LIMITATIONS OF OLD QUANTUM THEORY

The main shortcomings of the old quantum theory are that it could not

(i) be applied to non-periodic systems.

(ii) explain the spectral lines of system like hydrogen molecule and normal helium atom.

(iii) give any information about the transition probabilities and intensity of spectral lines. .

(iv) explain the process connected with the electron spin and Pauli's exclusion principle.

(v) explain the dispersion of light.

De-Broglie (1925) and Schrodinger's wave equation satisfied these matter waves.

Even though the spectral nature of light is present in a rainbow, it was not until 1666 that Isaac Newton showed that white light from the sun is composed of a continuum of colors (frequencies). Newton introduced the term "spectrum" to describe this phenomenon. His method to measure the spectrum of light consisted of a small aperture to define a point source of light, a lens to collimate this into a beam of light, a glass spectrum to disperse the colors and a screen on which to observe the resulting spectrum. This is indeed quite close to a modern spectrometer! Newton's analysis was the beginning of the science of spectroscopy (the study of the frequency distribution of light from different sources).

The first observation of the discrete nature of emission and absorption from atomic systems was made by Joseph Fraunhofer in 1814. He noted that when sufficiently dispersed, the spectrum of the sun was not continuous, but was actually missing certain colors as depicted in Fig. 3.2. These appeared as dark lines in the otherwise continuous spectrum, now known as Fraunhofer lines. (These lines were observed earlier (1802) by William H. Wollaston, who did not attach any significance to them.) These were the first spectral lines to be observed. Fraunhofer made use of them to determine standards for comparing the dispersion of different types of glass. Fraunhofer also developed the diffraction grating to enable not only greater angular dispersion of light, but also standardized measures of wavelength. The latter could not be achieved using glass prisms since the dispersion depended on the type of glass used, which was difficult to make uniform. With this, he was able to directly measure the wavelengths of spectral lines. Fraunhofer's achievements are all the more impressive, considering that he died at the early age of 39.

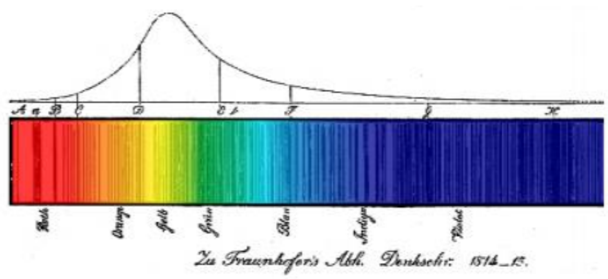

Figure 3.2: Fraunhofer spectrum of the sun. Note the dark lines in the solar spectrum.

The origin of the solar spectral lines were not understood at the time though. It was not until 1859, when Gustav Kirchoff and Robert Bunsen, realized that the solar spectral lines were due to absorption of light by particular atomic species in the solar atmosphere. They noted that several Fraunhofer lines coincided with the characteristic emission lines observed in the spectra of heated elements. By realizing that each atom and molecule has its own characteristic spectrum, Kirchoff and Bunsen established spectroscopy as a tool for probing atomic and molecular structure. There are two ways in which one can observe spectral lines from an atomic species. The first is to excite the atoms and examine the light that is emitted. Such emission spectra consist of many bright “lines” in a spectrometer, as depicted in Fig. 3.3. The second approach is to pass white light with a continuous spectrum through a glass cell containing the atomic species (in gas form) that we wish to interrogate and observe the absorbed radiation. This absorption spectrum will contain dark spectral lines where the light has been absorbed by the atoms in our cell, illustrated in Fig. 3.3. Note that the number of spectral lines observed by absorption is less than those found through emission.

The road to understanding the origins of atomic spectral lines began with a Swiss schoolmaster by the name of Johann Balmer in 1885, who was trying to understand the spectral lines observed in emission from hydrogen. He noticed that there were regularities in the wavelengths of the emitted lines and found that he could determine the wavelengths with the following

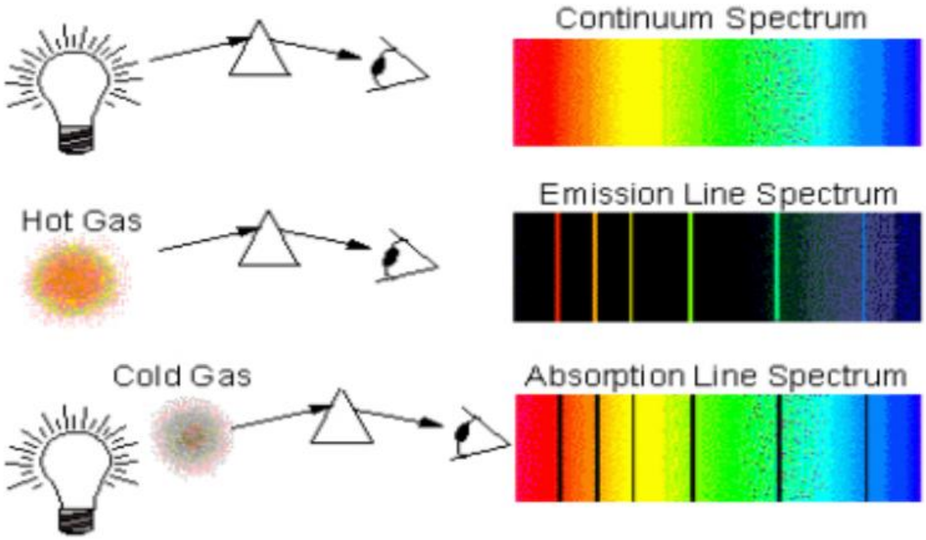

Figure 3.3: Spectra from various experimental setups demonstrating emission and absorption spectra. Spectrum from a white light source (top). Emission spectrum from a hot atomic gas vapor (could also be electrically excited). Absorption spectrum observed when white light is passed through a cold atomic gas.

formula

$$\lambda = \lambda_0 \left(\frac{1}{4} - \frac{1}{n^2} \right)^{-1}, \tag{3.1}$$

where n is an integer greater than two, and λ_0 is a constant length of 364.56 nm. This empirical result was generalized by Johannes Rydberg in 1900 to describe all of the observed lines in hydrogen by the following formula

$$\lambda = \left(\frac{R}{hc} \right)^{-1} \left(\frac{1}{m} - \frac{1}{n^2} \right)^{-1}, \tag{3.2}$$

where m and n are integers ($m < n$), R is known as the Rydberg constant ($R = 13.6$ eV), h is Planck's constant (6.626×10^{-34} Js) and c is the speed of light in vacuum. Although a concise formula for predicting the emission wavelengths for hydrogen were known, there was no physical description for the origin of these discrete lines. The leading theory of the day was that atoms and molecules had certain resonance frequencies at which they would emit, but there was no satisfactory description of the physical origins of these resonances. Furthermore, there were no other closed formulae to predict the emission spectral lines of other, more complex, materials. To take the next steps in understanding these questions required a model of the atom from which the radiation is emitted or absorbed.

BOHR'S ATOMIC MODEL

In 1911, fresh from completion of his PhD, the young Danish physicist Niels Bohr left Denmark on a foreign scholarship headed for the Cavendish Laboratory in Cambridge to work under J. J. Thomson on the structure of atomic systems. At the time, Bohr began to put forth the idea that since light could no long be treated as continuously propagating waves, but instead as discrete energy packets (as articulated by Planck and Einstein), why should the classical Newtonian mechanics on which Thomson's model was based hold true? It seemed to Bohr that the atomic model should be modified in a similar way. If electromagnetic energy is quantized, i.e. restricted to take on only integer values of hν, where ν is the frequency of light, then it seemed reasonable that the mechanical energy associated with the energy of atomic electrons is also quantized. However, Bohr's still somewhat vague ideas were not well received by Thomson, and Bohr decided to move from Cambridge after his first year to a place where his concepts about quantization of electronic motion in atoms would meet less opposition. He chose the University of Manchester, where the chair of physics was held by Ernest Rutherford. While in Manchester, Bohr learned about the nuclear model of the atom proposed by Rutherford.

To overcome the difficulty associated with the classical collapse of the electron into the nucleus, Bohr proposed that the orbiting electron could only exist in certain special states of motion - called stationary states, in which no electromagnetic radiation was emitted. In these states, the angular momentum of the electron L takes on integer values of Planck's constant divided by 2π, denoted by ~ = h/2π (pronounced h-bar). In these stationary states, the electron angular momentum can take on values ~, 2~, 3~, ..., but never non-integer values. This is known as quantization of angular momentum, and was one of Bohr's key hypotheses. Note that this differs from Planck's hypothesis of energy quantization, but as we will see it does lead to quantization of energy. For circular orbits, the position vector of the electron r is always perpendicular to its linear momentum p. The angular momentum **L** = **r** × **p** has magnitude L = rp = $m_e$vr in this case. Thus Bohr's postulate of quantized angular momentum is equivalent to

$$m_e v r = n\hbar, \tag{3.7}$$

where n is a positive integer. This can be solved to give the velocity

$$v = \frac{n\hbar}{m_e r}. \tag{3.8}$$

Using this result in Eq. (3.3),

$$\frac{m_e v^2}{r} = \frac{m_e}{r}\left(\frac{n\hbar}{m_e r}\right)^2 = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}, \tag{3.9}$$

we find a series of allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}n^2 = a_0 n^2. \tag{3.10}$$

Here $a_0 = 0.0529$ nm is known as the Bohr radius. Equation (3.10) gives the allowed radii for electrons in circular orbits of the hydrogen atom.

This is a significant and unexpected result when compared to the classical behavior discussed previously. A satellite in a circular orbit about the earth can be placed at any altitude (radius) by providing an appropriate tangential velocity. However, electrons are only allowed to occupy orbits with certain discrete radii. Furthermore, this places constraints to the allowed velocity, momentum, and total energy of the electron in the atom. By using Eq. (3.10) we can find the allowed velocity, momentum, and total energy in hydrogen are given by

$$v_n = \frac{\hbar}{m_e a_0 n}, \tag{3.11}$$

for the quantized velocity,

$$p_n = \frac{\hbar}{a_0 n}, \tag{3.12}$$

for the quantized momentum (note we assume nonrelativistic momentum), and

$$E_n = -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0}\frac{1}{n^2} = -\frac{E_1}{n^2}, \tag{3.13}$$

for the quantized energy levels. Here $E_1 = 13.6$ eV is the ground state energy of the system.

The energy levels are indicated schematically in Fig. 3.6. The electron energy is quantized, with only certain discrete values allowed. In the lowest energy level, known as the ground state, the electron has energy $E_1 = 13.6$ eV. The higher states, $n = 2, 3, 4, \ldots$ with energies -3.6 eV, -1.5 eV, -0.85 eV, ... are called excited states. The integer, n that labels both the allowed radius and energy level, is known as the *principle quantum number* of the atom. It tells us what energy level the electron occupies.

When the electron and nucleus are separated by an infinite distanc $(n \to \infty)$ we have $E = 0$. By bringing the electron in from infinity to particular state n, we release energy $E = -(E_{\text{final}} - E_{\text{initial}}) = |E_n|$ (not the minus sign comes from the energy being released). Similarly, if we star with an atom in state n, we must supply at least $|E_n|$ to free the electron This energy is known as the *binding energy* of the state n. If we supply mor

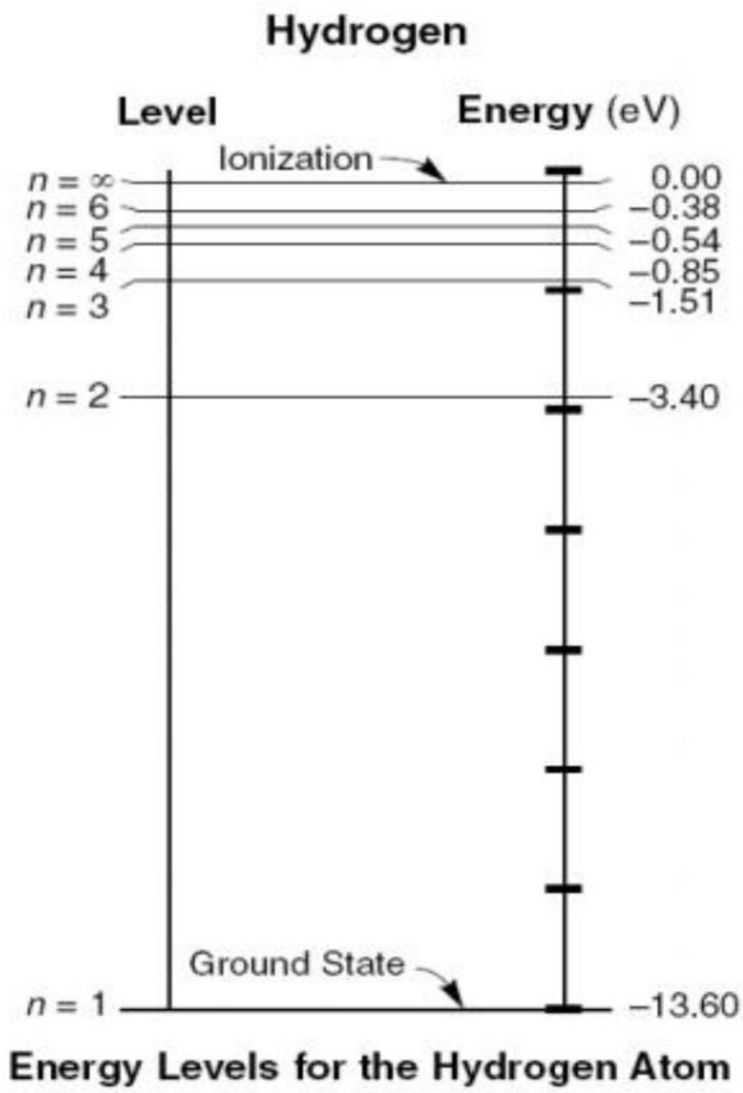

Figure 3.6: Schematic representation of the discrete allowed energy levels in the hydrogen atom.

energy than $|E_n|$ to the electron, then the excess beyond the binding energy will appear as kinetic energy of the freed electron.

The *excitation energy* of an excited state n is the energy above the ground state, $E_n - E_1$. For the first excited state, $n = 2$, the excitation energy is

$$\Delta E = E_2 - E_1 = -3.4 \text{ eV} - (-13.6 \text{ eV}) = 10.2 \text{ eV}. \tag{3.14}$$

Once Bohr had worked out that the energy levels of hydrogen were quantized, i.e. only allowed to take on discrete values, he was able to easily describe the spectral lines observed for hydrogen if he were to posit a second postulate: radiation can only be emitted when the atom makes a transition from one energy level, say n, to another with lower energy, $m < n$. The energy of the emitted photon will thus be given by the difference in energy between these two levels

$$E_{\text{ph}} = E_m - E_n = E_1 \left(\frac{1}{m^2} - \frac{1}{m^2} \right). \tag{3.15}$$

Using Planck's relation between energy and frequency, $E = h\nu$, we can see that the expected frequency spectral lines are

$$\nu = \frac{E_1}{h} \left(\frac{1}{m^2} - \frac{1}{m^2} \right), \tag{3.16}$$

or in terms of wavelength

$$\lambda = \frac{hc}{E_1} \left(\frac{1}{m^2} - \frac{1}{m^2} \right)^{-1}. \tag{3.17}$$

Comparison of this with Rydberg's empirical formula, Eq. (1.2), Bohr identified his ground state energy value, $E_1 = 13.6$ eV with the experimentally determined Rydberg constant, $R = 13.6$ eV. These two agreed well within experimental errors of the time.

Note that Bohr's second postulate, i.e. the energy of an emitted photon from an atom is given by the difference in energy level, contradicts the concepts of classical physics in which an oscillating charge emits radiation at its frequency of oscillation. For an electron in state n with energy E_n, its oscillation frequency is just $\nu_n = E_n/h$. Taken together, Bohr's postulates can be summarized as follows

Bohr's postulates

- Quantized angular momentum: $L = m_e vr = n\hbar$.
- Radiation is only emitted when an atom makes transitions between stationary states: $E_{\text{ph}} = E_m - E_n$.

By examining Eq. (3.12), we see that this can be rewritten as

$$\frac{h}{p_n} = 2\pi a_0 n = \frac{2\pi r_n}{n}. \tag{3.18}$$

As we will see when we discuss the wave nature of matter and the de Broglie wavelength, the quantization of angular momentum, which leads to allowed orbits with radii $r_n = a_0 n^2$ and momenta $p_n = \hbar/a_0 n = \hbar n/r_n$ implies that the circumference of the allowed states is an integer multiple of the de Broglie wavelength $\lambda_{\text{dB}} = h/p$

$$n\lambda_{\text{dB}} = 2\pi r_n \tag{3.19}$$

which follows easily from Eq. (3.18) above.