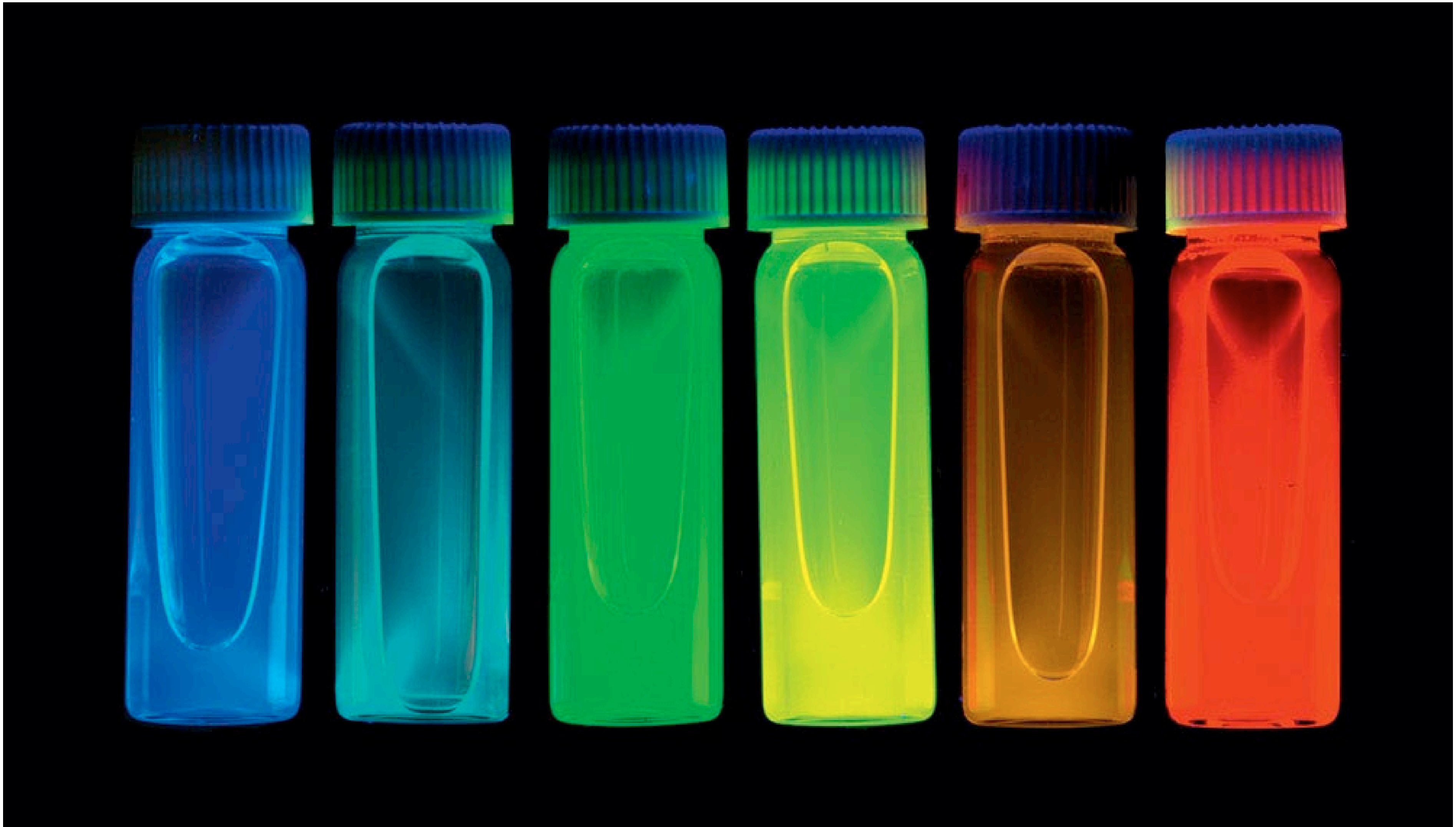
4

CHAPTER

INTRODUCTION TO QUANTUM MECHANICS

KAIST CHEMISTRY

Nanometer-Sized Crystals of CdSe



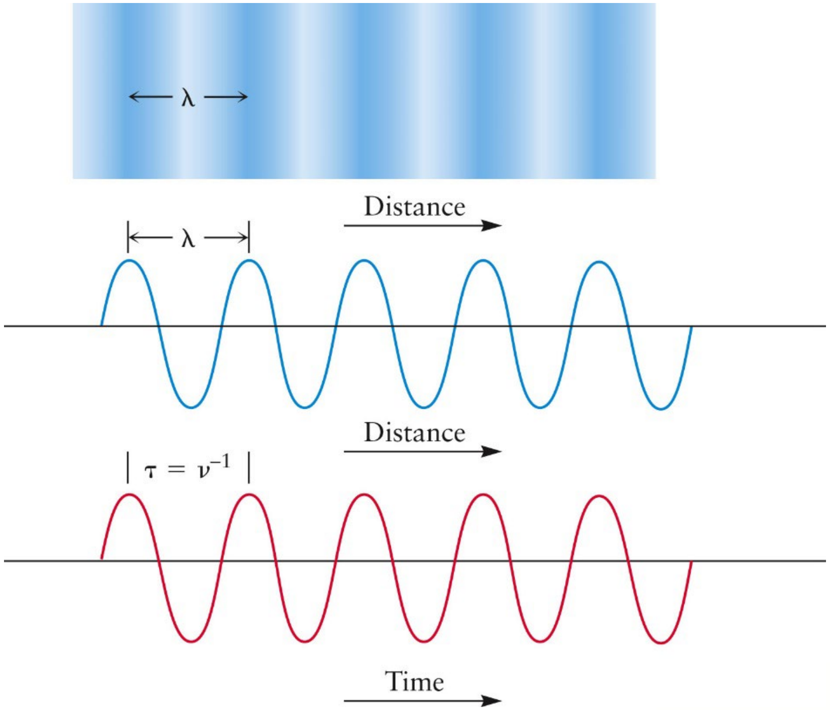
4.1 PRELIMINARIES: WAVE MOTION AND LIGHT

- **amplitude** of the wave: the height or the displacement
- **wavelength, λ** : the distance between two successive crests
- **frequency, ν** : units of waves (or cycles) per second (s^{-1})

TABLE 4.1

Kinds of Waves

Wave	Oscillating Quantity
Water	Height of water surface
Sound	Density of air
Light	Electric and magnetic fields
Chemical	Concentrations of chemical species



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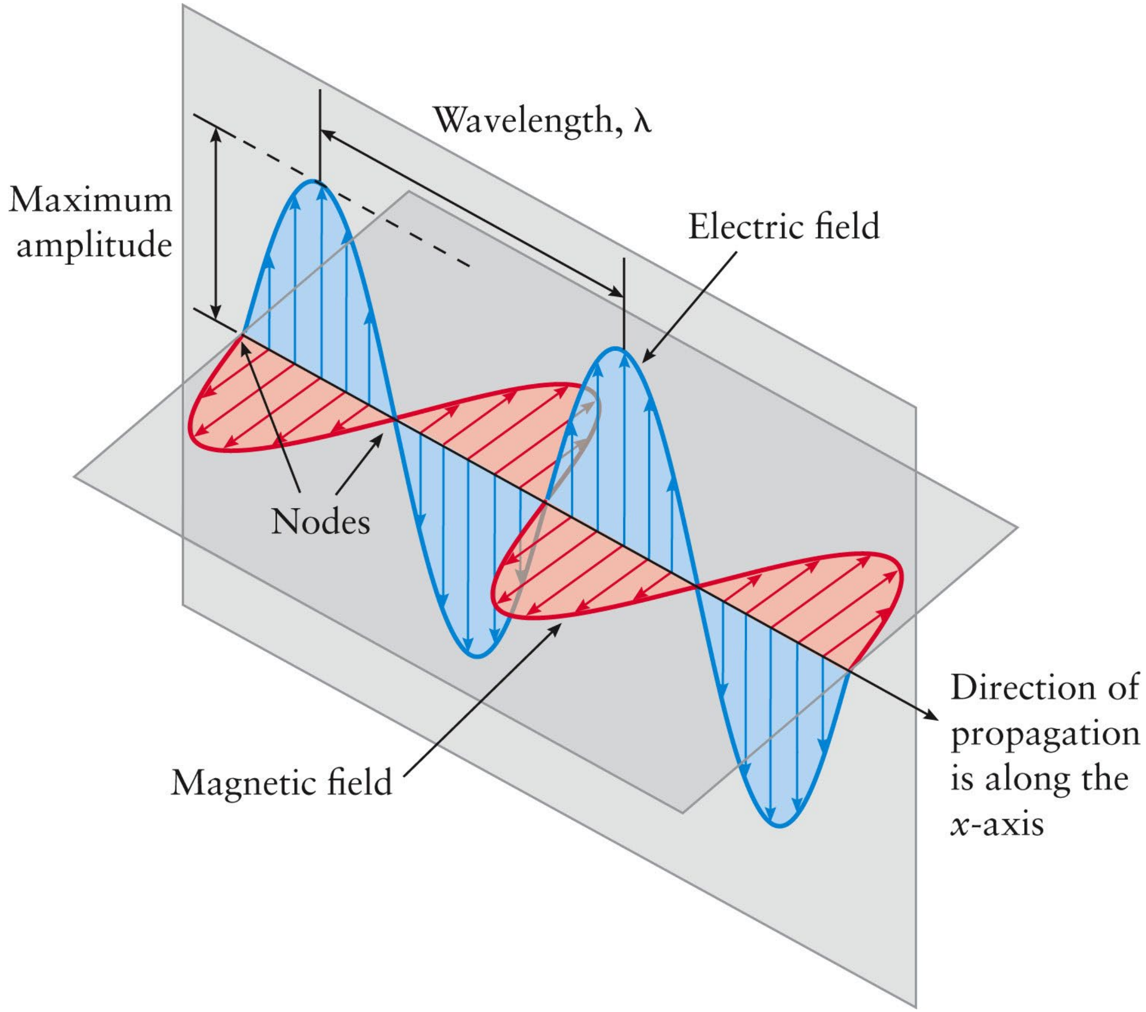
- speed $= \frac{\text{distance traveled}}{\text{time elapsed}} = \frac{\lambda}{\nu^{-1}} = \lambda\nu$



Electromagnetic Radiation

- A beam of light consists of oscillating **electric and magnetic fields** oriented perpendicular to one another and to the direction in which the light is propagating.

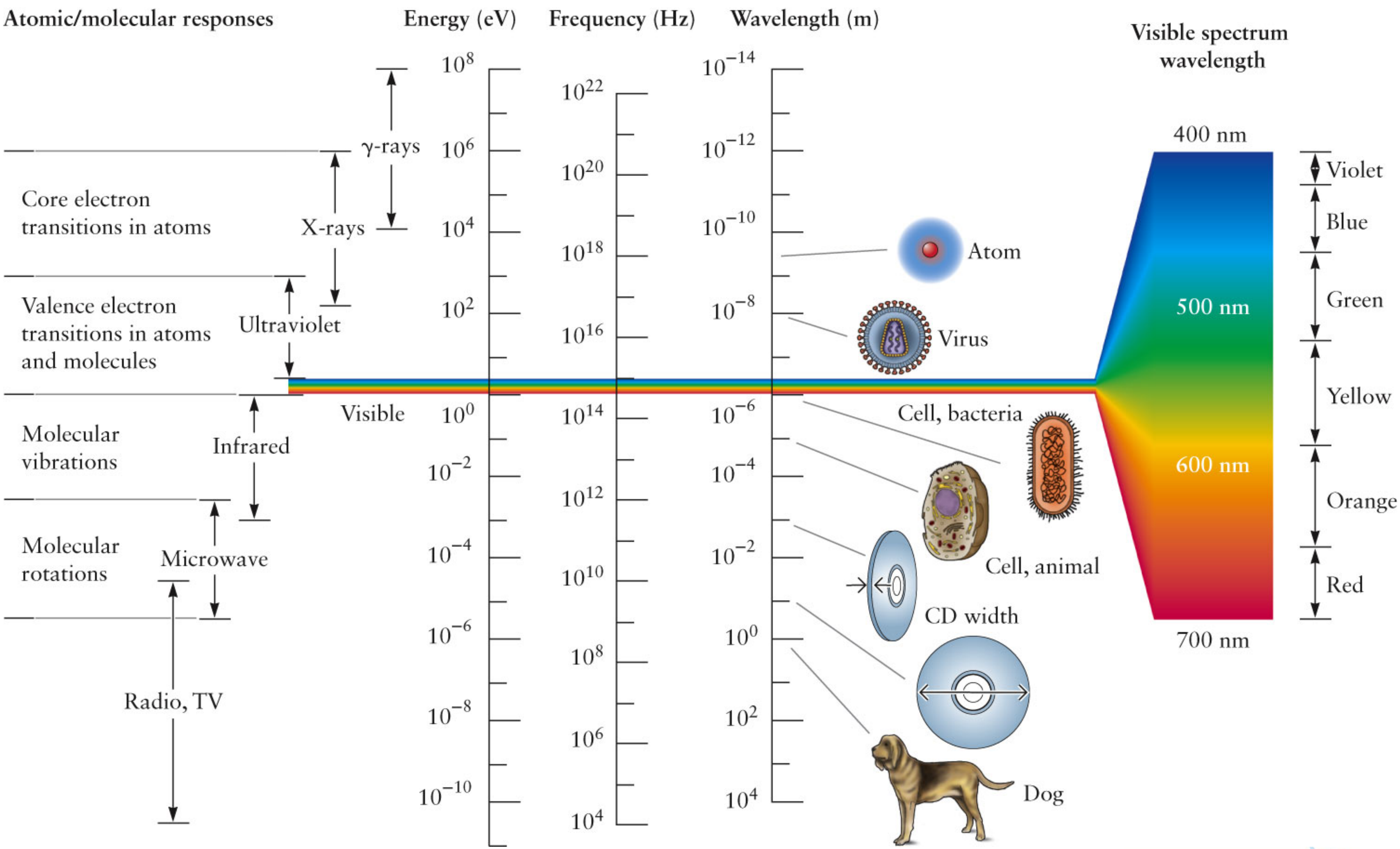
- **Amplitude** of the electric field

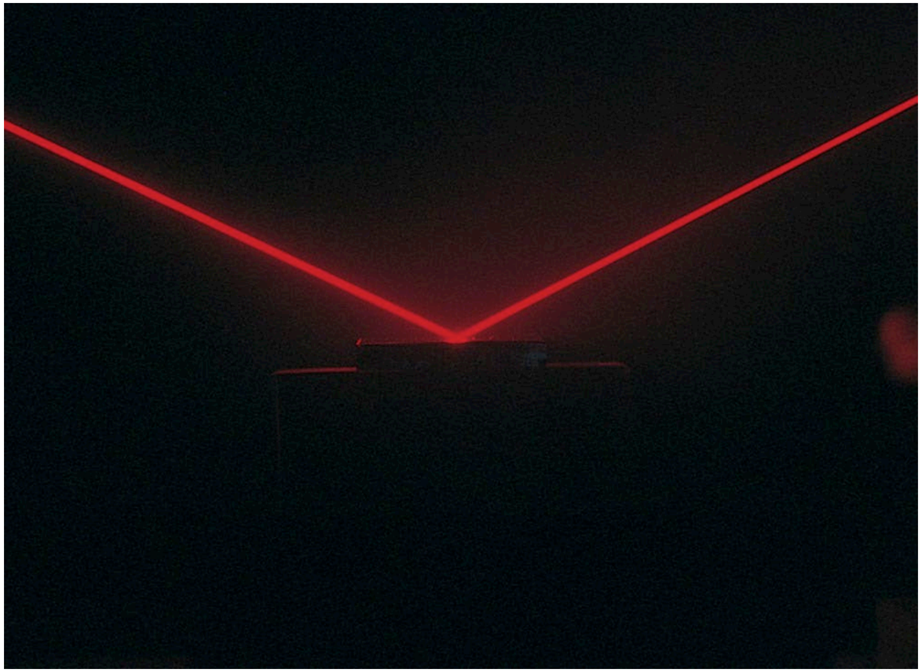
$$E(x,t) = E_{max} \cos[2\pi(x/\lambda - \nu t)]$$

- **The speed, c, of light** passing through a vacuum,

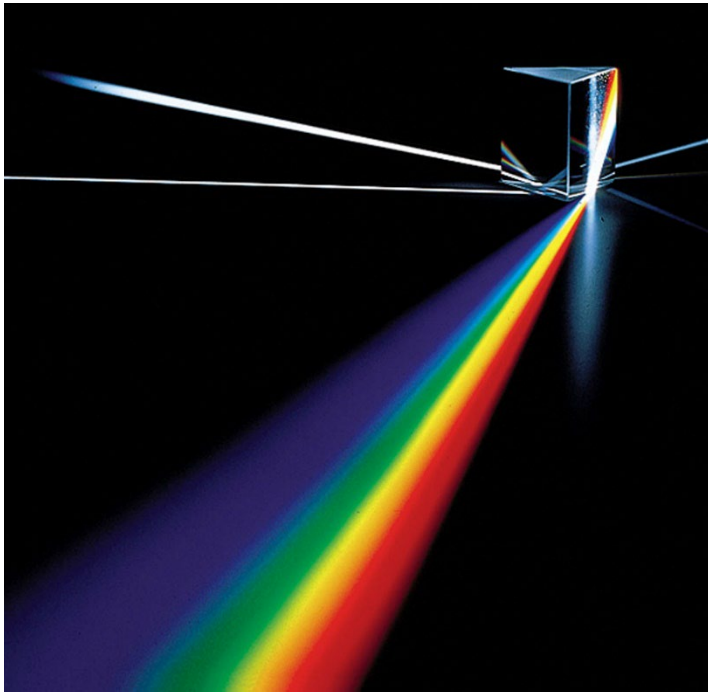
$$c = \lambda\nu = 2.99792458 \times 10^{8}\ ms^{-1}$$

is a universal constant; the same for all types of radiation.


Atomic/molecular responses
Energy (eV)
Frequency (Hz)
Wavelength (m)
Visible spectrum wavelength
γ-rays
X-rays
Ultraviolet
Visible
Infrared
Microwave
Radio, TV
Core electron transitions in atoms
Valence electron transitions in atoms and molecules
Molecular vibrations
Molecular rotations
10^8
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{22}
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^8
10^6
10^4
10^{-14}
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^0
10^2
10^4
Atom
Virus
Cell, bacteria
Cell, animal
CD width
Dog
400 nm
500 nm
600 nm
700 nm
Violet
Blue
Green
Yellow
Orange
Red



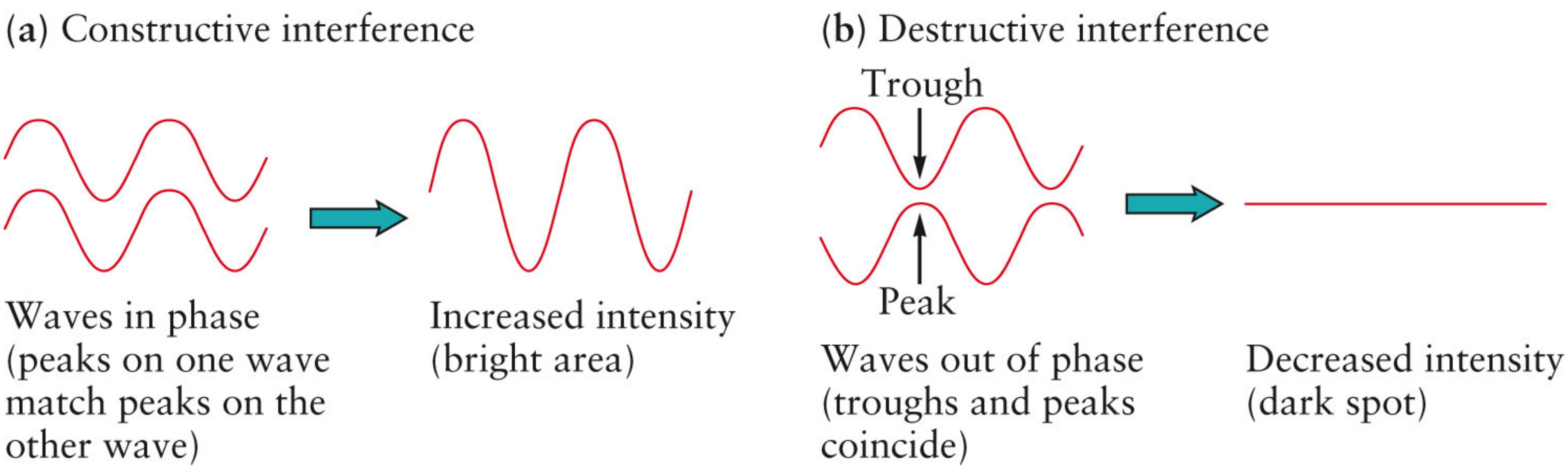
reflected by mirrors

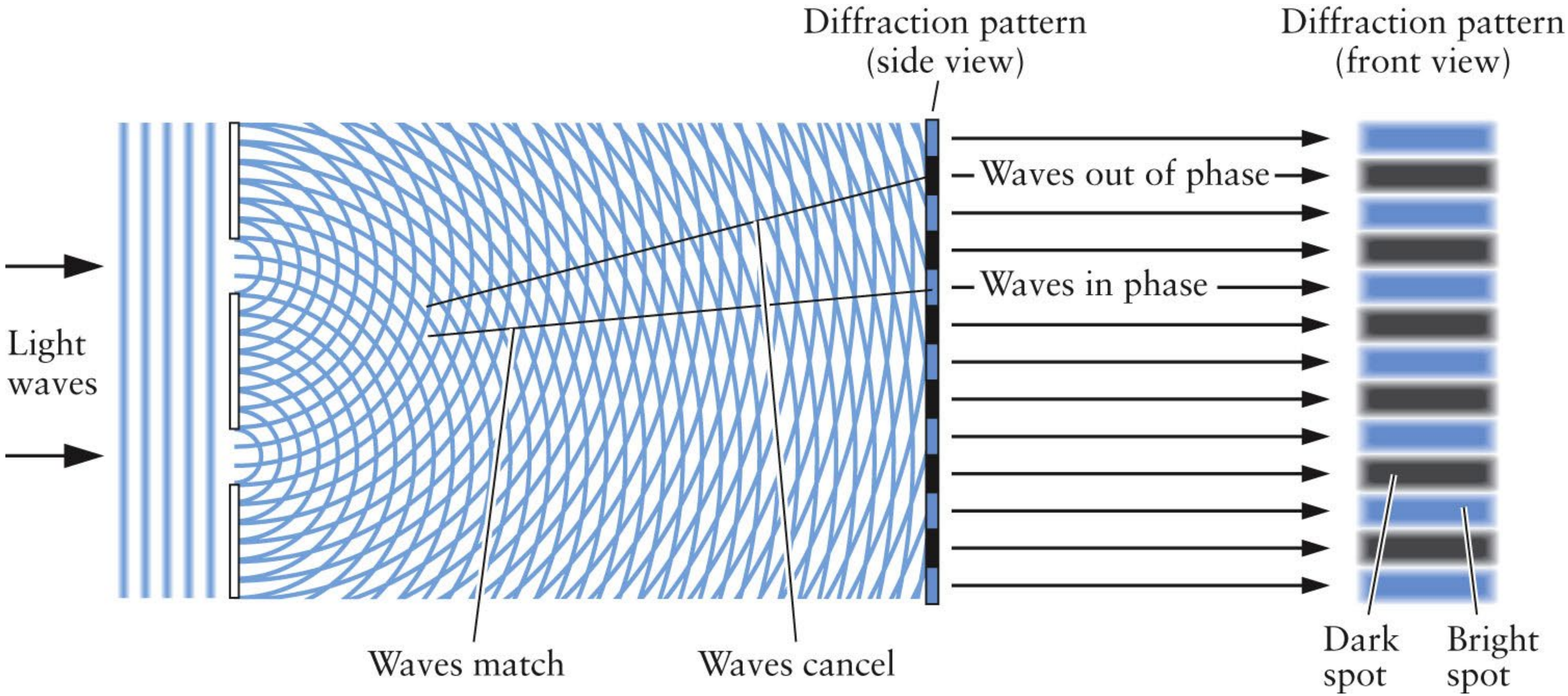


refracted by a prism

➢ Interference of waves

- When two light waves pass through the same region of space, they interfere to create a new wave called the **superposition** of the two.




Diffraction pattern
(side view)
Diffraction pattern
(front view)
Waves out of phase
Waves in phase
Light
waves
Waves match
Waves cancel
Dark
spot
Bright
spot

4.2 EVIDENCE FOR ENERGY QUANTIZATION IN ATOMS

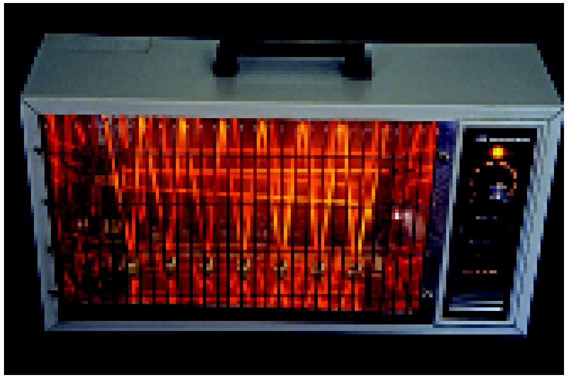
➢ Blackbody radiation

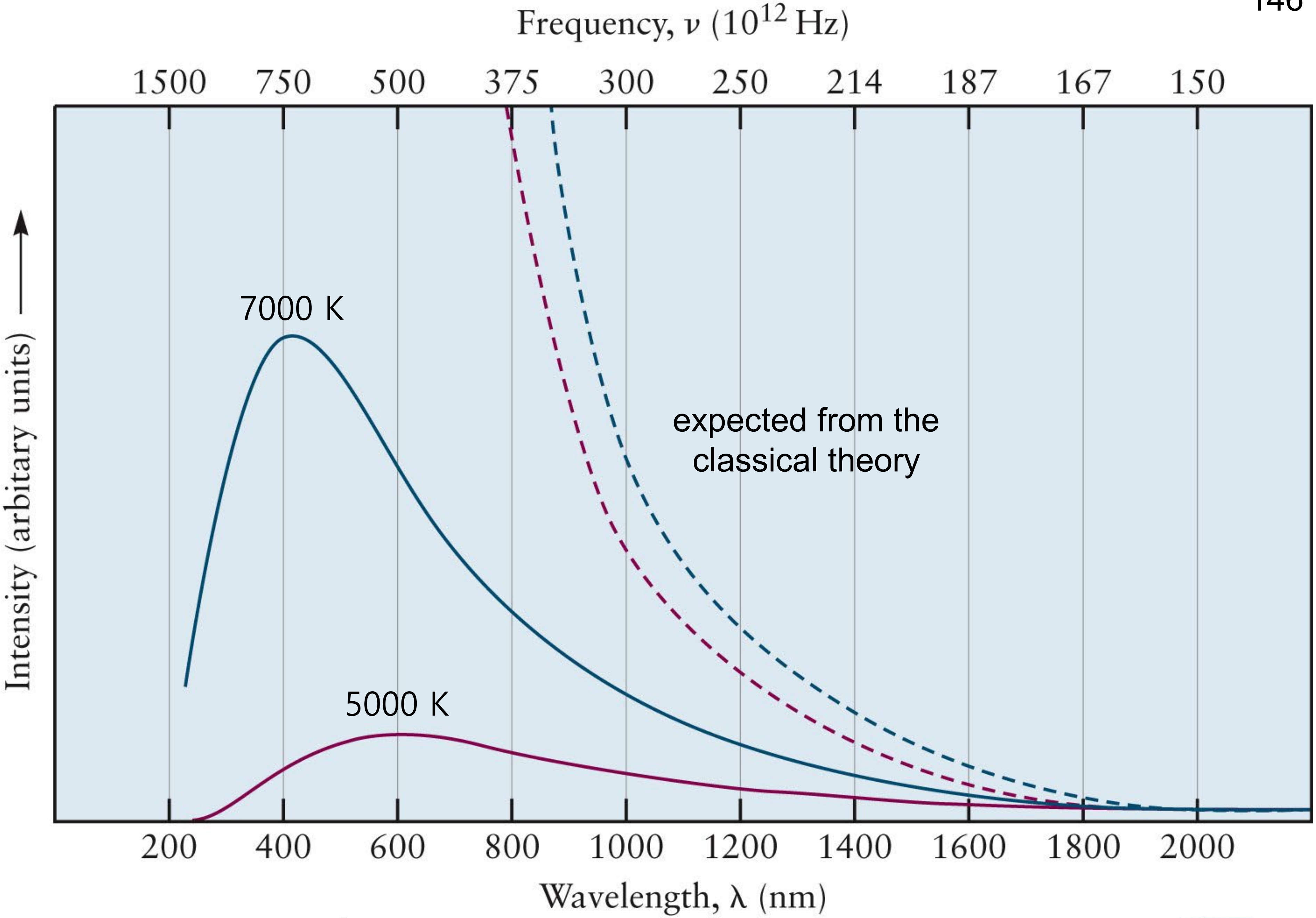
- Every objects emits energy from its surface in the form of thermal radiation. This energy is carried by electromagnetic waves.

- The distribution of the wavelength depends on the temperature.

- The maximum in the radiation intensity distribution moves to higher frequency (shorter wavelength) as T increases.

- The radiation intensity falls to zero at extremely high frequencies for objects heated to any temperature.




Frequency, ν (10^{12} Hz)
1500
750
500
375
300
250
214
187
167
150
Intensity (arbitary units)
7000 K
5000 K
expected from the
classical theory
200
400
600
800
1000
1200
1400
1600
1800
2000
Wavelength, λ (nm)

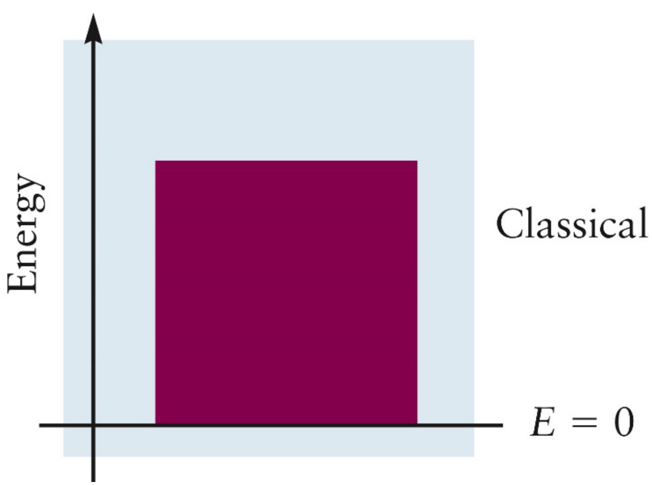
➢ Ultraviolet catastrophe

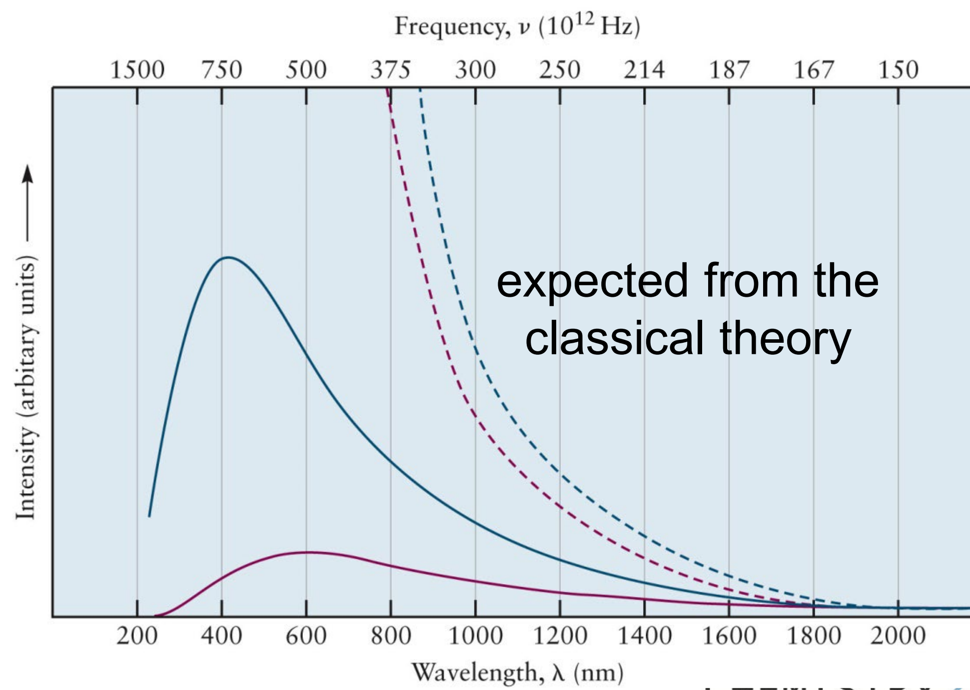
- From classical theory, $$\rho_T(\nu) = \frac{8\pi k_B T \nu^2}{c^3}$$

$\rho_T(\nu)$: intensity at ν, k_B: Boltzmann constant, T: temperature (K)

- Predicting **an infinite intensity at very short wavelengths**

↔ The experimental results fall to zero at short wavelengths





➢ Plank's quantum hypothesis

- The oscillator must gain and lose energy in quanta of magnitude hν, and that the total energy can take only discrete values:

$$\varepsilon_{OSC} = nh\nu \qquad n = 1, 2, 3, 4, \cdots$$

Plank's constant h = 6.62606896(3) x 10^{-34} J s

- Radiation intensity

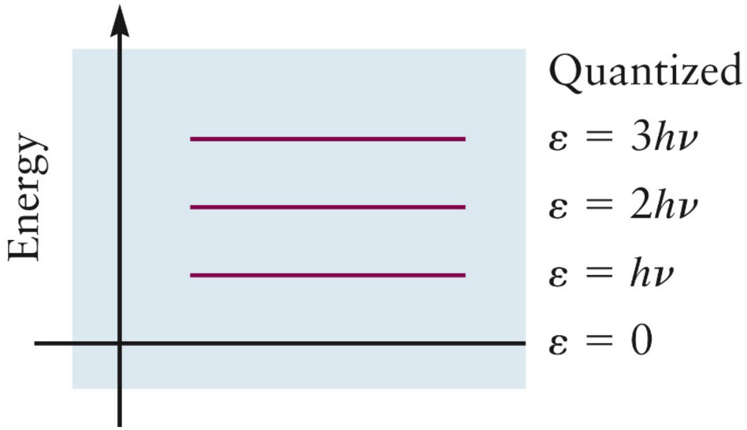
$$\rho_T(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT}-1}$$

When $h\nu/k_BT \ll 1$ (or T → ∞),

$$\rho_T(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{[1+\frac{h\nu}{k_BT}]-1} = \frac{8\pi k_BT\nu^2}{c^3}$$ = the classical result

➢ **Physical meaning of Plank's explanation**

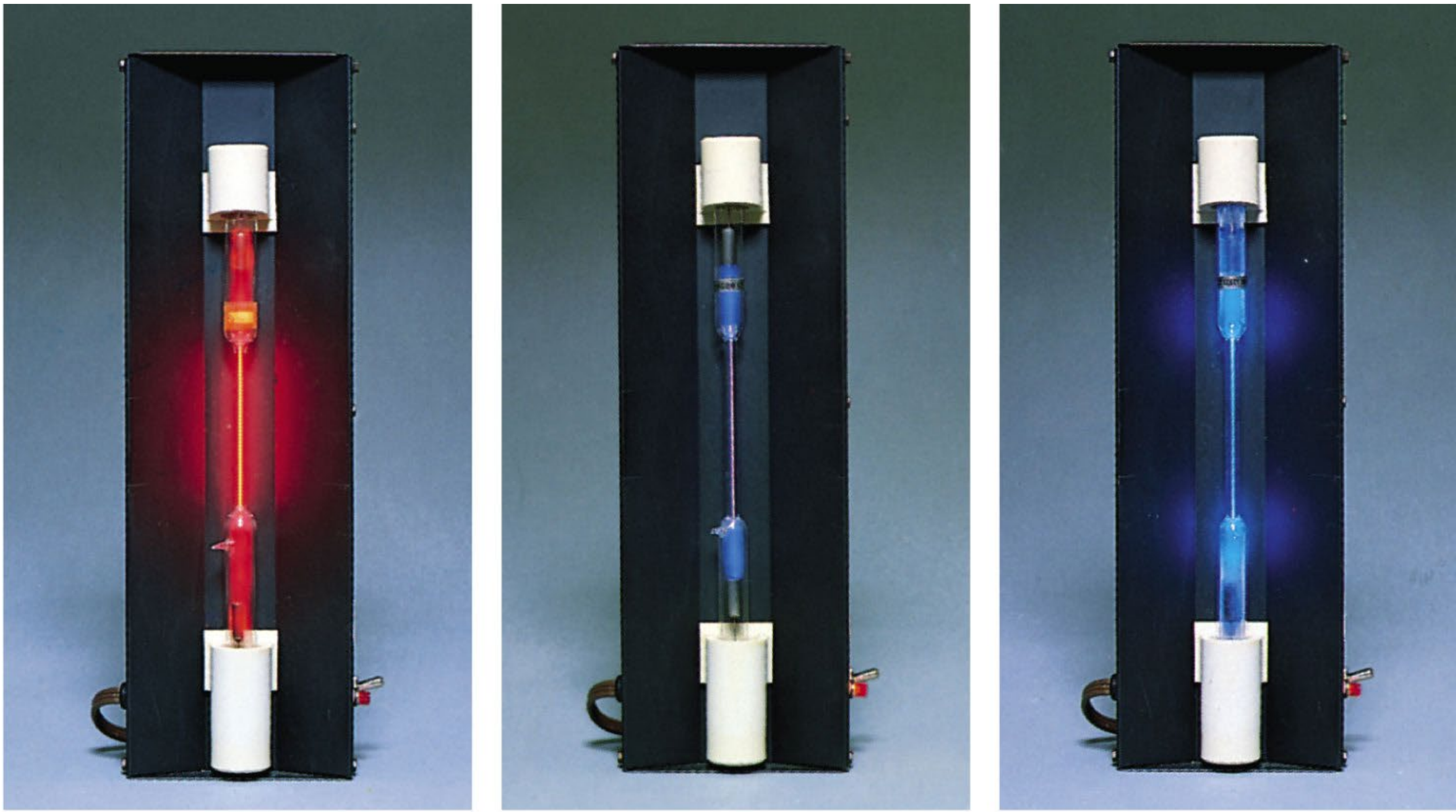
1. The energy of a system can take only discrete values.



2. A quantized oscillator can gain or lose energy only in discrete amounts $\Delta E = h\nu$.

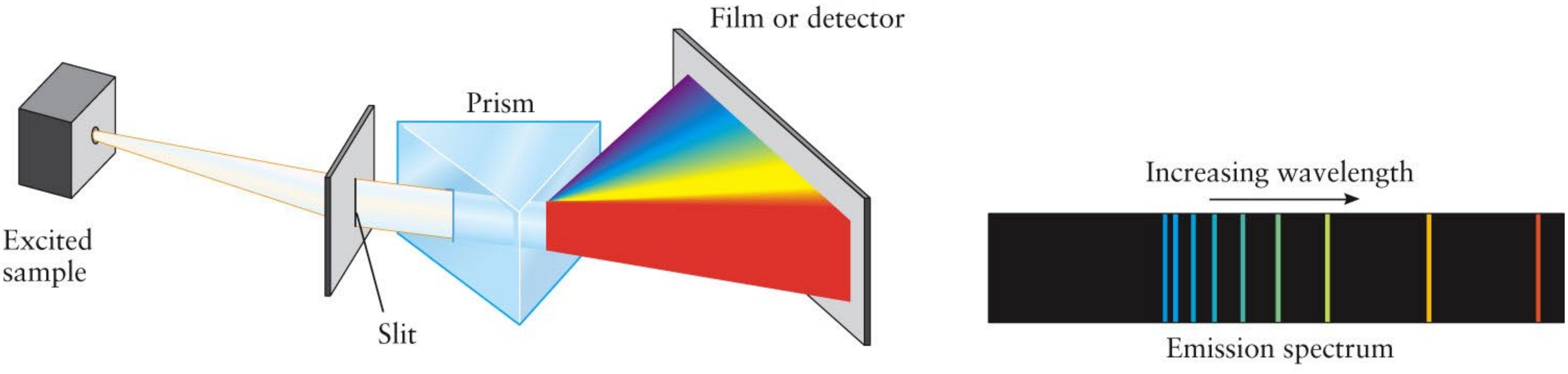
3. To emit energy from higher energy states, T must be sufficiently high.

Light from an electrical discharge

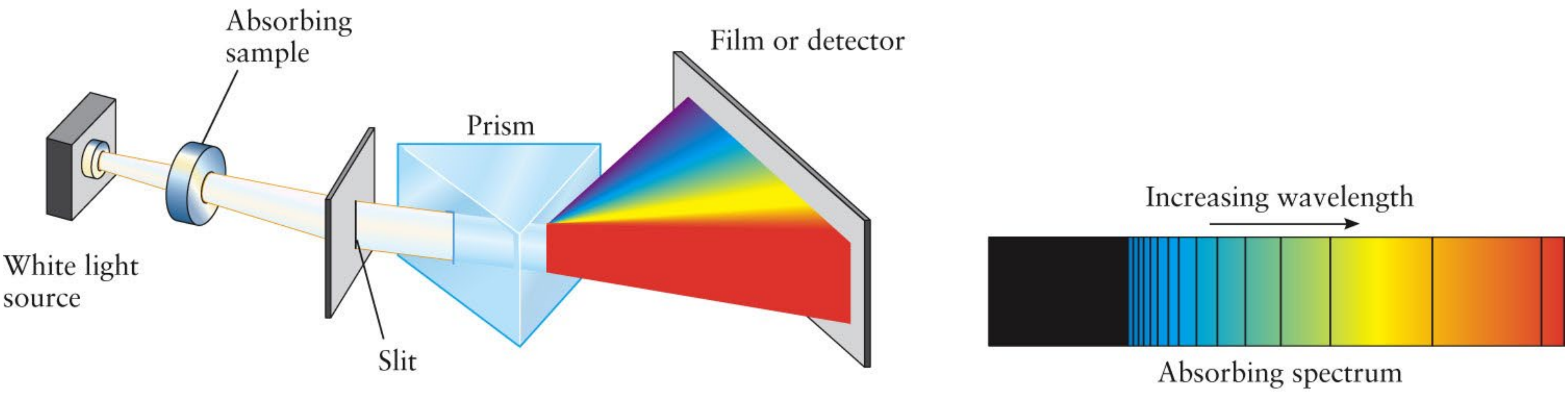


(a) Ne (b) Ar (c) Hg

Spectrograph



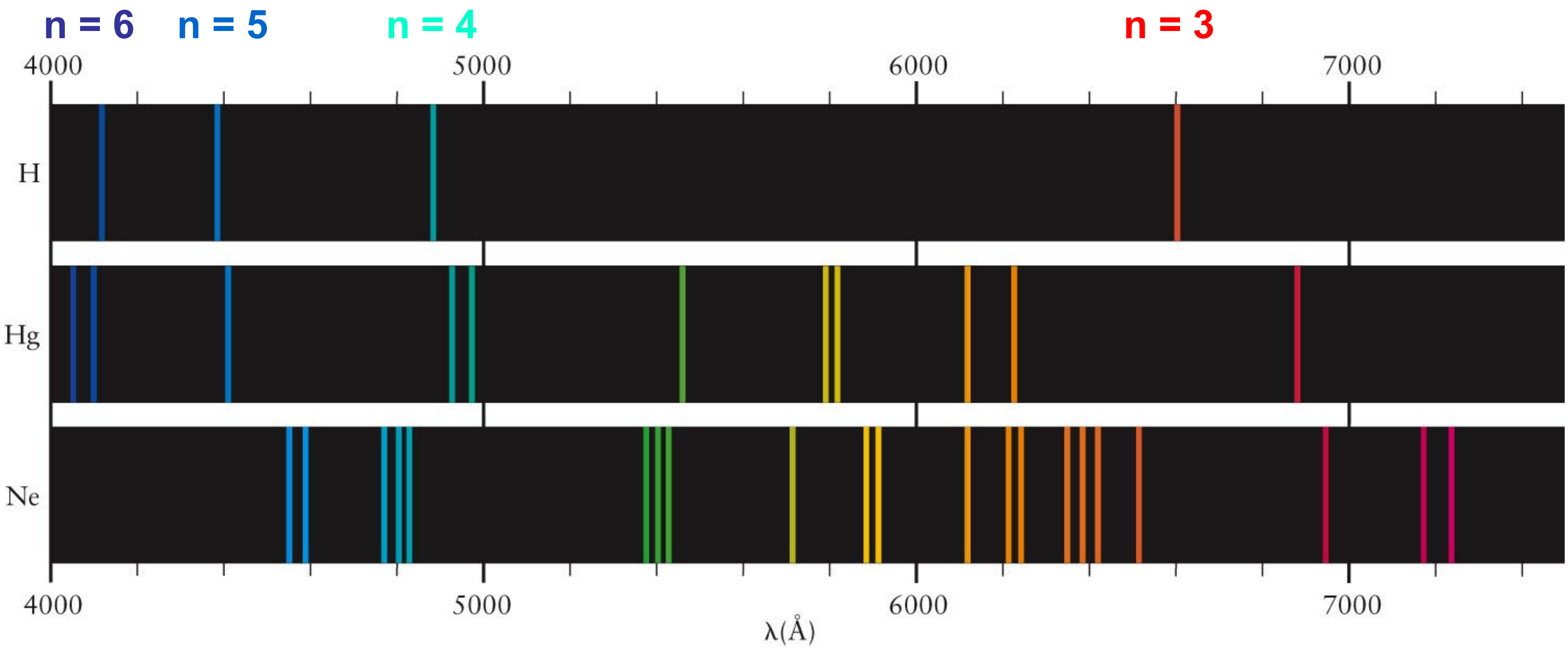
(a)



(b)

➢ Balmer series for hydrogen atoms

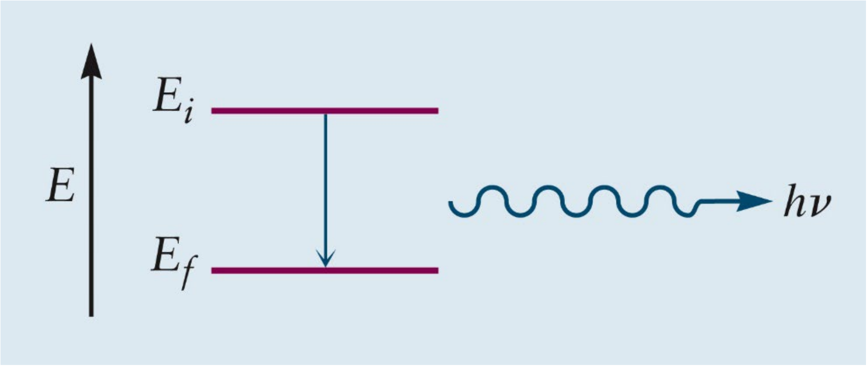
$$\upsilon = \left[\frac{1}{4} - \frac{1}{n^2}\right] \times 3.29 \times 10^{15}\ s^{-1} \quad n = 3, 4, 5, 6 \cdots$$



- **Bohr's explanation**

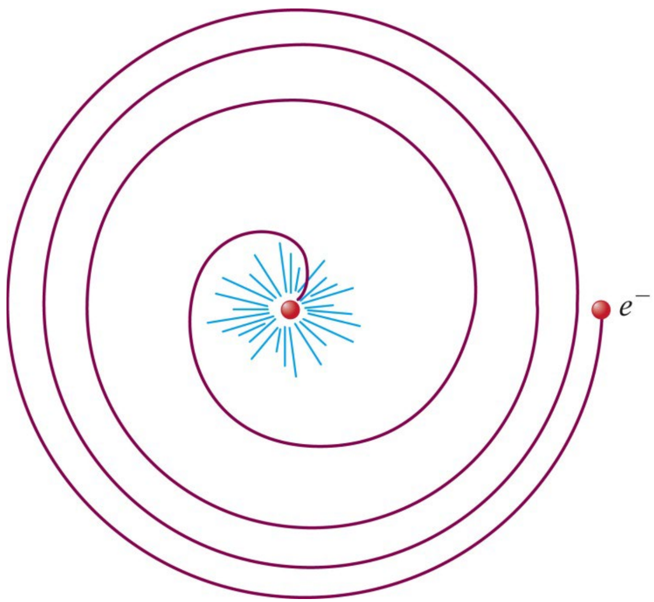
  The frequency of the light absorbed is connected to the energy of the initial and final states by the expression

$$\nu = \frac{E_f - Ei}{h} \quad \text{or} \quad \Delta E = h\nu$$

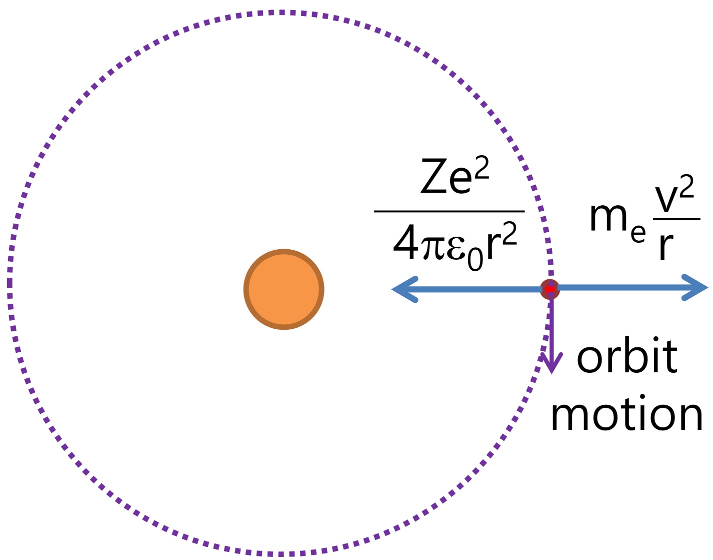


4.3 THE BOHR MODEL: PREDICTING DISCRETE ENERGY LEVELS IN ATOMS

- Starting from Rutherford's planetary model of the atom
- **the assumption** that an electron of mass m_e moves in a circular orbit of radius r about a fixed nucleus



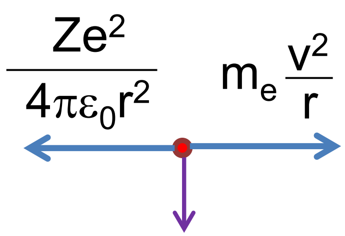
Classical theory states are not stable.



Bohr model

- The total energy of the hydrogen atom: kinetic + potential

$$E = \frac{1}{2}m_e v^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



- Coulomb force = centrifugal force

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2} = m_e\frac{v^2}{r}$$

- **Bohr's postulation**: angular momentum of the electron is quantized.

$$L = m_e vr = n\frac{h}{2\pi} \quad n = 1, 2, 3, \ldots$$

- Radius $r_n = \dfrac{\varepsilon_0 n^2 h^2}{\pi Z e^2 m_e} = \dfrac{n^2}{Z} a_0$

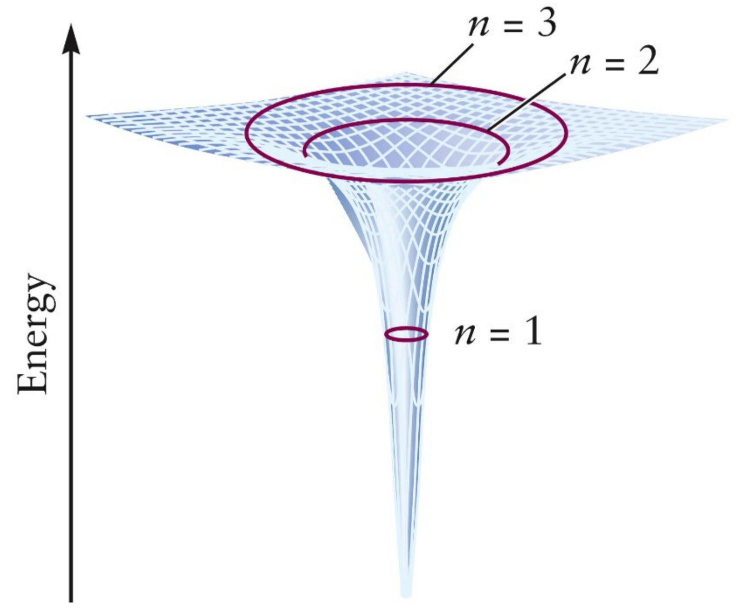
a_0 (Bohr radius) $= \dfrac{\varepsilon_0 h^2}{\pi e^2 m_e} = 0.529$ Å

- Velocity $v_n = \dfrac{nh}{2\pi m_e r_n} = \dfrac{Ze^2}{2\varepsilon_0^2 nh}$

- Energy $E_n = \dfrac{-Z^2 e^4 m_e}{8\varepsilon_0^2 n^2 h^2} = -R\,\dfrac{Z^2}{n^2}$

$n = 1, 2, 3, \ldots$

R (Rydbergs) $= \dfrac{e^4 m_e}{8\varepsilon_0^2 h^2} = 2.18\times10^{-18}$ J



- **Ionization energy**: the minimum energy required to remove an electron from an atom

In the Bohr model, the n = 1 state → the n = ∞ state

$\Delta E = E_{final} - E_{initial} = 0 - (-2.18\times10^{-18}\ J) = 2.18\times10^{-18}\ J$

$IE = N_A \times 2.18\times10^{-18}\ J = 1310\ kJ\ mol^{-1}$

EXAMPLE 4.3

Consider the n = 2 state of Li^{2+}. Using the Bohr model, calculate r, V, and E of the ion relative to that of the nucleus and electron separated by an infinite distance.

$$r = \frac{n^2}{Z}a_0 = \frac{4}{3}a_0 = 0.705\ \text{Å} \qquad v = \frac{nh}{2\pi m_e r_n} = \frac{2h}{2\pi m_e r_n} = 3.28\times10^{6}\ m\ s^{-1}$$

$$E_2 = -R\frac{Z^2}{n^2} = -R\frac{9}{4} = -4.90\times10^{-18}\ J$$

➢ Atomic spectra: interpretation by the Bohr model

- Light is emitted to carry off the energy hν by transition from E_i to E_f.

$$h\nu = \frac{-Z^2e^4m_e}{8\varepsilon_0^2h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

- Lines in the emission spectrum with frequencies,

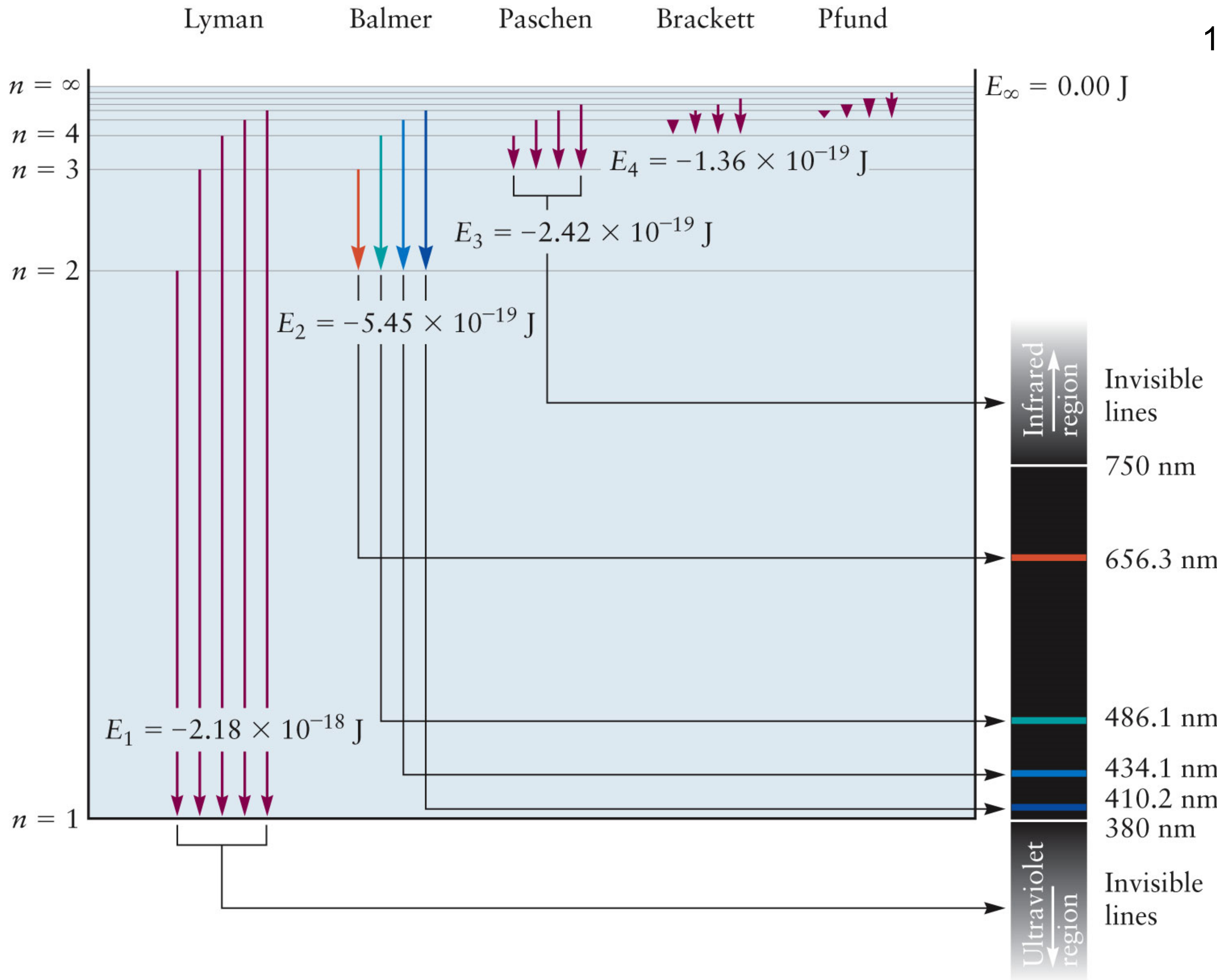
$$\nu = \frac{-Z^2e^4m_e}{8\varepsilon_0^2h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = (3.29\times10^{15}\ s^{-1})\ Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$n_i > n_f = 1, 2, 3, \ldots$ (emission)

- Lines in the absorption spectrum with frequencies,

$$\nu = \frac{-Z^2e^4m_e}{8\varepsilon_0^2h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = (3.29\times10^{15}\ s^{-1})\ Z^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$n_f > n_i = 1, 2, 3, \ldots$ (absorption)



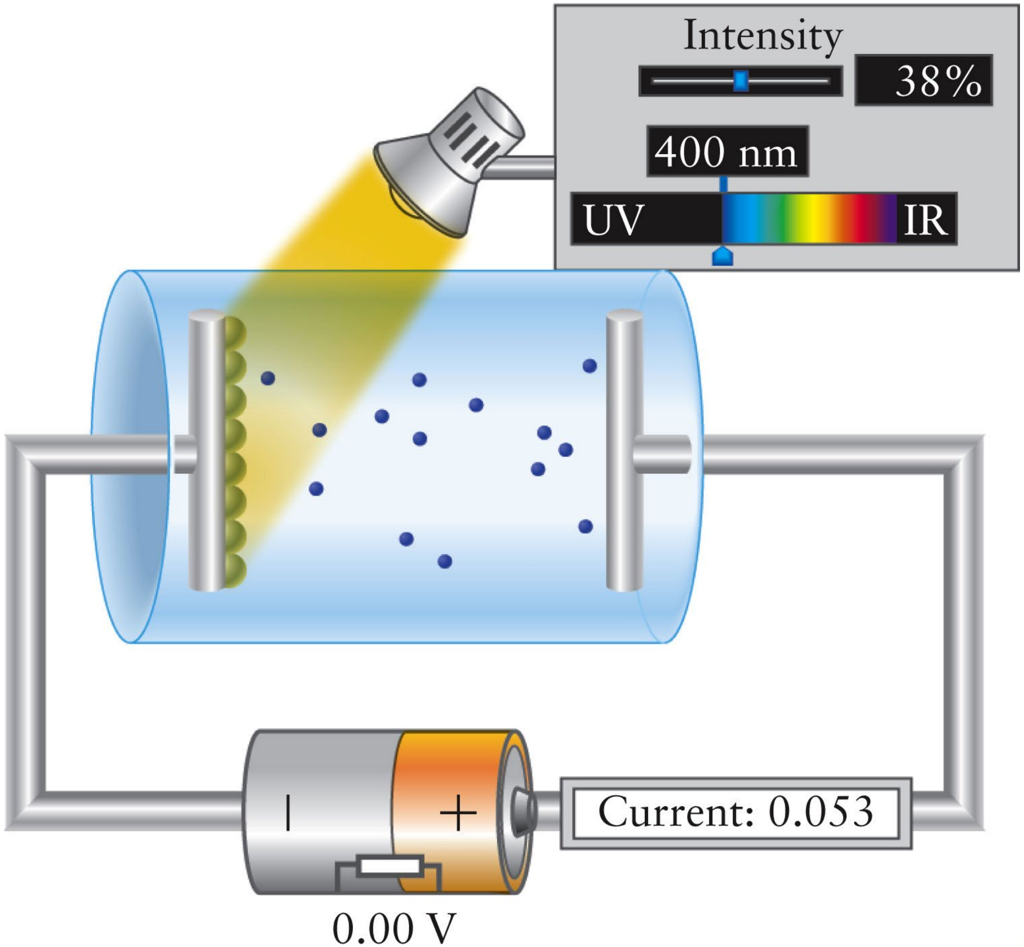
Lyman
Balmer
Paschen
Brackett
Pfund
n = ∞
n = 4
n = 3
n = 2
n = 1
E∞ = 0.00 J
E4 = −1.36 × 10^−19 J
E3 = −2.42 × 10^−19 J
E2 = −5.45 × 10^−19 J
E1 = −2.18 × 10^−18 J
Infrared region
Invisible lines
750 nm
656.3 nm
486.1 nm
434.1 nm
410.2 nm
380 nm
Ultraviolet region
Invisible lines

4.4 EVIDENCE FOR WAVE-PARTICLE DUALITY

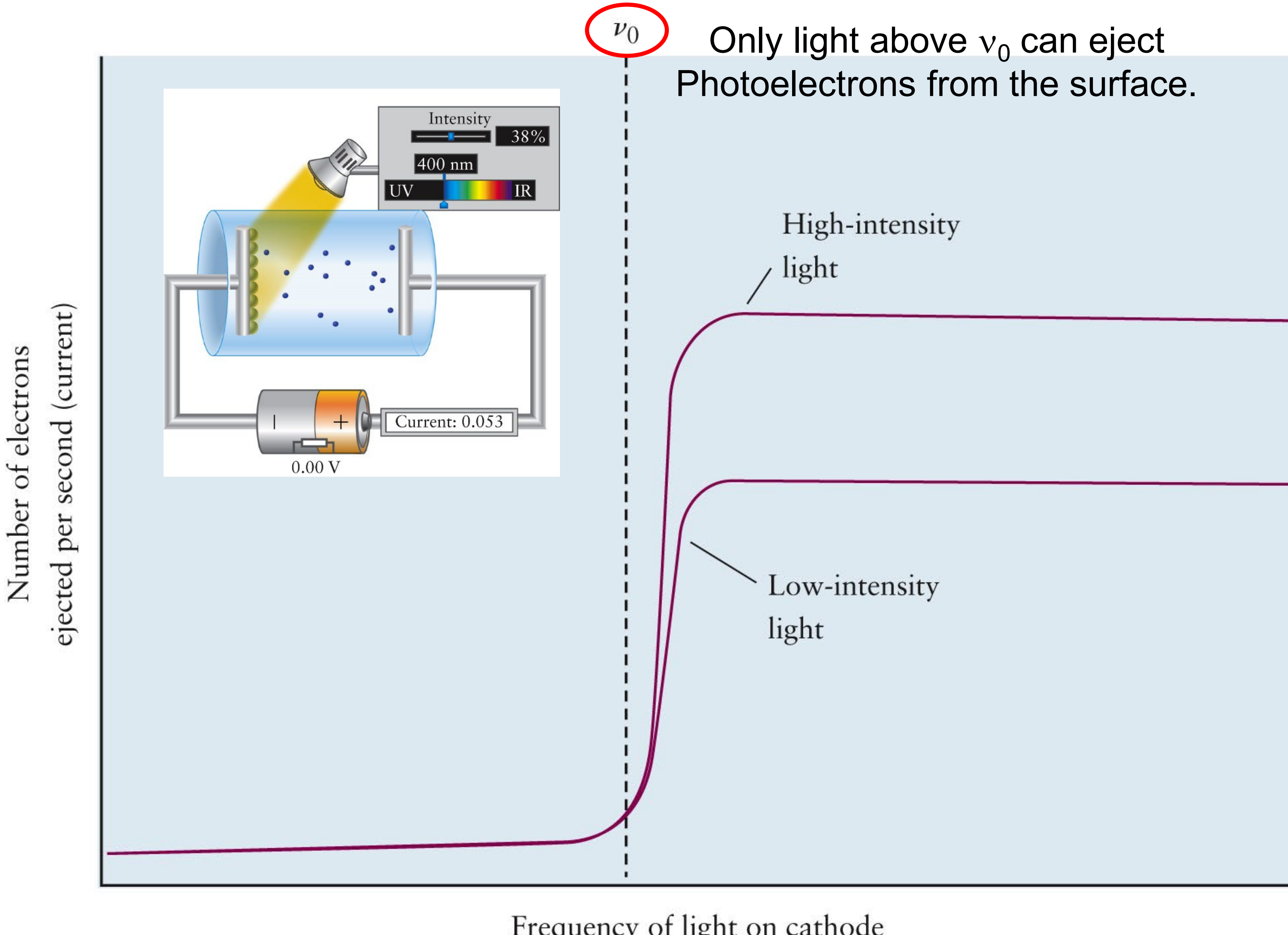
- The particles sometimes behave as waves, and vice versa.

➢ **The Photoelectron Effect**

- A beam of light shining onto a metal surface (photocathode) can eject electrons (photoelectrons) and cause an electric current (photocurrent) to flow.



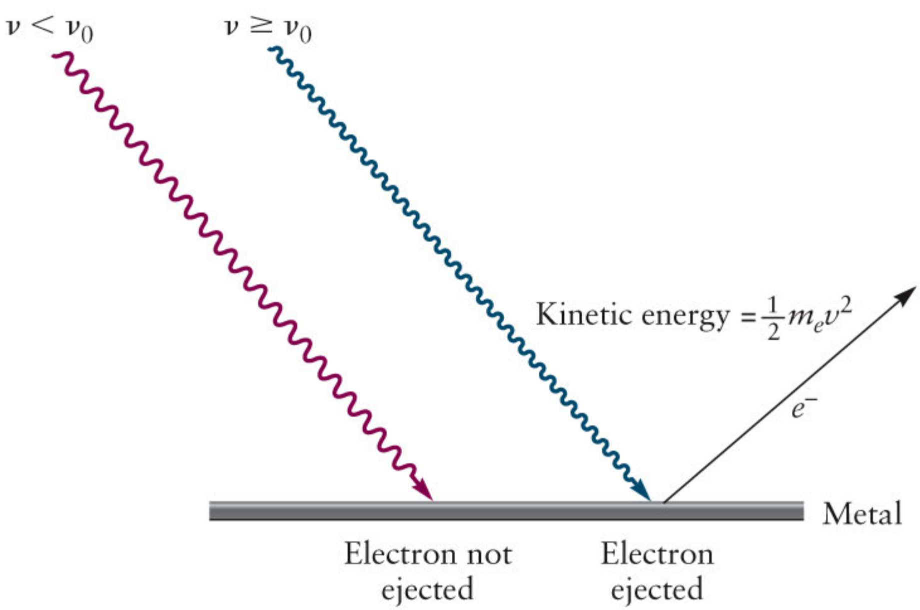
Only light above ν_0 can eject Photoelectrons from the surface.



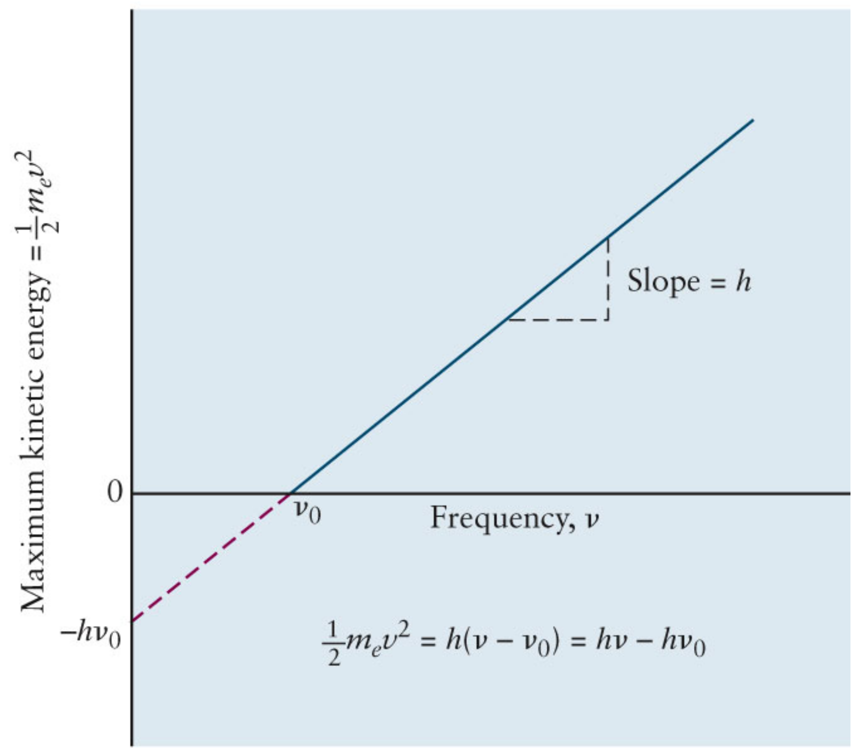
- Einstein's theory predicts that the maximum kinetic energy of photoelectrons emitted by light of frequency ν

$$E_{max} = \frac{1}{2} m v_e^2 = h\nu - \Phi$$

- Workfunction of the metal, Φ, represents the binding energy that electrons must overcome to escape from the metal surface after photon absorption.



(a)



(b)

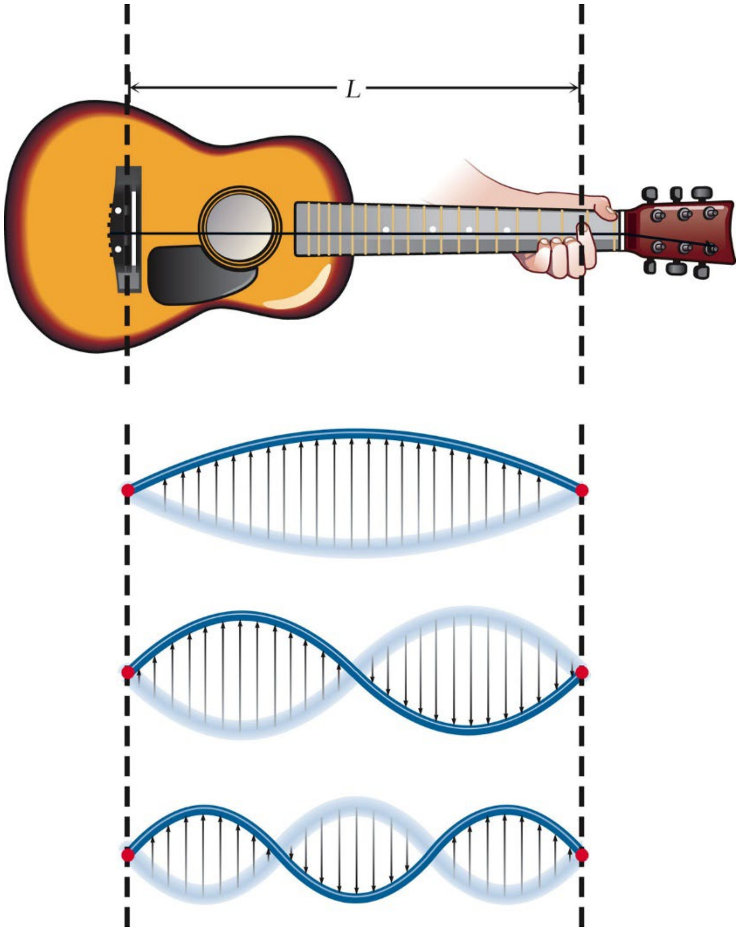
Standing Wave

- **Standing wave** under a physical boundary condition

$$n\frac{\lambda}{2} = L \qquad n = 1, 2, 3, \ldots$$

- **n = 1**, fundamental or first harmonic oscillation

- **node**, at certain points where the amplitude is zero.



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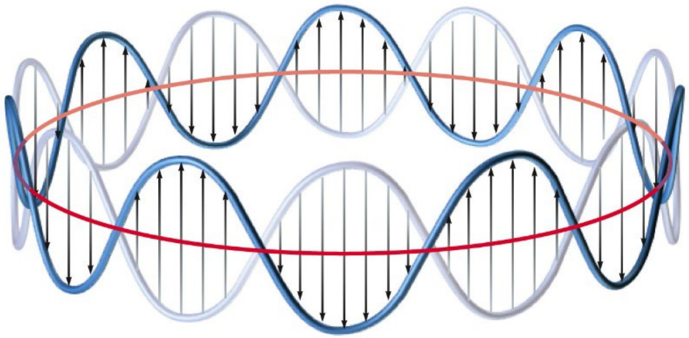
De Broglie Waves

- The electron with a circular standing wave oscillating about the nucleus of the atom.



$n\lambda = 2\pi r \qquad n = 1, 2, 3, \ldots$

From Bohr's assumption, $m_e vr = n\frac{h}{2\pi}$ $\qquad 2\pi r = n\frac{h}{m_e v}$

$$\boldsymbol{\lambda = \frac{h}{m_e v} = \frac{h}{p}}$$

EXAMPLE 4.3

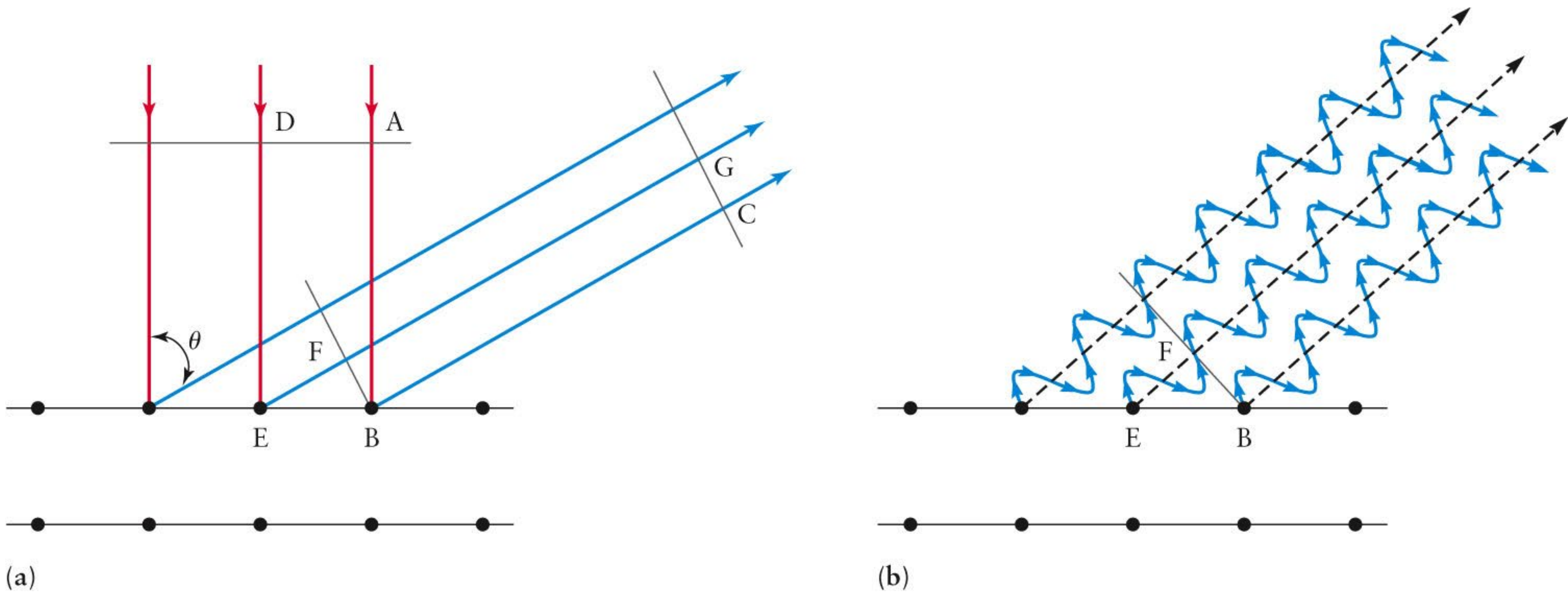
Calculate the de Broglie wavelengths of an electron moving with velocity 1.0 x 10^6 m s^{-1}.

7.3 Å

Electron Diffraction

- An electron with kinetic energy of 50 eV has a de Broglie wave length of 1.73 Å, comparable to the spacing between atomic planes.

$T = eV = \frac{1}{2}m_e v^2 = \frac{p^2}{2m_e}$ $\quad p = \sqrt{2m_e eV}$ $\quad \lambda = h/\sqrt{2m_e eV} = 1.73$ Å

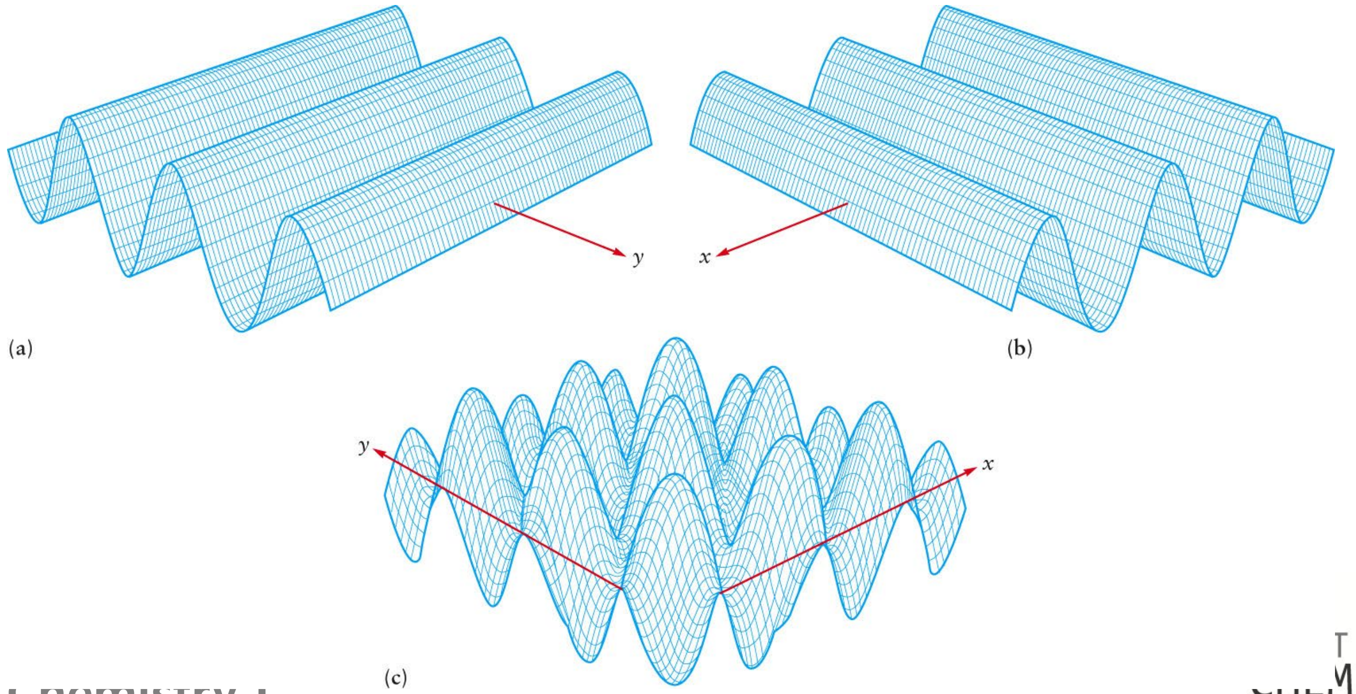


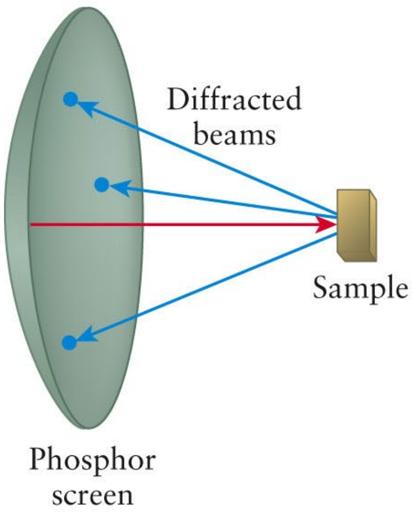
- The diffraction condition is

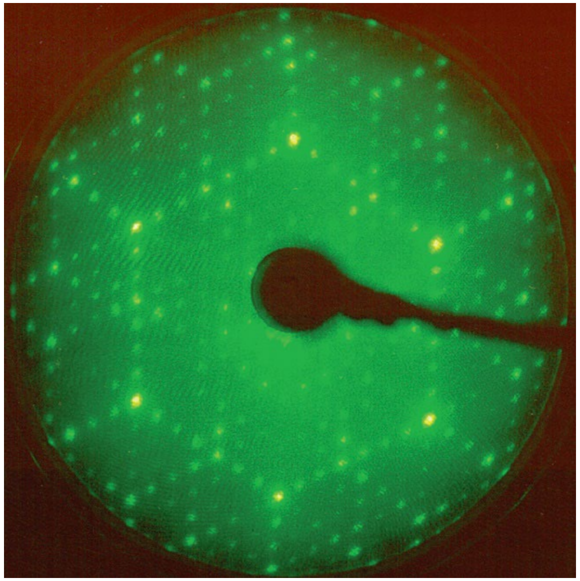
$$n\lambda = a \sin \theta$$

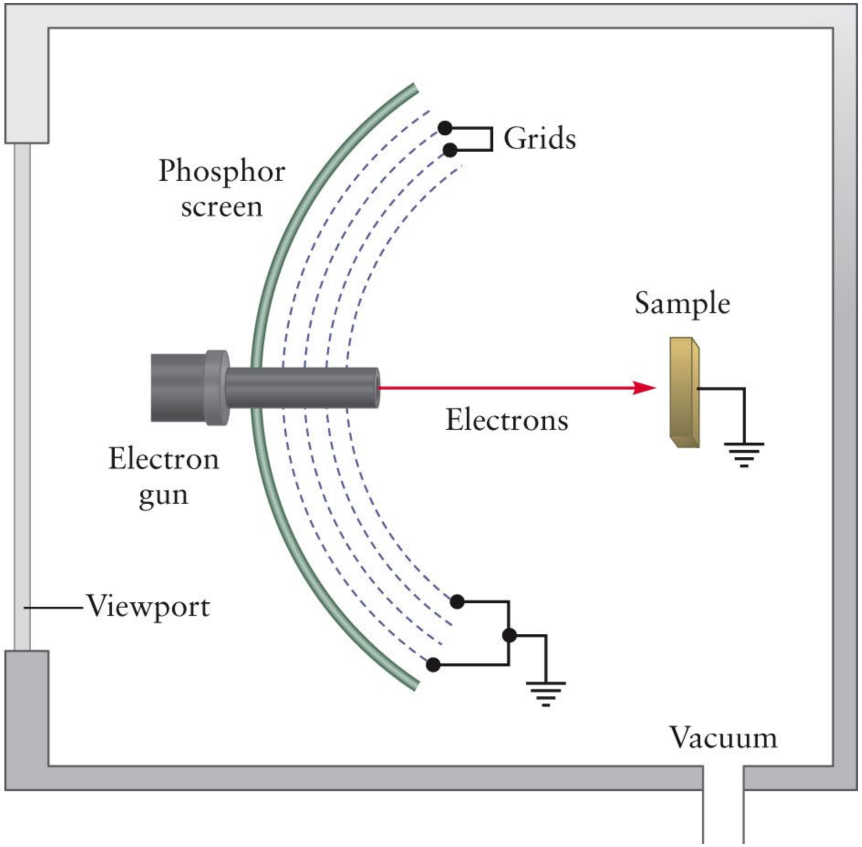
- For two dimensional surface with a along the x-axis and b along the y-axis

$$n_a\lambda_a = a \sin \theta_a \qquad n_b\lambda_b = b \sin \theta_b$$









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4.5 THE SCHRÖDINGER EQUATION

- **wave function** (ψ, psi): mapping out the amplitude of a wave in three dimensions; it may be a function of time.

- The origins of the Schrödinger equation:

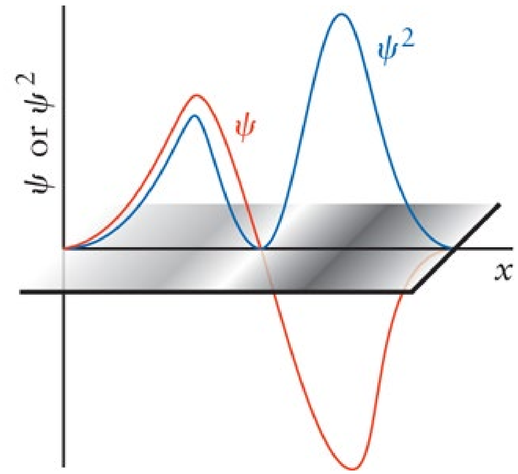
If the wave function is described as $\psi(x) = A\sin\frac{2\pi x}{\lambda}$,

$$\frac{d^2\psi(x)}{dx^2} = -A\left(\frac{2\pi}{\lambda}\right)^2 \sin\frac{2\pi x}{\lambda} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi(x)$$

$$= -\left(\frac{2\pi}{h}p\right)^2 \psi(x) \quad \Leftarrow \quad \lambda = \frac{h}{p}$$

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = \frac{p^2}{2m}\psi(x) = \mathrm{T}\psi(x) \quad \Leftarrow \quad T = \frac{p^2}{2m}$$

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad \Leftarrow \quad \mathrm{E} = \mathrm{T} + \mathrm{V(x)}$$



- **Born interpretation**: probability of finding the particle in a region is proportional to the value of ψ^2

- **probability density (P(x))**: the probability that the particle will be found in a small region divided by the volume of the region

  $P(x)dx$ = probability

1) Probability density must be normalized.

$$\int_{-\infty}^{+\infty} P(x)dx = \int_{-\infty}^{+\infty} [\psi(x)]^2 dx = 1$$

2) P(x) must be continuous at each point x.

3) $\psi(x)$ must be bounded at large values of x.

} boundary conditions

$\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$

How can we solve the Schrödinger equation?

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

➡ The allowed energy values E and wave functions $\psi(x)$

From the boundary conditions, energy quantization arises.
Each energy value corresponds to one or more wave functions.

The wave functions describe the distribution of particles
when the system has a specific energy value.

4.6 QUANTUM MECHANICS OF PARTICLE-IN-A-BOX MODELS

→ The simplest model problem for which the Schrödinger equation can be solved, and in which energy quantization appears

- **Particle in a box**

  - Mass m confined between two rigid walls a distance L apart

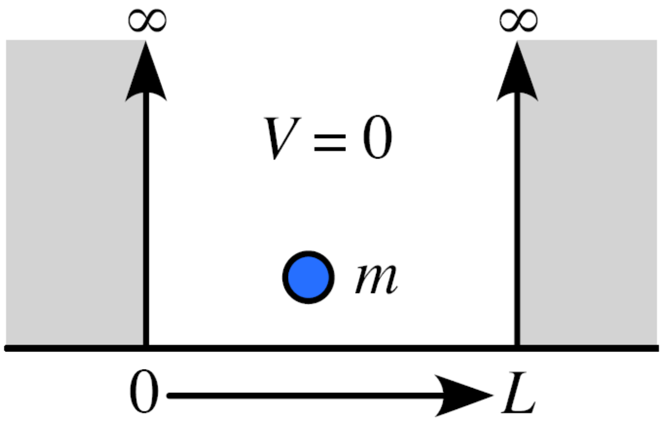
  - ψ = 0 outside the box at the walls (boundary condition)

Particle-in-a-box

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}$$

Find solutions of the form inside the box ($V = 0$):

$$\psi(x) = 0 \text{ for } x \leq 0 \text{ and } x \geq L$$



- Inside the box, where V = 0,

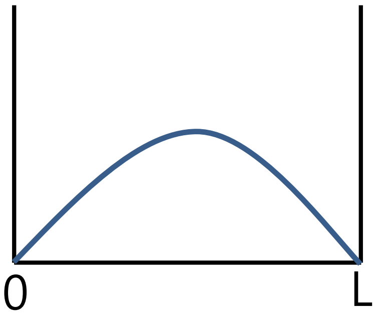
$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \frac{d^2\psi(x)}{dx^2} = -\frac{8\pi^2 mE}{h^2}\psi(x)$$

- From the boundary conditions, $\psi(x) = 0$ at x = 0 and x = L.

$$\psi(x) = \mathrm{A}\sin\mathrm{kx}; \quad \psi(L) = \mathrm{A}\sin\mathrm{kL} = 0$$

$kL = n\pi$ n = 1, 2, 3, …

➡ $\psi(x) = \mathrm{A}\sin\left(\frac{n\pi x}{L}\right)$ n = 1, 2, 3, ...



- For the normalization,

$$A^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = A^2\left(\frac{L}{2}\right) = 1 \qquad A = \sqrt{\frac{2}{L}}$$

$$\boldsymbol{\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \ldots}$$

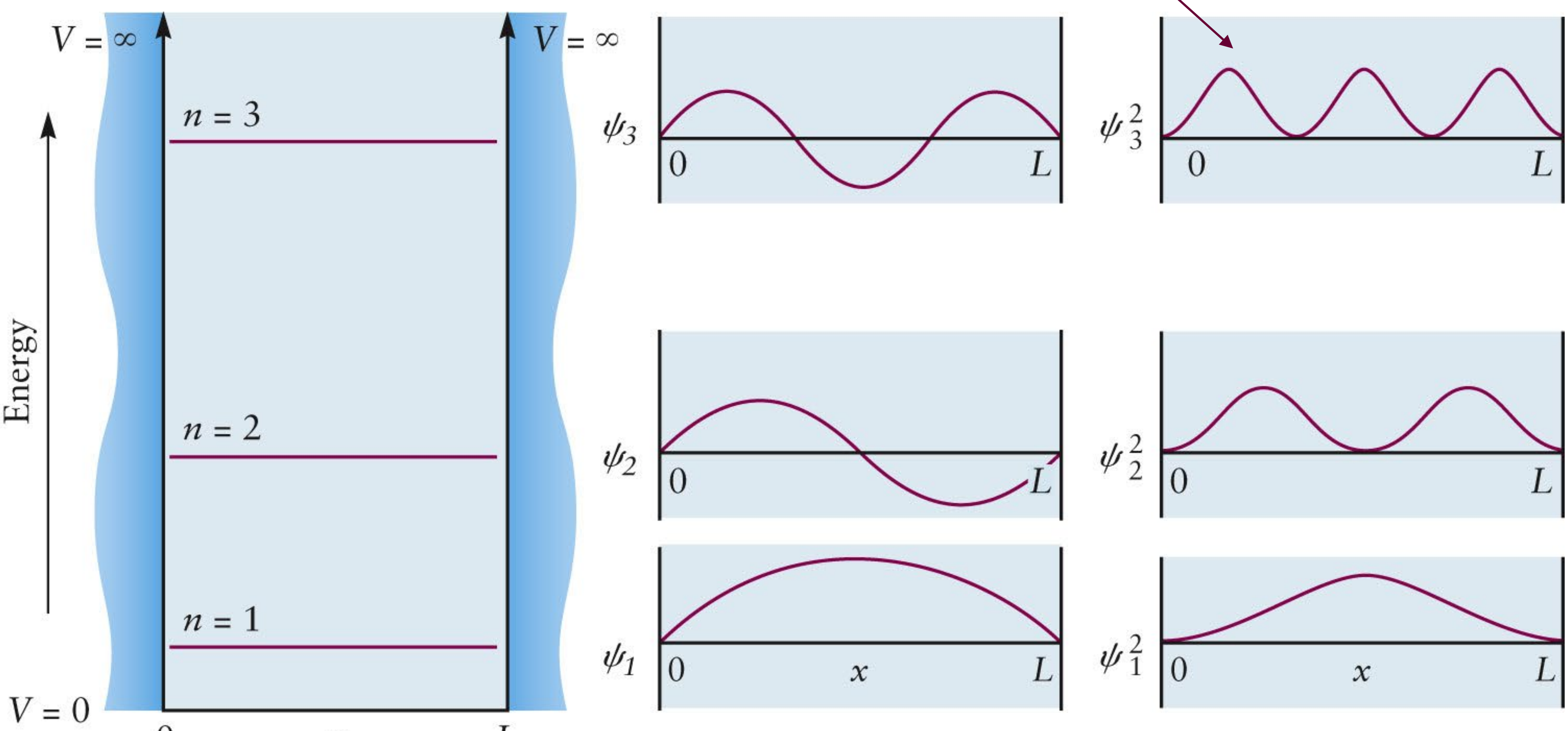
- The second derivative of the wave function:

$$\frac{d^2\psi_n(x)}{dx^2} = -\left(\frac{n\pi}{L}\right)^2\psi_n(x) = -\frac{8\pi^2 mE}{h^2}\psi(x)$$

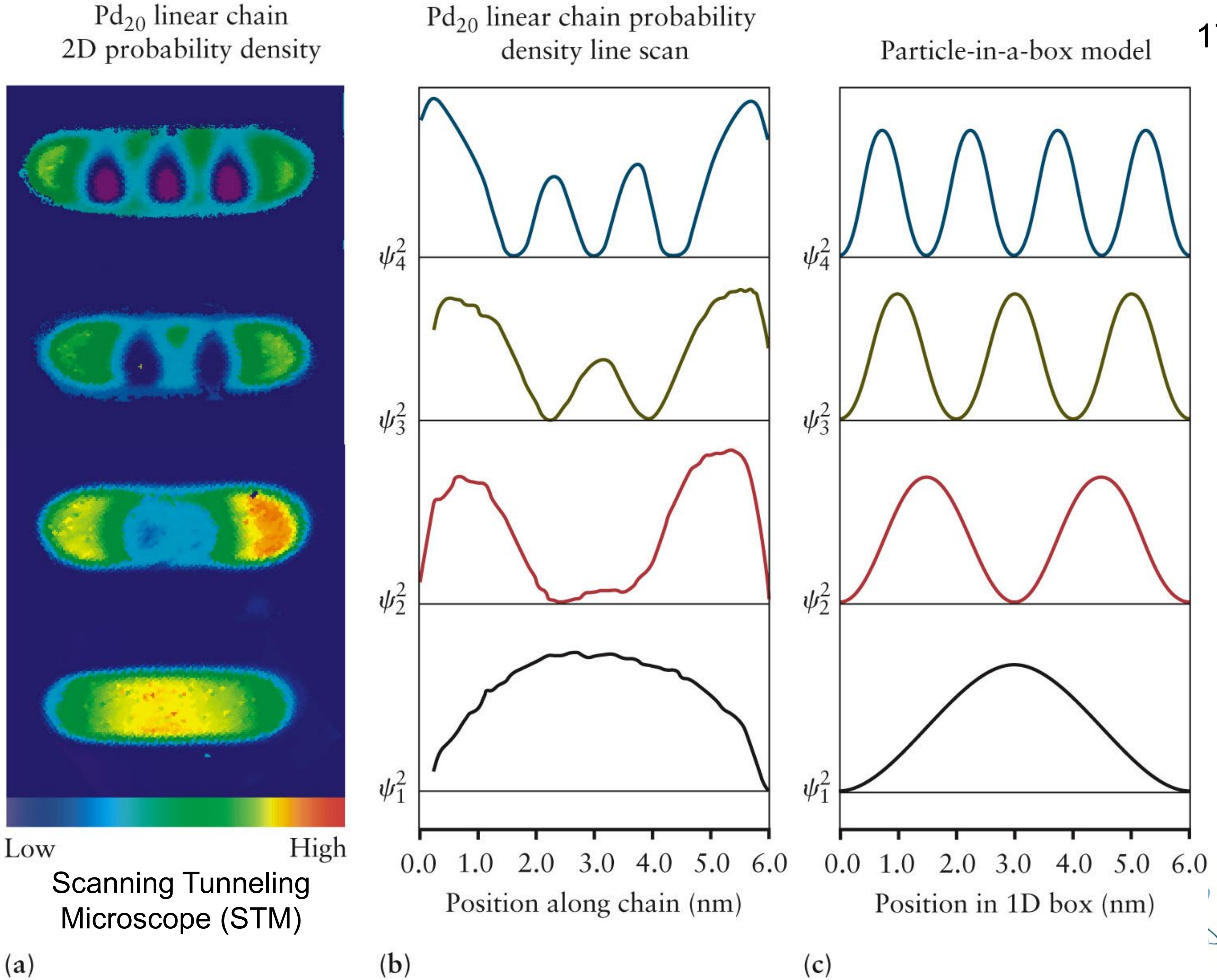
$$\boldsymbol{E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots}$$

Energy of the particle is quantized !

$\psi_n(x)$ has n - 1 nodes, and # of nodes increases with the energy.



(a) Energy levels (b) Wave functions (c) Probabilities


Pd20 linear chain
2D probability density
Low
High
Scanning Tunneling
Microscope (STM)
(a)
Pd20 linear chain probability
density line scan
ψ4²
ψ3²
ψ2²
ψ1²
0.0 1.0 2.0 3.0 4.0 5.0 6.0
Position along chain (nm)
(b)
Particle-in-a-box model
ψ4²
ψ3²
ψ2²
ψ1²
0.0 1.0 2.0 3.0 4.0 5.0 6.0
Position in 1D box (nm)
(c)