CONCEPTS IN QUANTUM PHYSICS

CHAPTER 2: ORIGIN OF QUANTUM THEORY

2.1. Introduction

The concept that matter's main building blocks are intangibly tiny particles known as atoms is generally traced back to Greek philosophers Democritus of Abdera and Leucippus of Miletus in the 5th Century BC. John Dalton, an English chemist, advanced the Greeks' atomic philosophy into the true scientific theory in the initial years of the nineteenth Century (Khrennikov, 2002; Holik et al., 2014). His article **New System of Chemical Philosophy** gave convincing phenomenological proof for the presence of atoms and applied the atomic philosophy to chemistry, giving the physical depiction of how the elements combine in order to form compounds reliable with the laws of multiple and definite proportions. Table 2.1 summarizes some early measurements (by Sir Humphrey Davy) on the comparative proportions of oxygen and nitrogen in 3 gaseous compounds (Valentini & Westman, 2005; Zurek, 2007).

Table 2.1. Oxides of Nitrogen

Compound	Percent O	Percent N	Ratio
I	70.50	29.50	0.418
II	55.95	44.05	0.787
III	36.70	63.30	1.725

These compounds are identified as NO_2, NO &N_2O, respectively. It is observed in data like these a confirmation of the atomic theory of Dalton: that compounds comprise of atoms of the constituent elements combined in the ratios of a small whole number. The mass ratios given in Table 2.1 are, with modern precision, 0.438, 0.875, and 1.750.

After over two thousand years of reasoning and speculation from indirect proof, it is now probable in a sense to really *see* individual atoms, as displayed for instance in Figure 2.1. The word "atom" is derived from the Greek word *atomos*, meaning "indivisible." It became obvious in the late nineteenth century, though, that the atom wasn't truly the critical particle of matter. The work of Michael Faraday had proposed the matter's electrical nature and the presence of subatomic particles. This became evident with the innovation of radioactive decay in 1896 by Henri Becquerel the emission of alpha (**α)**, beta (**β)**, and gamma (γ) particles from atoms. J. J. Thompson in 1897 acknowledged electron as the universal constituent of all the atoms and exhibited that it carried a negative (-) electrical charge, now designated as -*e*.

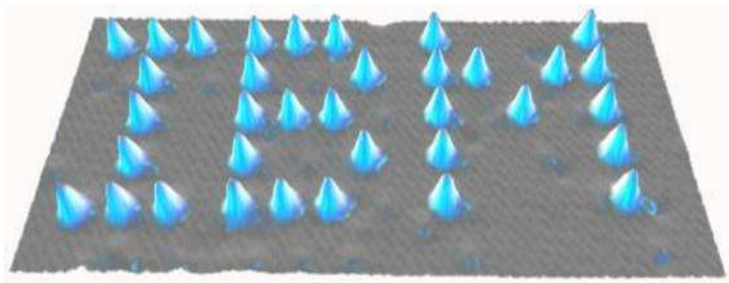

Figure 2.1. Image displaying electron clouds of the individual xenon (Xe) atoms on the nickel (110) surface produced by the scanning tunneling microscope at IBM Laboratories.

[Source:https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Quantum_Mechanics/01._Waves_and_Particles/Chapter_1%3A_Atoms_and_Photons%3A_Origin_of_Quantum_Theory]

To investigate the interior of an atom, in 1911 Ernest Rutherford bombarded the thin sheet of gold (Au) with the stream of positively (+ve) charged alpha (α) particles emitted by the radioactive source. The majority of the high energy alpha (α) particles passed through the foil of gold, but only some of them were detected strongly in a way that specified the existence of a small but immense positive (+ve) charge in the center of an atom (Figure 2.2). Rutherford anticipated the nuclear model of an atom (Luryi, 1991; Ladd et al., 2010). As now it is understood, an electrically-neutral atom having atomic number Z comprises of a nucleus of the positive charge $+Ze$, comprising almost the complete the mass of an atom, encircled by Z electrons of small mass, each having a charge $-e$. Hydrogen is the simplest atom, with $Z = 1$, comprising of a single electron $-e$ outside the single proton of charge $+e$.

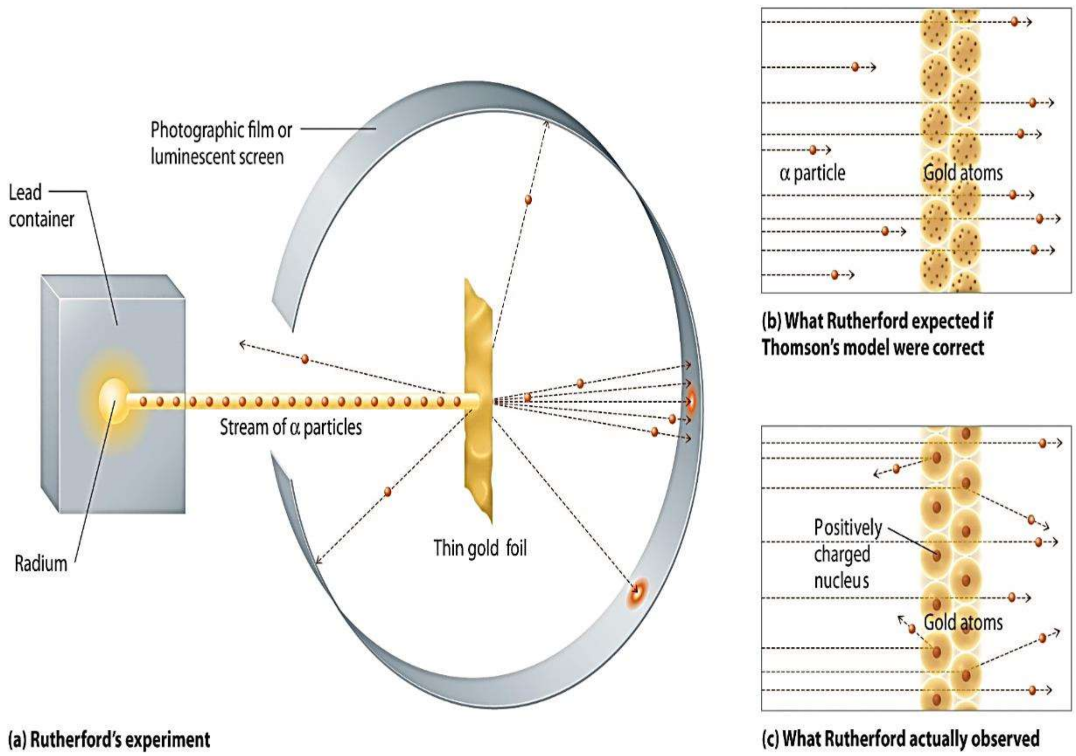

Figure 2.2. An Overview of Rutherford's Experiments

(a) An illustration of the apparatus used by Rutherford in order to detect deflections in the stream of alpha particles aimed at the thin gold foil target. The alpha particles were produced by the sample of radium. (b) If the model of the atom proposed by Thomson were correct, the alpha particles should have passed through the foil of gold. (c) But some of the alpha particles were deflected in several directions, as well as right back at the source. This could only be true if the positive (+ve) charge were more massive than the alpha particle. It recommended that the mass of the gold atom is focused in a very small section of space, which Rutherford called the nucleus.

[Source: https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s05-05-the-atom.html]

With the innovation of the neutron in 1932 by Chadwick, the structure of the atomic nucleus was explained. A nucleus of mass number A and atomic number Z was made up of Z protons and A-Z neutrons. Nuclei diameters are normally of the order of numerous times 10^{-15}m. From the viewpoint of an atom, which is normally 10^5 times larger, for most purposes, a nucleus behaves like a point charge $+Ze$ (Goyal et al., 2010).

During the 1960s, convincing evidence began to appear that neutrons and protons themselves had amalgamated structures, with main contributions by Murray Gell-Mann. According to the presently accepted "Standard Model," the neutron and protons are each made of 3 *quarks*, with compositions *add* and *uud*, respectively (Goyal & Knuth, 2011; Kawaguchi et al., 2012). The up quark *u* has the charge of +2/3e, whereas the down quark d has the charge of $-1/3e$. In spite of heroic experimental struggles, individual quarks haven't been isolated, obviously putting them in the same group with magnetic monopoles. By contrast, the electron preserves its status as an inseparable elementary particle (Dürr et al., 1998; Kaniadakis, 2002).

2.2. Electromagnetic Waves

Perhaps the greatest accomplishment of physics in the nineteenth century was James Clerk Maxwell's unification of the phenomena of magnetism, electricity, and optics in 1864 (Ron & Tzoar, 1963; Beckmann & Spizzichino, 1987; Tsang et al., 2004). In 1887 Heinrich Hertz was the first to validate experimentally the detection and production of the electromagnetic waves anticipated by Maxwell-specifically radio waves by an acceleration of the electrical charges. As displayed in Figure 2.3, electromagnetic waves comprise of mutually perpendicular magnetic and electric fields, **B and E** respectively, oscillating in synchrony at the high frequency and spreading in the direction of **E** x **B** (Tsang & Kong, 1980; Rakhmanov et al., 2008; Wait, 2013).

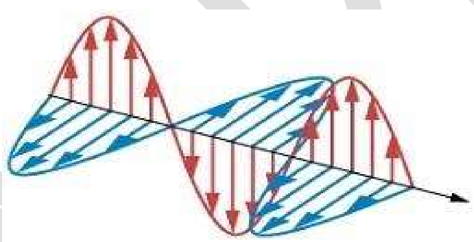

Figure 2.3. Schematic demonstration of the monochromatic linearly polarized electromagnetic wave.

[Source: https://en.wikipedia.org/wiki/Polarization_(waves)]

The wavelength λ is defined as the distance between consecutive maxima of the magnetic (or electric) field. The frequency ν signifies the number of oscillations in one second observed at the fixed point in space. The reciprocal of ν $\tau = 1/\nu$ signifies a period of oscillation-the time taken by one wavelength to pass the fixed point. The propagation speed of the wave is thus determined by $\lambda = c\tau$ or

$$\lambda\nu = c$$

Where $c = 2.9979 \times 10^8$m/sec, generally known as *the speed of light*, applicable to all of the electromagnetic waves in vacuum. Frequencies are expressed in Hz (hertz), defined as the no of oscillations in one second.

Electromagnetic radiation is known to occur in an enormous range of wavelengths including X-rays, ultraviolet, gamma rays, infrared, visible light, microwaves, and radio waves (Berenger, 1994; Tsang et al., 2004; Shukla et al., 2006; 2007; 2012).

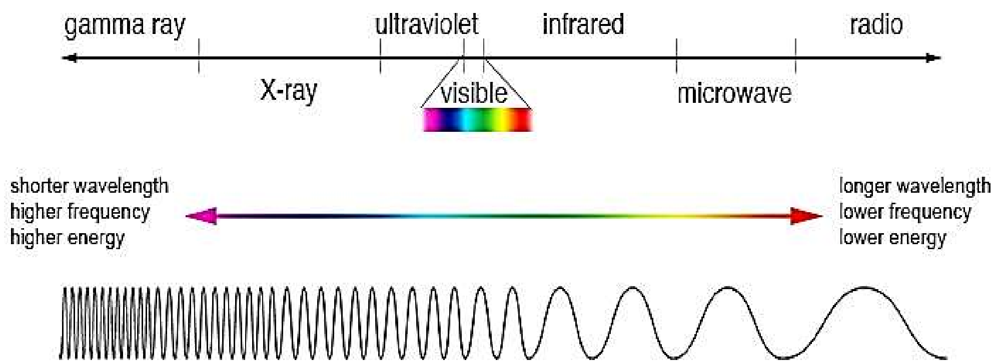

Figure 2.4. The electromagnetic spectrum, exhibiting wavelengths of different kinds of radiation

[Source: https://imagine.gsfc.nasa.gov/science/toolbox/emspectrum1.html]

2.3. 3 Failures of Classical Physics

A masterwork of Isaac Newton, *Principia*, published in 1687, can be well-thought-out to mark the commencement of modern physical science. Not only did Newton outline the fundamental laws governing gravitation and motion but he established the general philosophical worldview which saturated all scientific theories for 2 centuries afterward (Korolev, 2007; Norton, 2008). This thinking system about the physical world is called "Classical Physics." Its most distinguishing feature is the importance of cause and effect relationships (Boyer, 1969). Given adequate information regarding the current state of some part of the Universe, it must be possible, nevertheless in principle, to forecast its future behavior. This capability is called *determinism*. For instance, lunar and solar eclipses can be anticipated centuries ahead, within a precision of several seconds. The other pillar of classical physics is the theory of electromagnetism given by Maxwell (Carazza & Robotti, 2002; Earman, 2008; Virk, 2014).

The beginning of quantum theory can be manifested by 3 varied phenomena comprising electromagnetic radiation, which couldn't be sufficiently explained by the techniques of classical physics. The first among these phenomena was blackbody radiation, which directed to the involvement of Max Planck in 1900. Next among these was the photoelectric effect, treated in 1905 by Albert Einstein. A third was the beginning of line spectra, treated by Neils Bohr in 1913. A comprehensible formulation of the quantum mechanics was ultimately developed in 1925 and 1926, predominantly the work of Heisenberg, Schrödinger, and Dirac. The next sections of this chapter will define the early contributions to quantum theory by Einstein, Planck, and Bohr (Schiller, 1967; Billah & Scanlan, 1991).

2.3.1. Blackbody Radiation

It is a matter of experience that hot objects can emit radiation. A metal piece stuck into the flame can become red hot. At higher temperatures, the glow of metal can be defined as white-hot. Under even more severe thermal excitation the metal piece can emit principally blue light. The well-known pottery designer, Josiah Wedgwood, noted in 1782 that different materials usually turn red hot at the same temperature (Dicke et al., 1965; Smoot et al., 1977). The quantitative association between temperature and color is defined by *blackbody radiation law*. A blackbody is a perfect emitter and absorber of all probable wavelengths of the radiation. Figure 2.5 displays experimental wavelength distributions of the thermal radiation at various temperatures. Consistent with experience, the maximum in distribution, which defines the predominant color, increases with temperature (Silk, 1968; Gallagher & Cooke, 1979). This association is given by Wien's displacement law and can be expressed as:

$$T\lambda_{max} = 2.898 \times 10^{6} \text{ nmK}$$

Where the wavelength is given in nanometers (nm). At room temperature, the maximum takes place around 10 µm, in the IR region. In Figure 2.5, the estimated values of λ_{max} are 500n m at 5800 K, 1450 nm at 2000 K, and 2900 nm at 1000 K, the estimated surface temperature of the Sun. The λ_{max} of Sun is near the middle of the visible range (380-750nm) and is observed by eyes as white light (Ford et al., 1985; Dunbar & McMahon, 1998).

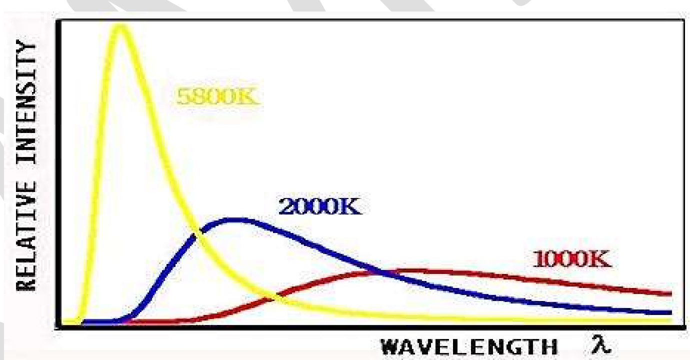

Figure 2.5. Intensity distributions of the blackbody radiation at 3 different temperatures. The total radiation intensity fluctuates as T4 (Stefan-Boltzmann law) thus the total radiation at 2 thousand K is normally 24 = 16 times than that at 1 thousand K

[Source: http://www.umich.edu/~chem461/QM%20Chap%201.pdf]

The origin of the blackbody radiation was the main challenge to nineteenth Century physics. Lord Rayleigh suggested that the electromagnetic field might be signified by the collection of oscillators of all probable frequencies. By simple geometry, the higher frequency modes of oscillation are increasingly abundant as it is feasible to fit the waves into an enclosure in a larger number of arrangements. Actually, no of oscillators increases very quickly as λ^{-4}. Rayleigh anticipated that every oscillator backed equally to the radiation. This agrees quite well with the experiment at low frequencies. But if higher frequencies and ultraviolet rays were produced in increasing numbers, one would get roasted by sitting in front of the fireplace! Fortunately, this does not happen, and the inappropriate theory is said to agonize from an "ultraviolet catastrophe" (Hun et al., 2008).

In 1900 Max Planck derived the accurate form of blackbody radiation law by presenting a bold postulate. He suggested that energies involved in emission and absorption of electromagnetic radiation didn't belong to the continuum, as inferred by Maxwell's theory, but were in reality composed of discrete bundles which he called quanta. Planck's idea is conventionally considered as marking the start of the quantum theory. A quantum linked with the radiation of frequency ν has energy

$$E = h\nu$$

Where the factor of proportionality $h = 6.626 \times 10^{-34}$ J sec is called the Planck's constant. For the development of a quantum theory of molecules and atoms, only this simple result is needed (Greenstein & Hartke, 1983).

2.3.2. The Photoelectric Effect

A familiar device in modern technology is photocell or electric eye, which runs a range of valuable gadgets, comprising automatic door openers. The principle indulges in the devices is the photoelectric effect, which was observed first by Heinrich Hertz in the laboratory in which he invented electromagnetic waves. Visible or UV radiation imposing on the clean metal surfaces can trigger electrons to be emitted from the metal. Such an effect isn't, in itself, unpredictable with classical theory as electromagnetic waves are recognized to carry momentum and energy. But the comprehensive behavior as the function of intensity and radiation frequency can'*t* be explained classically (Pratt et al., 1973; Sorokin et al., 2007).

The energy needed to eject an electron from the metal is defined by its *work function* Φ. For instance, sodium (Na) has $\Phi = 1.82$eV. The electron-volt is the appropriate energy unit on the atomic scale: 1 eV = 1.602×10^{-19}J. This resembles energy that an electron gathers when accelerated across the potential difference of one volt. The classical anticipation would be that the radiation of adequate intensity must cause the discharge of electrons from the metal surface, with the kinetic energies increasing with radiation intensity. Furthermore, the time delay would be projected between the absorption of the radiation and the ejection of the electrons (Glover et al., 1996; Miaja-Avila et al., 2006). The experimental facts are far different. It is discovered that the electrons are not ejected, no matter how high the intensity of radiation, unless the *frequency of radiation* surpasses some threshold value ν_0 for every metal. For sodium $\nu_0 = 4.39 \times 10^{14}$ Hz, as displayed in Figure 2.6. For frequencies above the threshold value, the ejected electrons attain kinetic energy given as:

$$\frac{1}{2} mv^2 = h(\nu - \nu_0) = h\nu - \Phi$$

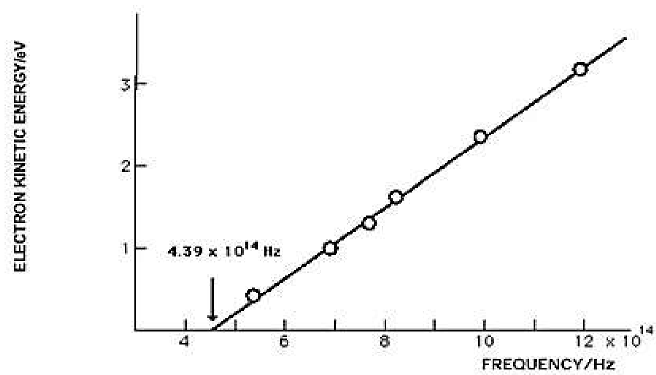

Figure 2.6. Photoelectric data for Na (sodium) (Millikan, 1916). The threshold frequency ν_0, discovered by extrapolation, equals 4.39 x 10 14Hz

[Source: http://www.umich.edu/~chem461/QM%20Chap%201.pdf]

Obviously, the work function Φ can be recognized with $h\nu_0$, equal to the 3.65 x 10^{-19}J=1.82 eV for Na (sodium). The kinetic energy *linearly increases* with a frequency above the threshold value but is independent of radiation intensity. Increased intensity does, though, increase the *no* of photoelectrons (Feibelman, 1975; Ho et al., 2005).

Einstein's explanation of the photoelectric effect in the year 1905 seems immaterially simple once stated. He accepted the hypothesis of Planck that the quantum of radiation normally carries an energy $h\nu$. Therefore, if an electron is bound in the metal having an energy Φ, the quantum of energy $h\nu_0 = \Phi$ will be adequate to dislodge it. And any surplus energy $h(\nu - \nu_0)$ will act as the kinetic energy of the ejected electron. Einstein thought that the radiation field did comprise of quantized particles, which Einstein called *photons*. Even though Planck himself never thought that quanta were real, the success of Einstein with the photoelectric effect advanced the idea of energy quantization greatly (Adawi, 1964; Clauser, 1974).

2.3.3. Line Spectra

The majority of what is identified about atomic and molecular structure and the mechanics has been inferred from spectroscopy. Figure 2.7 displays two different kinds of spectra. The continuous spectrum can normally be produced by a glowing gas or solid at high pressure. Blackbody radiation, for instance, is a continuum. An emission spectrum can only be produced by the gas at low pressure excited by collisions with the electrons or by heat. An absorption spectrum outcomes when light from the continuous source passes through the cooler gas, comprising of a sequence of dark lines typical of the composition of a gas. Frauenhofer between 1814 and 1823 found almost six hundred dark lines in the solar spectrum observed at high resolution. It is now fully understood that the lines are triggered by absorption by outer layers of the Sun (Doniach & Sunjic, 1970; Baldwin et al., 1981).

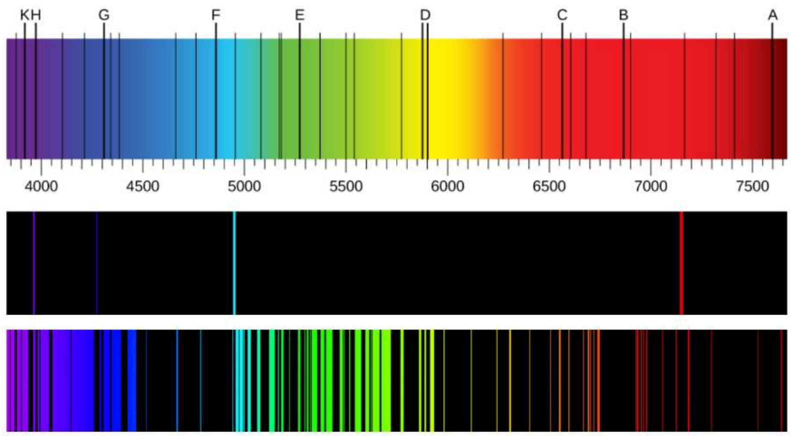

Figure 2.7. ***In the solar emission spectrum in the visible range (380 nm to 710 nm), Fraunhofer lines are perceived as black lines (vertical) at particular spectral positions in a continuous spectrum.***

Highly sensitive modern instruments detect thousands of such lines. The emission spectrum of the atomic hydrogen: The spectral positions of the emission lines are typical for hydrogen atoms.

[Source: http://www.umich.edu/~chem461/QM%20Chap%201.pdf]

Gases heated to luminosity were discovered by Kirkhoff, Bunsen, and others in order to emit light with a sequence of sharp wavelengths. The emitted light examined by a spectrometer seems like a multitude of narrow bands of color. These *line spectra* are representative of the atomic composition of a gas. The line spectra of various elements are displayed in the following figure (Kennicutt Jr, 1992; Cappellari & Emsellem, 2004).

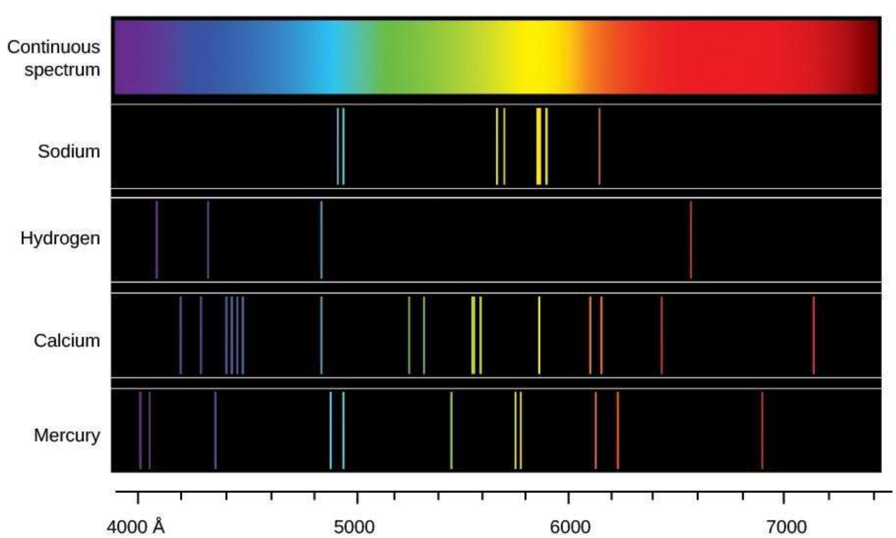

Figure 2.8. ***Emission spectra of various elements.***

[Source: https://courses.lumenlearning.com/astronomy/chapter/spectroscopy-in-astronomy/]

It is reliable with the classical theory of electromagnetics that the motions of electrical charges inside atoms can be linked with the emission and absorption of radiation. What is entirely enigmatic is how such kind of radiation can take place for discrete frequencies, instead of as a continuum. The breakthrough that clarified line spectra is attributed to Neils Bohr in 1913. Building on the concepts of Einstein and Planck, Bohr hypothesized that the levels of energy of atoms belong to the distinct set of values E_n, instead of a continuum as in classical mechanics. When the atom triggers a downward energy transition from higher energy level E_m to the lower energy level E_n, it instigated the emission of a photon having energy

$$h\nu = E_m - E_n$$

This is what interprets the distinct frequency ν values in the emission spectra of atoms. Absorption spectra are consistently linked with the eradication of a photon having the same energy and associated excitation of the atom from lower energy level E_n to higher energy level E_m. Figure 2.9 is a representation of the procedures of emission and absorption of photons by atoms. Absorption and emission processes take place at the same set frequencies (Van der Tak et al., 2007).

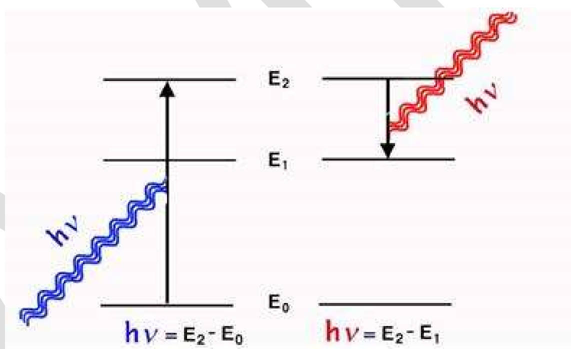

Figure 2.9. Origin of the line spectra. Absorption of photons displayed in blue triggers the atomic transition from E0 to E2. The transition from E2 to E1 triggers the emission of the photon displayed in red.

[Source: http://www.umich.edu/~chem461/QM%20Chap%201.pdf]

Rydberg (1890) discovered that all the lines of atomic hydrogen spectrum might be fitted to the simple empirical formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), n = 1, 2, 3\ldots, n_2 > n_1$$

where R, called the Rydberg constant, possesses the value 109,677 cm^{-1}. This formula was discovered to be effective for the hydrogen spectral lines in the ultraviolet and infrared regions, along with the 4 lines in the visible region. No simple formula has been discovered for any atom in addition to hydrogen. Bohr suggested a model for the levels of energy of the hydrogen atom which approved with Rydberg's formula for the radiative transition frequencies (Davidson, 1972). Motivated by Rutherford's nuclear atom, Bohr proposed a planetary model for a hydrogen atom. In his model, the electron goes near the proton in one of the sets of permitted circular orbits, as exhibited in Figure 2.10. A more essential understanding of the distinct nature of energy levels and orbits had to wait for the discoveries of 1925-26, but the model of Bohr provided a priceless stepping-stone to the advancement of quantum mechanics (Trager et al., 1998; Springobet al., 2005).

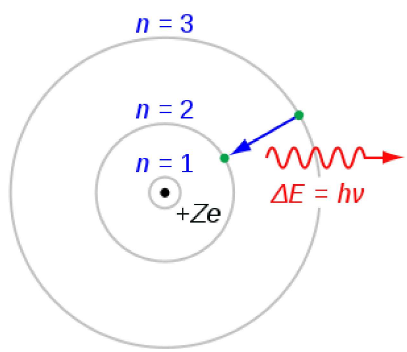

Figure 2.10. Bohr model of hydrogen atom displaying 3 lowest-energy orbits.

[Source: https://en.wikipedia.org/wiki/Bohr_model]

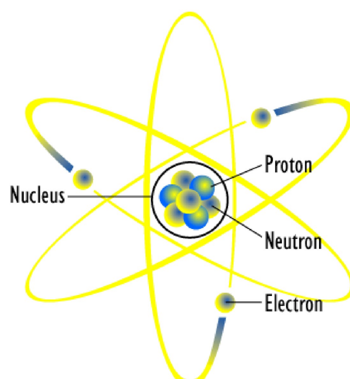

Figure 2.11. A stylized demonstration of the Bohr model for the multi-electron atom.

[Source: https://www.khanacademy.org/science/physics/quantum-physics/atoms-and-electrons/a/bohrs-model-of-hydrogen]

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