

Chapter 3

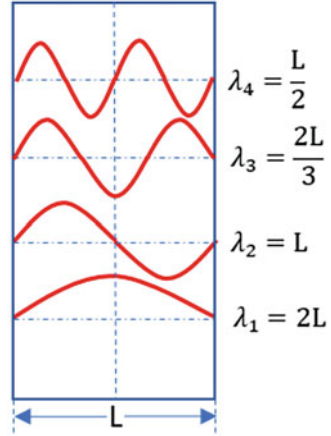
Quantization of Energy



3.1 Introduction

Until the discovery of the photoelectric effect in 1902 [1], everything seemed to be falling in place and physics moved forward with no qualms. The behavior of light and matter, the two facets of nature, could be accurately described by the wave theory and Newtonian mechanics, respectively. The discovery of the photoelectric effect, which unequivocally established the dual nature of light, viz., its ability to manifest both as a particle and wave, turned things around forever. It was not long before the dual nature of waves led to the realization of the dual nature of particles as well. This revolutionary insight into the behavior of particles, although it fetched a 1924 Nobel Prize in Physics to Louis de Broglie, dragged physics into rough weather. It is common knowledge that waves, when bounded by a constraint, can exist only at discrete frequencies or wavelengths. For example, in the case of a rope, rigidly clamped at the two ends, only waves, half of whose wavelength times an integer equals the rope's length, can be impressed upon it. Alternatively, an optical cavity can contain only that light whose wavelength also bears a similar relationship to the length of the cavity. Ascription of the wave nature to a particle, therefore, means that if the particle is confined within a region in space, the wavelengths that fit into this space will only be allowed. This restriction on wavelength, in turn, restricts the values of energy [17] that the particle can possess. While quantization of matter into lumps of atoms, molecules, and the like was well known, the very concept of discretization of its energy states seemed to have flummoxed the physics community in the early part of twentieth century. After all, quantization of energy of a particle would be analogous to having only certain specific speeds at which a car can travel, a soccer ball can be kicked, or a baseball can be struck! Fortunately, matter does not behave this way in our world despite its wavy nature. Where lies the catch then? This chapter has been planned to strike a sense of understanding, albeit qualitatively, to the mind of the readers on the implication of quantization of the energy states in the

Fig. 3.1 Discretization of the de Broglie wavelengths of a particle trapped in a box



macroscopic world we are familiar with. The chapter also mirrors the manifestation of the wave nature of a bound microscopic particle into the spectral emission from atoms and molecules that, in turn, would eventually lead to the realization of lasers.

3.2 A Bound Particle and Discretization of Its Energy

To gain deeper insight into the wavy matter, it is imperative that we consider a particle of mass m that is trapped inside a box and bouncing back and forth between its two walls spaced by a distance of L . We further assume that these two walls are infinitely rigid and the particle, therefore, cannot lose any energy on the walls every time it hits them. The situation is schematically illustrated in the traces of Fig. 3.1. Considering the wave picture, the wave length λ of this particle, which is analogous to the particle nature of light, called the de Broglie wave length, can be shown to be [18].

$$\lambda = h/mv \quad (3.1)$$

where h is Planck's constant and v is the velocity of the particle. Drawing an analogy to the waves set in a rope with its two ends rigidly clamped, we surmise that here too an infinite number of waves can be associated with the particle all of which will be characterized by zero displacements at the two rigid walls. It thus readily follows that the de Broglie wavelengths are intricately linked to the spacing L between the walls and the longest of them λ_1 , which also happens to be the fundamental of all these possible waves, will be obviously given by

$$\lambda_1 = 2L$$

And the next one will be $\lambda_2 = L$, and the next $\lambda_3 = \frac{2L}{3}$, the next $\lambda_4 = L/2$, and so on.

Upon generalizing all these into a single formula of permitted wavelengths, we obtain.

$$\lambda_n = \frac{2L}{n} \text{ (where } n \text{ is an integer)} \quad (3.2)$$

The kinetic energy of the particle can be expressed as

$$KE = \frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{h^2}{2m\lambda^2} \text{ (Substituting } mv \text{ from 3.1)} \quad (3.3)$$

As the particle has no potential energy, its total energy, upon combining Eqs. 3.2 and 3.3, can be expressed as

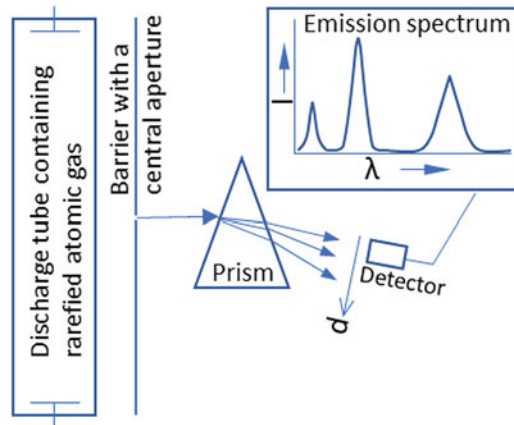
$$E_n = \frac{(nh)^2}{8mL^2} \quad n = 1, 2, 3, 4, \quad (3.4)$$

Obviously, therefore, the restriction on its wavelength also restricts the energy that the particle can possess. Each permitted energy is identified as an energy level, and the corresponding n is called its quantum number. An important inference that can be drawn from this equation is that Planck's constant being so small ($h = 6.64 \times 10^{-34}$ joule-sec) energy quantization becomes relevant only when m and L are also sufficiently small, a signature of the microscopic world comprising of electrons, atoms, molecules, and the likes.

To drive this point home, let us consider the typical case of a football of mass 0.1 kg moving between the two walls of a room spaced by 10 m. Upon plugging these values into Eq. 3.4, we obtain the minimum energy of the ball, which corresponds to $n = 1$, to be $\sim 5 \times 10^{-69}$ J. A 0.1 kg football possessing this KE will move with a velocity of $\sim 3 \times 10^{-33}$ m/s, which is vanishingly small and is practically indistinguishable from the one that is at rest! If this ball has to travel at a modest speed of 1 m/s, the corresponding energy level will have a quantum number on the order of 10^{33} . In the limit of such enormously high quantum numbers, the successive energy levels are positioned relatively so close, resulting practically in an energy continuum.¹ Thus, in the macroscopic world quantization of energy becomes inconsequential and Newtonian mechanics prevails.

¹A continuous sequence in which the adjacent energy levels are not perceptibly different from each other

Fig. 3.2 The emission of the fluorescent light after dispersion through a prism is scanned by a detector. The intensity recorded by the detector as a function of the wavelength of emission is also shown here for a narrow spectral range. In reality, the spectrum will obviously be much richer containing many more emission lines

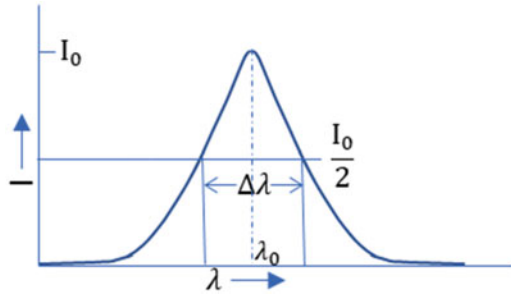


3.3 Spectral Emission from an Atomic Source

The fluorescent light sources are now in extensive use for illuminating our household and eye-catching displays at night throughout the world. The emission from such a source holds a wealth of science, the gradual decoding of which allowed physics to turn the sharp corner, stemming largely from the discovery of the photoelectric effect and a host of other great advances that soon followed. It is imperative at this point to delve a little into the emission of this source. To this end, we perform a simple experiment schematically described in Fig. 3.2. In fluorescent light (elaborated in Sect. 4.2, Chap. 4), an electric discharge is impressed upon a rarefied atomic gas contained in a glass tube. This causes the tube to emit light spontaneously all around it. By placing an opaque barrier with a central hole to one side of the tube, we select a narrow beam of light and allow it to disperse through an appropriately located prism. The intensity of this spatially dispersed light is then monitored by placing a detector on the other side of the prism and scanning it across the length d of the spatial spread. Based on the knowledge that we acquired on prismatic dispersion in the previous chapter, it is apparent that the spatial splitting of the beam is basically a spread of all the wavelengths it is made up of in space. It is therefore equivalent to saying that the distance d through which the detector is scanned can be directly translated to the wavelength λ . This exercise thus presents a record of the intensity of light emitted by the source as a function of its wavelength, known as the “emission spectrum” in the common parlance.

An oversimplified emission spectrum over a narrow range of wavelengths is also shown in Fig. 3.2 for clarity as well as palatability. A closer look at this spectrum readily points to the fact that the fluorescent source, under study here, basically emits light of three primary wavelengths over the displayed spectral range. Distinct also is the fact that the emission never occurs sharply on any of these wavelengths but rather spread into multiple wavelengths distributed around them. However, the feature that makes the emission of light by an atomic source most remarkable is the fact that it

Fig. 3.3 Line center (λ_0) and the full width at half maximum (FWHM, $\Delta\lambda$) of the emission



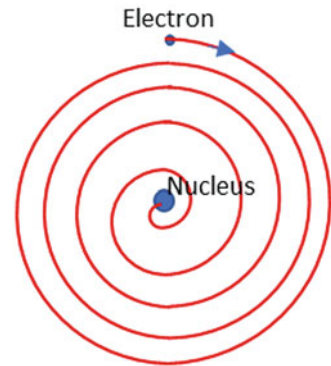
does not emit light of continuous wavelength, and, on the contrary, an element of discreteness is strikingly intrinsic to its emission spectrum. The atomic spectrum was first observed in 1853 by a Swedish physicist, Anders Angstrom (1814–1874), regarded as the founder of spectroscopy, for the hydrogen atom that would later play a pivotal role in providing the first insight into the structure of an atom.

The wavelength at which the intensity attains a peak I_0 is called the line center λ_0 , and the spread around it is called the emission width $\Delta\lambda$ and is usually defined as the width of the emission at half of its peak value, abbreviated as FWHM. The same has been pictorially illustrated in Fig. 3.3 for one of the emission wavelengths of the atomic source. The emission width is a direct measure of the monochromaticity or purity of the color of the corresponding emission. It is thus at once obvious that of the three different wavelengths of Fig. 3.2, the emission at the longest wavelength is least monochromatic and that at the smallest wavelength is the most. While the key features of the emissions remain invariant with different atomic sources, the number of emitted wavelengths and their corresponding emission widths vary from one atomic gas to the other. Gaining insight into the seemingly intricate physics underscoring the atomic spectra, which swayed some of the finest scientific minds over the years, is considered a major milestone in the evolution of science.

3.4 Bohr's Atom and Beyond: A Unique Handshake Between Matter and Radiation, the Two Faces of Nature

The classical physics pictures an electrically neutral atom as a tiny but enormously massive positively charged nucleus surrounded by electrons, at a great distance away, in numbers to exactly match the central positive charge. This notion, which emerged primarily from Rutherford's famed α -ray scattering experiment, however, suffers from an inherent limitation of rendering the atom unstable. An electron cannot be stationary as it would then be pulled by the positively charged nucleus into it so rapidly that the stable atom would collapse in just a flitting second. The atomic stability demands that the electron must orbit around the nucleus, akin to the

Fig. 3.4 Schematic illustration of an encircling electron, which, upon radiating energy, will spiral inward to impact the nucleus in a split second



rotation of planets around the Sun, and the attractive Coulomb force between the nucleus and electron provides the required centripetal force.² The mere rotation, however, cannot provide stability to the atom. According to classical electrodynamics, a rotating electron would lose its energy by emitting electromagnetic waves [19]. As a result of this energy loss, the orbiting radius of the electron reduces, and, in turn, it spirals inward colliding with the nucleus almost instantaneously (Fig. 3.4). Moreover, during the process of this atomic collapse, the electron must emit electromagnetic waves of continuously ascending frequency as its speed of rotation progressively increases. These are in stark contrast to the fact that atoms are indeed stable and, as we have seen, the atomic emission is discrete in frequency or wavelength and not continuous. In an attempt to resolve this impasse, Niels Bohr, having realized the inaptness of classical physics to describe the behavior of microscopic particles such as atoms, put a bold step forward in 1913 [4]. His courageous assertion that the energy levels of an atomic electron are quantized, and it can reside only in these levels, termed stationary states, without any dissipation of energy, confers stability to the atom. It is of interest to note here that the quantization of energy levels is a direct consequence of the wave nature of matter, a fact conceptualized by de Broglie, a decade later, in 1924. Example of waves impressed in a wire loop as illustrated in the traces of Fig. 3.5 will help you capture the underlying physics here. A wave, unless it joins itself as it travels around the loop (Fig. 3.5a), cannot be sustained as the destructive interference, the occurrence of which is inevitable here, will cause the vibration to die out. Consequently, the given wire loop is forbidden for the wave of this wavelength. It becomes obvious that only those waves can survive in the wire loop whose wavelength times an integer fits exactly into its circumference (Fig. 3.5b and c). Drawing an analogy, it becomes

²Centripetal force acts on a body that performs a curved motion and is directed toward the center of rotation. In case of planetary motion, the gravitational attraction between the Sun and the planet provides the centripetal force. If you tie an object to one end of a rope and rotate it by holding the other end, the tension developed in the taut rope supplies the centripetal force necessary to keep it moving. Centripetal force in case of a particle of mass m rotating at a velocity v in a circular path of radius r is given by $\frac{mv^2}{r}$.

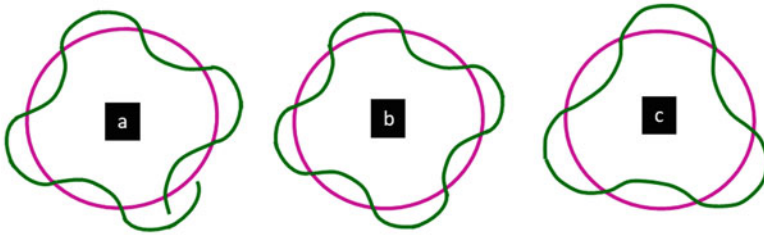
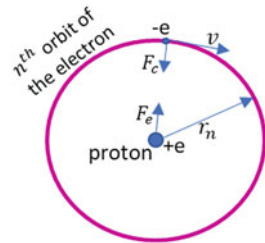


Fig. 3.5 Illustration of waves of different wavelengths vibrating in a circular loop of wire. (a) The vibration will die out due to destructive interference if the wave does not join on itself in the loop. (b) and (c) Only the waves whose wavelength fits an integer number of times within the loop will survive. Clearly, the values of the integer are 4 and 3 for (b) and (c), respectively

Fig. 3.6 Schematic of a hydrogen atom where the electron is revolving around the proton with a velocity v in the n^{th} stable orbit of radius r_n



readily apparent that an electron can also circle around the nucleus without any dissipation of energy only in those orbits that contain an integral number of its de Broglie wavelengths. Little surprise then that this notion of a wavy particle allowed tying up all the loose ends and physics quickly fell into place. The wave nature of a particle nevertheless gives the atom both its stability and size. Taking a cue from the analogy of the waves in a wire loop, the radius of the possible orbits of the electron could now be readily linked to its de Broglie wavelength λ mathematically as.

$$2\pi r_n = n\lambda \tag{3.5}$$

where n is an integer, called the quantum number, and r_n is the radius of the n^{th} stable orbit of the electron (Fig. 3.6). To simplify the analysis, we consider the case of a hydrogen atom, wherein a lone electron revolves around a proton. Upon substituting λ from Eq. (3.1), we obtain.

$$r_n = \frac{nh}{2\pi mv} \tag{3.6}$$

where m and v are the mass and velocity of the electron, respectively. The centripetal force F_c required to hold the electron in its orbit is provided by the electrical attraction F_e between the proton and the electron each containing a charge of magnitude e . It therefore readily follows that

$$\frac{mv^2}{r_n} = \frac{e^2}{4\pi\epsilon_0 r_n^2}$$

$$\text{i.e. } v = \frac{e}{\sqrt{4\pi\epsilon_0 m r_n}} \quad (3.7)$$

Eliminating “ v ” between (3.6) and (3.7), r_n , the orbital radii, can be expressed as.

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2} \quad (3.8)$$

The corresponding energy “ E_n ” of the electron will be the sum total of its kinetic and potential energy,³ i.e.,

$$E_n = KE + PE = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r_n}$$

Substituting “ v ” and “ r_n ,” respectively, from Eqs. (3.7) and (3.8), we find that.

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{me^4}{8\pi\epsilon_0^2 n^2 h^2} =$$

$$-\frac{E_1}{n^2} \left(\text{where } E_1 = \frac{me^4}{8\pi\epsilon_0^2 h^2} \text{ is the energy in the first orbit} \right) \quad (3.9)$$

Obviously, therefore, each stable orbit of the electron has a discrete energy associated with it. This fact has been illustrated in Fig. 3.7 for the first three stable orbits of the electron. The negative energy of the electron implies that the electron is bound by Coulomb attraction and work needs to be expended to make it free. For instance, the electron revolving in the first orbit has a negative energy of magnitude E_1 , and, therefore, to make it free exactly E_1 energy must be supplied from outside. A free electron is no longer bound by the attraction of the proton and thus will possess zero energy that, as evident from Eq. 3.9, corresponds to a quantum number of infinity. All the remaining energy levels lying between $n = 3$ and $n = \infty$ would pack to the capacity this slender energy space. This fact has also been highlighted in Fig. 3.7 by providing an enlarged view of this otherwise narrow energy space. As seen, with increasing n , the energy levels approach each other so closely that they eventually merge practically into a continuum. This is understandable; as the electron tends to be free, its de Broglie wavelength is no longer constrained with the so-called boundary conditions, and quantization of energy becomes practically irrelevant.

³Potential energy of the electron here is negative as it is being electrically attracted by the proton and equals the work required to be imparted in order to move the electron through a distance between r_n to infinity.

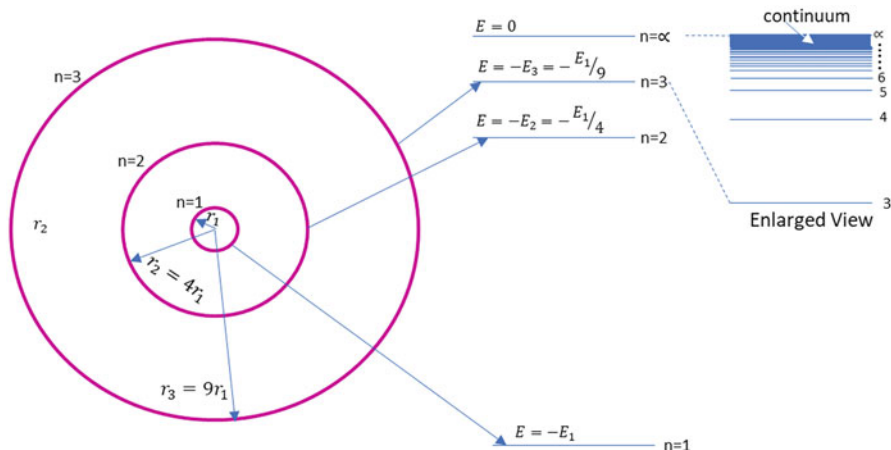


Fig. 3.7 First three electronic orbits in the hydrogen atom drawn to the scale of proportionality to n^2 . The corresponding energy levels are shown alongside and is drawn to the scale of inverse proportionality to n^2 . The zero-energy state of the electron obviously corresponds to a quantum number of infinity. An enlarged view here shows the stuffing of the energy space between $n = 3$ to ∞ with increasingly closely spaced energy levels leading eventually to a continuum

The very conceptualization of quantization of energy by Bohr, coming at a time when de Broglie was yet to enlighten the scientific world on the wavy behavior of the matter, was indeed a masterstroke and left an indelible mark in the evolution of knowledge. The perception of the energy quantization laid the groundwork for the interpretation of the atomic spectra that had eluded the scientific community for well over half a century. Bohr's exposition that the atomic spectra originate from a unique handshake between the wavy particle and corpuscular wave, the two most guarded secrets of nature until the beginning of the twentieth century, startled the scientific community. Many expressed their disbelief, and Einstein was no exception. A few such as Otto Stern (1888–1969) and Max von Laue (1879–1960), both German by birth and Nobel Laureates in Physics, offered to quit physics if Bohr were correct. That they had to retract the offer later is of course another story. Bohr's interpretation of atomic spectra in conjunction with de Broglie's formulation of matter waves provided the initial impetus for quantum mechanics to navigate the challenges of the microscopic world.

As we know now, the wavy electron in the hydrogen atom, under the influence of the proton's electric field, is able to reside without dissipation only in certain orbits, each labeled by a different integer called the orbital quantum number. As the electron is bound here, its total energy is always negative. An electron in the innermost orbit, identified as the orbit with quantum number $n = 1$, possesses the least energy and can be determined from Eq. (3.9) to be -13.6 eV .⁴ The energy of the electron rapidly

⁴eV is normally the unit used to express the energy of atomic particles and 1 eV is equivalent to $1.6 \times 10^{-19} \text{ J}$.

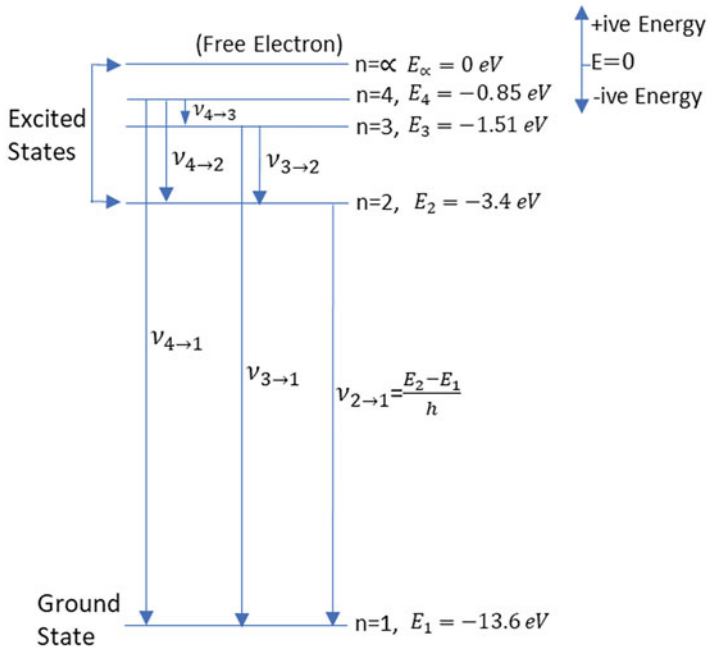


Fig. 3.8 All the stable atomic orbits of the electrons are characterized by negative energy. A few low-lying energy levels of a hydrogen atom are illustrated here along with their negative values of energy. Origin of spectral lines as the excited electron makes a transition to an energy level with lower energy is also schematically depicted

increases with increasing n and attains a value of zero as n tends to infinity. A few low-lying energy levels of a hydrogen atom and the corresponding energies are shown in Fig. 3.8. The electron under normal circumstances occupies the level with the lowest energy called the ground state. When energized by an extraneous source, the electron is excited and climbs up the energy ladder. Upon receiving an energy of 13.6 eV or more, the ground state electron will become free and no longer remain bound to the proton to form the hydrogen atom. This is equivalent to saying that the hydrogen atom has been ionized as the electron is stripped off. However, the plot thickens if the ground state electron acquires energy not sufficient to tear off the proton's attraction and escape, but just enough for it to jump into another low-lying energy level instead. For instance, what happens if the electron has climbed to the second orbit from the first: a gripping point that seemingly intrigued Neil Bohr's mind. His surmise of the electron spontaneously dropping down to the ground state releasing its energy of excitation as a photon of light is regarded as a brilliant piece of work as it finally cracked the physics behind the discreteness of atomic spectra. Digging a little deeper, we can readily conclude that this interpretation points to an exceptional hand clasp of particle and wave; it's like the wavy atom has created energy steps, akin to a ladder, for the photonic wave to climb down to the ground. If the electron makes a quantum leap from the second orbit ($n=2$, and energy $= -E_2$) to

the first ($n=1$, and energy = $-E_1$), the energy of the photon emerging from this transition will equal the difference of energy between these two levels. This can be mathematically expressed as

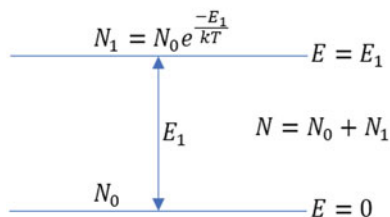
$$\begin{aligned}h\nu &= -E_2 - (-E_1) \\ \nu &= \frac{1}{h}(E_1 - E_2)\end{aligned}\tag{3.10}$$

where ν and h are the frequency of the emitted photon and the Planck's constant, respectively. If the electron, on the other hand, is excited to the next higher orbit of quantum number 3, it can return to the ground state by following two different routes, either making a direct transition from 3 to 1 or via level 2. This would thus result in the emission of three different photons. Clearly, the higher the level of excitation, the more numerous the pathways for the electron to return to its ground state. Every transition that the electron makes over its ground state-bound journey gives rise to the emission of a photon of different wavelength. The discreteness of the wavelength of light is thus intrinsic to the atomic spectra. Bohr's theory, however, neither sheds any light on how long the electron can reside in an excited state before making the spontaneous downward leap, nor does it say if some transitions are more probable than others or on the forbiddenness of any transition. The answers to these questions not only are central to understanding the other aspects of the atomic spectra, such as its varying richness from atom to atom, or as to why the width of one transition differs from another, but also have a strong bearing on the operation of a laser. These will be addressed at another place in the book.

3.5 Boltzmann Distribution

We now know that quantization of energy is a rule of nature that the inhabitants of the microscopic world very compliantly obey. Not that it doesn't exist in the macroscopic world, but we are unable to realize this as its effect becomes vanishingly small for the conventional objects. In addition to providing physical insight into the origin of quantization, the preceding sections also offered a quantitative formulation of this in the case of a hydrogen atom, the simplest of all the atoms. Although the theoretical approach to be followed in this context for atoms with higher atomic numbers will be qualitatively similar, the presence of multiple electrons and their associated de Broglie wavelengths will make the analysis understandably more complex. Notwithstanding this, the fact remains that no atom, small or large, can disobey the rule of energy discretization. The same will also apply to atoms from which one or more electrons have been stripped off. A molecule is an amalgamation of multiple atoms bonded together and will, nevertheless, have its own quantized electronic energy levels similar to that of an atom. As will be shown in a latter section of the book dealing with molecular lasers, a molecule, unlike an

Fig. 3.9 Distribution of total population “ N ” between two energy levels satisfying Boltzmann’s law



atom, can also vibrate and rotate at the same time. Similar to its electronic energy levels, the molecule’s vibrational and rotational levels are also quantized. An ensemble of atomic or molecular systems will comprise countless number of atoms or molecules. The obvious question that arises here is how these numerous species will be distributed among the discrete electronic energy levels in the case of atoms and the electronic, vibrational, and rotational energy levels in the case of molecules? To simplify the matter, let us stick at this point only to the case of distribution of species, atomic or molecular, among one set of discrete energy levels. (The specific cases of distribution of atoms and molecules into their respective energy levels will be addressed in a latter chapter dealing with atomic and molecular lasers.) Let us consider a situation wherein a total of N species are to be distributed within two energy levels as illustrated in Fig. 3.9. One of the energy levels is the ground level that for convenience has been scaled to a zero-energy state and the other is located at an energy of E_1 above it. It is a well-known fact that nature always acts in a manner so as to establish a situation with the lowest possible energy. In this example, the minimum energy condition will obviously be the one where all the N species settle into the ground energy state. There is a catch though! For any nonzero temperature, the system will contain a finite amount of thermal energy that essentially manifests by raising a fraction of the species to the levels with higher energy. In 1877, Ludwig Boltzmann⁵ (1844–1906), an Austrian physicist, succeeded in theoretically predicting the relation of the equilibrium population N_1 of any energy level to the ground level population N_0 as a function of the temperature, as

$$N_1 = N_0 e^{-\frac{E_1}{kT}} \text{ where } k \text{ is the Boltzmann's constant and } T \text{ is the temperature}$$

In reality, however, there would be an infinite number of energy levels, and consequently, the above formula can be generalized as

⁵Boltzmann chose to die by his own hand on September 5, 1906, when he was holidaying with his wife and daughter at a place close to the Italian town of Trieste. His suicide is blamed to a severe depression, he was suffering from, that stemmed basically from the strong opposition to his work on theorizing the population distribution. The irony is only a few weeks following this tragedy, his theory was experimentally verified. The suicide most certainly also drew a curtain on his getting a Nobel Prize that, incidentally, is not awarded posthumously.

$$N_j = N_0 e^{\frac{-E_j}{kT}} \quad (3.11)$$

where N_j is the population of the j^{th} energy level whose energy relative to the ground state is E_j .

In equilibrium, the population will be distributed among all these levels satisfying this equation termed Boltzmann's distribution law. It may be possible to disturb this state of thermal equilibrium by some extraneous means, but the condition of nonequilibrium will be short-lived as the system rapidly readjusts itself to return to its original equilibrium state. It becomes readily apparent from Eq. 3.11 that for any finite temperature T , population of an energy level exponentially reduces with the increase in its energy relative to the ground state. It is equivalent to saying that it is impossible to have an energy level with population exceeding that of any level beneath it. This is a valid statement for any highest conceivable temperature. Even in the limit of temperature tending to infinity, its population can at most match that of the level lying beneath and can never exceed it. In fact, in that limit, the population of all the levels will match that of the ground state. On the other hand, if the temperature starts falling, the low-lying levels will begin becoming increasingly populated at the expense of those in the upper levels. If the temperature goes all the way down to absolute zero, the entire population of the system will be realized in the ground state. The bearing of these facts in the realization of population inversion and, in turn, operation of a laser will be addressed in the next chapter.