

Wavefunction of the Hydrogen atom

- The proton/nucleus has a finite mass. Therefore the wavefunction would be a function of the coordinates of both the proton and the electron. If the mass of the proton is infinite then it doesn't move and we only have to treat the dynamics of the electron.
- The wavefunction of the hydrogen atom can be written as $\psi_{Hyd}(\vec{r}_p, \vec{r}_e, t)$ where \vec{r}_p , and \vec{r}_e are the coordinates of the proton and the electron, respectively.
- The wavefunction, which is a function of six coordinates and the time, is not describing a physical wave or displacement in space and time but rather a mathematical construction with the physical meaning given by the Born interpretation.

Wavefunction of the Hydrogen atom

- The total energy of the system includes the kinetic energies of the proton and the electron and the Coulomb potential energy.

$$E_{total} = \frac{p_e^2}{2m_e} + \frac{p_p^2}{2m_p} + V(|\vec{r}_p - \vec{r}_e|)$$

- The corresponding Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(|\vec{r}_p - \vec{r}_e|)$$

We used the Laplacian, $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, where ∇_p^2 acts only on the proton coordinates and ∇_e^2 acts only on the electron coordinates. In addition we define $r = |\vec{r}_p - \vec{r}_e|$ as the distance between the proton and the electron.

Wavefunction of the Hydrogen atom

- The corresponding Schrödinger equation is:

$$\left(-\frac{\hbar^2}{2m_p} \nabla_p^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(r) \right) \psi = i\hbar \frac{\partial \psi}{\partial t} = E_T \psi$$

- The total energy includes the kinetic energy due to motions of the center of mass and not only the energy due to the relative motion of the proton and the electron. In order to understand the spectrum of the hydrogen we have to ignore the motion of the center of mass, just as we did before in Bohr's model.
- The potential energy depends only on the relative coordinates of the proton and the electron.
- This enables us to rewrite the Schrödinger equation using the coordinates of the center of mass and the coordinates of the relative motion of the proton and the electron.

Wavefunction of the Hydrogen atom

- The COM coordinates are defined as:

$$X_{COM} = \frac{x_e m_e + x_p m_p}{m_e + m_p}$$

$$Y_{COM} = \frac{y_e m_e + y_p m_p}{m_e + m_p}$$

$$Z_{COM} = \frac{z_e m_e + z_p m_p}{m_e + m_p}$$

- The relative coordinates are defined as:

$$x = x_e - x_p$$

$$y = y_e - y_p$$

$$z = z_e - z_p$$

Wavefunction of the Hydrogen atom

- Using these coordinates we can write the total kinetic energy as:

$$\frac{P_{COM}^2}{2(m_e + m_p)} + \frac{p^2}{2\mu}$$

Where $\vec{P}_{COM} = (m_e + m_p) \frac{d\vec{r}_{COM}}{dt}$, $\vec{p} = \mu \frac{d\vec{r}}{dt}$ and the reduced mass is $\mu = \frac{m_e m_p}{m_e + m_p}$.

This enables us to write the Schrödinger equation as:

$$\left(-\frac{\hbar^2}{2(m_p + m_e)} \nabla_{COM}^2 - \frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \psi = i\hbar \frac{\partial \psi}{\partial t} = E_T \psi$$

- The wavefunction is a function of the coordinates of the COM, the relative coordinates and the time, $\psi(\vec{r}_{COM}, \vec{r}, t)$.
- The potential only depends on \vec{r} which enables the separation of variables.

Wavefunction of the Hydrogen atom

- Separating the variables we write the wavefunction as

$$\psi(\vec{r}_{COM}, \vec{r}, t) = \phi(\vec{r}_{COM})\vartheta(\vec{r})e^{-\frac{i(E+E_{COM})t}{\hbar}}$$

Where E_{COM} is the energy of the motion of the COM and E is the energy due to the relative motion of the proton and the electron.

This enables us to write the Schrödinger equation as two equations:

$$-\frac{\hbar^2}{2(m_p + m_e)}\nabla_{COM}^2\phi(\vec{r}_{COM}) = E_{COM}\phi(\vec{r}_{COM})$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right)\vartheta(\vec{r}) = E\vartheta(\vec{r})$$

- The eigenvalues of E are the energy levels in the COM reference frame (the same reference frame we used in Bohr's model).

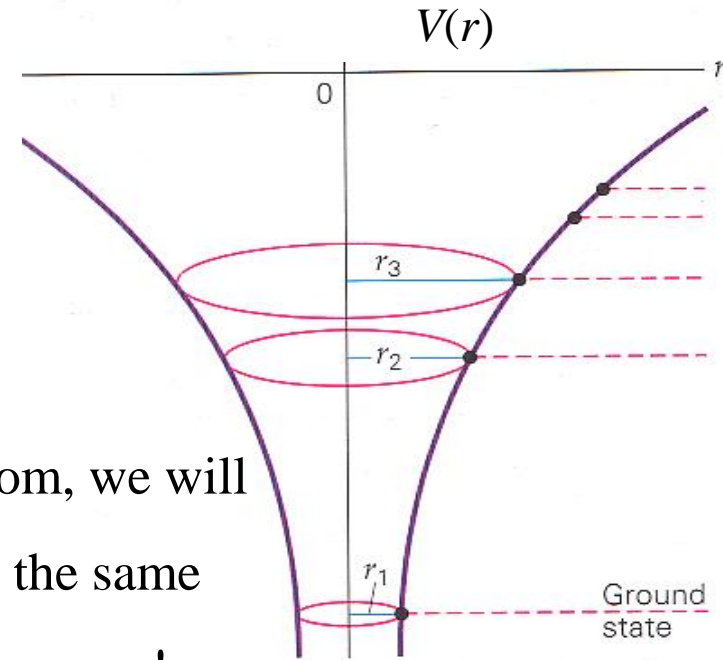
Hydrogen atom in Quantum Mechanics

The Three-dimensional potential well of the hydrogen atom is more complex than those we treated previously. The potential energy $V(r)$ results from the Coulomb interaction between a single electron and a proton in the nucleus. $V(r) = -\frac{e^2}{r}$

The potential is only a function of the radial distance r and doesn't depend on θ or ϕ . By definition, this is a central potential in which $V(\vec{r}) = V(r)$

By solving the Schrödinger equation for hydrogen atom, we will find that, surprisingly, the energy values are given by the same formula as that resulting from Bohr's model which is wrong!

$$E_n = -\frac{\mu c^2 \alpha^2 Z^2}{2 n^2} \approx -13.6 \text{eV} / n^2$$



Classical central force potential

In classical physics, a central force has an important feature: There is no torque, relative to the origin, on the object under the influence of the force, and therefore, the angular momentum does not vary with time.

The classical definition of the angular-momentum vector of a particle relative to some reference point is:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

\vec{r} is the position vector of the particle relative to the reference point and \vec{p} is the momentum of the particle relative to that point.

The components of angular momentum vector can be written explicitly as:

$$L_x = p_z y - p_y z, \quad L_y = p_x z - p_z x, \quad L_z = p_y x - p_x y$$

Classical central force potential

Conservation of angular momentum in classical mechanics

$$\vec{L} = \vec{r} \times \vec{p} = m\vec{r} \times \frac{d\vec{r}}{dt}$$

$$\frac{d}{dt}\vec{L} = m \frac{d\vec{r}}{dt} \times \frac{d\vec{r}}{dt} + m\vec{r} \times \frac{d^2\vec{r}}{dt^2} = \vec{r} \times \vec{F} = \vec{\tau}$$

$$\vec{F}(\vec{r}) = F_r(r)\hat{r} \Rightarrow \vec{\tau} = \vec{r} \times \vec{F} = \vec{r} \times F_r(r)\hat{r} = 0$$

$$\Rightarrow \vec{\tau} = \frac{d}{dt}\vec{L} = 0 \Rightarrow \vec{L} = \text{const}$$

We expect that the angular momentum will also be conserved in the quantum mechanics description of the same situation.

Quantum mechanical operator for angular momentum

- The momentum operators in the space basis are:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

- The position operators in the space basis are simply the coordinates:

$$\hat{x} = x, \hat{y} = y, \hat{z} = z$$

- Combining the two according to the definition of the angular momentum we may write the corresponding operators as:

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Quantum mechanical operator for angular momentum

- The commutation relations are:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

- The fact that the components of the angular momentum do not commute implies that we cannot simultaneously know the definite values of all the components.
- The Robertson-Schrödinger relation may be written as:

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

- The squared angular momentum may be written as:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

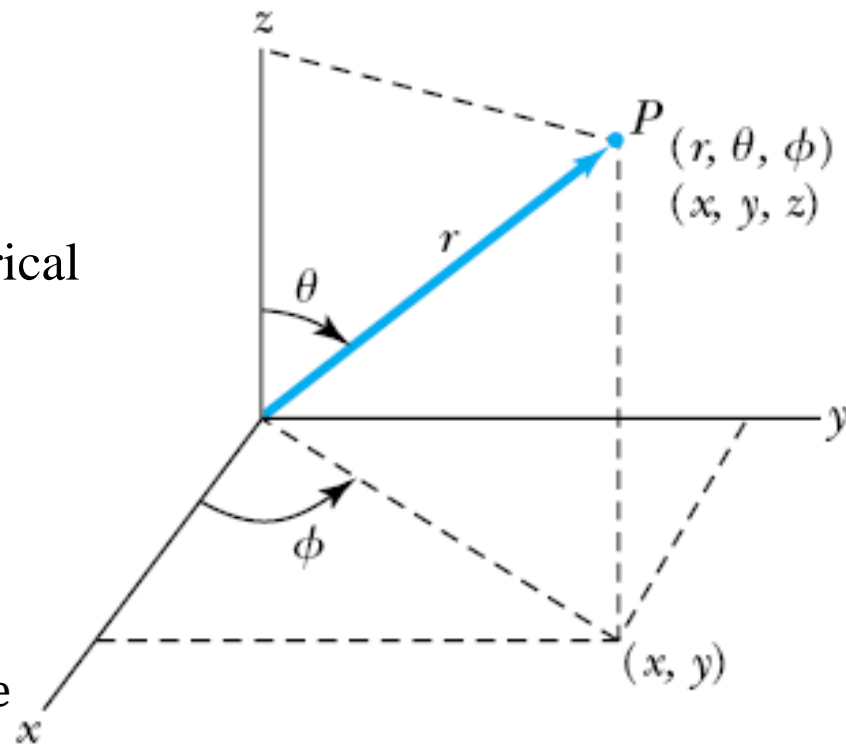
Spherical Coordinates

➤ It is useful to write the angular momentum operators in spherical coordinates. The spherical coordinates are defined as:

$$x = r \sin \theta \cos \phi \quad r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r \sin \theta \sin \phi \quad \theta = \cos^{-1} \left(\frac{z}{r} \right) \quad \text{polar angle}$$

$$z = r \cos \theta \quad \phi = \tan^{-1} \left(\frac{y}{x} \right) \quad \text{Azimuthal angle}$$



Using the chain rule we find:

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

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

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Angular momentum operator

- The operator for the squared angular momentum takes the following form in spherical coordinates:

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

- The eigenfunctions of the squared angular momentum operators are the spherical harmonics which are denoted as $Y_{l,m_l}(\theta, \phi) = N e^{im_l \phi} P_l^{m_l}(\cos(\theta))$ where $P_l^{m_l}(x)$ is the associated Legendre polynomial. N is a normalization

constant.
$$P_l^{m_l}(x) = \frac{(-1)^{m_l}}{2^l l!} (1 - x^2)^{\frac{m_l}{2}} \frac{d^{l+m_l}}{dx^{l+m_l}} (x^2 - 1)^l$$

- $\hat{L}^2 Y_{l,m_l}(\theta, \phi) = \hbar^2 l(l+1) Y_{l,m_l}(\theta, \phi)$ and $\hat{L}_z Y_{l,m_l}(\theta, \phi) = \hbar m_l Y_{l,m_l}(\theta, \phi)$
- The spherical harmonics are eigenfunctions of both the squared angular momentum and the z component of the angular momentum.

Angular momentum operator

- This implies that we can know the z component of the angular momentum and its magnitude simultaneously but not the other components!!
- It is also useful to define the following operators:

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial \theta} + i \cot(\theta) \frac{\partial}{\partial \phi} \right)$$

These operators act on the spherical harmonics such that

$$\hat{L}_{\pm} |l, m_l\rangle = \hbar \sqrt{l(l+1) - m_l(m_l \pm 1)} |l, m_l \pm 1\rangle$$

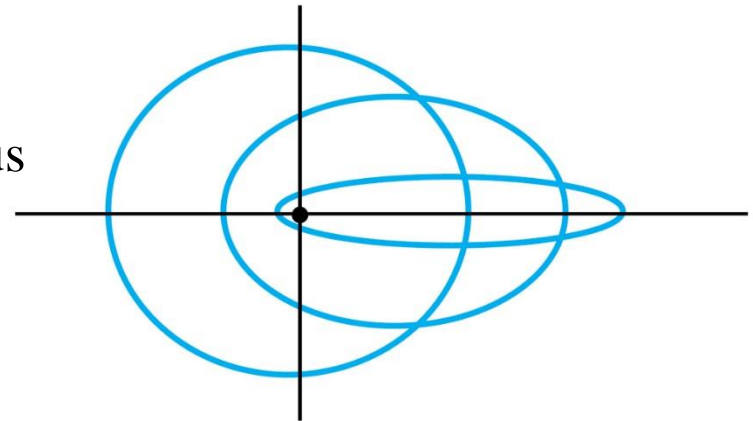
The indices take the values:

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

$$m_l = -l, -l+1, \dots, l-1, l$$

Orbital Angular Momentum Quantum Number l

- ▶ L is related to l by $L = \hbar\sqrt{l(l+1)}$
- ▶ In an $l = 0$ state, $L = \hbar\sqrt{0(0+1)} = 0$
- ▶ This disagrees with Bohr's semi-classical “planetary” model of electrons orbiting a nucleus
 $L = n\hbar$ with n being an integer ≥ 1



Classical orbits—which do not exist in quantum mechanics

Schrödinger equation for the central force potential

Schrödinger equation for this potential is as follows, using the reduced mass μ for the mass of the electron, as before:

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) \vartheta(\vec{r}) = E\vartheta(\vec{r})$$

Or

$$\nabla^2 \vartheta(\vec{r}) + \frac{2\mu}{\hbar^2} (E - V(r)) \vartheta(\vec{r}) = 0$$

To solve it we need to change the variables from the Cartesian coordinates (x,y,z) to spherical ones (r,θ,φ) where θ is the polar angle and φ is the azimuthal angle.

We will also need to transform the Laplacian operator.

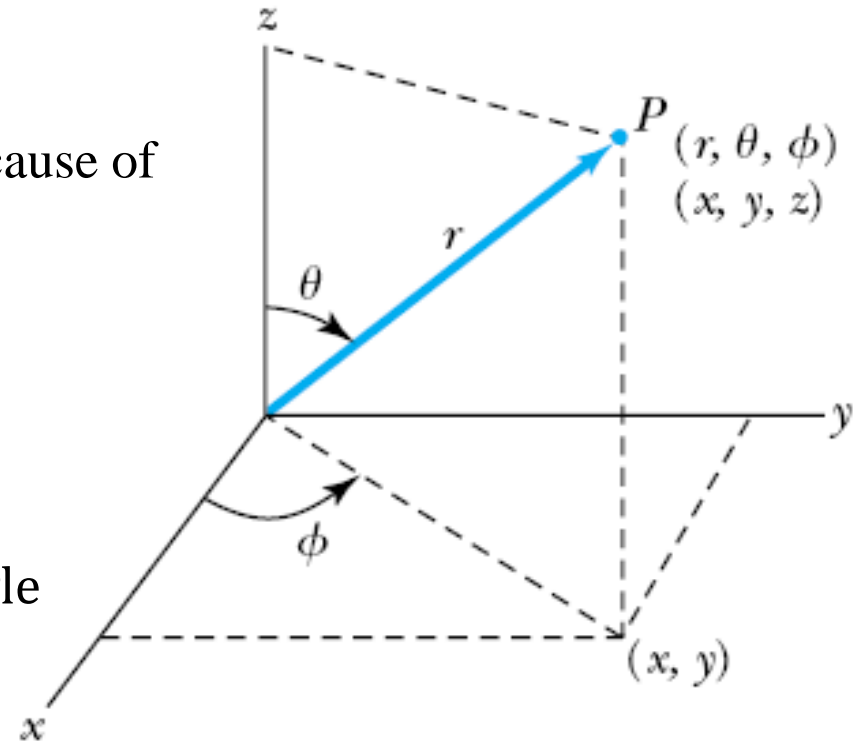
Spherical Coordinates

Transform to spherical polar coordinates because of the radial symmetry.

$$x = r \sin \theta \cos \phi \quad r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r \sin \theta \sin \phi \quad \theta = \cos^{-1} \left(\frac{z}{r} \right) \quad \text{polar angle}$$

$$z = r \cos \theta \quad \phi = \tan^{-1} \left(\frac{y}{x} \right) \quad \text{Azimuthal angle}$$



After several applications of the chain rule, the Laplacian operator in spherical coordinates can be written as:

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

Time-independent Schrödinger equation in spherical coordinates

In spherical coordinates, the time-independent Schrödinger equation appears more complicated:

$$\left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \vartheta(\vec{r}) + \frac{2\mu}{\hbar^2} (E - V(r)) \vartheta(\vec{r}) = 0$$

Laplacian operator (∇^2) in spherical coordinates

This complicated partial differential equation can be reduced to a set of one-dimensional differential equations. The equations for the angles θ and ϕ can be solved directly, without the need to introduce the Coulomb potential (central force) because the potential does not depend on the angles θ and ϕ .

Time-independent Schrödinger equation in spherical coordinates

It is important to note that the Laplacian in spherical coordinates can be written as:

$$\nabla^2 \equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\hbar^2 r^2} \hat{L}^2$$

$$\frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \vartheta(\vec{r}) + \frac{2\mu}{\hbar^2} (E - V(r)) \vartheta(\vec{r}) = 0$$

\hbar^{-2} times the squared angular momentum operator

Assume a Separable Solution for ψ_{Hyd}

- The wave function $\vartheta(\vec{r})$ is a function of r, θ, ϕ . This is a potentially complicated function.
- Assume instead that $\vartheta(\vec{r})$ is **separable**, that is, a product of three functions, each of one variable only. Remember that this is how we separated the time-dependent Schrödinger equation when the potential was time-independent:

$$\vartheta(r, \theta, \phi) = R(r)f(\theta)g(\phi)$$

Then, we can express the following partial derivatives with respect to the three variables r, θ and ϕ :

$$\frac{\partial \vartheta}{\partial r} = fg \frac{\partial R}{\partial r} \quad \frac{\partial \vartheta}{\partial \theta} = Rg \frac{\partial f}{\partial \theta} \quad \frac{\partial^2 \vartheta}{\partial \phi^2} = Rf \frac{\partial^2 g}{\partial \phi^2}$$

This will indeed work and yield a very elegant solution.

The Schrödinger Equation for Hydrogen using a separable solution

Start with Schrödinger's Equation and $\vartheta(r, \theta, \phi) = R(r)f(\theta)g(\phi)$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \vartheta}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \vartheta}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \vartheta}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V(r)) \vartheta = 0$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \vartheta}{\partial r} \right) = \frac{f(\theta)g(\phi)}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right)$$

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \vartheta}{\partial \theta} \right) = \frac{R(r)g(\phi)}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right)$$

$$\frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \vartheta}{\partial \phi^2} = \frac{R(r)f(\theta)}{r^2 \sin^2 \theta} \frac{\partial^2 g(\phi)}{\partial \phi^2}$$

$$\frac{2\mu}{\hbar^2} (E - V(r)) \vartheta = \frac{2\mu}{\hbar^2} (E - V(r)) R(r) f(\theta) g(\phi)$$

The Schrödinger Equation for central potential using a separable solution

Multiplying each term by $-\frac{r^2 \sin^2 \theta}{R(r)f(\theta)g(\phi)}$ and rewriting the equation, one finds:

$$-\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{\sin \theta}{f(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) - \frac{2\mu}{\hbar^2} \sin^2 \theta r^2 (E - V(r)) = \frac{1}{g(\phi)} \frac{\partial^2 g}{\partial \phi^2}$$

The RHS depends only on ϕ , while the LHS is independent of ϕ . Therefore, each side should be equal to a constant. We denote the constant as $-m_l^2$.

The Schrödinger Equation for central potential using a separable solution

The azimuthal equation is:

$$\frac{\partial^2 g(\phi)}{\partial \phi^2} = -m_l^2 g(\phi) \quad \text{Azimuthal equation}$$

We chose the solution to be:

$$g(\phi) = e^{im_l \phi}$$

The equation is satisfied by any value of m_l but in order for the solution to be single valued we have to request:

$$g(\phi) = g(\phi + 2n\pi) \Rightarrow e^{im_l \phi} = e^{im_l(\phi+2n\pi)} \Rightarrow e^{im_l(2n\pi)} = 1 \Rightarrow m_l \in \text{Integers}$$

$$m_l = 0, \pm 1, \pm 2, \dots$$

Solution of the Schrödinger Equation for central potential

$$-\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{\sin \theta}{f(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) - \frac{2\mu}{\hbar^2} \sin^2 \theta r^2 (E - V(r)) = \frac{1}{g(\phi)} \frac{\partial^2 g}{\partial \phi^2}$$

➤ Now set the RHS to $-m_l^2 = \frac{1}{g(\phi)} \frac{\partial^2 g}{\partial \phi^2}$

$$-\frac{\sin^2 \theta}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{\sin \theta}{f(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) - \frac{2\mu}{\hbar^2} \sin^2 \theta r^2 (E - V(r)) = -m_l^2$$

➤ Rearranging and dividing by $-\sin^2 \theta$:

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu}{\hbar^2} r^2 (E - V(r)) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{f(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right)$$

➤ Now, the LHS depends only on r , and the RHS depends only on θ . We can use the same method again since they are independent of each other!

Solution of the Schrödinger Equation for central force

$$\vartheta(r, \theta, \phi) = R(r)f(\theta)g(\phi)$$

$$\frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu}{\hbar^2} r^2 (E - V(r)) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{f(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right)$$

► Set each side equal to the constant $l(l + 1)$.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu}{\hbar^2} \left(E - V(r) - \frac{\hbar^2 l(l + 1)}{2\mu r^2} \right) R(r) = 0$$

Radial equation

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \left(l(l + 1) - \frac{m_l^2}{\sin^2 \theta} \right) f(\theta) = 0$$

Angular equation

$$\frac{\partial^2 g(\phi)}{\partial \phi^2} = -m_l^2 g(\phi) \Rightarrow g(\phi) = e^{im_l \phi}$$

Azimuthal equation

Therefore, we've separated the Schrödinger equation into three ordinary second-order differential equations, each containing only one variable.

Solution of the Radial Equation for H

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] R = 0 \quad \text{with} \quad V(r) = -\frac{e^2}{r}$$

► This radial equation is called the associated Laguerre equation and the solutions R are called associated Laguerre functions. There are infinitely many of them, for integer values of $n = 1, 2, 3, \dots$

► **Assume that the ground state has $n = 1$ and $l = 0$. Let's find this solution.**

► The radial equation becomes:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_{10}}{dr} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] R_{10} = 0$$

Solution of the Radial Equation for H

- The derivative of $r^2 \frac{dR}{dr}$ yields two terms:

$$\frac{d^2 R_{10}}{dr^2} + \frac{2}{r} \frac{dR_{10}}{dr} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{r} \right] R_{10} = 0$$

In which we have also inserted $V(r) = -\frac{e^2}{r}$ (note that for a nucleus with more than one proton we would just multiply the potential by Z , the total charge in units of e).

Solution of the Radial Equation for H

- Try a solution of the form $R_{10}(r) = Ae^{-\frac{r}{a_0}}$
- A is a normalization constant.
- a_0 is a constant with the dimension of length.
- Take first and second derivatives of R_{10} and insert into the radial equation.



- $$\frac{d^2 R_{10}}{dr^2} + \frac{2}{r} \frac{dR_{10}}{dr} + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{r} \right) R_{10} = 0 \Rightarrow \left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2} E \right) + \left(\frac{2\mu e^2}{\hbar^2} - \frac{2}{a_0} \right) \frac{1}{r} = 0$$

- To satisfy this equation for any r , both expressions in parentheses must be zero.

Solution of the Radial Equation for H

- Set the second expression equal to zero and solve for a_0 :

$$\left(\frac{2\mu e^2}{\hbar^2} - \frac{2}{a_0}\right) = 0 \Rightarrow a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.53\text{\AA} \quad \left(\text{in Bohr's model, } r_0 = \frac{\hbar^2}{m_e e^2}\right)$$

- Set the first expression equal to zero and solve for E :

$$\left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2} E\right) = 0 \Rightarrow E = -\frac{\hbar^2}{2\mu a_0^2} = -\frac{\mu e^4}{2\hbar^2} = -E_0 = -13.6\text{eV}$$

- The normalization is by

$$\int_0^\infty r^2 |R_{10}(r)|^2 dr = 1 \Rightarrow R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}}$$

Principal Quantum Number n

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] R = 0 \quad \text{General } l$$

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{r} \right) R \quad l = 0$$

- ▶ There are many solutions to the radial wave equation for $l = 0$, one for each positive integer, n .
- ▶ The result for the quantized energy is:

$$E_n = -\frac{\mu e^4}{2\hbar^2} \frac{1}{n^2} = -\frac{E_0}{n^2}$$

A negative energy means that the electron and proton are bound together as in the Bohr's model results.

The energy is independent of the quantum numbers l and m_l

Hydrogen Atom Radial Wave Functions

First few radial wave functions $R_{n\ell}$.

Subscripts on R specify the values of n and ℓ .

$$\int_0^{\infty} r^2 R_{n\ell}^*(r) R_{n\ell}(r) dr = 1$$

The radial wavefunctions are normalized, but they are not orthogonal. The orthogonality for the set of complete *w.f.*'s is contained in the angular part (i.e., the $Y_{\ell,m}(\theta, \phi)$).

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

Thornton and Rex, "Modern physics for scientists and engineers" Chapter 7.

Solution of the Angular and Azimuthal Equations

- ▶ The solutions to the azimuthal equation are: $g(\phi) = e^{im_l\phi}$
- ▶ Solutions to the angular and azimuthal equations are linked because both have m_l .

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta} \right) f(\theta) = 0$$

Angular equation

The angular equation is well known in the theory of differential equations as the associated Legendre equation whose solutions Y_{l,m_l} are listed on the next slide for various l and m_l . The $f(\theta)$ part of the $Y(\theta, \phi)$ is always a polynomial function of $\sin\theta$ and $\cos\theta$ of order l .

$Y_{l,m_l}(\theta, \phi) = f(\theta)g(\phi)$ are the so-called Spherical Harmonics and they form an orthonormal set:

$$\int_0^{2\pi} \int_0^\pi Y_{l_1,m_1}^*(\theta, \phi) Y_{l_2,m_2}(\theta, \phi) \sin\theta d\theta d\phi = \delta_{l_1,l_2} \delta_{m_1,m_2}$$

Normalized Spherical Harmonics

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta$
1	± 1	$\mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1)$
2	± 1	$\mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	± 2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$
3	± 1	$\mp \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
3	± 2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
3	± 3	$\mp \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \theta e^{\pm 3i\phi}$

Take sums and differences of $Y_{\ell m}$ for a particular ℓ to form an equivalent orthonormal basis set.



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

$$\ell = 1 \left\{ \begin{aligned} Y_{p_x} &= \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \cos \phi \\ Y_{p_y} &= \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \sin \phi \\ Y_{p_z} &= \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta \end{aligned}$$

$$\ell = 2 \left\{ \begin{aligned} Y_{d_{z^2}} &= \left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1) \\ Y_{d_{xz}} &= \left(\frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \cos \phi \\ Y_{d_{yz}} &= \left(\frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \sin \phi \\ Y_{d_{xy}} &= \left(\frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \sin 2\phi \\ Y_{d_{x^2-y^2}} &= \left(\frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \cos 2\phi \end{aligned}$$

Quantum Numbers and their names

- ▶ The three quantum numbers:
 - ▶ n : Principal quantum number
 - ▶ l : Orbital angular momentum quantum number
 - ▶ m_l : Magnetic (azimuthal) quantum number
- ▶ The restrictions for the quantum numbers:
 - ▶ $n = 1, 2, 3, 4, \dots$
 - ▶ $l = 0, 1, 2, 3, \dots, n - 1$
 - ▶ $m_l = -l, -l + 1, \dots, 0, 1, \dots, l - 1, l$

▶ Equivalently:

- ▶ $n > 0$
- ▶ $l < n$
- ▶ $|m_l| \leq l$

The energy levels are:

$$E_n = -\frac{\mu e^4}{2 \hbar n^2} = -\frac{E_0}{n^2} \approx -\frac{13.6\text{eV}}{n^2}$$

Orbital Angular Momentum Quantum Number l

▶ Energy levels are **degenerate** with respect to l (the energy is independent of l).

▶ Physicists use letter names for the various l values:

$l = \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \dots$

Letter = $s \quad p \quad d \quad f \quad g \quad h \dots$

▶ Atomic states are usually referred to by their values of n and l .

▶ A state with $n = 2$ and $l = 1$ is called a $2p$ state.

Probability density function

The radial function $R_{n,l}(r)$ and the spherical harmonics $Y_{l,m_l}(\theta, \phi)$ determine the probability density for the various quantum states. The total wave function $\vartheta_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m_l}(\theta, \phi)$ depends on n , l , and m_l .

- We use the wave functions to calculate the probability distributions of the electrons.
- The “position” of the electron is spread over space and is not well defined.
- We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element

$d\tau = r^2 \sin\theta dr d\theta d\phi$ is:

$$dP = \vartheta_{n,l,m_l}^*(r, \theta, \phi) \vartheta_{n,l,m_l}(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi$$

Probability density function

- $R_{n,l}^*(r)R_{n,l}(r)r^2 dr =$ probability of finding the electron at distance r within dr (the distance is between the electron and the nucleus).
- $Y_{l,m_l}^*(\theta, \phi)Y_{l,m_l}(\theta, \phi)\sin\theta d\theta d\phi =$ probability of finding an electron at θ and ϕ within $d\theta$ and $d\phi$.
- $\int_{\theta_1}^{\theta_2} \int_{\phi_1}^{\phi_2} |Y_{l,m_l}(\theta, \phi)|^2 \sin\theta d\theta d\phi =$ probability of finding an electron within the limits $\theta_1 \leq \theta \leq \theta_2$ and $\phi_1 \leq \phi \leq \phi_2$.