

## Chapter 1

Historical Background of Quantum Mechanics



Erwin Schrödinger (1887-1961)



## Historical Background of Quantum Mechanics

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**Quantum Mechanics:** the laws governing the behavior of microscopic particles such as electrons and nuclei.

**Quantum Chemistry** is the application of quantum mechanics to solve problems in chemistry. It has been applied in different branches of chemistry

## Why Study Quantum Mechanics?

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**Motions in macroscopic world is described by Newtonian mechanics (Classical Physics)**

**Motions in atomic world is not well described by classical physics !!**



## Classical Physics

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**developed before 1900**

- Classical mechanics
- Maxwell's theory of electricity
- Magnetism
- Electromagnetic radiation
- Thermodynamics
- Kinetic theory of gases



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In the late 19<sup>th</sup> century: believed that the theoretical structure of physics was complete

In the last quarter of the nineteenth century: various experimental results were obtained that could not be explained by classical physics.

**led to the development of quantum theory**

An understanding of atomic structure, chemical bonding, and molecular spectroscopy must be based on quantum theory

**Macroscopic world**

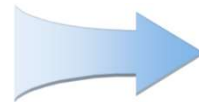
- Energy & matter continuous
- Wave phenomenon, particle
- Deterministic world
- Classic mechanics  
(Newtonian, Maxwell's Eq.)

**Atomic world**

- Energy & matter quantized
- Duality of wave & particle
- Probabilistic description
- Quantum mechanics  
(Schrodinger Eq.)

**Limits of Classical Physics**

- $C_{v,m}$  values of polyatomic molecules
- Blackbody radiation
- Photoelectric effect
- Compton effect ...



**Quantum  
mechanics**

## Blackbody radiation

When a solid is heated, it emits light.

Classical physics: light is a wave consisting of oscillating electric and magnetic fields, an **electromagnetic wave**.

$$\lambda\nu = c$$

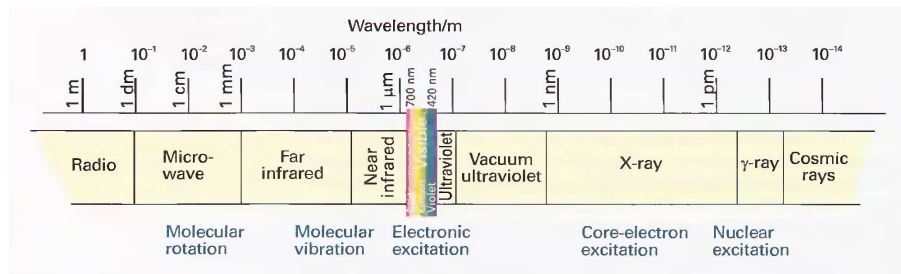
$c = 3.0 \times 10^8$  m/s (speed of light in vacuum)

human eye is sensitive to:  $4 \times 10^{14}$  to  $7 \times 10^{14}$  cycles/s.

Light  $\equiv$  electromagnetic radiation

## Blackbody radiation

- In classical physics: light is a wave consisting of oscillating electric and magnetic fields, an electromagnetic wave



The electromagnetic spectrum and the classification of the spectral regions.

## Blackbody radiation

- ✓ Different solids emit radiation at different rates at the same temperature.
- ✓ A **blackbody** is a body that absorbs all the electromagnetic radiation that falls on it.  $\approx$  a cavity with a tiny hole.
- ✓ Radiation that enters the hole is repeatedly reflected within the cavity (the radiation is absorbed)
- ✓ When the cavity is heated, its walls emit light, a tiny portion of which escapes through the hole.
- ✓ the rate of radiation emitted per unit surface area of a blackbody =  $f(T)$  independent of the material

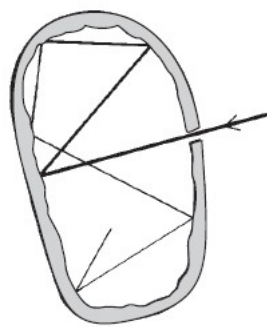
## Blackbody radiation

one can measure the amount of blackbody radiant energy emitted in a given narrow frequency range.

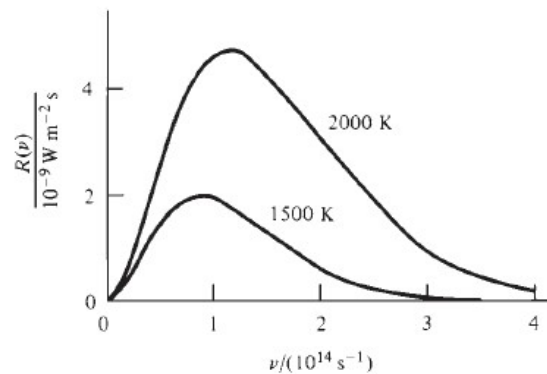
Let *frequency distribution* be described by the function  $R(\nu)$ , where  $R(\nu) d\nu$  is the energy with frequency in the range  $\nu$  to  $\nu + d\nu$  that is radiated per unit time and per unit surface area.

As  $T$  increases, the maximum in  $R(\nu)$  shifts to higher frequencies. When a metal rod is heated: red  $\rightarrow$  orange-yellow  $\rightarrow$  white  $\rightarrow$  blue-white.

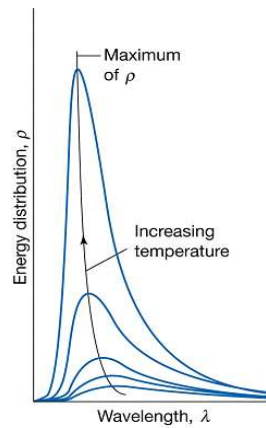
## Blackbody radiation



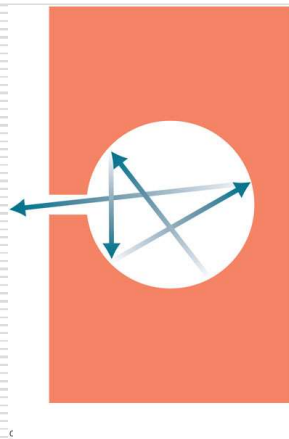
A cavity acting as a blackbody.



Frequency distribution of blackbody radiation at two temperatures.



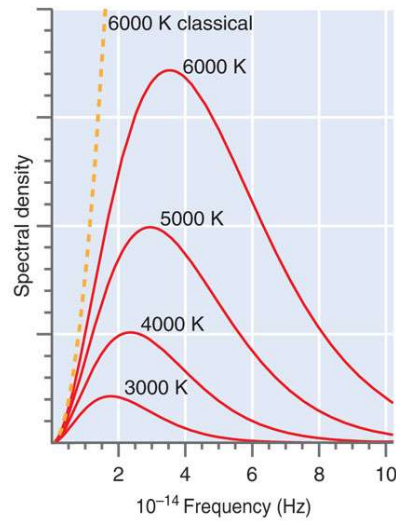
## Blackbody radiation



In June 1900, Lord Rayleigh:  
Using the equipartition-of-energy theorem (classical physics predicted)

$$R(\nu) = (2\pi kT/c^2)\nu^2$$

where  $k$  and  $c$  are Boltzmann's constant and the speed of light.  
energy radiated would increase without limit as  $\nu$  increases.  
Classical physics fails to predict the spectrum of blackbody radiation.



**R-J law lead to “Ultraviolet catastrophe”**

On October 19, 1900

Max Planck by trial and error:  $R(\nu) = a\nu^3/(e^{b\nu/T} - 1)$

a highly accurate fit to the observed curves

$a$  and  $b$  are constants with certain numerical values.

On December 14, 1900,

Planck presented a theory that yielded the formula

$a = 2\pi h/c^2$  and  $b = h/k$

$h$  was a new constant

$k$  is Boltzmann's constant

$$R(\nu) = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1}$$



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Planck considered: the walls contain electric charges that oscillated (vibrated) at various frequencies [Maxwell's electromagnetic theory of light]

Planck assumed that the energy of each oscillating charge could take on only the possible values  $0, h\nu, 2h\nu, 3h\nu, \dots$ , where  $\nu$  is the frequency of the oscillator and  $h$  is a constant (later called **Planck's constant**)

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$

by fitting the formula to the observed curves

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In classical physics, energy takes on a continuous range of values, and a system can lose or gain any amount of energy.

Planck restricted the energy of each oscillating charge to a whole-number multiple of  $h\nu$  and hence restricted the amount of energy each oscillator could gain or lose to an integral multiple of  $h\nu$ . (a **quantum** of energy)

*In classical physics, energy is a continuous variable. In quantum physics, the energy of a system is **quantized**, meaning that the energy can take on only certain values.*

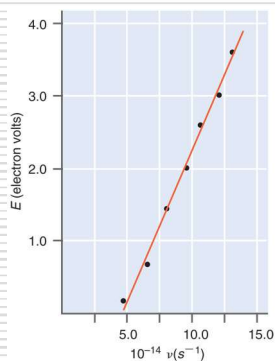
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## Photoelectric Effect

The person who recognized the value of Planck's idea was **Einstein** applied the concept of quantization to electromagnetic radiation and showed that this explained the experimental observations in the photoelectric effect.

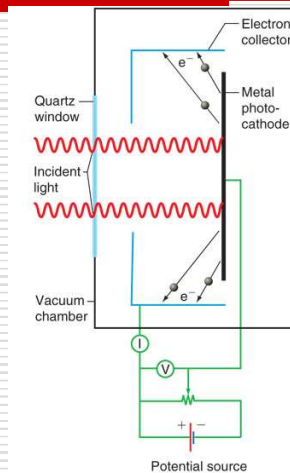
## Photoelectric Effect

Photoelectric Effect : Electron emitting when light radiation



- 1) # of emitted  $e^- \propto$  light intensity, but KE of  $e^-$  is independent to light intensity
- 2) No  $e^-$  emitting before a threshold frequency  $\nu_0$
- 3) KE of  $e^-$  depends on the frequency
- 4)  $e^-$  emitting with low light intensity, too

## Classical prediction of the photoelectric effect



## Einstein's hypothesis

- ✓ Einstein explained the photoelectric effect by extending Planck's concept of energy quantization to electromagnetic radiation.
- ✓ Einstein proposed that in addition to having wavelike properties, light could also be considered to consist of particlelike entities (**photons**), each having an energy  $h\nu$

$$E_{\text{photon}} = h\nu$$

$$h\nu = \Phi + \frac{1}{2}mv^2$$

*work function*  $\Phi$  : is the minimum energy needed by a n electron to escape the metal

$\frac{1}{2}mv^2$  : is the kinetic energy of the free electron.

$h\nu < \Phi$  : a photon does not have enough energy to allow an electron to escape the metal

The minimum frequency  $\nu_0$  at which the effect occurs is given by  $h\nu_0 = \Phi$ .

Photoelectric effect : the particle property of EM radiation

## Atomic spectra

### The Bohr Theory of the Hydrogen Atom

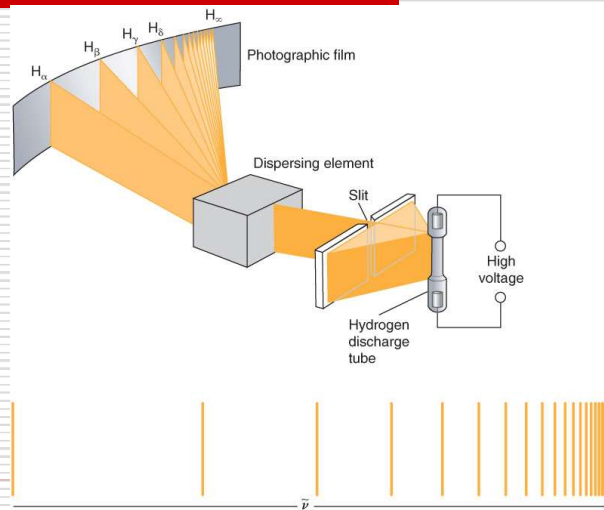
The next major application of energy quantization was the Niels Bohr's theory of the hydrogen atom.

A heated gas of hydrogen atoms emits electromagnetic radiation containing only certain distinct frequencies

Balmer, Rydberg, and others found that the following empirical formula correctly reproduces the observed H-atom spectral frequencies:

$$\frac{\nu}{c} = \frac{1}{\lambda} = R \left( \frac{1}{n_b^2} - \frac{1}{n_a^2} \right) \quad n_b = 1, 2, 3, \dots; \quad n_a = 2, 3, \dots; \quad n_a > n_b$$

## Atomic spectra



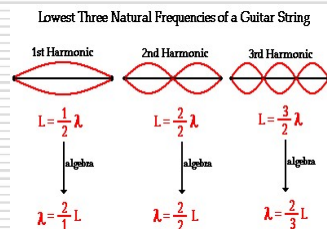
## The Bohr Theory of the Hydrogen Atom

- 1) An atom can take on only certain distinct energies  $E_1, E_2, E_3, \dots$  (stationary states)
- 2) An atom in a stationary state does not emit electromagnetic radiation
- 3) When an atom make a transition from a stationary state with energy  $E_{\text{upper}}$  to lower-energy stationary state with energy  $E_{\text{lower}}$ , it emits a photon of light  

$$E_{\text{upper}} - E_{\text{lower}} = h\nu$$
- 4) The electron in a stationary state moves in a circle around the nucleus and obeys the laws of classical mechanics.
- 5) The allowed orbits are those which the electron's angular momentum  $m_e v r$  equals  $nh/2\pi$

## The De Broglie Hypothesis

### Particles Exhibit Wave-Like Behavior



Quantization of energy does not occur in classical mechanics

Quantization does occur in waves in classical mechanics

In 1924, de Broglie suggested that a particle should have a wave length given by

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

$$E_{\text{photon}} = h\nu \rightarrow h\nu = mc^2 \rightarrow hc/\lambda = mc^2 \rightarrow \lambda = h/mc$$

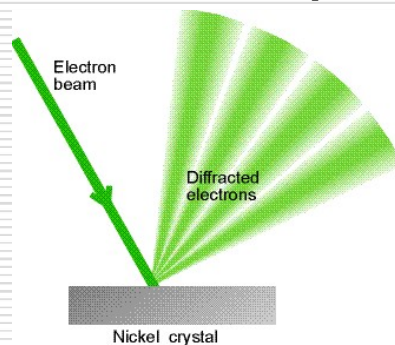
$$E_{\text{photon}} = mc^2$$

## The De Broglie Hypothesis

### Particles Exhibit Wave-Like Behavior

This relation was confirmed in 1927 by **Davisson** and **Germer**.

The wave character of particles  
Davisson and Germer's experiment.(1925)



They observed the diffraction pattern by a NiO crystal.



a characteristic property of wave.

Example:

What's the de Broglie wavelength of an electron moving at  $1.0 \times 10^6$  m/s?

Solution:

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.6 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(1.0 \times 10^6 \text{ m/s})} \\ &= 7 \times 10^{-10} \text{ m} = 7 \text{ \AA}\end{aligned}$$

For a macroscopic particle:  $m = 1.0$  g,  $v = 1.0$  cm/s  
 $\lambda = 7 \times 10^{-27}$  cm

Example:

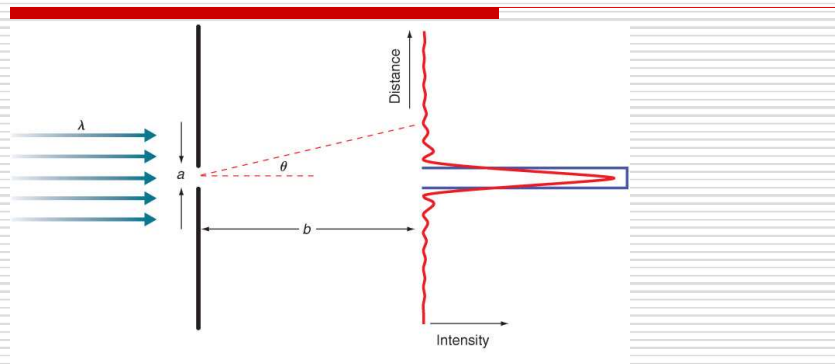
What's the magnitude of energy of  $e^-$  when  $\lambda = 0.30$  nm?

Solution:

$$\begin{aligned}E &= \frac{p^2}{2m} \\ E &= \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{(6.626 \times 10^{-34} \text{ Js})^2}{2(9.109 \times 10^{-31} \text{ kg})(3.0 \times 10^{-10} \text{ m})^2} \\ &= 2.7 \times 10^{-18} \text{ J or } 17 \text{ eV}\end{aligned}$$

## Particles Exhibit Wave-Like Behavior

### a) single-slit diffraction

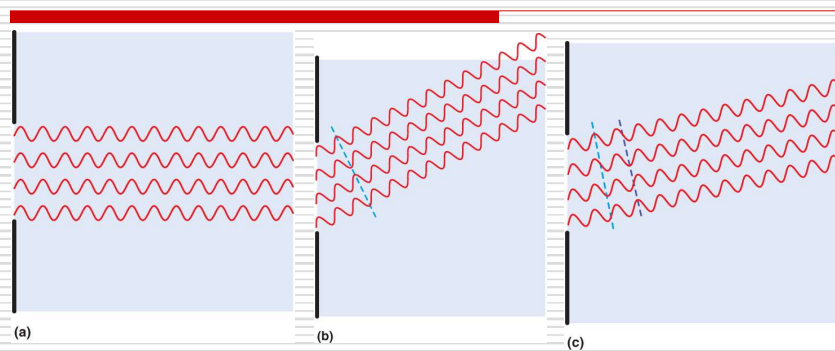


Diffraction : property of wave

**Red line** : intensity of diffracted light by single slit

**Blue line** : intensity of light when absence of diffraction

### Interference of single slit



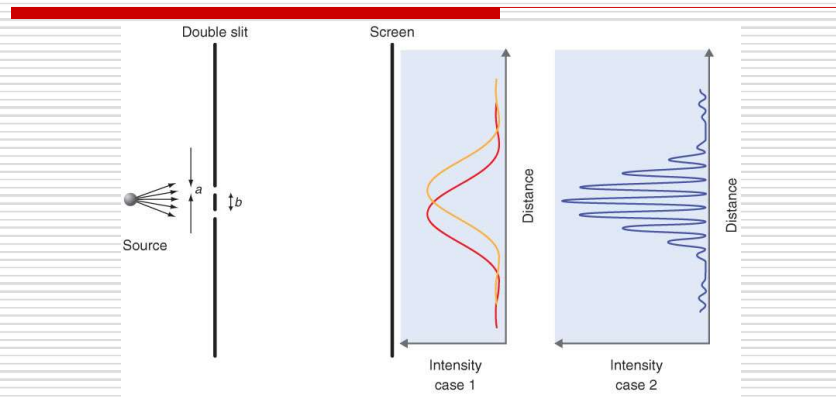
- a) Wave is perpendicular to slit
- b) Waves are perfect out of phase
- c) Waves in normal interference

Path distance :  $a \sin \theta$   
It must be same as  $n\lambda$

$$a \sin \theta = n\lambda, \sin \theta = \frac{n\lambda}{a}$$



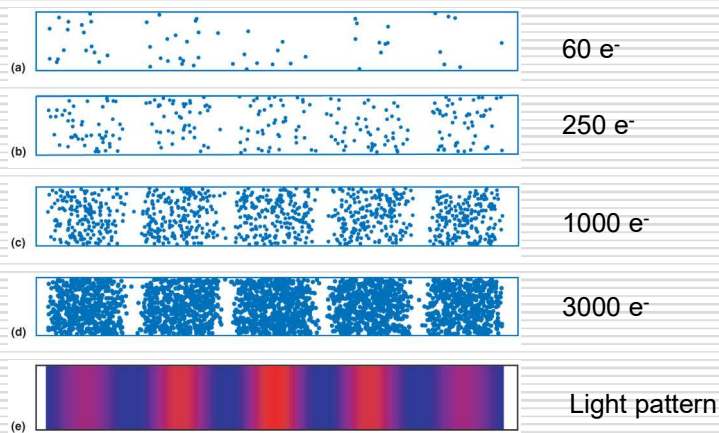
## b) double-slit diffraction



Case 1. one of slit is blocked

Case 2. both slit is opened

## c) double-slit electron diffraction (simulation)

Particle ( $e^-$ ) shows as a wave pattern

## Summary

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- ✓ Classical theory is not able to explain accurately atomic and molecular phenomena.
  - ✓ It is inevitable to introduce Quantum Mech to describe microscopic world accurately.
  - ✓ Be familiar with details of Quantum Mech.
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