

PHYS-454

The hydrogen atom

Introduction-a

- The study of the hydrogen atom is important in quantum mechanics because it is the only atom where the Schrödinger equation can be exactly solved in the limit where all the interactions, except the electrostatic, between the proton and the electron can be ignored.

Introduction-b

- The Schrödinger equation takes the form:

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

$$\nabla^2\psi + (\varepsilon - U(r))\psi = 0$$

$$\varepsilon = \frac{2mE}{\hbar^2} \quad U(r) = \frac{2mV(r)}{\hbar^2} \quad V(r) = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}$$

Introduction-c

- Since the interaction Hamiltonian depends only on r , the proper coordinate system for the study of this problem is the system of spherical coordinates, where:

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

- Since the mass of the proton is much larger than the electron's, the proton has been considered as a heavy motionless particle.

Solution of Schrödinger equation-a

- In solving the Schrödinger equation for the hydrogen atom we must take into account two important conservation principles:
- The conservation of energy
- The conservation of angular momentum since the Coulomb force between proton and electron is a central force.
- The Schrödinger equation is solved with the method of separating variables

Solution of Schrödinger equation-b

- The wavefunctions for the hydrogen electron are given by:

$$\psi_{nlm}(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{radial part}} \underbrace{Y_l^m(\theta, \phi)}_{\text{angular part}}$$

- As you may see they consist of a radial and an angular part

The angular part-a

- The angular part of the wavefunction is given by the so-called **spherical harmonics**:

$$Y_l^m(\theta, \phi) = \varepsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} P_l^m(\cos\theta) e^{im\phi}$$

$$\varepsilon = \begin{cases} (-1)^m, & m \geq 0 \\ 1 & m < 0 \end{cases}$$

$P_l^m(\cos\theta)$ the associated Legendre function

The angular part-b

- The associated Legendre functions polynomials are generated from the Legendre polynomials from the following relations:

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x)$$

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l$$

The angular part-c some associated Legendre polynomials

$$P_0^0 = 1$$

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

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

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

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

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

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

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

$$P_2^1 = 3\sin\theta\cos\theta \quad P_3^0 = \frac{1}{2}\sin\theta(5\cos^3\theta - 3\cos\theta)$$

The angular part-d

- The **spherical harmonics** are normalized and orthogonal to each other:

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

- The spherical harmonics are eigenfunctions of the square angular momentum operator and of the angular momentum operator along the z-direction

$$L^2 Y_l^m = \hbar^2 l(l+1) Y_l^m, \quad L_z Y_l^m = \hbar m Y_l^m$$

The angular part-e

the first few spherical harmonics

$$Y_0^0 = \left(\frac{1}{4\pi} \right)^{1/2}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$$

$$Y_3^0 = \left(\frac{7}{16\pi} \right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$$

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$$

$$Y_3^{\pm 1} = \mp \left(\frac{21}{16\pi} \right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$$

$$Y_2^0 = 3 \left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi} \right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$$

$$Y_2^{\pm 1} = \mp 3 \left(\frac{15}{8\pi} \right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi} \right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$$

The angular part-e

- The integer number l is known as **azimuthal quantum number** and gets the values

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

- The integer number m is known as **magnetic quantum number** and gets the values

$$m = -l, \dots, +l$$

The radial part-a

- The radial part of the solution is given by:

$$R_{nl}(r) = Ne^{-r/na_0} \left(\frac{2r}{na_0} \right)^l \left[L_{n-l-1}^{2l+1} \left(2r / a_0 \right) \right]$$

$$N = \sqrt{\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \quad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} m$$

Bohr radius

$L_{n-l-1}^{2l+1} \left(2r / a_0 \right)$ associated Laguerre polynomial

The radial part-b

- The associated Laguerre polynomials are generated from the Laguerre polynomials from the following relations:

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

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

The radial part-c

Some associated Laguerre polynomials

$$L_0^0 = 1$$

$$L_0^2 = 2$$

$$L_1^0 = -x + 1$$

$$L_1^2 = -6x + 18$$

$$L_2^0 = x^2 - 4x + 2$$

$$L_2^2 = 12x^2 - 96x + 144$$

$$L_0^1 = 1$$

$$L_0^3 = 6$$

$$L_1^1 = -2x + 4$$

$$L_1^3 = -24x + 96$$

$$L_2^1 = 3x^2 - 18x + 18$$

$$L_2^3 = 60x^2 - 600x + 1200$$

The radial part-c Discussion

- It can be shown that the radial part of the electrons wavefunction defines a function

$$u \equiv rR_{nl}(r)$$

which satisfies the so-called *radial equation*

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right]}_{\text{effective potential}} u = Eu$$

The radial part-c

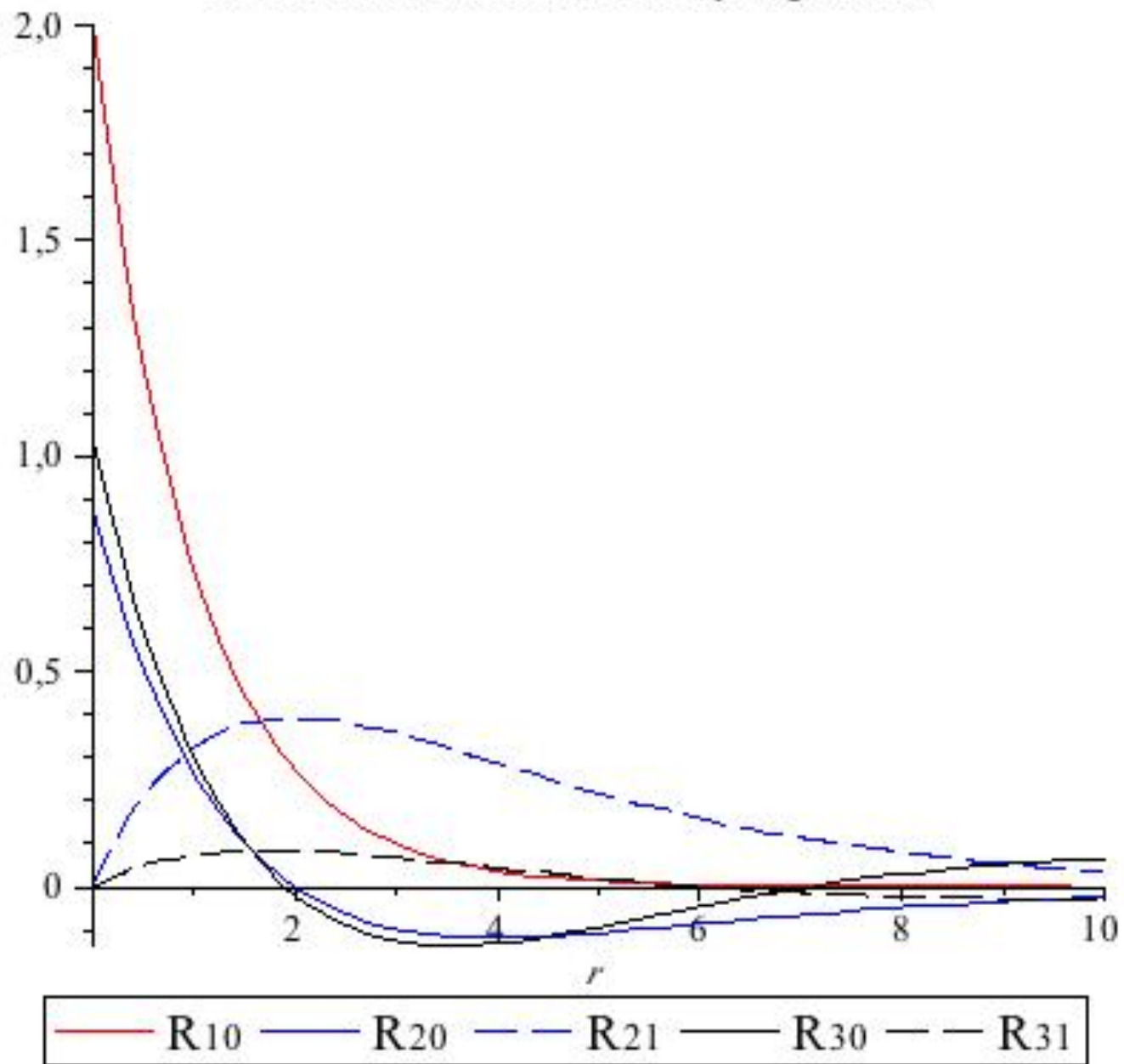
Discussion

- The functions u satisfy the following boundary conditions:

$$u(0) = 0, \quad u(\infty) = 0, \quad \text{while } 0 < r < \infty$$

- Thus the radial equation describes an one-dimensional motion where at 0 we have a “wall” and at infinity the wavefunction becomes zero.
- The radial equation contains the term $\hbar^2 l(l+1) / (2mr^2)$ which is the so called **centrifugal term**.

The first radial functions of the hydrogen atom



The total wavefunctions

- The total wavefunctions for the hydrogen atom are given by:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \left[L_{n-l-1}^{2l+1}\left(2r/na_0\right) \right] Y_l^m(\theta, \phi)$$

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin\theta dr d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

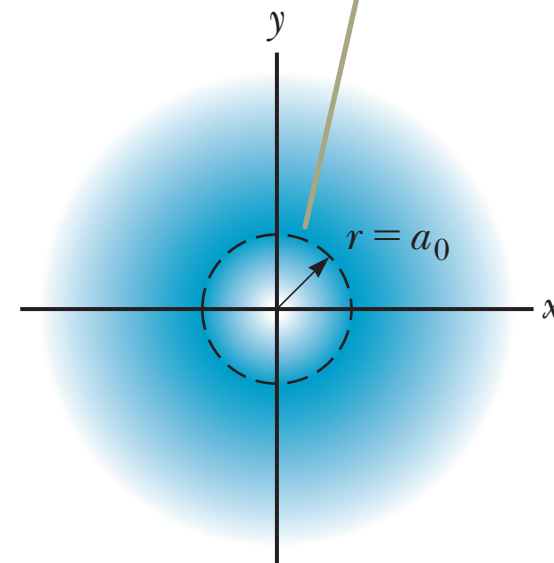
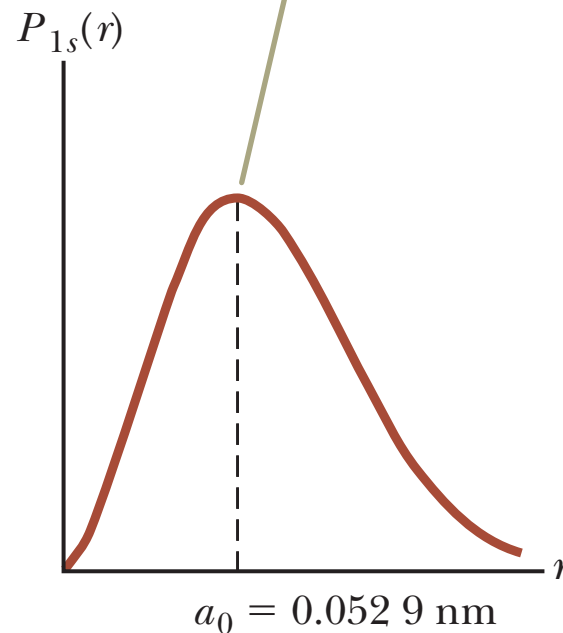
The probability has its maximum value when r equals the Bohr radius a_0 .

In this representation, the darkest color, representing the maximum probability, occurs at the Bohr radius.

$$P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr$$

$$P(r) = 4\pi r^2 |\psi|^2$$

$$P_{1s}(r) = \left(\frac{4r^2}{a_0^3}\right) e^{-2r/a_0}$$



a

b

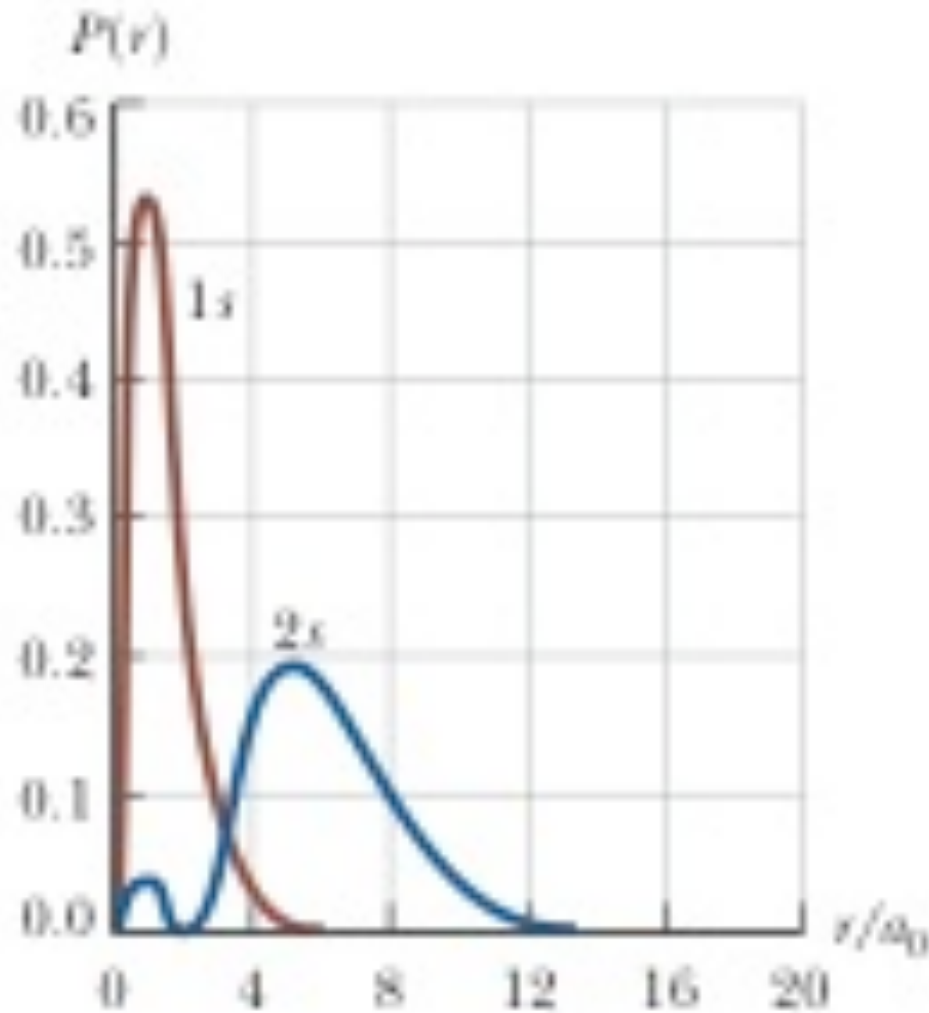
(a) The probability of finding the electron as a function of distance from the nucleus for the hydrogen atom in the 1s (ground) state. (b) The cross section in the xy plane of the spherical electronic charge distribution for the hydrogen atom in its 1s state.

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr$$

$$P(r) = 4\pi r^2 |\psi|^2$$



The radial probability density function versus r/a_0 for the 1s and 2s states of the hydrogen atom.

The energy spectrum of the hydrogen atom-a

- The energies of the electron states are given by the following formula:

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

- Where E_1 is the ground state energy given by

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}$$

- The number n is called the **principal quantum number**.

Interesting properties of the probability function

- For $n = 1$, the probability has one maximum exactly at $r = a_0$, the orbital radius of the first energy level in the Bohr model.
- For $(n = 2, l = 0, m = 0)$, the probability shows two maxima located at $r \neq n^2 a_0$.
- Only for states such that $n = l + 1$, the probability shows one maximum located at $r = n^2 a_0$, the orbital radius of the n^{th} energy level in the Bohr model.

The energy spectrum of the hydrogen atom-b

- One of the most impressive characteristic of the hydrogen atom energy spectrum is its *degeneracy*.
- By degeneracy we mean that there can be more than one states with the same energy. This is obvious since the energy does not depend on the numbers l and m .
- The principal quantum number n imposes the following restriction on the values of the azimuthal quantum number:

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

- We can prove that the number of different states that have the same energy is given by

$$d_n = n^2$$

The physical interpretation of quantum number l

- The Bohr model of hydrogen, however, postulates that the magnitude of the angular momentum of the electron is restricted to multiples of \hbar ; that is, $l = n\hbar$. This model must be modified because it predicts (incorrectly) that the ground state of hydrogen has one unit of angular momentum.
- According to quantum mechanics, an atom in a state whose principal quantum number is n can take on the following *discrete* values of the magnitude of the orbital angular momentum

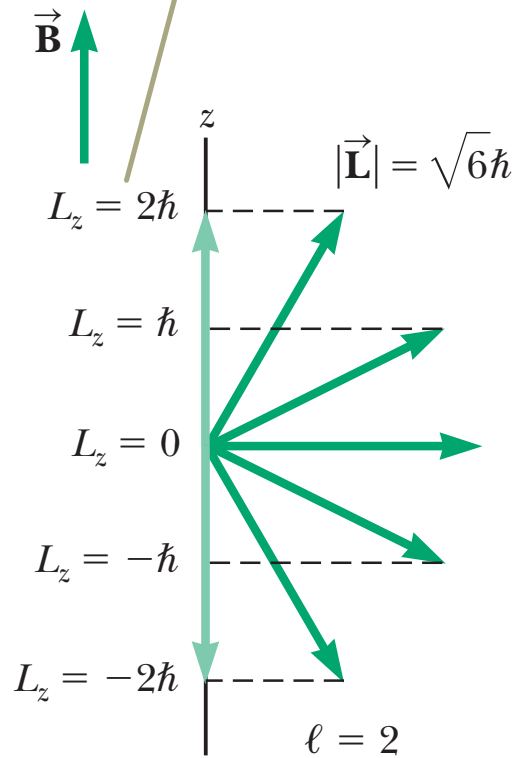
$$L = \sqrt{\ell(\ell + 1)}\hbar \quad \ell = 0, 1, 2, \dots, n - 1$$

The physical interpretation of quantum number m

- Spectral lines from some atoms are observed to split into groups of three closely spaced lines when the atoms are placed in a magnetic field.
- Suppose the hydrogen atom is located in a magnetic field. According to quantum mechanics, there are *discrete* directions allowed for the magnetic moment with respect to the magnetic field. Because the magnetic moment μ of the atom can be related to the angular momentum vector, the discrete directions of \mathbf{m} translate to the direction of \mathbf{L} being quantized. This quantization means that L_z (the projection of \mathbf{L} along the z axis) can have only discrete values.

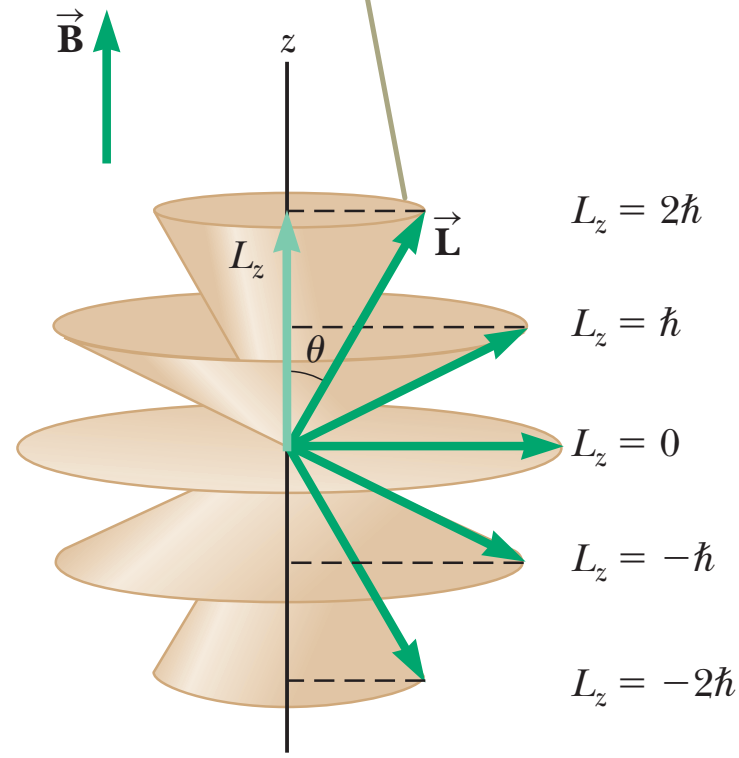
$$L_z = m_l \hbar$$

The allowed projections on the z axis of the orbital angular momentum $\vec{\mathbf{L}}$ are integer multiples of \hbar .



a

Because the x and y components of the orbital angular momentum vector are not quantized, the vector $\vec{\mathbf{L}}$ lies on the surface of a cone.



b

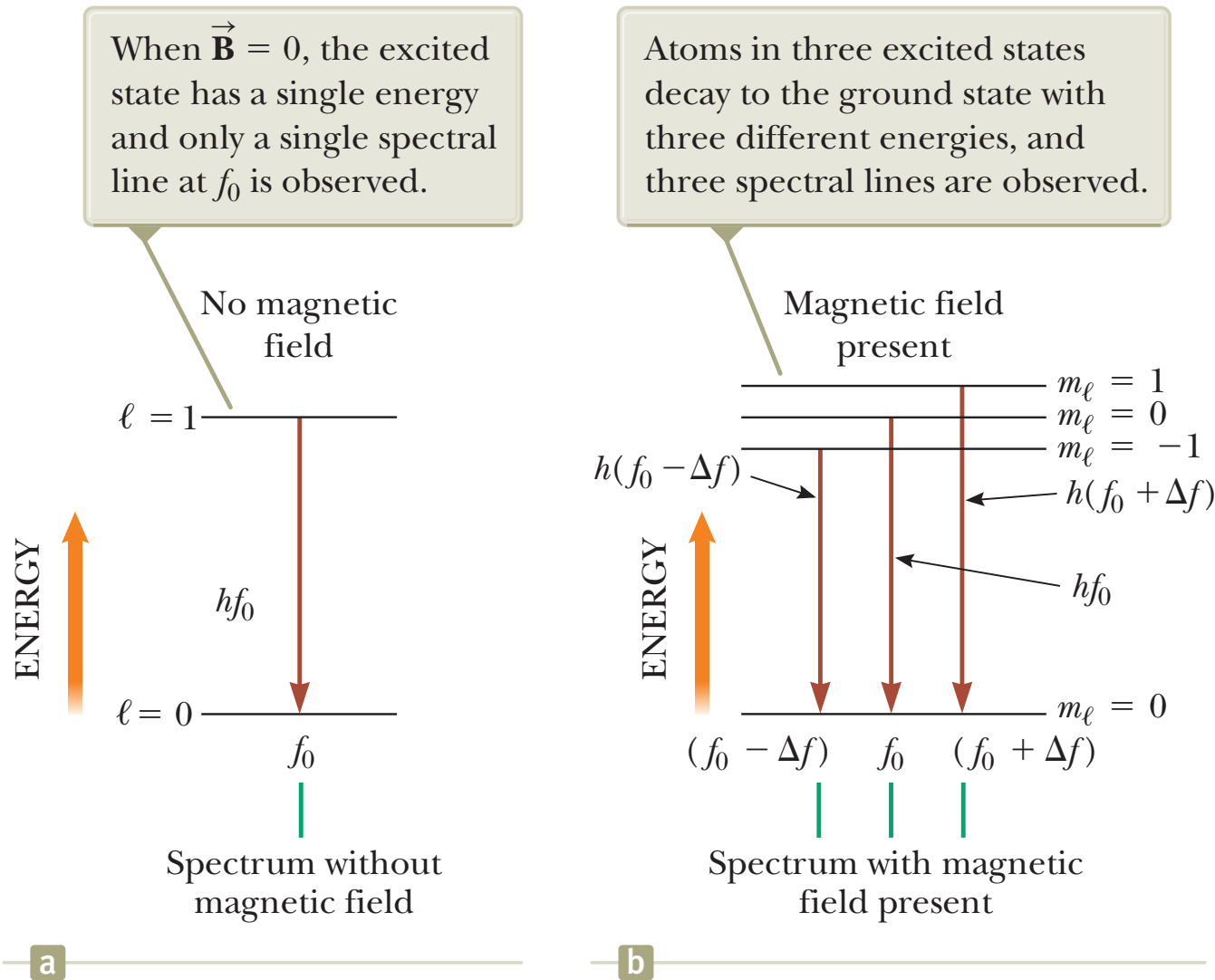
A vector model for $l=2$

The physical interpretation of quantum number m

- The quantization of possible orientations of \mathbf{L} with respect to an external magnetic field is often referred to as **space quantization**.
- Notice that \mathbf{L} can never be aligned parallel or anti-parallel to magnetic field \mathbf{B} because the maximum value of L_z is $l\hbar$ which is less than the magnitude of angular momentum $\{l(l+1)\}^{1/2}\hbar$.
- The vector \mathbf{L} does not point in one specific direction. If \mathbf{L} were known exactly, all three components L_x , L_y , and L_z would be specified, which is inconsistent with an angular momentum version of the uncertainty principle.

The physical interpretation of quantum number m

- If the atom is placed in a magnetic field, the energy $U_B = -\boldsymbol{\mu} \cdot \mathbf{B}$ is additional energy for the atom-field system. Because the directions of $\boldsymbol{\mu}$ are quantized, there are discrete total energies for the system corresponding to different values of m . This is the famous **Zeeman Effect**.
- The Zeeman effect can be used to measure extraterrestrial magnetic fields. For example, the splitting of spectral lines in light from hydrogen atoms in the surface of the Sun can be used to calculate the magnitude of the magnetic field at that location.
- The Zeeman effect is one of many phenomena that cannot be explained with the Bohr model but are successfully explained by the quantum model of the atom.



The Zeeman effect. (a) Energy levels for the ground and first excited states of a hydrogen atom. (b) When the atom is immersed in a magnetic field \mathbf{B} , the state with $l=1$ splits into three states, giving rise to emission lines at $f_0, f_0 + \Delta f$, and $f_0 - \Delta f$ where Δf is the frequency shift of the emission caused by the magnetic field.