on 3 spots on a screen at the other end of the magnetic channel as when \( m_e = +1 \) they are deviated down, when \( m_e = 0 \) they are not deviated & when \( m_e = -1 \) they are deviated up.
When Otto Stern & Walther Gerlach did their experiment, they were using ground state hydrogen for which $L = 0$ so on by one spot (no deflection) was expected. They however observed 2 spots & $Z = \ell (\ell + 1)$ so this was something new.

3) **Spin**

- Electrons possess an intrinsic angular momentum $S$ to which a magnetic dipole moment is related.
- Particles are each characterized by their intrinsic properties such as mass, electric charge, spin & others.
- A proper description of spin requires relativistic quantum mechanics (quantum field theory). It appears that:
  1. $S = \sqrt{S(S+1)} \frac{\hbar}{2}$ where $S$ is a quantum number, the value of which is a property of each particle. For the electron $S = \frac{1}{2}$ while for the photon $S = 1$.
  2. A spin $\frac{1}{2}$ particle has an angular momentum $S = \sqrt{\frac{3}{4}} \frac{\hbar}{2}$
  3. The intrinsic magnetic dipole moment is $m_s = g \frac{\hbar}{2\pi} S$ where $g$ is the gyromagnetic ratio. In the case of the electron $g \approx 2$, so $m_s = -\frac{e}{M_e} S$.
  4. $S_z = M_s \frac{\hbar}{2}$ with $M_s = -S, -S+1, \ldots, S-1, S$.

$M_s$ is the quantum number of spin. In the case of electrons $M_s = -\frac{1}{2}$ or $M_s = +\frac{1}{2}$. 
* The spin quantum number allows to understand the result of the Stern & Gerlach experiment.

\[ F = -\frac{e}{m_e} z \frac{\partial B_e}{\partial z} \hat{z} = -\frac{e}{m_e} m_s + \frac{\partial B_e}{\partial z} \hat{z} \quad m_s = -\frac{1}{2}, \frac{1}{2}. \]

* In order to specify the state in which the electron of a hydrogen atom is, we must add one quantum number:

\[ \psi_n, l, m_l, m_s. \]

If the energy does not depend on \( m_s \), this leaves the degree of degeneracy to \( 2n^2 \).

* In general the spin state is a linear combination of spin up \( |\uparrow\rangle \) & spin down \( |\downarrow\rangle \) so \( |\Psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle \)
& then \( |a|^2 \) is the chance probability of observing \( \uparrow \)
& \( |b|^2 \) is the chance probability of observing \( \downarrow \).

E) Systems with several identical particles:

1) Two particles in a box

* The wave function is a function of the positions of individual particles \( x_1 \) & \( x_2 \):

\[ \Psi(x_1, x_2) \]

* The Schrödinger equation reads

\[ \left( \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_2^2} \right) \Psi(x_1, x_2) + U_1(x_1, x_2) \Psi(x_1, x_2) = E \Psi(x_1, x_2) \]
To solve this, we make use once more of variable separation & rewrite the Schrödinger equation with \( \psi(x, y) = \psi_1(x) \psi_2(y) \)

\[- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(y)}{\partial y^2} + U(x, y) = \mathcal{E} \]

If \( U(x, y) \) contains terms of mutual interaction, which would typically depend on \(|x - y|\), the two variables do not separate. If on the other hand there are only external forces then \( U(x, y) = U_1(x) + U_2(y) \) & the problem appears as two independent Schrödinger equations, with energy \( \mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 \) & \( \psi(x, y) = \psi_1(x) \psi_2(y) \)

\[ \mathcal{E}_n = \frac{n^2 \hbar^2}{2m L^2} \]

\[ \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \]

In the case of the infinite square well of width \( L \).

2) Indistinguishable particles

Let's keep considering the problem of two particles in an infinite square well & assume the system is in the state \( n_1 = 3 \) & \( n_2 = 4 \) so \( \psi(x_1, x_2) = \psi_3(x_1) \psi_4(x_2) \)

The chance probability density of finding particle 1 in \( x \), a particle 2 in \( x_2 \) is \( |\psi(x_1, x_2)|^2 = |\psi_3(x_1)|^2 |\psi_4(x_2)|^2 \).

The chance probability of finding particle 1 in \( \frac{L}{2} \) is

\[ P_1(\frac{L}{2}) = |\psi_3(\frac{L}{2})|^2 \int |\psi_4(x_2)|^2 dx_2 = |\psi_3(\frac{L}{2})|^2 = 0 \]

while \( P_2(\frac{L}{2}) = |\psi_4(\frac{L}{2})|^2 \int |\psi_3(x_1)|^2 dx_1 = |\psi_4(\frac{L}{2})|^2 \neq 0 \)
* This is total nonsense - we are talking about two electrons, identical particles that are not distinguishable - How can we say one can be found in \( \frac{1}{2} \) while the other one can't?

This means the probability density must be unchanged during the exchange of the two particles & we must work under this restriction.

* There are two ways of doing this: we have states that are symmetric \( \Psi_s \) & states that are antisymmetric \( \Psi_a \)

\[
\Psi_s = \Psi_4(x_1) + \Psi_3(x_1) + \Psi_4(x_2) \Psi_3(x_2)
\]

\[\Psi_a = \Psi_4(x_1) \Psi_3(x_2) - \Psi_4(x_2) \Psi_3(x_1)\]

Clearly \( \Psi_s(x_1, x_2) = \Psi_s(x_2, x_1) \) & \( |\Psi_s(x_1, x_2)|^2 = |\Psi_s(x_2, x_1)|^2 \)

& \( \Psi_a(x_1, x_2) = -\Psi_a(x_2, x_1) \) & \( |\Psi_a(x_1, x_2)|^2 = |\Psi_a(x_2, x_1)|^2 \)

* In the case of 2 electrons in a potential well & including spin as one quantum number

\[
\Psi_s = \Psi_{m_1, m_1, s_1}(x_1) \Psi_{m_2, m_2, s_2}(x_2) + \Psi_{m_1, m_2, s_1}(x_1) \Psi_{m_2, m_1, s_2}(x_2)
\]

\[
\Psi_a = \Psi_{m_1, m_1, s_1}(x_1) \Psi_{m_2, m_2, s_2}(x_2) - \Psi_{m_1, m_2, s_1}(x_1) \Psi_{m_2, m_1, s_2}(x_2)
\]
3) Pauli exclusion principle

* Whether the wave function is symmetric or antisymmetric depends on the spin in a way that is explained by relativistic quantum mechanics.

(1) Particles with integer spin quantum number $s = 0, 1, 2, \ldots$ are called bosons & have a wave function that is symmetric under the exchange of two such particles.

(2) Particles with half integer spin quantum number $s = \frac{1}{2}, \frac{3}{2}, \ldots$ are called fermions & have a wave function that is antisymmetric under the exchange of two such indistinguishable particles.

* In the case of two fermions, the wave function is

$$\psi_A = \psi_n(x_1)\psi_m(x_2) - \psi_n(x_2)\psi_m(x_1)$$

If $n = n'$, $\psi_A = 0$ & we see that two fermions cannot have the same quantum numbers.

No two indistinguishable fermions may have the same set of quantum numbers in an isolated system.

This principle was discovered by Wolfgang Pauli in 1924 & he obtained the Nobel prize in 1945. This principle applies only to fermions & not to bosons.
E) The periodic table

1) Constructing the ground state of atoms.

* The lowest energy states get occupied first & up to what is permitted by the exclusion principle.
* The general quantum number structure describing the states of the hydrogen atom is preserved but the screening effect of inner electrons changes the potential energy, increasing the energy of states with larger \( l \) values.
* Electrons occupy the successive states following the value of \( n + l \) with priority the the lowest \( n \) when the values of successive \( n + l \) are equal.
* A given value of \( n \) defines a family of states referred to as a shell, within which the values of \( l \) correspond to subshells. Each subshell can host \( 2(2l+1) \) electrons, in accordance with the exclusion principle. The factor 2 corresponds to the two possible values of \( s^2 \) for given \( n, l, m_l \).

<table>
<thead>
<tr>
<th>Subshell</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3s</th>
<th>3p</th>
<th>4s</th>
<th>3d</th>
<th>4p</th>
<th>5s</th>
<th>4d</th>
<th>5p</th>
<th>6s</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n + l )</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>( 2(2l+1) )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>10</td>
<td>6</td>
<td>2</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

\( Z = 6 \) Carbon: \( 1s^2 \ 2s^2 \ 2p^2 \)

\( Z = 8 \) Oxygen: \( 1s^2 \ 2s^2 \ 2p^4 \)

\( Z = 11 \) Sodium: \( 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \)

As the number of electron increases however, some readjustment of the subshell energies take place so that for instance 3d levels fill up prior to 4s:

\( Z = 23 \) Ca: \( \ldots \ 4s^2 \ 3d^3 \) but \( Z = 24 \) Cr: \( \ldots \ 3d^5 \ 4s^1 \)
Each row of the periodic table corresponds to the filling up of one shell -
- For \( n = 1 \), \( l = 0 \) (s) Hydrogen & Helium
- For \( n = 2 \& 3 \), \( l = 0 \) & \( l = 1 \) (p) or 8 elements per row.
- For \( n = 4 \& 5 \), \( l = 0, 1 \& 2 \) (d) or 18 elements per row.
- For \( n = 6 \& 7 \), \( l = 0, 1, 2 \& 3 \) (f) are used & the additional \( 14 \) (\( 2(2x3+1) \)) elements are placed in separated rows corresponding to the so-called "rare earth" elements Lanthanides & Actinides

2) Chemical properties.