

Hydrogenic Atom - time-independent Schrödinger Equation

$$\frac{\partial^2 F}{\partial x^2} = \frac{1}{v_{ph}^2} \frac{\partial^2 F}{\partial t^2}$$

This is a wave equation. Let the wave function $F(x,t)$ be separable...

$$F(x,t) = \psi(x) f(t) \quad \text{where } f(t) = e^{-i\omega t}$$

$$\text{Then } \frac{\partial^2 F}{\partial x^2} = \frac{\partial^2 \psi(x)}{\partial x^2} f(t)$$

$$\text{and } \frac{\partial^2 F}{\partial t^2} = \psi(x) \frac{\partial^2 f}{\partial t^2} = -\omega^2 \psi(x) f(t)$$

$$\text{So } \frac{\partial^2 \psi}{\partial x^2} = -\frac{\omega^2}{v_{ph}^2} \psi(x) \quad \text{where } v_{ph} = \frac{\omega}{k}$$

$$\text{Since } k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = p/\hbar$$

$$\frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{p}{\hbar}\right)^2 \psi(x)$$

Consider a non-relativistic system with constant energy that is bound. Then, for a one-dimensional system,

$$E = V(x) + K = V(x) + p^2/2m$$

$$\text{or } p^2 = 2m(E - V(x))$$

$$\text{Then } \frac{\hbar^2}{2m(E-V)} \frac{\partial^2 \psi}{\partial x^2} + \psi = 0$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + (E - V(x)) \psi = 0$$

In three dimensions

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V(x,y,z) \psi = E \psi}$$

For a central force law, the potential function V is spherically symmetric, that is, $V(r) = -Ze^2/r$.
In spherical coordinates

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

There are spherically symmetric solutions that can be found using only the first (radial) term in $\nabla^2 \psi$

$$\nabla^2 \psi = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) = \frac{1}{r} \frac{\partial}{\partial r} \left[\psi + r \frac{d\psi}{dr} \right] = \frac{d^2 \psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr}$$

The spherically symmetric (radial) part of the Schrödinger Eq. is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dr^2} - \frac{\hbar^2}{m} \frac{1}{r} \frac{d\psi}{dr} - \frac{Ze^2}{r} \psi = E \psi$$

Guess a solution of the form $\psi(r) = e^{-r/a}$.
Then

$$-\frac{\hbar^2}{2ma^2} \psi + \frac{\hbar^2}{ma} \frac{\psi}{r} - \frac{Ze^2}{r} \psi = E \psi$$

Terms in $1/r$ must cancel, so $\frac{\hbar^2}{ma} = Ze^2$

$a = \frac{1}{Zm} \left(\frac{\hbar}{e} \right)^2$ If $Z=1$, "a" is the Bohr radius, 0.529 Å.

The constant terms must be equal, so

$$E = \frac{-\hbar^2}{2ma^2} = -\frac{Z^2 m e^4}{2\hbar^2} \quad \text{is the energy of the first Bohr orbit (ground state)}$$

The wave function is normalized so that the probability of finding the electron at a particular position is ψ^2 and

$$\int_0^{\infty} \psi^2(r) 4\pi r^2 dr = 1$$

Let the ground-state wave function be

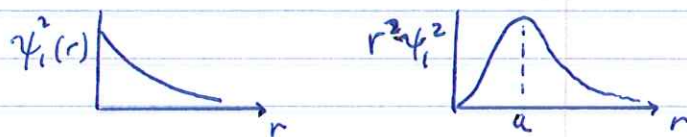
$$\Psi_1(r) = A_1 e^{-r/a}$$

$$\text{Then } 4\pi A_1^2 \int_0^{\infty} r^2 e^{-(2r/a)} dr = 1$$

The integral is $a^3/4$, so $A_1 = \frac{1}{\sqrt{\pi a^3}}$

The most probable place to find the electron is at the nucleus ($r=0$), but the most probable radius is found by maximizing the function

$$\Psi_1^2(r) 4\pi r^2 dr =$$



which is the probability of finding the electron at radius r to $r+dr$.

$$\frac{d}{dr} [r^2 e^{-2r/a}] = 2r e^{-2r/a} - \frac{2r^2}{a} e^{-2r/a} = 0$$

Therefore, $r=a$ is the most probable radius.

The most general wave functions of the hydrogenic atom are not spherically symmetric. They are

$$\Psi_{n\ell m}(r, \theta, \phi) = \underbrace{R_{n\ell}(r)}_{\text{real}} \underbrace{Y_{\ell m}(\theta, \phi)}_{\text{spherical harmonics}} e^{im\phi}$$

For each value of n , $\ell = 0, 1, \dots, n-1$ (n types)

For each value of ℓ , $m = 0, \pm 1, \dots, \pm \ell$ ($2\ell+1$ types)

The number of states (different wave functions) for each principal quantum number n is

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

$R_{nl}(r)$

n	l=0	l=1	l=2
1	$e^{-r/a}$
2	$\left(1 - \frac{r}{2a}\right) e^{-r/2a}$	$\frac{r}{a} e^{-r/2a}$...
3	$\left[1 - \frac{2r}{3a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right] e^{-r/3a}$	$\frac{r}{a} \left(1 - \frac{r}{6a}\right) e^{-r/3a}$	$\left(\frac{r}{a}\right)^2 e^{-r/3a}$

 $Y_{lm}(\theta, \phi)$

l	m		l	m	
0	0	$\frac{1}{\sqrt{4\pi}}$	2	0	$\sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
1	0	$\sqrt{\frac{3}{4\pi}} \cos\theta$	2	± 1	$\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{\pm i\phi}$
1	± 1	$\sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$	2	± 2	$\sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi}$

Y_{lm} are normalized so that $\iint |Y_{lm}|^2 \sin\theta d\theta d\phi = 1$

$P_{lm}(\mu)$ is the associated Legendre polynomial, where $\mu = \cos\theta$,

$$P_{lm}(\mu) = (1-\mu^2)^{m/2} \frac{d^m}{d\mu^m} P_l(\mu) \leftarrow \text{Legendre polynomial}$$

Note that $Y_{lm} = \text{constant}$ only for $l=0$, so the spherically symmetric solutions are

$$\psi_{n00} = R_{n0}(r)$$

Also $Y_{lm} = P_l(\cos\theta)$ only if $m=0$. You can see why m must be an integer; for ψ to be single valued as a function of ϕ

$$e^{im(\phi+2\pi)} = e^{im\phi}$$

$$e^{2\pi im} = 1$$

$$\cos(2\pi m) + i \sin(2\pi m) = 1 \Rightarrow m = 0, \pm 1, \dots$$

Momentum and Angular Momentum Operators

Writing the Schrödinger Equation as an operator on the wave function

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

or $H\psi = E\psi$, where H is the Hamiltonian, or energy operator. Operating on the wave function, H gives the energy of the state times the wave function.

Similarly, there is a momentum operator, $-i\hbar\nabla$, so that

$$-i\hbar\nabla\psi = \vec{p}\psi$$

We can write the components of the momentum operator

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

For a free particle $\psi_x \propto e^{ik_x x}$, so $p_x = \hbar k_x$, etc... We can define angular momentum operators from

$$\tilde{L} = \tilde{r} \times \tilde{p}$$

The position operator \tilde{r} is the position itself, with components x, y, z .

$$\begin{aligned} \tilde{L}_x &= y \tilde{p}_z - z \tilde{p}_y \\ \tilde{L}_y &= z \tilde{p}_x - x \tilde{p}_z \\ \tilde{L}_z &= x \tilde{p}_y - y \tilde{p}_x \end{aligned}$$

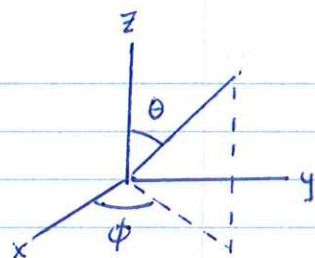
$$\tilde{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

or
$$\tilde{L}_x = \frac{\hbar}{i} \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \quad \text{in spherical coordinates}$$

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

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

The conversion of angular momentum operators from cartesian coordinates to spherical coordinates is tedious, and requires transforming the partial derivatives. For example, \tilde{L}_z :



$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$

$$\frac{\partial \psi}{\partial \phi} = \frac{\partial \psi}{\partial x} \frac{\partial x}{\partial \phi} + \frac{\partial \psi}{\partial y} \frac{\partial y}{\partial \phi} + \frac{\partial \psi}{\partial z} \frac{\partial z}{\partial \phi}$$

$$\frac{\partial \psi}{\partial \phi} = -r \sin \theta \sin \phi \frac{\partial \psi}{\partial x} + r \sin \theta \cos \phi \frac{\partial \psi}{\partial y}$$

$$\frac{\partial \psi}{\partial \phi} = -y \frac{\partial \psi}{\partial x} + x \frac{\partial \psi}{\partial y}$$

$$\Rightarrow \tilde{L}_z = -i\hbar \frac{\partial}{\partial \phi} = x \tilde{p}_y - y \tilde{p}_x \quad \left(\begin{array}{l} \text{The conversion of } \tilde{L}_x \text{ and} \\ \tilde{L}_y \text{ are more involved.} \end{array} \right)$$

The operator for the square of the total angular momentum can be written as

$$\begin{aligned}\tilde{L}^2 &= \tilde{L}_x \cdot \tilde{L}_x + \tilde{L}_y \cdot \tilde{L}_y + \tilde{L}_z \cdot \tilde{L}_z \\ &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]\end{aligned}$$

The notation $\tilde{L}_x \cdot \tilde{L}_x$ means operate on the wave function with \tilde{L}_x , then operate on the result with \tilde{L}_x .

That is,

$$\tilde{L}_x (\tilde{L}_x \psi)$$

When \tilde{L}^2 is applied to the wave function the result is

$$L^2 = l(l+1)\hbar^2 \quad \text{for the square of the total } L.$$

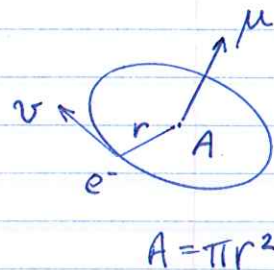
The z-component operator \tilde{L}_z gives simply

$$L_z = m\hbar$$

Why "m" is called the magnetic quantum number.

Consider the orbiting electron to be a current loop. It acts like a magnetic dipole with magnetic moment

$$\mu = \frac{IA}{c}$$



$$A = \pi r^2$$

The current is $I = \frac{-ev}{2\pi r}$

$$\text{So } \mu = \frac{-evA}{2\pi r c} = \frac{-evr}{2c}$$

But $\vec{L} = m\vec{r} \times \vec{v}$, so $\boxed{\vec{\mu} = \frac{-e}{2mc} \vec{L}}$

If an external magnetic field is applied, there will be a potential energy of

$$\boxed{\Delta E = -\vec{\mu} \cdot \vec{B}}$$

If the direction of the external B-field is chosen as z, then

$$\Delta E = \frac{e}{2mc} L_z B = \frac{e}{2mc} m_l \hbar B$$

(using here m_l as the magnetic quantum number, to distinguish it from m , the mass of the electron.)

So $\boxed{\Delta E = m_l \mu_B B}$, where $\mu_B = \frac{e\hbar}{2mc} = 9.27 \times 10^{-21} \frac{\text{erg}}{\text{G}}$

This is Zeeman splitting:

the "Bohr magneton"



Quantization of Angular Momentum (l, m)

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

$$L^2 = \ell(\ell+1) \hbar^2$$

Total angular momentum

$$L_z = m\hbar$$

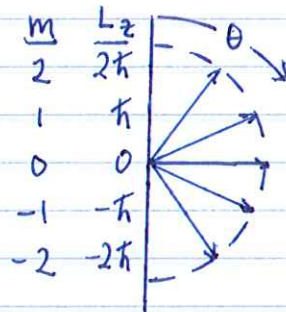
z-component

$Y_{\ell m}(\theta, \phi)$ is a constant only if $\ell=0$. Spherically symmetric states have zero angular momentum. For $\ell > 0$ the direction of angular momentum is quantized, in the sense that L_z is quantized.

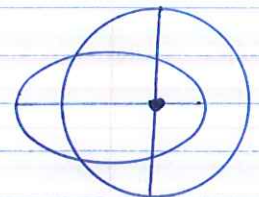
Example: $\ell=2$, $L = \sqrt{6} \hbar$

$$\sqrt{\ell(\ell+1)} \hbar \cos \theta = m\hbar$$

$$\cos \theta = m/\sqrt{6}$$



1. There are $2\ell+1$ values of m because L_z cannot exceed L .
2. L and L_z can be measured, but then the x and y components of L are unknown.
3. L is never equal to L_z because then the direction of L could be known.
4. This is similar to the uncertainty principle for position and momentum, except that L can be exactly zero.
5. ℓ is less than or equal to $n-1$. This can be understood according to a classical argument in which orbits with the same semimajor axis have the same energy E but different angular momentum L .
A circular orbit has maximum L .
A linear orbit has zero L .
The total energy of a circular orbit is $E = V + K = -K$, where ...



$$V = -\frac{Ze^2}{r}, \quad K = \frac{Ze^2}{2r} = -E$$

$$L_{\max}^2 = (mvr)^2 = 2mr^2K = 2m \frac{Z^2 e^4}{4K^2} K = \frac{m Z^2 e^4}{2|E|}$$

$$\text{So } 0 \leq L^2 \leq \frac{Z^2 m e^4}{2|E|}$$

But the quantized energy levels of the hydrogenic atom are:

$$E_n = \frac{Z^2 m e^4}{2\hbar^2} \frac{1}{n^2}, \quad \text{therefore } 0 \leq L^2 \leq (n\hbar)^2$$

$$\text{If } L^2 = l(l+1)\hbar^2, \quad \text{then } 0 \leq l(l+1) \leq n^2$$

$$\text{and } l \leq n-1$$

6. m is an integer because the wave function must be single-valued. (see page 158)

7. There is nothing special about the z -axis. Consider the states $l=1, m = -1, 0, +1$.

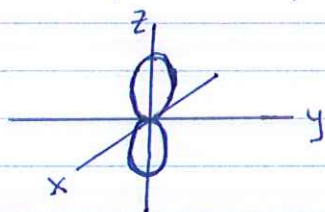
$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1,0} Y_{1,0}^* = \frac{3}{4\pi} \cos^2 \theta$$

$$Y_{1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

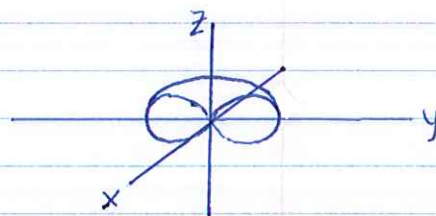
$$Y_{1,\pm 1} Y_{1,\pm 1}^* = \frac{3}{8\pi} \sin^2 \theta$$

Probability density is proportional to $Y Y^*$.



$$(l, m) = (1, 0)$$

"dumbbell"



$$(l, m) = (1, \pm 1)$$

"donut (torus)"

The sum of the probabilities of the three states is a constant

$$Y_{1,0} Y_{1,0}^* + Y_{1,1} Y_{1,1}^* + Y_{1,-1} Y_{1,-1}^* \\ = \frac{3}{4\pi} \cos^2\theta + \frac{3}{8\pi} \sin^2\theta + \frac{3}{8\pi} \sin^2\theta = 1$$

Also, since linear combinations of wavefunctions are allowed states, you can make a dumbbell shaped wave function along another axis, e.g., the x-axis, by using:

$$\frac{Y_{1,1} + Y_{1,-1}}{\sqrt{2}} = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi$$

Interpretation of the Radial wave functions

1. For any value of n , only wavefunctions with $l=0$ are non-zero at the origin. All others are zero at the origin. This is because only a particle with zero angular momentum can be at the origin.
2. For any value of n , the wave function with the largest value of l is the simplest, in the sense that it has one maximum, no nodes, and it also has one maximum in the radial probability distribution $r^2 R_{n,l}^2$.

$$R_{n,n-1} = \left(\frac{r}{a}\right)^{n-1} e^{-r/na}$$

The most likely value of r when $l=n-1$ is an^2

3. For smaller values of l , the electron goes both closer and farther from the nucleus than a state with large l . This is analogous to elliptical orbits.