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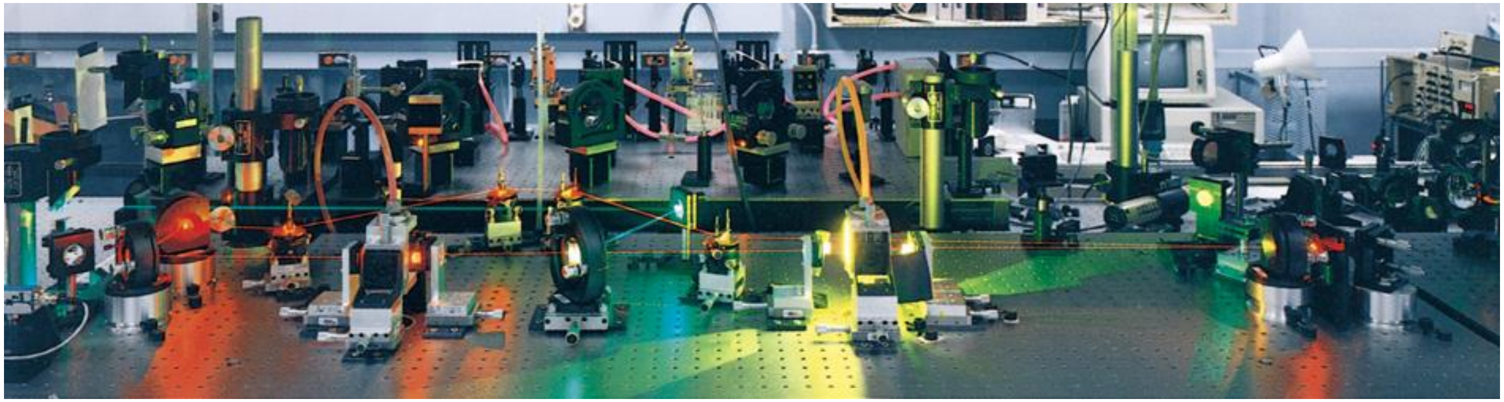
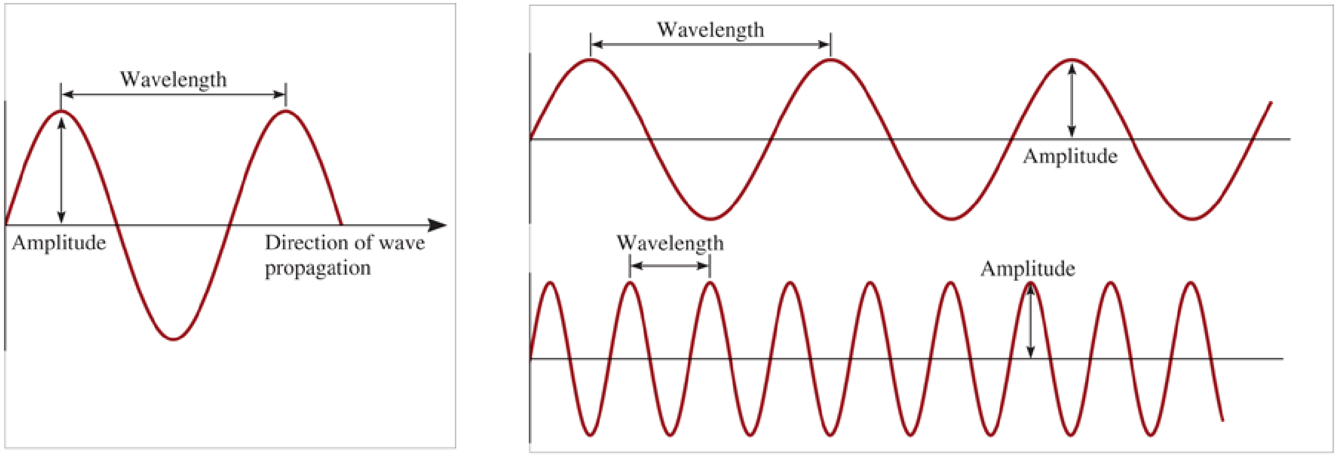


Quantum Theory and the Electronic Structure of Atoms

Chapter 7

Properties of Waves



(a) (b)

Wavelength (λ) is the distance between identical points on successive waves.

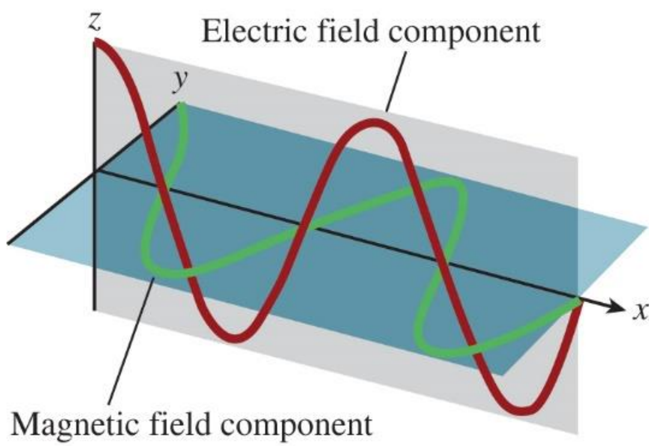
Amplitude is the vertical distance from the midline of a wave to the peak or trough.

Frequency (ν) is the number of waves that pass through a particular point in 1 second (Hz = 1 cycle/s).

The speed (u) of the wave = $\lambda \times \nu$

Light as a Wave

Maxwell (1873), proposed that **visible light consists of electromagnetic waves.**



Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.

Speed of light (c) in vacuum = 3.00×10^8 m / s

All electromagnetic radiation

$$\lambda \times \nu = c$$

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EXAMPLE 7.1

The wavelength of the green light from a traffic signal is centered at 522 nm. What is the frequency of this radiation?

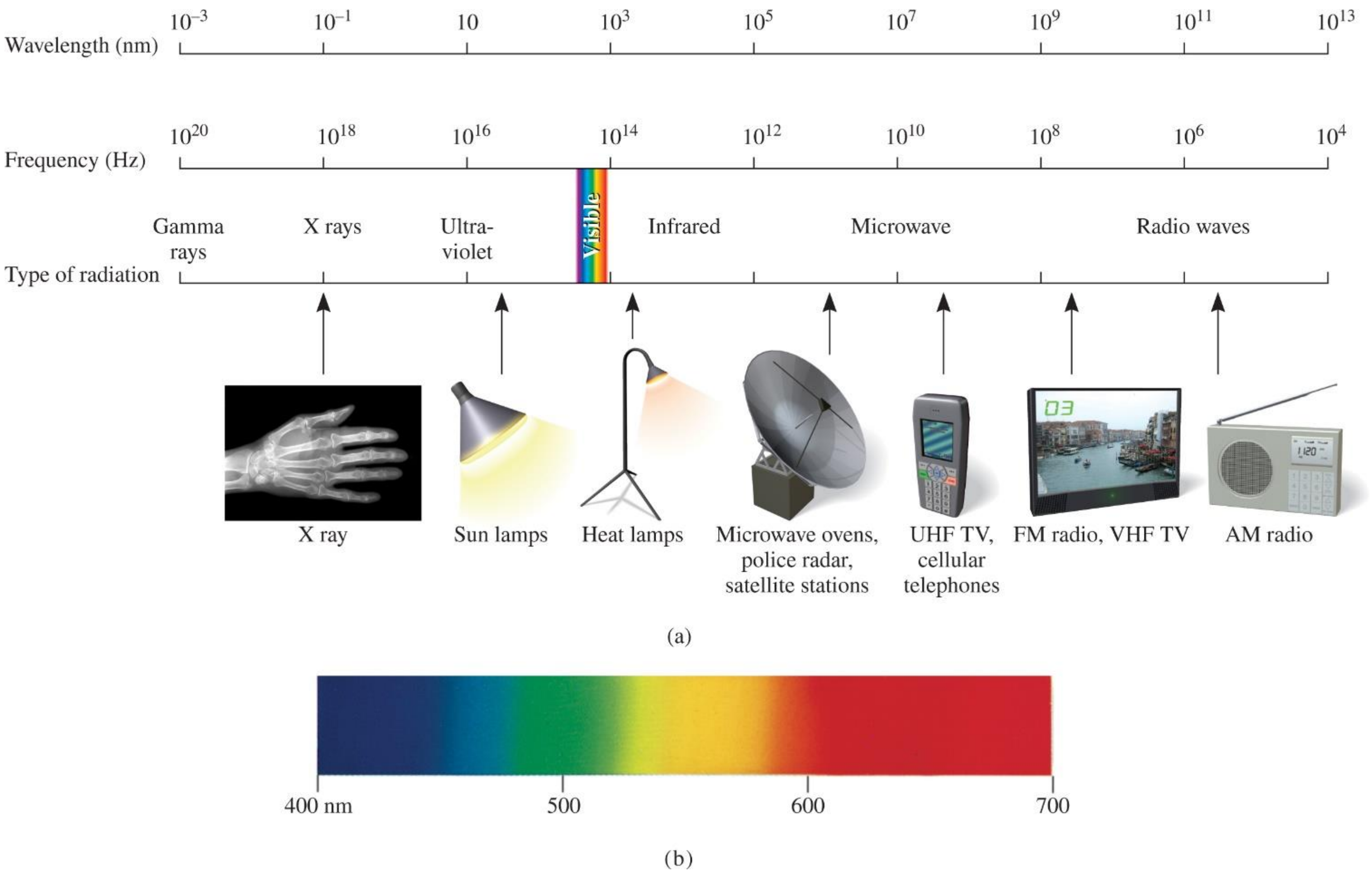
Solution Because the speed of light is given in meters per second, it is convenient to first convert wavelength to meters. Recall that 1 nm = 1×10^{-9} m (see Table 1.3). We write

$$\lambda = 522\ \cancel{\text{nm}} \times \frac{1 \times 10^{-9}\ \text{m}}{1\ \cancel{\text{nm}}} = 522 \times 10^{-9}\ \text{m}$$
$$= 5.22 \times 10^{-7}\ \text{m}$$

Substituting in the wavelength and the speed of light (3.00×10^{8} m/s), the frequency is

$$\nu = \frac{3.00 \times 10^{8}\ \text{m/s}}{5.22 \times 10^{-7}\ \text{m}}$$
$$= 5.75 \times 10^{14}/\text{s, or } 5.75 \times 10^{14}\ \text{Hz}$$

Electromagnetic Spectrum



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a: (X ray): Ted Kinsman/Science Source

“Photoelectric Effect” Solved by Einstein in 1905

Light has both:

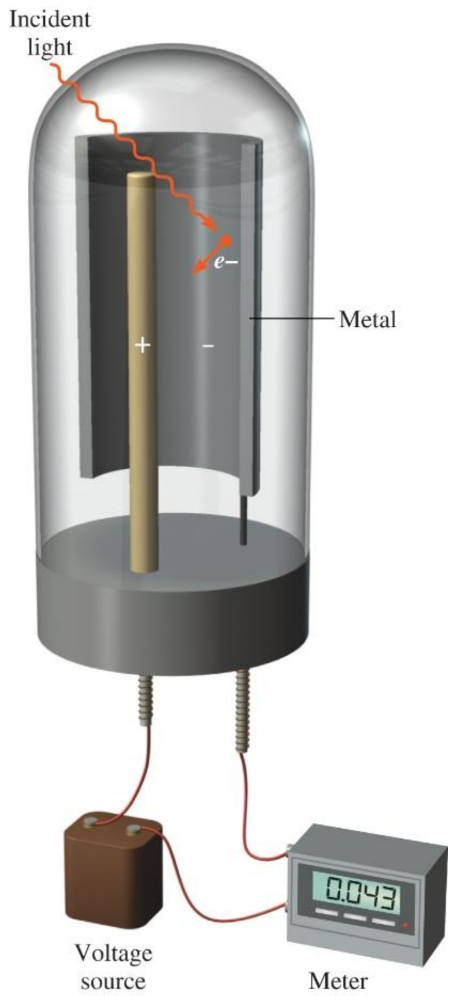
1. **wave nature**
2. **particle nature**

Photon is a “particle” of light

$$h\nu = \text{KE} + \text{W}$$

$$\text{KE} = h\nu - \text{W}$$

where W is the work function and depends how strongly electrons are held in the metal.



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EXAMPLE 7.2

Calculate the energy (in joules) of (a) a photon with a wavelength of 5.00×10^4 nm (infrared region) and (b) a photon with a wavelength of 5.00×10^{-2} nm (X ray region).

Strategy In both (a) and (b) we are given the wavelength of a photon and asked to calculate its energy. We need to use Equation (7.3) to calculate the energy. Planck's constant is given in the text and also on the back inside cover.

Solution (a) From Equation (7.3),

$$\begin{aligned} E &= h\frac{c}{\lambda} \\ &= \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^8\ \text{m/s})}{(5.00 \times 10^4\ \text{nm})\dfrac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}}} \\ &= \boxed{3.98 \times 10^{-21}\ \text{J}} \end{aligned}$$

This is the energy of a single photon with a 5.00×10^4 nm wavelength.

(b) Following the same procedure as in (a), we can show that the energy of the photon that has a wavelength of 5.00×10^{-2} nm is $\boxed{3.98 \times 10^{-15}\ \text{J}}$.

EXAMPLE 7.3

The work function of cesium metal is 3.42×10^{-19} J. (a) Calculate the minimum frequency of light required to release electrons from the metal. (b) Calculate the kinetic energy of the ejected electron if light of frequency $1.00 \times 10^{15}\ \mathrm{s}^{-1}$ is used for irradiating the metal.

Solution (a) Setting KE = 0 in Equation (7.4), we write

$$h\nu = W$$

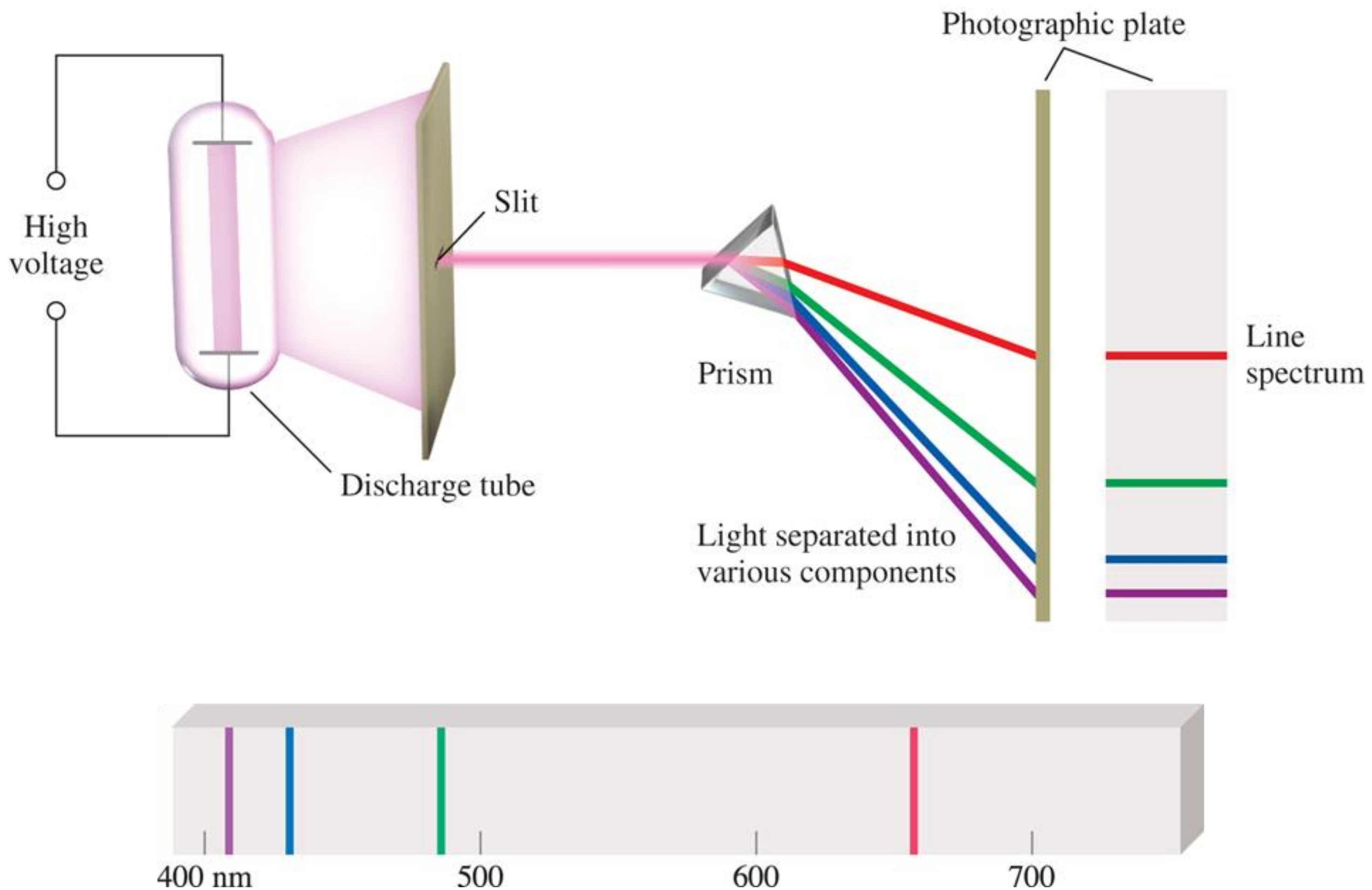
Thus,

$$\begin{aligned}\nu &= \frac{W}{h} = \frac{3.42 \times 10^{-19}\ \mathrm{J}}{6.63 \times 10^{-34}\ \mathrm{J \cdot s}} \\ &= 5.16 \times 10^{14}\ \mathrm{s}^{-1}\end{aligned}$$

(b) Rearranging Equation (7.4) gives

$$\begin{aligned}\mathrm{KE} &= h\nu - W \\ &= (6.63 \times 10^{-34}\ \mathrm{J \cdot s})(1.00 \times 10^{15}\ \mathrm{s}^{-1}) - 3.42 \times 10^{-19}\ \mathrm{J} \\ &= 3.21 \times 10^{-19}\ \mathrm{J}\end{aligned}$$

Line Emission Spectrum of Hydrogen Atoms



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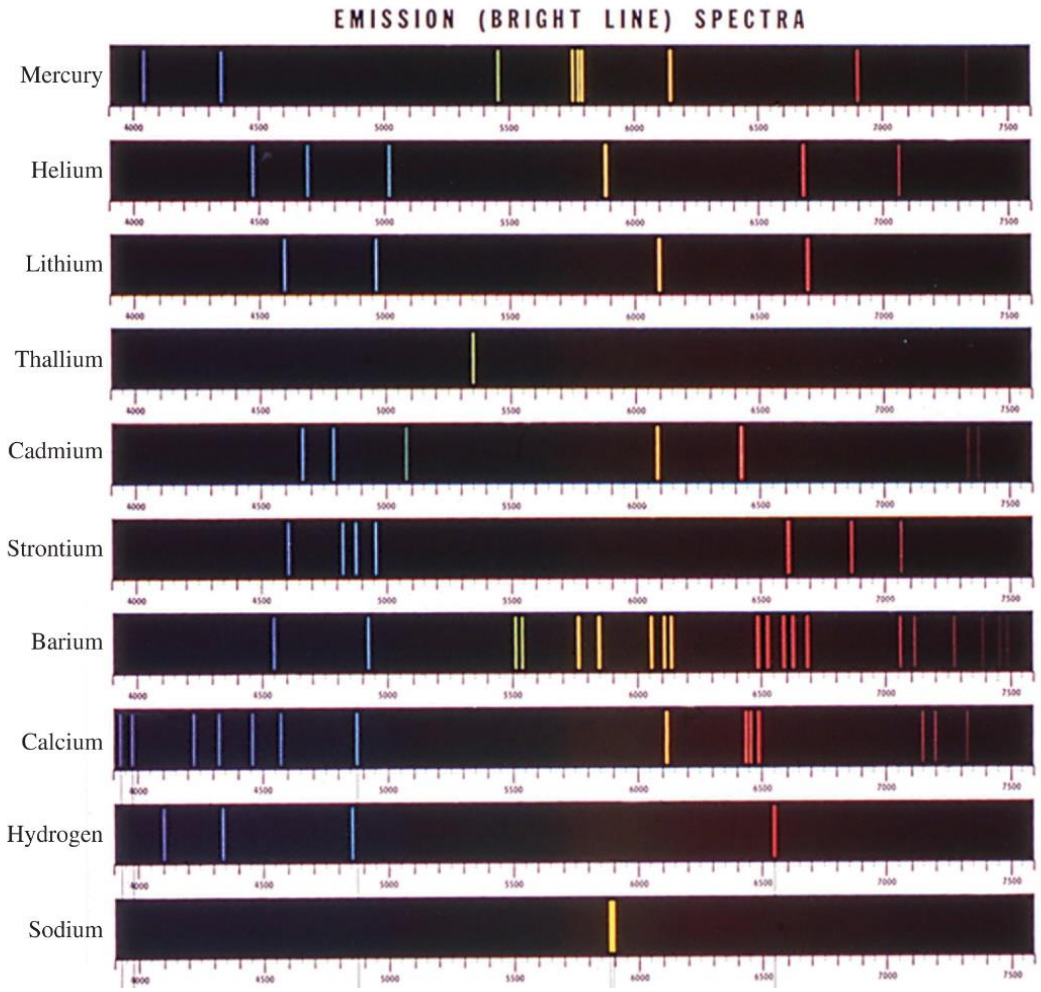
Emission Spectra of Some Elements



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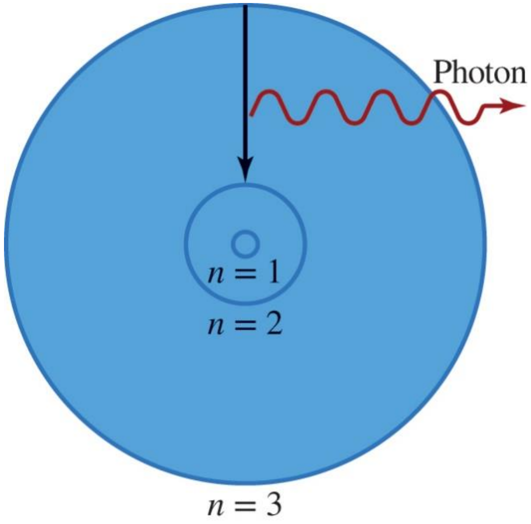
Courtesy of Wabash Instrument Corporation

Bohr's Model of the Atom (1913)

1. e^- can only have specific (quantized) energy values
2. light is emitted as e^- moves from one energy level to a lower energy level



$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

n (principle quantum number) = 1, 2, 3,….

R_H (Rydberg constant) $= 2.18 \times 10^{-18}$ J

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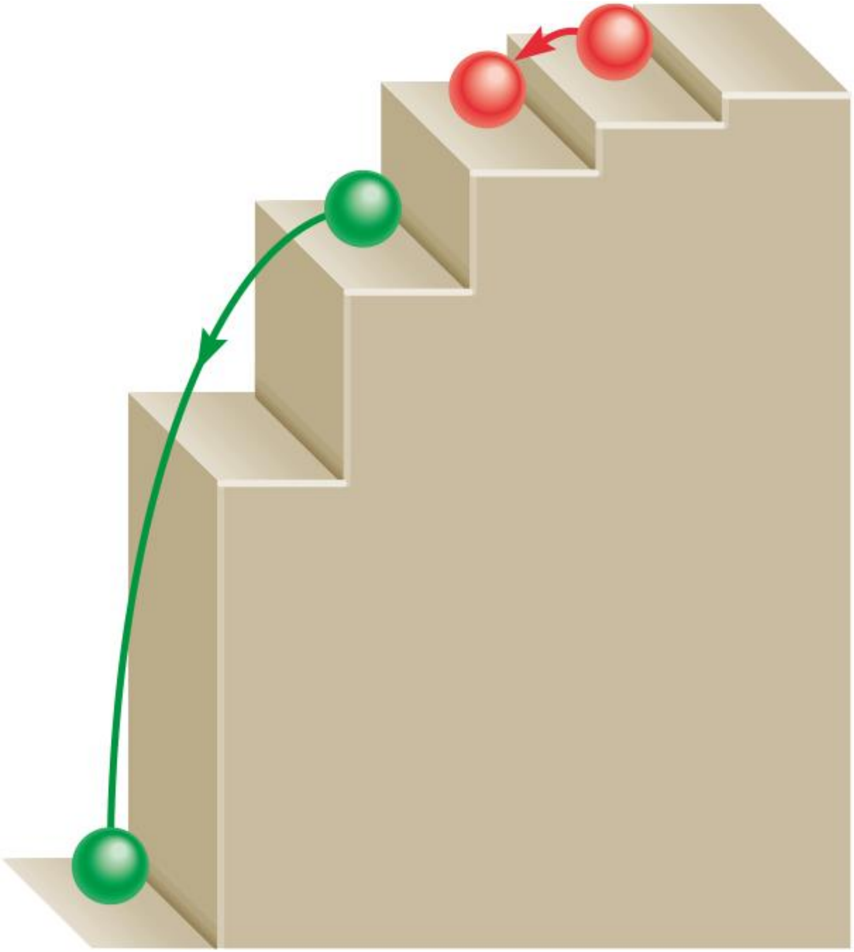
Quantized Energy

When an electron undergoes a transition, it can only exist in an energy level, not between energy levels, because energy levels of the atom are quantized.

A way to think about this is a ball on a staircase. The ball can only rest on steps, not between steps, much like how an electron can only exist in an energy level, not between energy levels.



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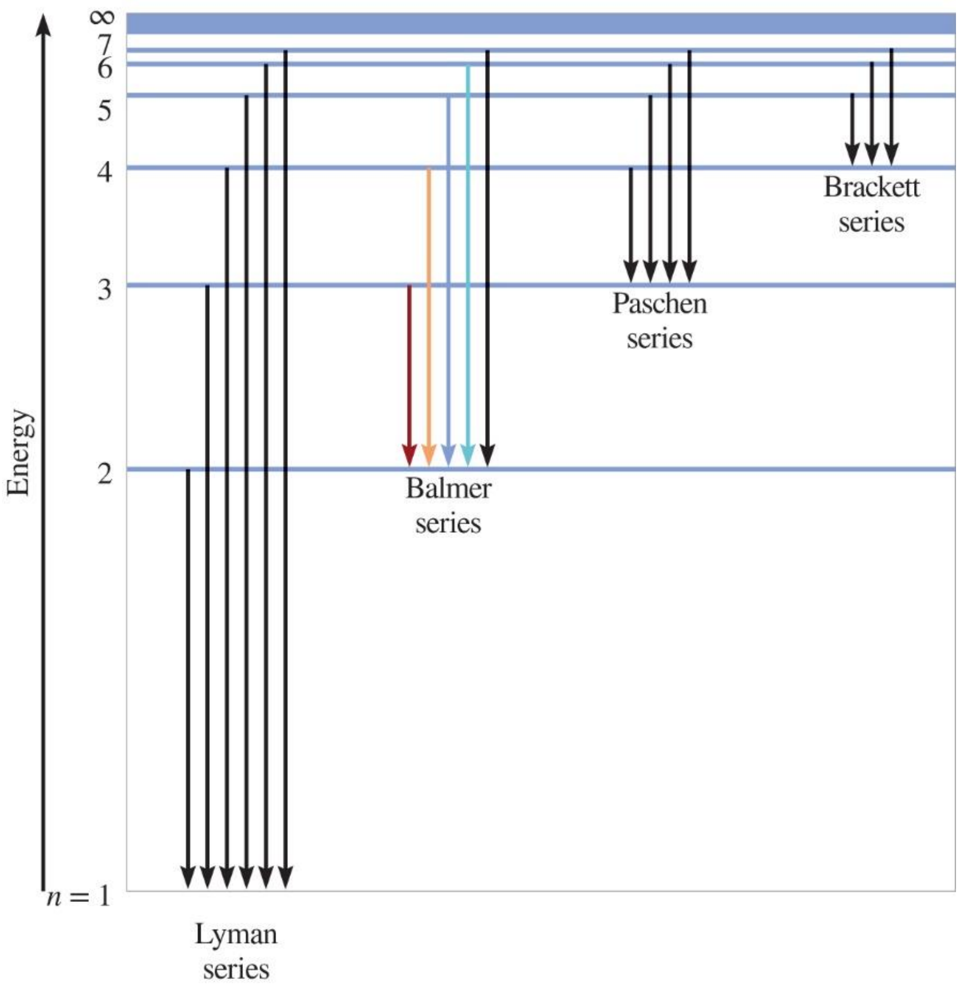
Energy Transitions of the Hydrogen Atom



$$E_{\text{photon}} = \Delta E = E_{\text{f}} - E_{\text{i}}$$

$$E_f = -R_{\text{H}}\left(\frac{1}{n_f^2}\right)$$

$$E_i = -R_{\text{H}}\left(\frac{1}{n_i^2}\right)$$

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

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Hydrogen Atom Emission Series

TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

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EXAMPLE 7.4

What is the wavelength of a photon (in nanometers) emitted during a transition from the $n_i = 5$ state to the $n_f = 2$ state in the hydrogen atom?

Strategy We are given the initial and final states in the emission process. We can calculate the energy of the emitted photon using Equation (7.6). Then from Equations (7.2) and (7.1) we can solve for the wavelength of the photon. The value of Rydberg's constant is given in the text.

Solution From Equation (7.6) we write

$$\begin{aligned}\Delta E &= R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\\ &= 2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{5^2} - \frac{1}{2^2}\right)\\ &= -4.58 \times 10^{-19}\ \text{J}\end{aligned}$$

(Continue..)

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The negative sign indicates that this is energy associated with an emission process. To calculate the wavelength, we will omit the minus sign for ΔE because the wavelength of the photon must be positive. Because $\Delta E = h\nu$ or $\nu = \Delta E/h$, we can calculate the wavelength of the photon by writing

$$\begin{aligned}
\lambda &= \frac{c}{\nu} \\
&= \frac{ch}{\Delta E} \\
&= \frac{(3.00 \times 10^{8}\ \text{m/s})(6.63 \times 10^{-34}\ \text{J} \cdot \text{s})}{4.58 \times 10^{-19}\ \text{J}} \\
&= 4.34 \times 10^{-7}\ \text{m} \\
&= 4.34 \times 10^{-7}\ \text{m} \times \left(\frac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}}\right) = \boxed{434\ \text{nm}}
\end{aligned}$$

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Quantization of Electron Energy

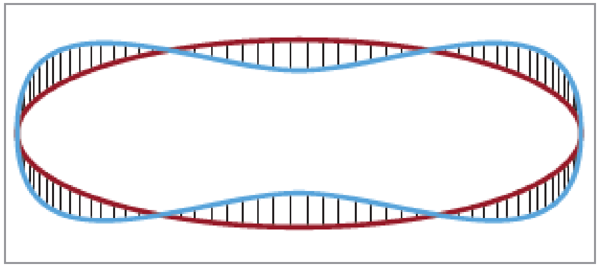
Why is e^- energy quantized?

De Broglie (1924) reasoned that e^- **is both particle and wave.**

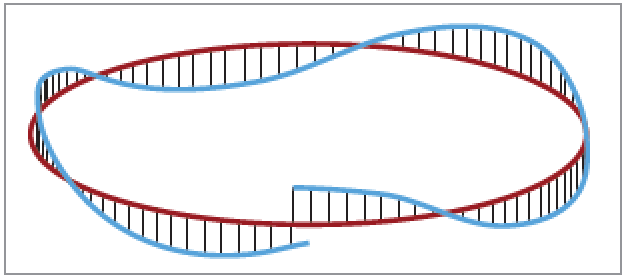
$$2\pi r = n\lambda \qquad \lambda = \frac{h}{mu}$$

u = velocity of e^-

m = mass of e^-



(a)



(b)

EXAMPLE 7.5

Calculate the wavelength of the "particle" in the following two cases: (a) The fastest serve in tennis is about 150 miles per hour, or 68 m/s. Calculate the wavelength associated with a 6.0×10^{-2}-kg tennis ball traveling at this speed. (b) Calculate the wavelength associated with an electron (9.1094×10^{-31} kg) moving at 68 m/s.

Strategy We are given the mass and the speed of the particle in (a) and (b) and asked to calculate the wavelength so we need Equation (7.8). Note that because the units of Planck's constants are J · s, m and u must be in kg and m/s ($1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$), respectively.

Solution (a) Using Equation (7.8) we write

$$\begin{aligned}\lambda &= \frac{h}{mu} \\ &= \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(6.0 \times 10^{-2} \text{ kg}) \times 68 \text{ m/s}} \\ &= \boxed{1.6 \times 10^{-34} \text{ m}}\end{aligned}$$

Comment This is an exceedingly small wavelength considering that the size of an atom itself is on the order of 1×10^{-10} m. For this reason, the wave properties of a tennis ball cannot be detected by any existing measuring device.

(Continued)

(b) In this case,

$$\lambda = \frac{h}{mu}$$

$$= \frac{6.63 \times 10^{-34}\ \text{J} \cdot \text{s}}{(9.1094 \times 10^{-31}\ \text{kg}) \times 68\ \text{m/s}}$$

$$= \boxed{1.1 \times 10^{-5}\ \text{m}}$$

Comment This wavelength (1.1×10^{-5} m or 1.1×10^{4} nm) is in the infrared region. This calculation shows that only electrons (and other submicroscopic particles) have measurable wavelengths.

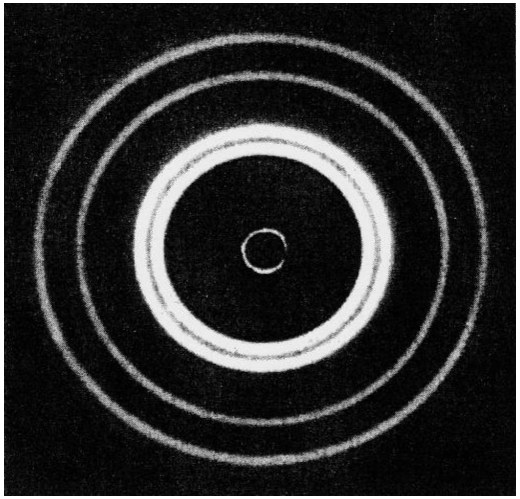
Practice Exercise Calculate the wavelength (in nanometers) of a H atom (mass = 1.674×10^{-27} kg) moving at 7.00×10^{2} cm/s.

Schrodinger Wave Equation 1

In 1926 Schrodinger wrote an **equation that described both the particle and wave nature of the** e^- Wave function (ψ) describes:

1. **energy of e^- with a given ψ**
2. **probability of finding e^- in a volume of space**

Schrodinger's equation can only be solved exactly for the hydrogen atom Must approximate its solution for multi electron systems.



Schrodinger Wave Equation 2

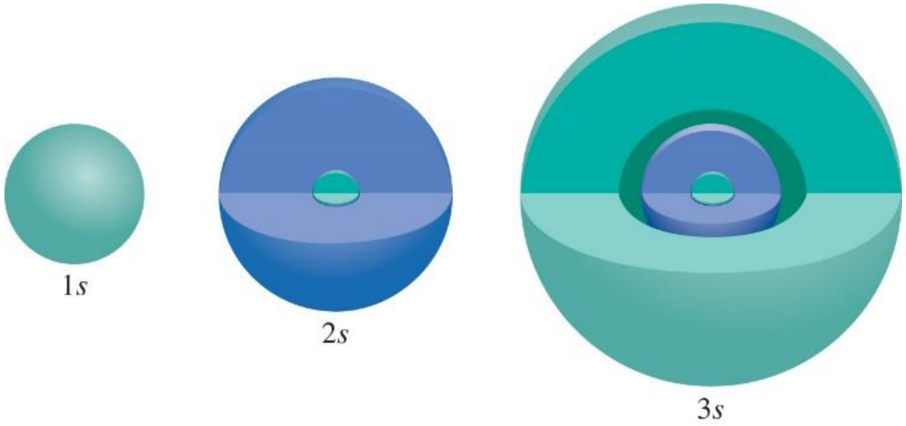
ψ is a function of four numbers called

quantum numbers $(\boldsymbol{n}, l, m_l, m_s)$

principal quantum number ***n***

n = 1, 2, 3, 4, ….

$\boxed{\text{distance of } e^- \text{ from the nucleus}}$



Schrodinger Wave Equation 3

quantum numbers $(n, \boldsymbol{l}, m_l, m_s)$

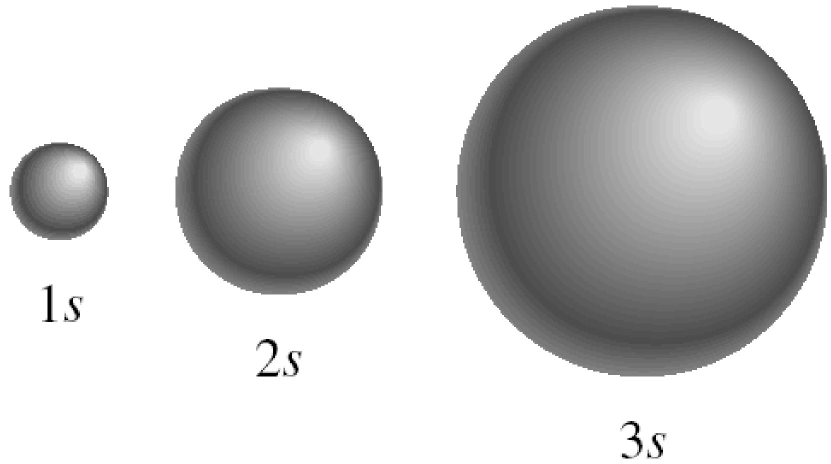
angular momentum quantum number ***l***

Angular momentum quantum number (l) descripts The shape of the "volume" of space that the e^- occupies

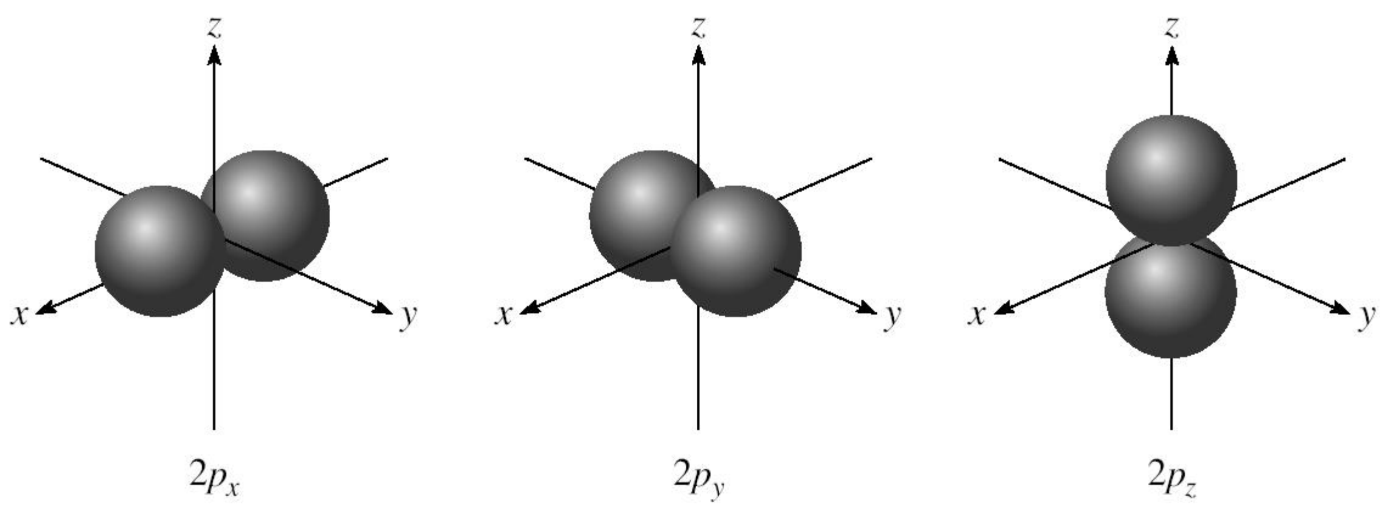
for a given value of *n*, *l* = 0, 1, 2, 3, … *n*-1

n = 1, *l = 0*	*l* = 0 *s* orbital
n = 2, *l* = 0 **or** 1	*l* = 1 *p* orbital
n = 3, *l* = 0, 1, **or** 2	*l* = 2 *d* orbital
n = 4, *l* = 0, 1, 2, **or** 3	*l* = 3 *f* orbital

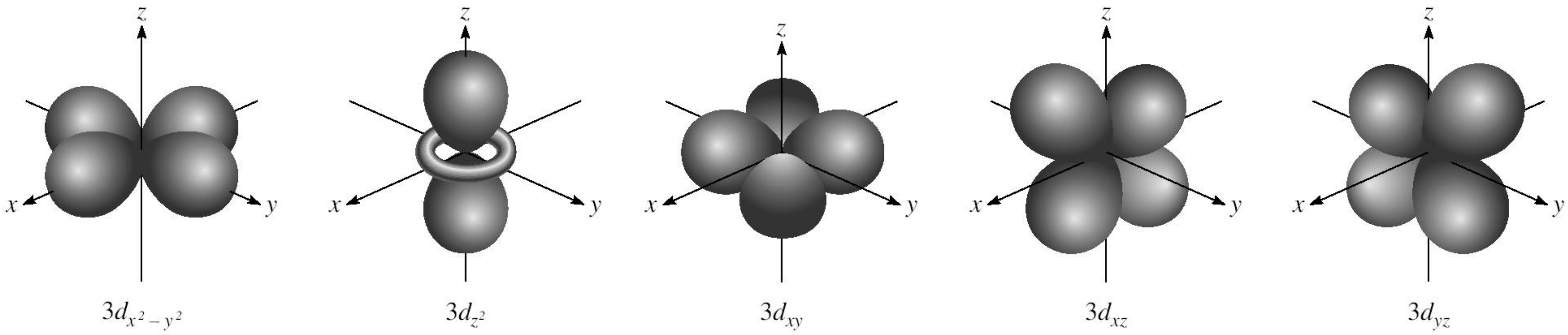
l = 0 (s orbitals)



l = 1 (p orbitals)



l = 2 (d orbitals)



Schrodinger Wave Equation 4

quantum numbers $(n, l, \boldsymbol{m_l}, m_s)$

magnetic quantum number $\boldsymbol{m_l}$

for a given value of l

$\boldsymbol{m_l} = -l, \; \ldots., \; 0, \ldots. + l$

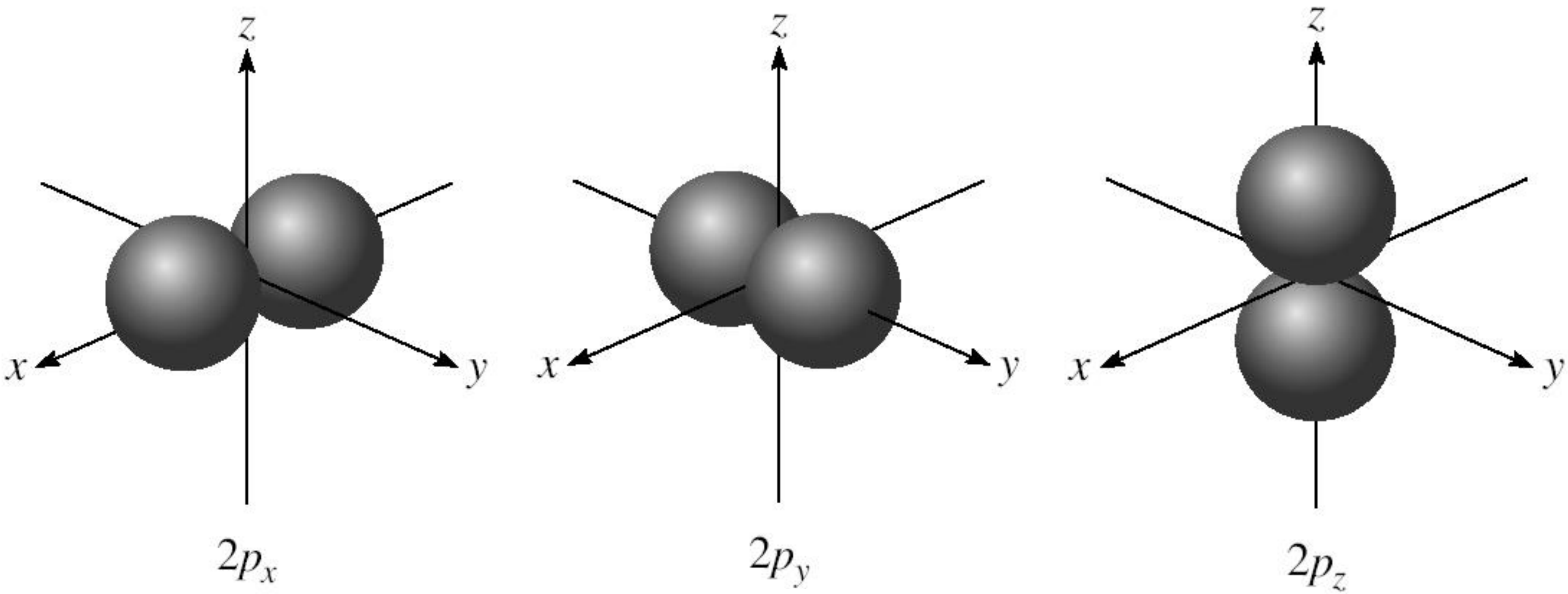
If $l = 1$ (p orbital), $\boldsymbol{m_l} = -1, 0,$ or $+1$

If $l = 2$ (d orbital), $\boldsymbol{m_l} = -2, -1, 0,$ or $+1$

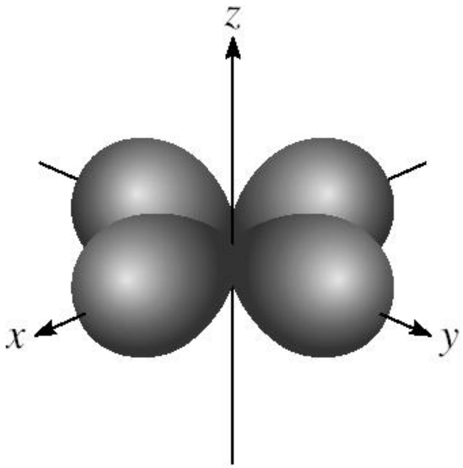
$\boxed{\text{orientation of the orbital in space}}$

m_l = -1, 0, **or** 1

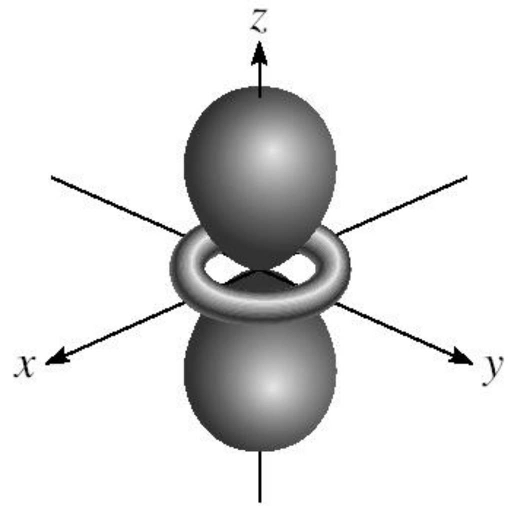
3 orientations in space



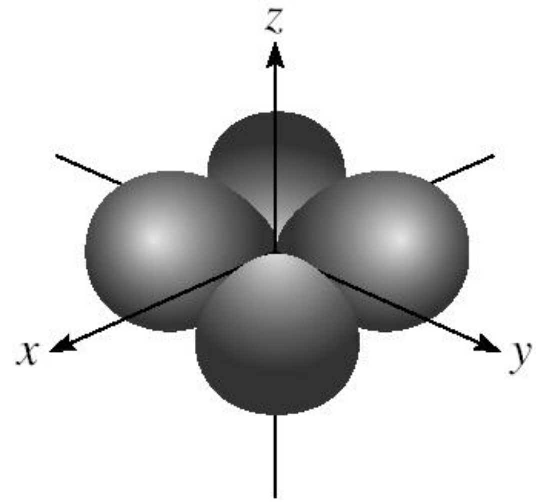
m_l = -2, -1, 0, 1, **or** 2 5 orientations in space



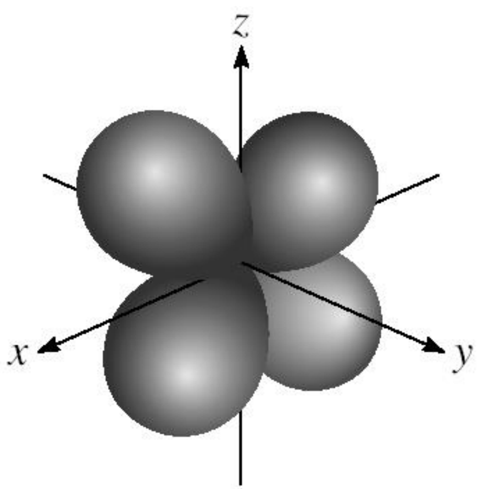
$3d_{x^2-y^2}$



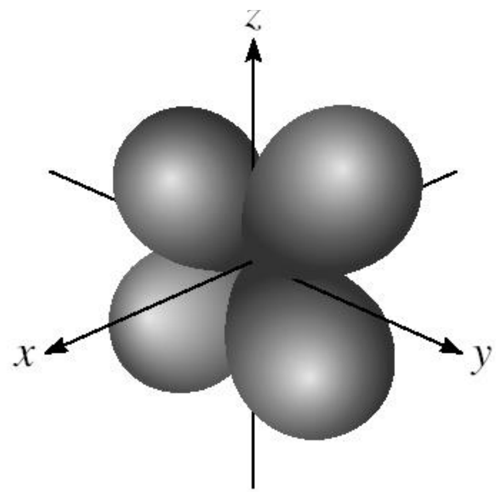
$3d_{z^2}$



$3d_{xy}$



$3d_{xz}$



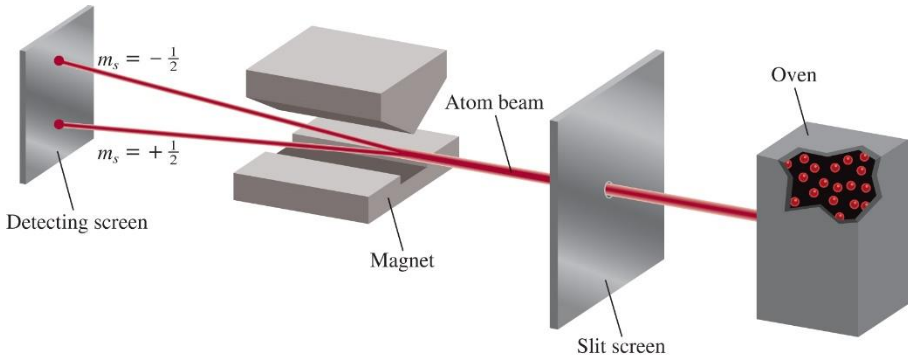
$3d_{yz}$

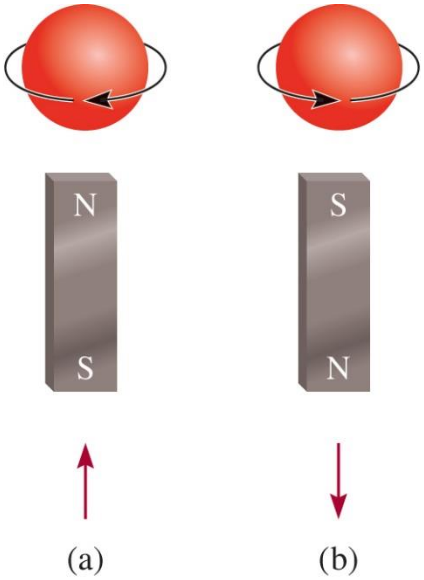
Schrodinger Wave Equation 5

$$\left(n, l, m_l, \boldsymbol{m_s}\right)$$

spin quantum number $\mathbf{m_s}$

$$\boldsymbol{m}_{\mathbf{s}} = +\frac{1}{2}\ \mathbf{or} -\frac{1}{2}$$





$$\boldsymbol{m}_{\mathbf{s}} = +\frac{\mathbf{1}}{\mathbf{2}} \quad \boldsymbol{m}_{\mathbf{s}} = -\frac{\mathbf{1}}{\mathbf{2}}$$

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Quantum Numbers: (n, l, m_l, m_s)

Existence (and energy) of electron in atom is described by its ***unique*** wave function ψ.

Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers.

Each seat is uniquely identified (E, R12, S8)
Each seat can hold only one individual at a time

TABLE 7.2 Relation Between Quantum Numbers and Atomic Orbitals

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

Quantum Numbers: (n, l, m_l, m_s)

Shell – electrons with the same value of ***n***

Subshell – electrons with the same values of ***n*** **and** ***l***

Orbital – electrons with the same values of ***n, l***, **and** ***ml***

How many electrons can an orbital hold?

If n, l, and m_l are fixed, then $m_s = \frac{1}{2}$ or $-\frac{1}{2}$

$\psi = (n, l, m_l, \frac{1}{2})$ or $\psi = (n, l, m_l, -\frac{1}{2})$

An orbital can hold **2 electrons**

How many 2*p* orbitals are there in an atom?

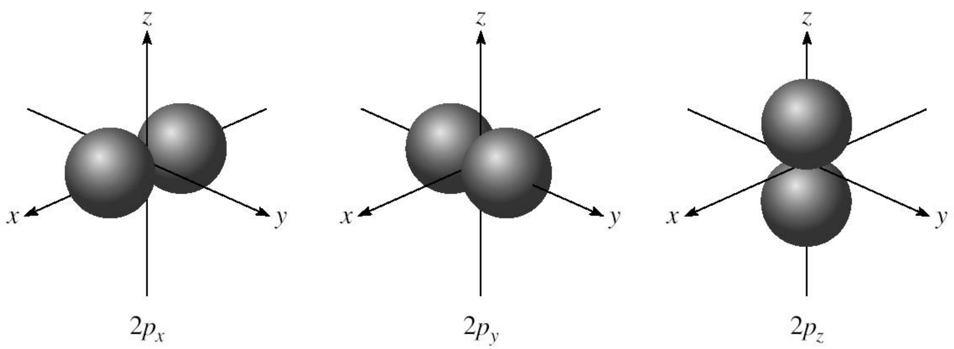
$n = 2$

2*p*

$l = 1$

If $l = 1$, then $m_l = -1, 0,$ or $+1$

<u>3 orbitals</u>



How many electrons can be placed in the 3*d* subshell?

$n = 3$

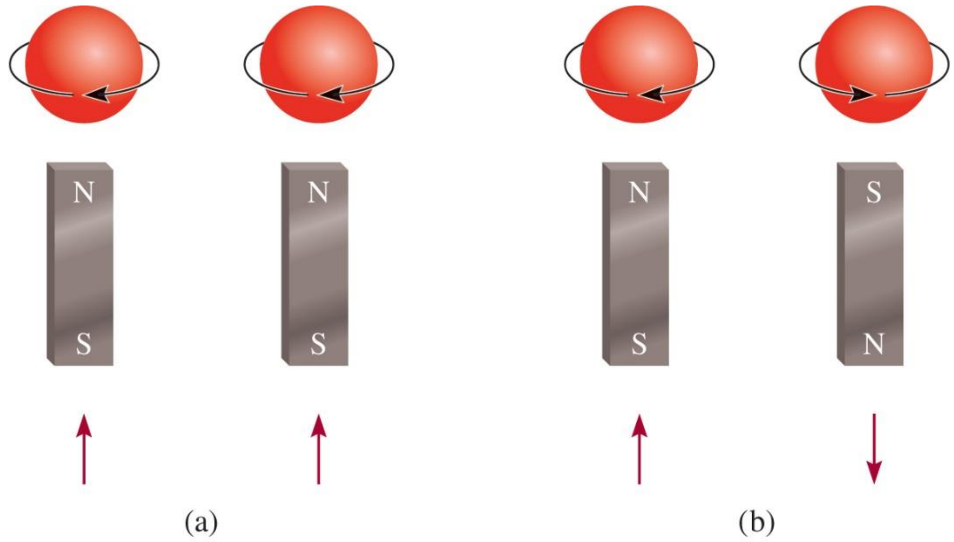
3*d*

$l = 2$

If $l = 2$, then $m_l = -2, -1, 0, +1,$ or $+2$

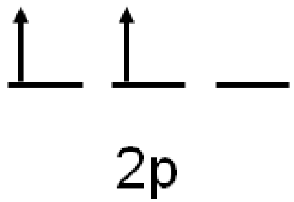
5 orbitals which can hold a total of **<u>10 e^-</u>**

Paramagnetism and Diamagnetism



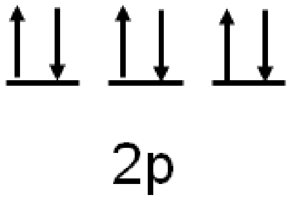
Paramagnetic

unpaired electrons



Diamagnetic

all electrons paired



EXAMPLE 7.8

Write the four quantum numbers for an electron in a 3*p* orbital.

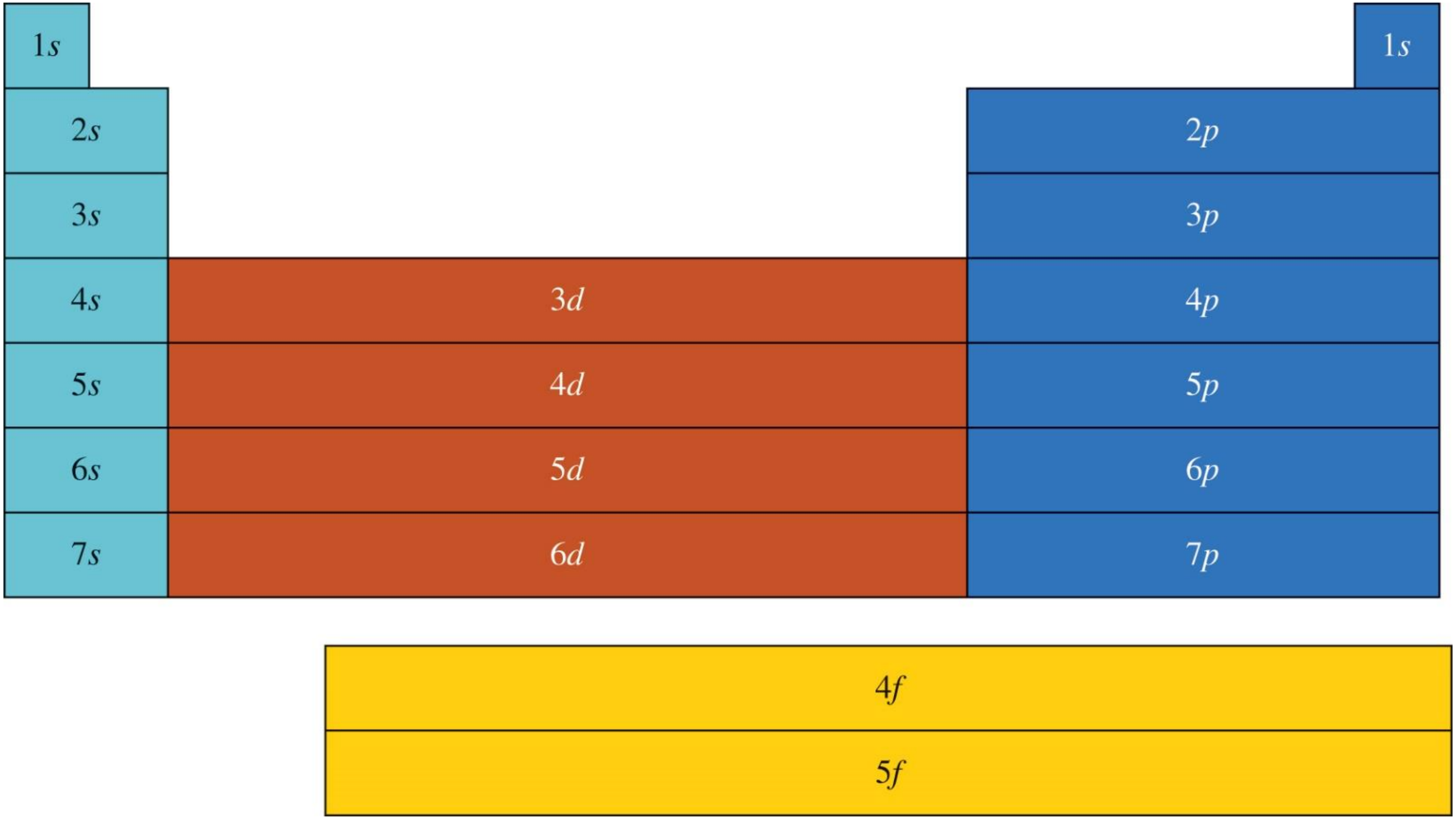
Strategy What do the "3" and "*p*" designate in 3*p*? How many orbitals (values of m_ℓ) are there in a 3*p* subshell? What are the possible values of electron spin quantum number?

Solution To start with, we know that the principal quantum number n is 3 and the angular momentum quantum number ℓ must be 1 (because we are dealing with a *p* orbital).

For $\ell = 1$, there are three values of m_ℓ given by -1, 0, and 1. Because the electron spin quantum number m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$, we conclude that there are six possible ways to designate the electron using the (n, ℓ, m_ℓ, m_s) notation:

$$
\begin{array}{ll}
(3, 1, -1, +\frac{1}{2}) & (3, 1, -1, -\frac{1}{2}) \\
(3, 1, 0, +\frac{1}{2}) & (3, 1, 0, -\frac{1}{2}) \\
(3, 1, 1, +\frac{1}{2}) & (3, 1, 1, -\frac{1}{2})
\end{array}
$$

Outermost subshell being filled with electrons



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What is the electron configuration of Mg?

Mg 12 electrons

1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2$ 2 + 2 + 6 + 2 = 12 electrons

Abbreviated as $[Ne]3s^2$ $[Ne]\ 1s^2 2s^2 2p^6$

What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2 3p^5$ 2 + 2 + 6 + 2 + 5 = 17 electrons

Last electron added to **3p** orbital

$n = \mathbf{3}$ $l = \mathbf{1}$ $m_l = \mathbf{-1, 0, \text{ or } +1}$ $m_s = \mathbf{\frac{1}{2} \text{ or } -\frac{1}{2}}$