

Chapter 2

Introduction to Quantum Mechanics

In 1802 *Dalton* formulated the *law of multiple proportions*, which states that if two elements combine in more than one proportion to form different compounds the masses of one of the elements with identical amounts of the second element are in the ratio of integral numbers. In 1833 *Faraday* found the *law of electrolysis* as a proof for the existence of an electrical elementary quantum of charge. These discoveries supported the postulation of the particle (atom, molecule) theory of matter. On this basis, during the second half of the nineteenth century, the *mechanical theory of heat* was first formulated by *Clausius* and was further developed by *Maxwell* and *Boltzmann*. Mechanical explanation of the pressure of a gas in a closed vessel, as well as the phenomenon of linear increase of pressure with temperature was possible in this way. In 1811 *Avogadro's hypothesis* was formulated, which stated that equal volume of different gases, under the same conditions of temperature and pressure, contains equal number of molecules. Russian Chemistry Professor Dimitric Mendeljeff [D. Mendelejeev, 'Ueber die Beziehungen der Eigenschaften zur den Atomgewichten der Elemente', *Z.f.Chemie* (in German), 1869, pp. 405–406] and German Chemist Julius Lothar Meyer independently published their Periodic Tables in 1869 and 1870, respectively. They arranged the elements columnwise on the basis of certain chemical properties, and it was found subsequently that these properties are dependent on the number of electrons on the outermost orbit around the nucleus of the element. Proceeding from *Rayleigh-Jeans law of radiation* for large wavelengths and from *Wien's law* for short wavelengths, *Planck* in 1900 combined these two laws semiempirically and found the famous law of radiation that bears his name. From his analysis, for the first time, the existence of an elementary quantum of radiation was found. A rigorous explanation of *Planck's law* was, however, left to *Albert Einstein*, who in the 1920s applied the results of a statistic developed by Indian scientist *Satyendra Nath Bose* to the light particles (photons). In 1905, based on astronomical experiments, Einstein also formulated his *theory of relativity* and gave for the first time a mass-energy equivalence principle. From the alpha particle scattering experiments in 1906–1913, *Rutherford* concluded that the mass of the atom should almost be totally concentrated around a very dense nucleus. He further suggested a simple model of an atom consisting of a very dense

nucleus around which the electrons move in orbits. The electrons are kept in orbits by a balance between the *centrifugal* and *Coulomb forces*. His theory, however, could not explain how the electrons could stay in orbit without any dipole radiation, which would result in their slowing down. An explanation for this was left to the Danish scientist, *Niels Bohr*, who, by drawing help from another branch of physics, namely, spectroscopy, could explain in 1913 the nature and radius of the electron orbit. This is discussed in detail in the following section.

Although the principles of radiation energy, quantum energy, and the energy-mass equivalence were known at the time of *Bohr*, particles and radiation energy were considered as two different natural objects. However, various experiments showed that under certain circumstances light behaved like particles, and particles exhibited the wave nature. Thus in 1924, *de Broglie* formulated his principle of *particle-wave dualism*. Based on this, in 1926, *Heisenberg* and *von Schrödinger* formulated, by two independent methods, the two important theories named after them and thus founded the basic principles of modern quantum mechanics.

2.1 Line, Band, and Continuous Spectra: Bohr's Atomic Theory

When the science of spectroscopy was in its infancy, the spectra were divided by their appearance, as given in Fig. 2.1, into *line*, *band*, and *continuous spectra*. Before man learnt the origin of these different types of spectra, which have been identified later as due to atomic, molecular, and solid body radiation, respectively, it was obvious from the line spectra of hydrogen, given schematically in Fig. 2.1a, that there must have been a relation between the wavelength and frequency of different lines.

The first series law of spectra in the visible region of hydrogen was found in 1885 by *Balmer*, a school teacher from Basel, and is given by the relation

$$\nu \propto (2^{-2} - n^{-2}), (n = 3, 4, 5, \dots). \quad (2.1)$$

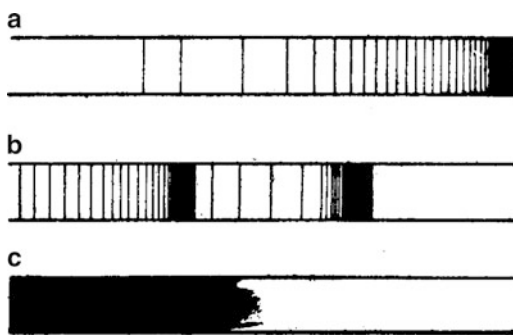


Fig. 2.1 Types of spectra:
(a) line, (b) band, and
(c) continuous spectra

Although this equation could not be explained by the *Rutherford model of atomic structure*, it was thought that the orbiting electron around the nucleus must represent a dipole and thus must be capable of radiation. The main difficulty, however, was that this model could not explain the occurrence of a discrete line radiation on account of their being no possibility of having stable orbits. In 1913 *Bohr* gave the solution to this problem by postulating that the electrons travel in certain stationary orbits in which they do not radiate energy and that in such an orbit the circular line integral of the electron angular momentum should be a multiple of the basic quantum number h . Thus the mathematical formulation of *Bohr's hypothesis* for a circular orbit of a hydrogen atom is

$$\oint M_e w_e ds = 2\pi M_e w r = nh, (n = 1, 2, 3, 4), \quad (2.2)$$

where w is the orbiting velocity of the electrons. Further, *Bohr* postulated that the atom emits (or absorbs) a quantum of electromagnetic radiation when the electron transits from one orbit to another. The frequency of the radiation is dependent on the energy difference ΔE between the two orbits and is given by

$$\Delta E = h\nu. \quad (2.3)$$

Total energy in an orbit consists of the potential and kinetic energies:

$$E = E_{\text{pot}} + E_{\text{kin}} = -C \frac{e^2}{r} + \frac{1}{2} M_e w^2, \quad (2.4)$$

where $C = 1/(4\pi\epsilon_0) = 8.986 \times 10^9 \text{ Vm(As)}^{-1}$.

The force balance equation (centrifugal force = Coulomb force) in the orbit for hydrogen atom (one proton, one electron) is

$$C \frac{e^2}{r^2} = M_e \frac{w^2}{r}. \quad (2.5)$$

From (2.2) and (2.5), we get two equations for orbital speed and radius,

$$w = r\omega = \frac{2\pi e^2 C}{nh} \quad (2.6)$$

and

$$r = \frac{C e^2}{M_e w^2} = \frac{n^2 h^2}{4\pi^2 e^2 M_e C}, \quad (2.7)$$

where $\omega = w/r$ is the *orbital radian frequency*. Substituting the approximate values for electrons, we get for *hydrogen atom*

$$w = 2.18 \times 10^6 / n, \text{ ms}^{-1} \quad (2.8)$$

and

$$r = 0.53 \times n^2, \text{\AA}. \quad (2.9)$$

Thus the *orbital frequency* for the hydrogen atom is

$$\nu_{\text{orb}} = \frac{w}{2\pi r} = \frac{6.563 \times 10^{15}}{n^3}, \text{s}^{-1}. \quad (2.10)$$

In the ground state ($n = 1$) for hydrogen atom, the collision cross section, therefore, is $\pi r^2 = 0.8825 (\text{\AA})^2$ and is of the same order of magnitude as it is obtained from the measurement of the transport properties. Substituting the relations for w and r , (2.6), (2.7), into (2.4), the total energy of the orbiting electron is

$$E = -\frac{2\pi^2 e^4 C^2 M_e}{n^2 h^2} \quad (2.11)$$

which, after substitution of relevant values for electrons in the hydrogen atom, gives

$$E = -2.17 \times 10^{-18} / n^2 [\text{J}] = -13.54 / n^2 \text{ eV}. \quad (2.12)$$

From (2.12) it is seen that for $n = 1$, E is a negative quantity, but for n going to infinity (ionization!), where the electron is at an infinite distance from the nucleus, E goes to zero. Thus, according to (2.12), the ionized atom has zero energy, whereas the bound atom has a negative energy. However, from convention, it is found convenient to put zero energy at the ground level ($n = 1$). This is done easily by subtracting the ground level energy and (2.11) becomes

$$E = \frac{2\pi^2 e^4 C^2 M_e}{h^2} \left(1 - \frac{1}{n^2} \right). \quad (2.13)$$

Now substituting (2.11) or (2.13) into (2.3), one gets

$$\nu = \frac{\Delta E}{h} = \frac{E'' - E'}{h} = \frac{2\pi^2 e^4 C^2 M_e}{h^3} \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right). \quad (2.14)$$

From the science of spectroscopy, the spectral frequency ν is where the transition from one energy level to the other takes place. If $n'' > n'$, a transition takes place from the higher energy level E'' to the lower energy level E' with consequent release of energy in emission. If, however, $n'' < n'$, the radiative transfer is due to absorption. While the frequency of the radiative energy is in s^{-1} , from the convention in spectroscopy, it is easier to work with the wave number $\bar{\nu} = \nu/c = 1/\lambda$ where λ is the wavelength. Thus, from (2.14), the wave number for hydrogen is given by the relation

$$\bar{\nu} = R'_H \left(\frac{1}{n'^2} - \frac{1}{n''^2} \right), \quad (2.15)$$

where

$$R'_H = \frac{2\pi^2 e^4 C^2 M_e}{h^3 c} = 10973731.2 \pm 0.8 \text{ m}^{-1} \quad (2.16)$$

is the so-called Rydberg constant for hydrogen. There is a small discrepancy, however, between the frequency and wavelength of radiation for hydrogen as given by (2.15) and experimental results. This discrepancy can be taken care of by introducing a small correction, which, as it is physically explained, is due to the electron and the nucleus moving around a common axis, instead of the electron only moving around the nucleus. The corrected Rydberg constant is now

$$R_H = R'_H \left[1 + \frac{M_e}{M_{\text{atom}}} \right] = 10967757.6 \pm 3.12, \text{ m}^{-1}. \quad (2.17)$$

From (2.15), it is now possible to calculate exactly the wavelength region of the spectra. In case $n' = 1$ and $n'' = n$, we get from (2.15)

$$\bar{\nu} = \lambda^{-1} = R_H \left[1 - \frac{1}{n^2} \right], n = 2, 3, 4, \dots \quad (2.18)$$

which is in a series form and is called after its discoverer, the *Lyman series* for the hydrogen atom radiation. The wavelengths of the Lyman series are given by the relation

$$\lambda = \frac{1}{R_H \left[1 - \frac{1}{n^2} \right]} = \frac{912}{\left[1 - \frac{1}{n^2} \right]}, \text{ \AA}, n = 2, 3, 4, \dots \quad (2.19)$$

For $n = 2, 3, 4, \dots$, the corresponding wavelengths are 1216, 1026, 972.8, ..., 912 Å. It is seen that all these lines are in the ultraviolet region. It is, therefore, not surprising that this series was discovered later. The earliest series discovered is the *Balmer series* given by the relation

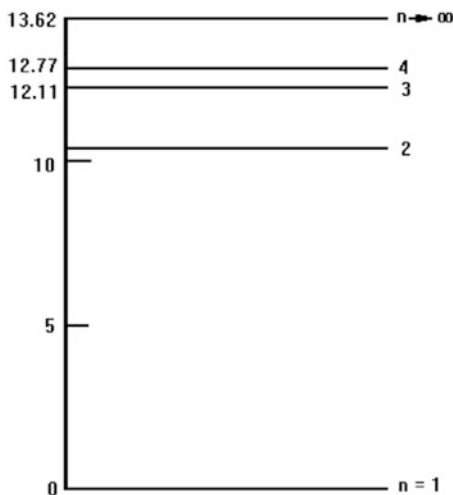
$$\lambda = \frac{1}{R_H \left[\frac{1}{2^2} - \frac{1}{n^2} \right]}, n = 3, 4, 5, \dots \quad (2.20)$$

which is in the visible region. Similarly there are other series as follows:

- *Paschen series*: $\bar{\nu} = \lambda^{-1} = R_H [1/3^2 - 1/n^2], n = 4, 5, 6, \dots$
- *Brackett series*: $\bar{\nu} = \lambda^{-1} = R_H [1/4^2 - 1/n^2], n = 5, 6, 7, \dots$
- *Pfund series*: $\bar{\nu} = \lambda^{-1} = R_H [1/5^2 - 1/n^2], n = 6, 7, 8, \dots$

Series with $n' > 5$ have no names, but the wavelengths for each of these series can be determined easily by the procedure given above.

Fig. 2.2 Energy levels for hydrogen atom



From (2.13) and the definition of the Rydberg constant, we see now that the energy level is given by the expression

$$E = R_H h c \left[1 - \frac{1}{n^2} \right] \quad (2.21)$$

in which the proportionality constant $R_H h c = 2.18148702 \times 10^{-18} \text{ J} = 13.62 \text{ eV}$.

For $n = 1, 2, 3, \dots$ the corresponding energy levels can be computed from (2.21), and these in electron volt (eV) are 0, 10.21, 12.11, 12.77, \dots , 13.62 eV. These energy levels for the hydrogen atom are shown in Fig. 2.2, with the corresponding values of n . One can show Fig. 2.2 with possible transitions, both in emission and absorption. For example, for the Lyman series, all transitions take place from a higher energy level to the ground level and in absorption from the ground level to a higher energy level.

The unit of the energy level in the present case is shown in J or eV, and these are not the only units currently in existence. We can write energy also in m^{-1} or in cm^{-1} , which is obtained by dividing (2.21) by (hc) . In fact, many of the energy level tables given in books of reference are in cm^{-1} , which is the reason to give in this book the conversion factor from cm^{-1} to J or eV. In other books the energy levels are given in K. These can be converted into J or eV by multiplying with the respective conversion factor.

Bohr's atomic model is successful in explaining the spectra of the hydrogen atom in a very lucid manner and with great accuracy. This is reflected in the fact, that the Rydberg constant is obtained theoretically with great accuracy. The model is also valid for all particles which are similar to the hydrogen atom, namely, a single electron around a nucleus like He^+ , Li^{++} , \dots , etc. In such cases, one can think of an electron around a nucleus of charge $+Ze$, where Z is the charge number. The reader

should work out, in analogy to those for hydrogen, the details of calculation to show that the Rydberg constant R'_H in such cases is to be multiplied simply by Z^2 to R'_H . Further it is found that for those atoms which have just one electron in the outermost orbit, which is the case for alkali atoms, the earlier analysis is valid, at least in principle. The failure of the Bohr model for the line spectra of multielectron atoms led Sommerfeld to consider that besides circular orbits, elliptical orbits may also be possible. To describe elliptical orbits more than one quantum number is needed. Hence, n is called the “principal quantum number” and can have values $n = 1, 2, 3, \dots$. In addition, the following are the other quantum numbers with possible values against each of them:

- $l = \text{angular quantum number} = 1, 2, \dots, (n - 1), n; n \text{ values}$
- $m = \text{magnetic quantum number}$
 $= -(l - 1), -(l - 2), \dots, -1, 0, 1, 2, \dots, (l - 2), (l - 1); (2l - 1) \text{ values}$
- $s = \text{spin quantum} = \pm 1/2; 2 \text{ values}$

In case we assume that the electron energy in an atomic structure is dependent on the value of the four quantum numbers n, l, m , and s and assuming, according to *Pauli principle*, that no two electrons in the ground state may have exactly the same energy, it is possible to determine the maximum number of electrons in the orbit (shell) in the ground state. For example, for $n = 1, l$ and m can have only 1 value each and s can have only two values. Therefore, the innermost orbit ($n = 1$) can have a maximum of only two electrons. Similarly for the next higher principal quantum number ($n = 2$), l can have two values (1 and 2), m can have only 4 values (1 value for $l = 1$ and 3 values for $l = 2$), and s can have two values for each l . Therefore, for the second orbit ($n = 2$), if $l = 1$, there can be only two values, and if $l = 2$, there can be only six values—a total of eight values. In a similar manner, we can show that for the next higher principal quantum number ($n = 3$), there can be a total of 18 values. These results can be generalized by writing $2n^2$ as the total number of electron energy values available in ground state and have some relevance with the chemical properties of the pure gas.

The *angular quantum numbers* are written, by convention, as $l = s, p, d, f, \dots$, instead of $l = 1, 2, 3, 4, \dots$. Even with modification from the single principal quantum number, Bohr’s atomic theory can explain and interpret the wave lengths of spectra due to hydrogen or hydrogen-like atoms. However, for many other cases, like the anomalies in *Zeeman effect*, *tunnel effect*, etc., where the particles go through a *potential barrier*, and so on, new theories had to be developed.

2.2 Wave-Particle Dualism and Wave Mechanics

In spite of success with the wave theory of light in providing explanations for phenomena such as interference and refraction, there are many phenomena such as the photoelectric effect that could not be explained by this theory. The explanation of these phenomena led to the quantum theory of radiation. *Max Planck* in A.D. 1900

postulated that in its interaction with matter, electromagnetic radiation behaved as though it consisted of particles, or quantum of energy, called photons, having an energy given by $E = h\nu$. This showed the dual character of electromagnetic radiation and led *de Broglie*, in 1924, to suggest that a similar dualism might exist for material particles and electrons. From the *mass-energy equivalence* relation of Einstein, $E = Mc^2$, we obtain the relation for momentum of photons as $Mc = h\nu/c = h/\lambda$. Assuming that this equation also applies to material particles and electrons, we have for a particle of mass M moving with velocity w the momentum $p = Mw = h/\lambda$, so that

$$\lambda = h/(Mw) = h/p. \quad (2.22)$$

This equation gives the wavelength λ of the hypothetical matter waves associated with the material particles and is the fundamental equation of *de Broglie's* theory. Equation (2.22) is now used to work out two specific cases. First, consider a man of mass 60 kg being stationary, which means $w = 0$ and the equivalent wavelength $\lambda \rightarrow \infty$. If the man walks at the speed of 5 km h^{-1} , then the equivalent wavelength is 10^{-35} \AA . For either of these cases, and also at other velocities in between, the equivalent wavelengths are either too small or too large to detect or to measure. Similarly, while investigating the particle nature of a light of wavelength $5,000 \text{ \AA}$ with the speed of light $w = c = 3 \times 10^8 \text{ ms}^{-1}$, the equivalent mass is $M = 10^{-37} \text{ kg}$, which is too small to be measured. Thus it is found that under most test conditions it is possible to recognize either the wave aspect or the particle aspect, but not both at the same time. This raises questions regarding the actual character of the universe bringing these to the realm of philosophical speculations, as is found in the *Upanishads*.

For monochromatic radiation the wavelength may be known, and thus from (2.22), the equivalent momentum can be determined. In 1927 *Heisenberg* put forward the uncertainty principle, which states that the exact simultaneous determination of the position and momentum of a particle is impossible. If Δx is the uncertainty involved in the measurement of the coordinate of a particle [in m] and Δp is the uncertainty in the simultaneous measurement of its momentum [in kgms^{-1}], then

$$\Delta x \cdot \Delta p \approx h, \text{ Js.} \quad (2.23)$$

It has been shown clearly from refraction experiments that the uncertainty is due to the *wave-particle dualism* and not due to errors in the measurement of certain quantities.

From (2.2) and (2.22), one can write further

$$2\pi M_e w r = nh = n M_e w \lambda \quad (2.24)$$

and thus, the circumference of the orbit is $2\pi r = n\lambda$ ($n = 1, 2, 3, \dots$). For $n = 1$, in the ground level, the circumference is equal to a certain wavelength λ . Similarly, for an arbitrary n , Bohr's quantum condition is reduced to the condition that there

must be an integer number of wavelengths that would just fit into the circular orbit. Such integer number of wavelengths would generate a standing wave instead of a stationary *Bohr orbit*. As a result, while the orbiting electrons move in a path of wave pattern, the orbit, as defined by the Bohr's quantum condition, becomes the path in which an electron has the maximum probability to stay.

This concept has further been exploited by *Schrödinger* by introducing a *wave function*, ψ , which satisfies the general wave equation

$$\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = \nabla^2 \psi, \quad (2.25)$$

where the velocity of propagation is $c = v\lambda = hv/(Mw)$. Now, if E is the total energy and U the potential energy, then

$$\frac{M}{2} w^2 = E - U \quad (2.26)$$

and, therefore,

$$Mw = \sqrt{2M(E - U)} = \frac{hv}{c}. \quad (2.27)$$

Thus, further,

$$c = \frac{hv}{\sqrt{2M(E - U)}}. \quad (2.28)$$

Let $\psi(x, y, z, t) = \bar{\psi}(x, y, z) \exp^{-2\pi j \nu t}$ in which $j = \sqrt{-1}$ and $\bar{\psi}$ is an amplitude function. Thus, from (2.25), the final form of *Schrödinger's wave equation* is

$$\nabla^2 \bar{\psi} + \frac{8\pi^2 M}{h^2} (E - U) \bar{\psi} = 0. \quad (2.29)$$

By comparison with classical problems of wave propagation, it is clear that the solution of $\bar{\psi}$ has the character of an *eigenfunction* and is complex. It has further been shown by theoretical physicists that the square of the absolute value obtained by multiplying with its *conjugate complex* $\bar{\psi}^*$ gives the probability of a particle being found at time t , in a volume element at x , y , and z formed between x and $x + dx$, y and $y + dy$, and z and $z + dz$. While the general analysis of (2.29) is outside the scope of this book, a few sample results will now be derived.

2.2.1 Rigid Rotors

For this case it is assumed that two equal masses are rotating around a common axis separated by a distance r . Further, let $U = 0$. Replacing M by $2M$, where M is the mass of a single atom, and if φ is the azimuthal coordinate, (2.29) becomes

$$\frac{d^2 \bar{\psi}}{d\varphi^2} + \frac{16\pi^2 M r^2}{h^2} E \bar{\psi} = 0. \quad (2.30)$$

Since solutions found are of the type $\bar{\psi}(\varphi) = \bar{\psi}(\varphi + 2\psi)$, condition for periodicity, the general solution sought is of a simple harmonic nature. That is, the trial solution is $\bar{\psi}(\varphi) = \exp^{jJ\varphi}$, where $j = \sqrt{-1}$. By substituting the trial solution into the differential equation one gets the particular solution

$$E_J = \frac{h^2}{16\pi^2 M r^2} J^2 = h c B J^2 = k_B \Theta_r J^2, \quad (2.31)$$

where $J = 0, \pm 1, \pm 2, \dots = \text{rotational quantum number}$, $B = \Theta_r k_B / (hc)$, and $\Theta_r = \text{characteristic rotational temperature}$.

It may be pointed out that $|J|$ is a measure of the number of nodes in the value of $\bar{\psi}$. Further the characteristic rotational temperature is inversely proportional to $M r^2$, which is the *mass moment of inertia*.

For a diatomic molecule, in which two masses, M_1 and M_2 , are connected to each other and are at a distance r_1 and r_2 , respectively, from the *center of gravity*, it is evident that $r_1 + r_2 = r$, the distance between the atoms, and $M_1 r_1 = M_2 r_2$. Therefore, one can show that the *mass moment of inertia* is

$$I = M_1 r_1^2 + M_2 r_2^2 = \mu r^2, \quad (2.32)$$

where $\mu = M_1 M_2 / (M_1 + M_2)$ is the *reduced mass*. Thus the *characteristic rotational temperature* and the moment of inertia for a homopolar diatomic molecule are related by the relation

$$\Theta_r = h^2 / [32\pi^2 k_B I]. \quad (2.33)$$

We discuss now the more general case when we determine for a given body the mass moment of inertia around various axes through the one and the same point (*center of mass*). We find, according to a theorem of mechanics, that there are three mutually perpendicular directions for which the moment of inertia is a maximum or minimum. These directions are called the *principal axes* and the corresponding moment of inertia as the *principal moments of inertia*, I_A , I_B , and I_C . Diatomic molecules and multiatomic molecules, in which two principal moments of inertia are equal and that of the third is zero or very small, are called *linear molecules*. If the three principal moments of inertia are all equal, then the molecule is called the

spherical top molecule, but if they are all unequal to each other, then the molecule is called the *asymmetric top (asymmetric rotor) molecule*. On the other hand, if at least two of the principal moments of inertia are equal, then it is a *symmetric top (symmetric rotor) molecule*.

In the more elaborate theory of quantum mechanics for a diatomic molecule J^2 in (2.31) is replaced by $J(J + 1)$. Thus the energy of a rigid diatomic rotor is

$$E_J = k_B J(J + 1) \Theta_r. \quad (2.34)$$

The frequencies of the spectral lines for transition between pure rotational energy levels can be calculated for rigid diatomic rotor from *Planck's radiation law*:

$$\begin{aligned} \nu &= \frac{\Delta E}{h} = \frac{E'' - E'}{h} = \frac{k_B \Theta_r}{h} [J''(J'' + 1) - J'(J' + 1)] \\ &= \frac{k_B \Theta_r}{h} (J'' - J')(J'' + J' + 1). \end{aligned} \quad (2.35)$$

Now the selection rule for such transitions is $\Delta J = \pm 1$. Thus, the equation for the frequencies of the lines due to transitions between pure rotational energy levels in a diatomic rotor is

$$\nu = \frac{2k_B \Theta_r}{h} J'' \quad (2.36)$$

for emission and

$$\nu = \frac{2k_B \Theta_r}{h} (J' + 1) \quad (2.37)$$

for absorption.

It is clear that these are equidistant lines. It may be pointed out that for homopolar molecules a change in the rotational quantum number does not mean any change in the electronic dipole moment, and as such for these molecules, transitions between pure rotational energy levels may take place by collision without radiation. However, the rotational bands may occur in Raman spectrum, as well as at the time of coupling with the electronic energy levels. In Table 2.1, the characteristic values of Θ_r and some other data for different diatomic molecular gases have been given, which have been determined from spectroscopical data. The electronic and vibrational energy levels are assumed to be in the respective ground state.

From the values of Θ_r given in Table 2.1 and (2.36) and (2.37), one can estimate the wavelength of radiation of lines for transition between pure rotational energy levels, $\lambda \approx hc / (2\Theta_r k_B) = 7.21 \times 10^7 / \Theta_r$, where λ is determined in Å. Thus it can be seen that these lines should appear in the wavelength range of 70 to $1.3 \times 10^5 \mu\text{m}$ (far infrared). Further, the energy difference for these transitions, $\Delta E \approx 2\Theta_r k_B J$ (in eV), is extremely small at small quantum numbers, but increases proportionately to the quantum number J .

Table 2.1 Characteristic data for different diatomic molecular gases

Gas	$\Theta_r(\text{K})$	$\Theta_v(\text{K})$	x	v_{\max}	$E_D(\text{eV})$	$\alpha(\text{K})$
H ₂	87.6	6333	0.0266	18.8	5.125	4.31e+0
N ₂	2.89	3400	0.0061	82.0	11.997	2.69e-2
O ₂	2.082	2280	0.0076	65.8	6.457	2.27e-2
Cl ₂	0.351	815	0.0070	17.2	0.605	2.86e-2
Br ₂	0.117	468	0.0033	40.3	0.812	2.44e-3
I ₂	0.054	309	0.0028	178.6	2.375	1.68e-4
OH	27.2	5375	0.0222	22.7	5.259	1.03e+0
CN	2.74	2981	0.0063	79.4	10.185	2.50e-2
CO	2.78	3130	0.0062	80.6	10.867	2.52e-2
NO	2.46	2745	0.0073	68.5	8.094	2.56e-2
HCl	15.26	4310	0.0174	28.7	5.332	1.61e-1

Table 2.2 Characteristic rotational data for multiatomic molecules

Molecule	Rotor					
	type	σ	$\Theta_r(\text{K})$	$\Theta_A(\text{K})$	$\Theta_B(\text{K})$	$\Theta_C(\text{K})$
HCN	(a)	1	0.213	0.213		
CO ₂	(a)	2	0.056	0.056		
CS ₂	(a)	2	0.016	0.016		
N ₂ O	(a)	1	0.060	0.060		
C ₂ H ₂	(a)	2	0.170	0.170		
SO ₂	(a)	2	0.949	0.949		
NH ₃	(b)	3	0.840	1.433	0.908	
BF ₃	(b)	3	0.027	0.050	0.024	
C ₂ H ₆	(b)	6	0.102	0.095	0.366	
H ₂ O ₂	(b)	2	0.188	0.118	1.449	
C ₂ H ₄	(b)	4	0.156	0.131	0.701	
CH ₄	(c)	12	0.517	0.757		
H ₂ O	(d)	2	1.527	2.090	4.005	1.337
H ₂ S	(d)	2	0.750	1.303	1.498	0.681

In addition, Table 2.2 contains rotational data for various molecules with more than two atoms, in which Θ_A , Θ_B , and Θ_C are characteristic temperatures along the principal rotational axis. The characteristic rotational temperature, Θ_r , is obtained from these values according to the following formulas:

- (a) *Linear molecules* ($\Theta_A = \Theta_B$): $\Theta_r = \Theta_A$
- (b) *Symmetric top molecules* ($\Theta_B = \Theta_C$): $\Theta_r = (\Theta_A \Theta_B^2 / \pi)^{1/3}$
- (c) *Spherical top molecules* ($\Theta_A = \Theta_B = \Theta_C$): $\Theta_r = \Theta_A / \pi^{1/3}$
- (d) *Asymmetric top molecules* ($\Theta_A \neq \Theta_B \neq \Theta_C$): $\Theta_r = (\Theta_A \Theta_B \Theta_C / \pi)^{1/3}$

In complex molecules, in addition, the rotation of one group of atoms relative to another (for example of the group CH₃ about the bond C–C in ethane) must be taken into consideration. Internal rotation may be hindered as well as free, because a

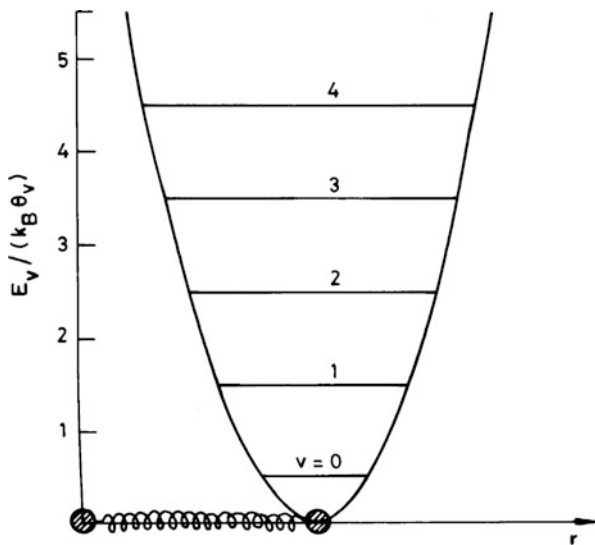


Fig. 2.3 Model and energy levels of a harmonic diatomic oscillator

molecule has a force field tending to orient a group of atoms in a definite position where the force inhibiting rotation is minimum to the position, where it is maximum, and is called the energy or potential barrier.

2.2.2 Harmonic Oscillator

Let there be two particles of equal mass M connected with a spring of spring constant k (Fig. 2.3). If the spring-mass system oscillates symmetric around a mean position, it is called a *harmonic oscillator*. From the theory of vibrations it can be shown that the frequency of oscillation for such a case is given by the relation

$$\nu = \frac{\sqrt{k/M}}{2\pi}. \quad (2.38)$$

Since the force $F = -kx = -dU/dx$, where U is the potential, $U = kx^2/2 = 2\pi^2 M \nu_{\text{osc}}^2 x^2$.

Thus (2.29) becomes

$$\frac{d^2 \bar{\psi}}{dx^2} + \frac{8\pi^2 M}{h^2} (E - 2\pi^2 M \nu_{\text{osc}}^2 x^2) \bar{\psi} = 0. \quad (2.39)$$

With $\xi = 2\pi x \sqrt{M\nu_{\text{osc}}/\hbar}$, $C = 2E/(\hbar\nu_{\text{osc}})$, the *wave equation* becomes

$$\frac{d^2\bar{\psi}}{d\xi^2} + (C - \xi^2)\bar{\psi} = 0. \quad (2.40)$$

Let there be a general trial function $\bar{\psi}(\xi) = H(\xi) \exp^{-\xi^2/2}$. Substituting this into the wave equation, the wave equation becomes

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (C - 1)H = 0. \quad (2.41)$$

This equation is solved with the boundary conditions

$$\xi \rightarrow \infty : \frac{d^2H}{d\xi^2} \rightarrow 0, \frac{dH}{d\xi} \rightarrow 0, H \text{ is finite.} \quad (2.42)$$

This equation is the so-called *Hermite equation*, which has a finite solution only when $(C - 1)/2$ is an integer. Assuming $(C - 1)/2 = v$, where v is an integer, we get $C = 2v + 1 = 2E/(\hbar\nu_{\text{osc}})$ and thus, the allowed vibrational energy levels of the diatomic harmonic oscillator are

$$E_v = \hbar\nu_{\text{osc}}(v + 1/2), v = 0, 1, 2, \dots, \quad (2.43)$$

where v is called the *vibrational quantum number* ($v = 0, 1, 2, 3, \dots$). From *Planck's radiation law*, the frequency of radiation is $\nu = |\Delta E|/\hbar = \nu_{\text{osc}}|\Delta v|$, and since from quantum mechanical considerations the most probable selection rule is $|\Delta v| = \pm 1$, the frequency of radiation is equal to the *frequency of oscillation* ($\nu = \nu_{\text{osc}}$) of a single line.

Defining a *characteristic vibrational temperature* $\Theta_v = \hbar\nu/k_B$, (2.43) becomes

$$E_v = k_B\Theta_v(v + 1/2). \quad (2.44)$$

Values of Θ_v for various diatomic gases given in Table 2.1 are applicable when the electron energy is in the ground level ($v = 0$). However, in the vibrational ground state ($v = 0$), the molecule possesses a nonzero vibrational energy $E_o = k_B\Theta_v/2$. Consistent with the convention adopted to measure the vibration energy from the ground state, we subtract this energy, and we get for the vibration energy as

$$E_v = vk_B\Theta_v. \quad (2.45)$$

It may now be seen that for pure vibrational transitions, the energy difference ($|\Delta v| = 1$) is about two to three orders of magnitude larger than for pure rotational transitions. Thus any vibrational transition is almost always accompanied by rotational transitions. For rigid rotors, it has already been pointed out that the spectral

frequency in emission is given by the relation $\nu = 2BcJ''$, where $B = \Theta_r k_B / hc$. For a not so rigid rotor, there is a new value of Θ_r or B for every combination of the electron and vibration energy levels. Since the difference between the electronic energy levels are quite large in comparison to the difference between the vibrational energy levels, it may be assumed that the transitions between the vibrational energy levels may take place at the ground electronic energy level. The change in the value of Θ_r for different values of the vibrational quantum number is given approximately by the formula

$$\Delta\Theta_r = (\Theta_r)_{v=0} - \alpha v, \quad (2.46)$$

where values of α for various diatomic molecular gases are given in Table 2.1. Thus for a not so rigid rotor with vibrational and rotational transitions, and with $\Delta J = J'' - J'$, the wave number of radiation is

$$\begin{aligned} \bar{\nu} &= \nu/c = B''J''(J'' + 1) - B'J'(J' + 1) + \bar{\nu}_v \\ &= (B'' - B')(J' + 1)J' + B''\Delta J(2J' + \Delta J + 1) + \bar{\nu}_v, \end{aligned} \quad (2.47)$$

where $\bar{\nu}_v = k_B \Theta_v \Delta v / (hc)$.

For the three cases of $\Delta J = -1, 0$, and $+1$, we get

$$\begin{aligned} \Delta J = -1 : \bar{\nu} &= (B'' - B')(J' + 1)J' - 2B''J' + \bar{\nu}_v, \\ \Delta J = 0 : \bar{\nu} &= (B'' - B')(J' + 1)J' + \bar{\nu}_v, \\ \Delta J = 1 : \bar{\nu} &= (B'' - B')(J' + 1)J' + 2B''(J' + 1) + \bar{\nu}_v. \end{aligned} \quad (2.48)$$

Actually, corresponding to these three cases, there are three branches of spectral lines which together give a band structure. This is further repeated in the hyperfine structure of the spectra in the case of an electronic transition coupled with transitions between vibrational-rotational energy levels. It may again be pointed out, as in the case of transitions between pure rotational energy levels, that for homopolar molecules such transitions without an electronic transition do not involve a change in electronic dipole moment. Thus, no electromagnetic wave radiation is possible for these homopolar molecules, except when these transitions are coupled with transitions between electronic energy levels also.

For *heteropolar diatomic molecules* with two atomic masses M_1 and M_2 connected with a spring of spring constant k , the two differential equations are

$$M_1\ddot{x}_1 + k(x_1 - x_2) = 0 \text{ and } M_2\ddot{x}_2 + k(x_2 - x_1) = 0. \quad (2.49)$$

Thus, $M_1\ddot{x}_1 + M_2\ddot{x}_2 = 0$. Let $x_1 = x_{m1} \cos(\omega t)$ and $x_2 = x_{m2} \cos(\omega t)$. Therefore, $x_{m2} = -M_1 x_{m1} / M_2$ and from the first differential equation, the *frequency of oscillation* is

$$\nu_{\text{osc}} = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad (2.50)$$

where the *reduced mass* is $\mu = M_1 M_2 / (M_1 + M_2)$.

For further analysis (2.43) and the subsequent text are valid. Figure 2.3 shows the energy levels which are the sum total of the kinetic and potential energies of the vibrating atoms in the molecule, calculated from (2.43), as a function of the vibrational quantum number. The wavelength range of the spectra for the transition between the two vibrational energy levels can easily be computed from the values of the characteristic vibrational temperature in Table 2.1, and this should be between 10^4 and 10^6 Å to which transitions between the rotational energy levels are superimposed as the hyperfine structure of the spectra. While the harmonic oscillator model is adequate as long as the ratio of T/Θ_v is small, the model fails with increasing temperature because the dissociation and the increase in the volume with temperature cannot be explained. Therefore, under these conditions the model of an anharmonic oscillator is studied, which is discussed in the next section.

For multiatomic molecules (number of atoms in the molecule > 2), there can be different characteristic temperature for each degree of freedom of vibration; values of the characteristic vibration temperature for a select number of gases are given in Table 2.3 with the associated *degeneracy* given within the parenthesis.

2.2.3 Anharmonic Oscillator

While the concept of vibration rests on the assumption of sufficiently small amplitude, actually the amplitudes are by no means infinitesimal small and for accurate calculations higher order terms in the potential energy are required. Energy levels for such an oscillator are modified from (2.43) and are given by the relation

$$E_v = (v + 1/2)h\nu_{\text{osc}} - x(v + 1/2)^2 h\nu_{\text{osc}}, \quad (2.51)$$

where x is a material constant and is acting as a correction factor in the harmonic oscillator model. The value of x is determined from the maximum value of $v = v_{\text{max}}$ when dissociation takes place. Since $v \rightarrow v_{\text{max}}$, $E_v \rightarrow E_D = \text{dissociation energy}$, and $dE_v/dv = 0$, it is evident that $v_{\text{max}} = (1 - x)/(2x)$ and $E_D = h\nu_{\text{osc}}/(4x)$. Thus from (2.51)

$$\frac{E_v}{E_D} = \frac{(1 + 2v)}{1 + 2v_{\text{max}}} \left[2 - \frac{(1 + 2v)}{1 + 2v_{\text{max}}} \right]. \quad (2.52)$$

For a harmonic oscillator $x \rightarrow 0$, $v_{\text{max}} \rightarrow \infty$, and $E_D \rightarrow \infty$, but for anharmonic oscillator as $v \rightarrow v_{\text{max}}$ the ratio E_v/E_D goes to one. Therefore, use of (2.52) is not meaningful, since there is no dissociation. However, for the purpose of comparison

Table 2.3 Characteristic vibrational temperature for selected multiatomic gases with degeneracy within parenthesis

Gas	$\Theta_{v,k} \text{ (K)}$											
	$k = 1$	2	3	4	5	6	7	8	9	10	11	12
H ₂ O	4170	1820	4290									
H ₂ S	3760	1860	1870									
SO ₂	1660	760	1920									
NO ₂	1900	930	2340									
CO ₂	1930	960	3390									
	(2)	(2)										
CS ₂	950	570	2190									
		(2)										
N ₂ O	1850	850	3200									
		(2)										
O ₃	1020	1500	2510									
	(2)	(2)	(2)									
C ₂ H ₂	4860	2840	4740	880	1050							
				(2)	(2)							
C ₂ N ₂	3350	1220	3100	730	330							
				(2)	(2)							
NH ₃	3800	1080	3900	1860								
			(2)	(2)								
BF ₃	1280	1010	2160	690								
			(2)	(2)								
H ₂ O ₂	4130	2070	2030	1250	4910	1970						
CH ₄	4200	2200	4350	1880								
		(2)	(3)	(3)								
C ₂ H ₄	4350	2340	1930	1190	4720	1510	1370	1360	4480	1430	4310	2080
SF ₆	1120	930	1390	890	760	520						

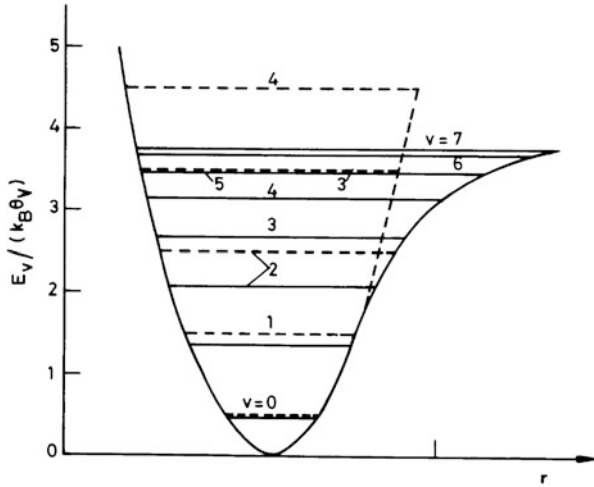


Fig. 2.4 Energy levels of an anharmonic oscillator ($v_{\max} = 7$)

with anharmonic oscillator, E_D is kept the same for both oscillators. Therefore for a harmonic oscillator, the expression taken is $E_v/E_D = (v + 1/2)/(4x)$. With a value of v_{\max} around seven, corresponding to a value of x around 0.0667, values of E_v/E_D are plotted in Fig. 2.4 along with energy levels and approximate potential distribution curves for both harmonic and anharmonic oscillators. It is seen that for a given value of the vibrational quantum number, a harmonic oscillator has a higher energy level than an anharmonic one. Further v_{\max} need not have a round figure, and is only an approximation obtained from the energy levels determined spectroscopically. From Table 2.1, it is clear that the above value of $v_{\max} = 7$ is no way near the actual value for a diatomic molecular gas, and the smallest value of v_{\max} is 18. This has the effect that the vibrational energy levels for small values of v are not much different for harmonic and anharmonic vibrational models. From (2.51), one obtains the equation for the wave number of the vibration spectra of an anharmonic oscillator for an energy level jump from quantum number v'' to v' as

$$\bar{\nu}_v = \frac{\nu_v}{c} = \frac{\Theta_v k_B}{hc} (v'' - v') [1 - x(v'' - v' + 1)]. \quad (2.53)$$

In emission, for $\Delta v = v'' - v' = 1$,

$$\bar{\nu}_v = \frac{\Theta_v k_B}{hc} [1 - 2x(v' + 1)]. \quad (2.54)$$

Since x is much smaller than one, for small values of v' , the spectral frequency of the vibrational lines is dependent only on the characteristic vibrational temperature of the gas. By accurately measuring the frequency of the spectral lines of vibration it is possible to determine Θ_v , x , and the dissociation energy. These are given in Table 2.1.

Table 2.4 Anharmonicity constants for some multi-atomic molecules

Gas	x_{11}	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}
CO ₂	-0.3	-1.3	-12.5	5.7	-21.9	-11.0
HCN	52.0	-2.8	-35.5	-4.2	-14.4	-19.5
N ₂ O	-3.2	-2.2	-13.7	4.7	-12.4	-26.1
H ₂ O	-43.8	-19.5	-46.3	-20.0	-155.	-19.8

While the expression for potential as given in (2.51) represents the potential energy of a diatomic molecule near the equilibrium position only, the expression for the potential curve better representing the vibration potential distribution given by Morse (for reference, see *Herzberg* [73]) is

$$U(r - r_e) = E_D (1 - \exp^{\beta(r-r_e)})^2, \quad (2.55)$$

where E_D is the dissociation energy. Note that as $r \rightarrow \infty$ and $U \rightarrow D_e$ and at $r = r_e$, equilibrium distance, $U = 0$.

While further we have assumed so far that there is no coupling between the rotational and vibrational energy levels, in actual practice this is not so. In the case of nonrigid rotor, the rotational energy for a diatomic molecule is

$$E_J = J(J + 1)k_B\Theta_r - 4k_B\Theta_r(\Theta_r/\Theta_v)^2 J^2(J + 1)^2 \quad (2.56)$$

in which Θ_r is calculated at the vibrational ground level and in which for most of the molecular species, the effect of the change of Θ_v at high rotational quantum number J is neglected.

For a multiple atomic gas, depending on the symmetry, there can be a number of values of v and x . In addition, there are cross-terms linking different modes of vibration, for which the vibration energy becomes

$$\begin{aligned} E_v &= E_v(v_1, v_2, v_3) \\ &= k_B \sum_{i=1}^3 \left[\Theta_{vi} \left(v_i + \frac{1}{2} \right) - \sum_{k=1}^3 x_{ik} \left(v_i + \frac{1}{2} \right) \left(v_k + \frac{1}{2} \right) \right] \end{aligned} \quad (2.57)$$

in which x_{ik} are the *anharmonicity constants*. For some typical molecules these are given in Table 2.4.

Finally, we would discuss the effect of putting the ground vibrational energy level to zero as per the convention. For the anharmonic oscillator, this results in the relation $v_{\max} = 1/(2x)$, but the relation between E_D and $h\nu_{\text{osc}}$ does not change. Equation (2.52) becomes

$$\frac{E_v}{E_D} = \frac{v}{v_{\max}} \left[2 - \frac{v}{v_{\max}} \right]. \quad (2.58)$$

Noting that the energy levels of a rotor are much smaller than the vibrational energy levels (for both harmonic and anharmonic vibration models), which, in turn, are much smaller than those of the electronic excitation, a pure rotational spectra of equidistant lines can be expected only in the far infrared region with very small change in the energy values. On the other hand, the rotation-vibration spectra (with most probable selection rule $|\Delta v| = 1$ giving a strong single rotation-vibration band in near infrared having larger change in the vibration energy values) have rotational lines as fine structures. Similarly, the electronic transitions are always accompanied by vibrational transitions (without the restriction of the previous selection rule), which in turn are accompanied by rotational lines as the hyperfine structure of the spectra; these are generally found in the visible and the ultraviolet regions.

While we have discussed, at least partially, the energy levels in molecules in the form of rotational, vibrational, and electronic energy, there are other energies like translational energy which we did not discuss. Further we have not discussed so far about the distribution of these energies among the molecules. This we would discuss further in the next chapter.

2.3 Exercise

- 2.3.1 Estimate the spectral wavelengths for He^+ and Li^{++} .
- 2.3.2 Calculate the wavelengths and energy exchanged in the Balmer series lines of hydrogen atom.
- 2.3.3 Calculate the spectral wavelengths in rotation and vibration separately for the heteropolar diatomic molecules OH, CN, CO, NO, and HCl.
- 2.3.4 Using the *characteristic vibrational temperature* for various molecules given in Tables 2.1 and 2.3, calculate the spectral wavelength of vibrational-rotational band and the corresponding energy.
- 2.3.5 Verify the values of dissociation energy of diatomic molecules given in Table 2.1, when the anharmonicity constant x is given.

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