# PHYS1001B College Physics IB

## Modern Physics IV Atomic Structure (Ch. 41)

# 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. How can one extra electron make these two elements so dramatically different?

# Outline

- 41-1 The Schrödinger Equation in Three Dimensions
- 41-2 Particle in a Three-Dimensional Box
- 41-3 The Hydrogen Atom
- 41-6 Many-Electron Atoms and the Exclusion Principle

# 41-1 The Schrödinger Equation in Three Dimensions

$$K = p^2/2m \qquad K = \frac{p_x^{\,2}}{2m} + \frac{p_y^{\,2}}{2m} + \frac{p_z^{\,2}}{2m}$$

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

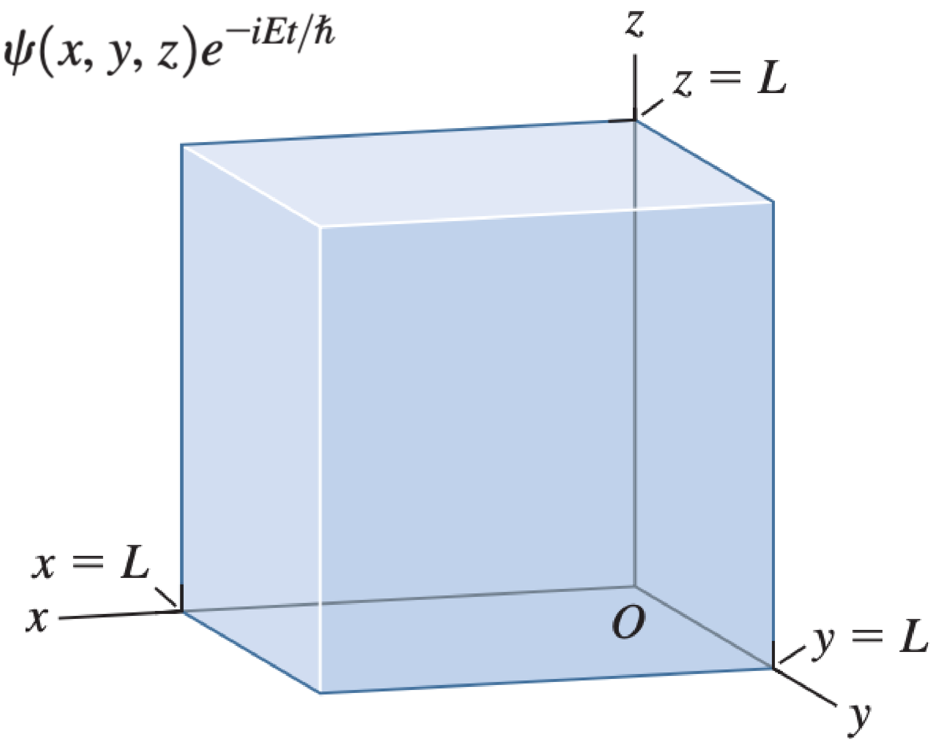
$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar}$$

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

Normalization condition $\displaystyle\int |\psi(x, y, z)|^2\, dV = 1$

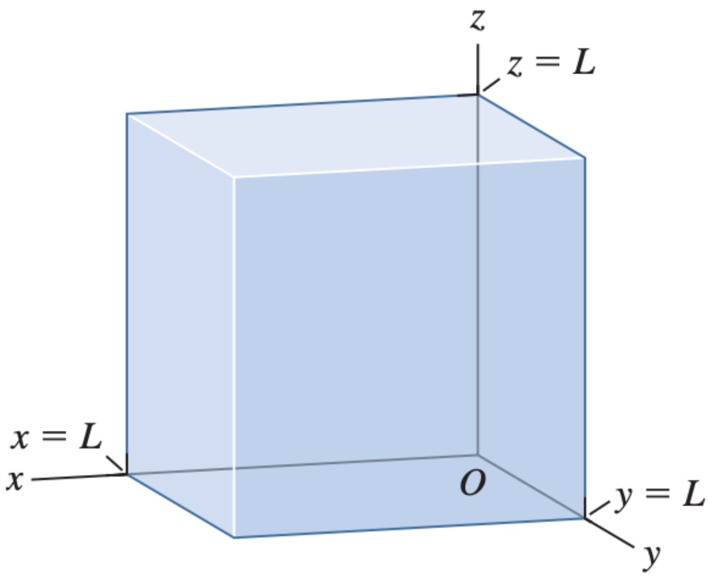
# 41-2 Particle in a Three-Dimensional Box

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar}$$




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

# 41-2 Particle in a Three-Dimensional Box

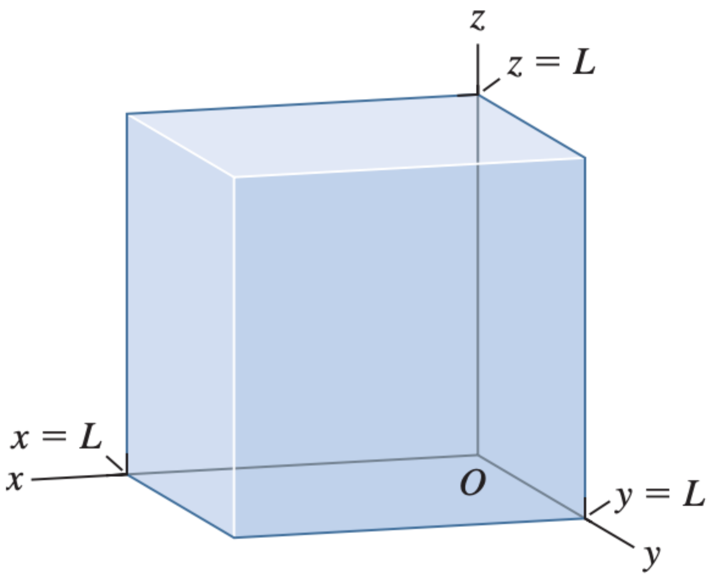



$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

$$-\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{d^2X(x)}{dx^2} + X(x)Z(z)\frac{d^2Y(y)}{dy^2} + X(x)Y(y)\frac{d^2Z(z)}{dz^2}\right)$$
$$= EX(x)Y(y)Z(z)$$

$$\left(-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}\right) + \left(-\frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}\right) = E$$

# 41-2 Particle in a Three-Dimensional Box




$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} = E_X X(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y(y)}{dy^2} = E_Y Y(y) \qquad E_X + E_Y + E_Z = E$$

$$-\frac{\hbar^2}{2m}\frac{d^2Z(z)}{dz^2} = E_Z Z(z)$$

$$X_{n_X}(x) = C_X \sin\frac{n_X \pi x}{L} \quad (n_X = 1, 2, 3, \ldots) \qquad E_X = \frac{{n_X}^2\pi^2\hbar^2}{2mL^2} \quad (n_X = 1, 2, 3, \ldots)$$

$$Y_{n_Y}(y) = C_Y \sin\frac{n_Y \pi y}{L} \quad (n_Y = 1, 2, 3, \ldots) \qquad E_Y = \frac{{n_Y}^2\pi^2\hbar^2}{2mL^2} \quad (n_Y = 1, 2, 3, \ldots)$$

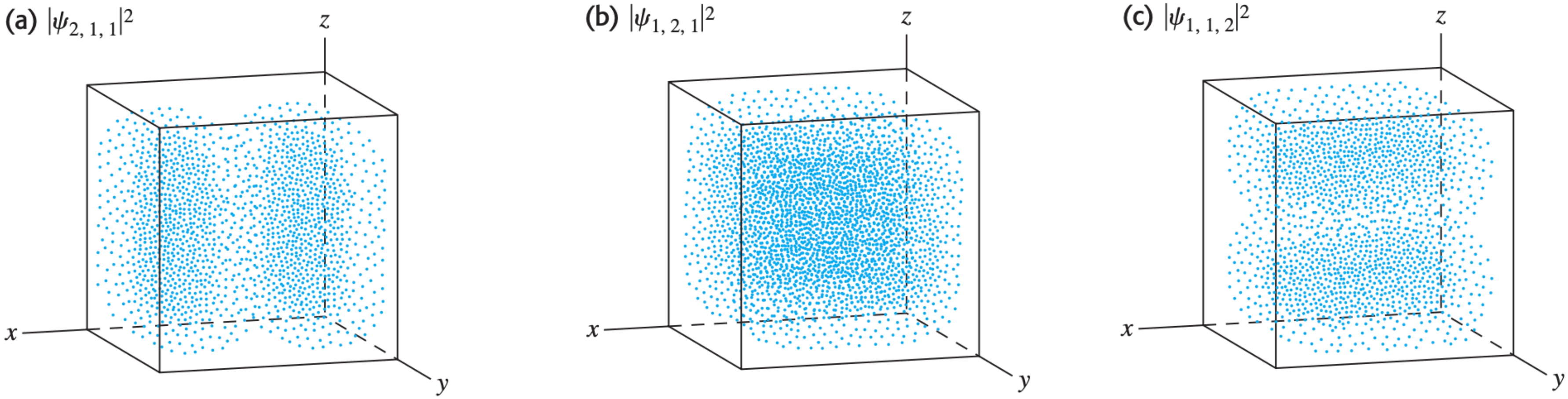
$$Z_{n_Z}(z) = C_Z \sin\frac{n_Z \pi z}{L} \quad (n_Z = 1, 2, 3, \ldots) \qquad E_Z = \frac{{n_Z}^2\pi^2\hbar^2}{2mL^2} \quad (n_Z = 1, 2, 3, \ldots)$$

# 41-2 Particle in a Three-Dimensional Box

$$\psi_{n_X,n_Y,n_Z}(x, y, z) = C\sin\frac{n_X\pi x}{L}\sin\frac{n_Y\pi y}{L}\sin\frac{n_Z\pi z}{L}$$

$$(n_X = 1, 2, 3, \ldots; n_Y = 1, 2, 3, \ldots; n_Z = 1, 2, 3, \ldots)$$

Probability distribution function $|\psi_{n_X,n_Y,n_Z}(x, y, z)|^2$ for $(n_X, n_Y, n_Z)$

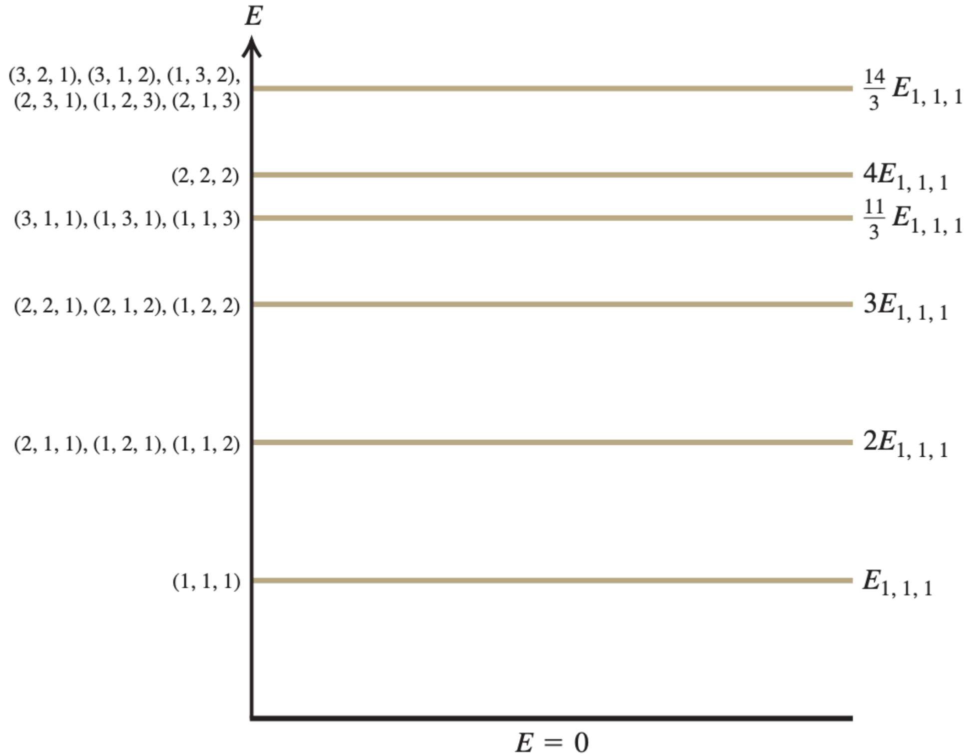



$$|\psi_{2,1,1}(x, y, z)|^2 = |C|^2\sin^2\frac{2\pi x}{L}\sin^2\frac{\pi y}{L}\sin^2\frac{\pi z}{L}$$

# 41-2 Particle in a Three-Dimensional Box

$$E_{n_X,n_Y,n_Z} = \frac{(n_X{}^2 + n_Y{}^2 + n_Z{}^2)\pi^2\hbar^2}{2mL^2} \quad (n_X = 1, 2, 3, \ldots;\ n_Y = 1, 2, 3, \ldots;\ n_Z = 1, 2, 3, \ldots) \tag{41.16}$$

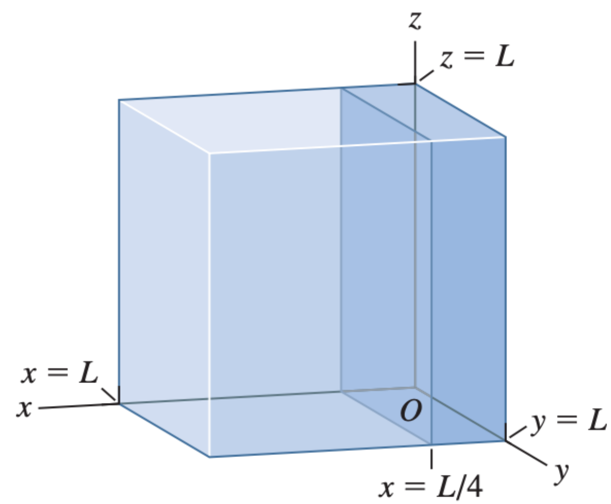
(energy levels, particle in a three-dimensional cubical box)



# Sample Problem

**Example 41.1** **Probability in a three-dimensional box**

(a) Find the value of the constant $C$ that normalizes the wave function of Eq. (41.15). (b) Find the probability that the particle will be found somewhere in the region $0 \le x \le L/4$ (Fig. 41.3) for the cases (i) $(n_X, n_Y, n_Z) = (1, 2, 1)$, (ii) $(n_X, n_Y, n_Z) = (2, 1, 1)$, and (iii) $(n_X, n_Y, n_Z) = (3, 1, 1)$.




**EXECUTE:** (a) From Eq. (41.15),

$$|\psi_{n_X,n_Y,n_Z}(x, y, z)|^2 = |C|^2 \sin^2 \frac{n_X \pi x}{L} \sin^2 \frac{n_Y \pi y}{L} \sin^2 \frac{n_Z \pi z}{L}$$

Hence the normalization condition is

$$\int |\psi_{n_X,n_Y,n_Z}(x, y, z)|^2\, dV$$
$$= |C|^2 \int_{x=0}^{x=L} \int_{y=0}^{y=L} \int_{z=0}^{z=L} \sin^2 \frac{n_X \pi x}{L} \sin^2 \frac{n_Y \pi y}{L} \sin^2 \frac{n_Z \pi z}{L}\, dx\, dy\, dz$$
$$= |C|^2 \left( \int_{x=0}^{x=L} \sin^2 \frac{n_X \pi x}{L}\, dx \right) \left( \int_{y=0}^{y=L} \sin^2 \frac{n_Y \pi y}{L}\, dy \right)$$
$$\times \left( \int_{z=0}^{z=L} \sin^2 \frac{n_Z \pi z}{L}\, dz \right) = 1$$

# Sample Problem

We can use the identity $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$ and the variable substitution $\theta = n_X \pi x/L$ to show that

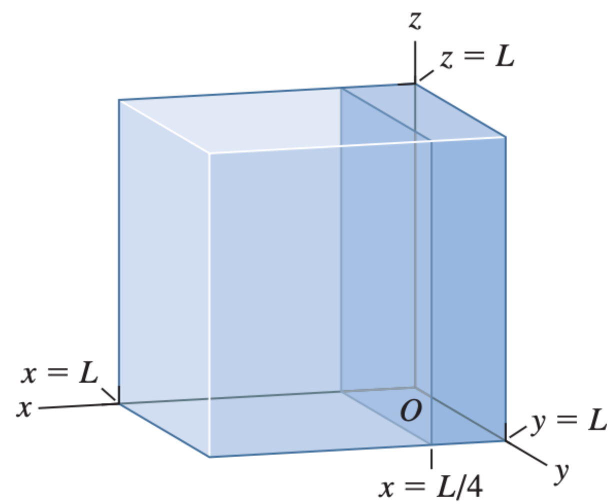
$$\int \sin^2 \frac{n_X \pi x}{L}\, dx = \frac{L}{2n_X\pi}\left[\frac{n_X \pi x}{L} - \frac{1}{2}\sin\left(\frac{2n_X\pi x}{L}\right)\right]$$

$$= \frac{x}{2} - \frac{L}{4n_X\pi}\sin\left(\frac{2n_X\pi x}{L}\right)$$

If we evaluate this integral between $x = 0$ and $x = L$, the result is $L/2$ (recall that $\sin 0 = 0$ and $\sin 2n_X\pi = 0$ for any integer $n_X$). The $y$- and $z$-integrals each yield the same result, so the normalization condition is

$$|C|^2\left(\frac{L}{2}\right)\left(\frac{L}{2}\right)\left(\frac{L}{2}\right) = |C|^2\left(\frac{L}{2}\right)^3 = 1$$

or $|C|^2 = (2/L)^3$. If we choose $C$ to be real and positive, then $C = (2/L)^{3/2}$.



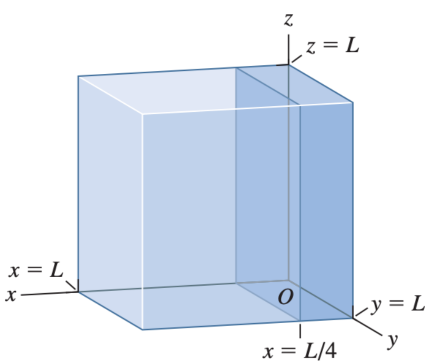
# Sample Problem

(b) We have the same $y$- and $z$-integrals as in part (a), but now the limits of integration on the $x$-integral are $x = 0$ and $x = L/4$:

$$P = \int_{0\le x\le L/4} |\psi_{n_X,n_Y,n_Z}|^2\,dV = |C|^2\left(\int_{x=0}^{x=L/4} \sin^2\frac{n_X\pi x}{L}\,dx\right)$$
$$\times\left(\int_{y=0}^{y=L} \sin^2\frac{n_Y\pi y}{L}\,dy\right)\left(\int_{z=0}^{z=L} \sin^2\frac{n_Z\pi z}{L}\,dz\right)$$

The $x$-integral is

$$\int_{x=0}^{x=L/4} \sin^2\frac{n_X\pi x}{L}\,dx = \left(\frac{x}{2} - \frac{L}{4n_X\pi}\sin\left(\frac{2n_X\pi x}{L}\right)\right]_{x=0}^{x=L/4}$$
$$= \frac{L}{8} - \frac{L}{4n_X\pi}\sin\left(\frac{n_X\pi}{2}\right)$$




Hence the probability of finding the particle somewhere in the region $0 \le x \le L/4$ is

$$P = \left(\frac{2}{L}\right)^3\left(\frac{L}{8} - \frac{L}{4n_X\pi}\sin\left(\frac{n_X\pi}{2}\right)\right)\left(\frac{L}{2}\right)\left(\frac{L}{2}\right)$$
$$= \tfrac{1}{4} - \frac{1}{2n_X\pi}\sin\left(\frac{n_X\pi}{2}\right)$$

This depends only on the value of $n_X$, not on $n_Y$ or $n_Z$. Hence for the three cases we have

(i) $n_X = 1$: $P = \tfrac{1}{4} - \dfrac{1}{2(1)\pi}\sin\left(\dfrac{\pi}{2}\right) = \tfrac{1}{4} - \dfrac{1}{2\pi}(1)$

$$= \tfrac{1}{4} - \frac{1}{2\pi} = 0.091$$

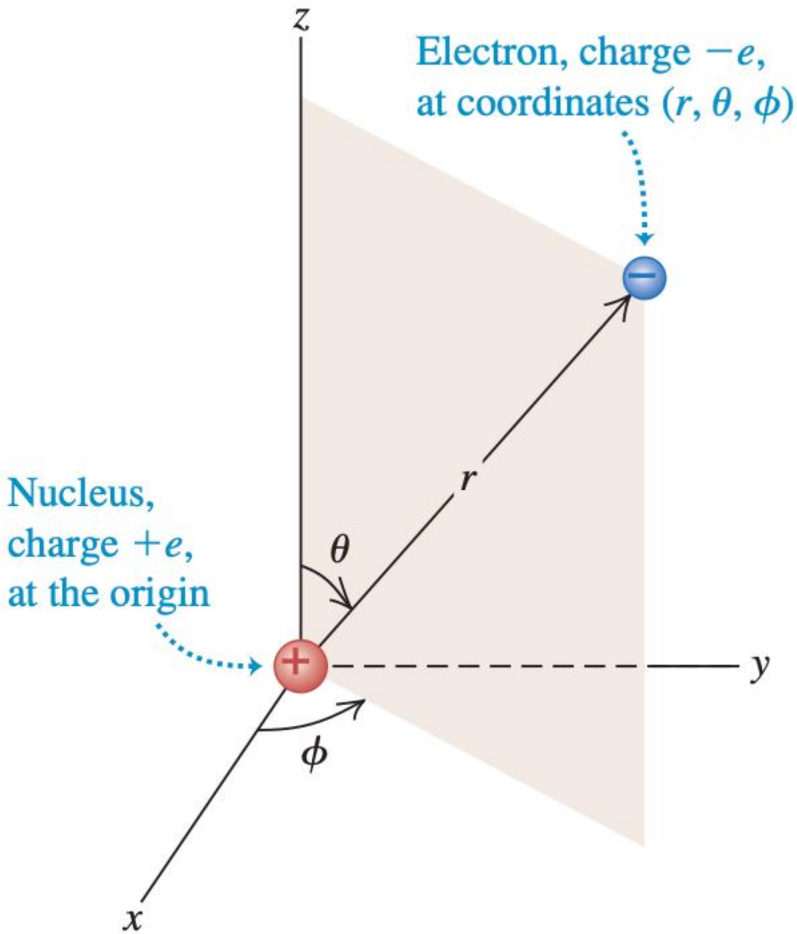
(ii) $n_X = 2$: $P = \tfrac{1}{4} - \dfrac{1}{2(2)\pi}\sin\left(\dfrac{2\pi}{2}\right) = \tfrac{1}{4} - \dfrac{1}{4\pi}\sin\pi$

$$= \tfrac{1}{4} - 0 = 0.250$$

(iii) $n_X = 3$: $P = \tfrac{1}{4} - \dfrac{1}{2(3)\pi}\sin\left(\dfrac{3\pi}{2}\right) = \tfrac{1}{4} - \dfrac{1}{6\pi}(-1)$

$$= \tfrac{1}{4} + \frac{1}{6\pi} = 0.303$$

# 41-3 The Hydrogen Atom




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

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$-\frac{\hbar^2}{2m_r r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left(\frac{\hbar^2 l(l+1)}{2m_r r^2} + U(r)\right)R(r) = ER(r)$$

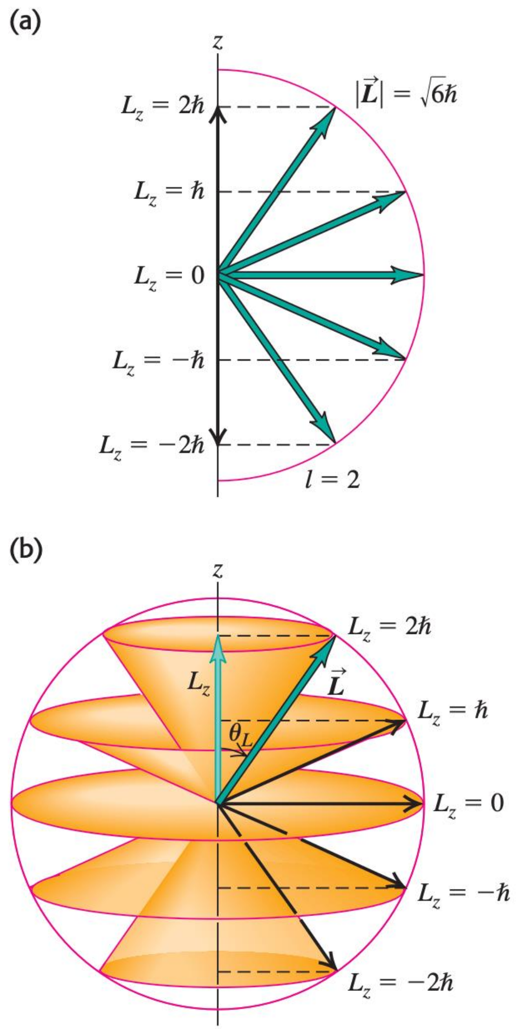
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta(\theta) = 0$$

$$\frac{d^2\Phi(\phi)}{d\phi^2} + m_l^2\Phi(\phi) = 0$$

$$\boxed{E_n = -\frac{1}{(4\pi\epsilon_0)^2}\frac{m_r e^4}{2n^2\hbar^2} = -\frac{13.60\text{ eV}}{n^2}}$$

$n$ the **principal quantum number**

# 41-3 The Hydrogen Atom




**orbital quantum number**

$$L = \sqrt{l(l+1)}\hbar \qquad (l = 0, 1, 2, \ldots, n-1)$$

**magnetic quantum number**

$$L_z = m_l\hbar \qquad (m_l = 0, \pm 1, \pm 2, \ldots, \pm l)$$

$l = 0$: $s$ states
$l = 1$: $p$ states
$l = 2$: $d$ states
$l = 3$: $f$ states
$l = 4$: $g$ states
$l = 5$: $h$ states

# 41-3 The Hydrogen Atom

**Table 41.1 Quantum States of the Hydrogen Atom**

| $n$ | $l$ | $m_l$ | Spectroscopic Notation | Shell |
|---|---|---|---|---|
| 1 | 0 | 0 | $1s$ | $K$ |
| 2 | 0 | 0 | $2s$ | $L$ |
| 2 | 1 | $-1, 0, 1$ | $2p$ | |
| 3 | 0 | 0 | $3s$ | $M$ |
| 3 | 1 | $-1, 0, 1$ | $3p$ | |
| 3 | 2 | $-2, -1, 0, 1, 2$ | $3d$ | |
| 4 | 0 | 0 | $4s$ | $N$ |
| and so on | | | | |

$n = 1$: $K$ shell

$n = 2$: $L$ shell

$n = 3$: $M$ shell

$n = 4$: $N$ shell

# Sample Problem

## Example 41.2 Counting hydrogen states

How many distinct $(n, l, m_l)$ states of the hydrogen atom with $n = 3$ are there? What are their energies?

**EXECUTE:** When $n = 3$, $l$ can be 0, 1, or 2. When $l = 0$, $m_l$ can be only 0 (1 state). When $l = 1$, $m_l$ can be $-1$, 0, or 1 (3 states). When $l = 2$, $m_l$ can be $-2$, $-1$, 0, 1, or 2 (5 states). The total number of $(n, l, m_l)$ states with $n = 3$ is therefore $1 + 3 + 5 = 9$. (In Section 41.5 we'll find that the total number of $n = 3$ states is in fact twice this, or 18, because of electron spin.)

The energy of a hydrogen-atom state depends only on $n$, so all 9 of these states have the same energy. From Eq. (41.21),

$$E_3 = \frac{-13.60\ \text{eV}}{3^2} = -1.51\ \text{eV}$$

# Sample Problem

**Example 41.3** **Angular momentum in an excited level of hydrogen**

Consider the $n = 4$ states of hydrogen. (a) What is the maximum magnitude $L$ of the orbital angular momentum? (b) What is the maximum value of $L_z$? (c) What is the minimum angle between $\vec{L}$ and the $z$-axis? Give your answers to parts (a) and (b) in terms of $\hbar$.

**EXECUTE:** (a) When $n = 4$, the maximum value of the orbital angular-momentum quantum number $l$ is $(n - 1) = (4 - 1) = 3$; from Eq. (41.22),

$$L_{\text{max}} = \sqrt{3(3 + 1)}\hbar = \sqrt{12}\hbar = 3.464\hbar$$

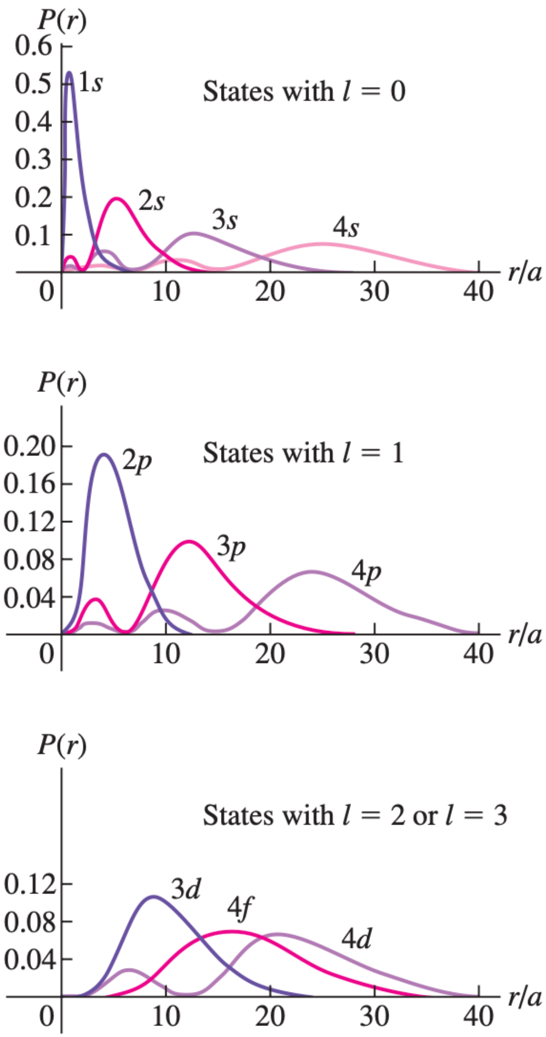
(b) For $l = 3$ the maximum value of $m_l$ is 3. From Eq. (41.23),

$$(L_z)_{\text{max}} = 3\hbar$$

(c) The *minimum* allowed angle between $\vec{L}$ and the $z$-axis corresponds to the *maximum* allowed values of $L_z$ and $m_l$ (Fig. 41.6b shows an $l = 2$ example). For the state with $l = 3$ and $m_l = 3$,

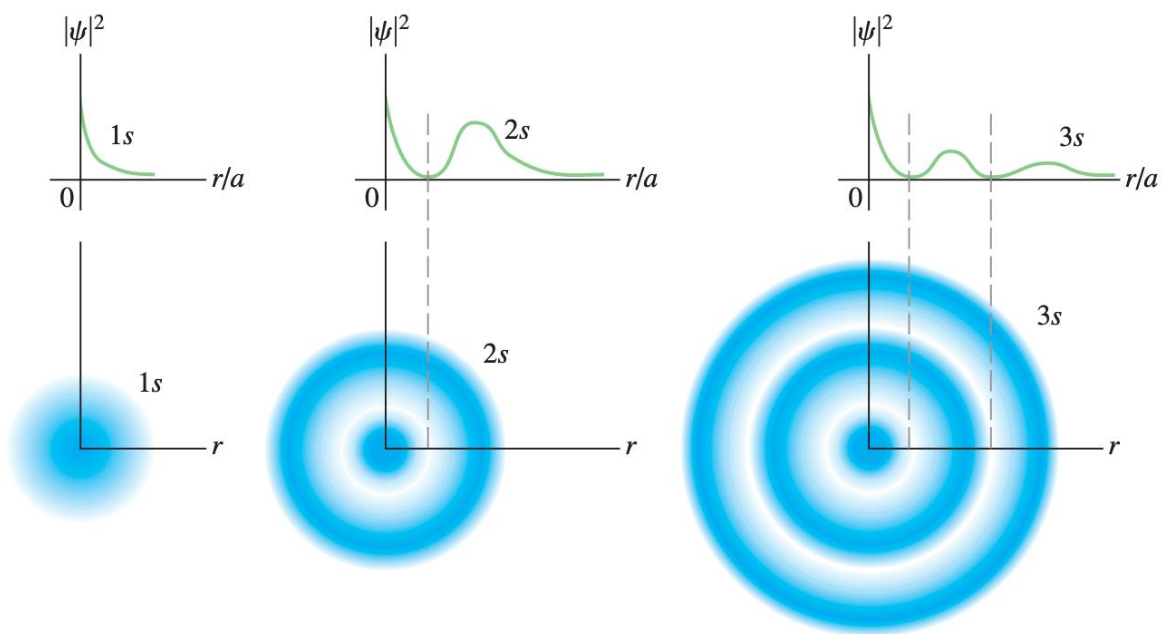
$$\theta_{\text{min}} = \arccos\frac{(L_z)_{\text{max}}}{L} = \arccos\frac{3\hbar}{3.464\hbar} = 30.0°$$

# 41-3 The Hydrogen Atom




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

$$a = \frac{\epsilon_0 h^2}{\pi m_r e^2} = \frac{4\pi\epsilon_0 \hbar^2}{m_r e^2} = 5.29 \times 10^{-11}\ \text{m}$$



# Sample Problem

## Example 41.4 A hydrogen wave function

The ground-state wave function for hydrogen (a 1$s$ state) is

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

(a) Verify that this function is normalized. (b) What is the probability that the electron will be found at a distance less than $a$ from the nucleus?

**EXECUTE:** (a) Since the wave function depends only on the radial coordinate $r$, we can choose our volume elements to be spherical shells of radius $r$, thickness $dr$, and volume $dV$ given by Eq. (41.24). We then have

$$\int_{\text{all space}} |\psi_{1s}|^2\, dV = \int_0^\infty \frac{1}{\pi a^3} e^{-2r/a}(4\pi r^2\, dr)$$

$$= \frac{4}{a^3}\int_0^\infty r^2 e^{-2r/a}\, dr$$

You can find the following indefinite integral in a table of integrals or by integrating by parts:

$$\int r^2 e^{-2r/a}\, dr = \left(-\frac{ar^2}{2} - \frac{a^2 r}{2} - \frac{a^3}{4}\right)e^{-2r/a}$$

Evaluating this between the limits $r = 0$ and $r = \infty$ is simple; it is zero at $r = \infty$ because of the exponential factor, and at $r = 0$ only the last term in the parentheses survives. Thus the value of the definite integral is $a^3/4$. Putting it all together, we find

$$\int_0^\infty |\psi_{1s}|^2\, dV = \frac{4}{a^3}\int_0^\infty r^2 e^{-2r/a}\, dr = \frac{4}{a^3}\frac{a^3}{4} = 1$$

The wave function *is* normalized.

(b) To find the probability $P$ that the electron is found within $r < a$, we carry out the same integration but with the limits 0 and $a$. We'll leave the details to you (Exercise 41.15). From the upper limit we get $-5e^{-2}a^3/4$; the final result is

$$P = \int_0^a |\psi_{1s}|^2\, 4\pi r^2\, dr = \frac{4}{a^3}\left(-\frac{5a^3 e^{-2}}{4} + \frac{a^3}{4}\right)$$

$$= (-5e^{-2} + 1) = 1 - 5e^{-2} = 0.323$$

# 41-6 Many-Electron Atoms and the Exclusion Principle

symmetric potential-energy function U(r): **central-field approximation**

$$n \geq 1 \quad 0 \leq l \leq n-1 \quad |m_l| \leq l \quad m_s = \pm\tfrac{1}{2} \qquad \text{(allowed values of quantum numbers)}$$

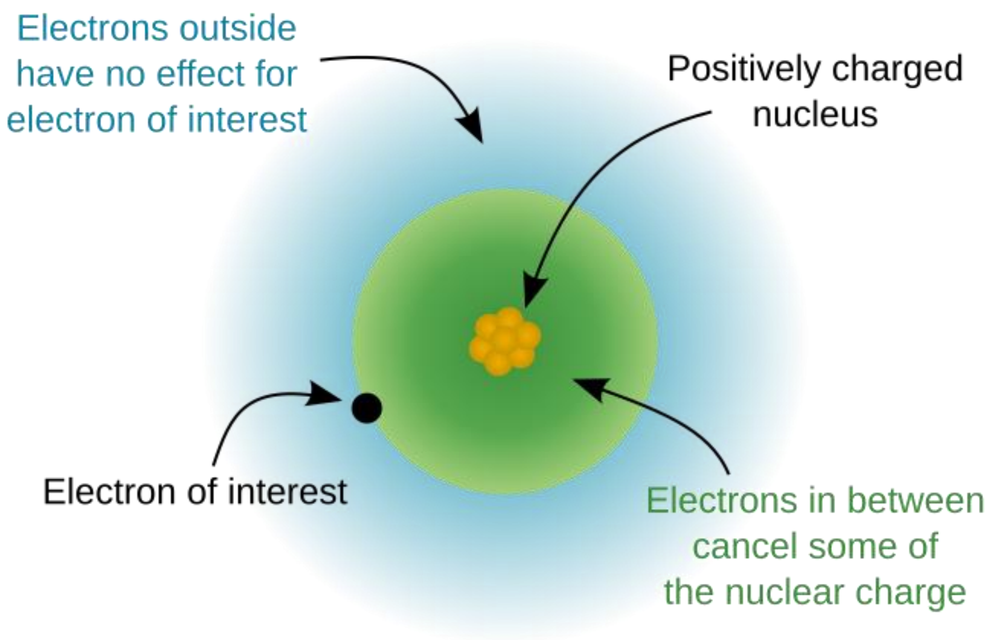
Exclusion principle
no two electrons can occupy the same quantum-mechanical state

$$(\boldsymbol{n}, \boldsymbol{l}, \boldsymbol{m}_{\boldsymbol{l}}, \boldsymbol{m}_{\boldsymbol{s}})$$

# 41-6 Many-Electron Atoms and the Exclusion Principle

| Element | Symbol | Atomic Number ($Z$) | Electron Configuration |
|---|---|---|---|
| Hydrogen | H | 1 | $1s$ |
| Helium | He | 2 | $1s^2$ |
| Lithium | Li | 3 | $1s^2 2s$ |
| Beryllium | Be | 4 | $1s^2 2s^2$ |
| Boron | B | 5 | $1s^2 2s^2 2p$ |
| Carbon | C | 6 | $1s^2 2s^2 2p^2$ |
| Nitrogen | N | 7 | $1s^2 2s^2 2p^3$ |
| Oxygen | O | 8 | $1s^2 2s^2 2p^4$ |
| Fluorine | F | 9 | $1s^2 2s^2 2p^5$ |
| Neon | Ne | 10 | $1s^2 2s^2 2p^6$ |
| Sodium | Na | 11 | $1s^2 2s^2 2p^6 3s$ |
| Magnesium | Mg | 12 | $1s^2 2s^2 2p^6 3s^2$ |
| Aluminum | Al | 13 | $1s^2 2s^2 2p^6 3s^2 3p$ |
| Silicon | Si | 14 | $1s^2 2s^2 2p^6 3s^2 3p^2$ |
| Phosphorus | P | 15 | $1s^2 2s^2 2p^6 3s^2 3p^3$ |
| Sulfur | S | 16 | $1s^2 2s^2 2p^6 3s^2 3p^4$ |
| Chlorine | Cl | 17 | $1s^2 2s^2 2p^6 3s^2 3p^5$ |
| Argon | Ar | 18 | $1s^2 2s^2 2p^6 3s^2 3p^6$ |
| Potassium | K | 19 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s$ |
| Calcium | Ca | 20 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ |

# 41-6 Many-Electron Atoms and the Exclusion Principle




Source: wikipedia

Electrons of inner shell screened the charge of protons

$$E_n = -\frac{{Z_{\text{eff}}}^2}{n^2}(13.6\ \text{eV}) \qquad \text{(energy levels with screening)}$$

# Sample Problem

**Example 41.8** **Determining $Z_{eff}$ experimentally**

The measured energy of a 3*s* state of sodium is −5.138 eV. Calculate the value of $Z_{eff}$.

**EXECUTE:** Solving Eq. (41.45) for $Z_{eff}$, we have

$$Z_{eff}^2 = -\frac{n^2 E_n}{13.6\ \text{eV}} = -\frac{3^2(-5.138\ \text{eV})}{13.6\ \text{eV}} = 3.40$$

$$Z_{eff} = 1.84$$