
Chapter 1**INTRODUCTION****1.1 General:**

The Spectroscopy is a branch of Physics which deals with the interaction of electromagnetic radiation with matter. It is presently going through an exciting time of renewed interest, which is being fueled by the rapid development of sophisticated experimental approaches. Recent development of powerful lasers to create complex excitations, thus allows one to study the highly excited levels with unprecedented resolution. New detecting techniques are constantly being developed with sensitivities far exceeding the limits of detectors which are not available a few years ago. The recent increasing interest in the role of anharmonicities and resonance couplings, made unavoidable by the study of higher lying rovibrational states and the experimental reality of avoiding inhomogeneous broadening makes the entire domain of direct interest to spectroscopists. To understand and analyze a physical system in its befitting manner molecular spectroscopy is an area of active interest from many stand points. Having its numerous connections with many other branches, molecular spectroscopy has been playing an important role both in experimental and theoretical approaches. At present the structure and dynamics of highly excited vibrational states of

polyatomic molecules is a subject of considerable interest. In studies of intra-molecular dynamics, benzene occupies an interesting position as text book example (Herzberg, 1945; Wilson, Decius and Cross, 1955; Page, Shen and Lee, 1987) of a molecule of intermediate size. The Benzene is a highly symmetric molecule and its overtone spectra and some of its isotopic derivatives have been at the starting point of the interesting discussion of the intra-molecular vibrational redistribution processes as visible in vibrational spectra. Benzene has also been considered as a prototype molecule for harmonic force field calculation (Bray, Berry, 1979; Page, Shen and Lee, 1988; Wilson, 1934) local mode theory (Rump and Mecke, 1939; Henry and Siebrand, 1968; Hayward, Henry and Siebrand, 1973) radiationless transitions, high resolution electronic spectroscopy (Collomon, Dunn and Mills, 1966; Schubert, Riedle, Neusser, 1989; Bruno, Riedle and Neusser, 1986) and high resolution infrared and Raman spectroscopy (Jensen and Brodersen, 1979; Hollinger and Welsh, 1978).

The present study leads to the vibrational analysis of Benzene, monomer and dimer of Benzene and three of its derivatives using Lie Algebraic approach which strongly relies on the traditional unitary group theory and hence examine the interactions that account for the Casimir and Majorana couplings and their consequences for fundamental and overtone spectra and dynamics. Our analysis follows the traditional approach of the Vibrational mode description of Wilson used in many papers on Benzene spectra.

Isotopically leveling Benzene causes the Benzene (h_6) modes to lose this identity due to alteration of the kinetic energy term in the Hamiltonian. A quantitative description of these modes can be obtained by expressing the Vibrational Hamiltonian of the heavy leveled Benzene. This expression involves diagonal and off-diagonal terms by Casimir and Majorana operators which provide a quantitative description of the normal modes of Benzene molecules and its derivatives.

1.2 Survey of literature:

During the last two decades, continuous interest in the spectroscopy of C-H stretch vibrations of polyatomic molecule has resulted in the accumulation of information concerning the dynamics of intra-molecular vibrational energy redistribution processes. These investigations concern a large number of molecules. Among them Benzene and its derivatives have been extensively studied and continued to arouse considerable interest (Bassi, Corbo, Lubich and Scotoni, 1997).

Developments of new modern spectroscopic techniques give the provisions of obtaining information on molecular Vibrational overtones and combination states (Choudhury *et al*, 2010). In view of this experimental technique one needs theoretical models to interpret experimental data. Traditional approaches by solving Schrödinger equation with interatomic potentials and Dunham's expansion (Dunham, 1932) becomes difficult to apply in the case of polyatomic molecules. To overcome the difficulties arised in analyzing the vibrational spectra by traditional methods, a third approach i.e. Vibron Model (the Algebraic Model) based on Lie Algebra (Iachello, 1981) was built in the second half of the 20th century. This new model based on one dimensional Vibron Model appears to describe the molecular spectra successfully even in complex situations.

The essence of the algebraic method can be traced to the Heisenberg's formulation of quantum mechanics (Heisenberg, 1925). The use of Lie Algebra as a tool to systematically investigate physical systems (the so called spectrum generating algebra) did not however developed fully until 1970's when it was introduced in a systematic fashion by Iachello, F and Arima, A in the study of spectra of atomic nuclei (interacting Boson model) (Iachello, 1974; Arima and Iachello, 1975; Iachello and Arima, 1987). Soon afterwards the algebraic method was extended to rotation-vibration spectra of polyatomic molecules (Van Roosmelen, Dieperink and Iachello, 1982). The basic idea in this new approach is that of expanding the Hamiltonian and the other operators in terms of set of Boson creation and annihilation operators characterizing the local/normal

modes of the system. Contrary to the potential (differential/wave formulation) approach, all manipulations here are algebraic.

The recent advent of high resolution spectroscopy, such as molecular-beam spectroscopy has led to a much more detailed understanding of Benzene overtone transitions, demonstrating the existence of well structured absorption spectra at least in the case of low order overtones (Page, Shen and Lee, 1988; Scotoni, Boschetti, Oberhofer and Bassi, 1991; Scotoni, Leonardi and Bassi, 1991). Algebraic models have shown to constitute a powerful tool for addressing the spectroscopic problems (Iachello and Levine, 1994; Iachello and Oss, 1992; Iachello and Oss, 1993). The algebraic model in its one-dimensional realization was used to analyze portions of vibration spectra of Benzene and some of its isotopic substituted forms (Bassi, Menegotti, Oss, Scotoni and Iachello, 1993). Several algebraic models with the help of Lie Algebra have been reported by different workers (Ogilvie, 1978; Halonen and Child, 1982; Iachello, Oss and Lemus, 1991; Iachello and Oss, 1990; Van Roosmelen, Benjamin and Levine, 1984; Michelot and Moret-Bailly, 1987; Leroy and Michelot, 1992; Lemus and Frank, 1994), but the interpretation of the spectra requires further improvement. The main advantage of the algebraic method is that anharmonicities in the energy spectra are put in from the very beginning and anharmonicities in the interactions between different modes are introduced automatically since they are already contained in the matrix elements of the step operators.

Since anharmonicities play crucial role in Vibrational spectroscopy, it is here that the algebraic methods have found their most useful applications and hence we have chosen the problem.

In this work, we present the Lie Algebraic method for determining the vibrational spectra of Benzene and its derivatives. The advantage of the algebraic approach is that the entire class of molecules can be described by a generic form of algebraic Hamiltonian where only the parameters are different for different molecules.

There is a considerable current research interest in the study of higher vibrational states of polyatomic molecules. The appearance of new experimental techniques to detect the higher vibrational excitation in polyatomic molecules requires theoretical methods for their interpretation. In integro differential techniques, the molecular Hamiltonian is parameterized in terms of internal co-ordinates (Wilson, Decious and Cross, 1955). The potential is modeled in terms of force field constant either through complex calculations involving molecular electronic energy of several configurations (Raynes, Lezzeretti, Zanasi, Sadlej and Fowler, 1987) or experimentally by fitting of spectroscopic data (Gray, Robiette, 1979). In case of polyatomic molecules the knowledge of force field is poor due to large number of force constants. The potential may be modeled by representing the anaharmonicity of bonds by a sum of anharmonic Hamiltonians, among these, Morse potential is commonly used. The first step towards the algebraic approach was given by Iachello, Levine and co-workers with the introduction of Vibron model where rotation-vibration spectra of molecules was described by $U(4)$ algebra. In 1984, Van Roosmelen et al proposed an algebraic model to describe the stretching vibrational modes of ABA molecules (Van Roosmelen, Benjamin and Levine, 1984). This model is based on the isomorphism between one dimensional Morse potential and $SU(2)$ algebra and corresponds to the algebraic version of the coupled Morse oscillator method developed by Halonen and Child. The use of $SU(2)$ model was not developed further to include in case of complex molecules until 1991 when Iachello and Oss proposed its extension to describe stretching vibrational modes of polyatomic molecules, such as Benzene like systems [Iachello and Oss, 1991(b)]. The algebraic approach of vibrational stretching mode in polyatomic molecules was also proposed by Moret, Michelot, Bailly and Leroy (Michelot, Moret and Bailly, 1987; Leroy and Michelot, 1992) using unitary group $U(n)$ with $(n-1)$ approach. An important step in the development of algebraic $SU(2)$ model was recent extension to incorporate bending modes.

In the past few years the results of Vibration spectra of HCN, OCS HCCF, HCCD, OCS and HCP (Sarkar *et al.*, 2006 ; 2007; 2008; 2009), CCl_4 , $SnBr_4$, CF_4 and

Propadiene (Choudhury *et al.*, 2008;2009), Ni(OEP), Ni(TPP), Ni Porphyrin(Karumuri *et al.*, 2008; 2009) have been reported by using algebraic approach with a few algebraic parameters. Also, vibrational spectra of molecules such as tri-fluoro benzonitrile, trifluoro-aniline and trifluoro benzoic acid dimmers were studied with a variety of experimental tools such as FTIR,IR, Raman spectra, DFT and SQMFF (Mukherjee *et al.*, 2008; 2009; 2010).

Although extensive studies on these systems have clarified several aspects, many other aspects require further theoretical explanations and there is enormous scope for improving the algebraic method for determining vibrational energy levels of Benzene and its derivatives.

1.3 Dynamics of Molecules and Normal Modes of Vibration:

In a molecule consisting of N atoms, there are $3N$ degrees of freedom or modes of vibration. The complete nuclear motion of N -atomic molecules can be described by $3N$ parameters. The translations of a molecule can always be described by three parameters and the rotation of any linear molecule can be described by two parameters and that of a non-linear molecule by three parameters. This means that there are always three translational and three (for linear molecules two) rotational degrees of freedom. The remaining $3N-6$ (for the linear case $3N-5$) degrees of freedom account for the vibrational motion of the molecule. They give the number of normal vibrations.

The translational and rotational degrees of freedom which do not change the relative positions of the atoms in the molecule are often called *non-genuine modes*. The remaining $3N-6$ (or $3N-5$) degrees of freedom are called *genuine modes*. In a crystal, all the $3N$ degrees of freedom of the molecule become oscillatory. The oscillations arising from translations and rotations of the molecule are known as translatory and liberatory lattice vibrations respectively. These vibrations are often referred to as external vibrations to distinguish them from the so called internal vibrations of the individual molecules. In General, all these vibrations in a crystal are governed by inter- and intra- molecular interactions. Although the dynamics of a molecule or a solid appears to be

complex it may be described in terms of simple modes of motion, known as *normal modes*.

Normal Modes of Vibration:

The random motion of molecular vibrations can always be decomposed into the sum of relatively simple components called *normal modes of vibration*. Each of the *normal modes* is associated with a certain frequency and thus, for a *normal mode* every atom of the molecule moves with the same frequency and in phase.

There are three characteristics of normal vibrations which are as follows:

- i. Their number,
- ii. Their symmetry,
- iii. Their types.

i. Their number:

Since vibration is only one of the possible forms of motion it has to be separated from the others, translation and rotation. For an N-atomic molecules there are always three translational and three (for linear molecule two) rotational degrees of freedom. The remaining $3N-6$ (for the linear case $3N-5$) degrees of freedom account for the Vibrational motion of the molecule. These give the number of normal vibrations.

ii. Their symmetry:

The close relationship between symmetry and vibration is expressed by the following rule:

Each normal mode operation forms a basis for an irreducible representation of the point group of the molecule. From the symmetry group of the molecule, the symmetry species of the *normal modes* can be determined without any additional information.

iii. Their types:

The *normal modes* can usually, though not always, be associated with a certain kind of motion. Those connected mainly with the changes in

bond lengths are the *stretching modes* and those with the changes of bond angles are the deformation. These deformation modes may be mainly either in-plane and out of plane. The simplest deformation mode is the *bending modes*.

1.4 Molecular Spectra and Vibrational Spectroscopy:

Molecular spectroscopy deals with the interaction of electromagnetic radiation with molecules. This results in transitions between rotational and vibrational energy levels in addition to electronic transitions. As a result, the spectra of molecules are much more complicated than those of atoms. Current interest in molecular spectroscopy is very great because numbers of known molecules are extremely large as compared with free atoms. As a result of the interaction of electromagnetic radiation with the molecules, electromagnetic radiation characteristics of the interacting system may be absorbed or emitted. In such a case, the experimental data consists of the nature (frequency or wavelength) and the amount (intensity) of the characteristic radiation absorbed or emitted. In spectroscopy, we correlate these data with the molecular and electronic structure of the substance and with intra-molecular and intermolecular interactions. Amplitude and periodicity are the two properties by which an electromagnetic radiation is characterized. The periodicity of an electromagnetic radiation is defined in terms of wavelength, wave number or frequency of the radiation. The wavelength (λ) is defined as the distance between any two consecutive points of the electromagnetic wave having same phase. We often characterize the electromagnetic radiation by the wave number ($\bar{\nu}$) which is defined as the number of waves contained per unit length, usually one centimeter. Dimension for wave number is reciprocal centimeter (cm^{-1}). The relation between wavelength and wave number is given by $\bar{\nu} = 1/\lambda$. It is known to us that all radiations travel uniformly with the velocity of light in vacuum (c) and the c/λ is termed as the frequency (ν) of the radiation. The frequency of a radiation is expressed as the number of waves that pass a

particular point per unit time (second). Thus, both the wave number and frequency are directly proportional to the energy of the radiation. As the name implies, an electromagnetic radiation has both an electric field (**E**) and a magnetic field (**H**) associated with it. Both **E** and **H** oscillate in a periodic manner (sinusoidally) at mutually perpendicular directions. All transverse directions for the electric and magnetic fields are equally represented in natural light. However, the electric vector is confined to a particular plane in case of a plane polarized light.

Elements of spectroscopy:

Any spectroscopic technique could be considered under the following heads:

- i. Radiation that interacts with the matter.
- ii. Energy levels that effect transitions among different energy levels.
- iii. Absorption (or emission) bands obtained as a result of these transitions.

The position, band width, number and intensity of the absorption (or emission) bands may be correlated with the molecular and electronic structure and bonding. By virtue of its different kinds of motion and intra-molecular interactions, an isolated molecule in space has various forms of energy. The molecule possesses translational energy by virtue of the motion of the molecule as a whole. The molecule possesses rotational energy due to bodily rotation of the molecule about an axis passing through the centre of gravity of the molecule. It may possess Vibrational energy due to periodic displacement of its atoms from their equilibrium positions. The molecule also may possess electronic energy since the electrons associated with each atom and bonds are in constant motion. In addition to these energies, the molecule further may possess nuclear energy and energy due to nuclear and electron spins. Having these much of information, as a first approximation, one can now express the total energy of a molecule as the sum of the constituent energies, i.e. ,

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} \quad (1.1)$$

We assume that the various types of energy associated with different motions of the molecule are independent of one another. It may be noted that a molecule can have many levels of these different energies. Absorption of a finite amount of energy, can take a molecule from one energy level to a higher energy level. It is known to us that there is a very big difference in mass between the electron and the nucleus. Due to this reason, it is permissible as a very good approximation, to regard the respective motions (of the electron and the nucleus) as mechanically separable. This approximation, as we know, is termed as the Born-Oppenheimer approximation (Banwell, 1992; Sathyanarayana, 2000). Born-Oppenheimer approximation tells us that in practice, we need not consider electrons explicitly in the treatment of molecular vibrations. Of course, one must note here that the presence of electrons does make itself felt in the dependence of the force constants on the electronic structure. For an electronic transition, the time required is about 10^{-15} s, on the other hand for a vibrational transition, the time required is about 10^{-13} s. From this data it is very much clear that the electronic transitions are about 10^{-2} times faster than the vibrational transitions.

The vibrational motion interacts with the rotational motion. These rotation-vibration interactions are however, generally very weak. In a typical rotational transition the energy involved is about 10^3 times smaller in magnitude than in a typical vibrational transition. The separation of rotational motions from vibrational motions thus represents a good approximation for vibrations of free molecules. For a rotational transition the time required (about 10^{-10} s) is higher than for a typical vibrational transition (10^{-13} s). Another important point is to be noted here that the energy due to nuclear and electron spins is negligible. It is now known to us that a system will continue to vibrate in exactly the same way irrespective of whether it is simultaneously undergoing translational motion uniformly through space in any direction. Translational motion is thus separable from the vibrational and other kinds of motion. And hence reasonably it's a good

approximation to consider the vibrational motions of polyatomic molecules independently of other types of motion. Now we consider two energy states of a system, let us say two vibrational energy levels labeled as E_1 and E_2 (Figure. 1.1). Here the subscripts 1 and 2 which distinguish the levels are referred to as 'quantum numbers'. The expressions we use to define the energy levels will involve one or more quantum numbers. The transition which takes the system from the lower level E_1 to the higher level, E_2 can occur provided an appropriate amount of energy $\Delta E = E_2 - E_1$ is absorbed by the system. In this context also one knows that if the system is already at the higher energy level E_2 by emission of energy ΔE , a transition to the lower energy level E_1 can take place. In this process, the frequency of the electromagnetic radiation absorbed (or emitted) is given by the Planck's equation,

$$\begin{aligned} \Delta E &= h\nu \\ \Rightarrow \nu &= \frac{\Delta E}{h} \end{aligned} \quad (1.2)$$

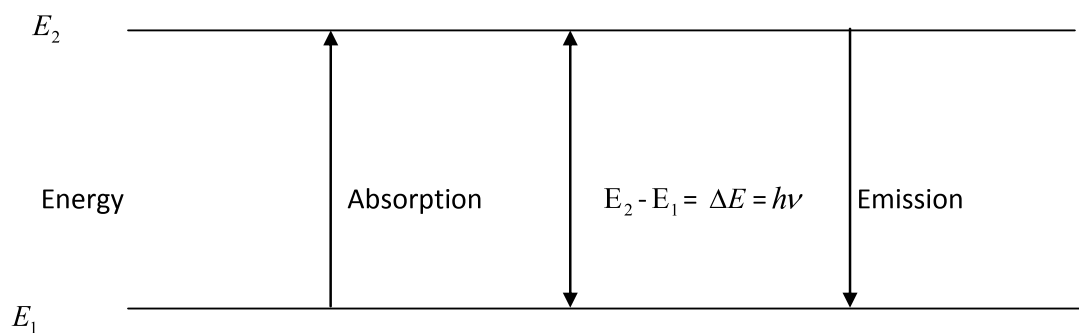


Fig. 1.1: Typical Transition

Equation (1.2) represents the basic equation of all spectroscopic studies. From this equation we see that a molecule in level E_1 by absorbing radiation of frequency, $\nu = \Delta E/h$ can occupy the energy level E_2 . If we use a detector to analyze the radiation it will reveal that the intensity of the beam has decreased after its interaction with the molecule. In case a radiation beam

containing a range of frequencies are used, only the radiation of frequency, $\nu = \Delta E/h$ would decrease in intensity and the intensity of the radiation of other frequencies would remain undiminished. It is thus clear that in absorption spectroscopy, one observes what frequencies of radiation are absorbed from the incident radiation as it passes through the sample. Thus one may have a plot of the intensity of the radiation absorbed against the frequency of the radiation, which is nothing but the absorption spectrum. Definitely there must be some mechanism by which the interaction between the incident electromagnetic radiation and the molecule takes place leading to the absorption of energy by the molecule producing changes in the nuclear, molecular or electronic energy. One may think that the interaction occurs through the electric or magnetic field associated with the electromagnetic radiation with appropriate electric or magnetic fields produced by changes taking place in the molecule. No absorption of radiation can occur, if there is no interaction between the molecule and the radiation. In this regard one should note that whether the interaction of the electromagnetic radiation with the system occurs or not is determined by the 'selection rules'. And thus this restriction on the appearance or otherwise of the absorption bands may give valuable information about the structure of the molecule under examination. It is already mentioned earlier that the frequency of the radiation absorbed or emitted depends on the energy difference (ΔE) between the two levels involved in the transition and this energy difference is different for rotational, vibrational, electronic, etc. energies. Consequently, the corresponding spectra occur in different regions of the electromagnetic spectrum. For the following, we discuss on the applications of vibrational spectroscopy.

Applications of vibrational spectroscopy:

Vibrational spectroscopy can provide the dynamic picture of a molecule. Vibrational spectroscopy is important principally because it is a fast

technique. Vibrational spectroscopy may be applied to many substances such as solid, as crystals or powder; liquids, solutions, melt; gases, films and adsorbed species. Due to this reason vibrational spectroscopy has very wide applications. The bandwidth, position, number and intensity of the absorption bands may be correlated with the electronic and molecular structure of the system. For the elucidation of molecular structure, vibrational spectroscopy may be considered as a valuable tool. Vibrational spectroscopy provides us important information about the intermolecular forces in condensed phase, the intra-molecular forces acting between the atoms in a molecule and the nature of the chemical bond. One should note here that the goal of high resolution molecular spectroscopy is the determination of molecular geometry and the potential energy function. To characterize and identify a molecule, vibrational spectra can be utilized directly and simply as molecular “fingerprints”. Due to this excellent ability of vibrational spectroscopy, we apply it in the study of simple inorganic, coordination and organic compounds. Also one must not forget that vibrational spectroscopy has contributed significantly to the growth of other areas like polymer science, catalysis, fast reaction dynamics, charge-transfer complexes, and nano material studies.

1.5 Principles of Vibrational Spectroscopy:

Conventional approach:

The spectroscopy of diatomic molecules (Herzberg, 1950) serves as a paradigm for the study of polyatomic molecules.

To have a simple understanding here first we discuss the basic principles of vibrational spectroscopy in relation to diatomic molecules and then extend the concepts developed, to polyatomic molecules as in the case of conventional approach.

1.6 Diatomic Molecules:

Harmonic oscillator:

We may compare the chemical bond between the atoms A and B to a spring in a diatomic molecule, A-B. To make the case more transparent, the ball and spring model of a diatomic vibrator is shown in Figure. 1.2. We assume that the spring obeys Hooke's law i.e., the force exerted by the spring on the particle is proportional to the displacement from the equilibrium position (r_0). Now from Hooke's law we may have the relation between the restoring force (F) and the displacement q (from r_0 to $r_0 + q$) as

$$F = -kq \quad (1.3)$$

here the proportionality constant 'k' is called the force constant. As molecular Vibrational amplitudes are small, here the simple harmonic approximation is generally a good one. We give the potential energy (V) as

$$\begin{aligned} V &= -\int Fdq \\ &= \frac{1}{2}kq^2 \end{aligned} \quad (1.4)$$

It is clear that the Eq. (1.4) relating potential energy to the displacement represents a parabola which is symmetrical about the equilibrium bond length, r_e . Newton's Second law gives us the familiar equation of a simple harmonic motion. According to classical mechanics the equation of motion is

$$m \frac{d^2q}{dt^2} = -kq \quad (1.5)$$

Equation (1.5) has a general solution

$$q = a \cos 2\pi\nu_0(t - t_0) \quad (1.6)$$

here a and t_0 are constants $\nu_0 = (1/2\pi) \sqrt{k/m}$ is the fundamental frequency of the oscillator. We can write the total energy E as

$$E = \frac{1}{2}kq^2 \quad (1.7)$$

From Eq. (1.7), we see that the vibrational energy of the nuclei depends only on the force constant k and the displacement q . Hence apparently any

energy value is allowed. This property that any positive energy value is allowed is the distinguishing mark of a classical harmonic oscillator.



Fig. 1.2: Diatomic oscillator: Ball and Spring Model.

It is known to us that the time – independent Schrödinger wave equation for a one – dimensional harmonic oscillator such as a particle of mass m executing simple harmonic vibration about the point $x = 0$ is given by

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (1.8)$$

Here E is the total Vibrational energy and x is the displacement. Now, using Eq. (1.4) in Eq. (1.8), we have the equation as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \quad (1.9)$$

We can now re-arrange the Eq. (1.9) such that it can be recognized as the Hermite differential equation. We know that the Hermite differential equation possesses solutions only for certain discrete values of its parameter. Applying the Schrödinger equation we are thus lead to the result that the energy of a harmonic oscillator is allowed to have only the values given by,

$$E_v = \left(v + \frac{1}{2}\right)h\nu = hc\bar{\nu}\left(v + \frac{1}{2}\right) \quad (\bar{\nu} \text{ in } cm^{-1}) \quad (1.10)$$

characterized by the vibrational quantum numbers v ($v = 0, 1, 2, \dots$). The Eq. (1.10) makes us clear that the quantum mechanical harmonic oscillator can have the energy only in positive half-integral multiples of $h\nu$. This gives discrete vibrational energy levels since all other conceivable energy values are not allowed. Hence a series of equally spaced and never ending vibrational levels are predicted and the molecule cannot dissociate. It is important to note that the lowest energy of a quantum-mechanical harmonic oscillator is $(1/2) h\nu$. We refer it as the zero point energy and it has its consequence in the Heisenberg uncertainty principle. Thus we see

that the energy levels of a quantum mechanical harmonic oscillator are equally spaced, the energy intervals between any two adjacent states being $h\nu$ (Figure. 1.3).

Selection rules:

Absorption of infrared radiation by a molecule results to the infrared absorption spectrum. Here the molecule undergoes a transition from one Vibrational energy state to another. Whether the absorption of radiation (by the molecules) can take place or not is determined by the selection rules.

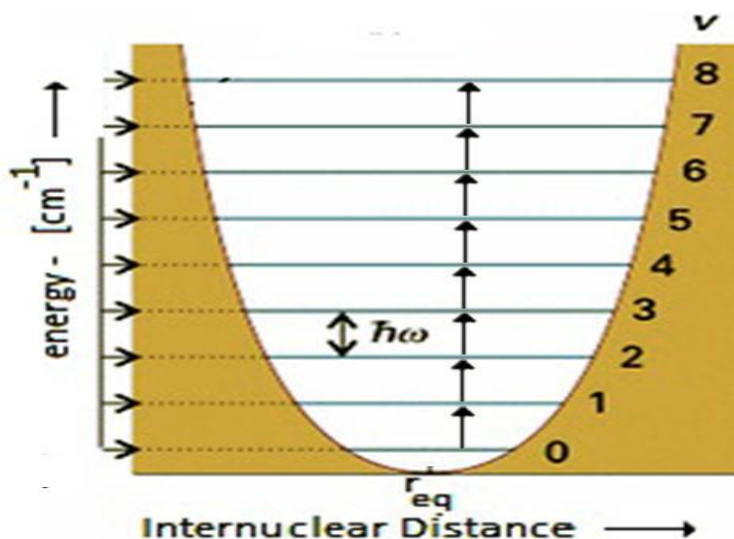


Fig. 1.3: The allowed Vibrational energy levels and transitions between them for a diatomic molecules undergoing simple harmonic motion. The energy interval between any two adjacent states here is $h\nu = \hbar\omega$

It is obvious that the field produced by the dipole oscillator (i.e. a vibrating molecule) consists of statistically fluctuating electric and magnetic dipole components mainly in the plane normal to the dipole axis and plane polarized in the direction of that axis. We may thus consider the vibrating molecule as producing a stationary alternating electric field whose magnitude changes periodically with a frequency equal to that of the vibrational frequency. The stationary alternating electric field (equation 1.8) produced by the vibrating molecule, interacts with the moving electric field

of the electromagnetic radiation. In case the diatomic molecule is homopolar, the stretching (or contraction) of the bond between the two atoms does not lead to any change in dipole moment and hence no fluctuating dipolar electric field is produced. Under such circumstances no interaction can take place with the electromagnetic radiation. On the other hand, for a heteroatomic molecule A-B, the electric dipole moment oscillates with the vibration frequency and hence radiation of this frequency can be absorbed. In this regard, it may be noted here that the energy absorbed must be such that the molecule would just exactly reach a higher allowed vibrational energy level.

This is equivalent to say that the radiation frequency must be identical to the frequency of the molecular vibration. The arrows in Figure.1.3 represent the transitions between adjacent levels, $0 \rightarrow 1$, $1 \rightarrow 2$, etc. Generally, the higher Vibrational level is denoted by v' and the lower level by v'' . It should be noted here that if the frequency of the radiation is not equal to the Vibrational frequency of the molecule, consideration of the interaction of the changing dipole moment and the moving alternating electric field shows that such an instantaneous interaction, will eventually be cancelled by one of exactly opposite phase. In a polyatomic molecule, the dipole moment change during a particular vibration may be dictated by the symmetry of the molecular vibration and hence this selection rule is often referred to as the symmetry selection rule (or gross selection rule). So far we have considered the transitions between adjacent levels. It may be noted that the transitions between nonadjacent levels are also energetically possible. The results of the quantum theory however, impose a restriction that the only allowed transitions for a harmonic oscillator are those between adjacent levels, that is, $\Delta v = \pm 1$. Often we refer this condition as the oscillator (or specific) selection rule. Using the Maxwell-Boltzmann distribution law, the number of molecules in the first excited state ($v' = 1$) relative to the number of molecules in the ground Vibrational state ($v'' = 0$) may be given by the following relationship:

$$\frac{N_1}{N_0} = \exp\left[-\frac{(E_1 - E_0)}{kT}\right] = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-h\nu}{kT}\right) \quad (1.11)$$

here ΔE is the energy difference between the two states, ν_1 , is the frequency in cm^{-1} of the excited Vibrational state, T is the temperature in Kelvin, k is the Boltzmann constant and h the Planck's constant. We know that at room temperature, kT corresponds to 200 cm^{-1} . Now, if ΔE is much larger than kT, the number of molecules (N_1) with energy E_1 is very much less than the number (N_0) with energy E_0 . From Boltzmann's law, it then follows that a great majority of the molecules are in their Vibrational ground state at room temperature. It is thus clear that at room temperature (T=300 K), the number of molecules in the excited Vibrational state falls off rapidly with the frequency of the excited vibration, but at lower temperatures, say at liquid nitrogen temperature (T=77K), the proportion falls off even more rapidly as seen from Table 1.1.

Now, as a consequence of the Boltzmann distribution law, most molecules would be found in the vibrational ground state ($v'' = 0$), the dominant transition in infrared spectroscopy is from $v'' = 0$ to $v' = 1$ and the transitions between adjacent states other than 0 and 1, though theoretically permitted, occur with very low probability because of the lower population. It may be noted here that the intensity of an absorption band is always proportional to the molecular population of the initial state from which the transition takes place. For a strictly harmonic oscillator however, such transitions say, from 1 to 2 are indistinguishable from the transitions between the levels 0 and 1 since all the energy levels of a harmonic oscillator are equally spaced.

**Table 1.1: Boltzmann population distribution as a function of frequency
(Sathyanarayana, 2000)**

Frequency (cm ⁻¹)	100	300	500	900
N ₁ /N ₀ at T = 300K	0.619	0.237	0.091	0.013
N ₁ /N ₀ at T = 77	0.139	0.003	0.001	

The transition from state $v'' = 0$ to state $v' = 1$ is known as the fundamental transition or simply as a fundamental. It should be noted here that the infrared fundamentals of interest (i.e. the Vibrational bands) occur between 4000 and 100 cm⁻¹.

Stretching Frequency:

We give the frequency of the stretching vibration for a diatomic molecule A-B as

$$\nu = \left(\frac{1}{2\pi c} \right) \sqrt{\frac{k}{\mu}} \quad (\text{in cm}^{-1}) \quad (1.12)$$

In equation (1.12), c is the velocity of light and μ is the reduced mass and is related to the masses of atoms A and B by $\mu = \frac{m_A m_B}{m_A + m_B}$. It may be noted

here that the vibrational stretching frequency is the characteristic of the diatomic molecule and is dependent on the force constant besides the masses of the two atoms concerned.

Anharmonic Oscillator:

The potential energy of a diatomic molecule in reality is more complex than that of a harmonic oscillator (equation. 1.4) since for larger values of displacement the molecule must dissociate. Figure 1.4 shows the potential energy of a diatomic molecule as a function of the internuclear distance r . In the same figure (Figure. 1.4) also we have shown the curve (parabola)

obtained from the equation (1.4) for a harmonic oscillator. Figure 1.4 shows that the true curve is steeper than the parabola at smaller inter-nuclear distances. The reason is, interatomic repulsive forces become larger in this region. Also we see from Figure. 1.4 that at large inter-nuclear distances, the true potential energy tends asymptotically to a constant value representing complete dissociation of the molecule into atoms. It is obvious that the true potential energy well is asymmetric. However, near the equilibrium inter-nuclear separation, the parabola is a good approximation to the energy of a real molecule. From this we get a clear cut indication which suggests, modification of the expression is required for the energy of a harmonic oscillator to include the effects of 'anharmonicity'. For the potential energy of an anharmonic oscillator a number of expressions have been suggested.

The Taylor series expansion is the simplest method to expand the Vibrational potential energy about the equilibrium position for small nuclear displacements. This is shown in the following expression

$$V = V_0 + \left(\frac{\partial V}{\partial q} \right)_0 q + \frac{1}{2} \left(\frac{\partial^2 V}{\partial q^2} \right)_0 q^2 + \left(\frac{1}{6} \right) \left(\frac{\partial^3 V}{\partial q^3} \right)_0 q^3 \quad (1.13)$$

here the subscript zero indicates that the values are evaluated at the minimum of the potential energy so that $\frac{\partial V}{\partial q} = 0$. V_0 is a constant independent of q and may be neglected since it does not affect the Vibrational frequencies. It may be noted that for the harmonic oscillator, we consider only the second derivative.

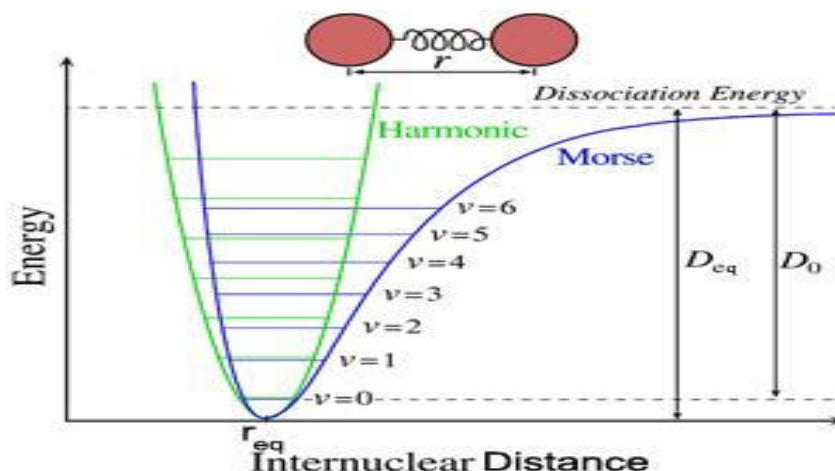


Fig. 1.4: The Morse Curve: The energy of a diatomic molecule executing anharmonic expansion and compressions.

For the potential energy of a diatomic anharmonic oscillator, a popular function is the 'Morse function' which is given by

$$V(r) = D_{eq} \left[1 - \exp \left\{ -\alpha (r - r_{eq}) \right\} \right]^2 \quad (1.14)$$

Here D_{eq} denotes the spectroscopic dissociation energy of the molecule and α is a constant characteristic of the internuclear bond in a specific electronic state. To the shape of the Morse curve (Figure. 1.4), a number of molecules can be fitted reasonably well. As r goes to zero, the Morse function approaches a very large finite value rather than becoming infinite. This defect is not significant since the behavior of the potential energy near $r = 0$ is unimportant. The potential energy becomes equal to the spectroscopic dissociation energy, D_{eq} when r tends to α .

In case of an anharmonic oscillator, the approximate solution to the Schrödinger equation expressing the Vibrational energy in terms of the harmonic frequency ν_e and an anharmonicity constant x_e is given by,

$$E = \left(\nu + \frac{1}{2} \right) h\nu_e - \left(\nu + \frac{1}{2} \right)^2 h\nu_e x_e \text{ (Joules)} \quad (1.15)$$

Eq. (1.15) provides a means of adjusting the observed frequency to the harmonic oscillator frequency. Here the second term is subtracted from

the first as expected from the convergence of the vibrational levels at higher quantum numbers. In two important ways, anharmonicity affects the molecular vibrations:

- i. The selection rule derived for the harmonic oscillator namely $\Delta V = \pm 1$ ceases to be a rigorous selection rule and transitions with $\Delta V = \pm 2, \pm 3$, etc., are allowed.
- ii. The vibrational levels are not spaced apart equally by the quantity $h\nu$ as shown in Figure. 1.5. Hence in this case, not only it may be possible to observe the transitions with $\Delta V = \pm 2, \pm 3$, etc., but also these transitions will not have exactly double, triple, etc. the frequency of the fundamental transition for which $\Delta V = \pm 1$.

In case a single vibrational quantum number changes by ± 1 , the transition is, as stated before, a fundamental transition and the corresponding frequency, a fundamental frequency usually denoted by the symbol ν . In case a single quantum number changes by ± 2 , the transition is said to be the first overtone. In case $\Delta V = \pm 3$, it is referred to as the second overtone and so forth. If two Vibrational quantum numbers change simultaneously in a polyatomic molecule, the resulting transition is referred to as a combination frequency. It is known that combination bands are of two kinds, sum band (let us say, $\nu_1 + \nu_2$) representing simultaneous changes in two (or more) Vibrational quantum numbers and a difference band (let us say, $\nu_1 - \nu_2$) representing a transition from an excited state $V'' = 1$ to $V' = 2$. Thus we see that presence of overtone and combination bands indicates the anharmonic character of the vibrations. In case overtone and combination bands are not observed, the harmonic approximation is an excellent one. It is obvious that the intensity of the overtone and combination bands is usually an order of magnitude weaker than that of the fundamentals. With respect to the first overtone, the second overtone is expected to be weaker. A gradual decrease in the intensity of the higher overtone bands is predicted in general.

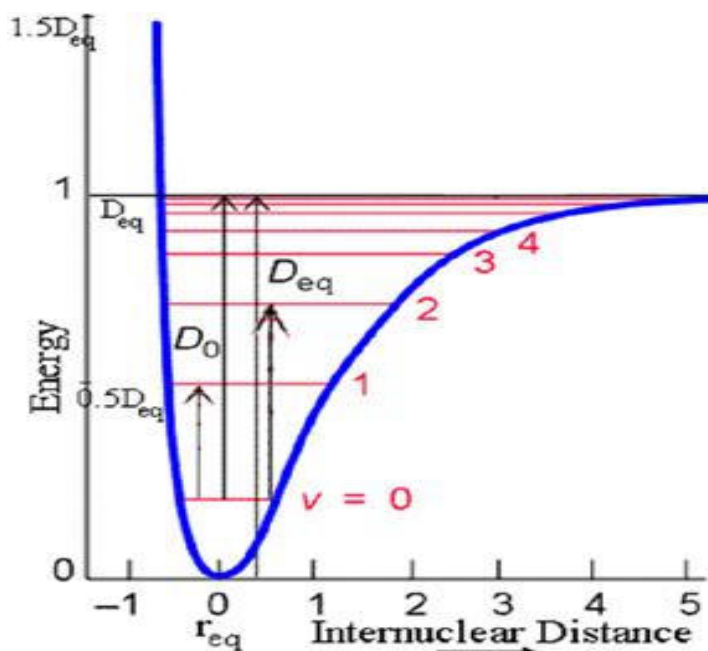


Fig. 1.5: The allowed vibrational energy levels and typical transitions between level for a diatomic molecule executing anharmonic oscillations.

The Eq. (1.15) which gives the energy of an anharmonic oscillator, may be rewritten as

$$E = \left(v + \frac{1}{2} \right) h\nu_e \left[1 - \left(v + \frac{1}{2} \right) x_e \right] \quad (1.16)$$

From Eq. (1.16) we see that the energy difference between the Vibrational states V and $V + 1$ is given by

$$\Delta E = [1 - 2 (1 + v) x_e] h\nu_e \quad (1.17)$$

Eq. (1.17) tells us that if x_e is positive, the energy spacing decreases with higher values of the vibrational quantum number V . The vibrational energy spacing increases, if x_e is negative. Usually, positive anharmonicities are observed for bond-stretching modes.

1.7 Structure of the benzene molecule:

Two scientists Kekul and J.Loschmidt thought of benzene's ring structure independently—a type of occurrence that is not unusual in science. The cyclic nature of benzene was finally confirmed by the crystallographer Kathleen Lonsdale. Benzene presents a special problem in that, to account for all the bonds, there must be alternating single and double covalent bonds between carbon atoms, which may be represented as:

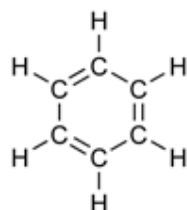


Figure 1.5A Benzene hexagonal structure with alternate single and double bonds

Using the technique known as X-ray diffraction, researchers discovered that all the carbon-carbon (C-C) bonds in benzene have the same length (140 picometers (pm)). The length of each C-C bond is greater than that of a double bond (134 pm) but shorter than a single bond (147 pm). The bond length of 140 pm, which is intermediate in length, is explained by the concept of "electron delocalization": the electrons for C-C bonding are distributed equally among the six carbon atoms. (One representation is that the structure exists as a superposition of two "resonance structures," rather than either form individually.)

This delocalization of electrons is known as *aromaticity*, which gives benzene great stability. This enhanced stability is a fundamental property of a class of molecules called "aromatic molecules," differentiating them from molecules that are not aromatic. To reflect the delocalized nature of the bonding, benzene is often depicted with a circle inside a hexagonal arrangement of carbon atoms (which are not labeled):

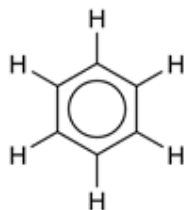


Figure 1.5B Benzene hexagonal structure with a ring formed by delocalized pi-electrons.

1.8. Vibrations of Polyatomic Molecules:

Energy and Spectral Transitions:

It can be seen that the energy level diagrams such as those used to describe transitions in a diatomic molecule (Figure. 1.3 or Figure. 1.6) can illustrate the vibrational transitions in polyatomic molecules except that there will be one such diagram for each of the $3N - 6$ fundamental vibrations of the molecule. Also it can be seen that the abscissa of each diagram is in the units of a normal coordinate. However, some of the potential energy curves will represent vibrations that are essentially stretching motions.

For a molecule (having N atoms), each vibrational energy is characterized by a set of $3N - 6$ vibrational quantum numbers $v_1, v_2, \dots, v_{3N-6}$. Now, if all the vibrational quantum numbers are equal to zero, the corresponding level is called the ground state vibrational level. Generally we refer the energy of this level as the zero point energy level, $E_v^0 (0, 0, \dots)$ and is not zero. If a polyatomic molecule has only one vibrational quantum number say, $v_k = 1$ and all other vibrational quantum numbers $v_i (i \neq k)$ are zero, the energy level is called the fundamental or the first harmonic level. Here we note that the band arising from a vibrational transition from the ground level to a fundamental level is known as a fundamental band or simply as a fundamental. Here, also it may be noted that each of the $3N - 6$ vibrational quantum numbers of a polyatomic molecule can independently be excited to a fundamental level from the ground state and each of these represents a fundamental

transition giving rise to a normal mode of vibration. For normal vibrations, it is the property that only one vibrational quantum number changes during a vibration. We describe each normal mode of vibration by a coordinate known as the normal coordinate and is generally denoted by Q . For a non-linear N -atom molecule, there are $3N - 6$ normal coordinates ($Q_1, Q_2, Q_3, \dots, Q_{3N-6}$). Here we note that corresponding to each normal vibration, there is a normal frequency generally denoted by ν and for a N -atom nonlinear molecule, there are $3N - 6$ normal vibrational frequencies $\nu_1, \nu_2, \nu_3, \dots, \nu_{3N-6}$. Here the symbol ν , should not be confused with stretching, since it is also used to denote a stretching vibration. For a polyatomic molecule, the procedure of calculation of normal vibrations - their frequencies and form - is referred to as normal coordinate analysis. Let us consider a triatomic molecule, for example SO_2 , having three vibrational quantum numbers ν_1, ν_2, ν_3 and $(0\ 0\ 0)$ represents the ground vibrational state. Here, the fundamental ν_1 corresponds to the transition $(0\ 0\ 0) \rightarrow (1\ 0\ 0)$ and ν_2 to $(0\ 0\ 0) \rightarrow (0\ 1\ 0)$ transition. $2\nu_2$, the overtone of the ν_2 fundamental, corresponds to the transition $(0\ 0\ 0) \rightarrow (0\ 2\ 0)$ and so forth. We write the first overtone of the fundamental say, ν_k as $2\nu_k$ although actually the frequency of the overtone may be slightly less than twice that of the fundamental. Similarly, the second overtone is written as $3\nu_k$. It may be noted that simultaneous excitation of more than one quantum number gives rise to a combination band. It is observed that the overtone and combination bands are useful in the determination of anharmonicity constants. We write the total vibrational energy for a polyatomic molecule as the sum of the individual energies for $3N - 6$ vibrations ($E_1 + E_2 + E_3 + \dots + E_{3N-6}$), i.e.

$$E_v = \sum_{i=1}^{3N-6} \left(\nu_i + \frac{1}{2} \right) h\nu_i \quad (1.18)$$

From Eq. (1.18), it is clear that for an N -atom molecule the zero-point energy $E_v^0(0, 0, \dots)$ may be given as simply

$$E_v^0 = \frac{1}{2} \sum_{i=1}^{3n-6} h\nu_i \quad (1.19)$$

1.9. Molecular Spectroscopy:

Different Approach of Study:

To understand and analyze a physical system in its befitting manner molecular spectroscopy is an area of active interest from many stand points. Having its numerous connections with many other branches, molecular spectroscopy has been playing an important role both in experimental and theoretical approaches. Being fueled by the rapid development of sophisticated experimental approaches, at present molecular spectroscopy is going through an essential change of renewed interest. Better initial-state preparation, improved light sources and specially designed pumping schemes, and more sensitive detection techniques are providing ever-improved resolution and a wider range of accessible final states. A close view reveals that in recent years the molecular spectroscopy is also undergoing a change in different direction. Not only better results, new ideas are also forth coming. One example of the changing attitudes is the increasing concern with time evolution. The time-energy uncertainty relation and the pursuit of higher resolution mean that traditional spectroscopy is implicitly equivalent to the study of the stationary states determined by the long-time limit of the intramolecular dynamics. The recent increasing interest in the role of anharmonicities and resonance couplings made unavoidable by the study of higher-lying rovibrational states and the experimental reality of avoiding inhomogeneous broadening (Quack, 1990) makes the entire time domain of direct interest to spectroscopists (Bitto and Huber, 1992). The very complementarity with the studies in the frequency domain (broad homogeneous spectral features \equiv early time dynamics and vice versa) makes lower-resolution spectra of interest. On the other hand, the traditional concerns of spectroscopy (Herzberg, 1945, 1950; Barrow, 1962;

King, 1964; Hollenberg, 1970; Herzberg, 1971; Bunker, 1979; Steinfeld, 1985) remain very much with us.

The formalism in modern spectroscopy discusses both level structure beyond harmonic limit and corresponding dynamics. A Hamiltonian is thus unavoidable since it is the generator of time evolution. There needs a practical method for the determination of the eigenvalues of the Hamiltonian. In case of traditional Dunham-like expansion (Dunham, 1932), the spectra are well approximated by a small number of constants. The fit of vibrational spectrum of triatomic molecule in its electronic ground state is expressed by the expansion

$$E(v_1, v_2, v_3) = \sum_i \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{i \leq j} x_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) + \sum_{i \leq j \leq k} y_{ijk} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right) \left(v_k + \frac{1}{2} \right) \quad (1.20)$$

Here, $E(v_1, v_2, v_3)$ is the energy level in wave number units. The Eq. (1.20) provides a fit to the observed levels within an error, which is almost experimental accuracy. The parameters in this expansion are directly related to a Hamiltonian. The familiar way of doing this proceeds in two steps. First, the electronic problem is solved in the Born-Oppenheimer approximation, leading to the potential for the motion of nuclei. Then the Schrödinger equation for the eigenvalues of this potential is solved. Since for any diatomic molecules the potential is a function of many coordinates, neither the first nor the second step is simple to implement. For a number of test cases this procedure has been carried out and for diatomic molecules of lower-row atoms it can challenge experiments in its precision. For larger molecules it is still not practicable to compute the required potential with sufficient accuracy. It is therefore often approximated using convenient functional forms. Not too far from deep equilibrium point, the potential is expanded in term of displacement coordinates relative to equilibrium configuration. There are two general methods which are presently used to describe molecular vibrations. In the traditional approach, based on integrodifferential techniques, the molecular Hamiltonian is parameterized in terms of internal coordinates (Wilson *et al.*, 1955). The potential is modeled in terms of force field

constants either through complex calculations involving the molecular electronic energy for several configuration (Raynes *et al.*, 1987) or experimentally, by fitting of spectroscopic data (Gray and Robiette, 1979). Although for diatomic molecules very accurate information on force fields is now available (Ogilvie, 1978), this is not the case for polyatomic molecules where the knowledge of force fields are poor due to the large number of force constants. The potential may also be modeled by representing the anharmonicity of the bonds, as a first approximation, by a sum of anharmonic Hamiltonians; among these the Morse potential is the most commonly used (Halonan and Child, 1982). The molecular rotation-vibration spectrum is provided by the Dunham expansion (Dunham, 1932). This is an expansion of energy levels in terms of vibration-rotation quantum numbers. For diatomic molecules, the expansion is

$$E(v, J) = \sum_{i,j} y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j \quad (1.21)$$

The coefficients y_{ij} are obtained by a fit to the experimental energy levels. But in this approach, there are few drawbacks namely (1) no Hamiltonian operator is available and (2) for large polyatomic molecules, one needs a large number of parameters obtained by fitting large experimental data base, which is not always available. (3) And this expansion does not contain any information about the wave function of individual states. Thus the matrix elements of operators cannot be calculated directly.

The second approach, called potential approach provides more sophisticated analysis. Here, energy levels are obtained by solving the Schrödinger equation with an interatomic potential. The potential V is expanded in terms of interatomic variables. For diatomic molecules, the possible expansion is (Iachello and Levine, 1982)

$$V(r) = \sum_n a_n \left(\frac{r-r_0}{b} \right)^n \quad (1.22)$$

The coefficients, a_n are obtained by a fit to the experimental energy levels. The solution of the Schrödinger equation also provides wave function $\psi(r)$

from which matrix elements of various operators can be calculated. In this approach, all manipulations are either differentiations or integrations.

The third approach to analyze molecular rotation-vibration spectra is based on the algebraic techniques. The success of the Interacting Boson Model of Arima and Iachello (Arima and Iachello, 1975, 1976; Iachello and Arima, 1974) has stimulated new interest in the study of many body systems governed by algebraic Hamiltonian. The algebraic Hamiltonian is written in terms of boson creation and annihilation operators characterizing the normal modes of the system. Contrary to potential approach, all manipulations are algebraic. The technical advantage of an algebraic approach is the comparative ease of algebraic operations. However, the result obtained by comparison with experiment is equally important. Another important advantage of this approach is that entire class of molecules can be described by general form of algebraic Hamiltonian where only the parameters are different for different molecules. The algebraic (or matrix) formulation of quantum mechanics is less familiar than differential (or wave) formulation. For diatomic molecules, the solution of Schrödinger equation with inter-atomic potential is very simple, thus, algebraic approach is not very much useful in application in diatomic molecules. But, in case of tri-atomic and polyatomic molecules, the algebraic approach gives very useful results in a simplified manner. The formalism necessary to analyze experimental data has been developed in two ways; (i) in the first case, the rotations and vibrations are treated together and the full three dimensional space of coordinates, \mathbf{r} and momenta \mathbf{p} is quantized with boson operators, giving rise to Lie algebras of $U(4)$ (Iachello and Levine, 1982; Iachello and Oss, 1996; Iachello, 1981) and products thereof (Roosmalen et al., 1982, 1983b) (ii) in the second case, rotations and vibrations are treated separately and each one dimensional space of coordinates \mathbf{x} and momenta p_x is quantized with boson operators, leading to one dimensional Lie algebras

$U(2)$ and products thereof (Roosmalen et al., 1984; Iachello and Oss, 1991).

1.10. Concept of a Group:

The concept of groups had its origin more than 150 years ago. The development of the theory of groups was mainly due to the famous mathematicians like Gauss, Cauchy, Abel, Hamilton, Cayley. After the advent of modern quantum mechanics in 1925, it did not find much use in physics for time being. The applications of group theory in physics were soon recognized and the new tool was put to use in the calculation of atomic structures and spectra by H. A. Bethe, E. P. Wigner and others. Group theory has now become indispensable in most branches of physics and chemical physics (Cornwell, 1997; Kim, 2004; Joshi, 2005).

Let us consider a set G of elements G_1, G_2, G_3, \dots is said to form a group if a law of multiplication of the elements satisfies the following conditions (Elliot and Dawber, 1979).

- (1) The product $G_1 G_2$ of any two elements is itself an element in the set i.e.

$$G_1 G_2 = G_4 \text{ for some } G_4 \text{ in } G \quad (1.23)$$

- (2) In multiplying three elements, G_1, G_2, G_3 together, it does not matter which product is made first. In other words,

$$G_1 (G_2 G_3) = (G_1 G_2) G_3 \quad (1.24)$$

where the products inside the bracket is carried out first.

- (3) One element of the set denoted by E and is called identity must have properties

$$E G_1 = G_1 \text{ and } G_1 E = G_1 \text{ for any } G_1 \text{ in the set } G \quad (1.25)$$

- (4) To each element G_1 in the set, there corresponds another element in the set, denoted by G_1^{-1} and is called the inverse of G_1 which has the properties

$$G_1 G_1^{-1} = E \text{ and } G_1^{-1} G_1 = E \quad (1.26)$$

It may be noticed that four properties satisfied by sets are very much similar in nature. In connection with a group, we may note the following terms:

- (i) The number of elements in a group is called its order.
- (ii) A group containing a finite number of elements is called a finite group.
- (iii) A group containing an infinite number of elements is called an infinite group. An infinite group may be either discrete or continuous; if the number of the elements in a group is denumerably infinite, the group is discrete; if the number of elements in a group is nondenumerably infinite, and the group is continuous (Cornwell, 1997; Kim, 2004; Joshi, 2005).

1.10.1 Lie Groups:

A group in which the law of composition and the law of inversion are continuous in all the group elements, is called a topological group. The dependence of the elements x_1, x_2 , etc., of a topological group G on its r continuous parameters can be written explicitly as

$$x_1 \equiv x_1(a_1, a_2, \dots, a_r), \quad x_2 \equiv x_2(b_1, b_2, \dots, b_r) \text{ etc.}$$

$$\text{Let } x_1 x_2 \equiv x_3(c_1, c_2, \dots, c_r) \text{ and } x_1^{-1} \equiv x_4(d_1, d_2, \dots, d_r)$$

The parameters of x_3 and x_4 can be expressed as functions of the parameters of

x_1 and x_2 , that is,

$$c_i \equiv c_i(a_1, a_2, \dots, a_r; b_1, b_2, \dots, b_r) \quad (1.27)$$

$$d_i \equiv d_i(a_1, a_2, \dots, a_r) \quad \text{for } 1 \leq i \leq r$$

A topological group is called an r -dimensional Lie group if there exists a neighborhood N of the identity element e such that the continuous parameters of the product of two elements and those of the inverse of an element in N are continuous differentiable functions of the parameters of the elements, that is, if c_i 's and d_i 's of Eq. (1.27) are analytic functions of a_i 's and b_i 's for elements in N provided that x_3 and x_4 lie in N when x_1 and

x_2 do. In addition, there will be laws for combining the other $n - r$ discrete parameters.

We see that it is convenient to choose the continuous parameters of a Lie group such that the image of the identity element e is the origin of the parameter space, i.e., $e \equiv x(0, 0, 0, \dots, 0)$. Having this parameterization, due to the analytical properties of the Lie groups, an element near the identity may be written as

$$x(0, 0, \dots, \varepsilon_j, \dots, 0) \simeq x(0, 0, \dots, 0) + i \varepsilon_j I_j (0, 0, \dots, 0), \quad (1.28)$$

to first order in ε_j . The first operator I_j can be obtained from (1.28) and is

$$\text{given by } I_j = \lim_{\varepsilon_j \rightarrow 0} \left[\left(\frac{1}{i\varepsilon_j} \right) \{ x(0, \dots, \varepsilon_j, \dots, 0) - x(0, 0, \dots, 0) \} \right]$$

For a Lie group, all the properties can be derived from the r operators I_j ($1 \leq j \leq r$) which need to be defined only near the identity element of the group.

We can arrive at an element of the group at a finite distance apart from the identity by the successive application of the product rule. Thus, let us say that we wish to generate the element $x(0, 0, \dots, a_j, \dots, 0)$. To do the same, let us first write $a_j = N\varepsilon_j$, where N is a large positive integer so that ε_j is a small quantity.

Then,

$$\begin{aligned} x(0, 0, \dots, a_j, \dots, 0) &= \left[x(0, 0, \dots, \varepsilon_j, \dots, 0) \right]^N \\ &= \left[e + i\varepsilon_j I_j \right]^N \\ &= \left[e + i \left(\frac{a_j}{N} \right) I_j \right]^N \end{aligned} \quad (1.29)$$

Now, allowing N to tend to infinity and using the algebraic identity

$$\lim_{N \rightarrow \infty} \left(1 + \frac{x}{N} \right)^N = \exp(x)$$

We have from Eq. (1.29)

$$x(0, 0, \dots, a_j, \dots, 0) = \exp(i a_j I_j) \quad (1.30)$$

which is an exact result. We are to understand the exponential function on the right-hand side of Eq. (1.30) as being formally equivalent to its expansion in the powers of the operator I_j . It may be noted that for a general element of the group, we can easily extend the above result to obtain

$$x(a_1, a_2, \dots, a_r) = \exp \left[\sum_{j=1}^r ia_j I_j \right] \quad (1.31)$$

Here we note that all the elements of the Lie group belonging to the subset containing the identity can be obtained by giving various values to the parameters a_j on the respective prescribed intervals. That is why the operators I_j are called the generators of the Lie group. Also we should note here that with r continuous parameters a Lie group has r generators.

1.10.2 Lie Algebras and Representations of Lie Groups:

Let us consider a Lie group with r continuous parameters a_k having the r generators I_1, I_2, \dots, I_r . It is seen that any element of the Lie group can be expressed in the form

$$x(a_1, a_2, \dots, a_r) = \exp \left[\sum_{k=1}^r ia_k I_k \right] \quad (1.32)$$

For a finite group, it is seen that all the properties of the group can be obtained from the structure of its multiplication table. It can be shown that for a Lie group, the commutators of its generators determine the structure of the group.

Thus, let us consider two particular elements of the Lie group of the form

$$x(0, 0, \dots, a_k, \dots, 0) = \exp(ia_k I_k)$$

$$x(0, 0, \dots, a_l, \dots, 0) = \exp(ia_l I_l)$$

Here, the product of these two elements $\exp(ia_k I_k) \exp(ia_l I_l)$, must belong to the group. Since the generators of a Lie group do not, in general

commute with each other (they commute only when the Lie group under consideration is abelian), there is no simple way of writing this product element. However, we may use the fact that such a product involves the commutator of I_k and I_l . Now, for the product $\exp(ia_k I_k) \exp(ia_l I_l)$ to belong to the group, it therefore follows that the commutator $[I_k, I_l]$ must be a linear combination of the generators, i.e.

$$[I_k, I_l] = \sum_{j=1}^r c_{kl}^j I_j, \quad l \leq k, \quad l \leq r \quad (1.33)$$

where c_{kl}^j are certain co-efficient. It is known that the commutators of pairs of generators of a Lie group determine the structure of the Lie group completely in analogy with the multiplication table for a finite group. Hence the coefficients c_{kl}^j are known as the structure constants of the Lie group. These structure constants are the characteristic property of the Lie group and do not depend on any particular representation of the generators. Since the generators of a Lie group themselves are not unique, hence these structure constants are also not unique. Eq. (1.33) provides us with a law of composition between any two elements of the vector space such that the resulting vector is also an element of the vector space. In fact, the set of real linear combinations of the generators of a Lie group is a Lie algebra.

A Lie algebra is a real r -dimensional vector space L with elements (x, y, z, \dots) endowed with a law of composition for any two elements of L denoted by $[x, y]$ such that

$$\left. \begin{aligned} [x, y] &\in L \\ [x, y] &= -[y, x] \\ [x, [y, z]] + [y, [z, x]] + [z, [x, y]] &= 0 \end{aligned} \right\} \quad (1.34)$$

for all $x, y, z \in L$. We refer the law of composition $[x, y]$ as the commutator of x and y .

The commutators of the generators of a Lie group defined in Eq. (1.33) satisfy the above properties, hence we obtain the following relations among the structure constants:

$$\left. \begin{aligned} c_{kl}^j &= -c_{lk}^j \\ \sum_{m=1}^r [c_{kl}^m c_{jm}^s + c_{lj}^m c_{km}^s + c_{jk}^m c_{lm}^s] &= 0 \end{aligned} \right\} \quad (1.35)$$

Since the generators I_k are Hermitian, Eq. (1.33) shows that the structure constants c_{kl}^j are purely imaginary.

It may be noted here that the importance of the Lie algebra lies in the fact that we may generate a representation of the Lie group by considering a matrix representation of the Lie algebra. Now, if we are able to find a set of r square matrices all of order p (let us say), such that they satisfy the commutation relations (1.33) with the given structure constants, then using these for the I_k 's in Eq. (1.32), we would generate a p -dimensional representation of the Lie group. Thus, we can take it as a general rule that a representation of a Lie algebra can be used to generate a representation of the associated Lie group.

Let us now apply the above discussion to $SU(2)$, as an example. The three generators of $SU(2)$ can be chosen to be the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.36)$$

Which are a set of three independent traceless Hermitian matrices of order 2. For the generators of $SU(2)$ we can then choose the set $(E, \sigma_x, \sigma_y, \sigma_z)$, where E is the unit matrix of order 2.

The generators of $SU(2)$ given in Eq. (1.36) satisfy the commutation relations

$$[\sigma_j, \sigma_k] = 2i \sum_l \varepsilon_{jkl} \sigma_l \quad (1.37)$$

Here \mathcal{E}_{jkl} is the fully antisymmetric tensor of rank 3 whose only nonvanishing elements are

$$\mathcal{E}_{123} = \mathcal{E}_{231} = \mathcal{E}_{312} = -\mathcal{E}_{213} = -\mathcal{E}_{132} = -\mathcal{E}_{321} = 1 \quad (1.38)$$

Here the indices j, k, l stand for any of x, y, z or for $1, 2, 3$. It should be noted here that the six equations in Eq. (1.38) is generally abbreviated into a single equation and is written as $\epsilon_{123} = 1$ and all permutations with proper signs. One can see here that the components of the tensor ϵ_{jkl} multiplied by $2i$ are evidently the structure constants of SU(2). Thus, the Lie algebra of SU(2) is the set of all real linear combinations of $\sigma_x, \sigma_y,$ and σ_z .

To make the conception more clear let us now look at the following three matrices:

$$\lambda_1 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \lambda_2 = \begin{bmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \lambda_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (1.39)$$

We can easily verify that all these three matrices satisfy the same commutation relations as the generators σ 's, i.e.

$$[\lambda_j, \lambda_k] = 2i \sum_l \mathcal{E}_{jkl} \lambda_l \quad (1.40)$$

Thus we see that the λ 's generate a representation of the Lie algebra of SU(2) and can therefore be used to generate a three-dimensional representation of SU(2) itself.

For a Lie group, the maximum number of mutually commuting generators is called its rank. Thus, the rank of SO(3) is 1 because no two of its generators, L_x, L_y and L_z commute with each other. On the same reasoning, the rank of SU(2) is also 1.

Casimir operator for a Lie group is the operator which commutes with all the generators of the Lie group. The number of independent Casimir operators of a Lie group is equal to its rank. Casimir himself recognized

that one such operator could always be constructed by taking a suitable bilinear combination of the generators.

Thus, the one and only Casimir operator of $SO(3)$ is $L^2 \equiv L_x^2 + L_y^2 + L_z^2$, which commutes with each of L_x , L_y and L_z . Similarly, the only Casimir operator of $SU(2)$ is $\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2$.

The Casimir operators of a Lie group can be diagonalized simultaneously with its generators. Hence the eigenvalues of the Casimir operators may be used to label the IR of the Lie group. The Casimir operator L^2 of $SO(3)$ thus has the eigenvalues $l(l+1)$, where l takes on all nonnegative integral values, and hence the IR of $SO(3)$ may be labeled by the index l . The Casimir operator σ^2 of $SU(2)$ has, in general, the eigenvalues $j(j+1)$ where j takes all nonnegative integral and half-odd-integral values [the representation (1.36) for the generators is a special case with $j = 1/2$]. Hence, the IR of $SU(2)$ can be labeled by j .

On the basis of the brief discussion on Lie groups and Lie algebras made in this section now we are in a position to summarize the properties of the Lie algebras which are given in the following section.

1.10.3 Properties of Lie Algebras:

(a) Definition:

Let us consider a set of operators as \hat{X}_a ($a = 1, \dots, r$). If this set of operators satisfying the commutation relations

$$[\hat{X}_a, \hat{X}_b] = \sum_c C_{ab}^c \hat{X}_c \quad (1.41)$$

where,

$$C_{ab}^c = -C_{ba}^c \text{ and } [\hat{X}_a, \hat{X}_a] = 0 \quad (1.42)$$

together with the Jacobi identity

$$[[\hat{X}_a, \hat{X}_b], \hat{X}_c] + [[\hat{X}_b, \hat{X}_c], \hat{X}_a] + [[\hat{X}_c, \hat{X}_a], \hat{X}_b] = 0 \quad (1.43)$$

It is said to form a Lie Algebra G

$$X_a \in G \quad (1.44)$$

In a similar way, a sub-algebra G' of G also can be defined.

Let us consider a subset Y_i of the X_a 's. Now, if

$$\left[\hat{Y}_i, \hat{Y}_j \right] = \sum_k C_{ij}^k \hat{Y}_k \quad (1.45)$$

the subset \hat{Y}_i of \hat{X} 's is said to form a sub-algebra G' of G .

We denote this situation by,

$$\hat{X}_a \in G, \hat{Y}_i \in G', G \supset G' \quad (1.46)$$

We say an algebra (or sub-algebra) as Abelian if all its elements commute

$$\left[\hat{X}_a, \hat{X}_b \right] = 0, \quad \forall \hat{X}_a \in G \quad (1.47)$$

(b) Generators and Realizations:

It is important to note that for the purpose of the definition of an algebra it is not necessary to specify any explicit form of the operators. If one writes the operators as differential operators, they are said to be the generators of the corresponding group of transformations. In such a case the resulting algebraic structure is said to be a realization (of the abstract algebra). We can also realize the abstract algebraic structure with a set of matrices or with products of creation and annihilation operators.

(c) Cartan's Classification:

Here we give the Cartan's classification of all the admissible, semi-simple, Lie algebras in Table 1.2. (Iachello and Levine, 1995)

Table 1.2: Admissible Lie Algebras:

Name	Label	Cartan Label
[Special] Unitary	[S] $U(n)$	$A_{(n-1)}$
[Special] Orthogonal	[S] $O(n)$, $n=\text{odd}$	$B_{(n-1)/2}$
[Special] Orthogonal	[S] $O(n)$, $n=\text{even}$	$D_{n/2}$
Symplectic	$Sp(n)$, $n=\text{even}$	$C_{n/2}$
Exceptional	G_2, F_4, E_6, E_7, E_8	G_2, F_4, E_6, E_7, E_8

Algebras should be denoted by lower case letters, and their associated groups of transformations by capital letters. We thus see that $\mathfrak{so}(3)$ denotes the algebra of special orthogonal transformations in three (3) dimensions, while $SO(3)$ denotes the associated group. However, it has become customary, to denote both groups and algebras by capital letters.

We note that the letter S denotes special transformations, that is, transformations with determinant +1. Also it should be noted that when dealing with algebras, the letter S is not important for orthogonal algebras, B and D types, while it is important for unitary algebras, since $U(n)$ and $SU(n)$ differ in the number of operators. One can see here that both orthogonal and special orthogonal algebras have the same number of operators. When dealing with orthogonal algebras, the letter S is deleted in the text to avoid unnecessary burdening of the notation.

(d) Number of Operators in the Algebra:

For any admissible Lie algebra, one knows the number of operators in the algebra, denoted by r (called the order of the algebra) and is given in Table 1.3.

**Table 1.3: Number of operators in the Lie algebras
(Iachello and Levine, 1995):**

Algebra	Number
$U(n)$	n^2
$SU(n)$	$n^2 - 1$
$SO(n)$	$\frac{1}{2} n(n - 1)$
$Sp(n)$	$\frac{1}{2} n(n + 1)$
G_2	14
F_4	52
E_6	78
E_7	133
E_8	248

(e) Isomorphic Lie Algebra:

Some algebras which have identical commutation relations are called isomorphic algebras. In the Table 1.4, the sign \oplus denotes direct sums of the algebra i.e. addition of the corresponding operators

Table 1.4 : Isomorphic Lie algebras (Iachello and Levine, 1995):

Cartan Notation	Isomorphic Algebra
$A_1 \approx B_1 \approx C_1$	$SU(2) \approx SO(3) \approx Sp(2)$
$B_2 \approx C_2$	$SO(5) \approx Sp(4)$
$D_2 \approx A_1 \oplus A_1$	$SO(4) \approx SU(2) \oplus SU(2) \approx SO(3) \oplus SO(3) \approx Sp(2) \oplus Sp(2)$
$A_3 \approx D_3$	$SU(4) \approx SO(6)$

(f) Examples of Lie Algebra:

It is known that the simplest example of a Lie algebra is the angular momentum algebra. One can see that this algebra is a realization of $SO(3)$ and has three elements, the three components of the angular momentum

$$G = J_x, J_y, J_z \quad (1.48)$$

With commutation relations

$$[J_x, J_y] = iJ_z, [J_y, J_z] = iJ_x, [J_z, J_x] = iJ_y \quad (1.49)$$

We see that $SO(3)$ has a (trivial) sub-algebra, $SO(2)$, composed of only one component, J_z (let us say),

$$G' = J_z \quad (1.50)$$

satisfying the (trivial) commutation relation

$$[J_z, J_z] = 0 \quad (1.51)$$

One should note here that the algebra of $SO(3)$ has only one independent Casimir invariant

$$C(SO(3)) = J_x^2 + J_y^2 + J_z^2 = J^2 \quad (1.52)$$

Hence it is an algebra of rank 1. Cartan called this algebra as B_1 .

It may be noted that the sub-algebra $SO(2)$ also has a (trivial) Casimir invariant, i.e., J_z itself,

$$C(SO(2)) = J_z^2 \quad (1.53)$$

which is also a trivial algebra of rank 1. This algebra was called as D_1 by Cartan.

It may be noted that the invariant operators are important because they are related to conserved quantities. As an example, here we may refer the case of angular momentum.

(g) Representations:

When we apply Lie algebras in the solutions of problems in physics and chemistry, we need to construct representations of the algebras. It is known that these are linear vector spaces over which the group elements act. We note that the representations of Lie algebras are characterized by a set of numbers (quantum numbers) that can take either integer or half-integer values. Those which take integer values are called tensor representations, while those that take half-integer values are called spinor representations. Another important point here we are to note is the concept of irreducible representations, i.e., vector spaces that transform into themselves by the operations of the algebra, and cannot be further reduced.

We note that the irreducible representations of unitary algebras, $U(n)$, are characterized by a set of n integers, corresponding to all possible partitions of an integer s ,

$$\lambda_1 + \lambda_2 + \dots + \lambda_n = s, \quad \text{with } \lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_n \quad (1.54)$$

We often arrange the integers λ s into a diagram, called a Young diagram (or tableau). In the Young diagram, the first row is λ_1 the second is λ_2 , and so on.

$$n \left\{ \begin{array}{l} \lambda_1 \\ \square\square\square\square \\ \lambda_2 \\ \square\square\square \\ \lambda_3 \\ \square\square \end{array} \right. \quad (1.55)$$

Also we can use another notation which is $[\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n]$. In this notation, for example, the diagram (1.55) may be stated as $[5, 3, 2]$.

It may be noted that the irreducible representations of special unitary algebras, $SU(n)$, are characterized by a set of integers, as in the case of $U(n)$, but with one fewer, i.e.,

$$\lambda_1 + \lambda_2 + \dots + \lambda_{n-1} = s, \quad \text{with } \lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_{n-1} \quad (1.56)$$

Also we note that the irreducible representations of $SO(n)$ are characterized by a set of integers, but corresponding to the partition

$$\mu_1 + \mu_2 + \mu_3 + \dots + \mu_v = s, \quad \text{with } \mu_1 \geq \mu_2 \geq \dots \geq \mu_v, \quad (1.57)$$

Where,

$$v = \begin{cases} \frac{n}{2}, n = \text{even} \\ n - \frac{1}{2}, n = \text{odd} \end{cases} \quad (1.58)$$

Similarly, the irreducible representations of $Sp(n)$ are also characterized by a set of integers

$$\mu_1 + \mu_2 + \mu_3 + \dots + \mu_v = s, \quad \text{with } \mu_1 \geq \mu_2 \geq \dots \geq \mu_v, \quad (1.59)$$

where $v = \frac{n}{2}$.

The summary of the discussion made in section **1.10.3(g)** is shown in Table 1.5, where the results for the exceptional algebras are also given. It

may be noted that the number of integers that characterize the representations is also equal to the rank of the algebra.

Table 1.5: Number of integers that characterize the tensor representations of Lie algebras:

Algebra	Number
U(n)	N
SU(n)	n - 1
SO(n), n=even	n/2
SO(n), n= odd	(n - 1)/2
Sp(n)	n/2
G ₂	2
F ₄	4
E ₆	6
E ₇	7
E ₈	8

Also it may be noted that there is a complication that arises only when dealing with orthogonal algebras in an even number of dimensions, SO(n), n = even. We see, the complication is that the partition (equation 1.57) is not sufficient to characterize uniquely the representations since there are, two equivalent representations (Hamermesh, 1962), when the last quantum number, μ_v , is different from zero. We denote this either by writing explicitly

$$[\mu_1, \mu_2, \mu_3, \dots, \pm \mu_v], \quad \mu_v > 0 \quad (1.60)$$

Or by writing simply

$$[\mu_1, \mu_2, \mu_3, \dots, |\mu_v|], \quad (1.61)$$

and remembering that there are two such states. In molecular physics SO(4) and SO(2) play an important role. Hence the complication (representation 1.60) cannot be overlooked. Here one should note that the complication (representation 1.60) has also an explicit physical meaning, since it is associated, for example, with the double degeneracy of π, δ orbitals or the Π, Δ vibrational states in linear molecules.

(h) Tensor Products:

We can form tensor products with the representations of Section

1.10.3(g) Generally we denote Tensor products by the symbol, \otimes

$$[\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n] \otimes [\lambda'_1, \lambda'_2, \lambda'_3, \dots, \lambda'_n] \tag{1.62}$$

It may be noted that there are definite rules on how to multiply representations of which we state here one (Hamermesh, 1962). Let us consider the product of any representation, for example,

$$\begin{array}{cc} \square & \square \\ & \square \end{array} \tag{1.63}$$

by a one-row representation, for example,

$$\square \quad \square \tag{1.64}$$

Let us draw the pattern for the first factor, using a symbol, for example, a ,

$$\begin{array}{cc} a & a \\ & a \end{array} \tag{1.65}$$

Let us assign another symbol, for example, b , to the second pattern. Let us apply b to a in all possible ways subject to the rule that no two bs appear in the same column,

$$\begin{array}{cccc} a & a & b & b \\ a & & a & b \\ & & & a \\ & & & b \end{array} \oplus \begin{array}{ccc} a & a & b \\ a & & b \\ & & a \end{array} \oplus \begin{array}{ccc} a & a & b \\ a & & b \\ & & a \end{array} \oplus \begin{array}{cc} a & a \\ & b \end{array} \tag{1.66}$$

Example:

$$[1] \otimes [1] = [2] \oplus [1, 1] \tag{1.67}$$

(i) Branching rules:

It is seen that for any given quantum mechanical problem one needs to find the complete set of quantum numbers that characterize uniquely the states of the system. It is clear that this corresponds to finding a complete chain of sub-algebras

$$G \supset G' \supset G'' \supset \dots \quad (1.68)$$

For solving this problem, there is a definite mathematical procedure (called the branching problem). When we apply the procedure, we need also to deal with the following question. For the sub-algebra G' , what are the representations contained in a given algebra G (branching rules). It may be noted that this problem is also completely solved, and there exist tables of branching rules.

(j) Examples of Representations of Lie Algebra:

Once again here we return to the simple example of the angular momentum algebra, $SO(3)$. The tensor representations of the algebra are characterized by one integer (Table 1.5), i.e., the angular momentum quantum number J . In a similar way the representations of $SO(2)$ are characterized by one integer (Table 1.5), i.e., M the projection of the angular momentum on the z axis. Thus the complete chain of algebras is

$$G \supset G' = SO(3) \supset SO(2), \quad (1.69)$$

And the complete set of quantum number is

$$\left. \begin{array}{cc} SO(3) \supset SO(2) \\ \downarrow \quad \downarrow \\ J \quad M \end{array} \right\} \quad (1.70)$$

Bracket notation of Dirac is used here following standard practice. Corresponding to (representation 1.70), the ket $|J M\rangle$ is also called a basis state.

It may be noted that according to the branching rules for $SO(3) \supset SO(2)$, in the representation J of $SO(3)$, the values of M are all the integers between $-J$ and $+J$. Again it should be noted that the

complication mentioned at the end of the Section **1.10.3.(g)**, is due to the fact that $SO(2)$ is in an even number of dimensions.

(k) Eigenvalues of Casimir Operators:

In the application of algebraic methods to problems in physics and chemistry another ingredient we need is the eigenvalues of Casimir operators in the representations of Section **1.10.3.(g)**. We give the known solution in Table 1.6.

(l) Examples of Eigenvalues of Casimir Operators:

In Table 1.6 we give the eigenvalues of the Casimir operator of $SO(3)$ in the representation J as

$$\langle C(SO(3)) \rangle = J(J+1). \quad (1.71)$$

This is a well known result. In a similar way, we can obtain the eigenvalues of the Casimir Operators of order 2 of $SO(4)$ in the representation τ_1, τ_2 as

$$\langle C(SO(4)) \rangle = \tau_1(\tau_1+2) + \tau_2^2. \quad (1.72)$$

Here we notice that once more a complication arises when dealing with orthogonal algebras in an even number of dimensions, since often these algebras have two Casimir Operators of order two. The two operators in such a case are distinguished by placing a bar over the second operator. We give the eigenvalues of this operator as

$$\langle \bar{C}(SO(4)) \rangle = \tau_2(\tau_1+1). \quad (1.73)$$

Table 1.6: Eigenvalues of some Casimir Operators of Lie Algebras (Iachello and Arima, 1987):

Algebra	Labels	Order	Eigenvalues
U(n)	$[f_1, f_2, f_3, \dots, f_n]$	1	$\sum_{i=1}^n f_i \equiv f$
		2	$\sum_{i=1}^n f_i (f_i + n + 1 - 2i)$
SU(n)	$[f_1, f_2, f_n, \dots, 0]$	2	$\sum_{i=1}^n \{(f_i - f/n)(f_i + 2n - 2i - f/n)\}$
SO(2n+1)	$[f_1, f_2, f_3, \dots, f_n]$	2	$\sum_{i=1}^n f_i (f_i + 2n + 1 - 2i)$
SO(2n)	$[f_1, f_2, f_3, \dots, f_n]$	2	$\sum_{i=1}^n f_i (f_i + 2n - 2i)$
Sp(2n)	$[f_1, f_2, f_3, \dots, f_n]$	2	$\sum_{i=1}^n f_i (f_i + 2n + 2 - 2i)$

1.11 Inception of Lie Algebraic Method in Modern Physics:

In the development of science, symmetry may be regarded as an extremely important concept (Iachello, 2004). From the both purely theoretical and computational viewpoints, the use of symmetry in physics and other related areas is widely recognized. It may be mentioned here that the word, symmetry does not necessarily have a geometric meaning when applied in modern physics. Also it should be noted here that symmetries beyond geometric ones appeared and started to demonstrate their usefulness after the introduction of quantum mechanics in the first part of the 20th Century. Beauty of symmetry is its connection to a possible invariance in a physical system. Such invariance of a physical

system leads directly to conserved quantities, which allow one to observe specific degeneracies in the energy spectrum and to introduce a meaningful labeling scheme for the corresponding eigenstates in a quantum mechanical framework.

To deal with the symmetry arguments, group theory is regarded as the most suitable tool. The continuous Lie groups and algebras are powerful mathematical techniques, particularly for addressing quantum mechanical problems embedded in a group theoretical framework. The matrix or algebraic formulation of quantum mechanics is already successful to show its greater suitability compared with the differential or wave formulation, at least in regard to matters inherent in symmetry problems. The use of Lie algebras in a systematic fashion was first introduced in the 1930's. Weyl, Wigner, Racah and others are the pioneer workers in this field. In particular, point and translation group theory played a fundamental role in solid-state physics, while continuous groups, especially unitary groups, were shown to be invaluable in studies related to nuclear and particle physics.

Interacting boson model, the highest expression of group theoretical methods in nuclear physics was introduced for even-even nuclei in 1974 (Iachello and Arima, 1974) and later the same was extended to more complex nuclear systems. Interacting boson model is important for its unprecedented power in describing virtually any kind of experimental situation in nuclear physics. We should note that the interacting boson model is the first example of a comprehensive theoretical model based on a dynamical symmetry environment. Details of dynamical symmetries in connection with molecular spectroscopy are discussed by many authors (Levine and Cooper, 1991; Iachello and Levine, 1995; Oss, 1996). A Hamiltonian is said to have a dynamical symmetry when its eigenvalues are an analytical function of the quantum numbers. An example of the latter is the finite Dunham-like expansion of the vibrational term values up to second order in the vibrational quantum

numbers, as given in reference (Dunham, 1932). The important point in a dynamical symmetry is that such an expansion can be derived from a Hamiltonian. For example, such a symmetry for triatomic molecules can be derived on the basis of an $U(4) \otimes U(4)$ Lie group. We must be clear about the point that a dynamical symmetry is but an approximation. Even we care to make it mainly for two primary reasons, one related with dynamics and the other with spectroscopy. The time-domain reason is the remarkable accuracy of the results provided by dynamical symmetry. For many molecules, the temporal evolution as predicted by dynamical symmetry is accurate for tens or even hundreds of vibrational periods. As the total energy increases, this will become less the case. Even so, it appears remarkable that in the range of the highest overtones currently accessible to direct excitation, the time evolution is regular for such a long time. It is known that there is no contradiction between the utility of dynamical symmetry in the time domain and its limited accuracy in the frequency domain. The same is best understood in terms of the time dependent approach to spectroscopy. This implies that the spectrum is generated via the time propagation of the nonstationary wave packet created at time zero. Highly resolved spectral details reflect long propagation times. The range of this "long" is determined by the magnitude of $\hbar = 5.31 \text{ ps cm}^{-1}$ or, in reduced units, by the typical stretch or bend frequencies which frequently exceed 10^3 cm^{-1} . Hence an rms accuracy of 10 cm^{-1} , not very satisfactory in the frequency domain, is sufficient to follow the molecule over many vibrational periods. An interesting implication of the validity of the dynamical symmetry over many vibrational period is the separation of time scales in the exploration of phase space. The second motivation for considering dynamical symmetry is that it provides a zero order or "deperturbed" set of states. We then can introduce perturbations, and one advantage of the algebraic approach is that this can be done in a systematic fashion. These perturbations can be related to "resonance coupling" of anharmonic,

uncoupled oscillators via a semi classical analysis. This provides a connection to the application of nonlinear mechanics to spectroscopy. Algebraic effort is utilized to ensure that zero order dynamical symmetry corresponds to anharmonic oscillators. For this reason, we see that in algebraic method an $SU(2)$ group is used for each one-dimensional oscillator and an $SU(4)$ group is used for each three-dimensional oscillator . We can describe a pair of coupled harmonic oscillator with a single $SU(2)$ group. No doubt that this leads to a simpler zero order basis but the characteristic effects of nonlinear mechanics then arise only from the perturbations. A familiar example of a resonance coupling is the Fermi resonance. In reference it has been shown regarding how to include this coupling by breaking the dynamical symmetry. As a result of the coupling, only the quantum number $(2v_1+v_2+2v_3)$ is conserved, while the individual stretch (v_1, v_3) and bend (v_2) quantum numbers are not. It should be noted that for non bending $(v_2 = 0)$ molecules, this coupling is the familiar with Darling-Dennison 2:2 resonance between the two stretch modes. Other types of resonances (example, 2:3 resonance) also can be described in an algebraic approach. It may be noted here that dynamical symmetries constitute a big step forward over a conventional use of symmetry arguments, especially those concerning the description and classification of energy spectra denoting specific degeneracy patterns. For a simple understanding one may think that the amount of information gained in going from a degeneracy symmetry to a dynamical one is similar to that obtained in going from a static to a dynamical study of forces acting in a conventional mechanical system. We should note here that dynamical symmetries contain within themselves both the degeneracy aspects of a physical system and the complete machinery for describing transitions among different states (that is, the dynamical behavior of the physical object at issue). In the extremely compact and convenient framework of Lie groups and algebras all these tasks can be carried out well. The use of group theoretical tools very often allows us to address

situations inaccessible by means of conventional methods of quantum mechanics.

It may be noted here that the interacting boson model is a beautiful example of how to specialize, the algebraic, second-quantized formulation of quantum mechanics from the aforementioned viewpoint. Such specialization involves recognizing, within the commutation relations of the creation and annihilation operators, certain Lie algebraic structures and to limit the choice of such operators within specific (invariant) bilinear forms. The existing mathematical apparatus concerning Lie algebras, tensor calculus, and related topics (such as the Wigner-Eckart theorem) is typically applied, in the case of nuclear physics and the interacting boson model, to the building block of the problem at issue, namely an object with five internal degrees of freedom (i.e. an electric quadrupole). Observable quantities like excitation spectra and transition probabilities are then obtained in terms of boson operators, whose transformation properties are closely connected with specific abstract symmetries. This type of boson operators are the algebraic version of both the monopole and quadrupole pairing character of the strong interaction between identical nuclear particles.

Very soon, the above mentioned strategy was applied in the world of molecules. First of all, in the last part of the 20th century, the algebraic models were introduced as a computational tool for the analysis and interpretation of experimental rovibrational spectral of small and medium-sized molecules (Wulfman, 1979; Levine and Wulfman, 1979; Iachello, 1981; Iachello and Levine, 1982; Roosmalen, 1982; Iachello and Levine, 1995; Iachello and Oss, 1991, 1996; Oss, 1996). The algebraic models are based on the idea of dynamic symmetry, which, in turn, is expressed through the language of unitary Lie algebras. With the application of these algebraic techniques, one obtains an effective Hamiltonian operator that conveniently describes the rovibrational degrees of freedom of the physical system. In this framework, any specific

mechanism relevant for the correct characterization of the molecular dynamics and spectroscopy can be accounted. The important point to be noted here is that the algebraic models contain the same physical information for both *ab initio* theories (based on the solution of the Schrödinger equation) and semiempirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). Compared with that of interacting boson model, it may be seen that the only difference between nuclei and molecules from the viewpoint of the building blocks used is that when dealing with molecules, one has to start with a diatomic unit. This is equivalent to that of considering boson operators related to the dipole character of the diatom. Consequently, a different dynamical symmetry (of smaller dimension than that of used in nuclear physics) is adopted in the description of molecular systems. It may be noted here that based on its firm footing, the algebraic techniques, at present can demonstrate their suitability to address successfully even quite difficult situations of molecular spectroscopy. It is also already confirmed that the algebraic techniques offer a concrete and complementary technique to conventional approaches.

1.12 The Lie Algebraic Method and the Role of Algebraic Method:

The Lie Algebraic Method:

In order to have a review of the Lie algebraic methods within the context of molecular spectroscopy, we start with the following brief description of it. The Lie algebraic methods have been useful in the study of problems in physics, especially after the development of quantum mechanics in the first part of the 20th century. The reason is, quantum mechanics makes use of commutators $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebras. And hence often it is termed that the essence of the algebraic methods can be traced to the Heisenberg's formulation of quantum

mechanics (Heisenberg, 1925). Let us consider a quantum mechanical problem in one-dimension with the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (1.74)$$

Instead of solving the differential equation $H\psi(x) = E\psi(x)$ directly, let us consider the case of a harmonic oscillator potential

$$V(x) = kx^2 / 2 \quad (1.75)$$

and introduce creation and annihilation operators

$$a^\dagger = \frac{1}{\sqrt{2}} \left(x - \frac{d}{dx} \right), \quad (1.76)$$

$$a = \frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right)$$

Along with a vacuum state $|0\rangle$. The Hamiltonian for the harmonic oscillator now may be written as

$$H = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \quad (1.77)$$

with eigenvalues

$$E(n) = \hbar\omega \left(n + \frac{1}{2} \right), \quad n = 0, 1, \dots, \infty \quad (1.78)$$

and eigenstates

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle. \quad (1.79)$$

The Harmonic frequency ω is given by

$$\omega = (k / m)^{1/2}. \quad (1.80)$$

For a generic potential, let us now expand $V(x)$ in power of x

$$V(x) = \sum_{i=2} k_i x^i \quad (1.81)$$

that is, in power of $a^\dagger, a, a^\dagger a$ and diagonalize it in the space $n = 0, 1, 2, \dots, N$.

The algebra formed with the set of four operators $a^\dagger, a, a^\dagger a, 1$ is called the Heisenberg-Weyl algebra H(2) (the identity 1 commutes with all operators) and has its commutation relation as

$$[a, a^\dagger] = 1; [a, a^\dagger a] = a; [a^\dagger, a^\dagger a] = a^\dagger \quad (1.82)$$

The method where the Hamiltonian operator is expanded in powers of operators of H(2) is called algebraic harmonic analysis (Kellman, 1995). All manipulations are done here algebraically rather than using differential operators. This is the most important advantage of the method. The matrix elements of the operators, a^\dagger, a are the key ingredients here in the algebraic manipulations. The matrix elements of the operators, a^\dagger, a (called step up and step down operators) are given by

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle; a |n\rangle = \sqrt{n} |n-1\rangle \quad (1.83)$$

This is all we need to calculate any observable within the framework of harmonic analysis. It is known to us that molecular potentials often deviate considerably from a harmonic potential. As a result, the expansion of $V(x)$ contains many parameters and the basis in which the diagonalization is done needs to be taken very large i.e. $N \rightarrow \infty$.

We can overcome this difficulty by considering other solvable potential functions which contain anharmonicity from the beginning. A function of this type is the Morse function

$$V(x) = V_0 \left[1 - \exp \left\{ -a(x - x_0) \right\} \right]^2 \quad (1.84)$$

With the help of a series of transformations, the Schrödinger equation with a Morse potential (Figure 1.6) can be written in terms of an algebra composed of four operators F_+, F_-, F_z, N satisfying commutation relations

$$[F_+, F_-] = 2F_z; [F_\pm, F_z] = \pm F_\pm \quad (1.85)$$

(The operator N commutes with all elements).

The four operators, as cited above, form a Lie algebra, called U(2), while the three operators F_+, F_-, F_z form a Lie algebra, called SU(2), isomorphic to the angular momentum algebra and hence called *quasi-spin algebra*.

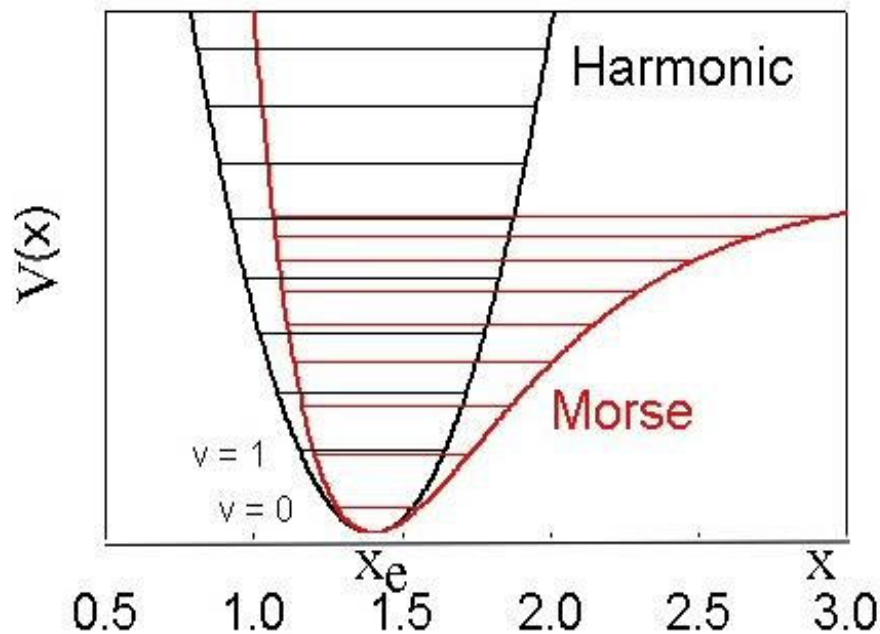


Fig. 1.6: The Morse potential and its approximation with a harmonic oscillator potential.

When written in terms of these operators, the Hamiltonian for the Morse oscillator takes the simple form

$$H = E_0 + AF_z^2 \quad (1.86)$$

Let us now introduce the vibrational quantum number n related to the eigenvalue M of F_z by $\nu = (n - m)/2$. The eigenvalues of H , in this situation, can be written as

$$E(\nu) = E_0 + AN^2 - 4A(N\nu - \nu^2),$$

$$\nu = 0, 1, \dots, \frac{N}{2} \text{ or } \frac{N-1}{2} \quad (\text{N even or odd}) \quad (1.87)$$

also the eigen function can be written as $|N, \nu\rangle$.

Now we are in a position to write the expression for the energy levels in the familiar form

$$E(\nu) = \hbar\omega_e \left(\nu + \frac{1}{2} \right) - \hbar\omega_e x_e \left(\nu + \frac{1}{2} \right)^2 \quad (1.88)$$

This represents an anharmonic oscillator with quadratic anharmonicities. The algebra $U(2)$ now provides a framework for performing algebraic anharmonic analysis. A generic potential can be expanded in terms of quasi-spin operators F_+ , F_- , F_z . All we need are the matrix elements of the step up and step down operators of $SU(2)$ given by

$$F_- |N, \nu\rangle = \sqrt{\nu(N-\nu+1)} |N, \nu-1\rangle; \quad (1.89)$$

$$F_+ |N, \nu\rangle = \sqrt{(N-\nu)(\nu+1)} |N, \nu+1\rangle$$

It may be noted here that for molecular potentials which are not very different from Morse potential, the expansion converges very quickly, that is, very few terms are needed to obtain an accurate description. The harmonic limit also can be easily recovered from $U(2)$ using a mathematical procedure called contraction $\frac{1}{N} \rightarrow 0$. By renormalizing the operators F_+ and F_- with $\frac{N_1}{2}$, their matrix elements go over those of the harmonic oscillator in the limit $N \rightarrow \infty$.

It should be noted here that the Morse function is not the only one that can be used to provide a basis for anharmonic analysis. The Pöschl-Teller function (Figure.1.7) is another function of interest in molecular physics, especially for bending vibrations. The Pöschl-Teller function, associated with the Lie algebra $U(2)$ is given by

$$V_x = -\frac{V_0}{\cosh^2 ax} \quad (1.90)$$

It may be noted here that the algebraic method can be applied to problems in any number of dimensions, in particular two and three dimensions where harmonic analysis is done in terms of the Weyl-Heisenberg algebras $H(3)$ and $H(4)$, and anharmonic analysis in terms of the Lie algebras $U(3)$ and $U(4)$.

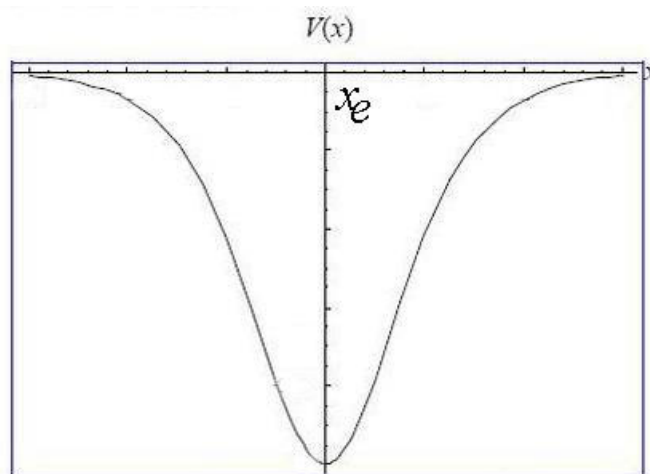


Fig. 1.7 : The Pöschl-Teller potential.

The Role of Algebraic method:

The Lie algebraic formulation discussed above can be used to study problems of relevance in physics and chemistry. Particularly, in case of molecules, the formulation can be used to analyze vibrational and rotational spectra. Electronic spectra also can be interpreted with the algebraic model. However, the field in which the algebraic method has had most impact is that of vibrational spectroscopy. To deal with the vibrational spectroscopy, following are the important advantages of the algebraic method:

- (a) In the energy spectra, from the very beginning anharmonicities are put in.
- (b) In the interactions between different modes, anharmonicities are introduced automatically since they are already contained in the matrix elements of the step operators.
- (c) The Lie algebraic methods allow us to calculate wave functions and thus observables other than energies, such as intensities of transitions (infrared, Raman, Franck-Condon).

In vibrational spectroscopy, anharmonicities play a very important role. This is the reason why the algebraic methods have found their most useful application here.

1.13. Vibrational Spectroscopy and The Lie Algebraic Method:

To discuss the vibrational spectroscopy within the context of the Lie algebraic methods, it is convenient to divide molecules according to their size. We denote molecules with $N = 2$ to 4 atoms as ‘small molecules’, molecules with $N = 5$ to 100 atoms as ‘medium-size molecules’, and molecules with $N > 100$ atoms as ‘macromolecules’.

Small Molecules:

The coordinate system chosen is an important aspect in the study of molecules. In the study of small molecules, the best set for vibrational analysis is provided by the internal coordinates. For a molecule, if N is the number of atoms, the number of internal coordinates is $3N - 6$. In case the molecule is linear, there are $3N - 5$ internal coordinates. The Lie algebraic method as applied to the vibrational spectroscopy of small molecules consists in quantizing each internal degree of freedom with the algebra of $U(2)$. For a set of n coupled one-dimensional degrees of freedom, the Hamiltonian is then written in terms of the quasi-spin operators $F_{+,i}$, $F_{-,i}$, $F_{z,i}$ for each degree of freedom i . Here a Hamiltonian often used is (Iachello and Oss, 1991)

$$H = E_0 + \sum_{i=1}^n A_i F_{z,i}^2 + \sum_{i<j=1}^n B'_{ij} F_{z,i} F_{z,j} + \sum_{i<j=1}^n B_{ij} (F_{+,i} F_{-,j} + F_{-,i} F_{+,j}) \quad (1.91)$$

In this Hamiltonian, the first term represents a set of n uncoupled anharmonic oscillators and the additional terms represent coupling between the modes. One can see here that apart from some over all constant, this Hamiltonian is the anharmonic version of the coupled harmonic oscillator Hamiltonian

$$H = E_0 + \sum_{i=1}^n A_i a_i^\dagger a_i + \sum_{i<j=1}^n B'_{ij} a_i^\dagger a_i a_j^\dagger a_j + \sum_{i<j=1}^n B_{ij} (a_i^\dagger a_j + a_i a_j^\dagger) \quad (1.92)$$

It may be noted here that any one of the above Hamiltonians (1.91 or 1.92) can be obtained from the other simply by a simple substitution.

For the linear molecules showing bending vibrations, the motion occurs in a plane perpendicular to the axis of the molecule, that is in two dimensions (Figure. 1.8). Therefore these vibrations are quantized with the algebra of $U(3)$. This algebra i.e. $U(3)$ is composed of nine operators. In case of linear molecules, we thus have one $U(2)$ for each stretching vibration and one $U(3)$ for each bending vibration. The Hamiltonian operator is expanded here in terms of the four operators of $U(2)$ and the nine operators of $U(3)$.

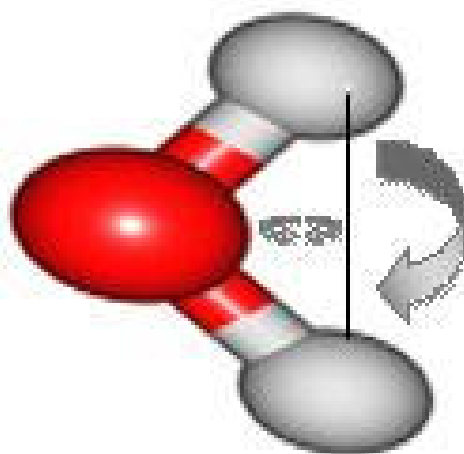


Fig. 1.8 : Bending Vibrations in polyatomic molecules (linear)

Recently this scheme has been used to study the bent and linear molecules. For bent triatomic molecules (SO_2 , S_2O) there are three one-dimensional degrees of freedom, quantized with $U(2) \times U(2) \times U(2)$. In case of linear triatomic molecules (CO_2) there are two one-dimensional stretching modes and one two dimensional bending mode, $U(2) \times U(2) \times U(3)$. In a similar fashion, we have for linear four-atomic molecules (C_2H_2) (Oss and Tamsamani, 1998), $U(2) \times U(2) \times U(2) \times U(3) \times U(3)$. It has been possible to extract the algebraic parameters by fitting the experimental energy levels. In the usual harmonic analysis these parameters play the role of the force-field constants.

For small molecules now let us see the results obtained so far. First of all, we consider the usefulness of the Lie algebraic methods and its comparison with that of usual harmonic analysis. For this, let us consider the Figure 1.9. In this figure the r.m.s. deviation for CO₂ is shown against the number of basis states (Sako *et al.*, 2000). The curve 'algebraic' notes the anharmonic analysis and the curve 'conventional' denotes the usual harmonic analysis. From this figure the convergence properties are very much clear. It is known that for CO₂ there are strong Fermi resonances between the double bending vibration and the symmetric stretch. From Figure.1.9 we note that for CO₂ the conventional analysis requires at least 1500 basis states to converge to a good r.m.s. deviation, whereas the algebraic analysis has already converged with less than 1000 states. The another important point of the algebraic method is its ability to calculate vibrational energies to very high quantum numbers. This is feasible here because we start from the beginning with an anharmonic basis. In this basis perturbations and couplings are small. This can be seen in the study of SO₂ where it has been possible to follow the vibrational states up to 20 quanta of vibration. The reliable calculation of highly excited states of molecules makes us capable to answer several important queries. One of the most important queries is on where and how the transition between normal modes and local modes occurs and whether or not chaotic properties emerge at some excitation energy. The analysis of SO₂ and H₂O shows that the transition from normal to local occurs in SO₂ at $\nu \approx 18$, whereas in case of H₂O it occurs already at $\nu \approx 2$ (Sako *et al.*, 2000). Most molecules with hydrogen bonds, in general, show local behavior for $\nu \geq 2$, although the much more complex dynamics observed in certain molecules (e.g. C₂H₂) are also well described in the algebraic methods (Oss and Tamsamani, 1998; Jacobson *et al.*, 1999).

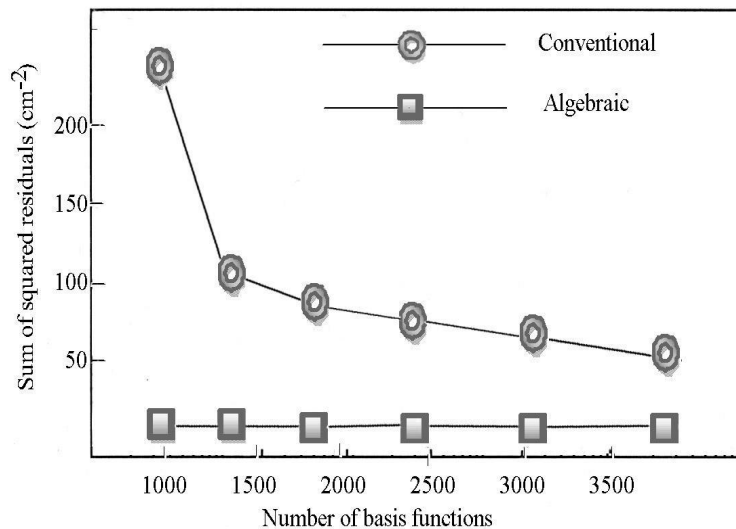


Fig. 1.9: Convergence properties of the algebraic method as compared with the conventional method.

As already mentioned, one of the main advantages of the algebraic method is that it permits a calculation of transition intensities (infrared, Raman and Franck-Condon). In molecular spectroscopy intensities of transitions have not been much used because of the fact that absolute calibration is often difficult. At present this difficulty has been removed. Recent experimental techniques are there which can extract transition intensities. Definitely, this new advancement will provide an enormous amount of information on the structure of molecules. To substantiate the comment, the recent study of Franck-Condon intensities in S_2O may be cited as an example (Muller *et al.*, 1999). In Lie algebraic method, in the study of transitions, we need a model of the transition operator. We need a dipole moment function in the study of infrared transitions.

In case of usual harmonic analysis in one-dimension often this is expanded in powers of the coordinate x

$$M(x) = \sum_{k=0} m_k x^k \quad (1.93)$$

Algebraically we write the above equation as

$$M = \sum_{k=0} m_k (a + a^\dagger)^k \quad (1.94)$$

It may be noted that this dipole moment function also suffers from the same problems of the potential function, that is, here also it becomes difficult to include anharmonicities. The dipole function is expanded in Lie algebraic method in terms of algebraic operators

$$M = \sum_{k=0} m_k (F_+ + F_-)^k. \quad (1.95)$$

In algebraic method the better form often used is

$$M = M_0 \exp[\alpha (F_+ + F_-)] \quad (1.96)$$

The algebraic method provides us a way to perform calculations of transition intensities in which the anharmonicities are included from the beginning both in the potential function and in the transition moment function. Application of this technique has provided an excellent description of 1000 Franck-Condon intensities in S_2O . This technique has made it possible also to extract information on the wave functions of both the upper and lower electronic manifold and information of the extent to which non-Condon effects play a role in these transitions (Iachello *et al.*, 2000).

Medium-size Molecules:

A convenient set of coordinates is provided by the local coordinates for medium size molecules. It may be noted here that this is in contrast to that of small molecules. For local coordinates we have the advantage to write the Hamiltonian operator in a simple form. However, local coordinates have the disadvantage that the spurious coordinates associated with overall translations and rotations must be removed. We must note that for medium-size molecules, discrete symmetries also play a major role. Due to these two difficulties, medium-size molecules present a real challenge to any calculation. To circumvent these difficulties several techniques have been devised. To circumvent the first difficulty, a technique often used is that of adding to the Hamiltonian a term proportional to the center of mass coordinates and letting the coefficient of that term go to a large value. In case the potential is harmonic, this removal of the center of mass

motion is exact. In other cases it is only approximate and there is a small error in the calculation of the vibrational modes which are admixed with the center of mass motion. In the study of benzene C_6H_6 , successfully the technique has been used (Iachello and Oss, 1993). To circumvent the second difficulty, we can construct symmetry adapted states and operators. Already several methods have been used to sort out this problem. The method introduced by Frank, Lemus and others has been used to formulate algebraic models directly in terms of symmetry adapted operators (Lemus and Frank, 1994; Perez-Bernal *et al.*, 1997; Frank *et al.*, 1999). Another method introduced by Chen, has been used to calculate vibrational states with up to $v = 10$ quanta of vibrations in octahedral molecules (UF_6) (Chen *et al.*, 1996). In this area the algebraic methods are found particularly useful since the conventional methods are found difficult to apply here. The algebraic methods made it possible to analyze several phenomena of particular importance in medium-size molecules, the most important one is the question of vibrational energy redistribution.

Macromolecules:

Local coordinates are the best choice for macromolecules. There is no problem in removing the spurious center of mass motion since its role is negligible when the overall mass of the molecule is large. Here the role of discrete symmetries is also less prominent in comparison to that of medium size molecules. Macromolecules till to be taken within the framework of the algebraic methods. The information on vibrational spectroscopy of these systems is also not fully acquired. Under such circumstances, a joint venture of theoretical and experimental studies is essential to have a deep understanding of the structure of macromolecules.

1.14. Plan of work:

The research work is organized into six chapters and brief discussions are given below:

Chapter 1 gives general introduction of molecular spectroscopy and different approaches of molecular spectroscopy. The chapter discusses the concept of Groups, Lie Groups, Lie Algebras, Representations of Lie Groups and Properties of Lie Algebras. It also presents the inception of Lie Algebraic method in modern physics and its application to molecular vibrational spectroscopy for polyatomic molecules.

Chapter 2 presents the formalism of Lie Algebraic theory of polyatomic molecules. This chapter discusses the formalism of Lie Algebraic methods to the concerned molecule Benzene.

Chapter 3 describes the study of vibrational spectra of Benzene using Lie Algebraic method. It also presents the application of one dimensional $U(2)$ Lie Algebraic method for the analysis of vibrational spectra of Benzene. In this chapter we have studied the stretching vibrational spectra of Benzene and calculated several fundamental frequencies of Benzene.

Chapter 4 presents the study of vibrational spectra of monomer and dimer of Benzene using Lie Algebraic method. In this chapter a comparative study of different fundamental frequencies (C-H stretch) of monomer and dimer of Benzene is provided between observed experimental and calculated fundamental frequencies.

Chapter 5 describes the study of vibrational spectra of derivatives of Benzene, fluorobenzene, deuterated Benzene and Mono deuterium substituted Benzene using Lie Algebraic method. In this chapter we have made comparative study of calculated and experimental fundamental frequencies of fluorobenzene, Deuterated Benzene and Mono Deuterium substituted Benzene.

Chapter 6 gives the conclusion and prologue to the future.