Today's class:

Fundamentals of Spectroscopy

This lecture follows the materials from the following book

- *Spectroscopy for the Biological Sciences, by Gordon G. Hammes, Wiley, 2005*
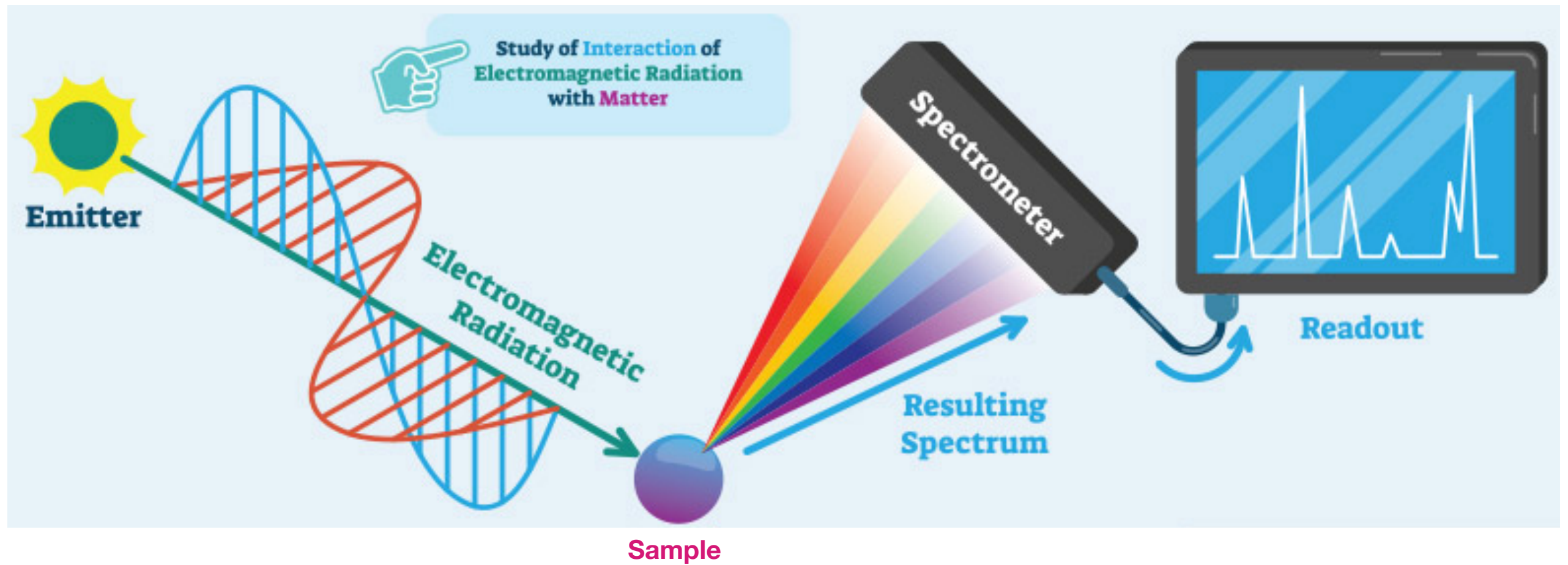
What is spectroscopy?
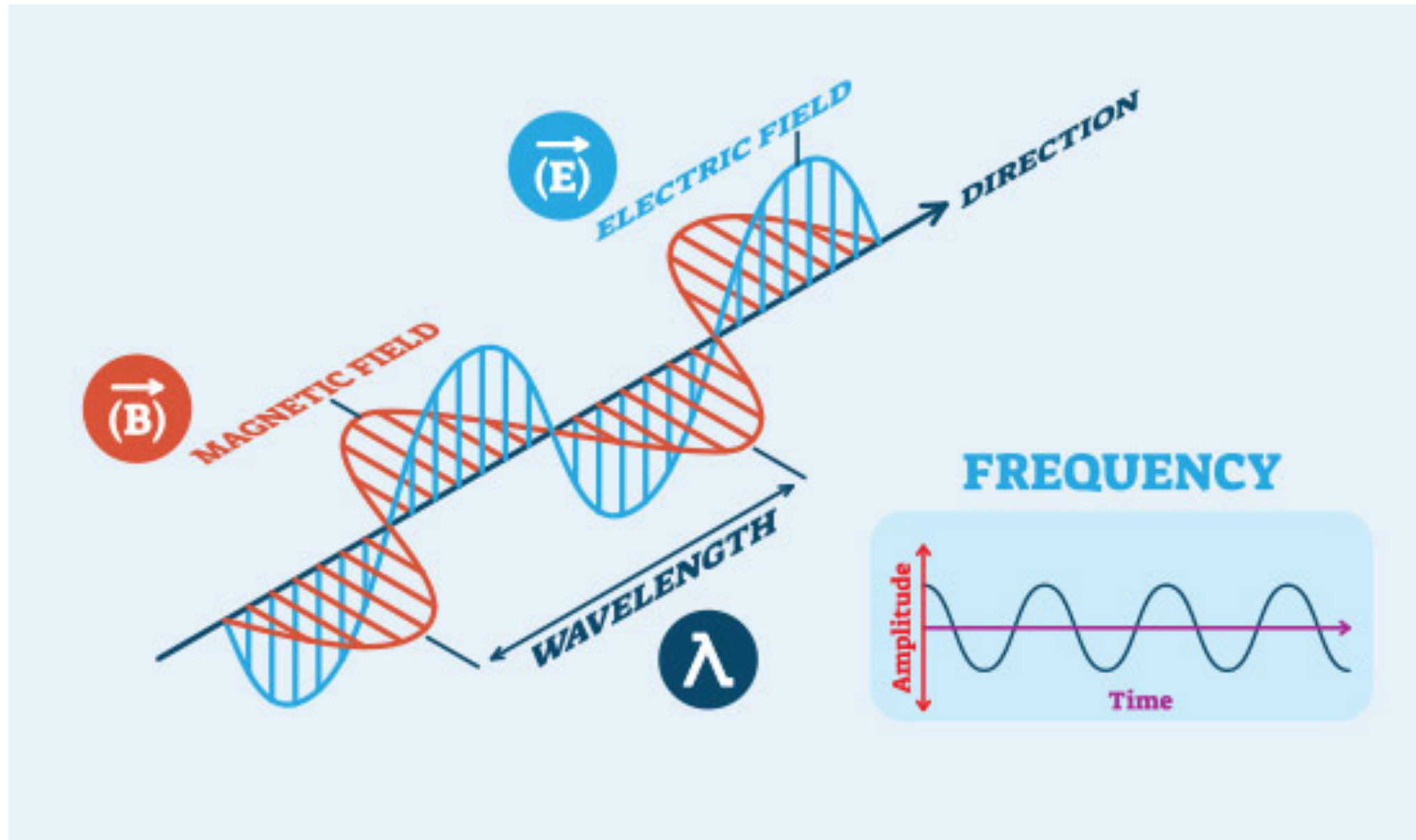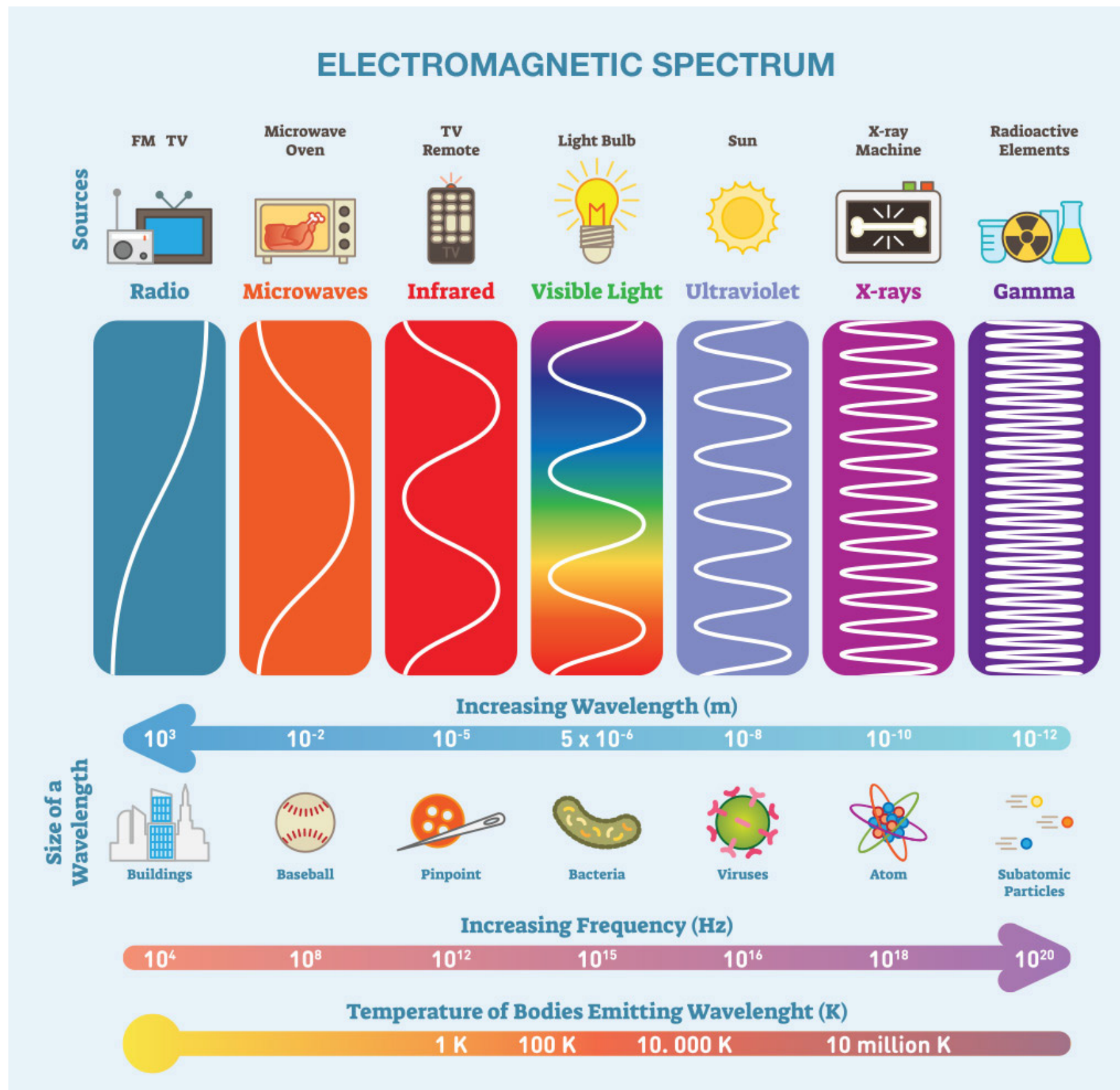

Image courtesy: pasco.com

Anatomy of a light beam
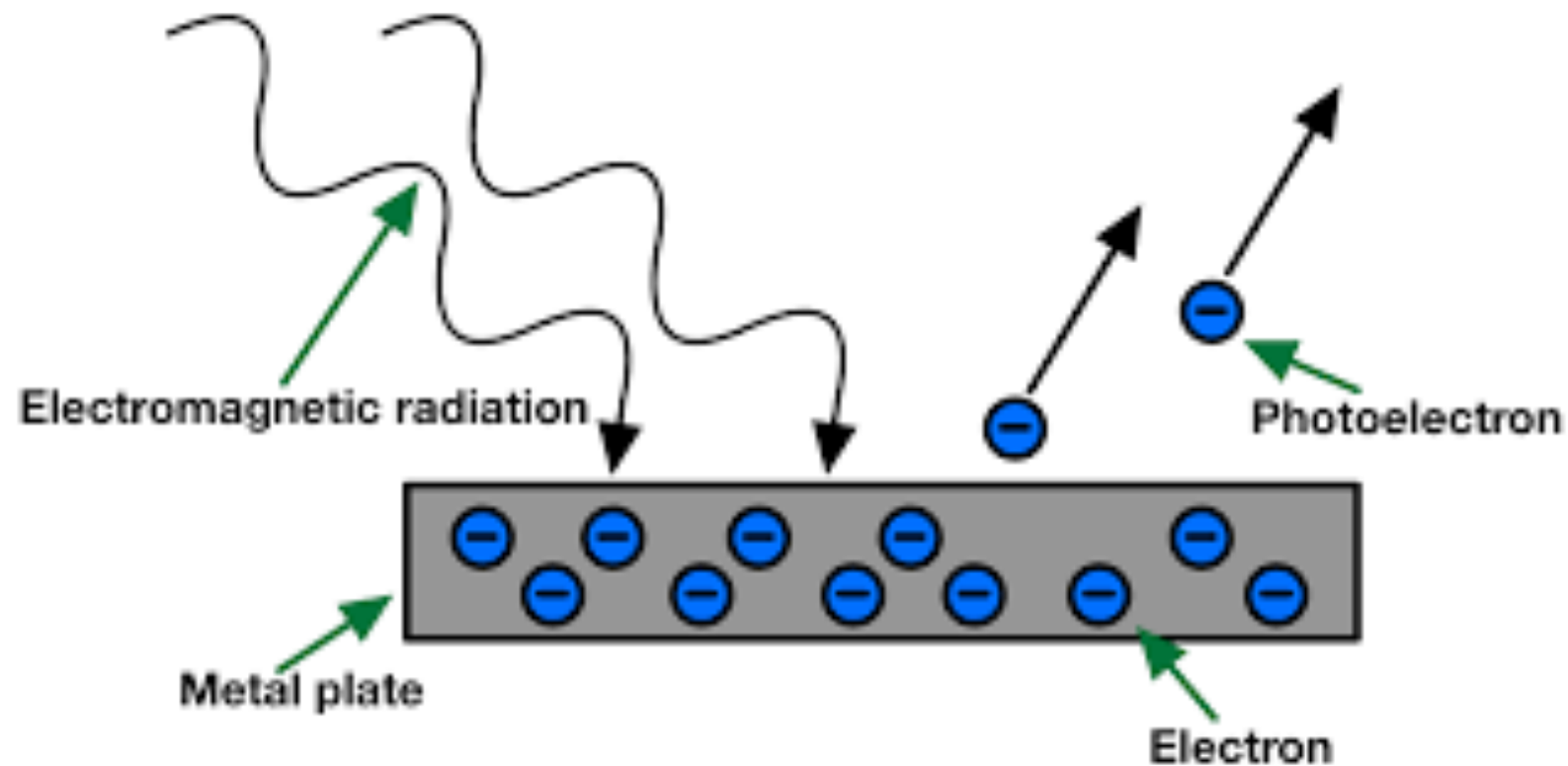

Image courtesy: pasco.com

Types of radiations by wavelength

Image courtesy: pasco.com

Quantum mechanics describes the interaction of light and matter

Photoelectric effect

Metals, like sodium, absorb light and emit electrons

Electromagnetic radiation

Photoelectron

Metal plate

Electron

Non-classical effects:

- Kinetic energy of electrons is independent of light intensity
- No of electrons $\propto$ light intensity but all e^- have same KE
- KE of photoelectron is zero until a threshold frequency ν_0
- As $\nu > \nu_0$, KE of photoelectron $\propto \nu$

# Einstein's explanation of the photoelectric effect

- Energy is absorbed only in discrete amounts of energy, $h\nu$ where h is the Planck constant

- A photon of energy $h\nu$ has the possibility of ejecting an electron, but a minimum energy is necessary called the work function ϕ characteristic of the metal.

- KE of photoelectron is then given by:

$$KE = h\nu - \phi$$
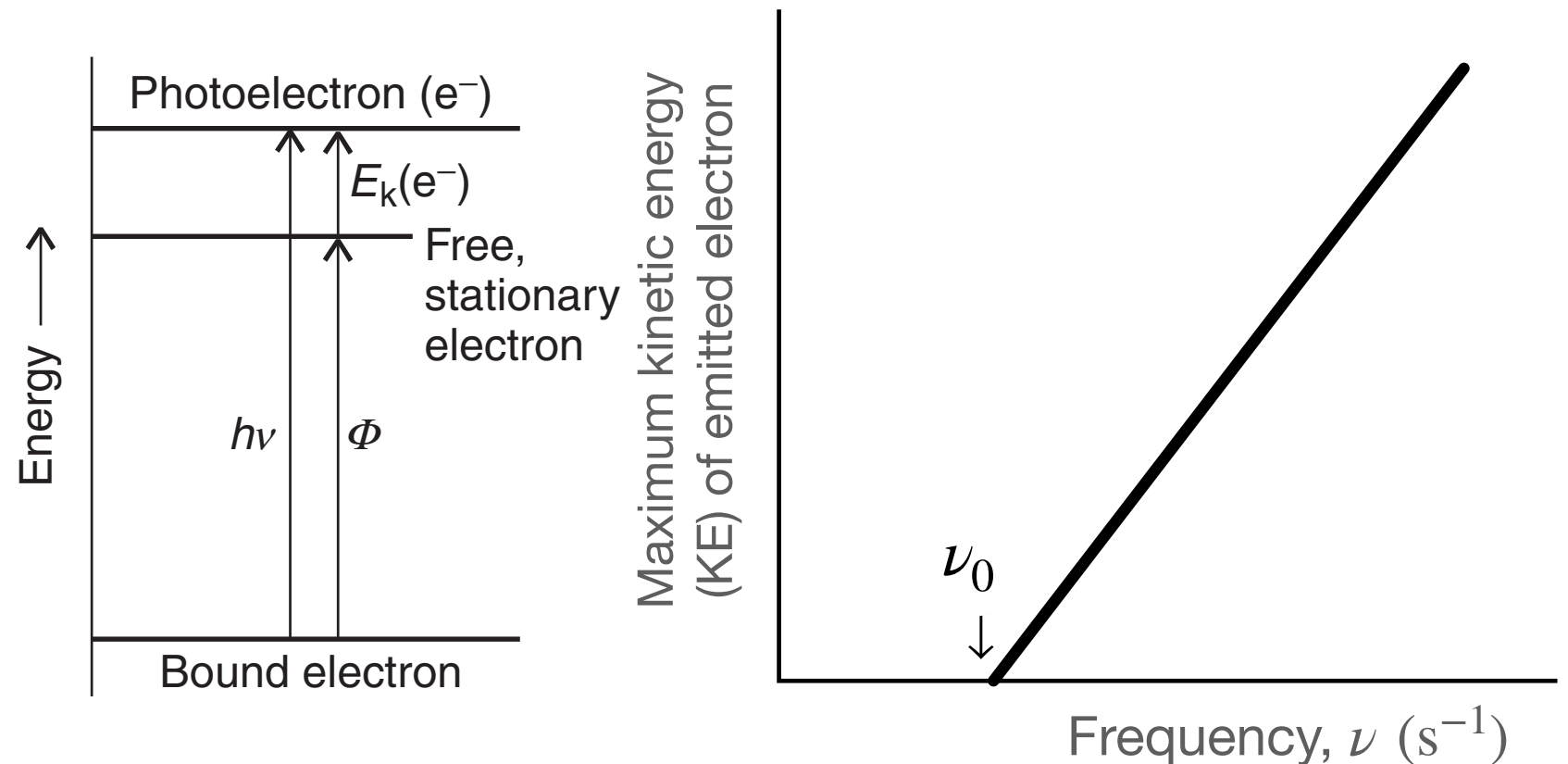
- Altering the light intensity would affect only the number of photoelectrons and not the kinetic energy.

- The slope of the experimental plot of KE vs frequency is h.

Light is quantized as photons *but* also a wave

Light photons

Electrons ejected from the surface

Sodium metal
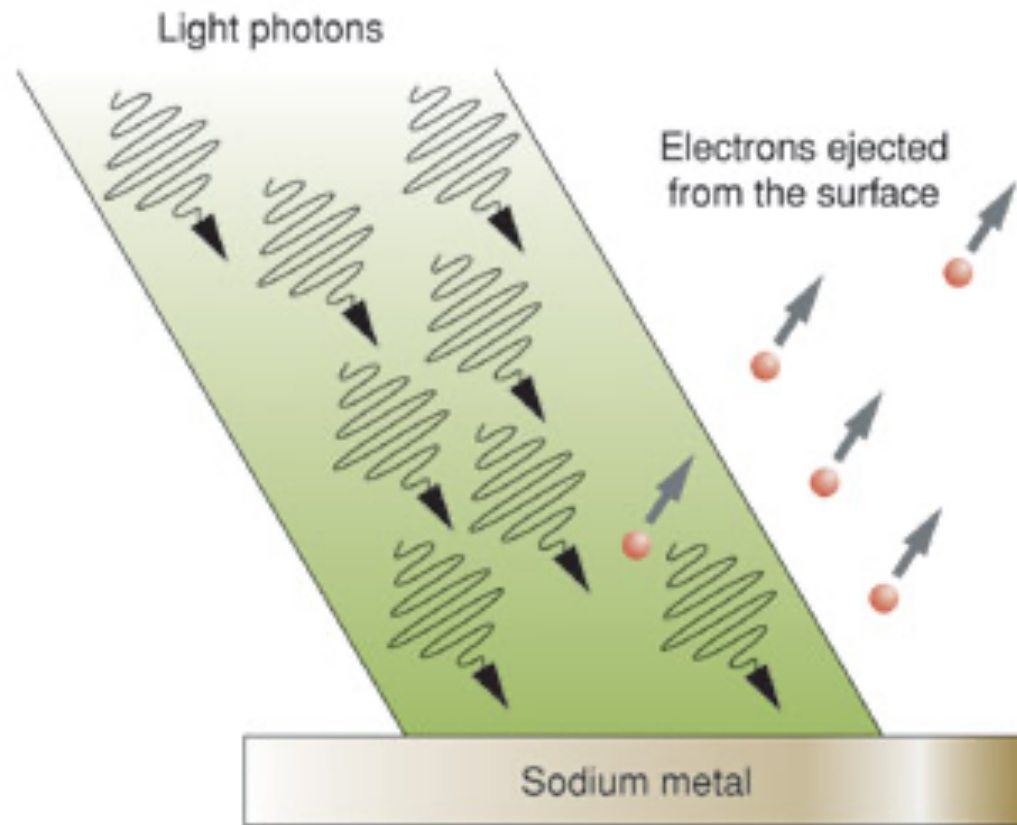
The photoelectric effect is strong evidence for the existence of photons and shows that light has certain properties of particles

Wave-particle duality of light

de Broglie hypothesis

All matter exhibits dual wave and particle character
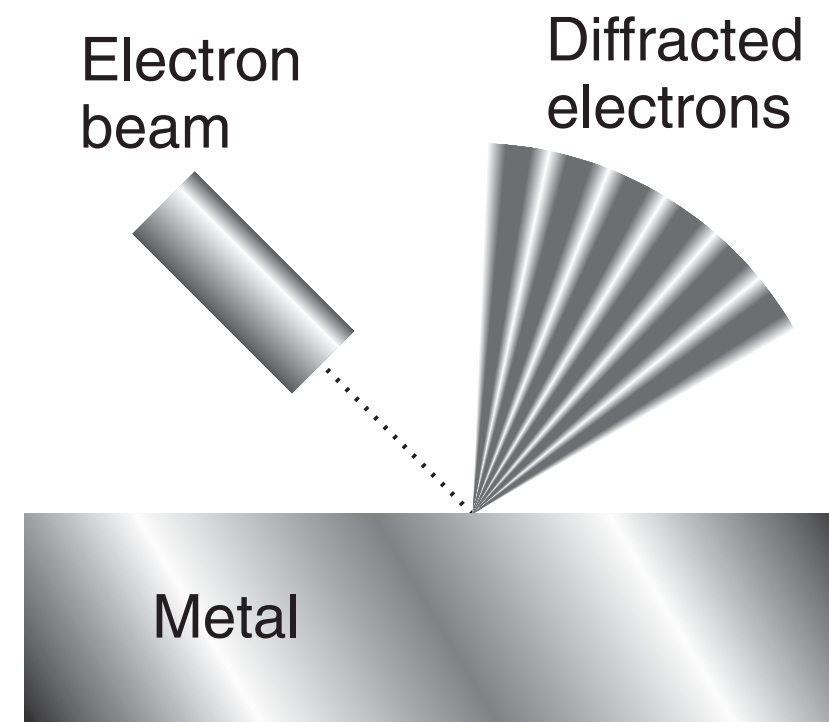
Louis de Broglie, 1924

de Broglie matter wave

de Broglie wavelength for any matter wave for a particle moving with linear momentum p is given by
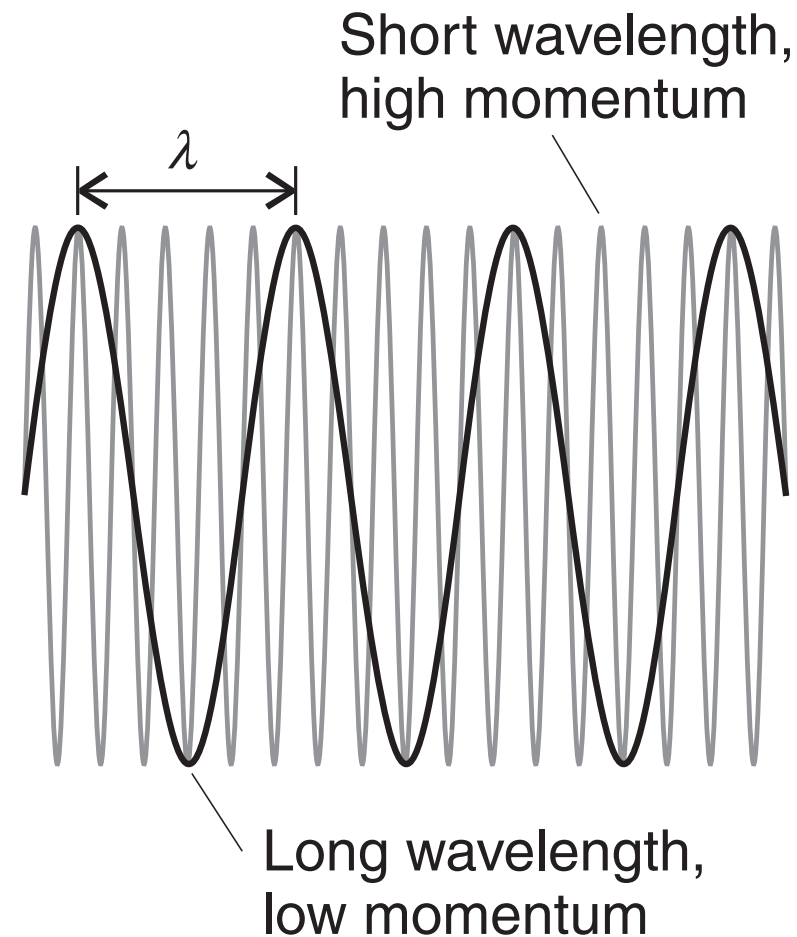
$$\lambda = \frac{h}{p}$$

h = Planck constant = 6.63×10^{-34} J . s

Wave character of electrons was proved by the famous Davisson-Germer experiment, 1927

Electron beam

Diffracted electrons

Metal

Matter wave is only significant for microscopic particles

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

Short wavelength,
high momentum

λ

Long wavelength,
low momentum

Comparison exercise

Compute de Broglie wavelength of
an E.coli cell with speed $10 \ \mu\text{m/s}$

$$\lambda \approx 6.63 \times 10^{-14} \text{ m}$$

Much smaller than the cell

Compute de Broglie wavelength of
electrons accelerated from rest
through a potential difference of 15 kV

$$\lambda \approx 10 \times 10^{-12} \text{ m}$$

Much bigger than a electron

The uncertainty principle

Heisenberg, 1927

Precise measurement of momentum and position
of a particle is limited by the following relation

$$\Delta p \Delta x \geq \frac{h}{2\pi}$$

This principle has no practical significance for macroscopic particles

Compute $\Delta x, \Delta p$ for

An E.coli cell with uncertainty in swimming speed $0.1\ \mu\text{m/s}$

an electron with uncertainty of speed $= 10^6\ \text{m/s}$

$\Delta x \approx 0.01\ \mathring{\text{A}}$

$\Delta x \approx 1\ \mathring{\text{A}}$

Much smaller than the size of the cell

Much bigger than a electron

Simplest quantum mechanical model of quantized energy levels

The particle in a box problem

U = ∞ | **U = 0** | U = ∞

0 | L

X $\longrightarrow$
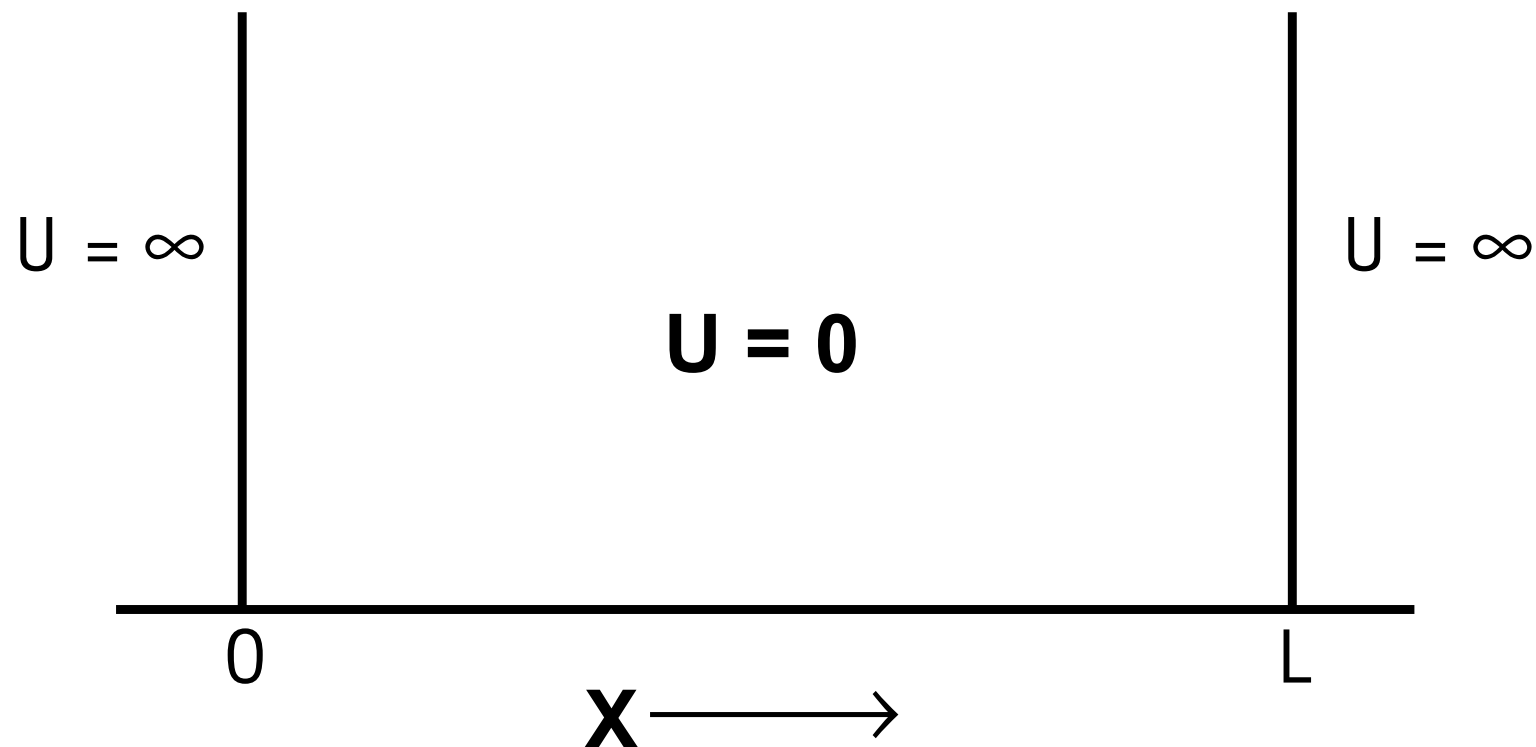
particle of mass *m* moving back and forth in a one-dimensional box of length *L*.

This is a useful model for delocalized elections on biomolecules with extended unsaturation
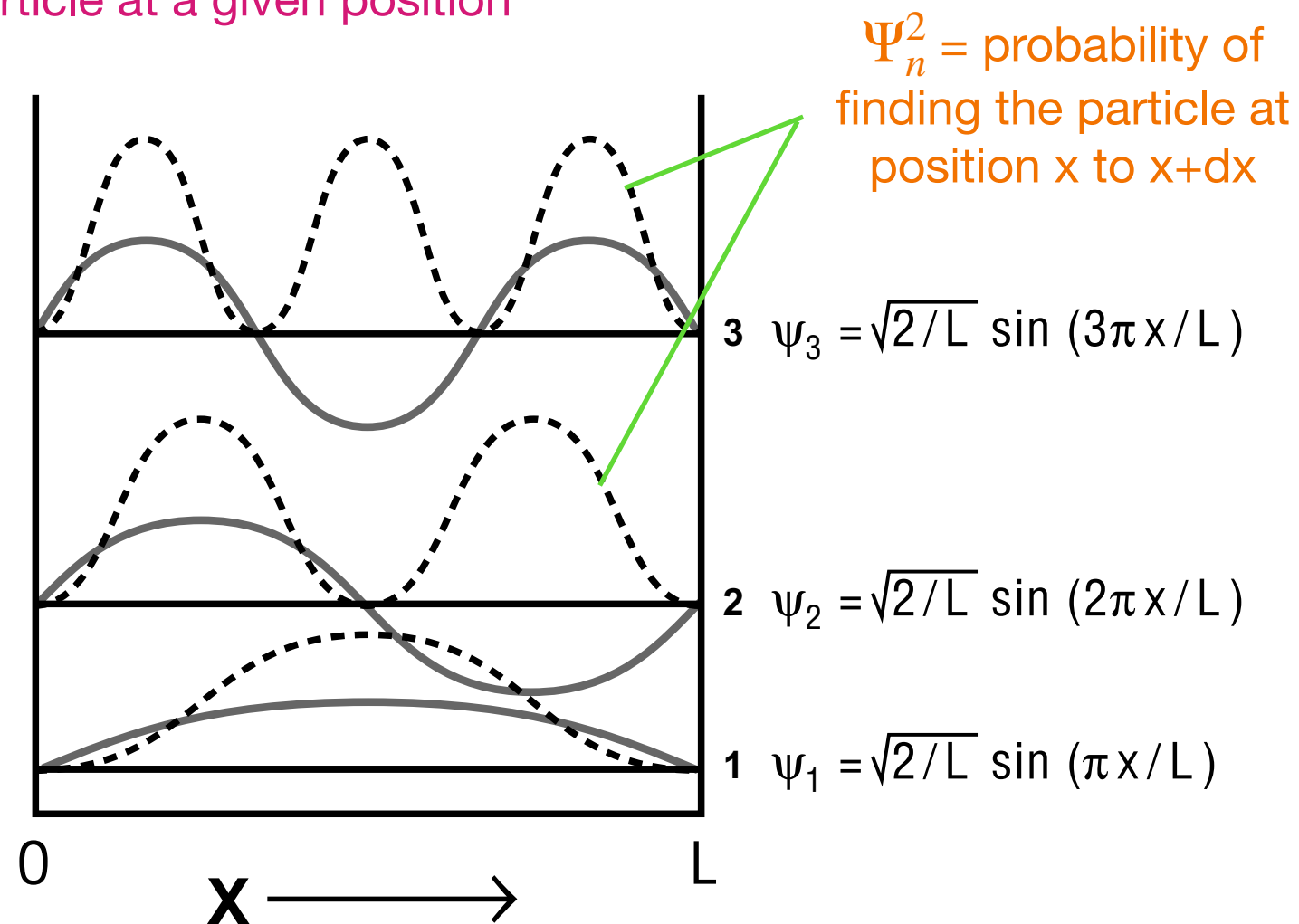
Schrödinger eq. In 1D: $H\Psi = E\Psi$ Hamiltonian: $H = -\dfrac{h^2}{8\pi^2 m}\dfrac{d^2}{dx^2} + U$

The particle in a box problem …*contd*

Solution to the 1D Schrödinger eq $$\Psi_n = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right) \qquad n = 1,2,3,...$$

From the wave function we can get the probability of finding the particle at a given position

Ψ_n^2 = probability of finding the particle at position x to x+dx

3   $\psi_3 = \sqrt{2/L} \ sin\ (3\pi x/L)$

2   $\psi_2 = \sqrt{2/L} \ sin\ (2\pi x/L)$

1   $\psi_1 = \sqrt{2/L} \ sin\ (\pi x/L)$

0   L

X $\longrightarrow$

The particle in a box problem …*contd*

The probability of finding the particle at any x between 0 and L for a given energy level

$$P(x) = \int_0^L \Psi_n^2 \, dx$$

Compute the probability of finding the particle between L/4 and 3L/4 at the lowest energy level

$$P_1 = \int_{L/4}^{3L/4} \Psi_1^2 \, dx = \frac{2}{L} \int_{L/4}^{3L/4} sin^2 \left(\frac{\pi x}{L} \right) dx$$

$$= \frac{2}{L} \left[\frac{\alpha x - sin\alpha x \; cos\alpha x}{2\alpha} \right]_{L/4}^{3L/4} \qquad \text{Where } \alpha = \frac{\pi}{L}$$

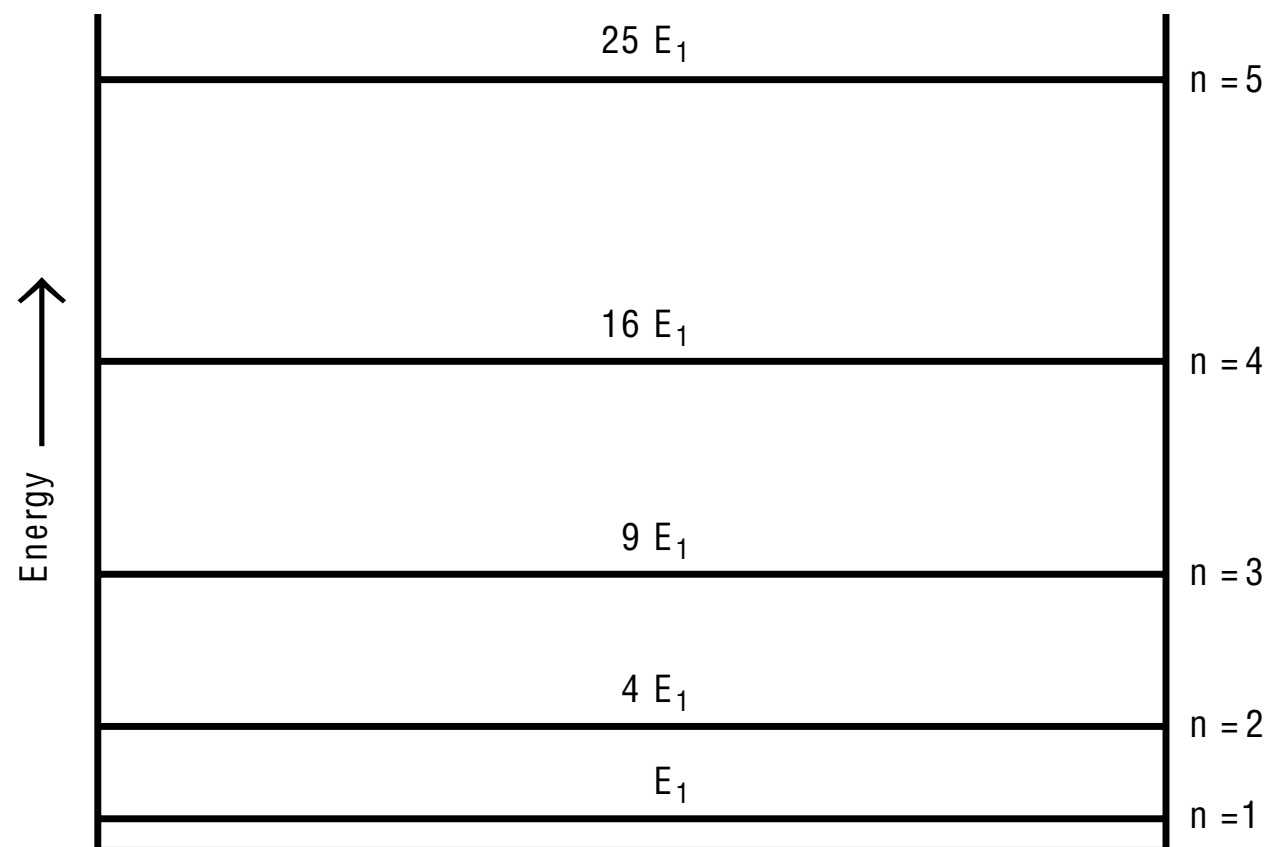This probability is independent of box size L but depends on the energy level

$$\approx 0.82$$

This probability for $n = 2$ becomes, $P_2 \approx 0.5$

The particle in a box problem ...*contd*

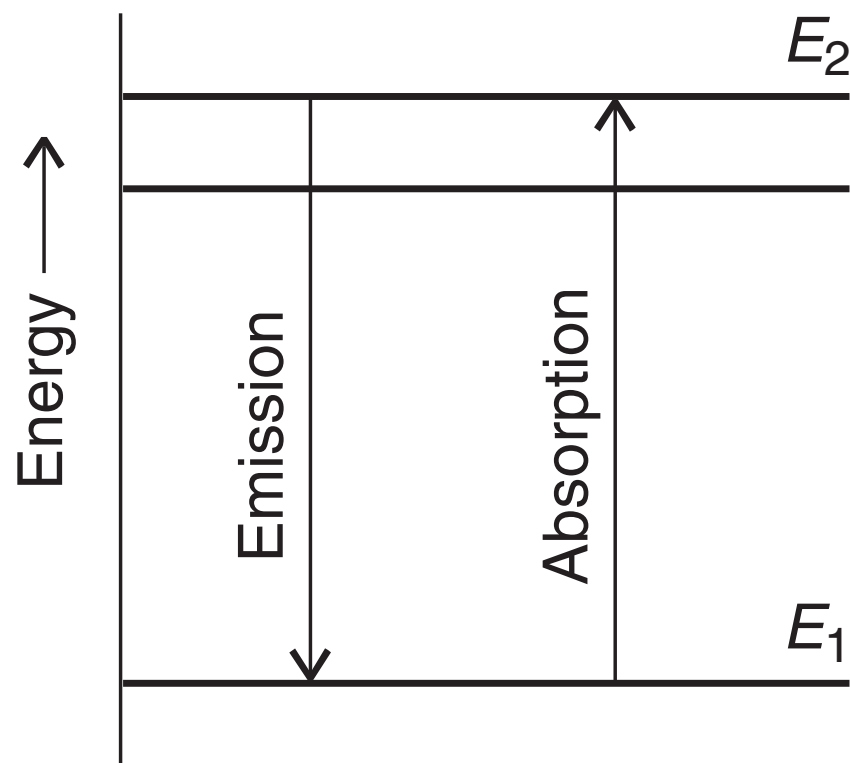Quantized energy levels for the particle

$$E_n = \frac{n^2 h^2}{8mL^2}$$

The spacing between the energy levels become negligibly small for macroscopic particles and quantum effects do not matter

This description can be used to calculate the energy of light absorption or emission for a particle jumping between energy levels

Transitions between energy levels

Energy ⟶

Emission

Absorption

E_2

E_1

Transitions happen only via absorption of emission of quantized packets of energy or photons

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\Delta E = E_2 - E_1$$

$$\lambda = \frac{hc}{E_2 - E_1}$$

For the particle in a box dropping from *n+1* to *n*

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2}$$

$$= \frac{h^2}{8mL^2}\left[(n+1)^2 - n^2\right]$$

$$= \frac{h^2}{8mL^2}(2n+1)$$

If the particle is a delocalized e^- moving on a molecule of length $L = 20$ Å and dropping from $n = 11$ to $n = 10$

$$\lambda = \frac{hc}{\Delta E} \approx 620 \text{ nm}$$

Visible light range!

Selection rules for transition between energy levels

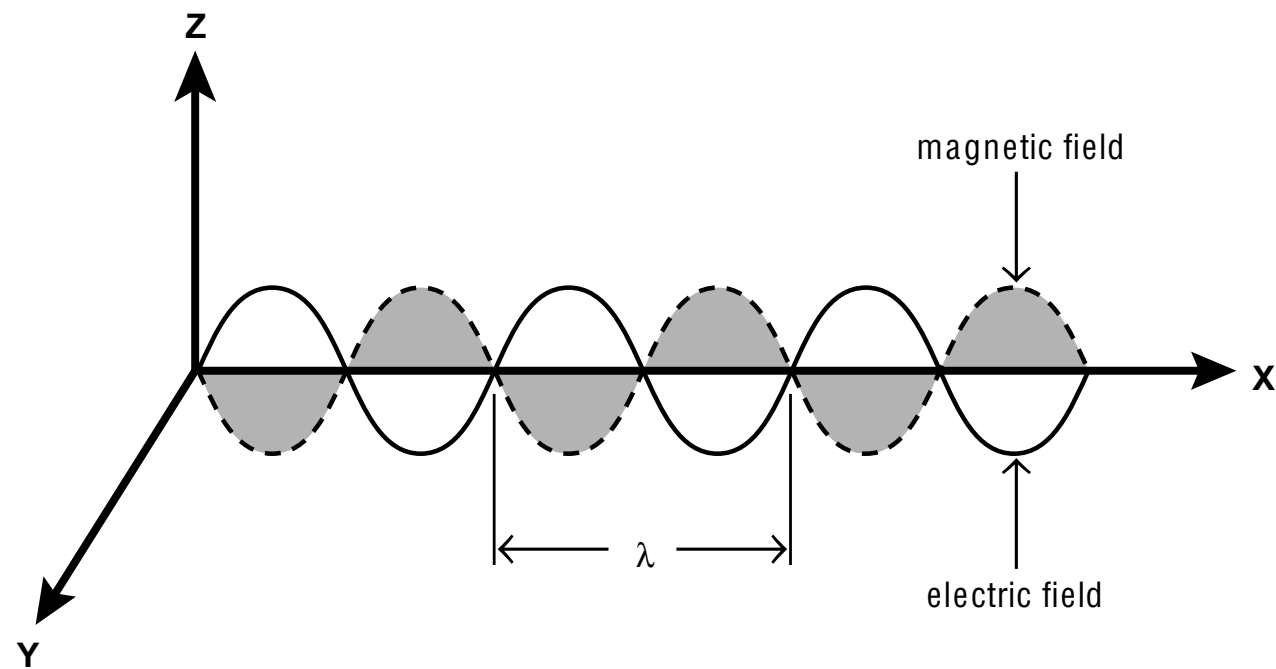Transition moment integral for particle in a box in 1D for transition between n=1 and n=2

$$\langle \mu \rangle = e \, \frac{2}{L} \int_0^L \sin \frac{2\pi x}{L} x \, \sin \frac{\pi x}{L} dx$$

This integral is zero for any even values of Δn

So the selection rule for this system is

$$\Delta n = \pm 1, \pm 3, \pm 5....$$

Wave properties of light

Light is an electromagnetic wave but also shows usual features of a periodic wave form

The electric field or the magnetic field can be described by a sine function in space
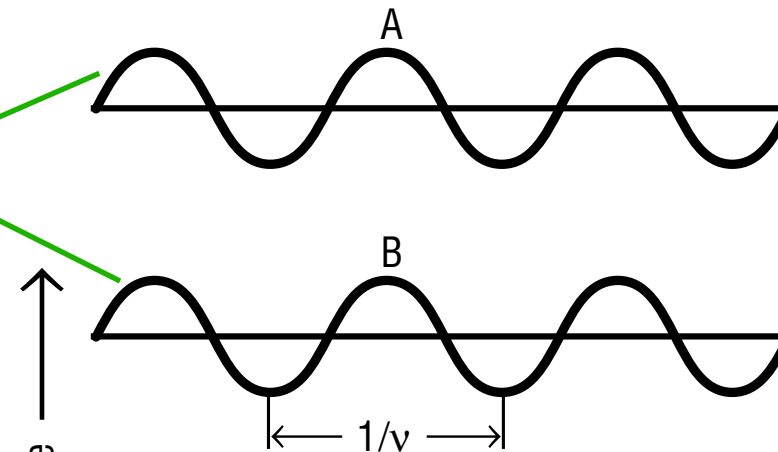
$$I = I_0 \, \sin\left(\frac{2\pi x}{\lambda}\right)$$

The light wave can be periodic in time also: $I = I_0 \, \sin(2\pi\nu t) = I_0 \, \sin(\omega t)$

For such a wave following properties are defined by this eq.

Amplitude = I, max. value = I_0

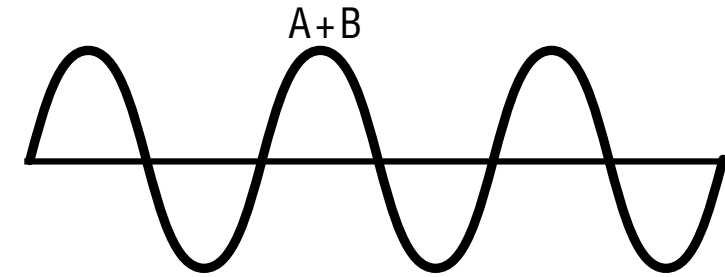Speed = $\lambda\nu = c$, angular freq = $\omega = 2\pi\nu$

Interference of waves

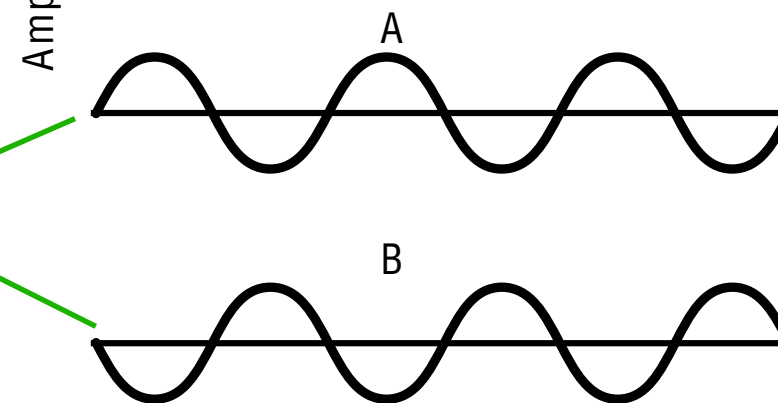light from two sources with same ν and I_0 starting with $I = 0$ at $t = 0$

A

B

← 1/ν →

Amplitude

Constructive interference

Phase angle $\delta = 0°$ or $2n\pi$

A+B

light from two sources with same ν and I_0, starting with $I = 0$ at $t = 0$ but opposing phase

A

B

Time
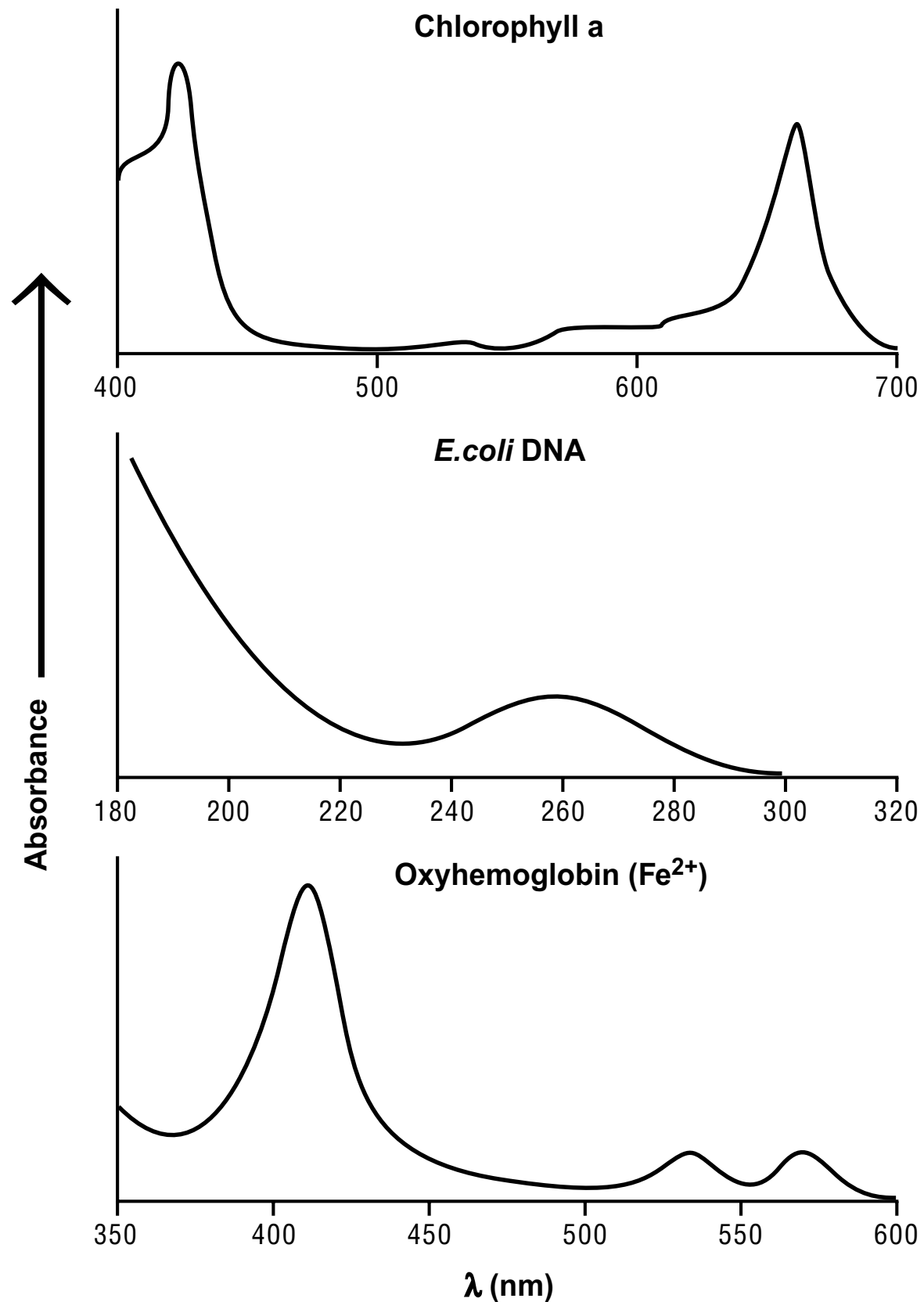
Destructive interference

Phase angle $\delta = (2n + 1)\pi/2$

A+B

General form of wave

$$I = I_0 \sin(\omega t + \delta)$$

Absorption spectrum of different biomolecules
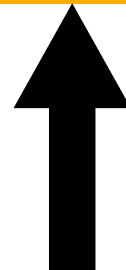
From frequency to the time domain

Frequency domain experiments can be time consuming and expensive

Frequency domain spectrum $I(\nu)$ can be transformed into a time-domain function $F(t)$ keeping all information intact and vice versa
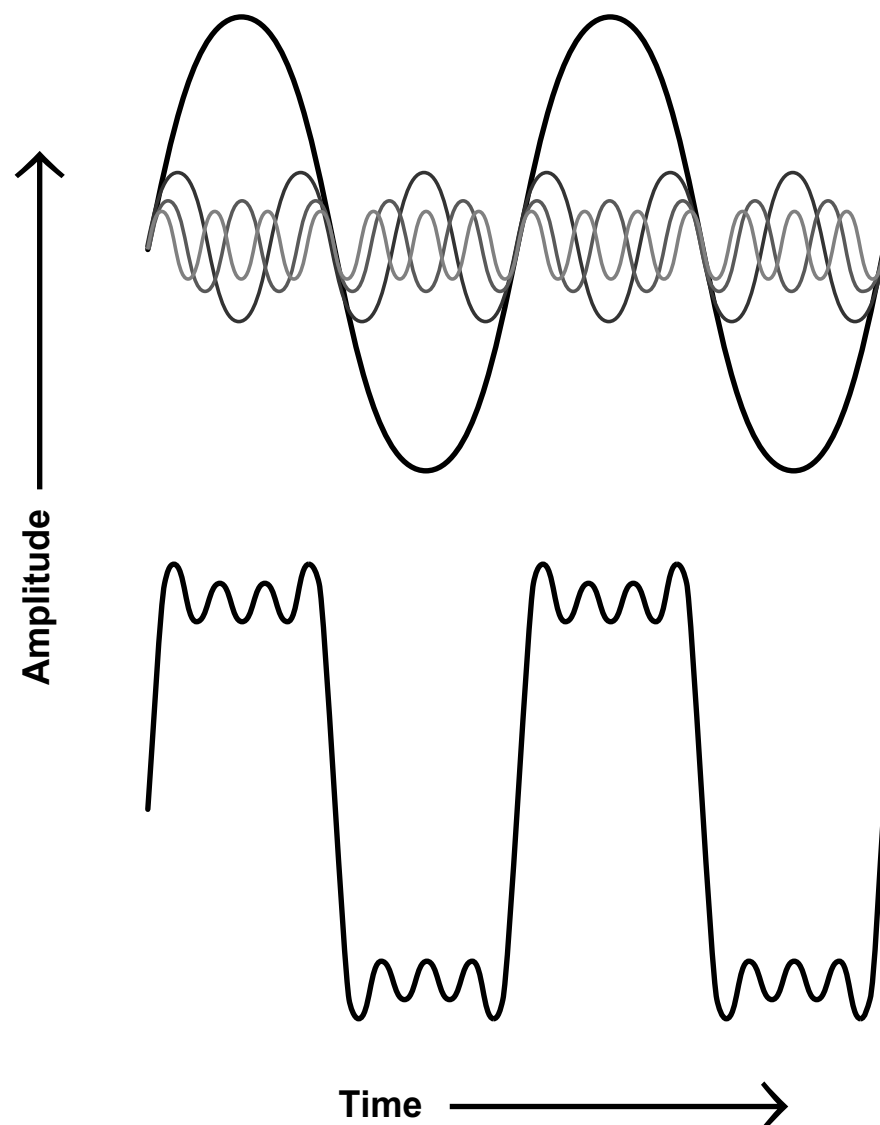
Fourier transform

Almost any generic wave form can be expressed as a sum of sines and cosines

Fourier series

Sum of many sine waves ≈ a square shaped 'pulse' wave

This transformation allows quick experiments based on short-time pulses and Fourier transform the response into the frequency spectrum

Time-saving and also allows many repeats to improved the quality of frequency spectrum by averaging

Power spectrum analysis

Frequency analysis of any generic time dependent signal

Amplitude

Time