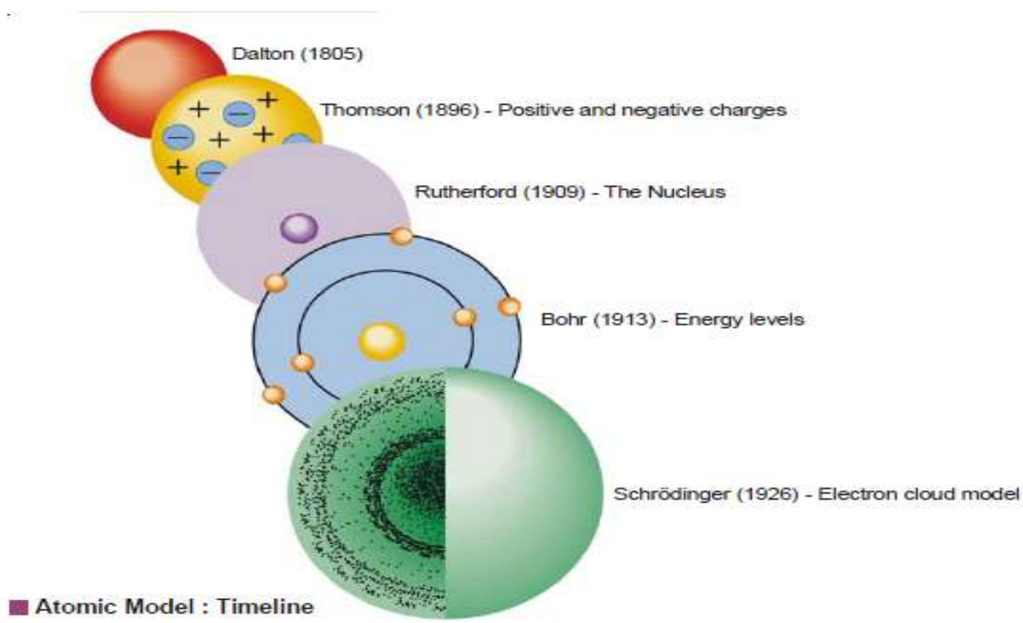
ATOMIC STRUCTURE

Modern Theories: The Quantum Theory and Atomic Structure.

Over a few remarkable decades, from around 1890 to 1930, a revolution took place in how we view the makeup of the universe. As seen, flaws appear in the established models as conflicting evidence mounts, more discoveries widen these flaws into cracks, and the conceptual structure crumbles gradually due to its inconsistencies. New insight, verified by experiment, then guides the building of a model more consistent with reality. So it was, when Dalton’s atomic theory established the idea of individual units of matter, and when Rutherford’s nuclear model substituted atoms with rich internal structure for “plum puddings.” Figure below summarizes the timeline of evolution of atomic structure based on the major contributor.



Rutherford model laid the foundation of the model picture of the atom. However, it did not tell anything as to the position of the electrons and how they were arranged around the nucleus. Rutherford recognized that electrons were orbiting around the nucleus. But according to the classical laws of Physics an electron moving in a field of force like that of nucleus, would give off radiations and gradually collapse into the nucleus. Thus Rutherford model failed to explain why electrons did not do so.

Neils Bohr, a brilliant Danish Physicist, pointed out that the old laws of physics just did not work in the submicroscopic world of the atom. He closely studied the behavior of electrons, radiations and atomic spectra. In 1913 Bohr proposed a new model of the atom based on the modern Quantum theory of energy. With his theoretical model he was able to explain as to why an orbiting electron did not collapse into the nucleus and how the atomic spectra were caused by the radiations emitted when electrons moved from one orbit to the other. Therefore, to understand the Bohr theory of the atomic structure, it is first necessary to acquaint ourselves with the nature of electromagnetic radiations and the atomic spectra as also the Quantum theory of energy.

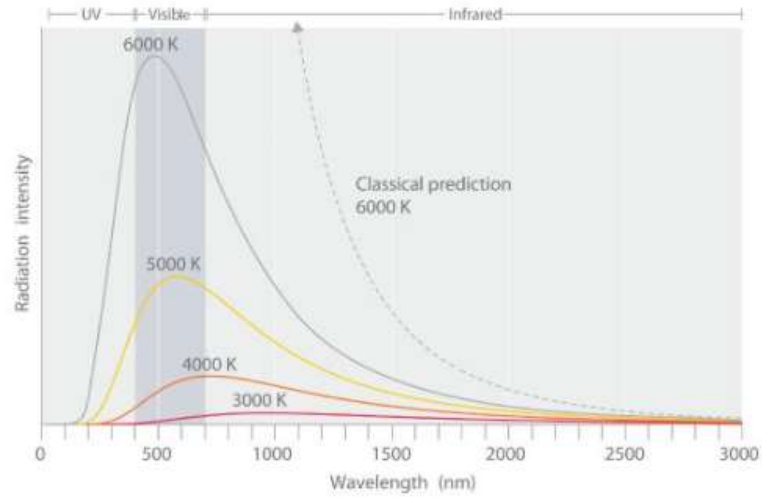
Planck's Quantum Theory

As progress in the science field was happening, Maxwell's suggestion about the wave nature of electromagnetic radiation was helpful in explaining phenomena such as interference, diffraction, etc. However, he failed to explain various other observations such as the nature of emission of radiation from hot bodies, photoelectric effect, i.e. ejection of electrons from a metal compound when electromagnetic radiation strikes it, the dependence of heat capacity of solids upon temperature, line spectra of atoms (especially hydrogen). Therefore, before stating or explaining Planck's Quantum Theory, some concepts must first be understood.

Black Body Radiation

Solids, when heated, emit radiation varying over a wide range of wavelengths. For example: when we heat solids, colour changes continue with a further increase in temperature. This change in colour happens from a lower frequency region to a higher frequency region as the temperature increases. For example, in many cases, it changes from red to blue. An ideal body which can emit and absorb radiation of all frequencies is called a black body. The radiation emitted by such bodies is called black body radiation.

Black-body radiation is the thermal electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment, emitted by a black body (an idealized opaque, non-reflective body). It has a specific spectrum of wavelengths, inversely related to intensity that depend only on the body's temperature, which is assumed for the sake of calculations and theory to be uniform and constant.



Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits

The thermal radiation spontaneously emitted by many ordinary objects can be approximated as black-body radiation. A perfectly insulated enclosure that is in thermal equilibrium internally contains black-body radiation and will emit it through a hole made in its wall, provided the hole is small enough to have a negligible effect upon the equilibrium.

In a dark room, a black body at room temperature appears black because most of the energy it radiates is in the infrared spectrum and cannot be perceived by the human eye. Since the human eye cannot perceive light waves below the visible frequency, a black body at the lowest just faintly visible temperature subjectively appears grey, even though its objective physical spectrum peak is in the infrared range. The human eye essentially does not perceive color at low light levels. When the object becomes a little hotter, it appears dull red. As its temperature increases further it becomes bright red, orange, yellow, white, and ultimately blue-white.

Thus, we can say that variation of frequency for black body radiation depends on the temperature. At a given temperature, the intensity of radiation is found to increase with an increase in the wavelength of radiation which increases to a maximum value and then decreases with an increase in the wavelength. This phenomenon couldn't be explained with the help of Maxwell's suggestions. Hence, Planck proposed Planck's quantum theory to explain this phenomenon.

The term *black body* was introduced by Gustav Kirchhoff in 1860. Black-body radiation is also called thermal radiation, *cavity radiation*, *complete radiation* or *temperature radiation*. Black-body radiation has a characteristic, continuous frequency spectrum that depends only on the body's temperature, called the Planck spectrum or Planck's law.

According to Planck’s quantum theory,

1. Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of the radiation.

Thus, the energy of radiation is expressed in terms of frequency as,

E = h v

Where,

E = Energy of the radiation

h = Planck’s constant (6.626×10^{-34} J.s)

v= Frequency of radiation

Further, Planck’s Law of Black body radiation can be mathematically expressed as follows:

$$B_\nu(T) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1},$$

where

$B_\nu(T)$ is the spectral radiance (the power per unit solid angle and per unit of area normal to the propagation) density of frequency ***v*** radiation per unit frequency at thermal equilibrium at temperature *T*.

h is the Planck constant;

c is the speed of light in a vacuum;

k is the Boltzmann constant;

v is the frequency of the electromagnetic radiation;

T is the absolute temperature of the body.

For a black body surface, the spectral radiance density (defined per unit of area normal to the propagation) is independent of the angle of emission with respect to the normal. However, this means that, following Lambert's cosine law, is the radiance density per unit area of emitting surface as the surface area involved in generating the radiance is increased by a factor with respect to an area normal to the propagation direction. At oblique angles, the solid angle spans involved do get smaller, resulting in lower aggregate intensities.

Interestingly, Planck has also concluded that these were only an aspect of the processes of absorption and emission of radiation. They had nothing to do with the physical reality of the radiation itself. Later in the year 1905, famous German physicist, Albert Einstein also reinterpreted Planck's theory to further explain the photoelectric effect. He was of the opinion that if some source of light was focused on certain materials, they can eject electrons from the material. Basically, Planck's work led Einstein in determining that light exists in discrete quanta of energy, or photons.

Photoelectric Effect

photoelectric effect is a phenomenon in which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. The effect is often defined as the ejection of electrons from a metal plate when light falls on it. In a broader definition, the radiant energy may be infrared, visible, or ultraviolet light, X-rays, or gamma rays; the material may be a solid, liquid, or gas; and the released particles may be ions (electrically charged atoms or molecules) as well as electrons.

The photoelectric effect was discovered in 1887 by the German physicist Heinrich Rudolf Hertz. In connection with work on radio waves, Hertz observed that, when ultraviolet light shines on two metal electrodes with a voltage applied across them, the light changes the voltage at which sparking takes place. This relation between light and electricity (hence *photoelectric*) was clarified in 1902 by another German physicist, Philipp Lenard. He demonstrated that electrically charged particles are liberated from a metal surface when it is illuminated and that these particles are identical to electrons, which had been discovered by the British physicist Joseph John Thomson in 1897.

Further research showed that the photoelectric effect represents an interaction between light and matter that cannot be explained by classical physics, which describes light as an electromagnetic wave. One inexplicable observation was that the maximum kinetic energy of the released electrons did not vary with the intensity of the light, as expected according to the wave theory, but was proportional instead to the frequency of the light. What the light intensity did determine was the number of electrons released from the metal (measured as an electric current). Another puzzling observation was that there was virtually no time lag between the arrival of radiation and the emission of electrons.

Consideration of these unexpected behaviours led Albert Einstein to formulate in 1905 a new corpuscular theory of light in which each particle of light, or photon, contains a fixed amount of energy, or quantum, that depends on the light's frequency. In particular, a photon carries an energy E equal to hf, where f is the frequency of the light and h is the Planck's constant.

Einstein assumed that a photon would penetrate the material and transfer its energy to an electron. As the electron moved through the metal at high speed and finally emerged from the material, its kinetic energy would diminish by an amount φ called the work function (similar to the electronic work function), which represents the energy required for the electron to escape the metal. By conservation of energy, this reasoning led Einstein to the photoelectric equation $E_k = hf - \varphi$, where E_k is the maximum kinetic energy of the ejected electron.

Although Einstein's model described the emission of electrons from an illuminated plate, his photon hypothesis was sufficiently radical that it was not universally accepted until it received further experimental verification. Further corroboration occurred in 1916 when extremely accurate measurements by the American physicist Robert Millikan verified Einstein's equation and showed with high precision that the value of Einstein's constant h was the same as Planck's constant. Einstein was finally awarded the Nobel Prize for Physics in 1921 for explaining the photoelectric effect.

In 1922 the American physicist Arthur Compton measured the change in wavelength of X-rays after they interacted with free electrons, and he showed that the change could be calculated by treating X-rays as made of photons. Compton received the 1927 Nobel Prize for Physics for this work. In 1931 the British mathematician Ralph Howard Fowler extended the understanding of photoelectric emission by establishing the relationship between photoelectric current and temperature in metals. Further efforts showed that electromagnetic radiation could also emit electrons in insulators, which do not conduct electricity, and in semiconductors, a variety of insulators that conduct electricity only under certain circumstances.

Principles of Photoelectric Effects

According to quantum mechanics, electrons bound to atoms occur in specific electronic configurations. The highest energy configuration (or energy band) that is normally occupied by electrons for a given material is known as the valence band, and the degree to which it is filled largely determines the material's electrical conductivity. In a typical conductor (metal), the valence band is about half filled with electrons, which readily move from atom to atom, carrying a current. In a good insulator, such as glass or rubber, the valence band is filled, and these valence electrons have very little mobility. Like insulators, semiconductors generally have their valence bands filled, but, unlike insulators, very little energy is required to excite an electron from the valence band to the next allowed energy band—known as the conduction band, because any electron excited to this higher energy level is relatively free. For example, the "bandgap" for silicon is 1.12 eV (electron volts), and that of gallium arsenide is 1.42 eV. This is in the range of energy carried by photons of infrared and visible light, which can therefore raise electrons in semiconductors to the conduction band. Depending on how the semiconducting material is configured, this radiation may enhance its electrical conductivity by adding to an electric current already induced by an applied voltage or it may generate a voltage independently of any external voltage sources.

Thermionic Emission

His is the discharge of electrons from heated materials, widely used as a source of electrons in conventional electron tubes (e.g., television picture tubes) in the fields of electronics and communications. The phenomenon was first observed (1883) by Thomas A. Edison as a passage of electricity from a filament to a plate of metal inside an incandescent lamp.

In thermionic emission, the heat supplies some electrons with at least the minimal energy required to overcome the attractive force holding them in the structure of the metal. This minimal energy, called the work function, is characteristic of the emitting material and the state of contamination of its surface.

Exercise A

1. Describe the relationship between the energy of a photon and its frequency.
2. How was the ultraviolet catastrophe explained?
3. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
4. The vibrational energy of a plucked guitar string is said to be *quantized*. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?
5. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

Answers

1. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.
2.
3.
4.
5. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

Exercise B

1. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?

a. 4.33×10^5 m

b. 0.065 nm

c. 786 pm

2. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?

a. 250 photons with a wavelength of 3.0 m

b. 4.2×10^6 photons with a wavelength of 92 µm

c. 1.78×10^{22} photons with a wavelength of 2.1 Å

3. A 6.023×10^{23} photons are found to have an energy of 225 kJ. What is the wavelength of the radiation?

4. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that 1 W = 1 J/s, how many photons are emitted by the transmitter each second?

Answers

1.

a. 4.59×10^{-31} J/photon, radio

b. 3.1×10^{-15} J/photon, gamma ray

c. 2.53×10^{-16} J/photon, gamma ray

2.

3. 532 nm

4.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation.