CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture-02, 10-01-2018

Planck Formula (1900)

$\rho(\lambda)d\lambda = (hc/\lambda)(e^{hc/\lambda kT} - 1)^{-1}(8\pi/\lambda^4)d\lambda$

Density of oscillators as before, but with $\nu = c/\lambda$, average energy is $h\nu/(e^{h\nu/kT} - 1)$.

Crucial assumption that Planck had to make was that an oscillator of frequency ν cannot be excited to any arbitrary energy, but only to integral multiples of a fundamental unit or quantum of energy $h\nu$, with $h = 6.626 \times 10^{-34}$ J s, the Planck constant, i.e., $E = nh\nu$, $n = 0,1,2,\ldots$.

Work out :

(i) Express Plank's distribution law in frequency domain.

(ii) Derive Stefan-Boltzman law from Plank's distribution law. Derive an expression for the Stefan-Boltzman constant.

(iii) Derive Wien's law from Plank's distribution law.

Success of Planck’s formula

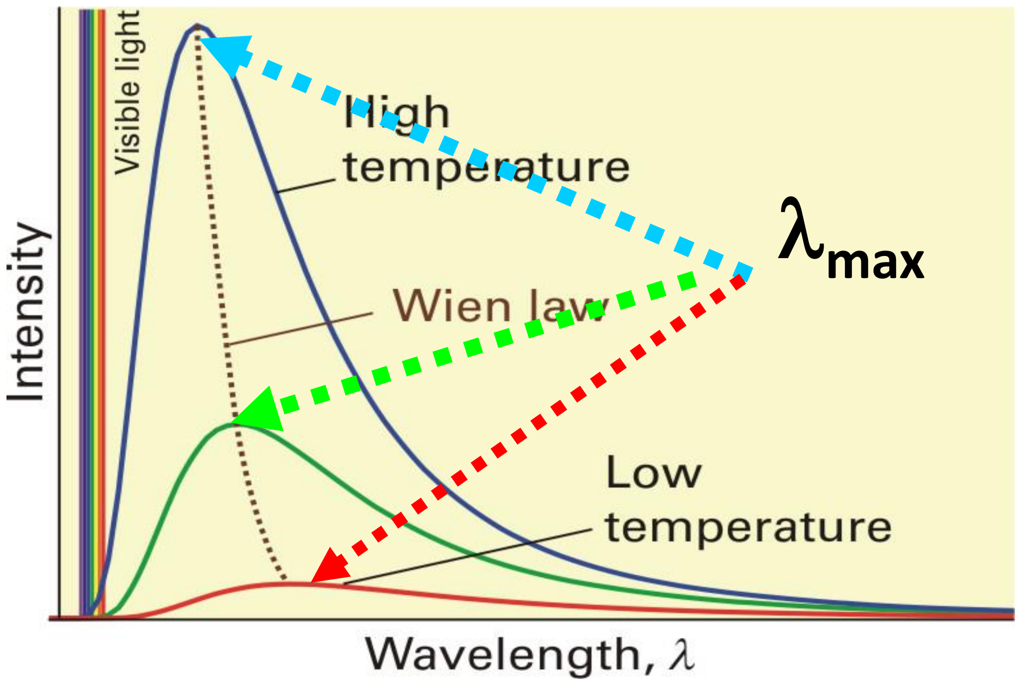
$$\rho(\lambda) = 8\pi\, hc / \{\lambda^5(e^{hc/\lambda kT} - 1)\}$$

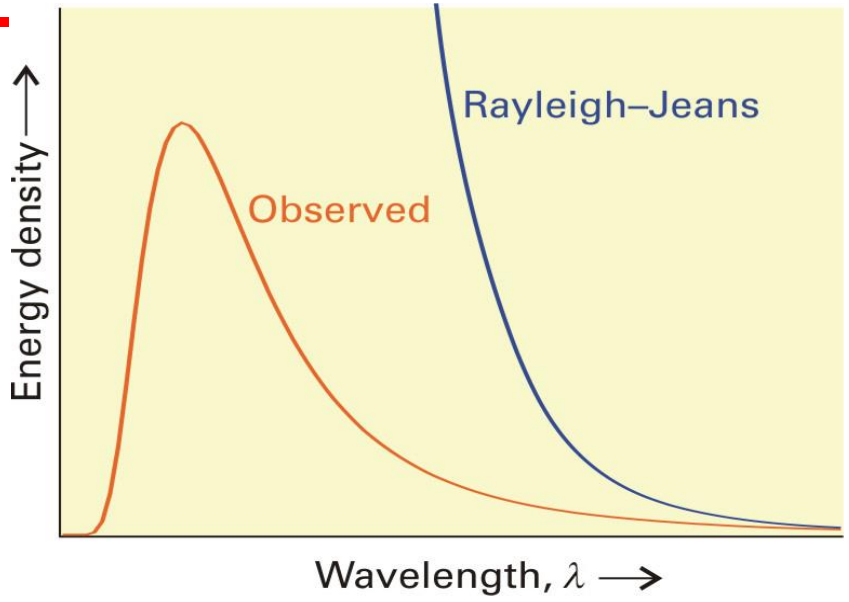
- Planck's hypothesis: An oscillator cannot be excited unless it receives an energy of at least hν (as this is the minimum amount of energy an oscillator of frequency *ν* may possess above zero.
- For high frequency oscillators (large ν), the amount of energy hν is <u>too large to be supplied by the thermal motion of the atoms</u> in the walls, and so they are not excited.
- Catastrophe avoided

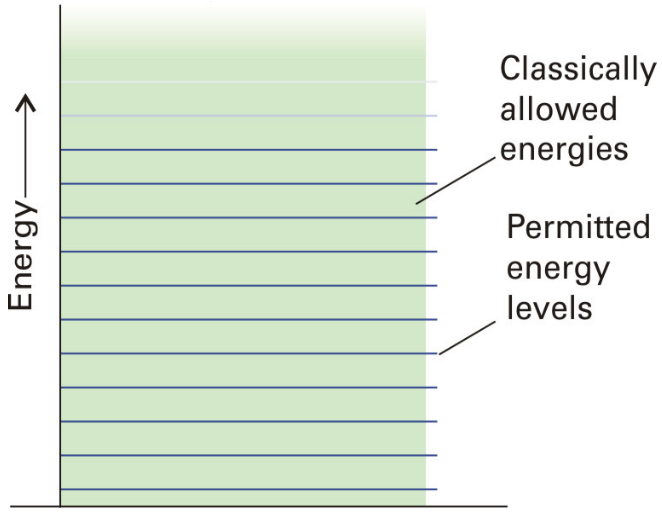
Simple application of the concept of black body

- Part of the sun that we can see is called the Photosphere and has a surface temperature of 5780 K. We can determine solar flux form every sq. m. of the surface.
- We can determine the Luminosity of a star (L)
- We may determine the maximum wavelength of Solar radiation, if we do consider that surface temperature of the Sun to be 5780 K

Summary: Lecture - 01



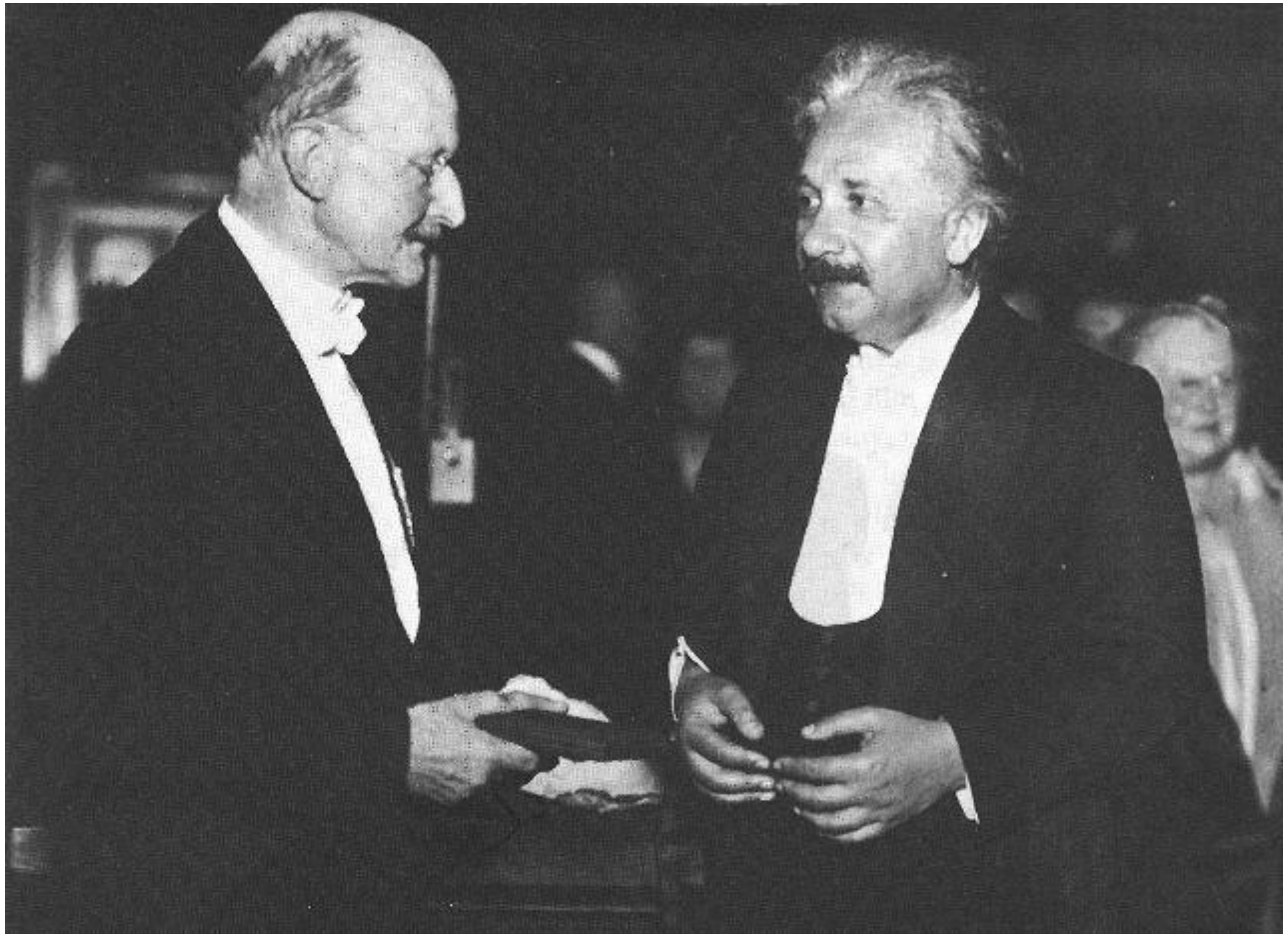




- Wien's Law: λ_{max}**T = 2.99 mm K (Constant)**
- Stefan-Boltzman Law: **M = aT^4**
- Rayleigh-Jeans: $\rho(\lambda)d\lambda = (8\pi kT/\lambda^4)d\lambda$
- Planck's Formula:

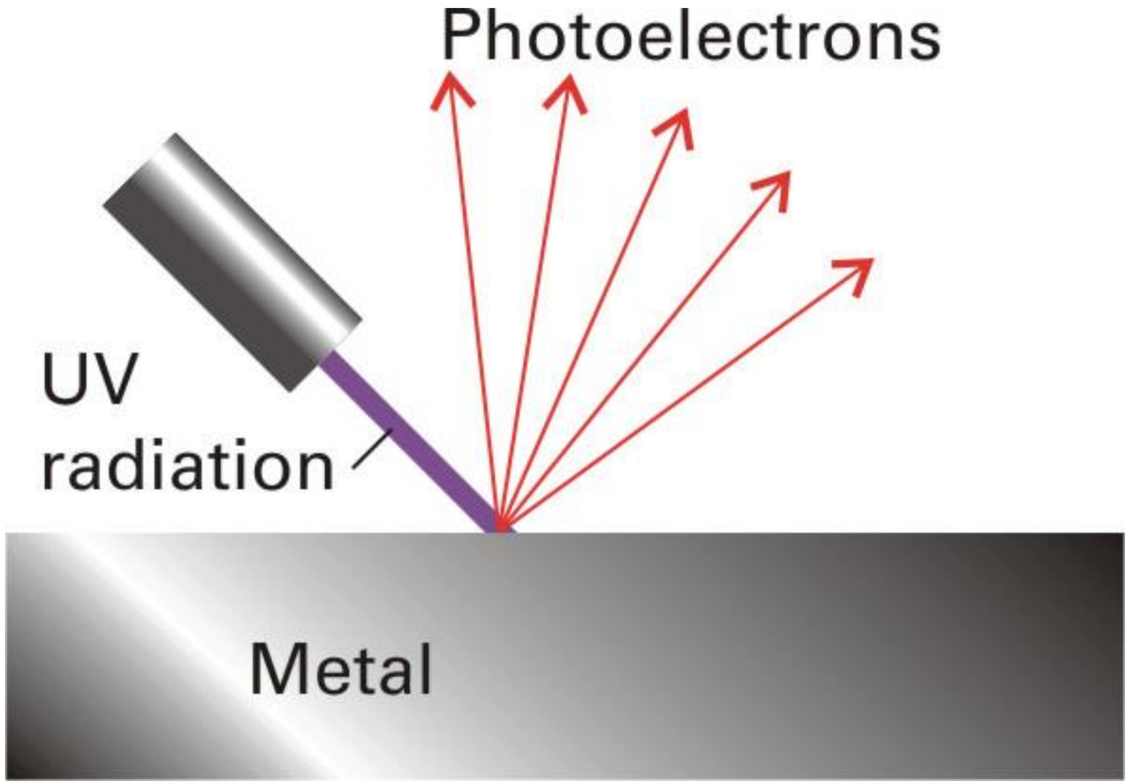
$$\rho(\lambda)d\lambda = (hc/\lambda)(e^{hc/\lambda kT} - 1)^{-1}(8\pi/\lambda^4)d\lambda$$

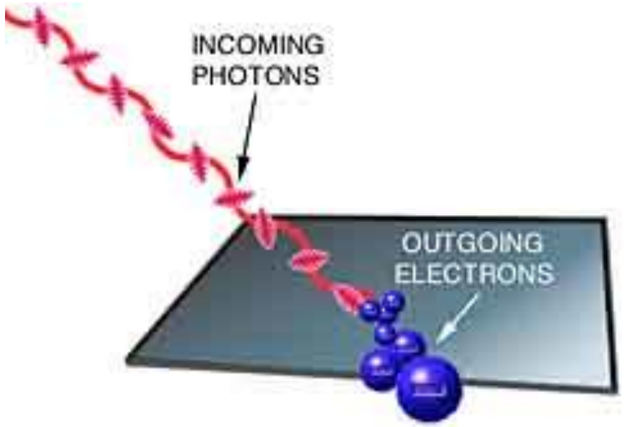
Extension of Planck's formula



Planck **Einstein**

Photoelectric effect (1886-1887)





Emission of electrons from metals when exposed to (ultraviolet) radiation.

Photoelectric effect-Observations

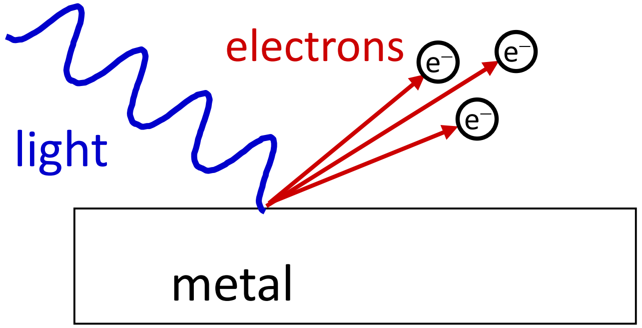
1. No emission of electrons if the frequency of radiation is below a threshold value characteristic of the metal, however high the intensity of the light.

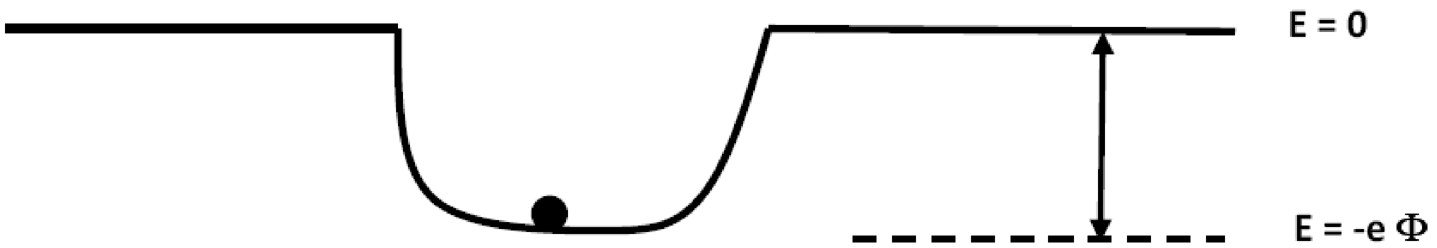
2. Kinetic energy of emitted electrons varies linearly with the frequency, and is independent of light intensity.

3. For frequencies above the threshold value, emission of electrons is instantaneous, no matter how low the intensity of the light.

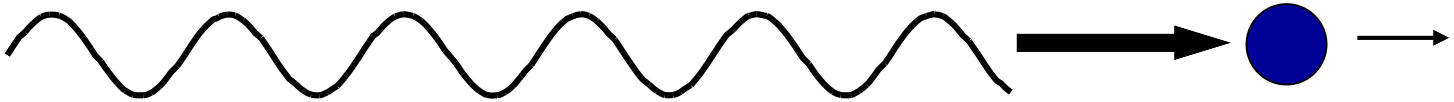
As the intensity increases, so does the amplitude of the oscillating electric field

Photoelectric effect - Classical Theory



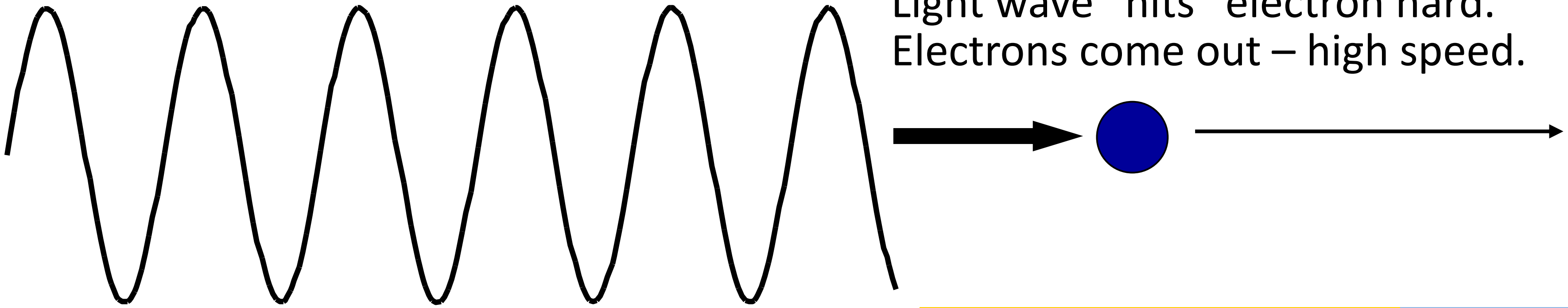


Low Intensity



Light wave “hits” electron gently.
Electrons come out – low speed.

High Intensity



Light wave “hits” electron hard.
Electrons come out – high speed.

Non-classical Explanation, 1905

1. **Light of frequency ν may be considered as a collection of particles, called photons, each of energy $h\nu$.**

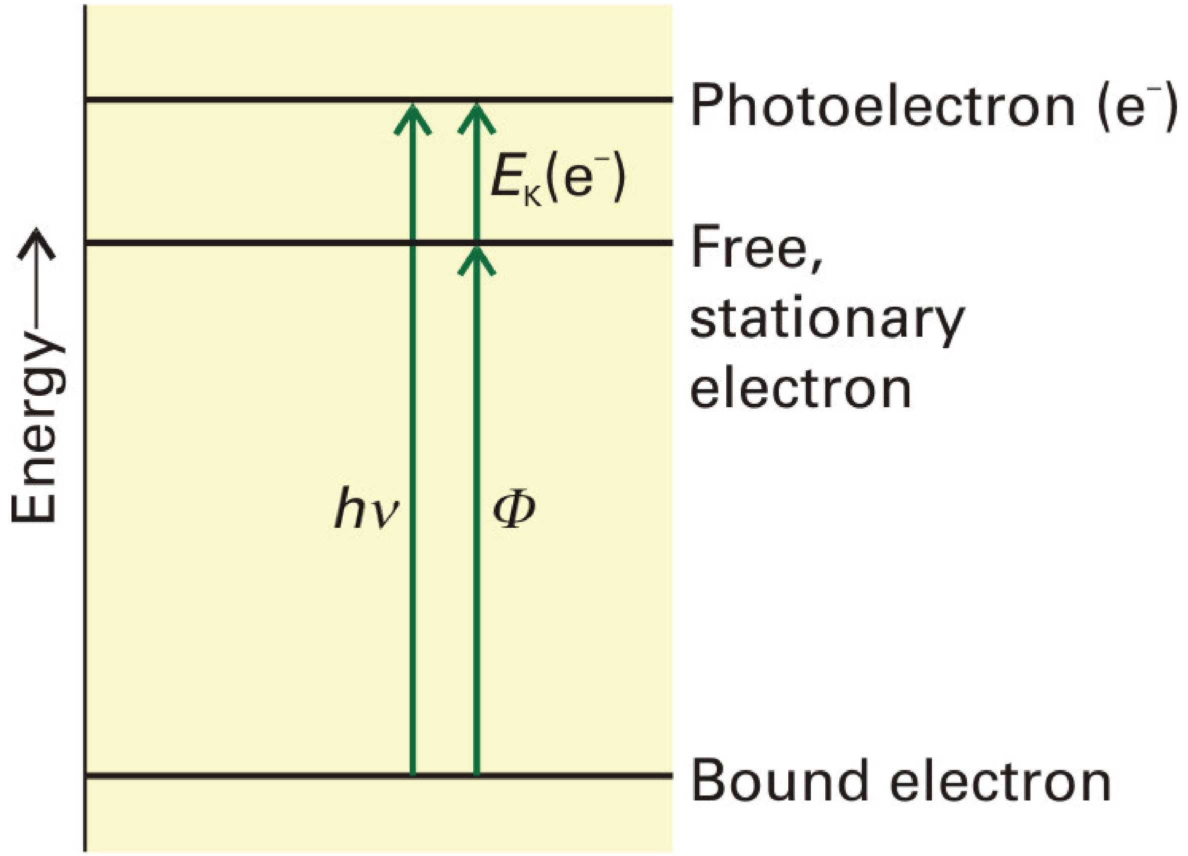
2. **If the minimum energy required to remove an electron from the metal surface is Φ (work function), then if $h\nu < \Phi$, no emission of electrons occurs.**

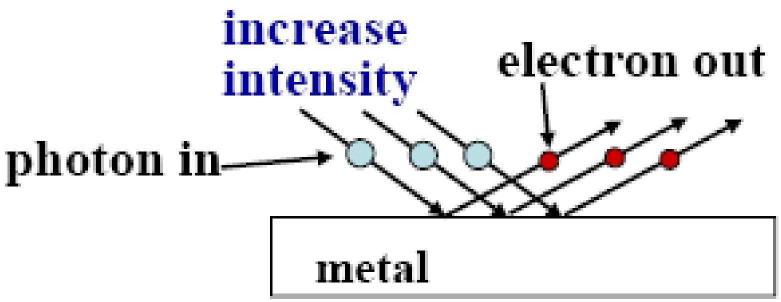
3. **Threshold frequency ν_0 given by $\Phi = h\nu_0$**

4. **For $\nu > \nu_0$, the kinetic energy of the emitted electron:**

$$E_k = h\nu - \Phi = h(\nu - \nu_0)$$

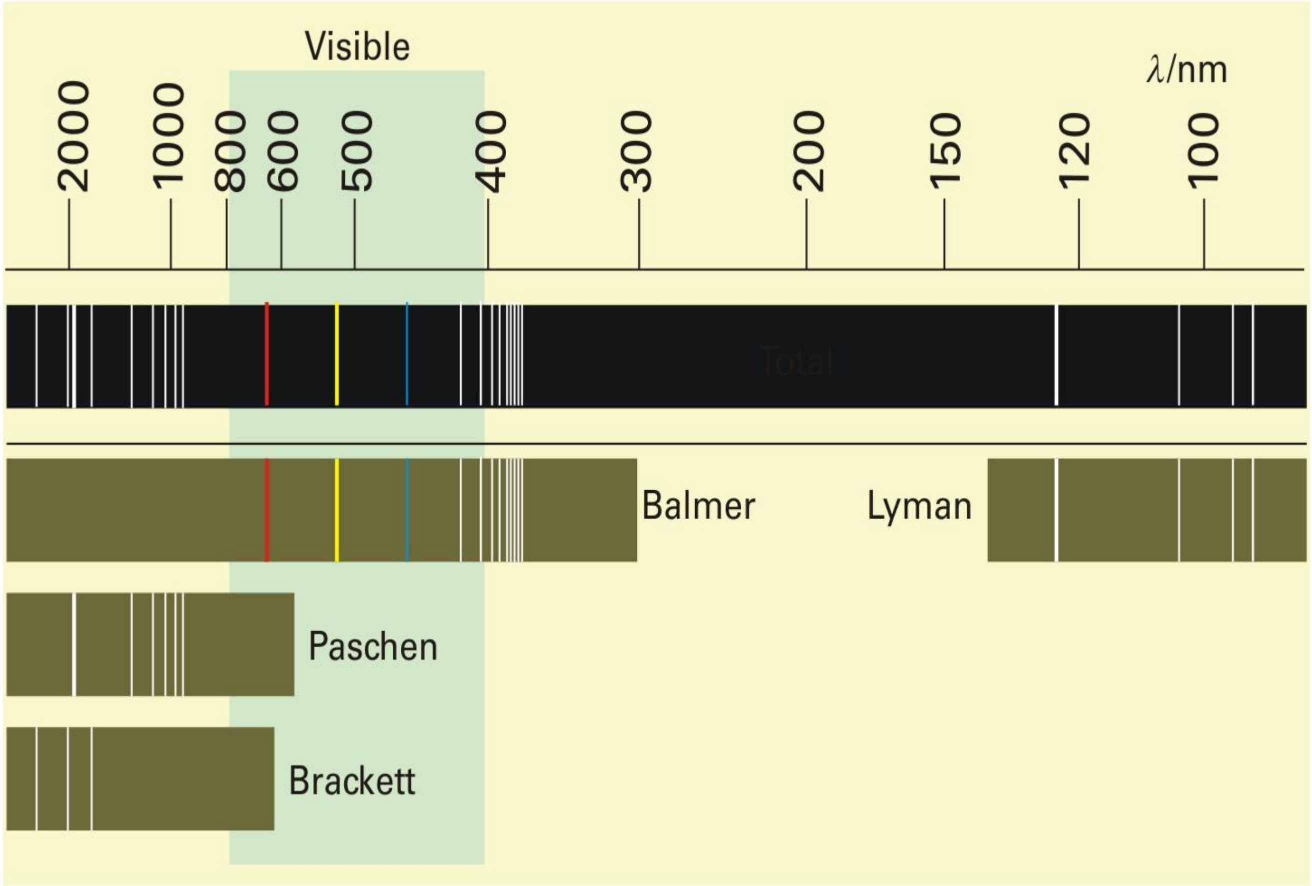
Explanation: Einstein, 1905

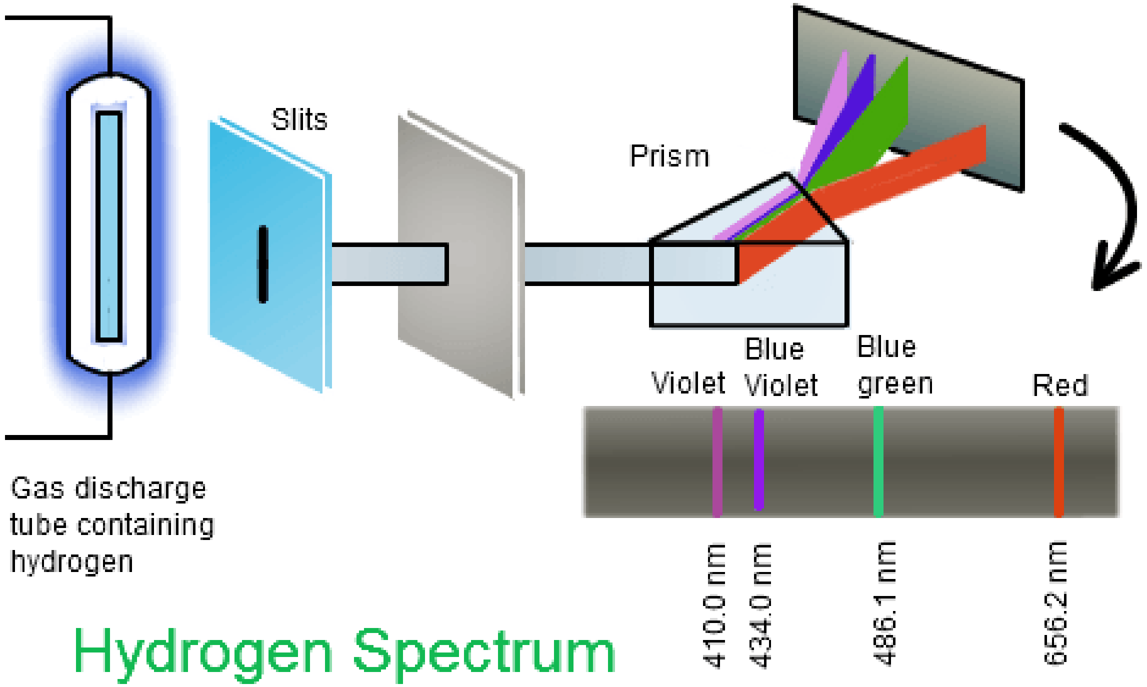




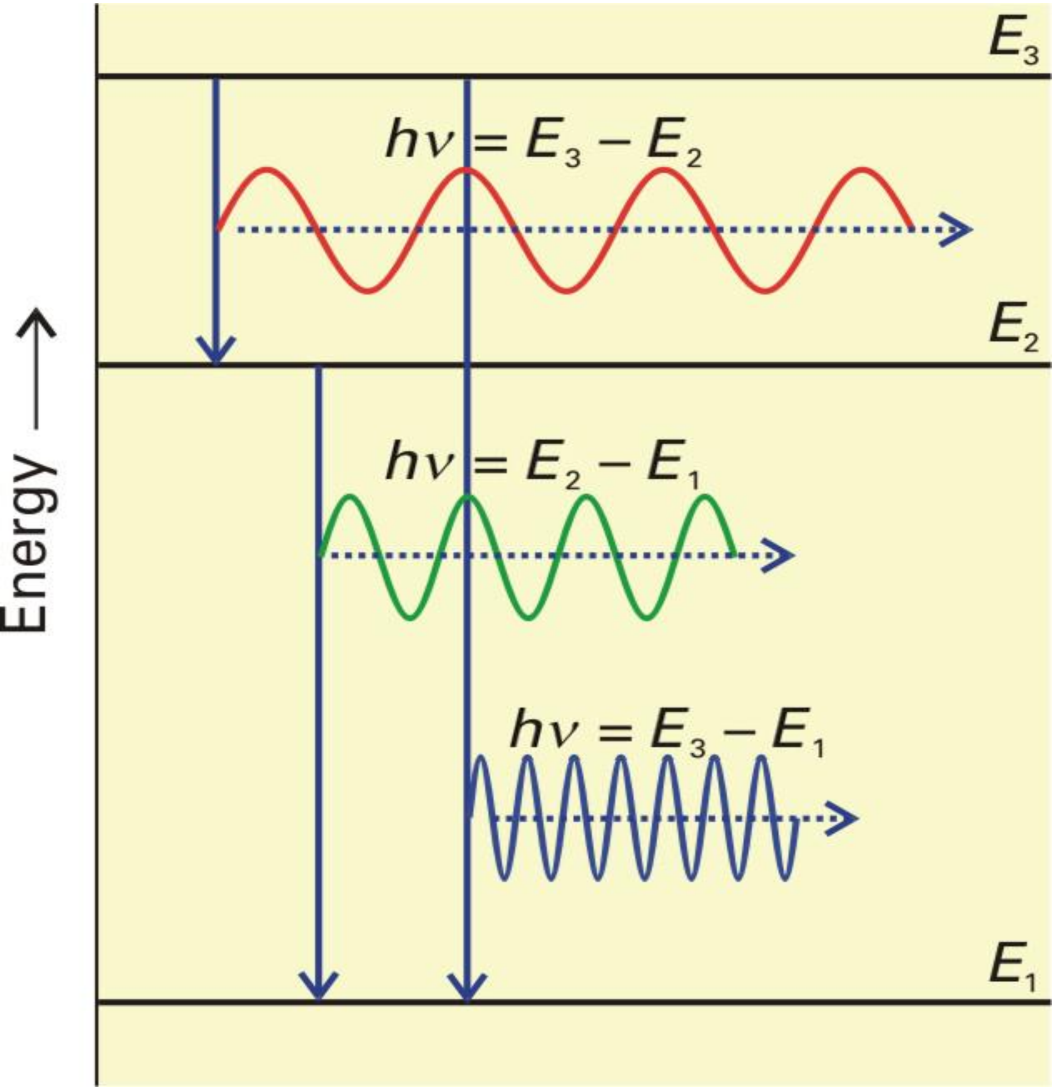
Work out: When Li is irradiated with light, one finds a stopping potential of 1.83 V for λ=3000 Å and 0.80 V for λ=4000 Å. Calculate (a) Planck's constant, (b) the threshold frequency, and (c) the work function of Li.

Line Spectrum of Hydrogen atom





Line Spectrum of Hydrogen atom



Transitions between quantized energy levels of atom or molecule, with absorption or emission of photon accounts for line spectra.

Line Spectrum of Hydrogen atom

The frequencies (in wave numbers) at which the lines occur in the spectrum of hydrogen are given by the formula

$$= 1/\lambda = R_H(1/n_1^2 - 1/n_2^2)$$

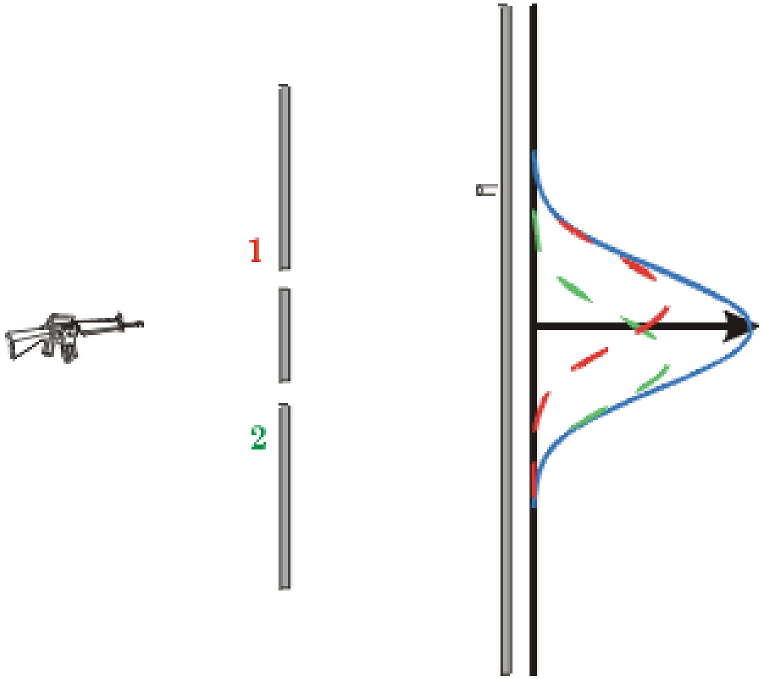
where R_H = 109677 cm^{-1} is the Rydberg constant, n_1 and $n_2 > n_1$ are positive integers, the various series corresponding to Lyman (n_1 = 1), Balmer (n_1 = 2), Paschen (n_1 = 3), Brackett (n_1 = 4), Pfund (n_1 = 5).

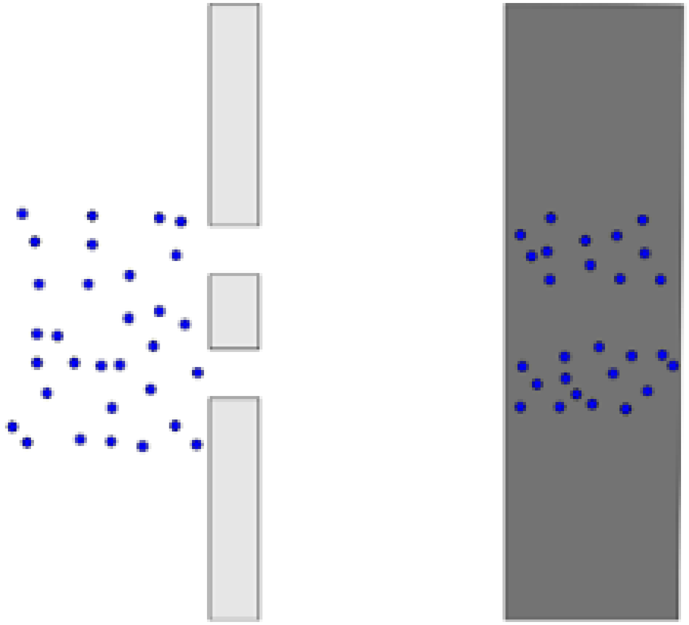
Bohr model of hydrogen like atom: Bohr proposed stable orbits for the electron, given by the quantization for angular momentum

$$\underline{mvr = nh/2\pi = n\hbar,\ n = 1,2,3,....}$$

Electron mass should be replaced by reduced mass in the Bohr theory

Two slit experiments



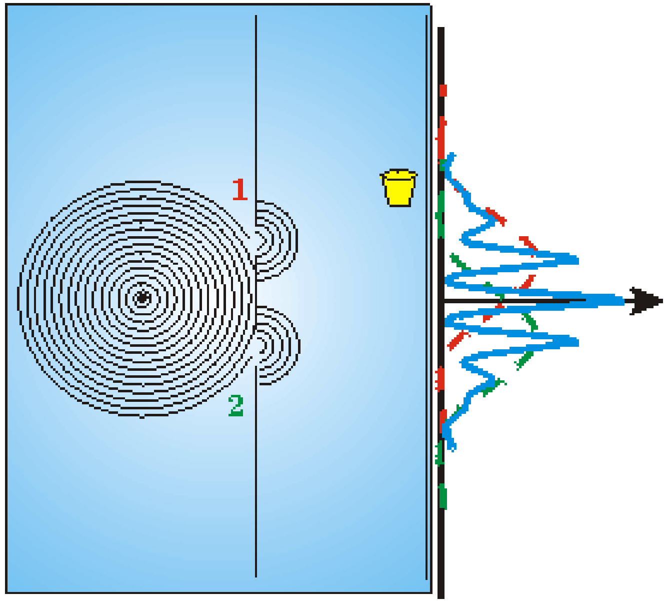


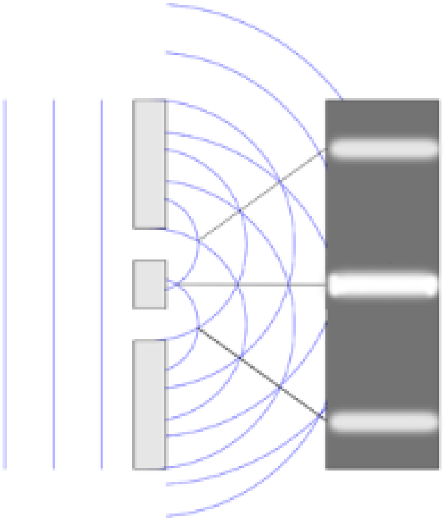
Experiment with Bullets/balls:

Arrive in identical discrete lumps – particles

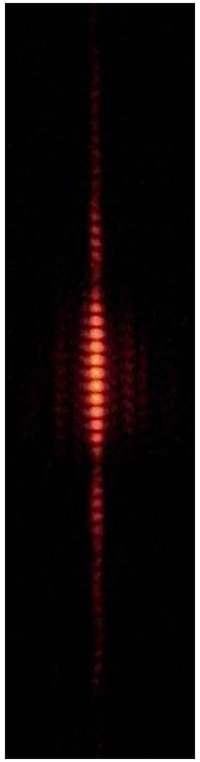
Distribution with both slits open is the sum of that with slit 1 alone open and that with slit 2 alone open – No interference.

Two slit experiments





Experiment with light of single wavelength

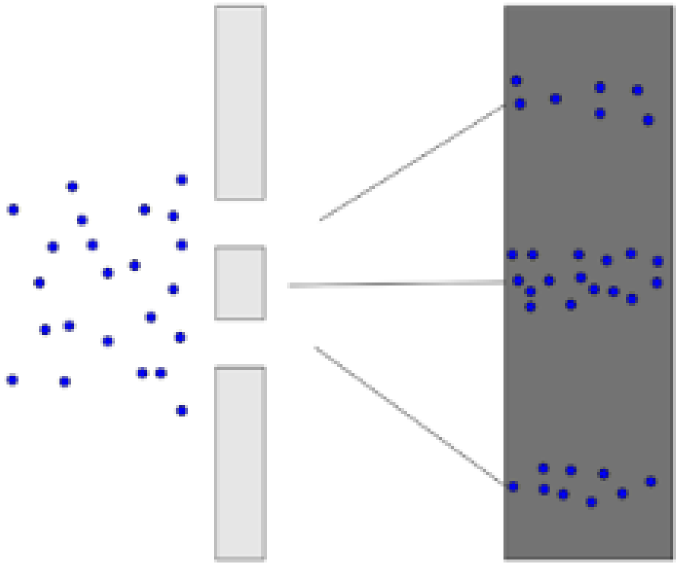


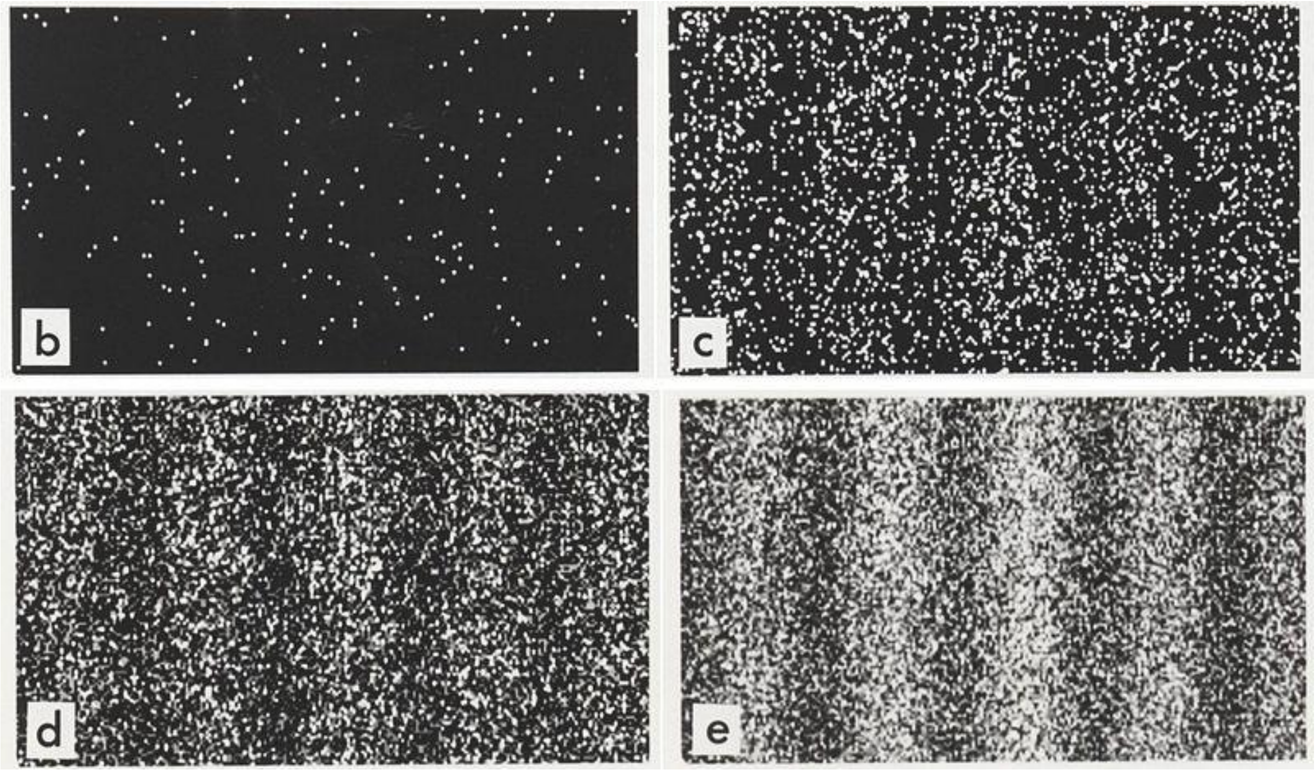
Experiment with water waves/light:

Intensity can be varied by changing amplitude of source – no lumps.

Clear indication of interference - waves

Two slit experiments with electrons



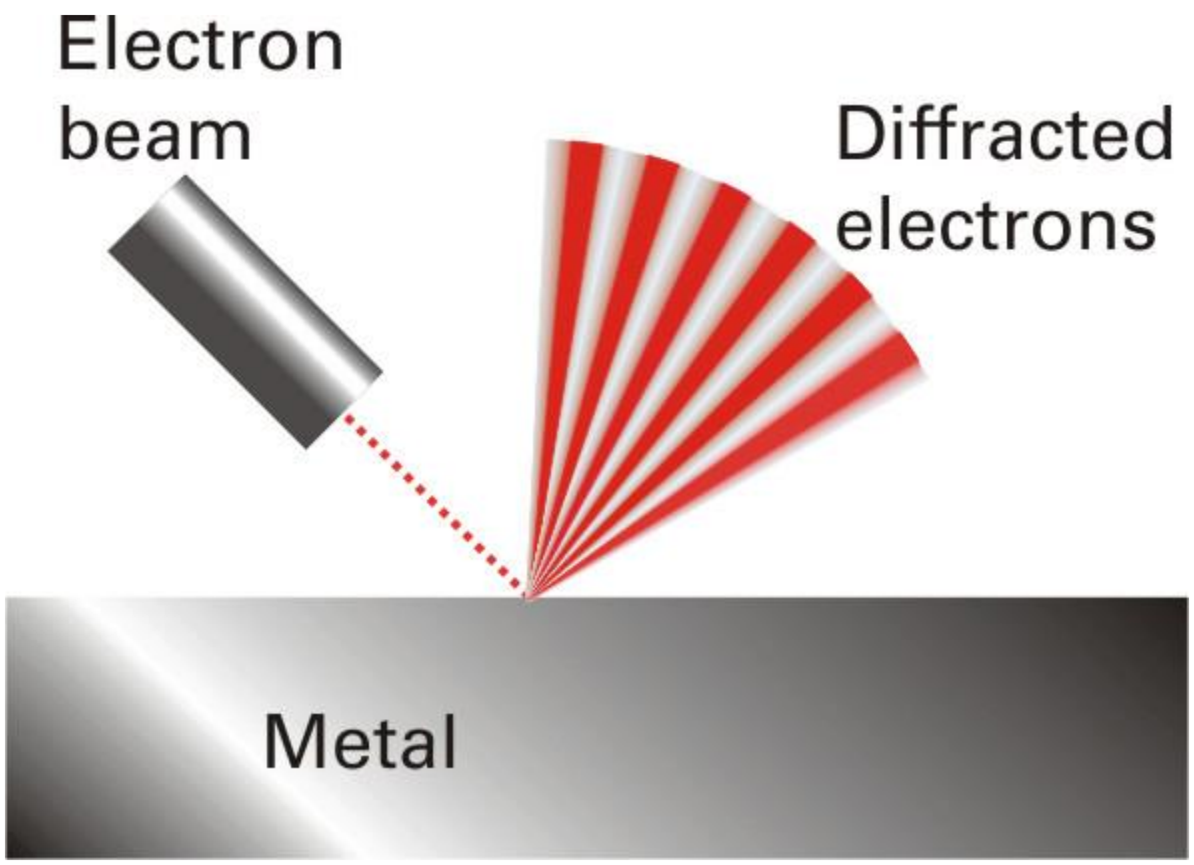


No. of e⁻ is increasing (b) > (c) > (d) > (e)

What do we learn?

1. Interference pattern remains even when e^- are fired one by one.
2. e- splits – passes through slits – interferes with itself – recombines -> **Weird!!**
3. So called particles "e-" combine characteristics of particles & waves

Electron Diffraction



(Detector)

Davisson and Germer 1925

Wave-Particle Duality

de Broglie: Just as light exhibits both ‘wave-like’ (diffraction), and ‘particle-like’ characteristics, so should all material objects.

For light (photon) $E = pc = hc/\lambda$

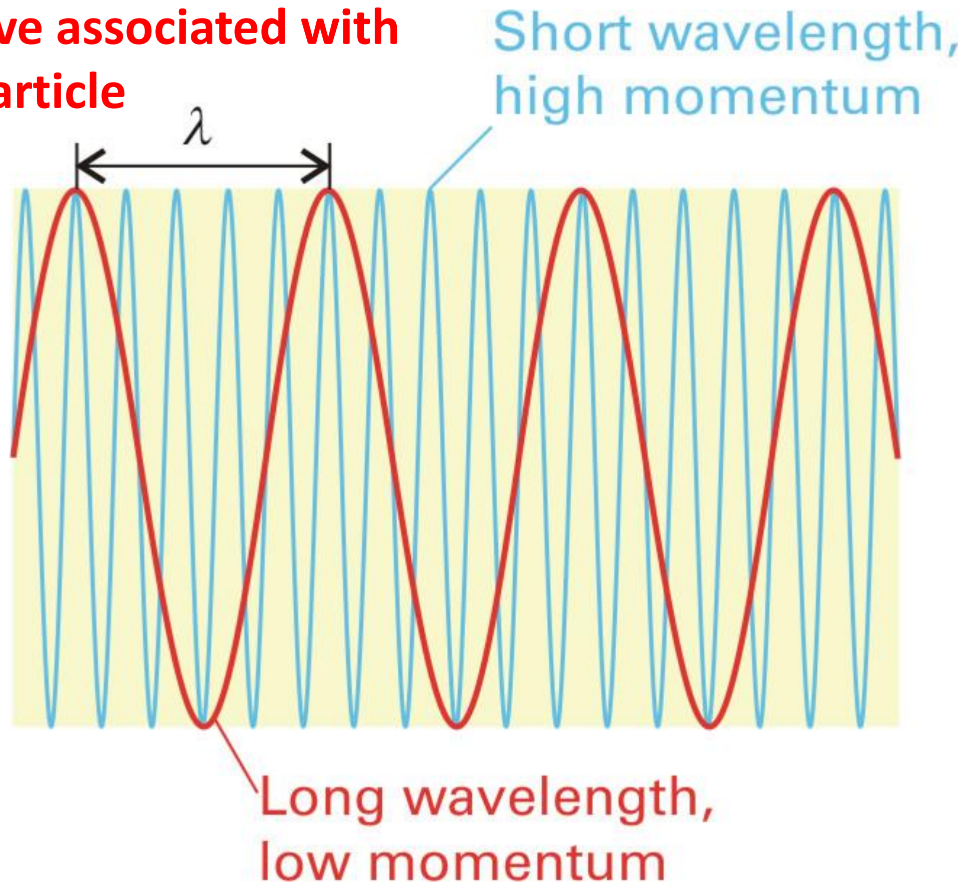
$\Rightarrow$ $$p = h/\lambda$$

de Broglie (1924) suggested that this is more generally true of all material objects. A particle moving with linear momentum p, has an associated ‘matter-wave’ of wave length

$$\lambda = h/p$$

Wave-Particle Duality

Wave associated with a particle



- Estimate the wavelength of e- that have been accelerated from rest through a potential difference of 40 kV:
  - 6.1×10^{-12} m
- Estimate the wavelength of a tennis ball of mass 57 g travelling at a speed of 80 km h^{-1}:
  - 5.2×10^{-34} m

Macroscopic objects are so massive that the de Broglie wave lengths are immeasurably small.

Wave-Particle Duality: Consequences

System has a dual potential nature, but the observed nature is particle-like or wave-like, depending on the nature of the observation.

Interference pattern observed even if electrons/photons sent one at a time, so in a sense each electron/photon interferes with itself– Position not sharply defined until it is actually observed.

Only the probabilities of particular results can be predicted, and these are the squares of probability amplitudes, or 'wavefunctions'.

Does the experiment with bullets show interference? Yes, but not seen due to the scale.

Matter wave

Classical one dimensional wave equation:

$$\frac{\delta^2\Phi}{\delta x^2} = \frac{1}{v^2}\frac{\delta^2\Phi}{\delta t^2}$$ ....Equn. 1

We can obtain the solution using the method of separation of variables

u is the potential energy associated with the particle of mass m

Solution: $\Phi(x,t) = \psi(x) \cos \omega t$ ....Equn. 2

$\psi(x)$ is the spatial factor of the amplitude or spatial amplitude of the wave

Substitute $\Phi(x,t)$ from Equn. 2 into Equn. 1

Idea of de Broglie matter wave: E_T = K.E. + P.E. = $\frac{p^2}{2m}$ + u(x); {u(x): Potential}

$$p = \sqrt{2m[E - u(x)]}$$ ....Equn. 3

Matter wave

Wave length associated with the particle having a momentum p is,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m[E - u(x)]}}$$

We'll finally obtain:

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - u(x)]\,\psi(x) = 0 \qquad \text{....Equn. 4}$$

Equation of state for a particle of mass m moving in a potential field of u(x)

$\psi(x) \Rrightarrow$ measure the spatial amplitude of the matter wave associated with a particle of mass "m"

$\Rrightarrow$ called **wave function** of the particle

State in classical- & quantum- mechanics

innovate achieve lead

Macroscopic objects:

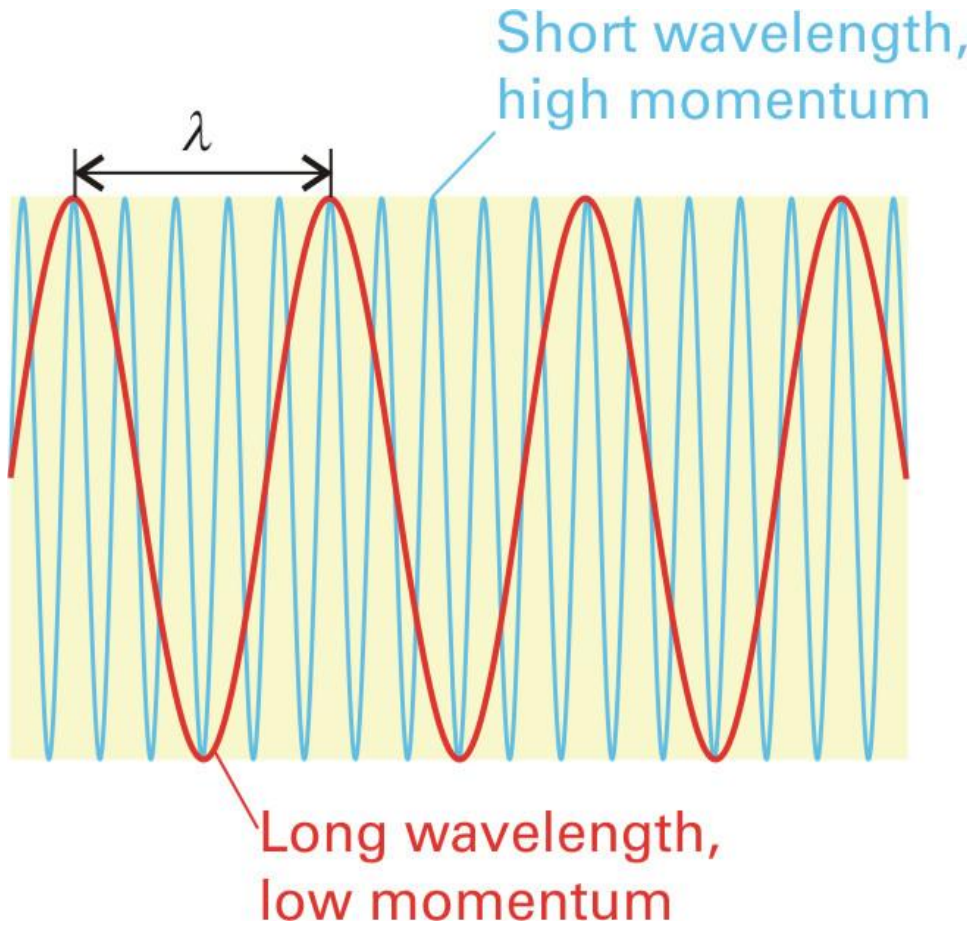
- Specification of the positon and momenta of each particle of the system at a particular time.
- Specification of the forces acting on the particles.

Microscopic particles:

- We can not determine simultaneously the exact positon and momenta of a microscopic particle ($\Delta p_x \Delta x \geq \hbar/2$)

Information required in classical mechanics to predict the future motion of a particle can not be obtained.

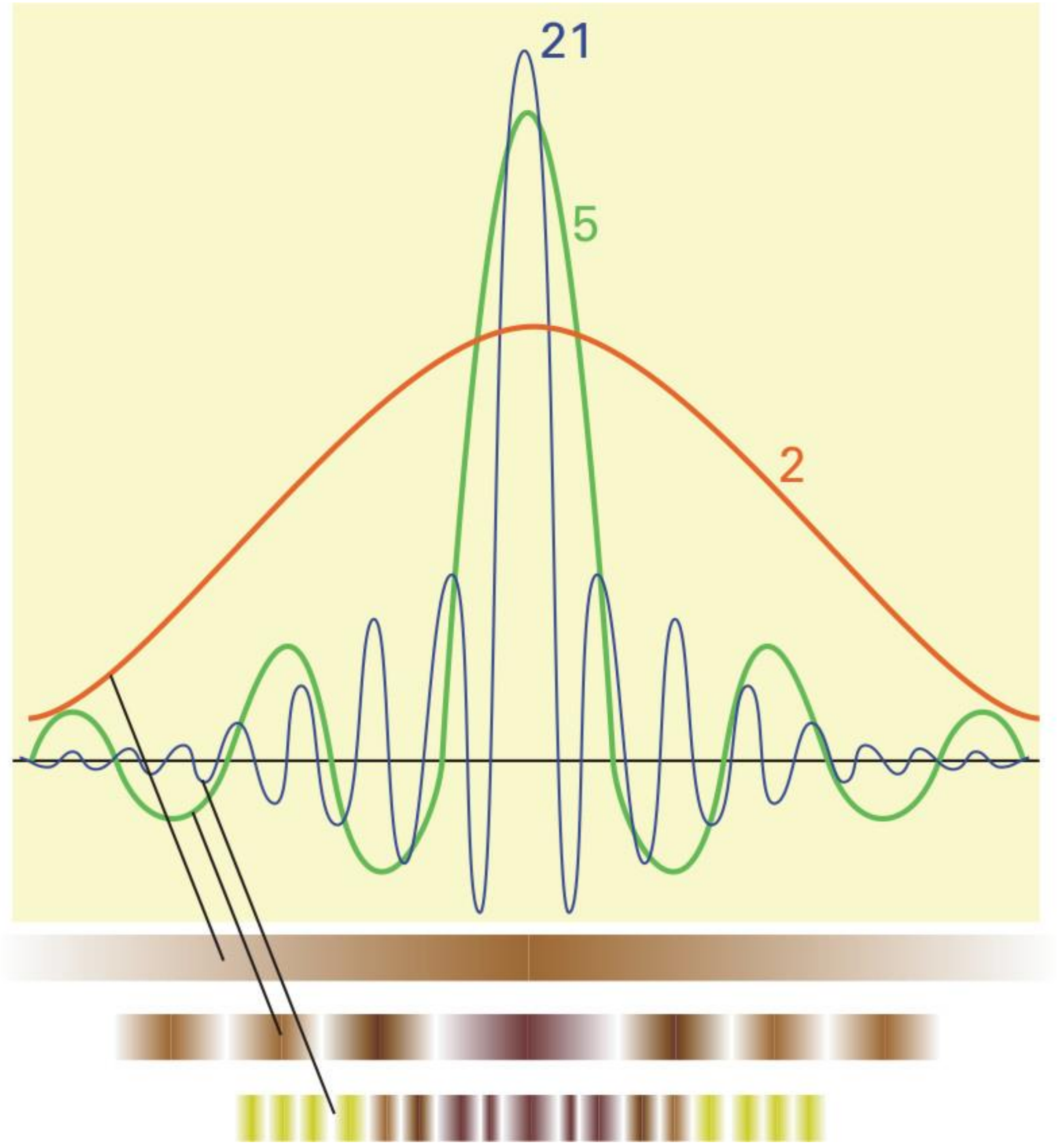
Uncertainty Principle



Definite wavelength ⇒ Definite momentum.

Since wave is spread out everywhere, no information about position.

Uncertainty Principle



Superposition of waves of definite wavelength to yield a localized wavefunction – momentum not precisely defined.

Summary

- Photoelectric effect: Particle nature of electromagnetic radiation
- Wave nature of particles
- Wave particle duality: $\lambda = \frac{h}{p}$
- **Equation of state for a particle of mass m moving in a potential field of u(x)**

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - u(x)]\,\psi(x) = 0$$

- Stationary states
- Schröndinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + u(x)\,\psi(x) = E\,\psi(x)$$