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Modern physics

6. Hydrogen atom in quantum mechanics



Outline

- 6.1. Hydrogen atom in quantum mechanics
- 6.2. Angular momentum and magnetic dipole moment
- 6.3. Electron spin

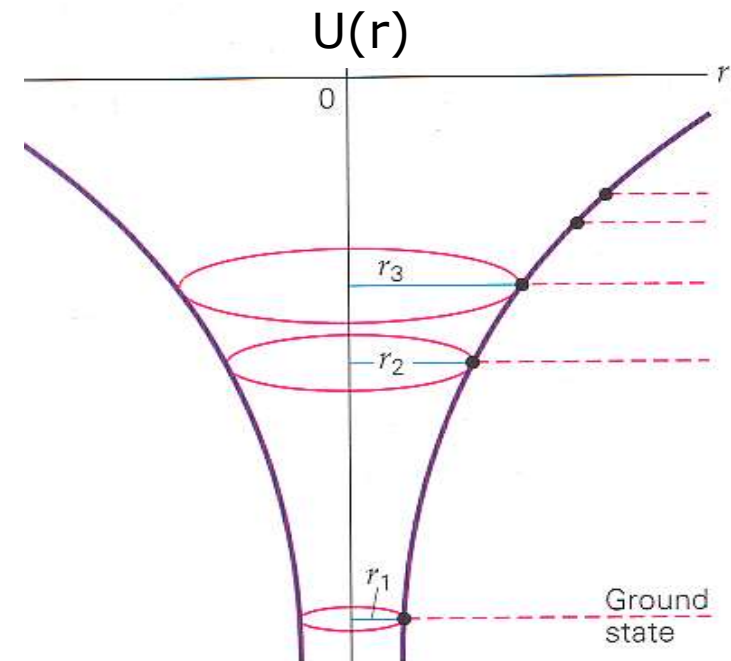
6.1. Hydrogen atom in quantum mechanics

Three-dimensional potential well of hydrogen atom is more complex than those treated previously (e.g. rectangular box). The potential energy $U(r)$ results from Coulomb interaction between a single electron and proton in nucleus.

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

This potential well does not have sharply defined walls. The potential is the only function of radial distance r . It means this is central potential

Amazingly, solving the Schrödinger equation for hydrogen atom, we will find the energy values are given by the same formula as that resulting from the (incorrect) Bohr model



$$r_n = 0.0529 \times n^2 \text{ [nm]}$$

$$E_n = -13.6/n^2 \text{ [eV]}$$

6.1. Hydrogen atom in quantum mechanics

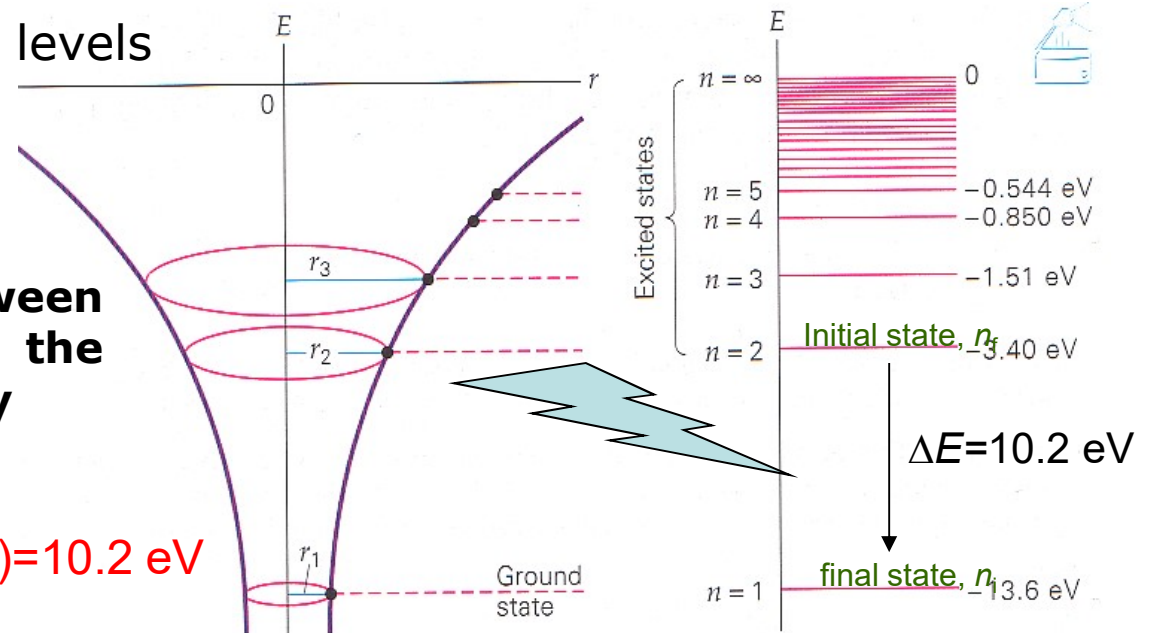
Therefore, the changes in the energy due to emission or absorption of light and the wavelengths for Balmer, Paschen, Lyman, etc. series will be correctly described by the same expressions as those derived from the Bohr model.

Energy difference between the levels

$$\Delta E = 13.6 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

For example, transition between $n_i=2$ and $n_f=1$ (as drawn in the picture) will release the energy

$$\Delta E = 13.6 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 13.6 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 10.2 \text{ eV}$$



6.1. Hydrogen atom in quantum mechanics

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, angular momentum does not vary with time

We expect that in quantum mechanics, the **angular momentum will be conserved** as well.

Schrödinger equation can be written for such potential:

$$-\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \psi(\vec{\mathbf{r}}) - \frac{e^2}{4\pi\epsilon_0 r} \psi(\vec{\mathbf{r}}) = E\psi(\vec{\mathbf{r}})$$

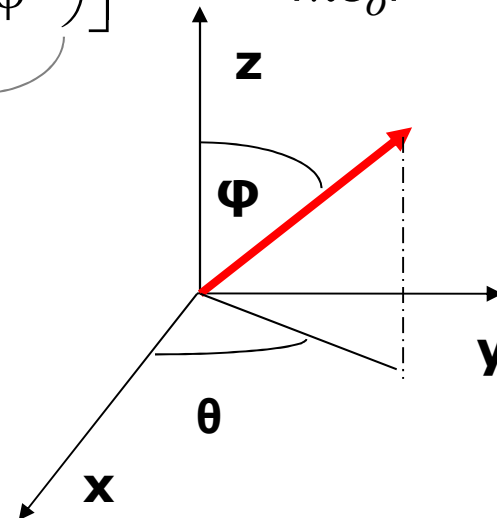
To solve it we need to change the variables from the Cartesian coordinates (x,y,z) to spherical ones (r,θ,φ) where θ is the polar angle and φ is the azimuthal angle.

6.1. Hydrogen atom in quantum mechanics

In spherical coordinates the time-independent Schrödinger equation takes a very complicated form (!):

$$-\frac{\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \right] \psi(\vec{r}) - \frac{e^2}{4\pi\epsilon_0 r} \psi(\vec{r}) = E\psi(\vec{r})$$

Laplacian in spherical coordinates



This complicated partial differential equation can be reduced to a set of one-dimensional differential equations in θ and φ that can be solved directly, without the need of introducing Coulomb potential because the potential does not depend on orientation (angles: θ , φ)

6.1. Hydrogen atom in quantum mechanics

We can use the same technique as before, separation of variables:

$$\underbrace{\psi(\vec{r}) = R(r)Y(\theta, \varphi)}_{\text{trial solution}}$$

We will refer to $R(r)$ as the **radial wave function** and $Y(\theta, \varphi)$ is known as a **spherical harmonic**.

Further on, we can separate θ and φ by assuming:

$$Y(\theta, \varphi) = F(\theta)\Phi(\varphi)$$

6.1. Hydrogen atom in quantum mechanics

Finally we get a set of three separated equations to solve: $\lambda = -\ell(\ell + 1)$

$$\underbrace{-\frac{\hbar^2}{2m_e} \left(\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + \lambda \frac{R(r)}{r^2} \right) - \frac{e^2}{4\pi\epsilon_0 r} R(r)}_{\text{ordinary differential eigenvalue equation for radial function } R(r)} = ER(r)$$

ordinary differential eigenvalue equation for radial function $R(r)$ with energy E as the eigenvalue

Each of these equations is an ordinary differential equation, involving single variables, θ and φ . They are easily solved even without the knowledge of the potential because the potential does not appear here.

$$\left\{ \begin{array}{l} \frac{d^2 F(\theta)}{d\theta^2} + \cot \theta \frac{dF(\theta)}{d\theta} - \frac{m_\ell^2}{\sin^2 \theta} F(\theta) = \lambda F(\theta) \\ \frac{d^2 \Phi(\varphi)}{d\varphi^2} = -m_l^2 \Phi(\varphi) \end{array} \right.$$

m_ℓ^2 and λ are the „separation“ constants related to quantum numbers



6.1. Hydrogen atom in quantum mechanics

Quantum numbers for the hydrogen atom

Although the energies of the hydrogen atom states can be described by the single quantum number n , the wave functions describing these states require **three quantum numbers**, corresponding to the three dimensions of the space in which electron can move.

Each set of quantum numbers (n, ℓ, m_ℓ) identifies the wave function of a particular quantum state.

Quantum number n , called the **principal quantum number** appears in the expression for the energy of the state

Quantum number ℓ , called the **orbital quantum number**, is a measure of the magnitude of the angular momentum associated with the quantum state

Quantum number m_ℓ called the **orbital magnetic quantum number** is related to the orientation in space of the angular momentum vector

6.1. Hydrogen atom in quantum mechanics

Symbol	Name	Allowed values
n	<i>Principal quantum number</i>	1,2,3...
ℓ	<i>Orbital quantum number</i>	0,1,2,3,...,n-1
m_ℓ	<i>Orbital magnetic quantum number</i>	$-\ell, -(\ell-1), \dots, +(\ell-1), +\ell$

The restrictions on the values of the quantum numbers for hydrogen atom are not arbitrary but come out of the solution to Schrödinger equation.

Example: for the ground state ($n=1$), $\ell=0$, $m_\ell=0$ (there is no other possibility).

The hydrogen atom in its ground state has zero angular momentum which is not predicted by Bohr model.

$$L=n\hbar, \text{ for } n=1,2,3\dots \text{ in Bohr model}$$

6.1. Hydrogen atom in quantum mechanics

Solutions of the time-independent Schrödinger equation - wave functions of the hydrogen atom

Spherical harmonics Y_{lm}

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{11} = \sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\varphi)$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(2i\varphi)$$

Radial eigenfunctions R_{nl}

$$R_{10} = \frac{2}{a^{3/2}} e^{-r/a} \quad \text{ground state}$$

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

$$R_{21} = \frac{1}{\sqrt{3}} \frac{1}{(2a)^{3/2}} \frac{r}{a} e^{-r/2a}$$

a is the Bohr radius $a = \frac{4\pi\hbar^2}{m_e e^2}$

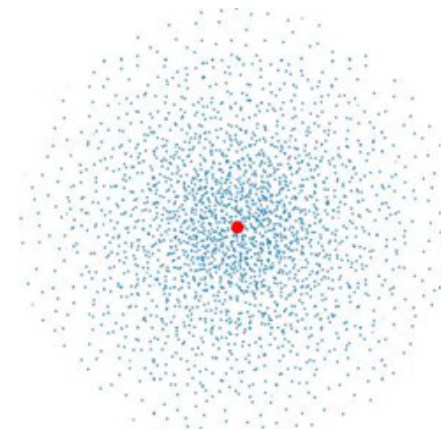
However, these functions do not have any physical meaning. We are interested in the probability density of finding an electron, i.e. $|\psi|^2$

6.1. Hydrogen atom in quantum mechanics

The Bohr idea that electrons in atoms follow well-defined orbits like planets moving around the Sun, is incorrect.

„Dot plot” suggests the probabilistic nature of the wave function and provides a useful mental model of the hydrogen atom in different states.

orbital 1s, volume probability density for the **ground state** of the hydrogen atom



$$|R_{10}(r)|^2$$

$$n = 1$$

$|R_{n\ell}(r)|^2 r^2 dr$ = probability of finding an electron within a gap of width dr about the radial distance r

$|Y_{\ell m}(\theta, \varphi)|^2 \sin \theta d\theta d\varphi$ = probability of finding an electron within an area $d\theta d\varphi$ about the angular location (θ, φ)

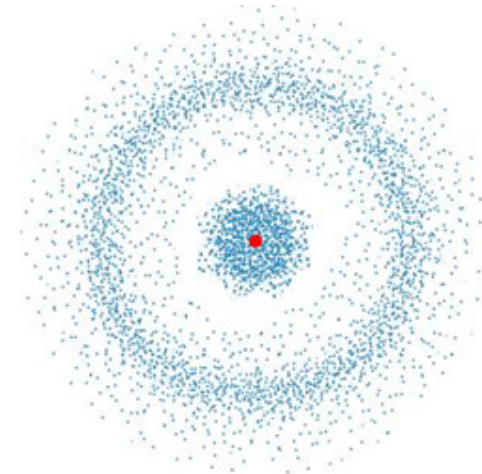
6.1. Hydrogen atom in quantum mechanics

Hydrogen atom states with $n=2$

There are four states of the hydrogen atom with $n=2$.

n	ℓ	m_ℓ
2	0	0
2	1	+1
2	1	0
2	1	-1

All quantum states with $\ell=0$ have spherically symmetric wave functions. If $\ell=0$, the angular momentum is zero, which requires that there is no preferred axis of symmetry for the probability density

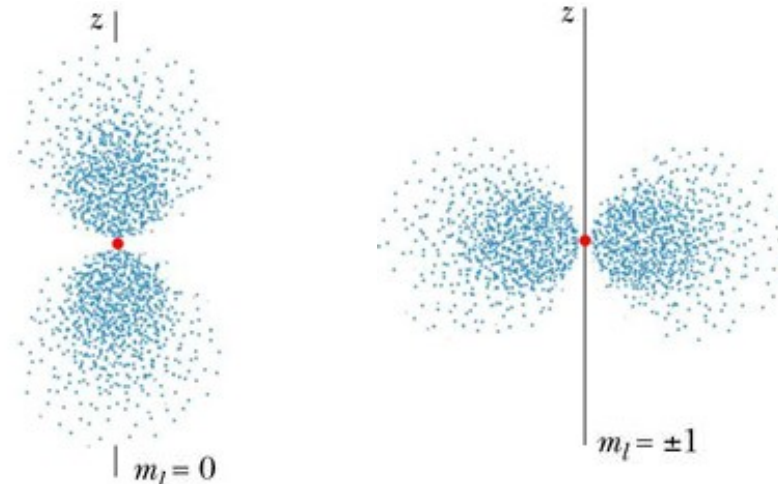


orbital 2s, volume probability density for the hydrogen atom in the quantum state with $n=2$, $\ell=0$, $m_\ell=0$; the gap in the dot density pattern marks a spherical surface over which the radial wave function is zero

6.1. Hydrogen atom in quantum mechanics

Three states of the hydrogen atom with $n=2$, $\ell=1$.

n	ℓ	m_ℓ
2	0	0
2	1	+1
2	1	0
2	1	-1



These plots are symmetric about z axis but they are not spherically symmetric. The probability densities for these three states are functions of r and the angular coordinate θ

What is there about the hydrogen atom that establishes the axis of symmetry?

orbitals $2p$, volume probability density for the hydrogen atom in the quantum state with $n=2$, $\ell=1$ and three different m_ℓ Probability density is symmetric about z axis

6.1. Hydrogen atom in quantum mechanics

Energy eigenvalues for hydrogen

The possible values of energy – the eigenvalues – that emerge from the radial Schrödinger equation

$$-\frac{\hbar^2}{2m_e} \left(\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + \lambda \frac{R(r)}{r^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r} R(r) = ER(r)$$

Z-atomic number (Z=1 for hydrogen)

are given by

$$E = -\frac{1}{2} m_e \left(\frac{Ze^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{(n_r + \ell + 1)^2}$$

where n_r is the new **radial quantum number**, $n_r=0,1,2..$

Principal quantum number n defined as

$$n \equiv n_r + \ell + 1$$

is always a positive integer

6.1. Hydrogen atom in quantum mechanics

Energy eigenvalues for hydrogen

In terms of the principal quantum number n ,

$$E = -\frac{1}{2} m_e c^2 (Z\alpha)^2 \frac{1}{n^2}$$

where $\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$ is fine-structure constant

This is exactly the form the bound-state energies take in the Bohr model

As the energy depends on n only, n^2 states have the same energy; we have n^2 degeneracy for hydrogen atom (electrons have spin which means that in fact the degeneracy is $2n^2$)

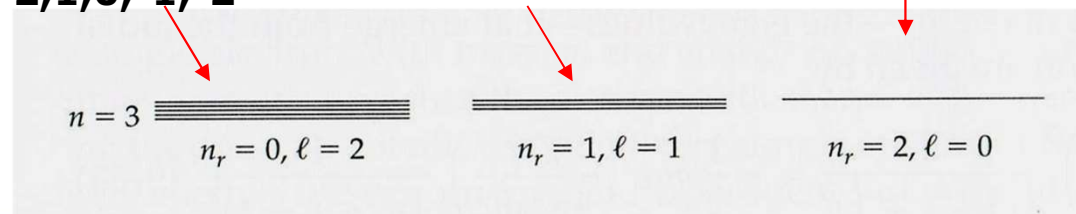
Example: for $n=3$

corresponds to five states
 $R_{32}(r)Y_{2m}(\theta,\varphi)$
 with $m=2,1,0,-1,-2$

corresponds to three states
 $R_{31}(r)Y_{1m}(\theta,\varphi)$
 with $m=1,0,-1$

corresponds to one state
 $R_{30}(r)Y_{00}(\theta,\varphi)$

Thus, there are a total of $5+3+1=9=3^2$ degenerate states with energy corresponding to $n=3$

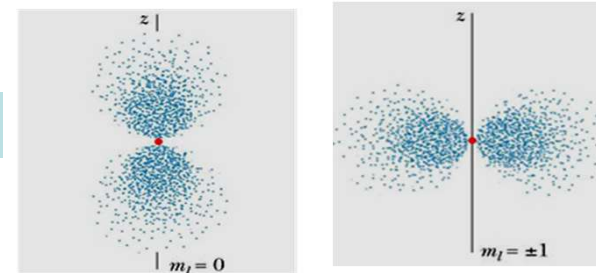


6.1. Hydrogen atom in quantum mechanics

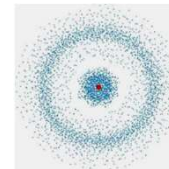
Hydrogen atom states with $n=2$

As the energy of a state depends only on the principal quantum number n and is independent of ℓ and m_ℓ for an isolated hydrogen atom there is no way to differentiate experimentally between the three states shown below

These three states (for $\ell=1$) are degenerate



Moreover the state with $\ell=0$ has also the same energy; this is 4-fold degeneracy



We can view all four states, given in table, as forming a spherically symmetric **shell** specified by the single quantum number n

n	ℓ	m_ℓ
2	0	0
2	1	+1
2	1	0
2	1	-1

6.1. Hydrogen atom in quantum mechanics

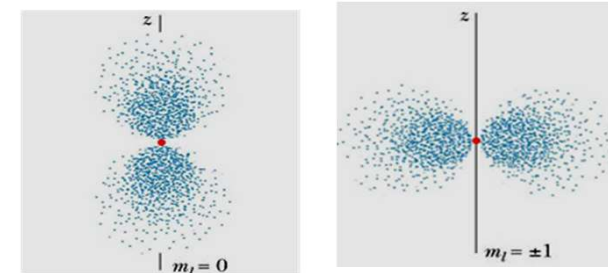
Hydrogen atom states with $n=2$

If we add the volume probability densities for the three states for which $n=2$ and $\ell=1$, the combined probability density turns out to be spherically symmetrical with no unique axis.

One can think of the electron spending one-third of its time in each of three states

One can think of the weighted sum of the three independent wave functions as defining a spherically symmetric **subshell** specified by the quantum numbers $n=2$ and $\ell=1$

The individual states will display their separate existence (the degeneracy will be lifted) only if we place the hydrogen atom in an external electric or magnetic field (Zeeman effect).



6.2 Angular momentum and magnetic dipole moment

The solutions of the angular part of Schrödinger equation – the spherical harmonics $Y_{nl}(\theta, \varphi)$ have a special physical significance related to the **angular momentum**.

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

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

\vec{p} is momentum of the particle

\vec{r} is the radius vector of the particle from the fixed point P

The vector product can be written component by component as follows

$$L_x = yp_z - zp_y \quad L_y = zp_x - xp_z \quad L_z = xp_y - yp_x$$

6.2 Angular momentum and magnetic dipole moment

In quantum mechanics we use the operators, for momentum:

$$p_x = -i\hbar \frac{\partial}{\partial x} \quad p_y = -i\hbar \frac{\partial}{\partial y} \quad p_z = -i\hbar \frac{\partial}{\partial z}$$

Then, the angular momentum operator is

$$L_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$L_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

We shall also be interested in the square of the angular momentum

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

6.2 Angular momentum and magnetic dipole moment

In spherical coordinates:
$$L^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right)$$

This operator involves only the angles and **not** the radial coordinate

The z-component of the angular momentum takes a particularly simple form in spherical coordinates:

$$L_z = -i\hbar \frac{\partial}{\partial \varphi}$$

We already know the eigenfunctions and possible eigenvalues of L^2 and L_z

The eigenvalue equation for L^2 is:
$$L^2 Y_{\ell m}(\theta, \varphi) = \underbrace{\hbar^2 \ell(\ell + 1)}_{\text{eigenvalues of } L^2 \text{ operator}} Y_{\ell m}(\theta, \varphi)$$

spherical harmonics are eigenfunctions of L^2 operator

6.2 Angular momentum and magnetic dipole moment

Therefore, an electron trapped in an atom has an orbital angular momentum:

$$L = \hbar \sqrt{\ell(\ell + 1)}$$



orbital quantum number

The projection L_z of angular momentum vector \mathbf{L} on an arbitrary 'z' axis is quantized and measurable and can give values:

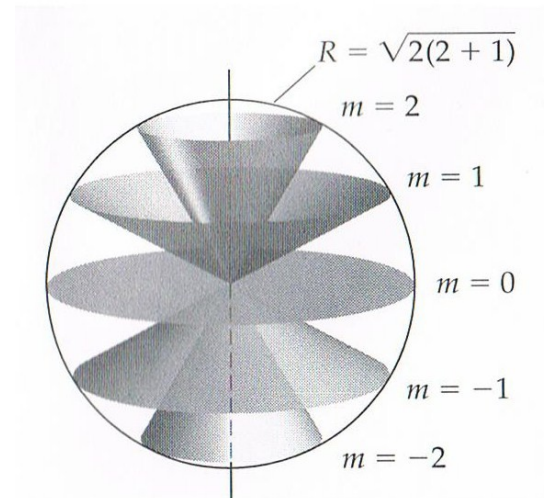
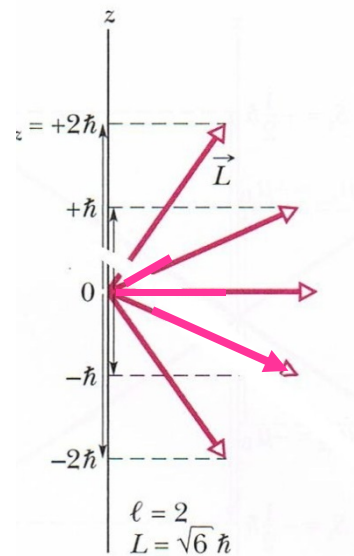
$$L_z = \hbar m_\ell$$



orbital magnetic quantum number

6.2 Angular momentum and magnetic dipole moment

This figure shows the five quantized components L_z of the orbital angular momentum for an electron with $\ell=2$, as well as the associated orientations of the angular momentum vector (however, *we should not take the figure literally* as we cannot detect \mathbf{L} this way)



6.2 Angular momentum and magnetic dipole moment

A magnetic dipole has an **orbital magnetic dipole moment** related to the angular momentum:

$$\vec{\mu}_{orb} = -\frac{e}{2m_e} \vec{L}$$

Neither $\vec{\mu}_{orb}$ nor \vec{L} can be measured

However, we can measure the components of these two vectors along a given axis.

We can measure, for instance, the z-components of orbital magnetic dipole moment and angular momentum vector along the axis that is given by the direction of the magnetic field B.

The components $\mu_{orb,z}$ are quantized and given by: $\mu_{orb,z} = -m_\ell \mu_B$

Bohr magneton $\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} \text{ J/T}$

6.3 Electron spin

Whether an electron is trapped in atom or is free,
it has an intrinsic *spin angular momentum*

The magnitude of spin is *quantized* and depends on a spin quantum number s , which is always $\frac{1}{2}$ for electrons, protons and neutrons.

In addition, the component of spin, measured along any axis is quantized and depends on a spin magnetic quantum number m_s , which can have only the value $+\frac{1}{2}$ or $-\frac{1}{2}$.

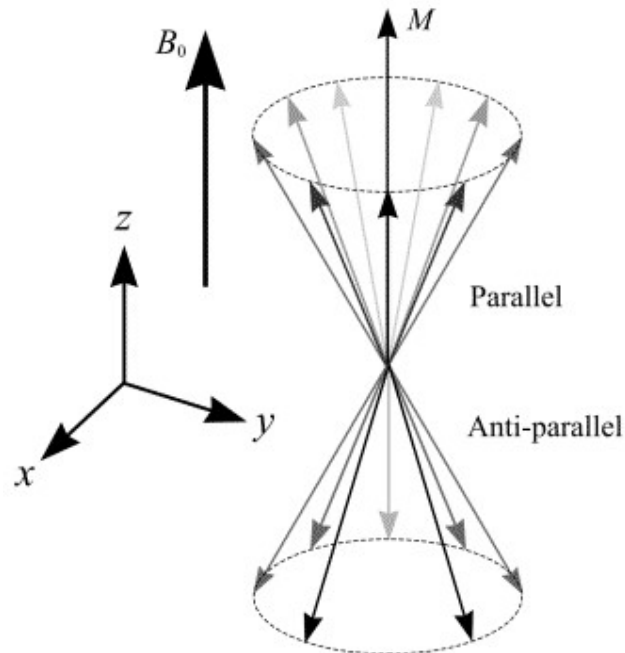


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Summary

Quantum number	Symbol	Allowed values	Related to
Principal	n	$1, 2, 3, \dots$	distance from the nucleus
Orbital	l	$0, 1, 2, \dots, (n-1)$	orbital angular momentum
Orbital magnetic	m_l	$0, \pm 1, \pm 2, \dots, \pm l$	orbital angular momentum (z component)
Spin	s	$\frac{1}{2}$	spin angular momentum
Spin magnetic	m_s	$\pm \frac{1}{2}$	spin angular momentum (z component)

NMR – nuclear magnetic resonance (application of science)



Upon absorption of a photon of energy hf the proton in the magnetic field can reverse its spin (change from spin-up state to the spin-down state) – spin-flipping

$$hf = 2\mu_z B$$

Because many substances have unique NMR signatures, this technique is used to identify unknown substances (i.e. forensic work of the criminal investigation)

Magnetic resonance imaging MRI has been applied in medical diagnosis with great success. Protons in the various tissues of human body, are found in different internal magnetic environments. Spin-flipping can be imaged in strong external magnetic field.

