From Classical to Quantum Mechanics
Chapter 12

The need for non-classical thinking - Quantum Mechanics:

Inability of classical mechanics to explain atomic and molecular phenomena, in particular three important physical observations.

1. Blackbody Radiation
2. The Photoelectric Effect
3. The Hydrogen Atom/Spectra

Objects at a temperature above 0 K emits 'light' in a range of wavelengths.

1. Blackbody Radiation: Objects at any temperature above 0 K emits light in a range of wavelengths.

If the object is perfectly 'black' (so it doesn't reflect any light to outside), it’s emissions are termed; blackbody radiation.

Background - electromagnetic theory (EMT) is highly successful in unifying the disciplines of magnetism, electricity and waves.

Light (EMT) - a wave of oscillating electrical and magnetic fields in orthogonal planes.

Black body: Ideally it is a heated closed container (of temperature, T), a pinhole can be made from which light is leaked/emitted. A perfect emitter of radiation.

All of the emitted radiation has been thermally equilibrated inside the container by many reflections.
Blackbody radiation.

Classical view.

Radiation is an electromagnetic wave, produced when an electric charge vibrates.

At larger temperatures the vibrations are more energetic – more light is emanated – brighter at all frequencies.

Classically the shape, the observed intensity distribution (i.e. presence of the maximum) of the spectrum cannot be explained.

Fact: The intensity of blackbody spectrum always becomes low at the high frequency end.

Classical approach leads to:

\[ \rho(\nu,2) \, d\nu = \frac{8\pi\nu^2}{c^2} \bar{E}_{\nu} \, d\nu \]

Heat is the kinetic energy of random motion, therefore:

\[ \bar{E}_{\nu} \propto KE \quad \bar{E}_{\nu} = kT \]

The Rayleigh-Jeans Law was successful in predicting the energy density at low frequencies, but failed at high frequencies – UV.

This inadequacy is known as the "UV catastrophe."

Planck’s insight: Matter is made of molecules/atoms that oscillate. Black body radiation arises from the vibrations of electrical dipoles (oscillators). Rate of vibration of an oscillator - \( \nu \). Dipoles vibrate in a range of \( \nu \) values.

\[ E \propto \nu \quad \Rightarrow \quad E = h\nu \]

Oscillators are ‘excited’ (or activated) only if they can acquire/absorb an energy of at least \( h\nu \) amount of energy.

Energy of an oscillator = a definite quantity of energy, termed as a quantum of energy, of the oscillator.

For the oscillators of higher frequencies to ‘come about into action’ requires high temperatures, because there is a minimum of energy for given oscillator.
Plank proposed that radiation is emitted or absorbed in packets of energy of definite size (quanta); i.e. light by way of energy is not continuous but made of ‘packets/particle’.

The energy of a quantum is proportional to the frequency of the oscillator.

Energy packet from a vibration of frequency $v$ is proportional to $v$, equal to $\hbar v$ (photon - a single quantum); $\hbar$ a proportionality constant.

Of the photon energy expression $\hbar v$, $\hbar$ is a proportionality constant!

$$h = 6.63 \times 10^{-34} \text{ J s}$$

The very small value of $h$, the Planck’s constant, is the reason, that the ‘character’ of energy packets of radiation was noticed before.

Correspondence Principle (a detour).

As temperature increases quantum system morphs into the classical system, because for $kT >> \hbar v : \bar{E}_{\text{osc}} \rightarrow k_{B}T$

$$\bar{E}_{\text{osc}} = \frac{\hbar v}{\hbar v / k_{B}T} - 1 = \frac{\hbar v}{1 + \hbar v / k_{B}T} \approx k_{B}T$$

$$\rho(v,T) \ dv = \frac{8\pi \hbar v^{3}}{c^{3}} \frac{1}{\hbar v / k_{B}T - 1} \ dv$$

Valid @ all frequencies and $T$.

In the region $kT >> \hbar v : \bar{E}_{\text{osc}} \rightarrow k_{B}T$

$$\bar{E}_{\text{osc}} = \frac{\hbar v}{\hbar v / k_{B}T} - 1 = \frac{\hbar v}{1 + \hbar v / k_{B}T} \approx k_{B}T$$

2. The Photoelectric Effect:

Phenomenon: Shining light on the surface of a metallic substance results in the metal absorbing the light energy and electrons escaping from the metal surface.

Classically, light carries energy and when using low light intensities there would be a time delay for sufficient light energy to build up and be used to eject an electron.

$$KE \text{ of ejected electron increases with light intensity.}$$

Experimentally, if light of a certain frequency can eject electrons from a metal, the intensity of light intensity makes no difference just to eject electrons. Also, no time delay for electron generation as the classical theory predicts.
Einstein inferred - light energy proportional to $\nu$ !!!. Einstein employing Planck’s idea proposed that light energy comes as packets (quanta). Each packet is called a photon has an energy equal to $\beta \nu$ ($\beta = h =$ Planck’s constant).

Therefore the energy of light is ‘packed’ in the photons (particle).

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

A low intensity light has fewer photons but that does not alter the energy of an individual photon. For a specific frequency light, if a single photon has enough energy to eject an electron from a metallic surface, then electrons will be ejected when the photons hit the metal.

3. The Hydrogen Atom/Spectra:

Hydrogen atom consists of a positively charged proton at the center, with a negatively charged electron cloud around it (Rutherford) – The nuclear atom.

The electrical attraction between the proton and the electron (centrifugal force) keeps the nucleus and the electrons in the atom ‘together’.

However classical physics predicts, because the moving/orbiting electron possesses an acceleration and it should also emit electromagnetic radiation.

Classical physics predicts

Therefore the electron should continually lose energy and eventually lose all of its kinetic energy and spiral down into the nucleus. Emission spectrum is ‘continuous’ with a range of frequencies.

This is contrary to observation.

Atoms emits light that consists of few discrete colors.
When sample hydrogen gas is heated it emits light that consists of just a few colors.

If theory doesn't agree with nature, there are two choices: change the theory, or change nature. Unfortunately, all attempts to change nature have failed. The only choice left is - change the theory.

Bohr – made a bold assumption – to explain the atomic spectra, the electron revolves around the atom in well defined circular orbits.

\[
\frac{1}{R_H} \left( \frac{1}{n^2} - \frac{1}{n_i^2} \right), \quad n > n_i
\]

\[n = \text{integers only}!!\]

Light emanating from the energized atoms is of well defined frequencies (wavelengths) contrary to classical understanding.

Photons emanating from the energized atoms is quantized, contrary to classical understanding.

\[
\bar{v} (\text{cm}^{-1}) = R_H (\text{cm}^{-1}) \left( \frac{1}{n^2} - \frac{1}{n_i^2} \right), \quad n > n_i
\]

Determining orbits – radii ?

\[
\text{Coulombic attraction} = \text{Centrifugal force}
\]

\[
\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}
\]

Invoking wave-particle duality of e’s; for a nondestructive wave to exist in the orbit, the circumference = \( n\lambda \).

\[
2\pi r = n\lambda = n\frac{h}{p}
\]

\[
m_e \lambda r = nh, \quad \text{where } n = 1,2,3 \ldots
\]
Bohr’s derivation for the energy of the H-atom amounts to the tinkering of a classical mechanics model with a condition on the angular momentum.

Angular momentum condition lead to the discrete energy levels.

Bohr orbits, \( n \) defines the orbit.

Current equivalence of Bohr orbit: stationary states - spaces where electrons can exist

Correspondence Principle.

As \( n \) increases quantum system morphs into a classical system.

Radius: \( r = \sqrt{\frac{n^2 \hbar^2}{2 \pi m_e^2}} \)

Total energy of atom:

\[ E_{total} = E_{kinetic} + E_{potential} = \frac{1}{2} m_v n^2 - \frac{e^2}{4 \pi \varepsilon_0 r} \]

\[ E_{total} = \frac{1}{2} \left( \frac{e^2}{4 \pi \varepsilon_0 r} \right) - \left( \frac{e^2}{4 \pi \varepsilon_0 r} \right) = - \frac{e^2}{8 \pi \varepsilon_0 r} \]

\[ E_n = - \frac{m_e e^4}{8 \varepsilon_0 \hbar^2 n^2} \quad n = 1, 2, 3, \ldots \]

The particle character of photons would associate a momentum, \( p = mv \), for the photon.

For free moving particles, the relationship between the wave character (described by a wavelength, \( \lambda \)) and the particle character of the described by its momentum, \( p \); was shown to be related by De Broglie as,

\[ \lambda = \frac{h}{p} \]

\[ 2\pi r = n\lambda = n\frac{h}{p} \quad n = 1, 2, 3, \ldots \]

\[ 2\pi = n\frac{h}{p} = n\frac{h}{mv} \]

\[ 2\pi mvr = nh \]

\[ mvr = \frac{nh}{2\pi} = n\hbar \]

Angular momentum is restricted to an integer multiple of a fixed unit – \( n\hbar/2\pi \) - Quantization.

Stationary state, \( n = 6 \)

\[ = n\lambda \], yes

\[ = n\lambda \], no

Properties of light: Diffraction.

Single slit experiment

\[ \sin \theta = \frac{n\lambda}{a} \quad n = \pm 1, \pm 2, \pm 3, \pm \ldots \text{ maxima} \]

The phenomenon of diffraction is a wave character. Light as well as matter (electron) beams behave as waves.
A characteristic feature that distinguishes quantum mechanics from classical mechanics is the wave-particle duality of atomic systems.

The experiment performed on atomic and molecular systems determines whether the wave or the particle behavior is operational.

The quantization of energy is the other characteristic feature of quantum mechanics.