CHAPTER 7 QUANTUM THEORY OF THE ATOM

Dr. Yuan Dan

7. Quantum Theory of the Atom

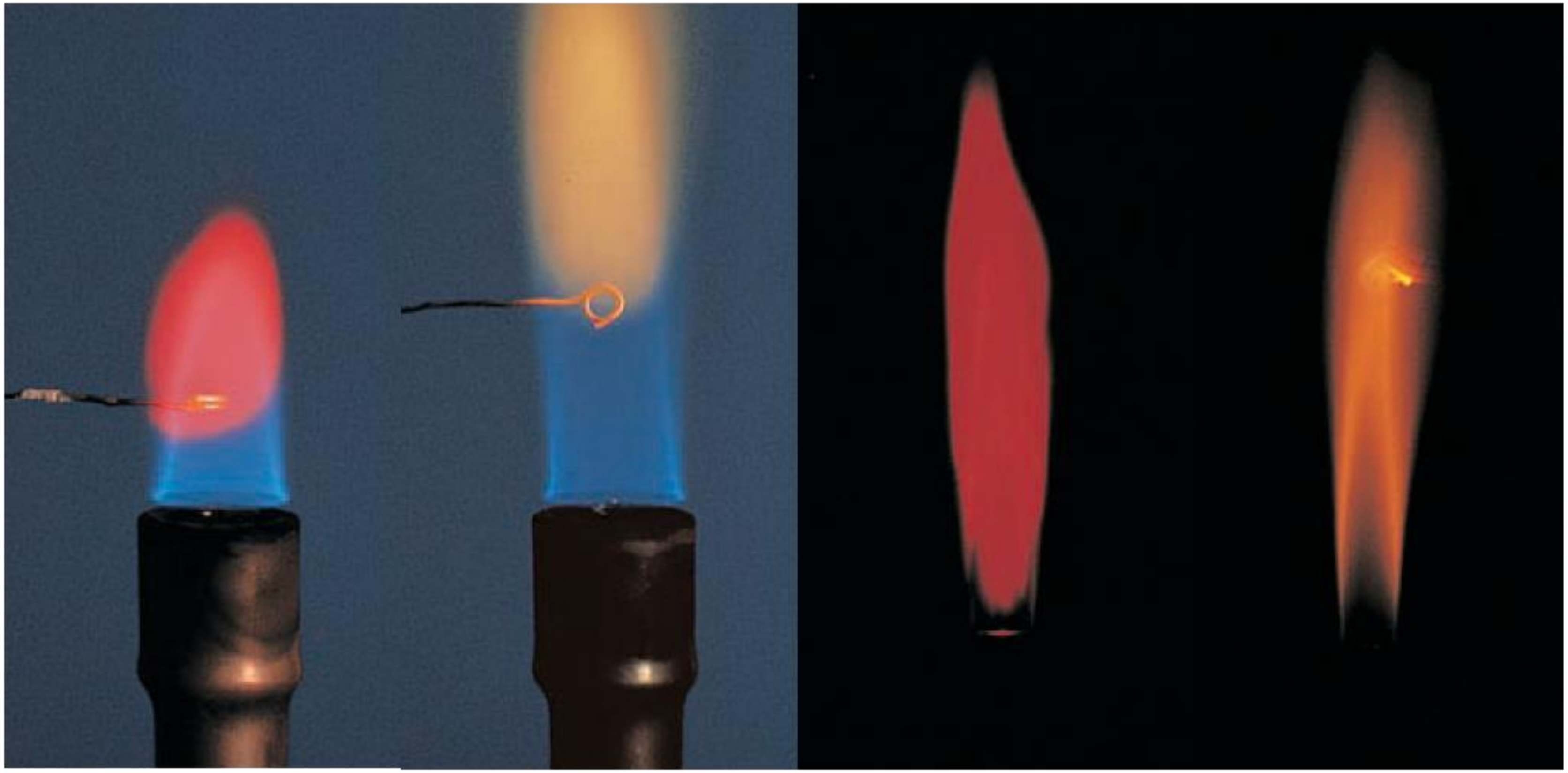


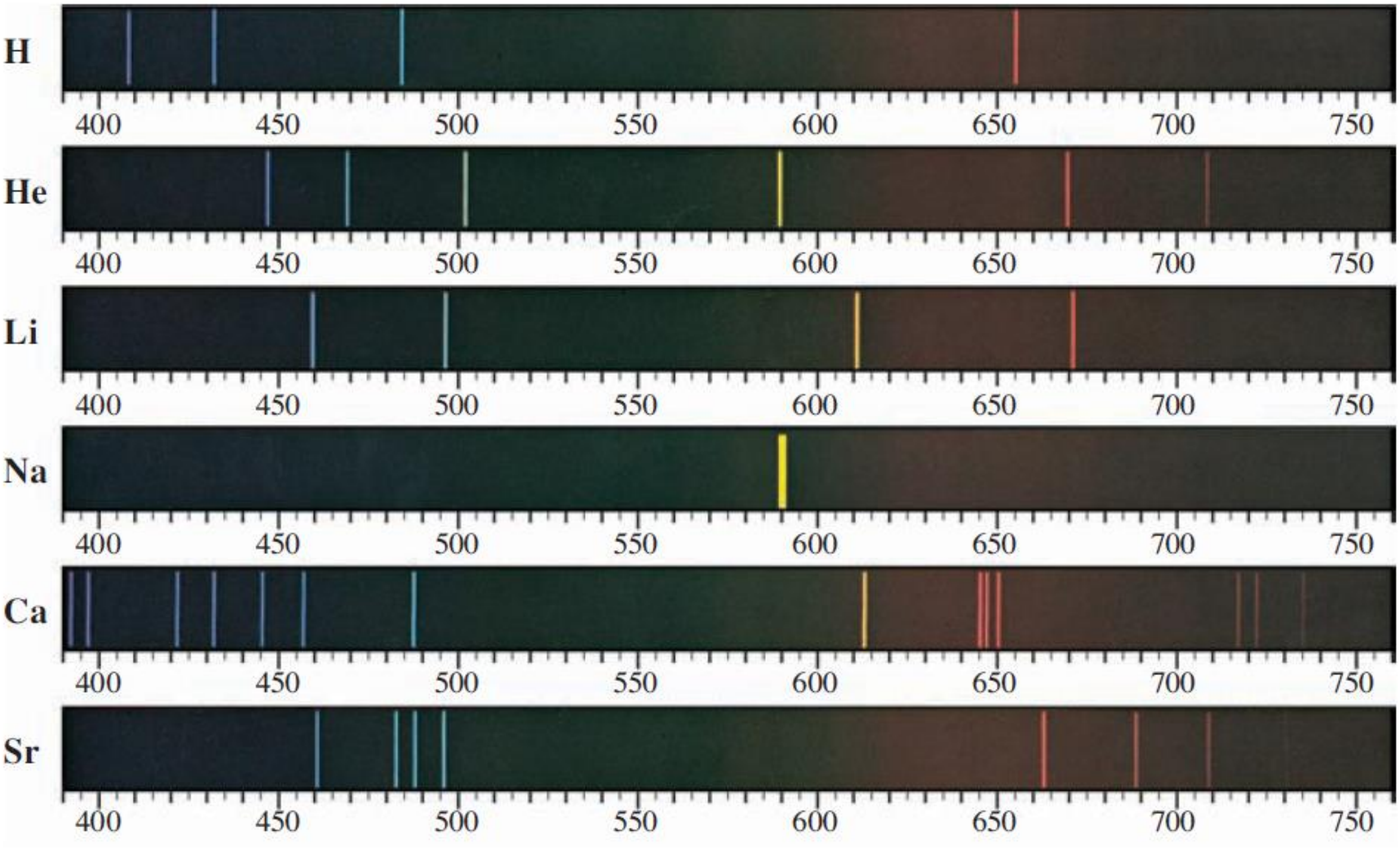
FIGURE 7.1

Flame tests of Groups IA and IIA elements

A wire loop containing a sample of a metal compound is placed in a flame. *Left to right:* flames of lithium (red), sodium (yellow), strontium (red), and calcium (orange).

7. Quantum Theory of the Atom

- Emission (line) spectra of some elements resolved (separated) by means of a prism



7. Quantum Theory of the Atom

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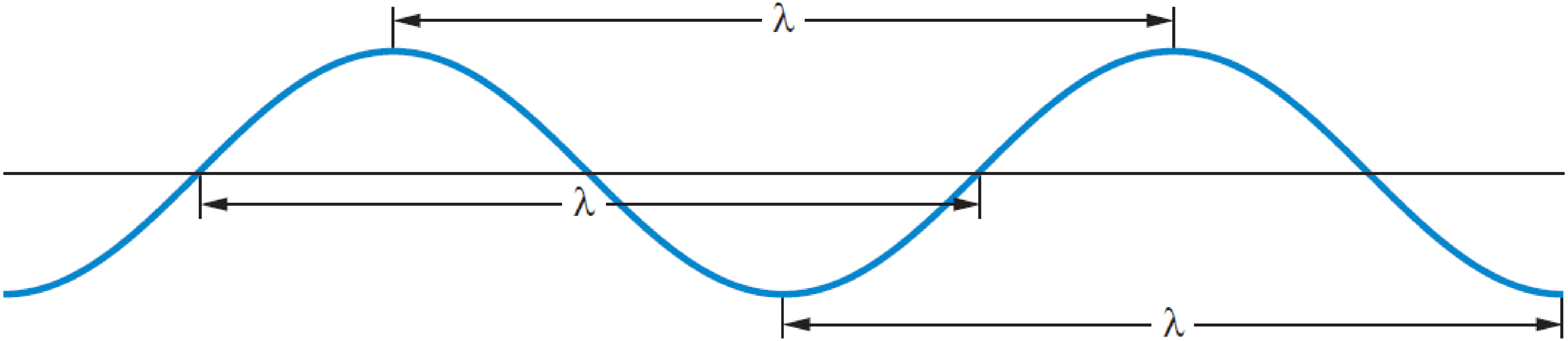
7.1 The Wave Nature of Light

- A wave is a continuously repeating change or oscillation in matter or in a physical field.
- Light is also a wave. It consists of oscillations in electric and magnetic fields that can travel through space.
- Visible lights, X-rays, and radio waves are all forms of electromagnetic radiation.

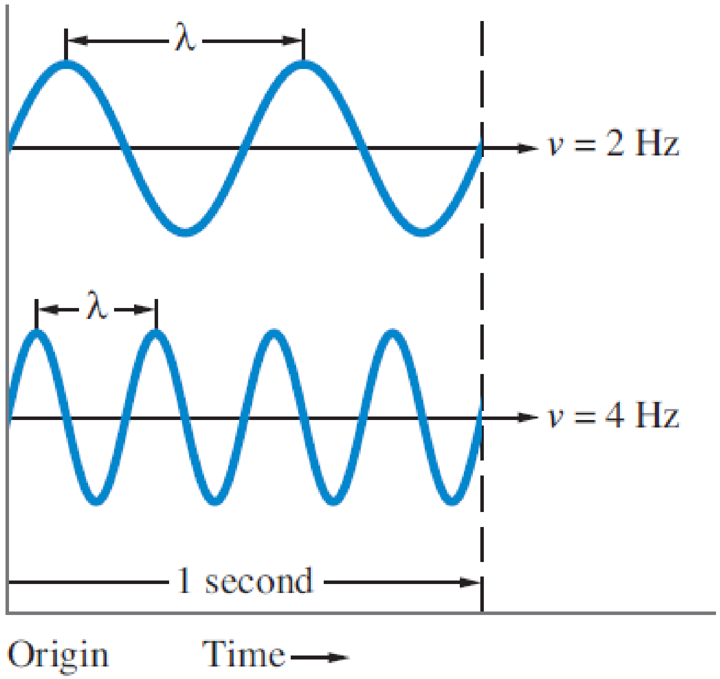
7.1 The Wave Nature of Light

- Wavelength (λ): the distance between any two adjacent identical points of a wave.



7.1 The Wave Nature of Light

- Frequency (ν): the number of wavelengths of that wave that pass a fixed point in one unit of time (usually one second).
- Unit: s^{-1}, also *hertz* (Hz)



wavelength and frequency are inversely related: the greater the wavelength, the lower the frequency, and *vice versa*

7.1 The Wave Nature of Light

$$c = \nu\lambda$$

- The speed of light waves in vacuum is a constant:

  3.00 X 10^8 m/s

P266 Example 7.1

What is the wavelength of the yellow sodium emission, which has a frequency of 5.09×10^{14}/s?

$$\lambda = \frac{3.00 \times 10^{8}\ \text{m}/\cancel{\text{s}}}{5.09 \times 10^{14}/\cancel{\text{s}}} = 5.89 \times 10^{-7}\ \text{m, or } \mathbf{589\ nm}$$

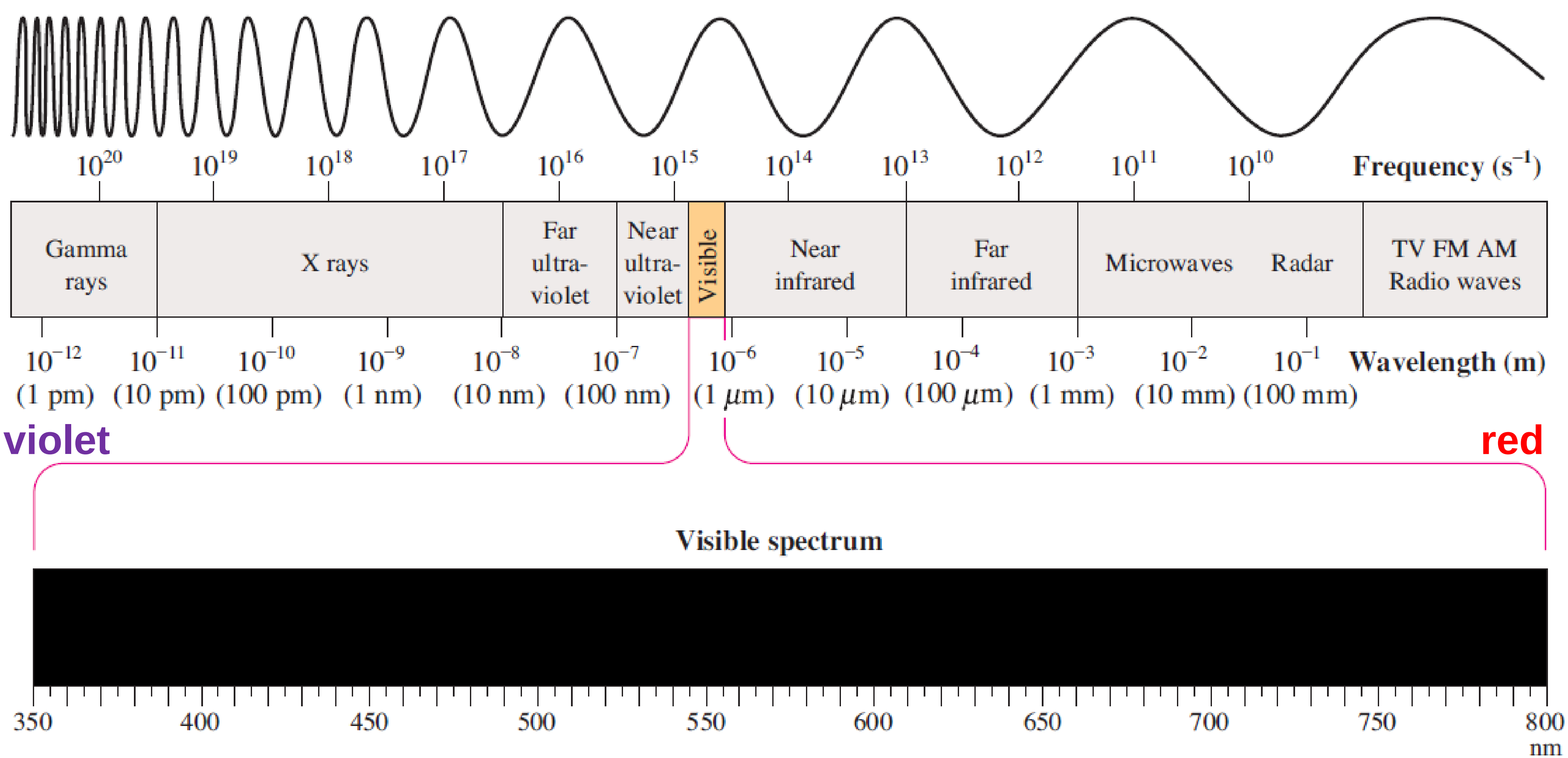
P266 Example 7.2

What is the frequency of violet light with a wavelength of 408 nm?

$$\nu = \frac{3.00 \times 10^8 \cancel{m}/\mathrm{s}}{408 \times 10^{-9} \cancel{m}} = \mathbf{7.35 \times 10^{14}/s}$$

7.1 The Wave Nature of Light

- Electronic spectrum: the range of frequencies or wavelengths of electromagnetic radiation



7.2 Quantum Effects and Photons

- Light is…

  Newton: a beam of particles

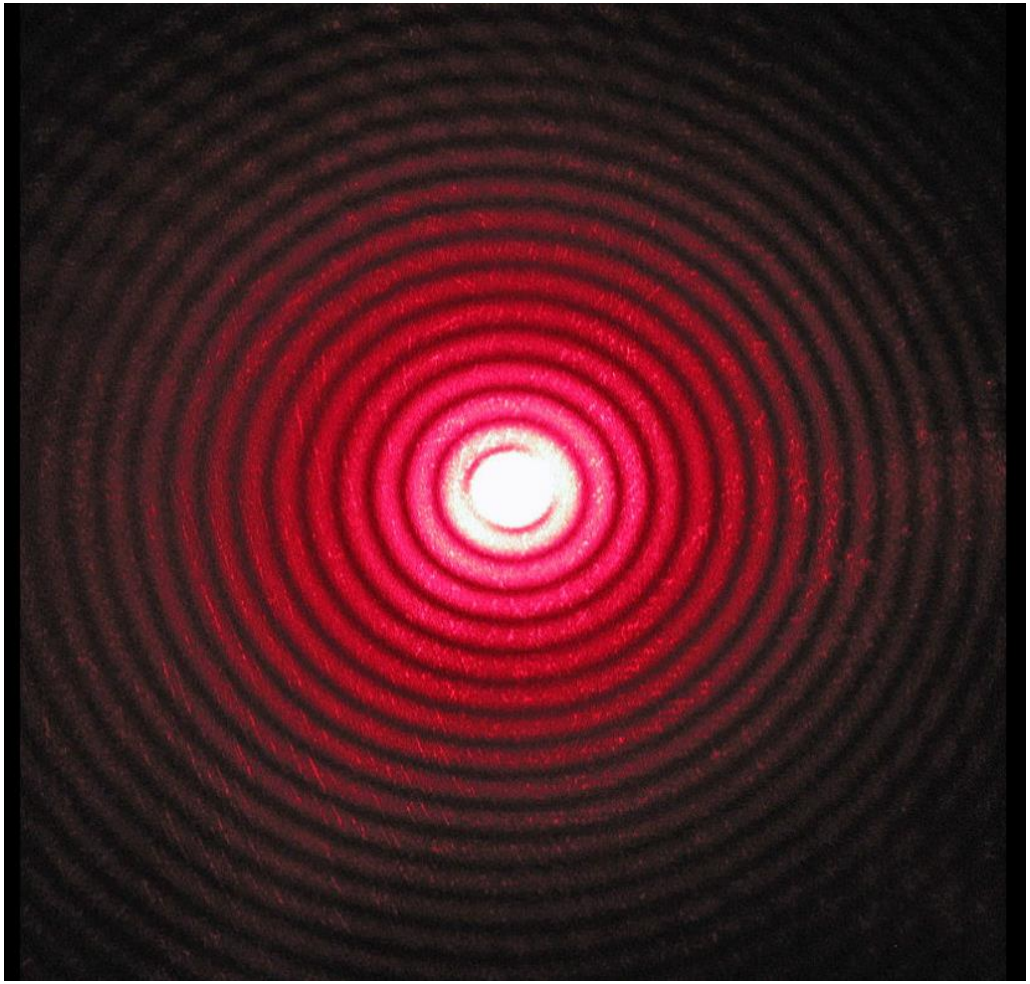
  Young: like waves – diffraction

  Einstein: light has both wave and particle properties (photoelectric effect)

  - Diffraction is a property of waves in which the waves spread out when they encounter an obstruction or small hole about the size of the wavelength.

7.2 Quantum Effects and Photons

- Diffraction



7.2 Quantum Effects and Photons

- Planck's Quantization of Energy
  - An atom could have only certain energies of vibration, *E*

$$E = nh\nu, \qquad n = 1, 2, 3, \ldots$$

  - *h*: Plank's constant, a physical constant relating energy and frequency, having the value

    6.63×10^{-34} J·s

  - *n*: quantum numbers
  - The vibrational energies of the atoms are said to be quantized; that is, the possible energies are limited to certain values.

7.2 Quantum Effects and Photons

- Photoelectric Effect (by Einstein)
  - Light consists of photons, or particles of electromagnetic energy, with energy *E* proportional to the observed frequency of the light.

$$E = h\nu$$

  - The wave-particle duality of light: *E* is the energy of a light particle or photon; ν is the frequency of the associated wave.

7.2 Quantum Effects and Photons

- Photoelectric Effect (by Einstein)
  - Photoelectric effect: the ejection of electrons from the surface of a metal or from another material when light shines on it.
  - Electrons are ejected only when the frequency of light exceeds a certain threshold value characteristic of the particular metal.

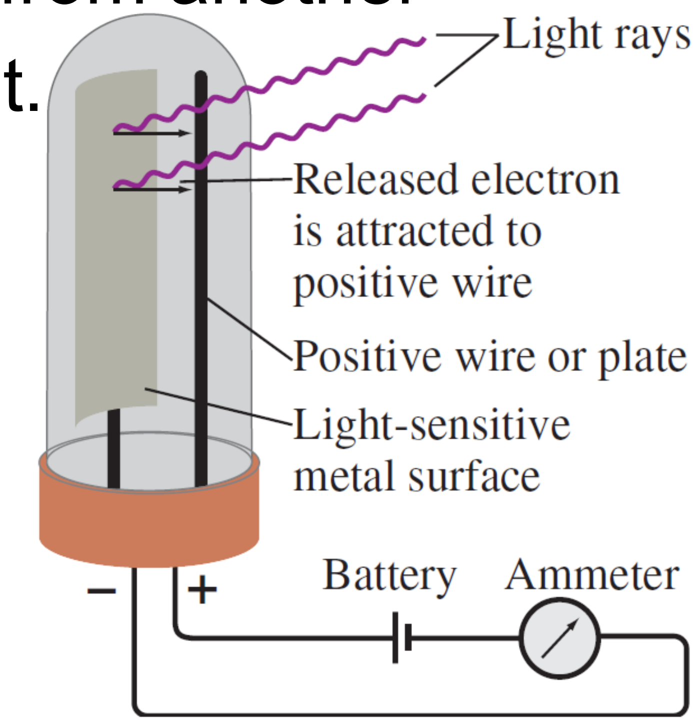


FIGURE 7.6
The photoelectric effect

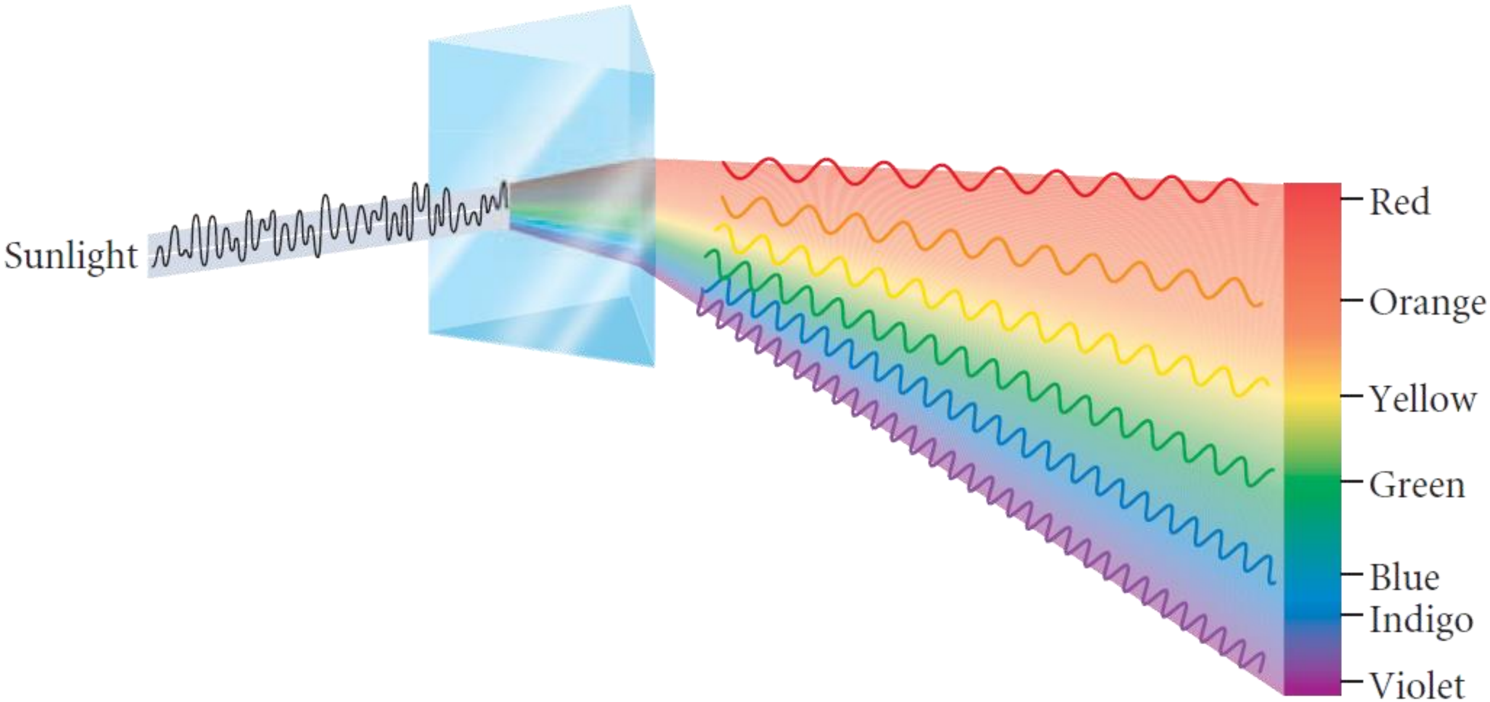
P269 Example 7.3

The red spectral line of lithium occurs at 671 nm (6.71×10^{-7} m). Calculate the energy of one photon of this light.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \cancel{\text{m}}/\text{s}}{6.71 \times 10^{-7}\ \cancel{\text{m}}} = 4.47 \times 10^{14}/\text{s}$$

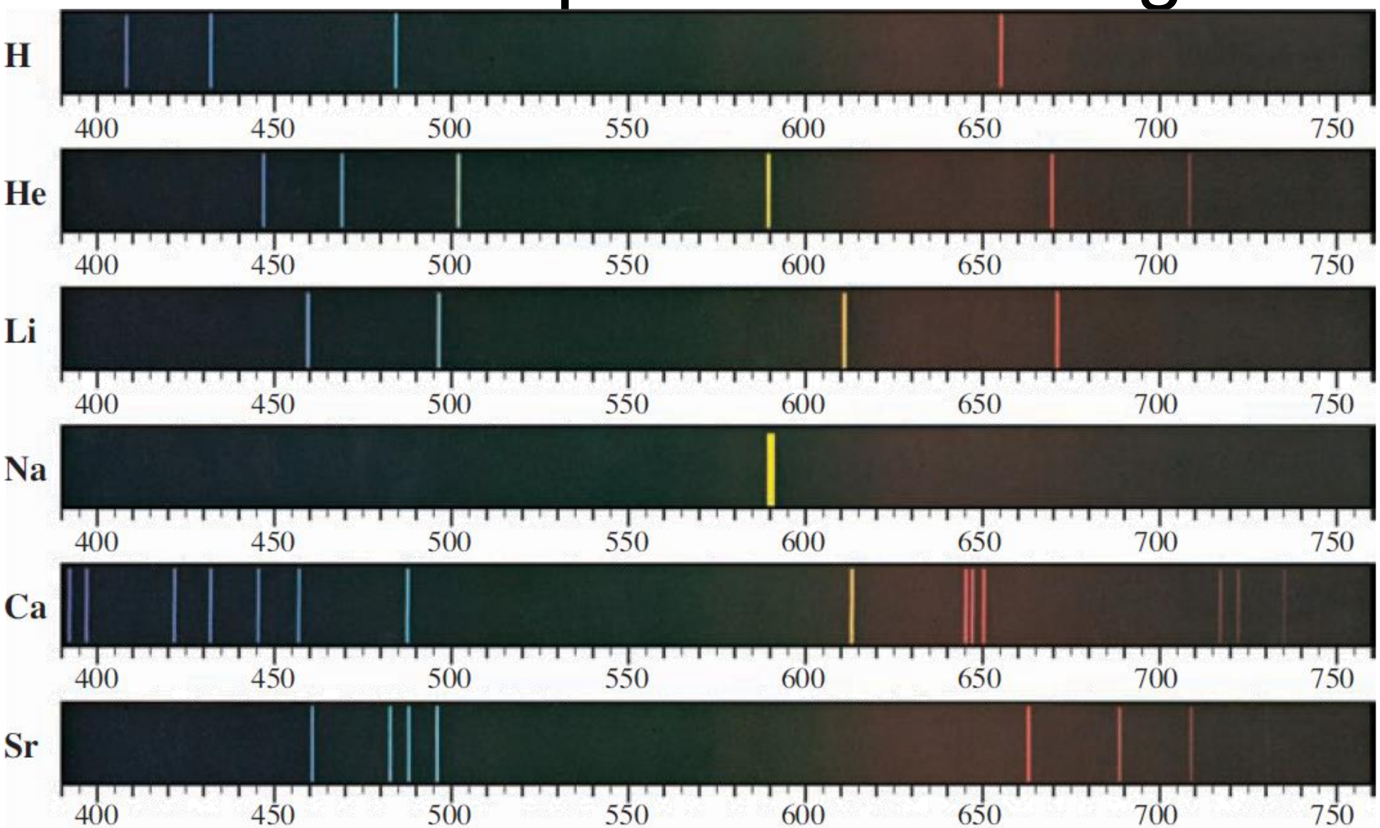
7.3 The Bohr Theory of the Hydrogen Atom

- The light emitted by a heated solid. E.g., A heated tungsten filament in a lightbulb
- Continuous spectrum: a spectrum containing light of all wavelengths



7.3 The Bohr Theory of the Hydrogen Atom

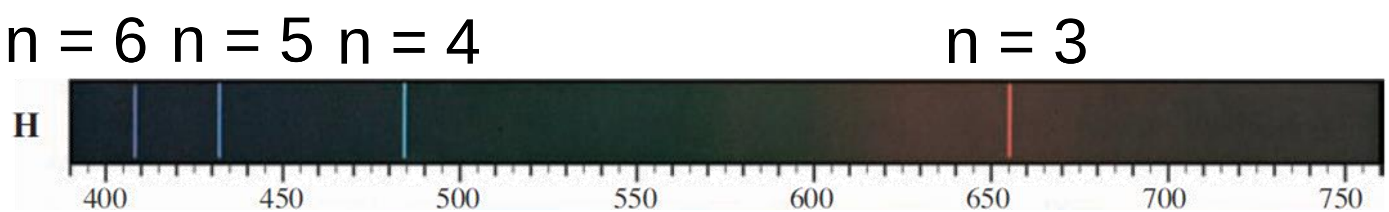
- The light emitted by a heated gas
- Line spectrum: a spectrum showing only certain colors or specific wavelengths of light.



7.3 The Bohr Theory of the Hydrogen Atom

- The visible spectrum of hydrogen:

$$\frac{1}{\lambda} = 1.097 \times 10^7/\text{m}\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$



7.3 The Bohr Theory of the Hydrogen Atom

- Bohr's Postulates
  - To solve problems of 1) the stability of the hydrogen atom (the atom exists and its electron does not continuously radiate energy and spiral into the nucleus); 2) the line spectrum of the atom.

7.3 The Bohr Theory of the Hydrogen Atom

- Bohr's Postulates
  - Energy-level Postulate: an electron can have only specific energy values in an atom.

$$E = -\frac{R_H}{n^2} \qquad n = 1, 2, 3, \ldots \infty \qquad \text{(for H atom)}$$

  - R_H = 2.179 X 10^{-18} J
  - n: principle quantum number, integral values from 1

7.3 The Bohr Theory of the Hydrogen Atom

- Bohr's Postulates

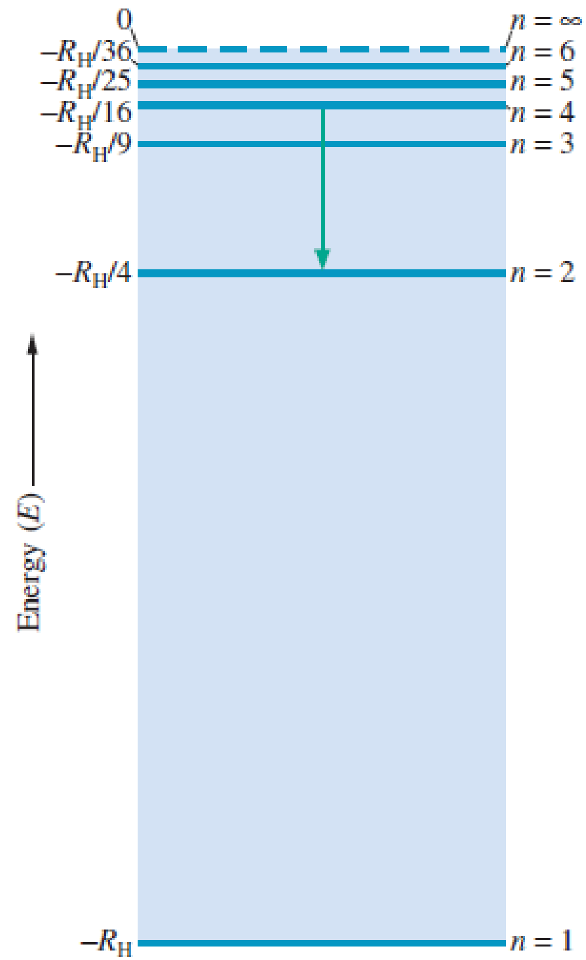


FIGURE 7.10

Energy-level diagram for the electron in the hydrogen atom

7.3 The Bohr Theory of the Hydrogen Atom

- Bohr's Postulates
  - Transitions Between Energy in an atom can change e from one energy level to a By so doing, the electron un

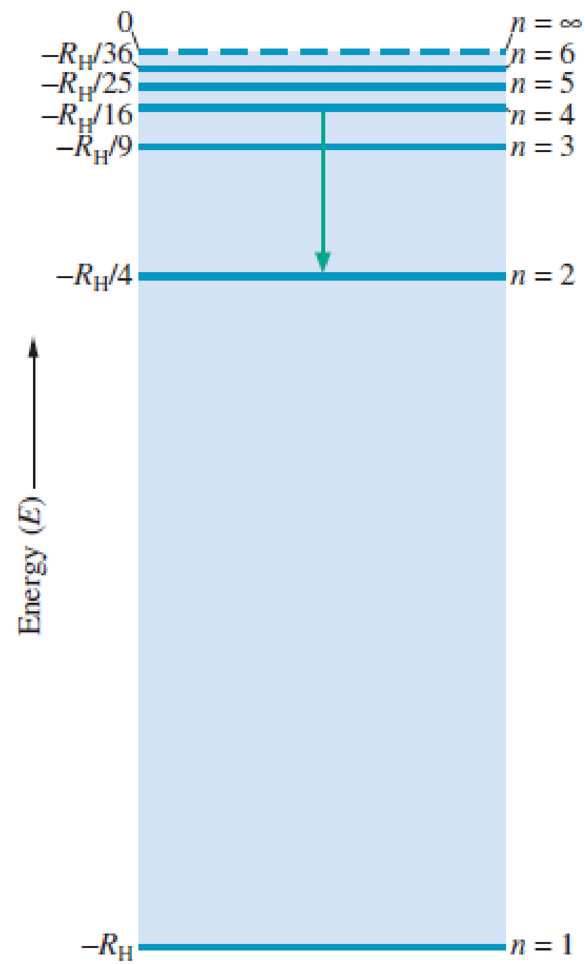


FIGURE 7.10

Energy-level diagram for the electron in the hydrogen atom

7.3 The Bohr Theory of the Hydrogen Atom

- Bohr's Postulates
  - Transitions Between Energy Levels: An electron in an atom can change energy only by going from one energy level to another energy level. By so doing, the electron undergoes a transition.

$$\text{Energy of emitted photon} = h\nu = -\Delta E = -(E_f - E_i)$$

$$h\nu = R_H\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right)$$

P273 Example 7.4

What is the wavelength of light emitted when the electron in a hydrogen atom undergoes a transition from energy level n = 4 to level n = 2?

$$E_i = \frac{-R_H}{4^2} = \frac{-R_H}{16} \qquad \text{and} \qquad E_f = \frac{-R_H}{2^2} = \frac{-R_H}{4}$$

$$\left(\frac{-R_H}{16}\right) - \left(\frac{-R_H}{4}\right) = \frac{-4R_H + 16R_H}{64} = \frac{-R_H + 4R_H}{16} = \frac{3R_H}{16} = h\nu$$

$$\nu = \frac{3R_H}{16h} = \frac{3}{16} \times \frac{2.179 \times 10^{-18}\ \cancel{J}}{6.626 \times 10^{-34}\ \cancel{J}\cdot s} = 6.17 \times 10^{14}/s$$

$$\lambda = \frac{3.00 \times 10^8\ m/\cancel{s}}{6.17 \times 10^{14}/\cancel{s}} = 4.86 \times 10^{-7}\ m, \text{ or } \mathbf{486\ nm}$$

7.4 Quantum Mechanics

- A theory that applies to submicroscopic (that is, extremely small) particles of matter, such as electrons.
- Stimulated by the discovery of the de Broglie relation.
- Particle of matter of mass *m* and speed *v* has an associated wavelength, by analogy with light:

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

7.4 Quantum Mechanics

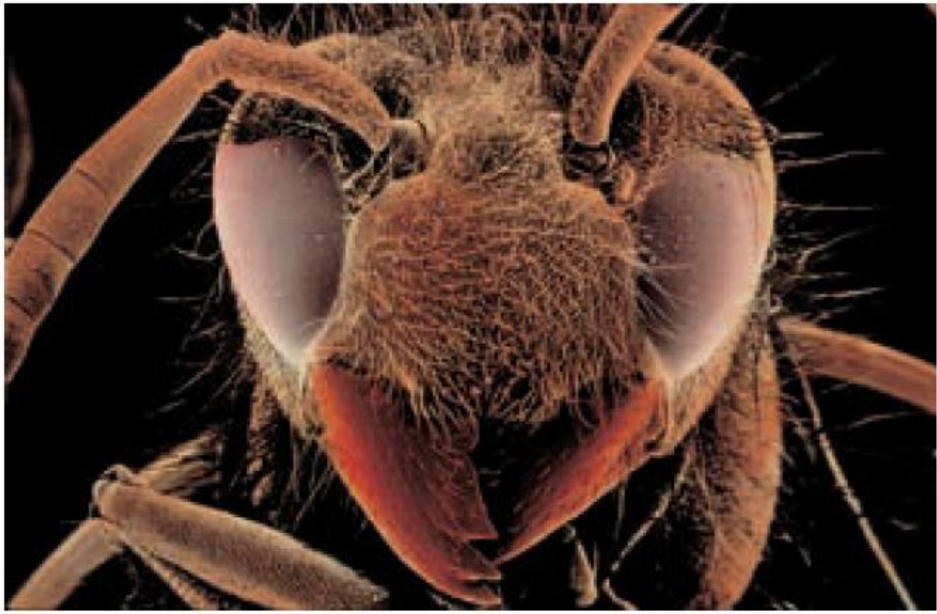
- Particle of matter of mass *m* and speed *v* has an associated wavelength, by analogy with light:

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

  - Baseball, 0.145 kg, 27 m/s, 10^{-34} m
  - Electron, 9.11×10^{-31} kg, 10^{-12} m

7.4 Quantum Mechanics

- Electron microscope: To resolve detail the size of several hundred picometers, we need a wavelength on that order.



P278 Example 7.5

a. Calculate the wavelength (in meters) of the wave associated with a 1.00-kg mass moving at 1.00 km/hr.

b. What is the wavelength (in picometers) associated with an electron, whose mass is 9.11×10^{-31} kg, traveling at a speed of 4.19×10^{6} m/s? (This speed can be attained by an electron accelerated between two charged plates differing by 50.0 volts; voltages in the kilovolt range are used in electron microscopes.)

$$1.00\,\frac{\text{km}}{\text{hr}} \times \frac{1\ \text{hr}}{3600\ \text{s}} \times \frac{10^{3}\ \text{m}}{1\ \text{km}} = 0.278\ \text{m/s}$$

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{1.00\ \text{kg} \times 0.278\ \text{m/s}} = \mathbf{2.38 \times 10^{-33}\ m}$$

P278 Example 7.5

a. Calculate the wavelength (in meters) of the wave associated with a 1.00-kg mass moving at 1.00 km/hr.

b. What is the wavelength (in picometers) associated with an electron, whose mass is 9.11×10^{-31} kg, traveling at a speed of 4.19×10^{6} m/s? (This speed can be attained by an electron accelerated between two charged plates differing by 50.0 volts; voltages in the kilovolt range are used in electron microscopes.)

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}\ \mathrm{J \cdot s}}{9.11 \times 10^{-31}\ \mathrm{kg} \times 4.19 \times 10^{6}\ \mathrm{m/s}} = 1.74 \times 10^{-10}\ \mathrm{m} = \mathbf{174\ pm}$$

7.4 Quantum Mechanics

- de Broglie relation: applies quantitatively only to particles in a force-free environment
- Erwin Schrödinger's theory: could be used to find the wave properties of electrons in atoms and molecules.
- Quantum mechanics or wave mechanics: The branch of physics that mathematically describes the wave properties of submicroscopic particles.

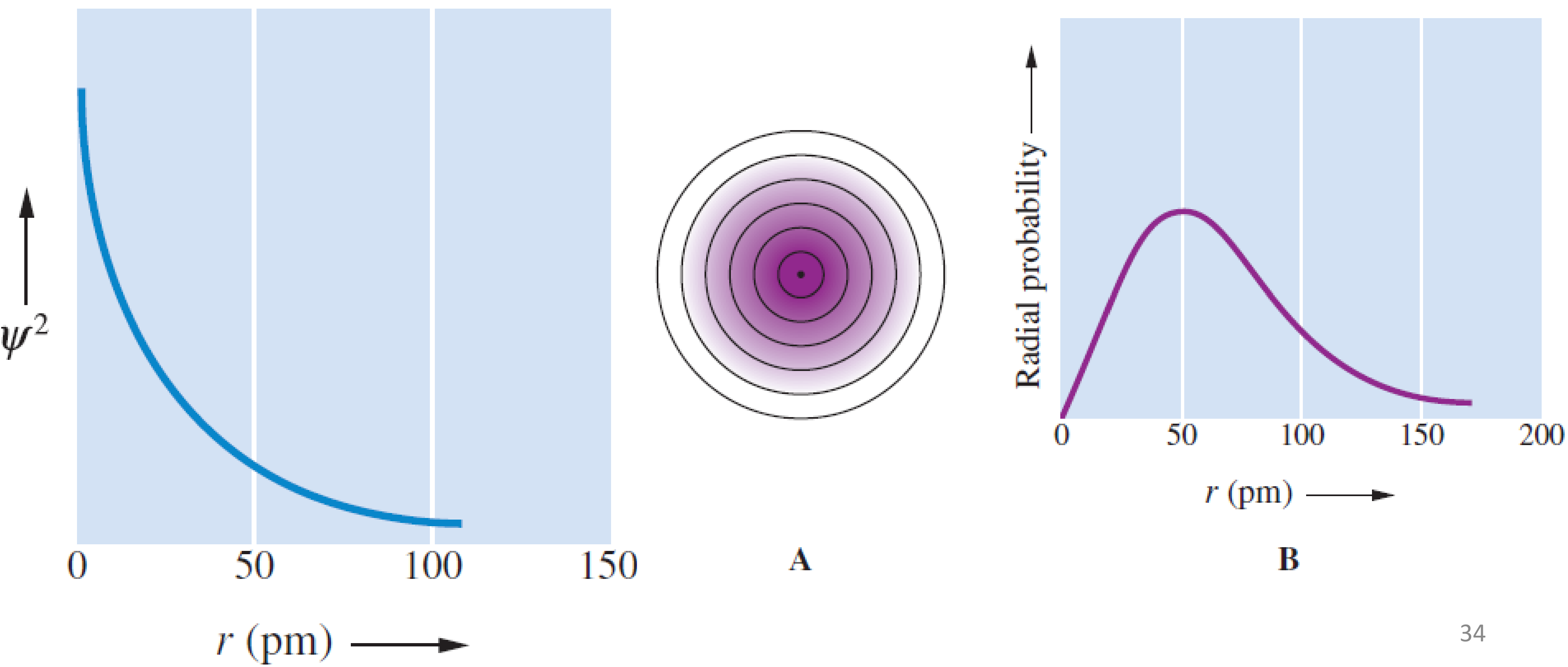
7.4 Quantum Mechanics

- Heisenberg pointed out: it is impossible to know simultaneously, with absolute precision, both the position and the momentum of a particle such as an electron.
- Heisenberg's uncertainty principle: a relation that states that the product of the uncertainty in position and the uncertainty in momentum of a particle can be no smaller than Planck's constant divided by 4π.

$$(\Delta x)(\Delta p_x) \geq \frac{h}{4\pi} \Rightarrow (\Delta x)(\Delta v_x) \geq \frac{h}{4\pi m}$$

7.4 Quantum Mechanics

- Make statistical statements on the probability of finding an electron at a certain point in a hydrogen atom.



7.5 Quantum Numbers and Atomic Orbitals

- According to quantum mechanics, each electron in an atom is described by four different quantum numbers, three of which (n, l, and m_l) specify the wave function that gives the probability of finding the electron at various points in space.
- A wave function for an electron in an atom is called an atomic orbital.
- An atomic orbital is pictured qualitatively by describing the region of space where there is high probability of finding the electrons.

7.5 Quantum Numbers and Atomic Orbitals

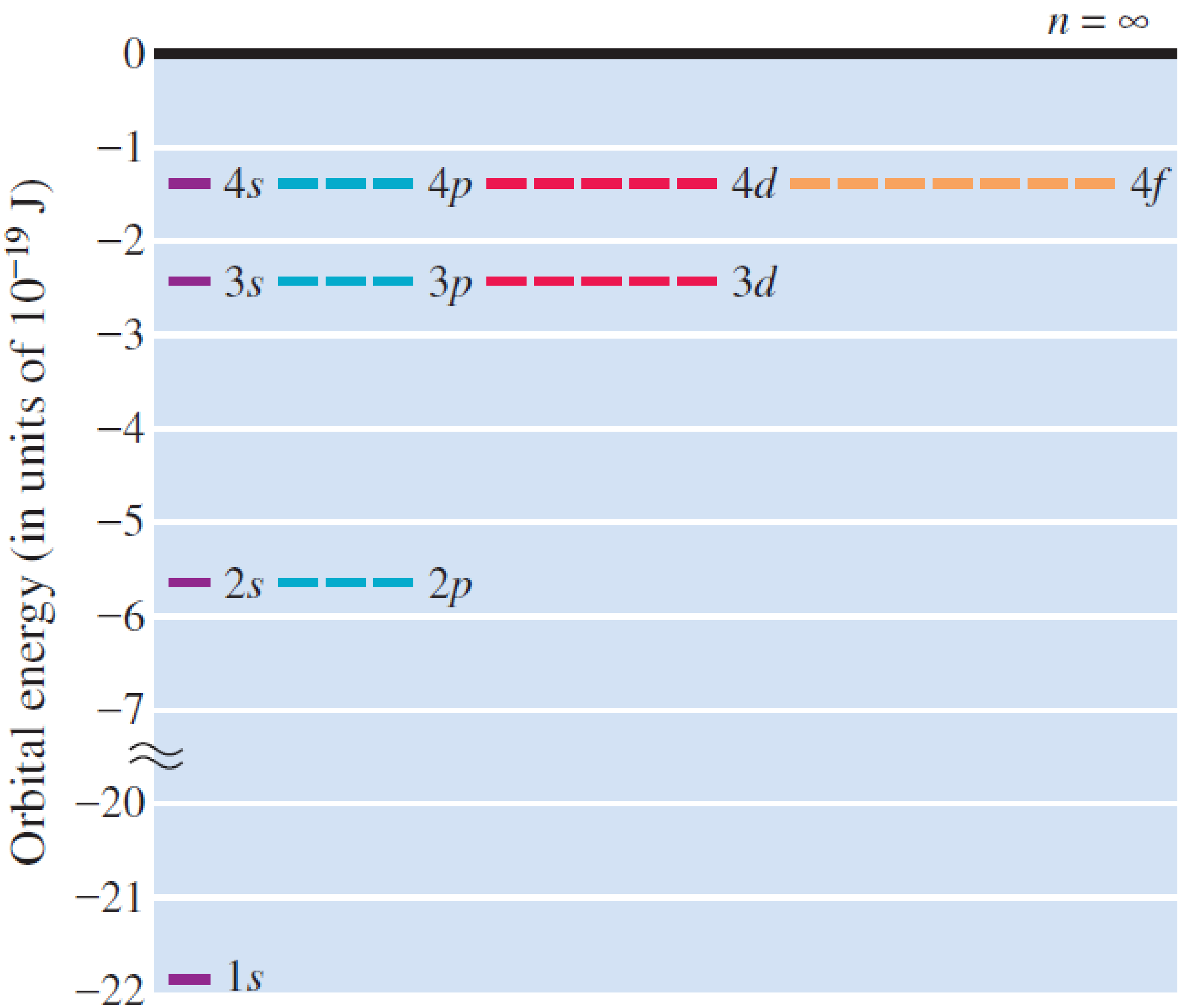
- Principal Quantum Number (*n*): The energy of an electron in an atom depends principally on n.
- n = 1, 2, 3, and so on.
- The size of an orbital also depends on n. The larger the value of n is, the larger the orbital.

7.5 Quantum Numbers and Atomic Orbitals

- **Angular Momentum Quantum Number (l)**: This quantum number distinguishes orbitals of given n having different shapes; it can have any integer value from 0 to n-1.
- For a given n, the energy of an orbital increases with l.
- Orbitals of the same n but different l are said to belong to different subshells of a given shell.

Letter	*s*	*p*	*d*	*f*	*g* . . .
l	0	1	2	3	4 . . .

7.5 Quantum Numbers and Atomic Orbitals



7.5 Quantum Numbers and Atomic Orbitals

- **Magnetic Quantum Number (m_l)**: This quantum number distinguishes orbitals of given n and l - that is, of given energy and shape but having a different orientation in space; the allowed values are the integers from $-l$ to $+l$.
- The orbitals have the same shape but different orientations in space.
- All orbitals of a given subshell have the same energy.
- There are $2l+1$ orbitals in each subshell of quantum number l.

7.5 Quantum Numbers and Atomic Orbitals

- A fourth quantum number (m_s) refers to a magnetic property of electrons called spin.
- This quantum number refers to the two possible orientations of the spin axis of an electron; possible values are +1/2 and -1/2 .

7.5 Quantum Numbers and Atomic Orbitals

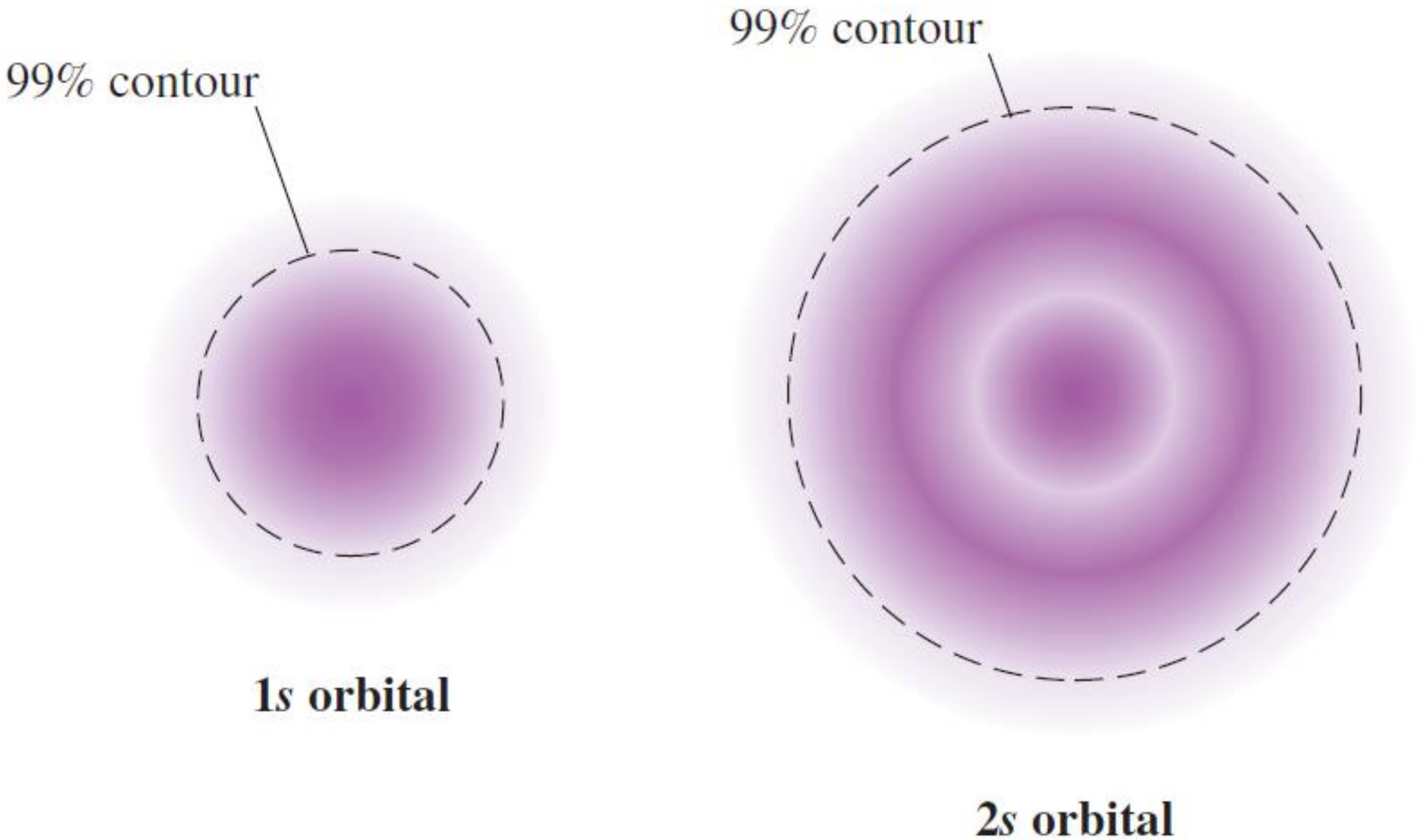
TABLE 7.1 **Permissible Values of Quantum Numbers for Atomic Orbitals**

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	$-1, 0, +1$	2p	3
3	0	0	3s	1
3	1	$-1, 0, +1$	3p	3
3	2	$-2, -1, 0, +1, +2$	3d	5
4	0	0	4s	1
4	1	$-1, 0, +1$	4p	3
4	2	$-2, -1, 0, +1, +2$	4d	5
4	3	$-3, -2, -1, 0, +1, +2, +3$	4f	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

7.5 Quantum Numbers and Atomic Orbitals

- Atomic Orbital Shapes



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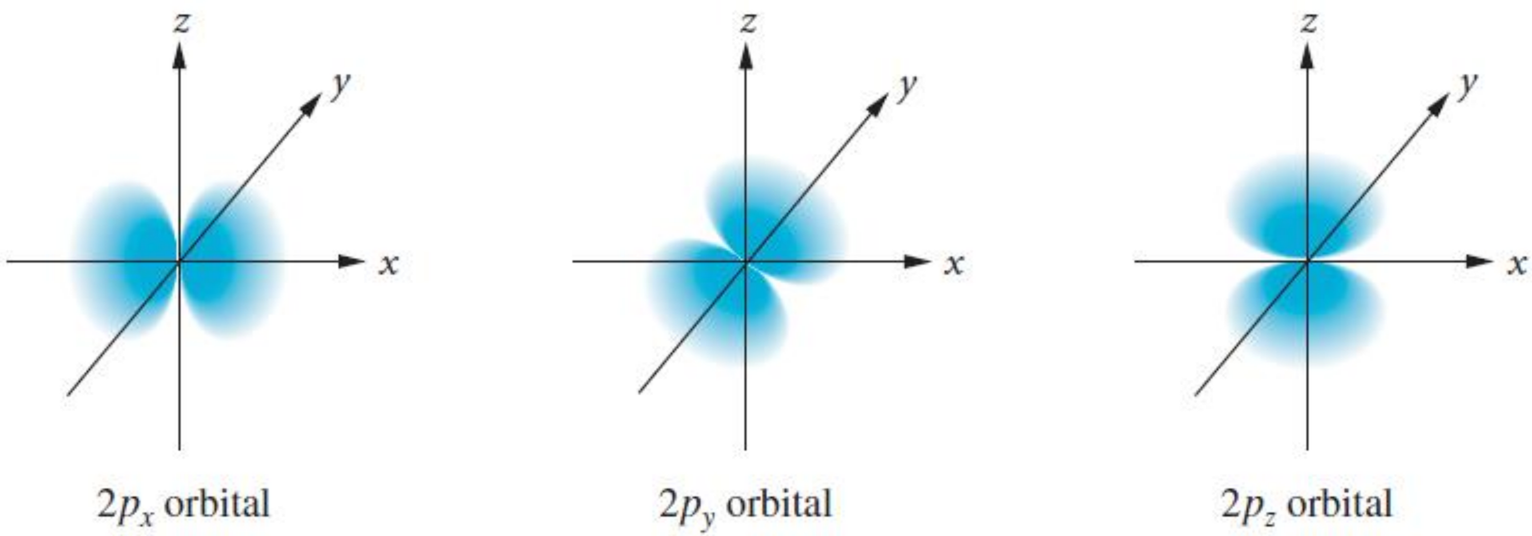
- Atomic Orbital Shapes



7.5 Quantum Numbers and Atomic Orbitals

- Atomic Orbital Shapes