Chapter 2

FORMALISM OF LIE ALGEBRAIC THEORY OF POLYMATIC MOLECULES

2.1. One dimensional Algebraic Model for Polyatomic Molecules:

The Lie algebraic methods have been useful in the study of problems in physics at the end of the 19th century and especially after the development of quantum mechanics in the last part of the 20th century. In the last few years, Lie algebraic method has been introduced as a computational tool for the analysis and interpretation of experimental rovibrational spectra of small and medium-size molecules (Iachello, 1981; Iachello and Levine, 1982). This method is based on the idea of dynamic symmetry, which, in turn, is expressed through the language of Lie algebras. By applying algebraic techniques, one obtains an effective Hamiltonian operator that conveniently describes the ro-vibrational degrees of freedom of a physical system. Within this framework, any specific mechanism relevant to the correct characterization of the molecular dynamics and spectroscopy can be accounted for. The algebraic methods are formulated in such a way that they contain the same physical information of both *ab initio* theories (based on the solution of the SchrÖdinger equation) and of semiempirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). However, by employing the powerful

method of group theory, the results can be obtained in a more rapid and straightforward way.

Iachello, Arima (Iachello and Arima, 1974; Arima and Iachello, 1975) and Wulfman (Wulfman, 1973; Levine *et al*., 1979) have played a significant role in the algebraic approach to molecules. Wulfman is the pioneer who reported on the algebraic approach to molecules (the approach to the Morse oscillator) in 1979. Later, in 1981 Iachello used Lie algebraic methods in a systematic study of the spectra of molecules (the vibron model). This introduction was based on the second quantization of the Schrodinger equation with a three-dimensional Morse potential and described the rotation-vibration spectra of diatomic molecules and polyatomic molecules (Roosmalen, Iachello, Levine and Dieperink, 1983b; Roosmalen, Benjamin and Levine, 1984). Using Lie algebraic method, Sarkar and Karumuri (Sarkar *et al*, 2006; Karumuri, 2012; Karumuri *et al*, 2010a; Choudhury et al, 2010) reported better results for the vibrational energy levels of HCN, HCCF, HCCD, $SnBr_4$, Cu[TPP], $Cu[TPP]^+$ than those reported earlier. Moreover, The $U(2)$ algebraic model was also particularly successful in explaining separately the stretching and bending vibrations of polyatomic molecules such as octahedral, benzene and pyrrole-like molecules (Lubich and Oss, 1996; Ping, 1997). As such, the approach is particularly appropriate for many challenges of modern spectroscopy, hence we used the $U(2)$ algebraic model to study some of the vibrational spectra of benzene, monomer and dimer of benzene and two of its derivatives and at the same time try to confirm that the $U(2)$ Algebraic model stands itself as an alternative approach to the traditional Dunham expansion and potential approach for polyatomic molecules. In potential approach, the interpretation of experimental data by solving Schrödinger equation with interatomic potentials becomes increasingly difficult as the number of atoms in the molecule increases, whereas, in Dunham expansion no Hamiltonian operator is available and in this expansion for large polyatomic molecules, one needs a large number of parameters to

obtain by fitting large experimental data base, which is not always available. The Dunham expansion can be readily obtained as

$$E(\upsilon) = \omega_e\left(\upsilon + \frac{1}{2}\right) - \omega_e x_e\left(\upsilon + \frac{1}{2}\right)^2 \tag{2.1}$$

where ω_e and $\omega_e x_e$ are the spectroscopic constants. This above expansion does not contain any information about the wave function of individual states. Thus, the matrix elements of operators cannot be calculated directly.

To construct the Hamiltonian operator in the algebraic framework in *n* dimensional harmonic oscillator one has to replace the usual $_i$ and p_i space coordinates with differential quantum operators x_i , $-i\hbar\partial/\partial x_i$ (*i* = 1,……., *n*). This corresponds to the algebraic realization which is obtained in terms of a second quantization by replacing the differential space-momentum operators with creation and annihilation operators. For a harmonic oscillator the followings are the rules of replacement

$$a_i = \frac{x_i + \partial/\partial x_i}{\sqrt{2}}, \quad a_i^\dagger = \frac{x_i - \partial/\partial x_i}{\sqrt{2}} \tag{2.2}$$

By virtue of the quantum nature, both the operators x_i and p_i satisfy certain commutation relations, which contain within themselves the specific aspects of the physical interaction between particles, lead to a set of precise commutation relations of the operators a_i and $a_i^\dagger$.

The following expression representing the Hamiltonian operator, in terms of the operators a_i and $a_i^\dagger$

$$H = N + \frac{n}{2}, \text{ where the number operator } \mathrm{N}=\sum_{i=1}^{n} a_i a_i^\dagger \tag{2.3}$$

Considering the larger degeneracy and dynamical groups, the algebraic Hamiltonian operator can be written in terms of n^2 annihilation—creation operators *ai* and $a_j^\dagger$ (*i*, *j* =1, ……., *n*). Thus it can be easily shown that,

$$\left[\hat{H}, \hat{a}_i^\dagger \hat{a}_j\right] = 0 \tag{2.4}$$

These commutation relations are an unequivocal sign of symmetry for the Hamiltonian operator, *H*. Such symmetry is made clear through a detailed study of group theoretical properties of the bilinear forms $a_i^\dagger a_j$. In proper expansion over bilinear forms of (boson) creation and annihilation operators, the Hamiltonian operator can still be represented. The general rule is that one has to introduce a set of $(n+1)^2$ boson operators b_i and $b_j^\dagger$ (*i, j* = 1, ……, *n*+1) satisfying the commutation relations

$$\left[b_i, b_j^\dagger\right] = \delta_{ij}, \quad \left[b_i, b_j\right] = \left[b_i^\dagger, b_j^\dagger\right] = 0 \tag{2.5}$$

The Algebraic (second-quantized) version Hamiltonian operator now can be written as

$$H = E_0 + \sum_{i,j} e_{ij} b_i^\dagger b_j + \sum_{i,j,h,k} f_{ijhk} b_i^\dagger b_j^\dagger b_h b_k + ... \tag{2.6}$$

This expression includes terms up to two body interactions. The algebraic Hamiltonian (Eq. (2.3)) of the (*n*-dimensional) harmonic oscillator is, of course a special case of Eq. (2.6). One observes that it is possible to arrange the above Hamiltonian in the framework of a dynamical algebra by explicitly introducing the bilinear products

$$G_{ij} = b_i^\dagger b_j, \quad i, j = 1, ..., n+1 \tag{2.7}$$

Where the operators G_{ij} satisfy the commutation relations

$[G_{ij}, G_{hk}] = G_{ik}\delta_{jh} - G_{hj}\delta_{kl}$ and hence representing the unitary algebra U(n+1). Now it is possible to write the Hamiltonian operator in terms of the generators

$$H = E_0 + \sum_{i,j} e_{ij} G_{ij} + \sum_{i,j,h,k} f_{ijhk} G_{ih} G_{jk} + ... \tag{2.8}$$

In this situation it is worthy to notice that the algebraic Hamiltonian (Eq. (2.6)) expressed in terms of elements of *U*(*n*+1), is completely general and holds for any *n*-dimensional problem. This means that the dynamical group for any three dimensional problem is *U(4)*, while for any one-dimensional situation the dynamical group is *U(2)*. In Eq. (2.8) the basic idea is to choose the parameters e_{ij}, f_{ijhk}, …… in such a way that only certain operators of the sub-algebras of the dynamical algebras are taken into

account. As a matter of fact, if one includes in this expansion only the invariant or Casimir operators of the sub-algebras, the Hamiltonian operator can be written as

$$H = E_0 + AC + A'C' + A''C'' + \ldots\ldots \tag{2.9}$$

In which the *C's* are invariant operators of the sub-algebras *G'*,*G"*, ……. of the dynamical algebra *G*. Starting from *U*(2), we introduces two dynamical symmetries, *(a)* and *(b)* corresponding to the chains

$$(a)\ U(2) \supset U(1) \tag{2.10}$$

$$(b)\ U(2) \supset O(2) \tag{2.11}$$

Chain *(a)* is characterized by the following algebraic ket:

$$\left| \begin{matrix} U(2) \supset U(1) \\ N \qquad\quad \mathrm{n} \end{matrix} \right\rangle \text{ where } \mathrm{n} = \mathrm{N}, \mathrm{N}-1, \ldots . 0 \tag{2.12}$$

By virtue of the boson character of the algebraic realization of U(2), one just has to use symmetric irreducible representations of the algebra. Similarly, the chain (b) is characterized by the following algebraic ket:

$$\left| \begin{matrix} U(2) \supset O(2) \\ N \qquad\quad \mathrm{m} \end{matrix} \right\rangle \text{ where } \mathrm{m} = \pm \mathrm{N}, \pm \mathrm{N}-2, \ldots . \pm 1 \text{ or } 0 \tag{2.13}$$

Based on both the chains, the dynamical symmetric Hamiltonian operator has the following form:

$$H^{(a)} = E_0 + e_1 C^{(1)}_{U(1)} + e_2 C^{(2)}_{U(1)} \tag{2.14}$$

$$H^{(b)} = E_0 + A_1 C^{(1)}_{O(2)} + A_2 C^{(2)}_{O(2)} \tag{2.15}$$

The eigenvalues of those Hamiltonian operator using chain (*a*) and chain (b) are

$$E^{(a)}(n) = E_0 + e_1 n + e_2 n^2, \quad \text{where } \mathrm{n} = N, N-1, \ldots 0 \tag{2.16}$$

$$E^{(b)}(m) = E_0 + A_1 m + A_2 m^2, \quad \text{where } \mathrm{m} = \pm N, \pm N-2, \ldots \pm 1 \text{ or } 0 \tag{2.17}$$

Interesting situation arises when we chose $A_1 = 0$, $A \equiv A_2 \neq 0$ in Eqs. (2.15) and (2.17), it is now possible to put the spectrum in a one-to-one correspondence with the bound state spectrum of the one dimensional Morse potential. This can be done by choosing in Eq. (2.17) only the positive branch of the quantum number *m.* Correspondingly we obtain,

$$E^{(b)}(m) = E_0 + Am^2, \quad \text{where m} = N, N-2, \ldots 1 \text{ or } 0 \tag{2.18}$$

Now, one can easily recognize the Morse spectrum by introducing the usual vibrational quantum number

$$\upsilon = \frac{N-m}{2} = 0, 1, \ldots, \frac{N}{2} \text{ or } \frac{N-1}{2} (N \text{ even or odd}) \tag{2.19}$$

Using the function of υ, Eq. (2.18) becomes

$$E^{(b)}(\upsilon) = E_0 + A(N-2\upsilon)^2 = e_0 - 4A\upsilon(N-\upsilon), \text{where } e_0 = E_0 + AN^2 \tag{2.20}$$

Comparing Eq. (2.20) directly with the Dunham expansion (Eq. (2.1)), we obtain,

$$e_0 = \frac{\omega_e}{2}\left(1 - \frac{x_e}{2}\right), \quad A = -\frac{\omega_e x_e}{4}, \quad N = \frac{1}{x_e} - 1 \tag{2.21}$$

We generalize the U(n+1) algebra for *N* interacting oscillators, the corresponding product is

$$U_1(2) \otimes U_2(2) \otimes \ldots . \otimes U_N(2) \tag{2.22}$$

Consequently the algebraic Hamiltonian for *N* uncoupled anharmonic oscillators, based on the $U(2) \supset O(2)$ dynamic symmetry, will be given by

$$H_{uncoupled} = \sum_{i=1}^{N} A_i C^{(2)}_{O_i(2)} \tag{2.23}$$

We also introduce the algebraic local basis

$$\left| m_1, m_2, \ldots . m_n \right\rangle, \qquad m_i = N_i, N_i - 2, \ldots . , \qquad i = 1, \ldots, N \tag{2.24}$$

or, equivalently, the local vibrational basis

$$\left| \upsilon_1, \upsilon_2, \ldots, \upsilon_n \right\rangle, \quad \upsilon_i = 0, 1, 2, \ldots . , \quad i = 1, \ldots . , N \tag{2.25}$$

In the above basis, the eigenvalues can be computed according to Eq. (2.20)

$$E_{uncoupled}\left(\upsilon_1, \ldots . , \upsilon_n\right) = -4\sum_{i=1}^{N} A_i \upsilon_i (N_i - \upsilon_i) \tag{2.26}$$

The local basis as given by Eq. (2.25) can be arranged in polyads, characterized by a well defined total vibrational number $\Sigma_{i=1}^{n} \nu_1 \equiv p$. This means that within the same polyads i.e., for given *p*, single basis states are expressed in terms of integers partitions of *p* in *N* parts. We now have to

account for some type of interaction among the local modes. In the *N* oscillator case, we expect to deal with coupling terms involving pairs of oscillators; this is equivalent to considering algebraic lattices, starting from the product as shown in Eq. (2.22), of the following types,

$$O_2(2)\otimes O_2(2)\otimes .....\otimes O_N(2) \supset \begin{cases} O_{12}(2)\otimes O_3(2)\otimes ...\otimes O_N(2) \\ O_{13}(2)\otimes O_2(2)\otimes ...\otimes O_N(2) \\ . \\ . \\ . \\ O_{1N}(2)\otimes O_2(2)\otimes ...\otimes O_{N-1}(2) \end{cases} \tag{2.27}$$

and

$$U_1(2)\otimes U_2(2)\otimes .....\otimes U_N(2) \supset \begin{cases} U_{12}(2)\otimes U_3(2)\otimes ...\otimes U_N(2) \\ U_{13}(2)\otimes U_2(2)\otimes ...\otimes U_N(2) \\ . \\ . \\ . \\ U_{1N}(2)\otimes U_2(2)\otimes ...\otimes U_{N-1}(2) \end{cases} \tag{2.28}$$

Thus it leads to the following Hamiltonian operator for *N* interacting oscillators,

$$H = E_0 + \sum_{i=1}^{N} A_i C^{(2)}_{O_i(2)} + \sum_{i<j=1}^{N} A_{ij} C^{(2)}_{O_{ij}(2)} + \sum_{i=1}^{N} \lambda_{ij} M_{ij} \tag{2.29}$$

Consider now a molecule with *n* bonds. In the algebraic model, here each bond is replaced by the corresponding U(2) algebra. Our concentration lies on the explicit problem of the construction of a straightforward generalization of the Hamiltonian operator for the benzene and its derivatives. According to the general algebraic description for one-dimensional degrees of freedom, a dynamically-symmetric Hamiltonian operator for *N* interacting (not necessarily equivalent) oscillators can be written as (Sen *et.al*., 2011; 2012)

$$H = E_0 + \sum_{i=1}^{N} A_i C_i + \sum_{i<j}^{N} A_{ij} C_{ij} + \sum_{i<j}^{N} \lambda_{ij} M_{ij} \tag{2.30}$$

In this expression, one finds three different classes of effective contributions. The first one, $\sum_{i=1}^{n} A_i C_i$ is devoted to the description of *n* independent, anharmonic sequences of vibrational levels (associated with *N* independent, local oscillator) in terms of the operators C_i . The second one, $\sum_{i<j}^{n} A_{ij} C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij}. The third one, $\sum_{i<j}^{n} \lambda_{ij} M_{ij}$ describes anharmonic, non-diagonal interactions involving pairs of local oscillators in terms of the operators M_{ij}. The C_i, C_{ij} operators are invariant (Casimir) operators of certain Lie algebras, while the M_{ij} are invariant (Majorana) operators associated with coupling schemes, involving algebras, arising from a systematic study of the algebraic formulation of the one-dimensional model for *N* interacting oscillators. Our work relies on the local (uncoupled oscillators) vibrational basis, which can be written as,

$$\left|v\right\rangle \equiv \left|v_1 v_2 v_3 .... v_n\right\rangle \tag{2.31}$$

In which the aforementioned operators have the following matrix elements,

$$\begin{aligned}
&\left\langle v\right|C_i\left|v\right\rangle = -4v_i(N_i - v_i)\\
&\left\langle v\right|C_{ij}\left|v\right\rangle = -4(v_i + v_j)(N_i + N_j - v_i - v_j)\\
&\left\langle v'\right|M_{ij}\left|v\right\rangle = (v_i N_i + v_j N_j - 2v_i v_j)\lambda_{v'_i v_i}\lambda_{v'_j v_j}\\
&\left\langle v'\right|M_{ij}\left|v\right\rangle = -\left[\left(v_i + 1\right)\left(N_i - v_i\right)v_j\left(N_j - v_j + 1\right)\right]^{1/2} \times \delta_{v'_i - v_i}\delta_{v'_j + v_j}\\
&\left\langle v'\right|M_{ij}\left|v\right\rangle = -\left[\left(v_j + 1\right)\left(N_j - v_j\right)v_i\left(N_i - v_i + 1\right)\right]^{1/2} \times \delta_{v'_i + v_i}\delta_{v'_j - v_j}
\end{aligned} \tag{2.32}$$

Here, in particular, the above expressions depend on the numbers N_i popularly known as Vibron numbers (vibration rotation quantum number). Such numbers have to be seen as predetermined parameters of well-defined physical meaning, as they relate to the intrinsic anharmonicity of a single, uncoupled oscillator through the simple relation.

2.2. Hamiltonian for Bending Vibration:

We emphasize once more that the quantization scheme of bending vibrations in U(2) is rather different from U(4) and implies a complete separation between rotations and vibrations. If this separation applies, one can quantize each bending oscillator *i* by means of an algebra $U_i(2)$ as in Equation (2.13). The Pöschl-Teller Hamiltonian is

$$H(P_s, s) = \frac{P_s^2}{2\mu} - \frac{D}{\cosh^2(\alpha s)} \tag{2.33}$$

Where we have absorbed the λ (λ -1) part into D, and can be written, in the algebraic approach, as

$$H_i = \varepsilon_{0_i} + A_i C_i \tag{2.34}$$

This Hamiltonian is identical to that of stretching vibration [Eq. (2.30)]. The only difference is that the coefficients A_i in front of C_i are related to the parameters of the potential, D and α, in a way that is different for Morse and Pöschl-Teller potentials. The energy eigenvalues of uncoupled Pöschl-Teller oscillators are, given by

$$E = \sum_i \varepsilon_i = E_0 - \sum_i 4A_i \left(N_i \nu_i - \nu_i^2 \right) \tag{2.35}$$

One can then proceed to couple the oscillators as done previously and repeat the same treatment.

2.3. Local to Normal-mode Transition and the Locality Parameter:

The local-to-normal transition is governed by the dimensionless locality parameter (**ξ**). The local-to-normal transition can be studied for polyatomic molecules, for which the Hamiltonian is,

$$H = H^{local} + \lambda_{12} M_{12} = A_i C_i + A_{ij} C_{ij} + \lambda_{ij} M_{ij} \tag{2.36}$$

For these molecules, the locality parameters are

$$\xi_i = (2/\pi) \tan^{-1} \left[8\lambda_{ij} / (A_i + Aij) \right], i, j = 1, 2, 3, ... \tag{2.37}$$

corresponding to the two bonds. A global locality parameter for XYZ molecules can be defined as the geometric mean.

$$\xi = (|\xi_1 \xi_2|)^{1/2} \tag{2.38}$$

With this definition, due to Child and Halonen, local-mode molecules are near to the ξ = 0 limit, normal mode molecules have $\xi \rightarrow 1$.