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Intramolecular Vibrational Spectra of Benzene and Its Derivatives in CC, CH and CD Local Mode Interaction

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Lie algebraic method is based on the idea of dynamic symmetry, which can be expressed in terms of $U(2)$ Lie algebra. By applying algebraic approach, an effective Hamiltonian operator can be obtained which conveniently describes the rovibrational degrees of freedom of benzene and its derivatives. Here, every CC, CH, CD bonds of the molecule are replaced by a corresponding $U(2)$ Lie algebra and finally the local Hamiltonian is constructed considering the invariant Casimir and Majorana operators. The fundamental modes are then calculated using this Hamiltonian to fit the results of the theoretical as well as experimental observations.

Keywords: Lie Algebra, Hamiltonian, Casimir and Majorana Operators, Benzene.

1. INTRODUCTION

The structure and dynamics of highly excited vibrational states of polyatomic molecules is a subject of considerable current interest. One of the queries in the study of the vibrational spectra of polyatomic molecules is the determination of the normal modes of vibration. For an N-atom molecule the number of these modes is $n = 3N - 6$ and under the Born-Oppenheimer approximation each one can be described in terms of the displacements of all the nuclei from their equilibrium positions in a given electronic state of the molecule. In case of highly symmetric benzene molecule, the overtone spectra of it and some of its isotopic derivatives have been at the starting point of the interesting discussions of intramolecular vibrational redistribution as visible in vibrational spectra. This present work aims to present an algebraic model of intramolecular vibrational spectra associated with local modes CC, CH and CD interactions in benzene and compare the calculated results with that of theoretical as well as experimental approaches.[1–3]

It is nearly 50 years since Ingold et al.[4] carried out the first comprehensive study of the vibrational spectrum of benzene. They measured the vapour and liquid infrared spectra of several deuterium labeled benzenes. Their correlation of bands between labeled molecules and careful comparison of vapor and liquid frequencies allowed a vibrational analysis which in large part still stands today. Mair and Hornig[5] then made a major contribution to the early vibrational assignments by giving definite

and plausible frequencies for the infrared and Raman forbidden fundamentals.

Benzene has also been considered as a prototype molecule for harmonic force-field calculations,[6–8] local mode theory,[9–11] radiation less transitions, high resolution electronic spectroscopy[12–14] and high resolution infrared and Raman spectroscopy.[15, 16] The force-field calculations are available for in-plane and out-of-plane modes of benzene and also for many substituted benzenes and its derivatives. Moreover, there have been the advanced *ab initio* studies of its harmonic and anharmonic potential functions.

The present work leads to the vibrational analysis of benzene and two 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 standard Fermi couplings along with Casimir and Majorana couplings and their consequences for fundamental and overtone spectra and dynamics. Our work relies strictly on the normal mode analysis of benzene carried out by Pulay et al.[17] Our analysis follows the traditional approach of the vibrational mode descriptions of Wilson used in many papers on benzene spectra.[18] Isotopically labeling benzene causes the benzene (h_6) modes to lose their 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 labeled benzenes in terms of the normal coordinates of benzene. This expression involves diagonal and off-diagonal terms by Casimir and Majorana operators which provide a quantitative description of the normal modes of benzenes molecules and its derivatives.

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2. *U*(2) ALGEBRAIC MODEL

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.[19, 20] 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 Schrodinger 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[21, 22] and Wulfman[23, 24] 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.[25, 26] Using Lie algebraic method, Sarkar and Karumuri[27–30] 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 explain separately the stretching and bending vibrations of polyatomic molecules such as octahedral, benzene and pyrrole-like molecules.[31, 32] Recently, we have reported the vibrational spectra of polyatomic fullerenes C_{60}, C_{70} and C_{80}[33, 34] using Lie algebraic method. As such, the approach is particularly appropriate for many challenges of modern spectroscopy, hence in this paper we used the $U(2)$ algebraic model to study some of the vibrational spectra 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 Hamitonian 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

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

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 can not be calculated directly.

To construct the Hamiltonian operator in the algebraic framework in n dimensional harmonic oscillator one has to replace the usual x_i and p_i space coordinates with differential quantum operators x_i, $-i\hbar \partial/\partial x_i$ $(i = 1, \ldots, n)$. 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

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

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 $a_i^\dagger$

$$H = N + \frac{n}{2}, \quad \text{where the number operator } N = \sum_{i=1}^{n} a_i a_i^\dagger \quad (3)$$

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

$$[\widehat{H}, \widehat{a_i^\dagger} \widehat{a_j}] = 0 \quad (4)$$

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 $b_j^\dagger$ $(i, j = 1, \ldots, n+1)$ satisfying the commutation relations

$$[b_i, b_j^\dagger] = \delta_{ij}, \quad [b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0 \quad (5)$$

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

$$H = E_0 + \sum_{i,j} e_{ij} b_i^\dagger b_j + \sum_{i,j,h,k} f_{ijhk} b_i^\dagger b_j^\dagger b_h b_k + \cdots \quad (6)$$

This expression includes terms up to two body interactions. The algebraic Hamiltonian (Eq. (3)) of the (n-dimensional) harmonic oscillator is, of course a special case of Eq. (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

$$G_{ij} = b_i^\dagger b_j, \quad i, j = 1, \ldots, n+1 \quad (7)$$

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

$$H = E_0 + \sum_{i,j} e_{ij} G_{ij} + \sum_{i,j,h,k} f_{ijhk} G_{ih} G_{jk} + \cdots \quad (8)$$

In this situation it is worthy to notice that the algebraic Hamiltonian (Eq. (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. (8) the basic idea is to choose

the parameters e_{ij}, f_{ijhk}, ... in such away 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

$$H = E_0 + AC + A'C' + A''C'' + \cdots \qquad (9)$$

In which the $C's$ are invariant operators of the subalgebras $G', G'', \ldots$ of the dynamical algebra G. Starting from $U(2)$, we introduces two dynamical symmetries, (a) and (b) corresponding to the chains

$$\text{(a) } U(2) \supset U(1) \qquad (10)$$

$$\text{(b) } U(2) \supset O(2) \qquad (11)$$

chain (a) is characterized by the following algebraic ket:

$$\left| \begin{matrix} U(2) \supset U(1) \\ N \qquad n \end{matrix} \right\rangle \text{ where } n = N, N-1, \ldots 0 \qquad (12)$$

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:

$$\left| \begin{matrix} U(2) \supset U(1) \\ N \qquad m \end{matrix} \right\rangle \text{ where } m = \pm N, \pm N-2, \ldots, \pm 1 \text{ or } 0 \qquad (13)$$

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

$$H^{(a)} = E_0 + e_1 C_{U(1)}^{(1)} + e_2 C_{U(1)}^{(2)} \qquad (14)$$

$$H^{(b)} = E_0 + A_1 C_{O(2)}^{(1)} + A_2 C_{O(2)}^{(2)} \qquad (15)$$

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

$$E^{(a)}(n) = E_0 + e_1 n + e_2 n^2, \quad \text{where } n = N, N-1, \ldots 0 \qquad (16)$$

$$E^{(b)}(m) = E_0 + A_1 m + A_2 m^2, \quad \text{where,}$$

$$m = \pm N, \pm N-2, \ldots, \pm 1 \text{ or } 0 \qquad (17)$$

Interesting situation arises when we chose $A_1 = 0$, $A \equiv A_2 \neq 0$ in Eqs. (15) and (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. (17) only the positive branch of the quantum number m. Correspondingly we obtain,

$$E^{(b)}(m) = E_0 + Am^2, \quad m = N, N-2, \ldots, 1 \text{ or } 0 \qquad (18)$$

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

$$v = \frac{N-m}{2} = 0, 1, \ldots, \frac{N}{2} \text{ or } \frac{N-1}{2} \text{ (N even or odd)} \qquad (19)$$

Using the function of v, Eq. (18) becomes

$$E^{(b)}(v) = E_0 + A(N-2v)^2 = e_0 - 4Av(N-v), \quad \text{where}$$

$$e_0 = E_0 + AN^2 \qquad (20)$$

Comparing Eq. (20) directly with the Dunham expansion (Eq. (1)), we obtain,

$$e_0 = \frac{\omega_e}{2}\left(1 - \frac{x_e}{2}\right), \quad A = -\frac{\omega_e x_e}{4}, \quad N = \frac{1}{x_e} - 1 \qquad (21)$$

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

$$U_1(2) \otimes U_2(2) \otimes \cdots \otimes U_N(2) \qquad (22)$$

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

$$H_{\text{uncoupled}} = \sum_{i=1}^{N} A_i C_{O_i(2)}^{(2)} \qquad (23)$$

We also introduce the algebraic local basis

$$|m_1, m_2 \ldots m_N\rangle, \quad m_i = N_i, N_i - 2, \ldots, \quad i = 1, \ldots N \qquad (24)$$

or, equivalently, the local vibrational basis

$$|v_1, v_2 \ldots v_N\rangle, \quad v_i = 0, 1, 2 \ldots, \quad i = 1, \ldots, N \qquad (25)$$

In the above basis, the eigenvalues can be computed according to Eq. (20)

$$E_{\text{uncoupled}}(v_1, \ldots, v_N) = -4\sum_{i=1}^{N} A_i v_i (N_i - v_i) \qquad (26)$$

The local basis as given by Eq. (25) can be arranged in polyads, characterized by a well defined total vibrational number $\sum_{i=1}^{N} v_i \equiv p$. This means that within the same polyads i.e., for given p, single basis states are expressed in terms of intergers 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. (22), of the following types,

$$O_2(2) \otimes O_2(2) \otimes \cdots \otimes O_N(2)$$

$$\supset \begin{cases} O_{12}(2) \otimes O_3(2) \otimes \cdots \otimes O_N(2) \\ O_{13}(2) \otimes O_2(2) \otimes \cdots \otimes O_N(2) \\ \vdots \\ O_{1N}(2) \otimes O_2(2) \otimes \cdots \otimes O_{N-1}(2) \end{cases} \qquad (27)$$

and

$$U_1(2) \otimes U_2(2) \otimes \cdots \otimes U_N(2)$$

$$\supset \begin{cases} U_{12}(2) \otimes U_3(2) \otimes \cdots U_N(2) \\ U_{13}(2) \otimes U_2(2) \otimes \cdots \otimes U_N(2) \\ \vdots \\ U_{1N}(2) \otimes U_2(2) \otimes \cdots \otimes U_{N-1}(2) \end{cases} \qquad (28)$$

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

$$H = E_0 + \sum_{i=1}^{N} A_i C_{O_i(2)}^{(2)} + \sum_{i \langle j=1}^{N} A_{ij} C_{O_{ij}(2)}^{(2)} + \sum_{i=1}^{N} \lambda_{ij} M_{ij} \qquad (29)$$

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[33, 34]

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i\langle j}^{n} A_{ij} C_{ij} + \sum_{i\langle j}^{n} \lambda_{ij} M_{ij} \qquad (30)$$

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, $\sum_{i\langle j}^{n} A_{ij} C_{ij}$ leads to cross-anharmonicities between pairs of distinct local oscillators in terms of the operators C_{ij}. The third one, $\sum_{i\langle j}^{n} \lambda_{ij} M_{ij}$ 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,

$$|\nu\rangle \equiv |\nu_1 \nu_2 \nu_3 \ldots \nu_n\rangle \qquad (31)$$

In which the aforementioned operators have the following matrix elements,

$$\langle\nu| C_i |\nu\rangle = -4\nu_i(N_i - \nu_i)$$

$$\langle\nu| C_{ij} |\nu\rangle = -4(\nu_i + \nu_j)(N_i + N_j - \nu_i - \nu_j)$$

$$\langle\nu'| M_{ij} |\nu\rangle = (\nu_i N_i + \nu_j N_j - 2\nu_i \nu_j)\delta_{\nu_i' \nu_i}\delta_{\nu_j' \nu_j}$$

$$\langle\nu'| M_{ij} |\nu\rangle = -[(\nu_i + 1)(N_i - \nu_i)\nu_j(N_j - \nu_j + 1)]^{1/2} \qquad (32)$$
$$\times \delta_{\nu_i' - \nu_i}\delta_{\nu_j' + \nu_j}$$

$$\langle\nu'| M_{ij} |\nu\rangle = -[(\nu_j + 1)(N_j - \nu_j)\nu_i(N_i - \nu_i + 1)]^{1/2}$$
$$\times \delta_{\nu_i' + \nu_i}\delta_{\nu_j' - \nu_j}$$

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.

3. HAMILTONIAN FOR CC, CH, CD BONDS OF THE MOLECULES

Our significance lies on the quantization scheme of steching 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 identify each oscillator by means of an algebra $U(2)$ which leads the general form of Hamiltonian of the concerned molecules, given by

$$H = A_{CD}\sum_{i=1}^{6} C_i^{CD} + A_{CD}'\sum_{i\langle j=1}^{6} C_{ij} + \sum_{i\langle j=1}^{6}\lambda_{ij} M_{ij}$$

$$+ A_{CC}\sum_{i=1}^{6} C_i^{CC} + A_{CC}'\sum_{i\langle j=1}^{6} C_{ij} + \sum_{i\langle j=1}^{6}\lambda_{ij}' M_{ij} + A_{CH}\sum_{i=1}^{6} C_i^{CH}$$

$$+ A_{CH}'\sum_{i\langle j=1}^{6} C_{ij} + \sum_{i\langle j=1}^{6}\lambda_{ij}'' M_{ij} \qquad (33)$$

4. SYMMETRY PERSONALIZED OPERATORS

In polyatomic molecules, the geometric point group symmetry of the molecule plays an important role. States must transform according to representations of the point symmetry group. In the absence of the Majorana operators M_{ij}, states are degenerate. The introduction of the Majorana operators has two important contributions: (1) it splits the degeneracies of figure and (2) in addition, it generates states with the appropriate transformation properties under the point group. In order to achieve this result the λ_{ij} must be chosen in an appropriate way that reflects the geometric symmetry of the molecule. The total Majorana operator

$$S = \sum_{i<j}^{n} M_{ij} \qquad (34)$$

Considering the molecule benzene (C_6H_6) and two of its derivatives (i.e., C_6H_5D, C_6D_6) the Majorana Part of C—C is given by the following matrix structure

$$\begin{pmatrix} N(\lambda' + \lambda'' + \lambda''') & -N\lambda' & -N\lambda'' \\ -N\lambda' & N(2\lambda' + \lambda'' + \lambda''') & -N\lambda' \\ -N\lambda'' & -N\lambda' & N(2\lambda' + \lambda'' + \lambda''') \\ -N\lambda''' & -N\lambda'' & -N(\lambda' + \lambda'') \\ 0 & -N\lambda''' & -N\lambda'' \\ 0 & 0 & -N\lambda''' \end{pmatrix}$$

$$\begin{pmatrix} -N\lambda''' & 0 & 0 \\ -N\lambda'' & -N\lambda''' & 0 \\ -N\lambda', & -N\lambda'' & -N\lambda''' \\ N(\lambda' + 2\lambda'' + \lambda''') & -N\lambda' & -N\lambda'' \\ -N\lambda' & N(2\lambda' + \lambda'' + \lambda''') & -N\lambda' \\ -N\lambda'' & -N\lambda' & N(\lambda' + \lambda'' + \lambda''') \end{pmatrix}$$

$$(35)$$

Similarly for the interacting bond C—D and C—H, the respective matrix structures are given by

$$\begin{pmatrix} N(\lambda' + \lambda'') & -N\lambda' & -N\lambda'' \\ -N\lambda' & 2N\lambda' & -N\lambda' \\ -N\lambda'' & 0 & N(\lambda'' + \lambda') \end{pmatrix} \qquad (36)$$

and

$$\begin{pmatrix} N\lambda' & -N\lambda' \\ -N\lambda' & N\lambda' \end{pmatrix} \qquad (37)$$

5. LOCAL TO NORMAL TRANSITION: THE LOCALITY PARAMETER (ξ)

The local-to-normal transition is governed by the dimensionless locality parameter (ξ). The local-to-normal transition can be studied[31–38] for polyatomic molecules, for which the Hamiltonian is

$$H = H_{local} + \lambda_{ij} M_{ij} = A_i C_i + A_{ij} C_{ij} + \lambda_{ij} M_{ij} \qquad (38)$$

For these molecules, the locality parameters are

$$\xi = \frac{2}{\pi} \tan^{-1} \left[\frac{8\lambda_{ij}}{A_i + A_{ij}} \right], \quad i, j = 1, 2, 3 \ldots \qquad (39)$$

corresponding to the number of bonds.

With this definition, considering the case of Child and Halonen,[39] local mode molecules are near to the $\xi = 0$ limit, normal mode molecules have $\xi \rightarrow 1$.

6. RESULTS AND DISCUSSION

In the algebraic theory, we introduce the vibron number N which is directly related to the anharmonicity of local CC, CH and CD stretching bonds. The quantum numbers v_i corresponds to the number of quanta in each oscillator, while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i \qquad (40)$$

For a particular polyad, the total vibrational quantum number is always conserved.

The value of vibron number N for C_6H_6, C_6D_6 and C_6H_5D can be calculated by the following relation[23]

$$N_k = \frac{\omega_e}{\omega_e x_e} - k \quad (k = 1, 2, 3 \ldots) \qquad (41)$$

where, ω_e and $\omega_e x_e$ are the spectroscopic constants[40, 41] of poly-atomic molecules of stretching interaction of the molecule considered. The value of N has to be taken as the initial guess. Depending on the specific molecular structure one can expect a change of 20% of the value of N.

The value of the parameter A can be obtained from the single-oscillator fundamental mode as

$$E(v = 1) = -4A(N - 1) \qquad (42)$$

Lastly, one has to obtain an initial guess for the parameters λ and λ' of the Majorana operators, the role of which is to degenerate the local modes and the value of the parameters can be calculated by considering the following matrix structure of the molecules.

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) & & -\lambda N \\ \quad +3(\lambda+\lambda')N & & \\ -\lambda N & & -4A(N-1) - 4A'(2N-1) \\ & & \quad +3(\lambda+\lambda')N \\ -\lambda N & & -\lambda N \\ -\lambda N & & -\lambda N \end{pmatrix}$$

$$\left. \begin{array}{cc} -\lambda N & -\lambda N \\ -\lambda N & -\lambda N \\ -4A(N-1) - 4A'(2N-1) & -\lambda N \\ \quad +3(\lambda+\lambda')N & \\ -\lambda N & -4A(N-1) - 4A'(2N-1) \\ & \quad +3(\lambda+\lambda')N \end{array} \right) \qquad (43)$$

To obtain an initial guess for the parameter λ and λ', we comprise the following relations from above matrix equation,[42]

$$\lambda = \frac{E_3 - E_1}{2N} \qquad (44)$$

and

$$\lambda' = \frac{E_2 - E_1}{6N} \qquad (45)$$

Table I. Fitting algebraic parameters for CC, CD, CH bonds of benzene (C_6H_6) and two of its derivatives (C_6H_5D, C_6D_6).

Bonds	C—C	C—D	C—H
Vibron number	$N_{C_6H_6} = 43$	$N_{C_6D_6} = 59$	$N_{C_6H_5D} = 53$
Algebraic parameters [cm^{-1}]	$A_{CC} = -2.38$	$A_{CD} = -1.49$	$A_{CH} = -1.93$
	$A'_{CC} = -0.1056$	$A'_{CD} = -0.1932$	$A'_{CH} = -8.2986$
	$\lambda = 3.21$	$\lambda = 2.00$	$\lambda = 1.87$
	$\lambda' = 0.81$	$\lambda' = 0.43$	$\lambda' = 0.61$

Table II. Calculated and observed harmonic and fundamental frequencies [cm^{-1}] of benzene (C_6H_6).

Mode [Wilson No.]	Symmetry	$\bar{\nu}_{obs}$ [Ref. 1]	$\bar{\nu}_{cal}$	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	Mode character
1	A_1	993.1	995.4	-2.3	Breathing
2	A_1	3073.9	3069.8	4.1	CH stretch in-phase
3	A_2	1350.0	1338.7	11.3	CH bend In-phase
12	B_1	1010.0	1002.7	7.3	CCC trigonal bend
13	B_1	3057.0	3055.2	1.8	CH trigonal stretch
14	B_2	1309.4	1309.5	-0.1	CC stretch
15	B_2	1149.7	1137.1	12.6	CH trigonal bend
6	E_2	608.1	608.3	-0.2	CCC bend
7	E_2	3056.7	3047.9	8.8	CH stretch
8	E_2	1601.0	1600.2	0.8	CC stretch
9	E_2	1177.8	1167.8	10.0	CH bend
18	E_1	1038.3	1033.4	4.9	CH bend
19	E_1	1484.0	1480.4	3.6	CC stretch
20	E_1	3064.4	3062.5	1.9	CH stretch
11	A_2	674.0	675.5	-1.5	CH wagg.in-phase
4	B_2	707.0	704.7	2.3	CCCC puckering
5	B_2	990.0	988.1	1.9	CH trigonal wagg
10	E_1	847.1	839.1	8.0	CH wagg
16	E_2	398.0	399.4	-1.4	CCCC torsion
17	E_2	967.0	966.2	0.8	CH wagg

Table III. Calculated and observed harmonic and fundamental frequencies [cm^{-1}] of benzene derivative C_6D_6.

Mode [Wilson No.]	Symmetry	$\bar{\nu}_{obs}$ [Ref. 2]	$\bar{\nu}_{cal}$	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	Mode character
1	A_1	945.0	947.2	-2.2	Breathing
3	A_2	1059.0	1061.8	-2.8	CCH(D)wagg
12	B_1	970.0	978.0	-8.0	CCC trigonal bend
14	B_2	1282.0	1282.4	-0.4	CC stretch
15	B_2	824.0	825.8	-1.8	CCH(D) trigonal wagg
6	E_2	580.0	581.2	-1.2	CCC bend
8	E_2	1557.0	1556.0	1.0	CC stretch
9	E_2	869.0	878.8	-9.8	CCH(D) wagg
18	E_1	814.0	810.4	3.6	CCH(D) wagg
19	E_1	1333.0	1344.0	-11.0	CC stretch
11	A_2	496.0	497.4	-1.4	CCH(D) wagg
4	B_2	599.0	596.6	2.4	CCC puckering
5	B_2	829.0	830.3	-1.3	CCH(D) trigonal wagg
10	E_1	660.0	665.0	-5.0	CCH(D) wagg
16	E_2	345.0	345.2	-0.2	CCC bend
17	E_2	787.0	779.6	7.4	CCH(D) wagg

Table IV. Calculated and observed harmonic and fundamental frequencies [cm^{-1}] of benzene derivative C$_6$H$_5$D.

Mode [Wilson No.]	Symmetry	$\bar{\nu}_{obs}$ [Ref. 3]	$\bar{\nu}_{cal}$	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	Mode character
16	A_2	401.0	402.4	−1.4	CCC out-of plane bending
11	B_1	596.7	596.4	0.3	CH out-of plane bending
6	A_1	600.0	600.4	−0.4	CCC in-plane bending
4	B_1	692.6	693.8	−1.2	CCC puckering
10	A_2	838.4	837.9	0.5	CH out-of plane bending
17	B_1	919.7	916.3	3.4	CH out-of plane bending
1	A_1	971.8	966.7	5.1	ring breathing
5	B_1	983.0	985.3	−2.3	CH out-of plane bending
12	A_1	992.1	1003.1	−11.0	CCC trigonal bending
18	A_1	1028.6	1025.5	3.1	CC stretching
15	B_2	1163.3	1165.5	−2.2	CH in-plane bending
9	A_1	1176.1	1176.7	−0.6	CH in-plane bending
14	B_2	1292.6	1285.9	6.7	CC stretching
3	B_2	1329.7	1325.0	4.7	CH in-plane bending
19	A_1	1470.7	1473.5	−2.8	CH in-plane bending
8	A_1	1599.7	1599.5	0.2	CC stretching
13	A_1	2271.9	2270.5	1.4	CD stretching
2	A_1	3053.8	3057.8	−4.0	CH stretching
7	A_1	3071.8	3069.2	2.6	CH stretching
20	A_1	3090.8	3091.4	−0.6	CH stretching

By using a numerical fitting procedure (in a least square sense) one can adjust the values of the parameters N, A, λ, λ' and A' to fit the experimental result.

The fitting algebraic parameters used in the study of vibrational spectra of benzene and two of its derivatives are given in Table I, where, Tables II–IV show the calculated frequencies of benzene and two of its derivatives with the corresponding deviations considering the different theoretical and experimental perspectives.

7. CONCLUSIONS

In this work we have studied the stretching vibrational spectra of benzene and two of its derivatives by the algebraic model considering coupled one dimensional Morse oscillators describing the CC, CH, and CD stretching and bending vibrations of the molecules. This study shows that the Algebraic model is an alternative approach of other theoretical and experimental models. More interestingly, the hurdle of complicated integrations in the solution of coupled differential Schrödinger equations of polyatomic molecules can be avoided by making use of this algebraic model. Moreover the number of parameters in this case is also much less as compared to the traditional Dunham expansion calculations. So with the further advancement of this $U(2)$ algebraic model, the other modes of vibrations of the molecules also can be explained and predicted for the interest of further experimental study. Thus, it can be concluded that $U(2)$ algebraic method is one of the successful alternative theoretical approach to

explore the previously unknown vibrational states of polyatomic molecules.

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Successful Applications of Lie Algebraic Model to Analyze the Vibrational Spectra of Fluorobenzene

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The article is aimed at calculating the stretching vibrational spectra of fluorobenzene (C_6H_5F) using one-dimensional algebraic model. The Model Hamiltonian so constructed which seems to describe the C-C, C-F C-H, H-F stretching modes accurately using a relatively small set of well-defined parameters.

Key Words: algebraic model, fluorobenzene, Hamiltonian, vibrational spectra

INTRODUCTION

Spectroscopic investigation of fundamental and overtone transitions of stretching modes of benzene and its partially substituted derivatives are an important source of information on intramolecular vibrational redistribution (IVR) processes. These investigation processes include I.R spectroscopy (1,2), FTIR and Raman Spectra, DFT, and SQMFT (3,4). At the same time, many theoretical approaches including quantum chemical calculation as well as semi-empirical programs have been attempted by several researchers (4,5). In spite of rigorous studies by all these techniques on these molecules have given insight several aspects many other aspects require further theoretical explanation. In this article, we used an alternative approach (algebraic approach) to describe the vibrational spectra of molecules like fluorobenzene. In the last two decades, algebraic models, such as Lie algebraic methods (5,6) and boson-realization model (7), have been proposed for the description of vibrations, rotations, and

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Table 1: Fitting algebraic parameters of fluorobenzene (C_6H_5F)

Vibron number	Algebraic parameters (cm^{-1})		
N	A	λ'	λ
49.52	-30.43	0.05	0.376

rotation–vibration interactions in polyatomic molecules. In the Lie algebraic approach, $U(4)$ and $U(2)$ algebraic models have been extensively used (7). The $U(4)$ model deals with the rotation and the vibration simultaneously but it becomes quite complicated when the number of atoms in a molecule are more than four. The $U(2)$ model was particularly successful in explaining stretching vibration of diatomic and polyatomic molecules such as benzene (7).

In this article, we use the $U(2)$ algebraic model to calculate the normal fundamental and overtone modes of vibrations of fluorobenzene and hence find the accuracy of the results with respect to the experimental observations (1,2).

THE ALGEBRAIC MODEL

A complete description of the theoretical foundations is needed to formulate the algebraic model for a vibrating molecule. We apply the one-dimensional algebraic model, consisting of a formal replacement of the interatomic, bond coordinates with unitary algebras. To say it differently, the second-quantization picture suited to describe anharmonic vibrational modes is specialized through an extended use of Lie group theory and dynamical symmetries. By means of this formalism, one can attain algebraic expressions for eigenvalues and eigenvectors of even complex Hamiltonian operators, including inter-mode coupling terms as well as expectation values of any operator of interest (such as electric dipole and quadrupole interactions). Algebraic models are not *ab initio* methods, as the Hamiltonian operator depends on a certain number of a priori undetermined parameters. As a consequence, algebraic techniques can be more convincingly compared with semi-empirical approaches making use of expansions over power and products of vibrational quantum numbers, such as a Dunham-like series. However, two noticeable advantages of algebraic expansions over conventional ones are that (i) algebraic modes lead to a (local) Hamiltonian formulation of the physical problem at issue (thus permitting a direct calculation of eigenvectors in this same local basis) and (ii) algebraic expansions are intrinsically anharmonic at their zero-order approximation. This fact allows one to reduce drastically the number of arbitrary parameters in comparison to harmonic series, especially when facing medium- or large-size molecules. However, it also should be noticed that, as a possible drawback of purely local Hamiltonian formulations (either algebraic or not) compared with

3

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traditional perturbative approaches, the actual eigenvectors of the physical system. Yet, for very local situations, the aforementioned disadvantage is not a serious one. A further point of importance here is found in the ease of accounting for proper symmetry adaptation of vibrational wave functions. This can be of great help in the systematic study of highly excited overtones of not-so small molecules, such as the present one. Last but not least, the local mode picture of a molecule is enhanced from the very beginning within the algebraic framework. This is an aspect perfectly lined up with the current tendencies of privileging local over normal mode pictures in the description of most topical situations.

THE ALGEBRAIC HAMILTONIAN

According to the general algebraic description for one-dimensional degrees of freedom, a dynamically symmetric Hamiltonian operator for n interacting (not necessarily equivalent) oscillators of a polyatomic molecule in terms of Morse anharmonic oscillators by introducing the $U(2)$ algebra for each bonds can be written as (8–12):

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i\langle j}^{n} A_{ij} C_{ij} + \sum_{i\langle j}^{n} \lambda_{ij} M_{ij}, \tag{1}$$

Table 2: Calculated and experimental normal fundamental frequencies (cm^{-1}) of fluorobenzene (C$_6$H$_5$F)

Normal fundamental level	$\bar{\nu}_{obs}$ (1)	$\bar{\nu}_{cal}$	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	$\frac{\|\bar{\nu}_{obs}-\bar{\nu}_{cal}\|}{\bar{\nu}_{obs}} \times 100\%$
ν_1	3047.9	3048.17	−0.27	0.008%
ν_2	3060.3	3058.15	2.15	0.071%
ν_3	3061.3	3062.25	−0.95	0.031%
ν_4	3067.3	3067.10	0.20	0.001%
ν_5	3069.6	3068.45	1.15	0.037%
ν_6	3070.6	3071.33	−0.73	0.023%
ν_7	3076.0	3075.24	0.76	0.024%
ν_8	3079.1	3078.20	0.90	0.029%
ν_9	3079.4	3079.56	−0.16	0.005%
ν_{10}	3080.1	3081.69	−1.59	0.051%
ν_{11}	3084.9	3083.17	1.73	0.056%
ν_{12}	3090.3	3089.58	−0.72	0.023%
ν_{13}	3094.0	3094.55	−0.55	0.017%
ν_{14}	3104.0	3102.85	1.15	0.037%
ν_{15}	3109.6	3108.22	1.38	0.44%
ν_{16}	3111.0	3112.36	−1.36	0.043%
ν_{17}	3112.1	3113.20	−1.10	0.035%

Δ (RMS) $= 1.12$cm^{-1}.

4   *S. K. Singha et al.*

Table 3: Calculated and experimental normal overtone frequencies (cm^{-1}) of fluorobenzene (C$_6$H$_5$F)

Normal Overtone level	$\bar{\nu}_{obs}$ (2)	$\bar{\nu}_{cal}$	$\bar{\nu}_{obs} - \bar{\nu}_{cal}$	$\frac{|\bar{\nu}_{obs} - \bar{\nu}_{cal}|}{\bar{\nu}_{obs}} \times 100\%$
ν_1	5905.80	5906.20	−0.40	0.007%
ν_2	5920.70	5921.05	−0.35	0.006%
ν_3	5943.10	5943.43	−0.33	0.005%
ν_4	5949.30	5950.96	−1.66	0.027%
ν_5	5956.90	5958.49	−1.59	0.026%
ν_6	5968.50	5966.23	2.27	0.038%
ν_7	5974.10	5973.34	0.76	0.012%
ν_8	5983.70	5981.08	2.62	0.043%
ν_9	5991.40	5988.40	3.00	0.050%
ν_{10}	5997.10	5995.72	1.38	0.023%
ν_{11}	6003.10	6003.04	0.06	0.001%
ν_{12}	6005.90	6003.25	2.65	0.044%
ν_{13}	6011.60	6010.57	1.03	0.017%
ν_{14}	6018.80	6018.10	0.70	0.011%

Δ(RMS). = 1.95 cm^{-1}.

where C_i, C_{ij}, and M_{ij} are the invariant algebraic operators. In the local basis the operators C_i are the diagonal matrix with eigenvalues

$$\langle N_i, v_i \,|C_i|\, N_i, v_i \rangle = -4 \left(N_i v_i - v_i^2 \right). \tag{2}$$

The couplings between the bonds are introduced by the operators C_{ij} and M_{ij}, called Casimir and Majorana operators, respectively. The role of the Majorana operators M_{ij} is to introduce off-diagonal couplings between pairs of local modes. In the simplest case of equivalent interacting bonds, the Majorana operator naturally leads to a solution for symmetrized coupled modes, in which the invariance of the Hamiltonian operator, under bond exchange, is explicitly taken into account. A rather appealing feature of this algebraic model is that such a "symmetrizing" property of the Majorana operator, actually quite a trivial one for two equal bonds, can readily be extended to any molecular geometry, even a very complex one. The key point is that the basic information characterizing the specific molecular geometry can easily be incorporated by introducing proper linear combinations of Majorana operators.

In purely local limit of N oscillators, these oscillators are somehow correlated with each other through the C_{ij} operators, which account for (diagonal) cross-anharmonicities, represented by the following equation:

$$C_{ij} = C_i - N_{ij} \left(\frac{C_i}{N_i} + \frac{C_j}{N_j} \right), \tag{3}$$

where $N_{ij} = N_i + N_j$

95   Furthermore, following Eq. (3), it should be noted that one basically subtracts
96   from C_i those terms arising from uncoupled single-oscillator contributions. In
97   the special case of a pair of equivalent oscillators i and $j (N_i = N_j)$, the above
98   equation can be replaced by the following matrix elements:

$$\langle v_i v_j \left| C_{ij} \right| v_i v_j \rangle = -4(v_i - v_j)^2 \tag{4}$$

99   i.e., the matrix elements do not depend on $N_i(N_j)$. As a result, C_{ij} will ac-
100   count for different contributions throughout different polyads and within the
101   same polyad; the most important aspect of C_{ij} is the dependence of its matrix
102   elements on the product $v_i v_j$.
103   The quantum numbers v_i correspond to the number of quanta in each os-
104   cillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^{n} v_i. \tag{5}$$

105   For a particular polyad, the total vibrational quantum number is always con-
106   served.
107   In Eq. (1), the invariant Casimir (C_{ij}) and Majorana (M_{ij}) operators have
108   the following matrix elements (9,10):

$$\left.\begin{aligned}
&\langle N_i, v_i; N_j, v_j \left| C_{ij} \right| N_i, v_i; N_j, v_j \rangle = -4\left[\left(v_i + v_j \right)\left(N_i + N_j \right) - \left(v_i + v_j \right)^2 \right] \\
&\langle N_i, v_i; N_j, v_j \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2 v_i v_j \\
&\langle N_i, v_i + 1; N_j, v_j - 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle \\
&\quad = -\sqrt{v_j \left(v_i + 1 \right) \left(N_i - v_i \right) + \left(N_j - v_j + 1 \right)} \\
&\langle N_i, v_i - 1; N_j, v_j + 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle \\
&\quad = -\sqrt{v_i \left(v_j + 1 \right) \left(N_j - v_j \right) + \left(N_i - v_i + 1 \right)}.
\end{aligned}\right\} \tag{6}$$

109   Thus, the eigenvalues of the Hamiltonian can be easily evaluated and provide
110   a description of n coupled anharmonic vibrators.

111   **RESULTS AND DISCUSSIONS**

112   In general, the eigenvalue problem for H must be solved analytically with spec-
113   trum generating algebra or dynamical algebra which describes, within a cer-
114   tain approximation, realistic rotation-vibration spectra in one (stretch) and
115   three dimensions (stretch and bend). As the dynamical algebra can be incor-
116   porated by the language of Lie algebra and thus after the introduction of $U(2)$
117   Lie algebra to describe n stretching bonds, two possible chains of molecular
118   dynamical groups of fluorobenzene are as (11–13):

$$U^1(2) \otimes \dots \dots \otimes U^n(2) \supset O^1(2) \otimes \dots \dots \otimes O^n(2) \supset O(2), \tag{7}$$

6   *S. K. Singha et al.*

$$U^1(2) \otimes \ldots \otimes U^n(2) \supset U(2) \supset O(2), \tag{8}$$

119   which correspond to local and normal coupling, respectively. The coupling to
120   final $O(2)$ group in the first chain is carried out though different intermediate
121   couplings $O^{ij}(2)$ and the second chain arises from all the possible couplings of
122    $U^i(2)$ groups to obtain a total $U(2)$ group, which in turn contains the final $O(2)$
123   group.
124   To find the vibrational frequencies of fluorobenzene, we use the algebraic
125   parameters A, A', λ, λ', and N, to study the vibrational spectra of fluorobenzene
126   molecules where N is the vibron number. After considering the common cou-
127   pled and uncoupled bond-bond interaction in the molecular configuration in
128   case of fluorobenzene and also considering the Majorana couplings, on the ba-
129   sis of the symmetry of the molecules, the numbers of algebraic parameters are
130   reduced to four. In this regard, one should note that this is the unique beauty
131   of the algebraic model where one needs only a fewer parameters to describe
132   the vibrational spectra of a molecule with a good accuracy.
133   The values of Vibron number (N) can be determined by the relation

$$N_i = \frac{\omega_e}{\omega_e x_e} - 3 \; (i = 1, 2 \ldots \ldots) \quad \left[x_e = \frac{1}{N+2} \right], \tag{9}$$

134   whereand $\omega_e x_e$ are the spectroscopic constants.
135   For fluorobenzene molecules in normal mode, we can have the values of ω_e
136   and $\omega_e x_e$ for each bond from the study of Nakamoto (14) and that of Huber and
137   Herzberg (15). Using the values of ω_e and $\omega_e x_e$ for each bond, we can have the
138   initial guess for the value of the vibron number N. It may be noted here that in
139   the algebraic approach, there is provision to change (not more than $\pm 20\%$) the
140   value of N to get better accuracy. This is equivalent to change the single-bond
141   anharmonicity according to the specific molecular environment, in which it can
142   be slightly different.
143   To obtain a starting guess for the parameter A we use the expression for
144   the single-oscillator normal mode which is given as

$$E(\nu = 1) = -4A(N-1). \tag{10}$$

145   Using Eq. (16), A can be obtained as

$$A = -\frac{E_1}{4(N-1)}. \tag{11}$$

146   To obtain the initial guess for λ, whose role is to split the initially degener-
147   ate local modes, placed here at the common value E, used in Eq. (17). Following
148   the simple Hamiltonian matrix structure (Eq. (18)) leads to finding out the cor-
149   responding algebraic parameters:

$$\begin{pmatrix} -4A(N-1) - 4A'(2N-1) + \lambda N & -\lambda N \\ -\lambda N & -4A(N-1) - 4A'(2N-1) + \lambda N \end{pmatrix}. \tag{12}$$

150   From the above matrix structure, we easily find that

$$\lambda = \frac{E_3 - E_1}{2N} \qquad (13)$$

151   and for hyperfine splitting of the spectrum, the corresponding algebraic
152   parameter is

$$\lambda' = \frac{E_2 - E_1}{6N}. \qquad (14)$$

153   To achieve the better results, a numerical fitting procedure (in a least-
154   square sense) is required to obtain the parameters A, A' λ, and λ', as given by
155   Eqs. (11), (13), and (14). Initial guess for A' may be taken as zero.
156   The following tables show the fitting algebraic parameters along with the
157   results based on experimental (opto-thermal spectrum) (1,2) and calculated vi-
158   brational transitions of normal fundamental and overtone modes of fluoroben-
159   zene are compared.

160   **CONCLUSION**

161   In this article, using the one-dimensional $U(2)$ algebraic model, we calculate
162   the number of fundamental and overtone frequencies of fluorobenzene which
163   is one of the derivative of benzene molecule. It is revealed from our study that
164   compared to other traditional approaches, the algebraic models require only a
165   fewer data for the analysis of a system. All these data can be obtained from the
166   database (observed energy levels). The calculated RMS deviations suggested
167   the accuracy of the algebraic model.
168   For the systematic study of problems in Chemical Physics, algebraic mod-
169   els have provided a new tool. Using this model many molecular systems have
170   been analyzed in the last 30 years. In the coming years the model may be ap-
171   plied in the analysis of larger and more complex systems like macromolecules:
172   polymers. In the algebraic model, anharmonicities in the energy spectra are
173   put in from the very beginning. This is the main advantage of the model. An-
174   harmonicities play important role in other physical systems like liquids and
175   surfaces. Applications of the algebraic models may be extended to cover these
176   situations in coming days. The basic idea in the algebraic model is to simplify
177   the analysis of a complex system using the powerful mathematical methods.
178   This property may help the researchers to expand the applications of the alge-
179   braic models in the analysis of floppy molecules, macromolecules, and polymers
180   including biomolecules and biopolymers in the near future.

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