Experimental Facts that Led to the Development of Quantum Theory

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This part of the course is based on Refs. [1], [2] and [3].

1. Introduction

By the late 19^{th} century, classical physics was at its full glory. **Isaac Newton**'s laws (which were re-formulated and generalized by Leonhard Euler, Joseph-Louis Lagrange and Sir William Rowan Hamilton to enable them to tackle much more complicated problems) provided an excellent description of a very wide mechanical phenomena, both here on earth as well as the motion of planets; People such as Ludwig Boltzmann and William Thomson (lord Kelvin) incorporated thermodynamics and statistical mechanics into the realm of mechanics.

In addition, the wave nature of light was investigated, formulated and established by people such as Thomas Young, Augustin-Jean Fresnel and Christiaan Huygens. **James Clerk Maxwell** unified earlier experiments by André-Marie Ampére and Michael Faraday into one, complete theory of electromagnetism; Maxwell was able to show that the electric and magnetic fields obey a wave solution, thereby unifying EM with light - this was later demonstrated experimentally by Heinrich Hertz and by Guglielmo Marconi, who invented the modern radio transmission.

A very famous statement is attributed to Albert Michelson (who invented the Michelson interferometer), who claimed, in 1894 that

"The more important fundamental laws and facts of physical science have all been discovered, and these are now so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote . . . Our future discoveries must be looked for in the sixth place of decimals."

Similarly, Lord Kelvin is quoted in 1900 saying that

"There is nothing new to be discovered in physics now. All that remains is more and more precise measurement."

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This was just about to dramatically change.

2. Basic experiments with light: wave-particle duality

2.1. Light as wave: Young's double slit experiment

Already in 1801, Thomas Young demonstrated that light behaves as a wave. The basic apparatus is simple: a coherent light source [1] illuminates a plate pierced by two parallel slits, and the light passing through the slits is observed on a screen behind the plate.

Once passing through the two slits, the light waves interfere, producing bright and dark bands on the screen (see Figure 1). This can be understood only when one accepted the wave nature of light: bright patterns occur in places of constructive interference, and dark ones occur in regions of destructive interference (see Figure 2).

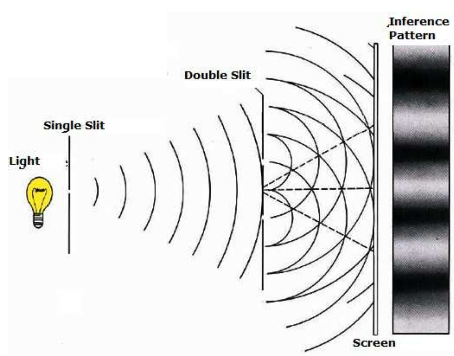

Fig. 1.— Basic apparatus of Young's double slit experiment. Young uses the sun as the source of light, and first passed it through a single slit, to make it somewhat coherent. He then passed the light through a double slit, and observed the interference pattern - dark and bright.

Knowledge of the distance between the two slits, d and the location of the bright / dark patterns, enable a quick calculation of the wavelength of the light waves, λ (see Figure 3). Since the screen can be considered very far away (relative to d), the angle θ between the path taken by each ray to the screen and the normal to the screen is about the same for

[1] A coherent light is a light in which all of its waves have a constant phase difference. Today, the most common coherent light source is a laser beam. Of course, these didn't exist in Young's time, and instead he used the sun rays, which he passed through a single slit to make it somewhat coherent.

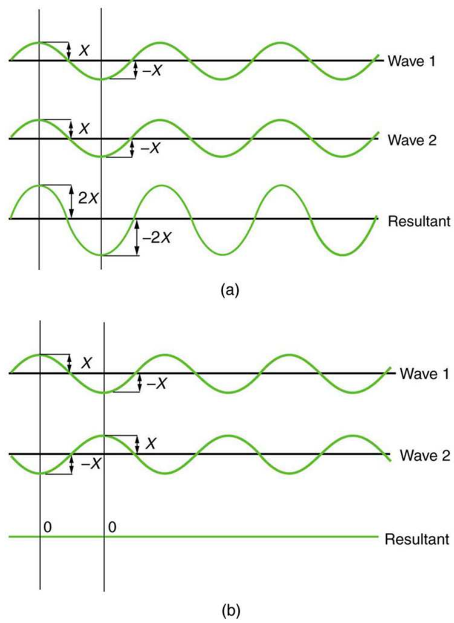

Fig. 2.— Top: pure constructive interference is obtained when two identical waves are in phase. Bottom: when two identical waves are exactly out of phase (shifted by half wavelength), a pure destructive interference occurs.

the two paths. Thus, the difference in path length for waves traveling from two slits to a common point on a screen is $\Delta l = d \sin\theta$.

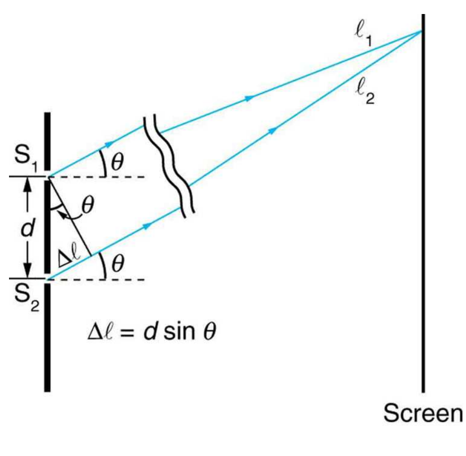

Fig. 3.— For a very far screen, the angle θ between the two paths to the same location is nearly the same. The difference in path length is thus $\Delta l \approx d \sin\theta$.

A constructive interference is obtained when

$$d \sin\theta = m\lambda, \quad \text{for} \;\; m = 0, 1, 2, 3, ..., -1, -2, -3, ... \tag{1}$$

and a destructive interference is obtained for

$$d \sin\theta = \left(m + \frac{1}{2}\right)\lambda, \quad \text{for} \;\; m = 0, 1, 2, 3, ..., -1, -2, -3, ... \tag{2}$$

(see Figure 4).

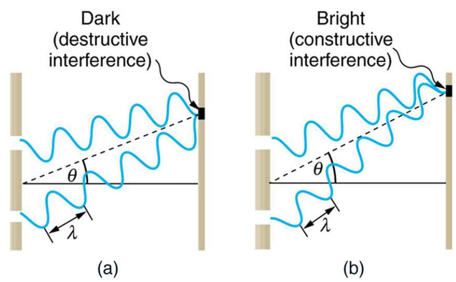

Fig. 4.— A constructive interference (bright fringe) occurs when $d \sin\theta = m\lambda$, where λ is the wavelength and $m = 0, 1, -1, 2, -2, ...$ A destructive interference occurs when $d \sin\theta = (m + 1/2)\lambda$. Knowing d and θ thus enables to determine the wavelength, λ of light.

The overall conclusion from Young's experiment is that

Light is a wave.

This conclusion was widely accepted during the 19^{th} century. It was theoretically explained by Maxwell, whose electromagnetic theory predicts the existence of waves.

2.2. Black body radiation: the birth of quantum mechanics

Every body at thermal equilibrium with temperature $T > 0$ °K (above absolute zero) emits electromagnetic radiation. Furthermore, when radiation falls on a body, some of it is absorbed, while some is reflected (if the body is transparent, some may be transmitted). By definition, a **black body**, is a body that absorbs all the radiation falling upon it.

Black body radiation is the radiation emitted by a black body that is in thermal equilibrium (with temperature T) with its environment. In 1860, it was shown by Gustav

Kirchhoff that for a black body emitter, **the ratio of emissive power to absorption coefficient is a universal function of the wavelength and temperature only**, or

$$\frac{j_\lambda}{\alpha_\lambda} = f(T, \lambda), \tag{3}$$

where λ is the wavelength. This is known as *Kirchhoff's law*. It follows that black body radiation has universal properties that do not depend on the properties of the emitter (apart from its temperature).

Using thermodynamical arguments, in 1879 J. Stefan (and later L. Boltzmann) derived the formula for the total emitted power from a black body at temperature T:

$$F(T) = \sigma T^4, \tag{4}$$

where $\sigma = 5.67 \times 10^{-8}$ W m^{-2} °K^{-4} is a constant known as *Stefan's constant*. Equation 4 is known as *Stefan-Boltzmann law*.

Stefan-Boltzmann's law can be put in a slightly different form,

$$u(T) = aT^4, \tag{5}$$

where $u(T)$ is the *energy density* (amount of energy stored per unit volume) inside the black body, and

$$a \equiv \frac{4\sigma}{c} = 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ °K}^{-4} \tag{6}$$

is known as the *radiation constant* (c is of course the speed of light).

The spectrum of the black body, $f(T, \lambda)$ still needs to be determined. It is obvious that

$$F(T) = \int_0^\infty f(T, \lambda) d\lambda \tag{7}$$

Rayleigh and Jeans used the classical physics arguments to derive $f(T, \lambda)$ (more precisely, they looked at the energy density, $u(T, \lambda) = \frac{4}{c} f(T, \lambda)$). They considered the radiator as a cavity containing standing electromagnetic waves. The spectral distribution of the energy density $u(T, \lambda)$ can be written as

$$u(T, \lambda) = n(\lambda) \times \langle \epsilon(T, \lambda) \rangle. \tag{8}$$

Here, $n(\lambda)$ is the number density of standing waves (modes per unit volume per unit wavelength) supported by the cavity; and $\langle \epsilon(T, \lambda) \rangle$ is the average energy in the mode with wavelength λ. (so, the energy density is simply written the density of waves times the energy in each wave).

Classical arguments lead to $n(\lambda) = 8\pi/\lambda^4$. [2] As for the average energy of each wave, the classical argument is as follows: each wave can have any energy, $0 \leq \epsilon \leq \infty$. However, the system is in thermal equilibrium, so we need to weight each energy by the probability $e^{-\epsilon/k_B T}$. The average energy is therefore

$$\langle \epsilon \rangle = \frac{\int_0^\infty \epsilon e^{-\epsilon/k_B T}}{\int_0^\infty e^{-\epsilon/k_B T}} = k_B T. \tag{9}$$

Rayleigh and Jeans thus obtained the **wrong** result: $u(T, \lambda) = \frac{8\pi}{\lambda^4} k_B T$. As it turns out, this result is correct in the limit of long wavelengths, but it diverges near the peak and at short wavelength - this is known as "the ultraviolet catastrophe" (see Figure 5). The total energy (summing over all wavelengths) per unit volume is infinite, which is clearly incorrect.

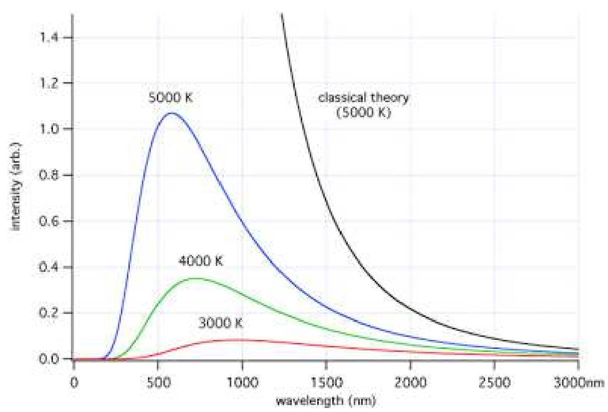

Fig. 5.— The spectrum of a black body at different temperatures. The black line corresponds to the Rayleigh-Jeans formula, which is valid for long wavelength, but diverges at short wavelength ("the ultraviolet catastrophe").

In 1900, **Max Planck** **postulated** that the energy of an oscillator of given frequency ν (recall that $\nu = c/\lambda$) cannot take **any** energy between 0 and ∞, but can only take **discrete values**:

$$\boxed{\epsilon = n\epsilon_0 = nh\nu,} \tag{10}$$

where n is a discrete number (positive integer or 0): $n = 0, 1, 2, 3, ...$ and ϵ_0 is a **quantum** of energy, related to the frequency by $\epsilon_0 = h\nu$. Here, h is a fundamental constant of nature,

[2] A very similar derivative was carried towards the end of PY2104, when we derived the distribution of ideal gas (Maxwell distribution). The derivation can be found in my PY2104 lecture notes available online, as well as, of course, in many textbooks.

known as **Planck's constant**, and is

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

Using this hypothesis, Planck calculated the average energy of a mode,

$$\langle \epsilon \rangle = \frac{\sum_{n=0}^{\infty} n\epsilon_0 e^{-n\epsilon_0/k_B T}}{\sum_{n=0}^{\infty} e^{-n\epsilon_0/k_B T}} = \frac{\epsilon_0}{e^{\epsilon_0/k_B T} - 1} = \frac{hc/\lambda}{e^{hc/\lambda k_B T} - 1} \tag{11}$$

when multiplying this by the density of states calculated (correctly !) by Rayleigh and Jeans, Planck was able to recover the observed spectrum of a black body emitter.

Using Taylor expansion, it is further easy to show that Planck's formula (Equation 11) reduces to the Rayleigh-Jeans formula (Equation 9) in the limit of long wavelength, $\lambda \gg hc/k_B T$.

The units of Planck's constant, h are [energy]×[time] = [length]×[momentum] = *action*.

Thus, the overall conclusion from Planck's work, is that

$$\boxed{\textbf{Energy is quantized.}}$$

For an electromagnetic wave of frequency ν, the **only** possible energies are integer multiples of the quantum $h\nu$,

$$\boxed{\epsilon = n \times h\nu.}$$

This realization of Planck that the energy of waves is quantized - which was initially rejected by most physicists at that time - marks the birth of quantum mechanics.

2.3. The Photoelectric effect

In 1887, Heinrich Hertz observed that when ultraviolet light falls on metallic electrodes, it creates a spark. It was later shown that charged particles - electrons - are ejected from the metallic surface when irradiated by electromagnetic waves, creating the spark. This is known as the **photoelectric effect** (see Figure 6).

Placing the electrodes in a vacuum chamber and applying a potential, V, the electrons emitted produce a current that can be measured. The produced current (called *photocurrent*), I, varies with the potential, V (see Figure 7). When V increases, I increases, until it saturates - this can be explained by that all the released electrons reached the cathode.

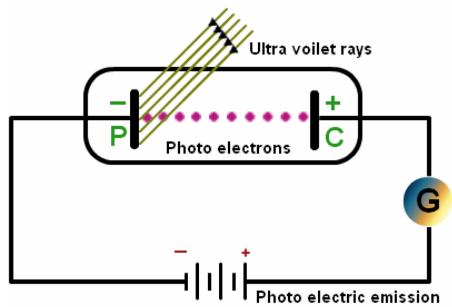

Fig. 6.— Schematic drawing of the apparatus used by Lenard. UV light falls onto a metallic surface P, inside an evacuated glass tube. As a consequence, the metal emits electrons, which are attracted to the cathode, C, by the electric potential, thereby producing a current.

When the voltage is **reversed**, there is a negative voltage, $-V_0$, below which there is no current: no electrons arrive to the cathode. This potential is known as the *stopping potential*.

In a series of experiments conducted by Lenard in 1900, he found that the photocurrent I is proportional to the intensity of the incident light (see Figure 7). This is to be expected in the framework of classical mechanics, as the number of electrons emitted per unit time is proportional to the intensity of the incident light.

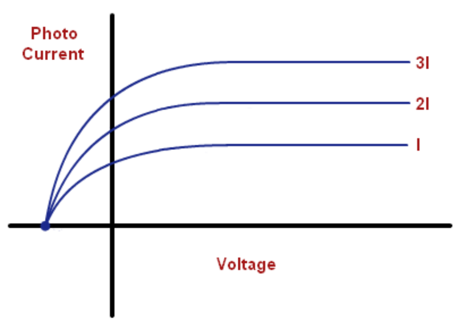

Fig. 7.— The photocurrent, I as a function of the potential, V, for various light intensities. Below $-V_0$, no current is observed. Above that, the current grows, until it saturates.

Classical theory, though, **fails to explain** the following experimental results:

1. The existence of a minimum frequency, ν_t of the radiation (equivalent to maximum wavelength, λ_t), below which no emission of electrons take place. This is irrespective of the intensity.

2. While the photocurrent, I depends on the intensity of the incoming light, it is independent on its wavelength (for wavelength shorter than λ_t, of course).

3. The stopping potential, V_0 depends **linearly** on the frequency ν of the radiation, but is **independent** on its intensity.

4. Electron emission takes place immediately once the light shines on the surface, without delays.

These experimental facts **are in contradiction** to the prediction of classical theory, according to which:

1. Light being a wave, its intensity $\rightarrow$ energy is determined by its amplitude. Thus, larger amplitude implies larger energy that is gained by the electrons. The energy of the electrons, hence the stopping potential, should depend on the the intensity of light, in contradiction to result (3) above.

2. The velocity of the emitted electron should not depend on the frequency of the emitted light. Electrons should be able to gain energy from the radiated light at all frequencies - contradicting result (1) above.

3. An electron would be emitted once it gets sufficient energy necessary for emission. This could take time - in contradiction to the instantaneous emission (result 4 above).

4. The EM wave acts on all electrons in the surface equally. Thus, given enough time, *all* electrons should be able to collect enough energy and eject. Thus, at late enough times, the current should not depend on the intensity - contradicting point (2) above.

In a seminal paper in 1905, **Albert Einstein** proposed a solution: by extending the idea of Max Planck, Einstein proposed that **the electromagnetic waves themselves are quantized**. Light consists of quanta - called **photons** - each having energy

$$E = h\nu = \frac{hc}{\lambda}. \tag{12}$$

The photons are **localized**: when interacting with particles, they give **all** their energy to the particle at once.

This was later demonstrated by another effect - the **Compton effect**.

Note that Planck "only" assumed that the energy of each mode (wave) is quantized, while treating the electromagnetic field as classical and continuous. Einstein took an extra step, by assuming that the electromagnetic field itself is quantized, thereby introducing quanta of light - photons.

The conclusion from the works of Planck and Einstein is that

> **In interactions between light and matter, radiation appears to be composed of particles - photons, having discrete energies.**

Combined with Young's double slit experiment, this established the **dual nature of light**: both as wave and as particle.

So, is light a wave or particle ? It is both. We will shortly show how quantum mechanics treats *both* wave and particle aspects of light in a self consistent way.

3. The particle - wave nature of matter

Following Young's experiment, in the 19^{th} century light was treated as waves. In contrast, matter was treated as discrete particles - similar to "billiard balls". However, this classical treatment turned out to be incomplete not only for light, but for matter as well.

3.1. Bohr's atomic model, old quantum mechanics

3.1.1. Spectral lines

In 1752, Thomas Melville showed that the light emitted from burned material, such as salts, is composed of several discrete wavelength; we call these today **emission lines**. It was later discovered that when light passes through a material, discrete **absorption lines** are seen.

About a hundred years later, in 1859, Gustav Kirchhoff (the same one who worked on black body radiation), showed that for a given material, the same lines are emitted and absorbed. Thereby, he introduced modern spectroscopy (and enabled, e.g., astronomers to determine the chemical composition of stars).

These spectral lines do not appear at random wavelength. Rather, it was shown by Johann Balmer, and later on (1889) by Johannes Rydberg that they appear at wavelength given by

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \tag{13}$$

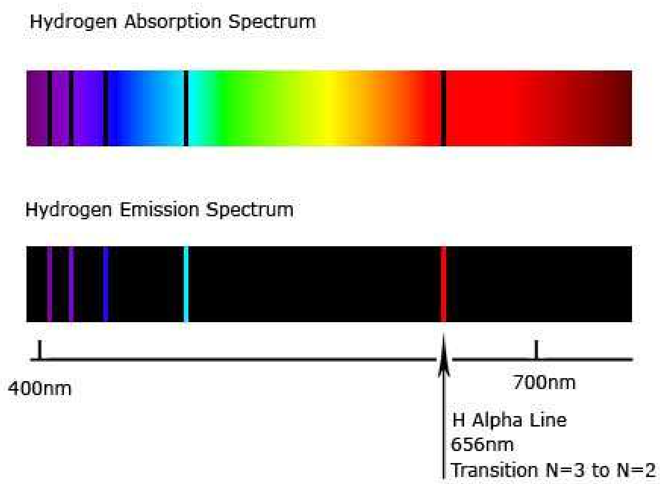

Fig. 8.— Absorption (top) and emission (bottom) lines from the hydrogen atom.

where $R_H = 1.097 \times 10^7$ m^{-1} is known as **Rydberg constant**, and n_1, n_2 are discrete numbers, $n_1 = 1, 2, 3, ...$ and $n_2 > n_1$.

3.1.2. The nuclear atom

In a series of experiments in 1911, **Ernst Rutherford** demonstrated that all the positive charge and nearly all the mass of an atom is concentrated in its tiny nucleus, which is 4 orders of magnitude smaller than the size of the atom (see Figure 9).

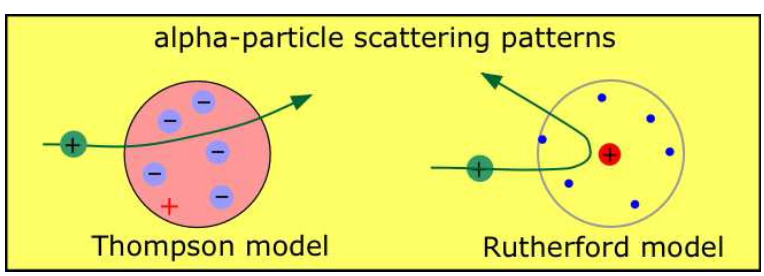

Fig. 9.— Rutherford demonstrated that all the positive charge and almost all the mass of the atom are in its tiny nucleus.

This result is **contradictory** to classical theory in various ways.

1. Positive charges repeal each other, so what holds them in the nucleus ?
2. There is no stable configuration of positive and negative charges at rest. Thus, electrons must *move* around the kernel. However, in this circular motion they are accelerated, thereby they must emit radiation. It can be shown that they lose all their energy to radiation within $\sim 10^{-10}$ s. After that time, they must collapse to the nucleus.

3.1.3. Bohr's atomic model

In 1913, **Niels Bohr** combined the quantum concepts of Planck and Einstein and was able to explain both Rutherford's results as well as the observed spectra of the hydrogen atom.

Bohr **postulated** that the electrons cannot circulate around the nucleon in *any* orbit, as classical EM allows, but only in a certain set of stable orbits, which he called **stationary states**. For each state there is an associated energy E_i.

Bohr further postulated that once in a stable state, the electron does not emit any radiation. Radiation can be emitted or absorbed when an electron transits between different orbits = different energy levels. The frequency of radiation is given by

$$h\nu = E_f - E_i \tag{14}$$

where E_i and E_f are the energies of the atom in the initial and final states (see Figure 10).

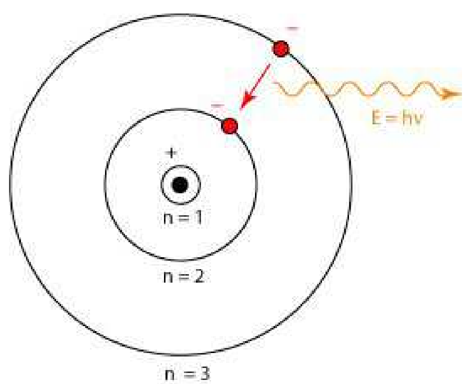

Fig. 10.— Bohr's atomic model. Electrons can move only in discrete orbits around the nucleus. When in such an orbit, no radiation is emitted. Radiation can only be emitted when an electron transients between different orbits, with frequency given by $h\nu = E_f - E_i$.

Further postulating that the *magnitude of the angular momentum of the electron's trajectory is also quantized*, namely $L = nh/2\pi$, where $n = 1, 2, 3, ...$, Bohr was able to derive Rydberg's constant,

$$R_H = \frac{m_e q^4}{8\epsilon_0^2 h^3 c}, \tag{15}$$

where m_e is the mass of the electron, q is its charge, ϵ_0 is the permittivity of free space, c is the speed of light and h is Planck's constant.

The conclusion from Bohr's work is that

The motion of atomic system: electrons orbits and their angular momentum are quantized (discrete).

This conclusion was further tested and extended by Otto Stern and Walther Gerlach. In their famous experiment, conducted in 1922, they showed that not only the total angular momentum is quantized, but each of its components, e.g., L_z is quantized as well. Their experiment further showed that electrons have *intrinsic* angular momentum, called **spin**, which is also quantized, and can take only 2 different values ($+1/2$ and $-1/2$).

Although the basic principle that the motion is quantized is essentially correct, Bohr's quantum theory encountered several difficulties (e.g., it only works for the Hydrogen atom, but not for the Helium), and was replaced in the 1920's by a more modern version of quantum mechanics, which was constructed based on it. Bohr's model is thus known today as the **old quantum theory**.

3.2. De-Broglie and the wave nature of particles

Following the realization that light exhibits both wave-like and particle-like behaviors, in 1923, **Louis de Broglie** hypothesized that **material particle may posses a wave-like properties** as well. In analogy to Einstein's work, de-Broglie proposed that for a particle of energy E and momentum $\vec{p}$ there is an associated **matter wave**, of frequency

$$\boxed{\nu = \frac{E}{h}}, \tag{16}$$

and wavelength

$$\boxed{\lambda = \frac{h}{|p|}}. \tag{17}$$

We note that for photons, $E = pc$ and $\nu = c/\lambda$, and thus each of these relations leads to the other. As opposed to that, for matter waves, both are needed.

The wavelength $\lambda = h/p$ is known as **de Broglie wavelength** of a particle.

Note that de-Broglie idea provides a qualitative explanation to the quantization of angular momentum proposed by Bohr in explaining the value of Rydberg's constant. If an electron circulates the nucleon at a stable, circular orbit of radius r, its associated wave must be such that a whole number of wavelengths fit into $2\pi r$. Thus, $n\lambda = 2\pi r$. Using $\lambda = h/p$ and $L = r \times p$, we immediately find $L = nh/2\pi$, which was postulated by Bohr.

For macroscopic particles, de Broglie wavelength is tiny: For example, the de Broglie wavelength of a 1 kg body moving at $v = 1$ m s^{-1} is $\lambda \approx 6.6 \times 10^{-34}/1 \approx 10^{-33}$ m. This is far too small to be detected.

However, for microscopic particles, the de Broglie wavelength is much larger. An electron ($m_e = 9.1 \times 10^{-31}$ kg) accelerated by a potential of 1 Volt, has de-Broglie wavelength of 12.3 Angstrom. This wavelength is similar to that of X-rays, and is comparable to the spacing of atoms in a crystal lattice. In 1927, Clinton Davisson and Lester Germer performed the scattering experiments on a nickel crystal, demonstrating the constructive and destructive interference, thereby proving the wave nature of electrons. The conclusion is that

All matter particles possess wave-like characteristics.

We note that this wave nature directly relates to Planck's constant h, as $\lambda = h/p$. In the limit $h \to 0$, $\lambda \to 0$, and all particles obey the laws of classical mechanics. This is similar to the fact that *geometrical optics* is obtained as a *short-wavelength approximation of wave optics*.

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