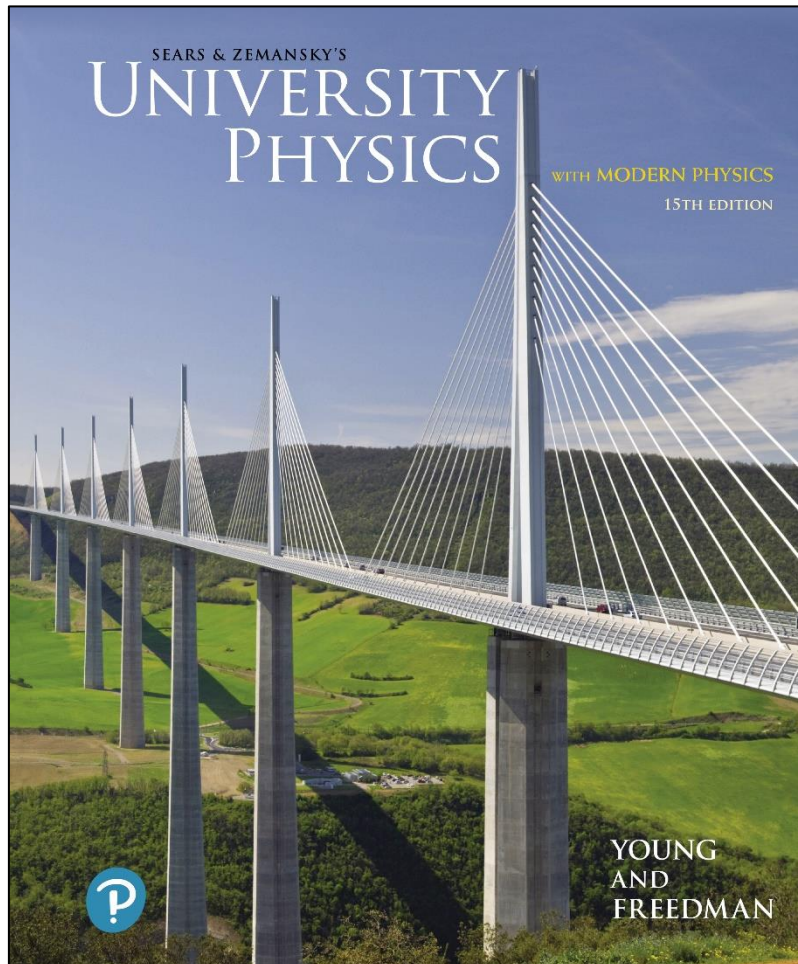


University Physics with Modern Physics

Fifteenth Edition



Chapter 41

Quantum Mechanics II: Atomic Structure

Learning Outcomes

In this chapter, you'll learn...

- how to extend quantum-mechanical calculations to three-dimensional problems, such as a particle trapped in a cubical box.
- how to describe the states of a hydrogen atom in terms of quantum numbers.
- how magnetic fields affect the orbital motion of atomic electrons.
- how to analyze the structure of many-electron atoms.
- what happens when the quantum-mechanical states of two particles become entangled.

Introduction

- Lithium (with three electrons per atom) is a metal that burns spontaneously in water, while helium (with two electrons per atom) is a gas that undergoes almost no chemical reactions.
- The Pauli exclusion principle is responsible.
- Helium is inert because its two electrons fill the K shell; lithium is very reactive because its third electron must go into the L shell and is loosely bound.



The Schrödinger Equation in 3-D

- Electrons in an atom can move in all three dimensions of space.
- If a particle of mass m moves in the presence of a potential energy function $U(x, y, z)$, the Schrödinger equation for the particle's wave function $\psi(x, y, z, t)$ is:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi(x, y, z, t)}{\partial x^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial y^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial z^2} \right) + U(x, y, z) \Psi(x, y, z, t) = i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t}$$

(general three-dimensional Schrödinger equation)

The Schrödinger Equation in 3-D: Stationary States

- If a particle of mass m has a definite energy E , its wave function $\psi(x, y, z, t)$ is a product of a time-Independent wave function $\psi(x, y, z)$ and a factor that depends on time but not position.
- The function $\psi(x, y, z)$ obeys the time-independent Schrödinger equation in three dimensions:

Time-independent three-dimensional Schrödinger equation:

Planck's constant
divided by 2π

Time-independent wave function

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right)$$

Particle's mass

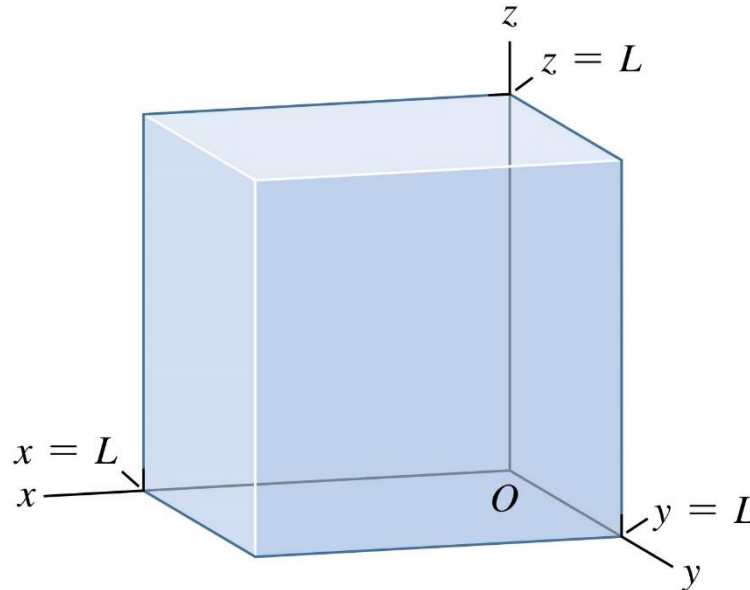
$$+ U(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

Potential-energy function

Energy of state

Particle in a Three-Dimensional Box (1 of 5)

- Consider a particle enclosed within a cubical box of side L .
- The potential energy is zero inside the box, but infinite outside.



Particle in a Three-Dimensional Box

(2 of 5)

- For a particle enclosed in a cubical box with sides of length L , three quantum numbers n_x , n_y , and n_z label the stationary states.
- The stationary-state wave functions are:

$$\psi_{n_x, n_y, n_z}(x, y, z) = C \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$$
$$(n_x = 1, 2, 3, \dots; n_y = 1, 2, 3, \dots; n_z = 1, 2, 3, \dots)$$

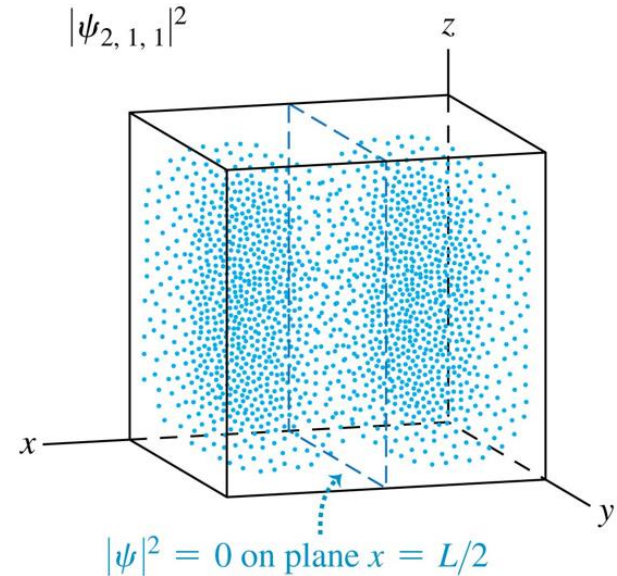
- The value of the constant C is determined by the normalization condition:

$$\int |\psi(x, y, z)|^2 dv = 1$$

(normalization condition for a stationary state in three dimensions)

Particle in a Three-Dimensional Box (3 of 5)

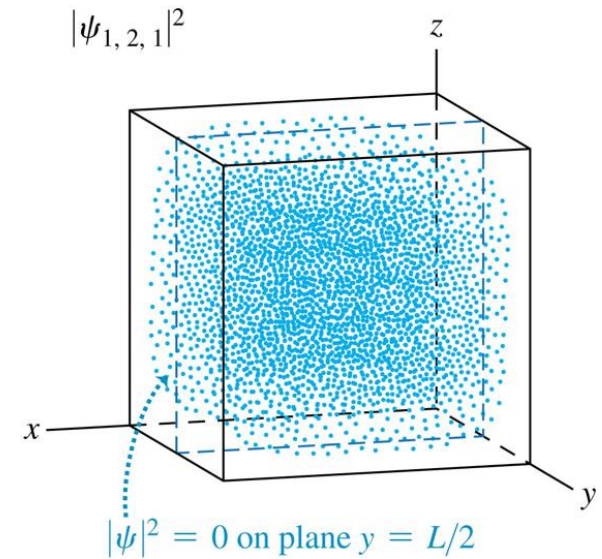
- Shown is the probability distribution for $(n_x, n_y, n_z) = (2, 1, 1)$.
- The value of $|\psi|^2$ is proportional to the density of dots.



Particle in a Three-Dimensional Box

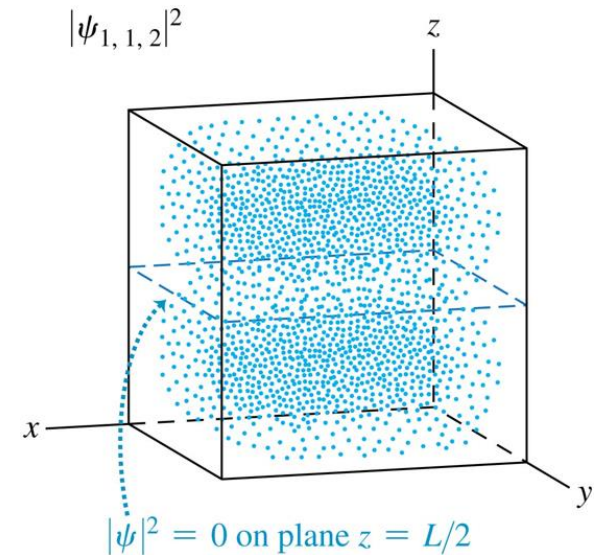
(4 of 5)

- Shown is the probability distribution for $(n_x, n_y, n_z) = (1, 2, 1)$.
- The value of $|\psi|^2$ is proportional to the density of dots.



Particle in a Three-Dimensional Box (5 of 5)

- Shown is the probability distribution for $(n_x, n_y, n_z) = (1, 1, 2)$.
- The value of $|\psi|^2$ is proportional to the density of dots.



Energy Levels and Degeneracy

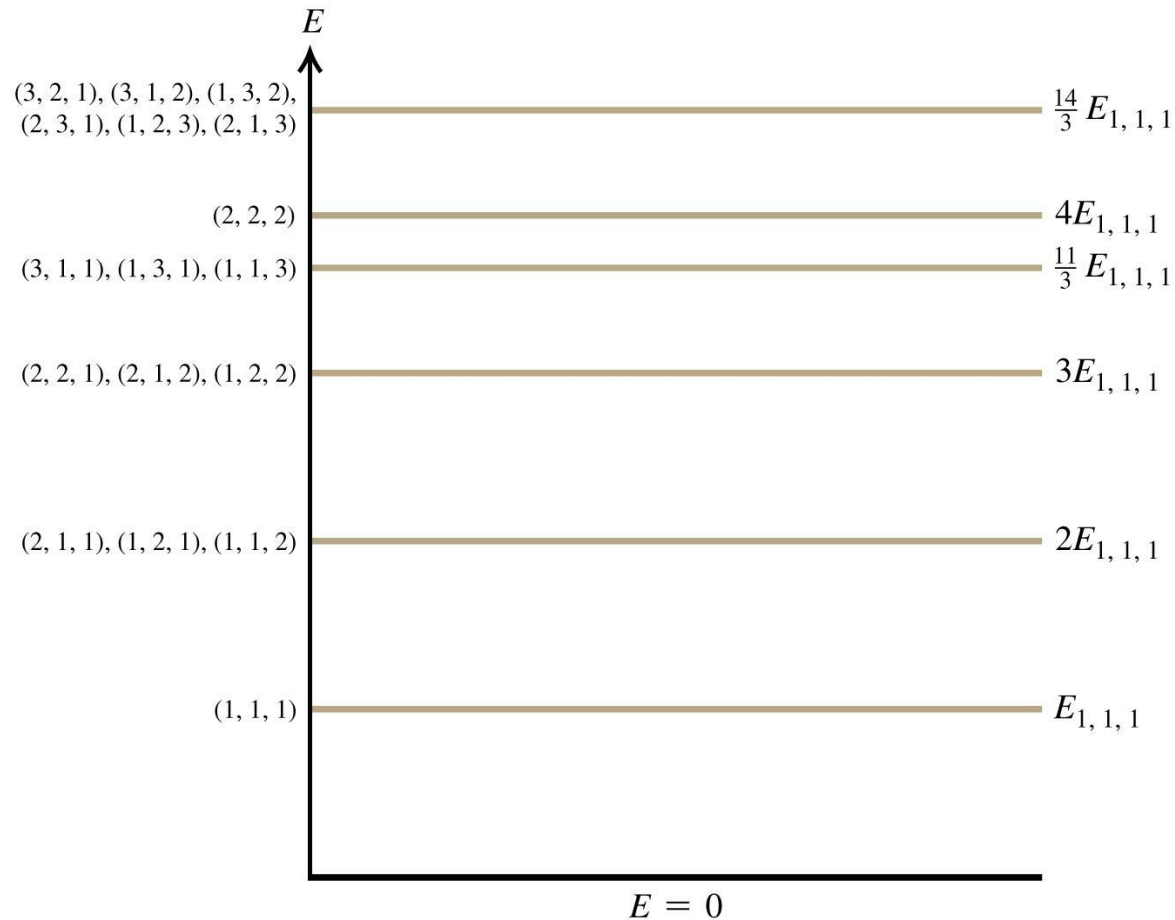
- The allowed energies for a particle of mass m in a cubical box of side L are:

The diagram shows the equation for energy levels in a three-dimensional cubical box. The equation is $E_{n_x, n_y, n_z} = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2}$. Annotations include: 'Energy levels, particle in a three-dimensional cubical box' pointing to the left side of the equation; 'Quantum numbers n_x, n_y, n_z can each equal 1, 2, 3, ...' pointing to the terms in the numerator; 'Planck's constant divided by 2π ' pointing to \hbar ; 'Particle's mass' pointing to m ; and 'Length of each side of box' pointing to L .

$$E_{n_x, n_y, n_z} = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2}$$

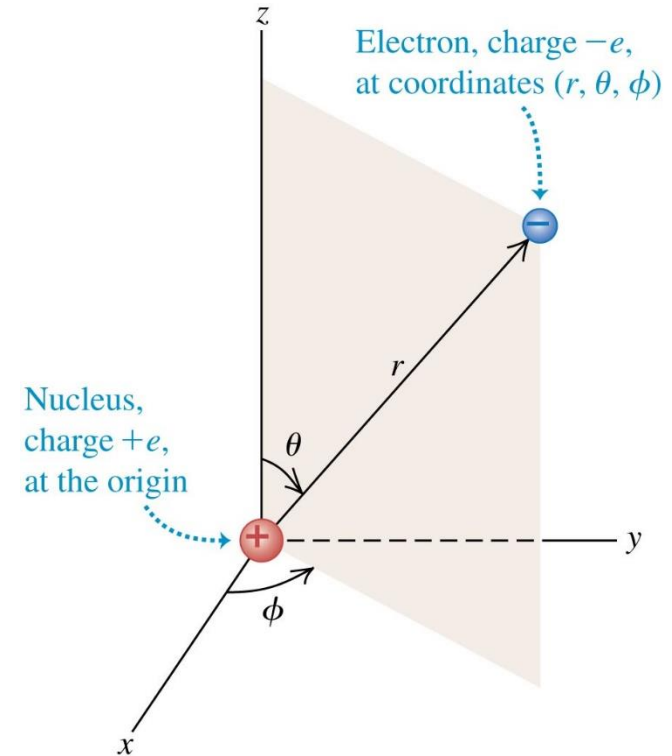
- The next slide shows the six lowest energy levels.
- Note that most energy levels correspond to more than one set of quantum numbers (n_x, n_y, n_z) .
- Having two or more distinct quantum states with the same energy is called degeneracy, and states with the same energy are said to be **degenerate**.

Energy Levels for a Particle in a Cubical Box



The Hydrogen Atom: Quantum Numbers

- The Schrödinger equation for the hydrogen atom is best solved using coordinates (r, θ, ϕ) rather than (x, y, z) .
- The stationary states are labeled by three quantum numbers:
 - n (which describes the energy),
 - l (which describes orbital angular momentum), and
 - m_l (which describes the z-component of orbital angular momentum).



The Schrödinger Equation for the Hydrogen Atom

- The potential energy for an electron in a hydrogen atom is:

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

- Solutions to the Schrödinger equation with this potential turn out to have energies identical to those from the Bohr model, with the electron rest mass m replaced by the reduced mass m_r .
- The allowed energies of the stationary states are:

The diagram shows the equation for the energy levels of hydrogen, $E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m_r e^4}{2n^2 \hbar^2} = -\frac{13.60 \text{ eV}}{n^2}$. Labels with arrows point to various parts of the equation: 'Energy levels of hydrogen' points to E_n ; 'Reduced mass' points to m_r ; 'Magnitude of electron charge' points to e^4 ; 'Electric constant' points to $(4\pi\epsilon_0)^2$; 'Principal quantum number ($n = 1, 2, 3, \dots$)' points to n^2 ; and 'Planck's constant divided by 2π ' points to \hbar^2 .

- We call n the **principal quantum number**.
- [Video Tutor Solution: Example 41.2](#)

Quantization of Orbital Angular Momentum (1 of 2)

- For an electron in a hydrogen atom with energy E_n and principal quantum number n , the possible values of orbital angular momentum L are:

Magnitude of orbital angular momentum, hydrogen atom

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

Orbital quantum number

Planck's constant divided by 2π

Principal quantum number ($n = 1, 2, 3, \dots$)

- The permitted values of the component of \vec{L} in the z-direction are:

z-component of orbital angular momentum, hydrogen atom

$$L_z = m_l \frac{\hbar}{2\pi} \quad (m_l = 0, \pm 1, \pm 2, \dots, \pm l)$$

Orbital magnetic quantum number

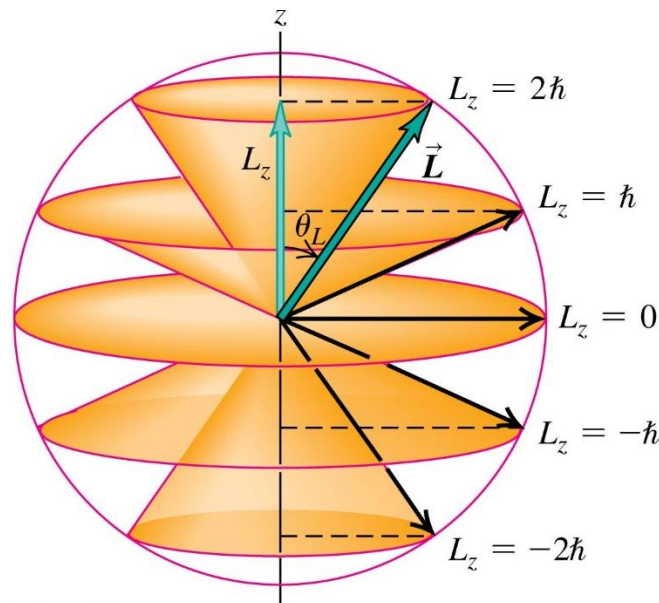
Planck's constant divided by 2π

Orbital quantum number

Quantization of Orbital Angular Momentum

(2 of 2)

- If the orbital quantum number $l = 2$, then the magnetic quantum number m_l can equal -2 , -1 , 0 , 1 , or 2 .
- These cones show the possible directions of \vec{L} for different values of L_z .



Quantum States of the Hydrogen Atom

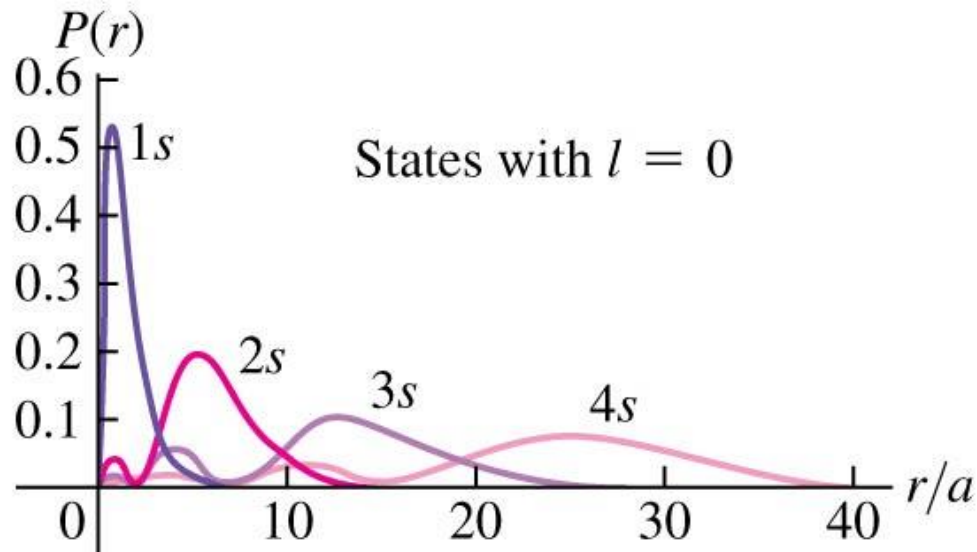
- Table 41.1 (below) summarizes the quantum states of the hydrogen atom.
- For each value of the quantum number n , there are n possible values of the quantum number l . For each value of l , there are $2l + 1$ values of the quantum number m_l .

Table 41.1 Quantum States of the Hydrogen Atom

n	l	m_l	Spectroscopic Notation	Shell
1	0	0	1s	<i>K</i>
2	0	0	2s	<i>L</i>
2	1	-1, 0, 1	2p	
3	0	0	3s	
3	1	-1, 0, 1	3p	<i>M</i>
3	2	-2, -1, 0, 1, 2	3d	
4	0	0	4s	<i>N</i>

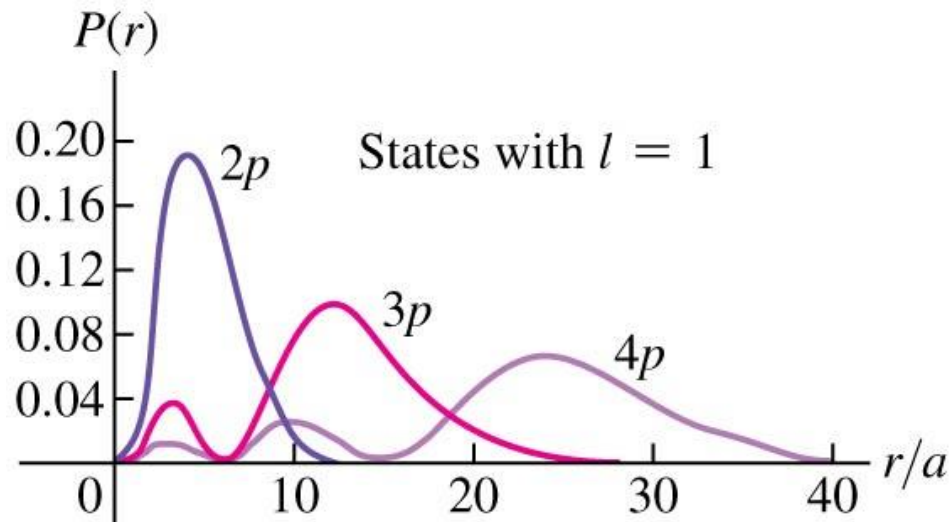
Electron Probability Distributions: $l = 0$

- Shown are radial probability distribution functions $P(r)$ for several hydrogen-atom wave functions, plotted as functions of the ratio r/a .
- Here a is the Bohr radius, $a = 5.29 \times 10^{-11} \text{m}$.



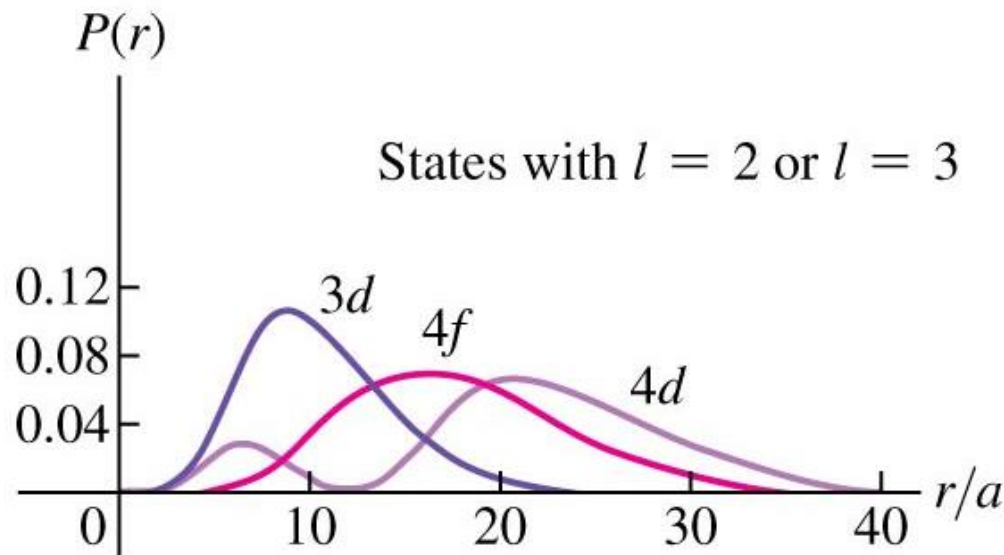
Electron Probability Distributions: $l = 1$

- Shown are radial probability distribution functions $P(r)$ for several hydrogen-atom wave functions, plotted as functions of the ratio $\frac{r}{a}$.
- Here a is the Bohr radius, $a = 5.29 \times 10^{-11} \text{m}$.



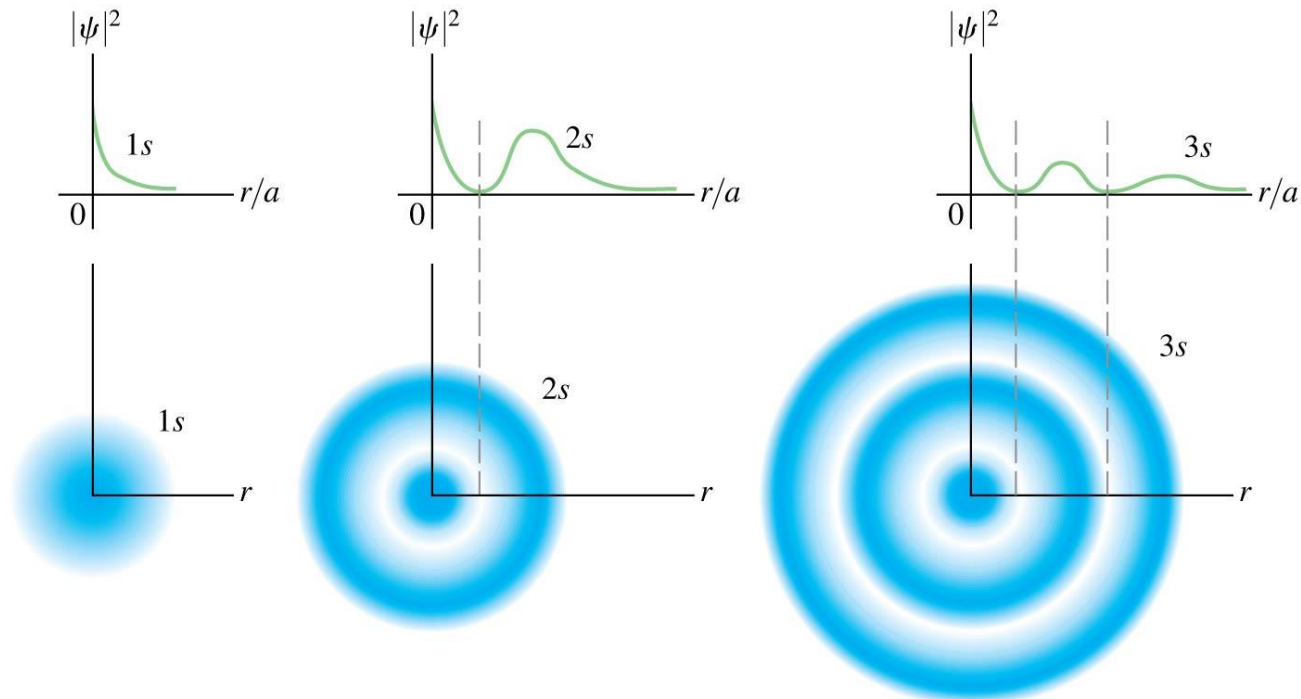
Electron Probability Distributions: $l = 2$ or 3

- Shown are radial probability distribution functions $P(r)$ for several hydrogen-atom wave functions, plotted as functions of the ratio $\frac{r}{a}$.
- Here a is the Bohr radius, $a = 5.29 \times 10^{-11} \text{m}$.



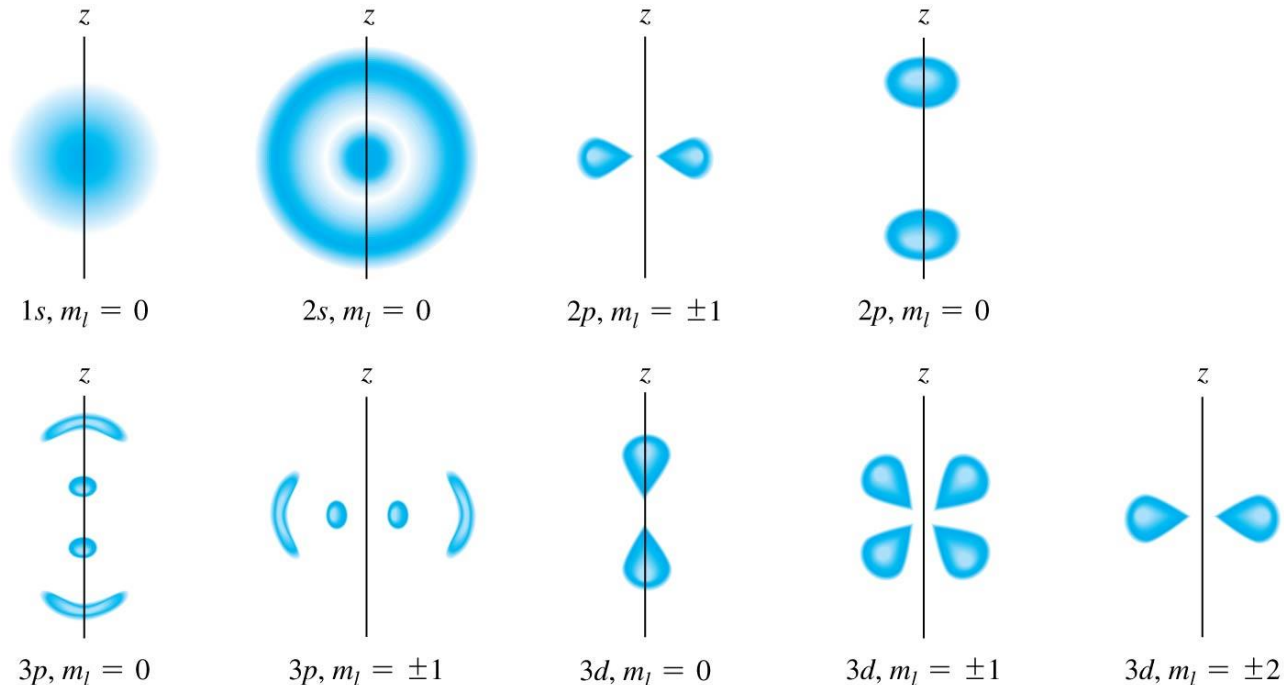
The Hydrogen Atom: Probability Distributions (1 of 2)

- Shown are three-dimensional probability distributions for the spherically symmetric 1s, 2s, and 3s hydrogen-atom wave functions.



The Hydrogen Atom: Probability Distributions (2 of 2)

- The p states ($l = 1$) and d states ($l = 2$) of the hydrogen atom have wave functions that are **not** spherically symmetric.



Magnetic Moments and the Zeeman Effect

(1 of 2)

- Electron states with nonzero orbital angular momentum ($l = 1, 2, 3, \dots$) have a magnetic dipole moment due to the electron motion.
- These states are affected if the atom is placed in a magnetic field.
- The result, called the **Zeeman effect**, is a shift in the energy of states with nonzero m_l .
- The magnetic field shifts the energy of each orbital state by an amount U :

Orbital magnetic interaction energy $\rightarrow U = -\mu_z B = m_l \frac{e\hbar}{2m} B = m_l \mu_B B$

Magnetic dipole component in direction of \vec{B}

Magnetic-field magnitude

Magnitude of electron charge

Planck's constant divided by 2π

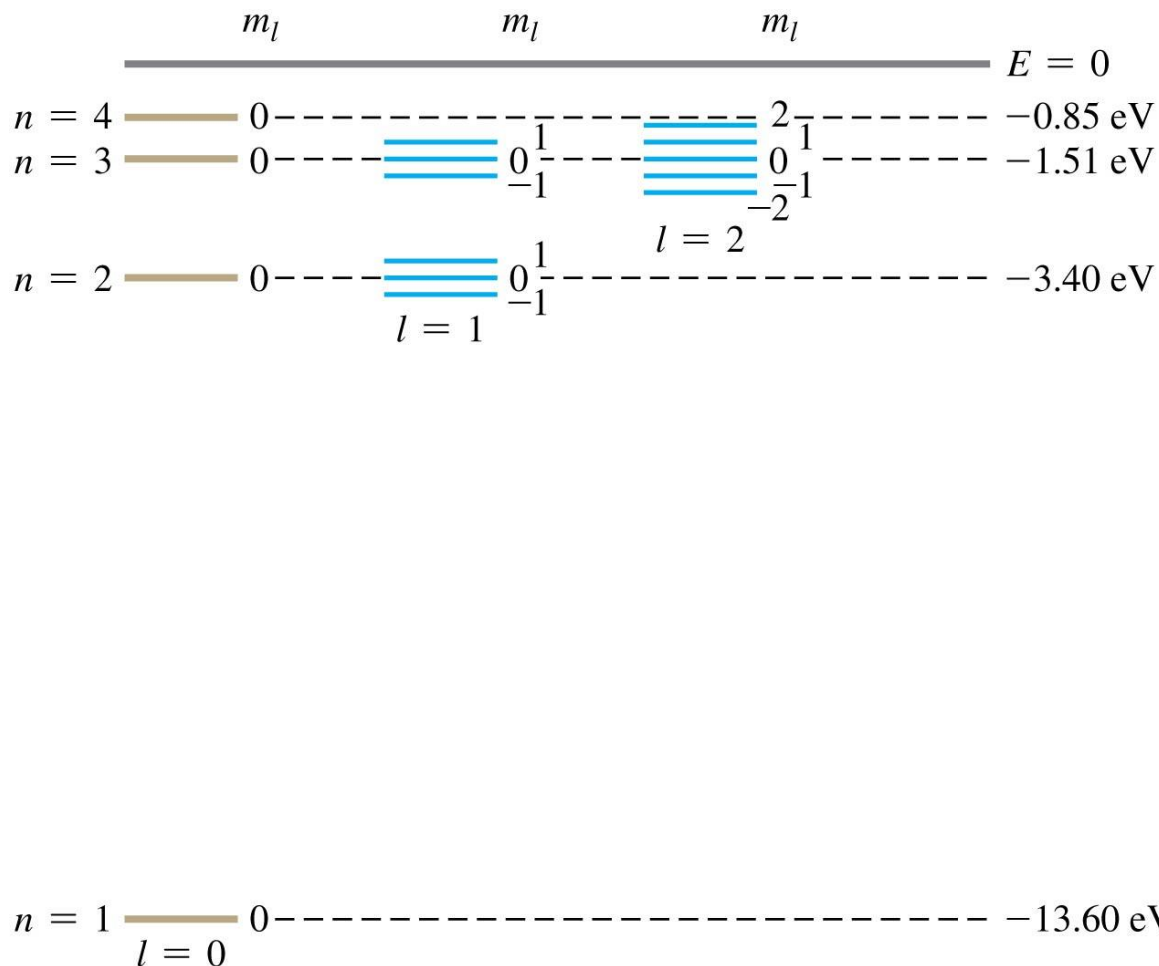
Bohr magneton

Orbital magnetic quantum number = $0, \pm 1, \pm 2, \dots, \pm l$

Electron mass

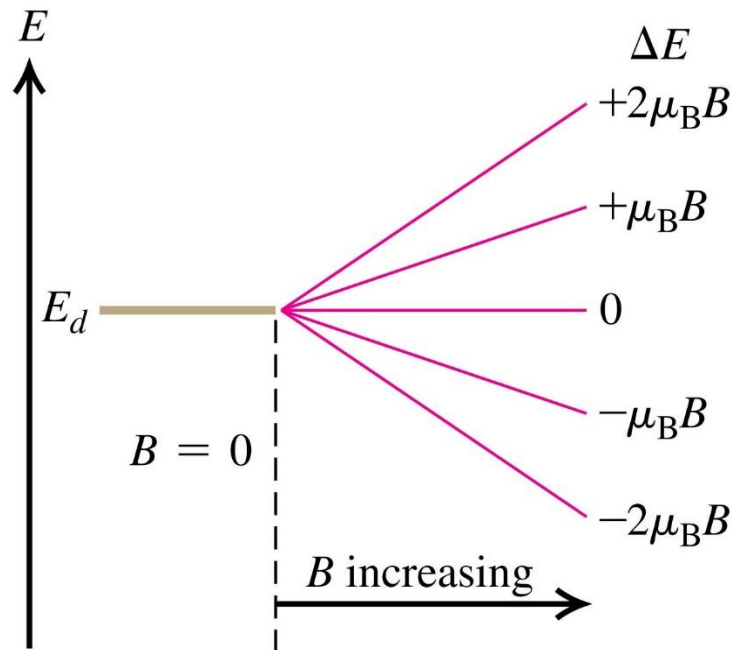
- [Video Tutor Solution: Example 41.5](#)

Magnetic Moments and the Zeeman Effect (2 of 2)



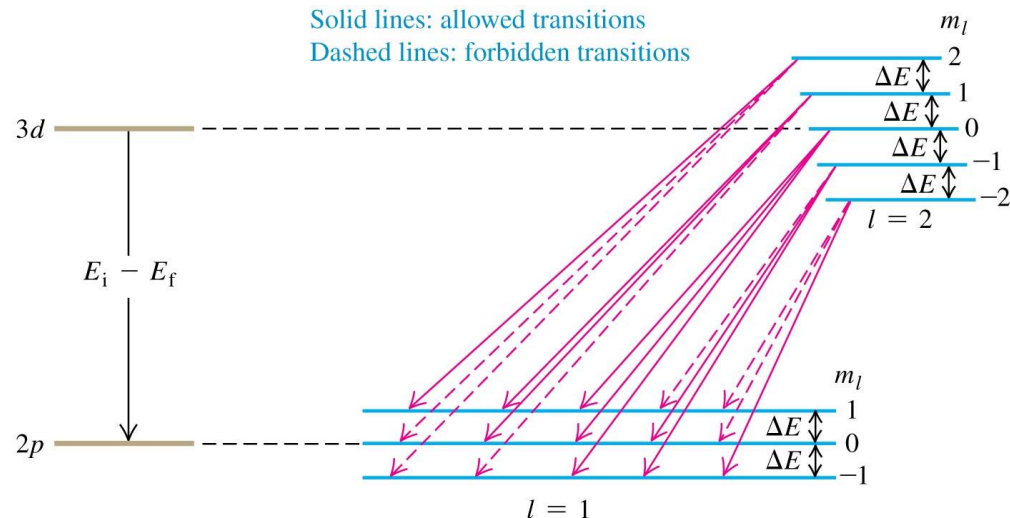
The Zeeman Effect and Selection Rules (1 of 2)

- This figure shows how the splitting of the energy levels of a d state ($l = 2$) depends on the magnitude B of an external magnetic field, assuming only an orbital magnetic moment.



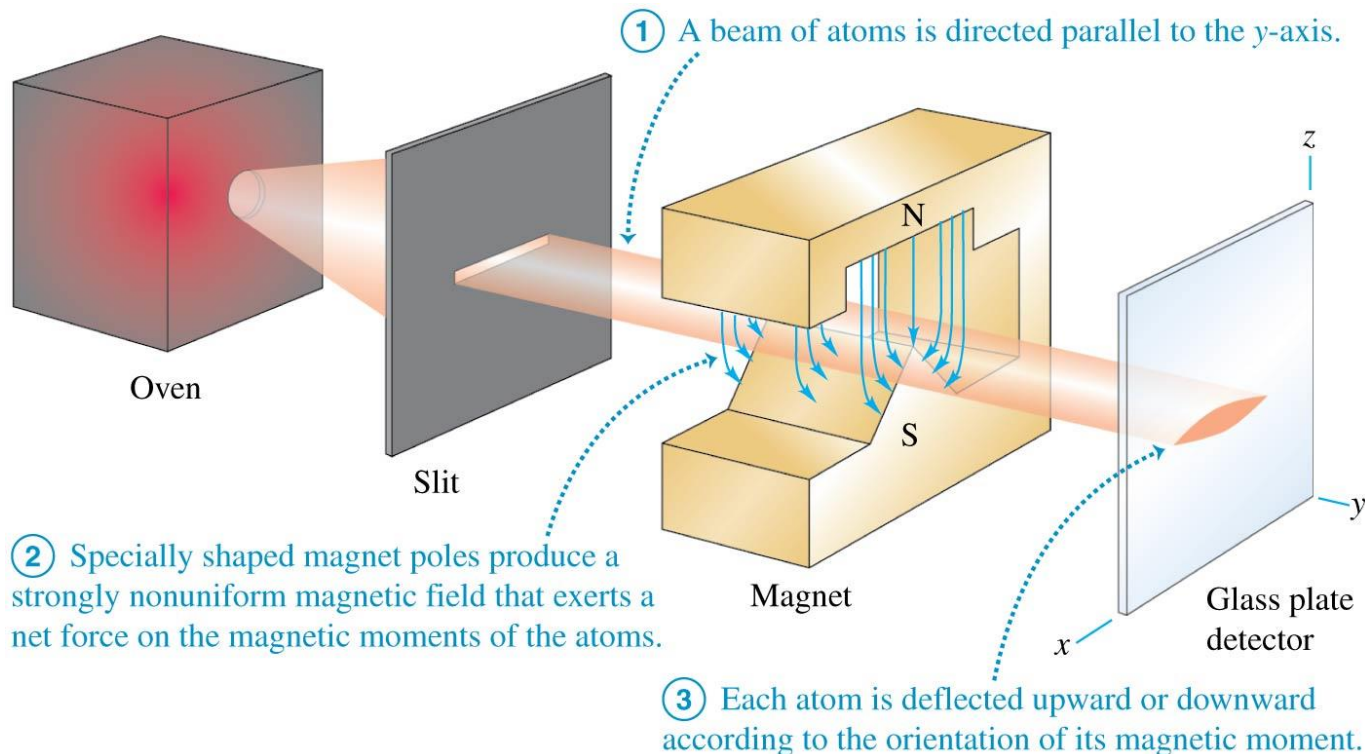
The Zeeman Effect and Selection Rules (2 of 2)

- Shown below is the cause of the normal Zeeman effect. The magnetic field splits the levels, but selection rules allow transitions with only three different energy changes, giving three different photon frequencies and wavelengths.



Electron Spin and the Stern-Gerlach Experiment

- The experiment of Stern and Gerlach demonstrated the existence of electron spin.



Electron Spin

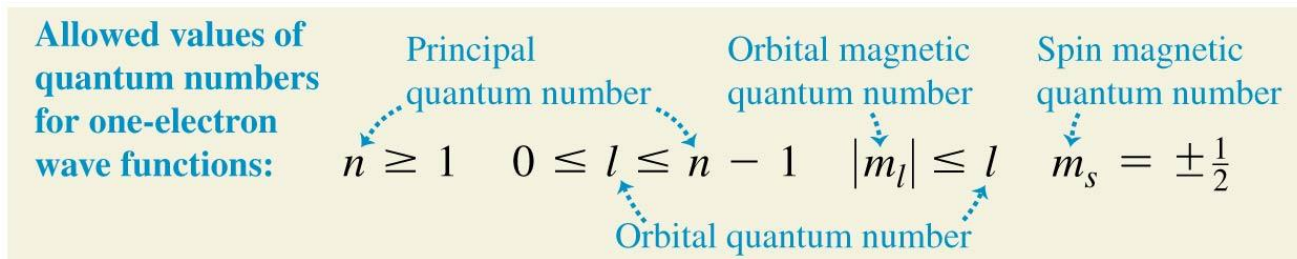
- In addition to orbital angular momentum, an electron also has spin angular momentum, \vec{S} .
- Suppose we have an apparatus that measures the z-component of \vec{S} , S_z .
- We find that the only possible values are:

z-component of spin angular momentum of electron $\rightarrow S_z = m_s \hbar$ \leftarrow Spin magnetic quantum number = $\pm \frac{1}{2}$
Planck's constant divided by 2π

- The spin magnetic quantum number, m_s , has only two possible values: $+\frac{1}{2}$ and $-\frac{1}{2}$.
- The electron is often called a “spin-one-half particle.”

Quantum States and the Pauli Exclusion Principle (1 of 2)

- The restrictions on the values of the quantum numbers for an electron are:



- The **Pauli exclusion principle** states that no two electrons can occupy the same quantum-mechanical state in a given system.
- That is, no two electrons in an atom can have the same values of all four quantum numbers (n , l , m_l , m_s).

Quantum States and the Pauli Exclusion Principle (2 of 2)

- The table lists some of the sets of quantum numbers for electron states in an atom. Because of the exclusion principle, the “number of states” is the same as the maximum number of electrons that can be found in those states.

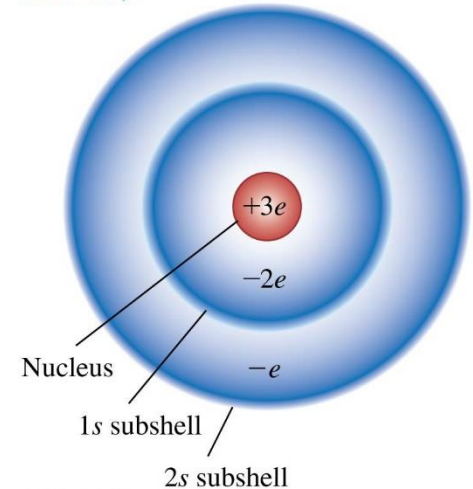
TABLE 41.2 Quantum States of Electrons in the First Four Shells

n	l	m_l	Spectroscopic Notation	Number of States	Shell	
1	0	0	1s	2	K	
2	0	0	2s	2		
2	1	-1, 0, 1	2p	6	8	L
3	0	0	3s	2		
3	1	-1, 0, 1	3p	6	18	M
3	2	-2, -1, 0, 1, 2	3d	10		
4	0	0	4s	2	32	N
4	1	-1, 0, 1	4p	6		
4	2	-2, -1, 0, 1, 2	4d	10		
4	3	-3, -2, -1, 0, 1, 2, 3	4f	14		

A Multielectron Atom

- Shown is a sketch of a lithium atom, which has three electrons.
- The allowed electron states are naturally arranged in **shells** of different size centered on the nucleus.
- Due to the Pauli exclusion principle, the 1s subshell of the *K* shell ($n = 1, l = 0, m_l = 0$) can accommodate only two electrons (one with $m_s = +\frac{1}{2}$, one with $m_s = -\frac{1}{2}$).
- Hence the third electron goes into the 2s subshell of the *L* shell ($n = 2, l = 0, m_l = 0$).

On average, the 2s electron is considerably farther from the nucleus than the 1s electrons. Therefore, it experiences a net nuclear charge of approximately $+3e - 2e = +e$ (rather than $+3e$).



Screening in Multielectron Atoms

- An atom of atomic number Z has a nucleus of charge $+Ze$ and Z electrons of charge $-e$ each.
- Electrons in outer shells “see” a nucleus of charge $+Z_{\text{eff}} e$, where $Z_{\text{eff}} < Z$, because the nuclear charge is partially “screened” by electrons in the inner shells.
- So an electron that spends all its time completely outside a positive charge $Z_{\text{eff}} e$ has energy levels:

Effective (screened) atomic number

Energy levels of an electron with screening

$$E_n = -\frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV})$$

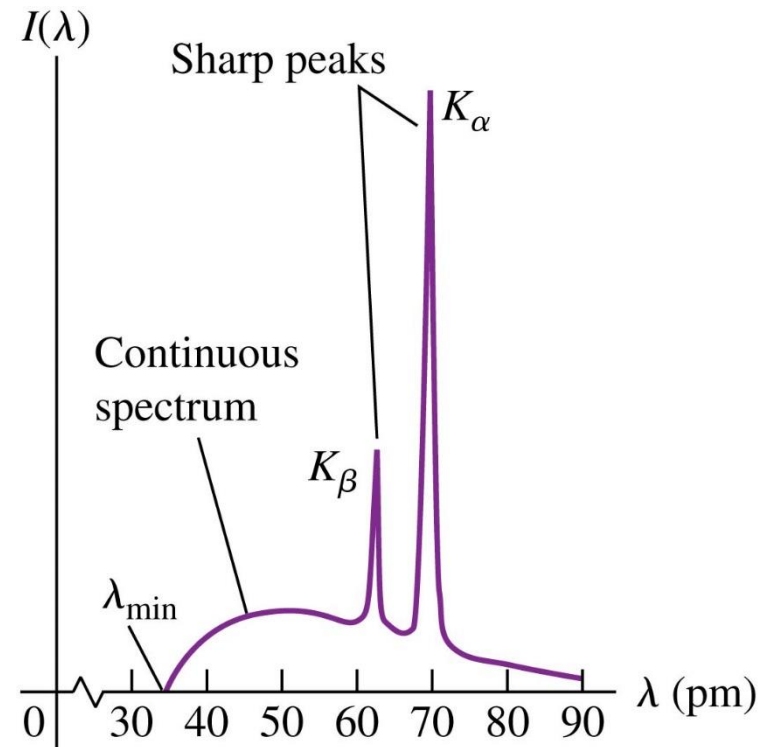
Principal quantum number

The diagram features a light yellow background. On the left, the text 'Energy levels of an electron with screening' is written in blue. A blue dotted arrow points from this text to the E_n term in the equation. Above the equation, the text 'Effective (screened) atomic number' is written in blue, with a blue dotted arrow pointing to the Z_{eff} term. Below the equation, the text 'Principal quantum number' is written in blue, with a blue dotted arrow pointing to the n^2 term in the denominator.

- [Video Tutor Solution: Example 41.9](#)

X-Ray Spectroscopy

- When atoms are bombarded with high-energy electrons, x rays are emitted.
- There is a continuous spectrum of x rays as well as strong **characteristic x-ray emission** at certain definite wavelengths.
- The two sharp spikes shown are characteristic for molybdenum.



X-Ray Spectroscopy: Moseley's Law (1 of 2)

- Moseley showed the following relation for the x-ray frequency of K_α emission:

Moseley's law:

$$f = (2.48 \times 10^{15} \text{ Hz})(Z - 1)^2$$

Frequency of K_α line in characteristic x-ray spectrum of an element

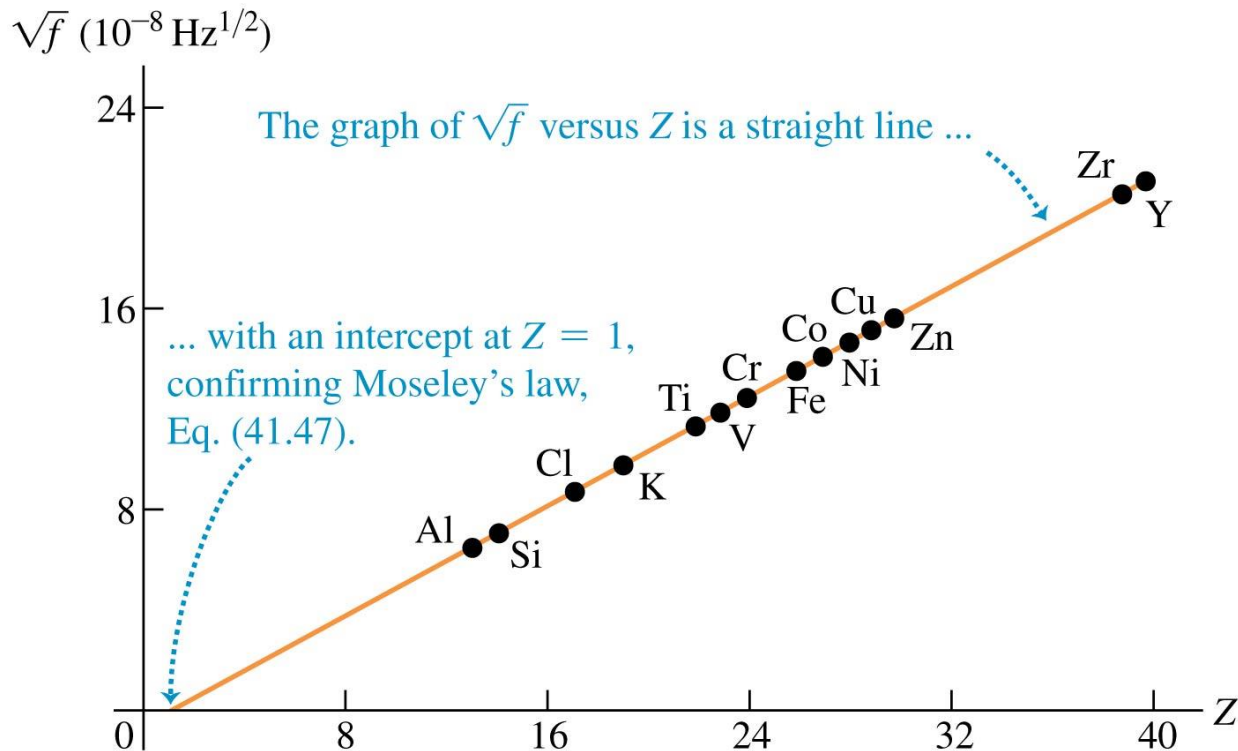
Atomic number of element

- This is consistent with our model of multielectron atoms.
- Bombarding an atom with a high-energy electron can knock an atomic electron out of the innermost K shell.
- K_α x rays are produced when an electron from the L shell falls into the K -shell vacancy.
- The energy of an electron in each shell depends on Z , so the x-ray energy released does as well.

X-Ray Spectroscopy: Moseley's Law

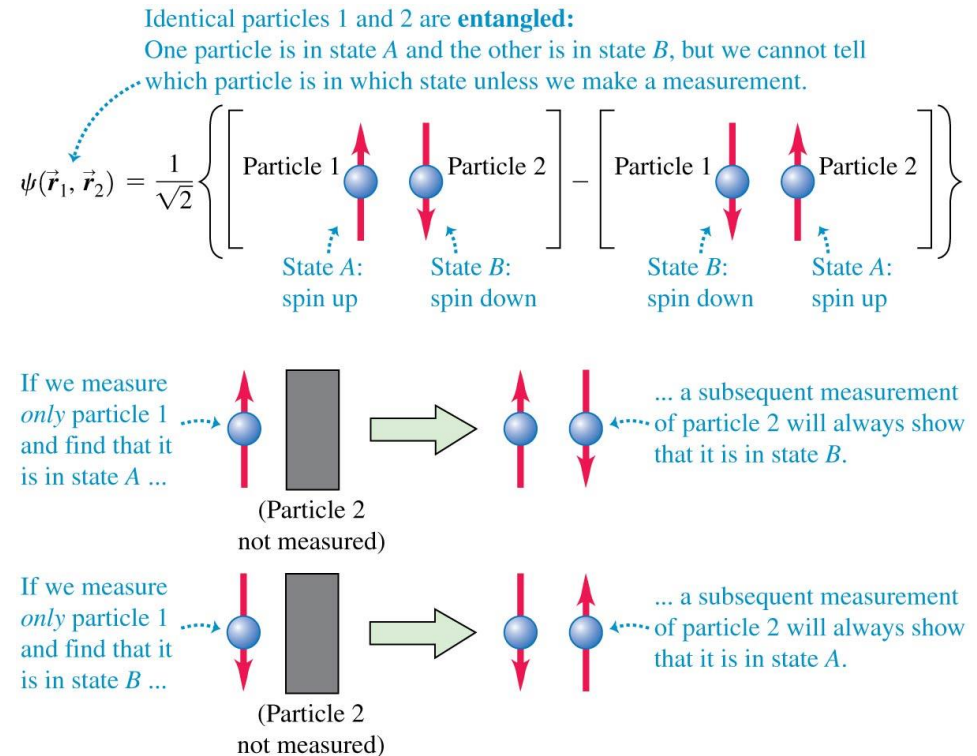
(2 of 2)

- Shown below is the square root of Moseley's Measured frequencies of the K_{α} line for 14 elements.



Quantum Entanglement

- If two particles are in an entangled state, making a measurement of one particle determines the result of a subsequent measurement of the other particle.



Because the two particles are entangled, measuring the state of particle 1 determines the state of particle 2. This is true even if the two particles do not interact.