2 Introduction

At the start of the 20th century, people began to notice that classical physics was not perfect. In 1900, Lord Kelvin gave a speech on ”Nineteenth-Century Clouds over Dynamical Theory of Heat and Light,” where he pointed out a few problematic phenomena. Around that time, some important scientific discoveries were made (e.g., quantization of energy, wave-particle duality, etc.), which provide crucial information necessary to start the development of the quantum mechanics. We shall cover some of the topics in this chapter.

2.1 Black Body Radiation

At ∼1900, use of classical physics allows to predict the amount of radiation emitted by black body as a function of frequency (ν)

$$\underset{\substack{\uparrow \\ \text{given freq } \nu, \\ \text{Temp } T}}{d\rho(\nu,T)} = \frac{8\pi\nu^2}{c^3}\underbrace{K_B T}_{\substack{\downarrow \\ \text{Average E}}} d\nu \cdots \text{①}$$

radiating E density (per unit vol)

① predicts red line in Figure 1.

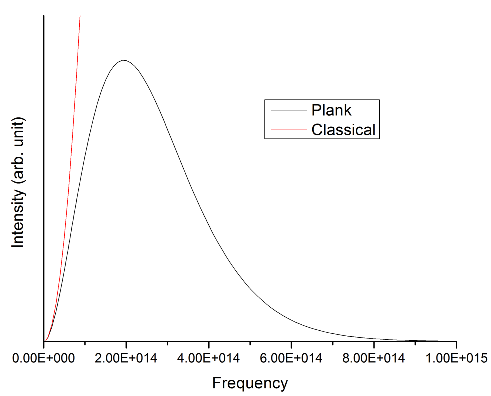

Figure 2: Black Body Radiation

Basically, this model (based on classical physics) predicts that every object emits high-frequency light (ultraviolet and above). Since you are still alive and reading this textbook, we know that we are not bombarded by harmful gamma rays all the time. In other words, classical physics can’t explain black body radiation correctly.

Failure of the classical model is called "the ultraviolet catastrophe". Plank's solution to this problem was quantization.

$\int f(x)dx \to \sum_i f(x_i)$

$\uparrow$ $\uparrow$

Classical Quantized

Using the result of statistical mechanics (Physical Chemistry Part II)

$$\underbrace{\int E f_r(E) dE}_{= K_B T} \to \frac{h\nu}{e^{\frac{h\nu}{KT}}-1}$$

Now ① becomes

$$d\rho(\nu, T) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{\frac{h\nu}{KT}}-1}d\nu \cdots \text{①'}$$

HW: Use ① & ①' (Excel) to create Figure 1.

According to Plank, we are less likely to get bombarded by harmful gamma rays. This is a good news for readers who wish to study physical chemistry. In addition, this formula predicts experimental results correctly.

2.2 Photoelectric Effect

Classical physics treats light as propagating electromagnetic wave.

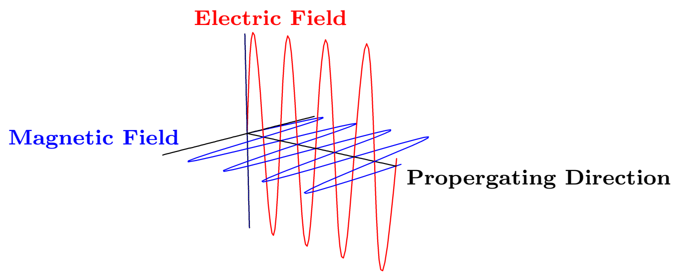

Figure 3: Electromagnetic Wave

Based on this concept, following experiment was performed.

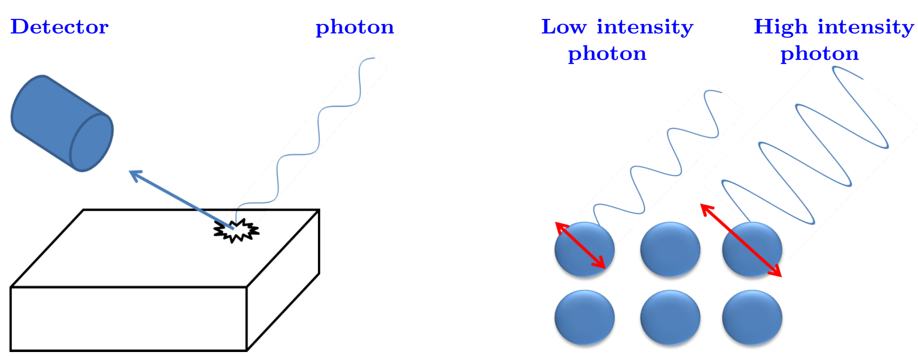

Figure 4: Photelectric Effect

Expectation

Higher Intensity $\rightarrow$ Produce more energetic e^- $\rightarrow$ K.E. of e^- is higher
light (wave)

Result

Higher intensity U.V. light (wave) $\rightarrow$ e^- with same K.E. $\quad \Rightarrow\Leftarrow$

Einstein's solution

Each photon possesses energy $\quad E = h\nu$

$\uparrow$

light <u>particle</u>

$$\Downarrow$$

$$KE = \frac{1}{2}mv^2 = h\nu - \underset{\substack{\uparrow \\ \text{minimum energy required to remove } e^- \text{ from surface}}}{\phi}$$

ϕ is surface dependent and it is usually called as work function.

2.3 Line Spectra of Hydrogen

In 1900, a flame analysis was used to identify the type of atoms in a sample. However, scientists at that time didn't know how it worked.

<< You have seen these in Genenal Chemistry I.>>

Using experimental results, they came up with the formulas to fit the line spectra.

Balmer	$\nu = 109,680(\frac{1}{2^2} - \frac{1}{n^2})cm^{-1}$
Lyman	$\nu = 109,680(\frac{1}{1^2} - \frac{1}{n^2})cm^{-1}$
Paschen	$\nu = 109,680(\frac{1}{3^2} - \frac{1}{n^2})cm^{-1}$

$\Downarrow$ generalization

$$\nu = \frac{1}{\lambda} = 109,680(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2})cm^{-1}$$

$\nwarrow$ Rydberg formula

2.4 Bohr's Atomic Model (Hydrogen)

In Bohr's Atomic Model, electron (e^{-1}) orbits around proton in circular orbit (similar to the solar system).

Two types of force act on e^{-1} attraction (⊕ ⊖)
&
centrifugal force

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}$$

Einstein		de Broglie		Bohr
Light is both wave & particle.	=>	Everything is wave & particle. $\lambda = \frac{h}{mv}$	=>	Since e^{-1} is wave, circumference must be integer multiple of λ. $2\pi r = n\lambda$

$$2\pi r = n\lambda$$
$$\Downarrow$$
$$m_e v r = \frac{nh}{2\pi}$$
$$\Downarrow$$

<u>HW</u>
Derive these ->

$$r = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2}$$
&
$$E_n = \frac{m_e e^4}{8{\epsilon_0}^2 h^2 n^2}$$

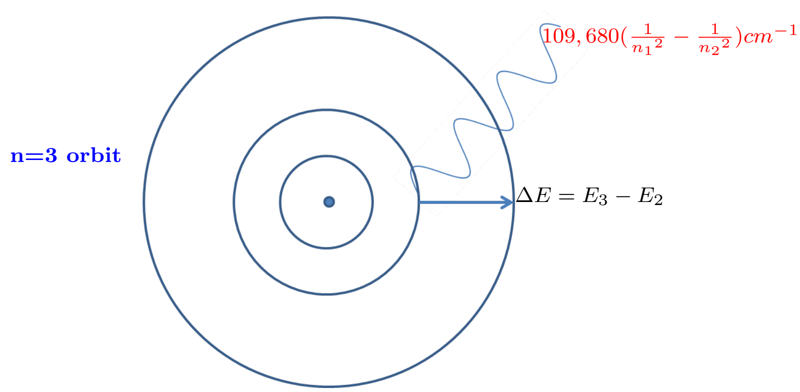

Figure 5: Bohr Model

2.5 Uncertainty Principle

Around 1920, Heisenberg showed,

$$\Delta x \Delta p \geq \hbar/2$$

The basic concept of the uncertainty principle is closely related to Fourie transform. Proof can be found in the appendix, but we will cover this later again from a different perspective.