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A study of the stretching vibrational spectra of fullerene dimers $C_{60}O$ and $C_{60}O_2$ by *U*(2) Lie algebra

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The vibrational energy levels of the fullerene dimers $C_{60}O$ and $C_{60}O_2$ were calculated considering the local Hamiltonian of the Morse potential using algebra. Here, each bond of the molecules was replaced by a corresponding Lie algebra and finally the Hamiltonian was constructed considering the interacting Casimir and Majorana operators. The fundamental stretching modes of vibration of both dimers $C_{60}O$ and $C_{60}O_2$ were then calculated using the algebraic Hamiltonian. This study leads to explore few fundamental hitherto unknown vibrational energy levels of both the fullerene dimers.

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1. Introduction

Lie algebraic methods have been useful in the study of problems in Physics ever since Lie algebras were introduced by M. Sophus Lie (1842 – 1899) at the end of the 19th century, especially after the development of Quantum Mechanics in the first part of the 20th century. This is because quantum mechanics makes use of commutators $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebras. The essence of the algebraic method can be traced to the Heisenberg formulation of quantum mechanics [1]. The use of Lie algebras as a tool to systematically investigate physical systems (the so called spectrum generating algebras) did not however develop fully until the 1970's when it was introduced in a systematic fashion by F. Iachello and A. Arima in the study of spectra of atomic nuclei (interacting boson model) [2,3, 4, 5]. In 1981 F. Iachello introduced Lie algebraic methods in the systematic study of spectra of molecules (vibron model) [4]. This introduction was based on the second quantization of the Schrodinger equation with a three dimensional Morse potential and described rotation – vibration spectra of diatomic Molecules [5]. Soon afterwards the algebraic method was extended to rotation – vibration spectra of polyatomic molecules [6]. In the intervening years much work was done. Most notable advances were the extension to two coupled one-dimensional oscillators [7] and its generalization to many coupled one-dimensional oscillators [8], which led to a simple treatment of vibrational modes in polyatomic molecules, and the extension to two dimensional oscillators [9] which allowed a simpler description of bending modes in linear molecules. The situation up to 1995 was reviewed in reference [9]. After 1995, the brief review work of F. Iachello and S. Oss [9,10,11] reflects the scenario of the field up to 2002 along with the perspectives for the algebraic method in the first decade of the 21st century.

Apart from the Lie algebraic method, already there are two other well known methods:

1. Dunham Expansion and
2. Potential Approach method.

A simple analysis of molecular vibration spectra is provided by the Dunham expansion [10, 11, 12]. This is an expansion of the energy levels in terms of vibration quantum numbers. This expansion does not contain any information about the wave functions of individual states. Thus matrix elements of operators cannot be directly calculated.

A second analysis is provided by the potential approach (differential / wave formulation). Here energy levels are obtained by solving the Schrodinger equation with an interatomic potential. The potential V is expanded in terms of interatomic variables. The solution of the Schrodinger equation also provides wave functions ψ (r) from which matrix elements of various operators can be calculated. In the potential approach (differential / wave formulation), all manipulations are either differentiations or integrations.

The very recent approach to the analysis of molecular vibration spectra is based on algebraic (rather than differential) techniques. However, a similar approach has had in the description of vibrational spectra of nuclei [12]. The basic idea in this new approach is that of expanding the Hamiltonian (and other operators) in terms of a 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 Lie algebraic formulation can be used to attack problems of relevance in Physics and Chemistry. In particular, in molecules it can be used to analyze rotational and vibrational spectra. For the treatment of electronic spectra, additional ingredients, describing the electron spin, are needed. An algebraic model of electronic spectra was introduced in 1989 [12, 13,14] but it has not been exploited much up to this point. Instead the field in which the algebraic method has had most impact is that of vibrational spectroscopy. The reason is that the main advantages of the algebraic method are: the anharmonicities in the energy spectra are put in from the very beginning; anharmonicities in the interactions between different modes are introduced automatically since they are already contained in the matrix elements of the step operators; the method allows one to calculate wave functions and thus observables other than energies, such as intensities of transitions (infrared, Raman, Franck-Condon).

Since, anharmonicities play a crucial role in vibrational spectroscopy; it is here that algebraic methods have found their most useful application. And hence, we have chosen the problem: “A study of the stretching vibrational spectra of fullerene dimers $C_{60}O$ and $C_{60}O_2$ by U(2) Lie algebra”.

2. Review of Lie algebraic method

First of all, the Lie algebraic set up required to study the vibrational spectra of molecules will be built up. Then the Hamiltonian for the specific molecule for the specific mode (local, normal, local to normal transition) will be derived. In next step, eigenvalues will be derived related to the Hamiltonian. Using the eigenvalues, different vibrational energy levels will be calculated as functions of vibrational quantum numbers. Final conclusion will be drawn after comparing these results (calculated) with the corresponding experimental ones. Vibrational parameters for molecules will also be worked out.

Vibrational energy states of molecules are studied with a variety of experimental tools such as IR and Raman spectroscopy, Franck-Condon spectroscopy. Infrared and Raman spectroscopy provide informations on the vibrational modes built on the ground state electronic configuration; Franck-Condon spectroscopy provides information on the vibrational modes built on two electronic manifolds.

When dealing with molecules, an important aspect is what coordinate system is to be chosen. For small molecules the best set for vibrational analysis is provided by the internal coordinates. If N is the number of atoms, the number of internal coordinates is 3N-6. If the molecule is linear there are 3N-5 internal coordinates. The 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) [U, unitary matrix]. For bending vibrations of linear molecules the motion occurs in the plane perpendicular to the axis of the molecule, that is in two dimensions. These vibrations are therefore quantized with the algebra of U(3). The algebra of U(3) is composed of nine operators. For linear molecules one thus has one U(2) for each stretching vibration and one U(3) for each bending vibration. The expansion of the Hamiltonian operator is done in terms of the four operators of U(2) and the nine operators of U(3). This scheme has been used recently to study bent and linear molecules. [15,16,17,18] In bent triatomic molecules (SO_2, S_2O) there are three one dimensional degrees of freedom, quantized with U(2)xU(2)xU(2) while in linear triatomic molecules (CO_2) there are two one-dimensional stretching modes and one two-dimensional bending mode, U(2)xU(2)xU(3). Similarly, in linear four-atomic molecules (C_2H_2)[17, 18] one has U(2)xU(2)xU(2)xU(3)xU(3). By fitting the experimental energy levels it has been possible to extract the algebraic parameters. These parameters play the role of the force-field constants in the usual harmonic analysis [18].

In our work we shall write the Hamiltonian as an (algebraic) operator using the appropriate Lie algebra. This is unlike the more familiar differential operator of wave mechanics. It is important to note that the Hamiltonian will be presented by “matrix representation”.

3. One dimensional algebraic model

Even though the Lie algebras were introduced at the end of the nineteenth century, the use of Lie algebras as a tool to systematically investigate physical systems (the so called spectrum generating algebras) did not however develop fully until the 1970’s. In 1970’s Lie algebras were introduced in a systematic fashion by A. Arima and F. Iachello in the study of spectra of atomic nuclei (interacting boson model) [16]. Wulfman played a great role in the introduction of the algebraic approach to molecular Spectroscopy [17, 18]. He is the pioneer to publish the first paper on the algebraic approach to molecular Spectroscopy (the algebraic approach to the Morse oscillator) in 1979 [9, 17, 18]. Later, in 1981, F. Iachello used Lie algebraic methods in the systematic study of spectra of molecules (vibron model) [17, 18]. This use was based on the second quantization of the Schrodinger equation with a three dimensional Morse potential and described rotation-vibration spectra of diatomic molecules [17, 18]. Soon afterwards the algebraic method was extended to rotation vibration spectra of polyatomic molecules [17]. In the intervening years much work was done. Most notable advances were the extension to two coupled one-dimensional oscillators [17] and its generalization to many coupled one dimensional oscillator [18], which led to a simpler treatment of vibrational modes in polyatomic molecules, and the extension to two-dimensional oscillators [17, 18] which allowed a simpler description of bending modes in linear molecules. The situation up to 1995 was reviewed in the study of F. Iachello and R. D. Levine [8]. The study of F. Iachello and S. Oss [9] presented a brief review of the work done up to 2000. The study of Iachello and Oss [9] also provided perspectives for the algebraic method in the first decade of the 21st century.

Recently, using Lie algebraic method [17, 18] reported better results for the vibrational energy levels of HCN, HCCF, SnBr4, CCl4 than those reported earlier. Moreover, The U(2) algebraic model model was particularly successful in explaining stretching vibrations of polyatomic molecules such as octahedral, benzene and pyrrole-like molecules [12,13,14]. As such, the approach is particularly appropriate for many challenges of modern spectroscopy. Hence in this paper we used the algebraic model to study some of the vibrational spectra of fullerene dimers $C_{60}O$ and $C_{60}O_2$.

The interpretation of experimental data by solving Schrödinger equation with interatomic potentials becomes increasingly difficult as the number of atoms in the molecule increases. Similarly, Dunham expansion contains large numbers of parameters which cannot be determined from the few available data. In this section, we use the U(2) algebraic model which is introduced as an alternative approach to the traditional Dunham expansion and Schrödinger equation for polyatomic molecules.

According to Iachello and Levine [8] the algebraic theory of polyatomic molecules consists of the separate quantization of rotations and vibrations in terms of vector coordinates $r_1, r_2, r_3, \ldots$ quantized by the algebra

$$G \equiv U_1(2) \otimes U_2(2) \otimes U_3(2) \qquad (1)$$

For the stretching vibrations of polyatomic molecules corresponding to the quantization of anharmonic Morse oscillators, we have the classical Hamiltonian

$$h(p, x) = \frac{p2}{2\mu} + D[1-\exp(-\alpha\, x)]^2 \qquad (2)$$

It can be put into one-to-one correspondence with the representation of the algebra U(2) $\supset$ O(2) characterized by the quantum numbers $|N, m\rangle$ with the provision that one takes only the positive branch of m, i.e., $m = N$, N - 1, N – 2,....., 1 or 0 for N = odd or even (N = integer). However, to have complete description of molecular vibrations we need both stretching and bending modes. This is achieved by considering the isomorphism of U(2) Lie algebra with the solution of Schrödinger equation with another potential called Poschl-Teller potential. This potential is very much applicable for calculating bending vibrations where Morse potential is not appropriate. The eigenstates of Schrödinger equation with Hamiltonian operator is

$$h(p, x) = \frac{p2}{2\mu} - \frac{D}{\cosh^2 \alpha x} \qquad (3)$$

It can also be put into one-to-one correspondence with the representation of U(2) $\supset$ O(2), characterized by the quantum numbers $|N, m\rangle$ with the provision that one takes only the positive branch of m, i.e., $m = N$, N -1, N - 2……, 1 or 0 for N = odd or even (N = integer). In the above equation, the coordinate x is the product of the radius of bender r times the bending angle θ, i.e., $x = r\theta$. For molecules like C_{60} and their oxides, we introduce U(2) Lie algebra to describe n stretching bonds (C-C). The two possible chains of molecular dynamical groups in these molecules are

$$U^1(2) \otimes \ldots \otimes - U^n(2) \supset O^1(2) \otimes \ldots \otimes O^n(2) \supset O(2) \qquad (4)$$

$$U^1(2) \otimes \ldots\ldots \otimes U^n(2) \supset U(2) \supset O(2) \qquad (5)$$

which correspond to local and normal coupling respectively. The coupling to final O(2) group in the first chain is carried out though different intermediate couplings $O^{ij}(2)$ and the second chain arises from all the possible couplings of $U^i(2)$groups to obtain a total U(2) group, which in turn contains the final O(2) group [11]. For these two situations the Hamiltonian operator can be diagonalized analytically. The common algebraic model Hamiltonian in the case of stretching for these molecules can be considered as [17, 18, 19]

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i \langle j}^{n} A_{ij} C_{ij} + \sum_{i \langle j}^{n} \lambda_{ij} M_{ij} \qquad (6)$$

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

$$\langle N_i, v_i | C_i | N_i, v_i \rangle = -4\left(N_i v_i - v_i^2\right) \qquad (7)$$

The couplings between the bonds are introduced by the operators C_{ij} and M_{ij} called Casimir and Majorana operators respectively. The Casimir operator has only the diagonal matrix element, where as the Majorana operators have both diagonal and non-diagonal matrix elements, which are given by

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = -4\left[(v_i + v_j)(N_i + N_j) - (v_i + v_j)^2\right]$$

$$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2 v_i v_j$$

$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_j (v_i + 1)(N_i - v_i) + (N_j - v_j + 1)}$$

$$\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -\sqrt{v_i (v_j + 1)(N_j - v_j) + (N_i - v_i + 1)} \qquad (8)$$

Thus the eigenvalues of the Hamiltonian can be easily evaluated which provide a description of n coupled anharmonic vibrators.

4. Results and discussion

In this work we use four algebraic parameters $i.e. A, A', \lambda, \lambda' \,\&\, N$, to study the vibrational spectra of the fullerene dimers $C_{60}O$ and $C_{60}O_2$ where N is the vibron number.

The values of Vibron number (N) can be determined by the relation,

$$N_i = \frac{\omega_e}{\omega_e x_e} - 2, \quad (i = 1, 2 \ldots\ldots) \qquad (9)$$

Where ω_e and $\omega_e x_e$ are the spectroscopic constants of polyatomic molecules of stretching interaction of the molecule considered [20, 21]. This numerical value must be seen as initial guess; depending on the specific molecular structure, one can expect changes in such an estimate, which, however, should not be larger than $\pm 20\%$ of the original value (Eq. (9)). It may be noted that during the calculation of the fundamental vibrational frequencies of fullerene dimers $C_{60}O$ and $C_{60}O_2$ the value of N is kept fixed and not used as free parameter.

To obtain a starting guess for the parameter A we use the expression for the single-oscillator fundamental mode which is given as,

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

Using the relation (9), $\bar{A}$ can be obtained as,

$$\bar{A} = \frac{\bar{E}}{4(1-N)} \tag{11}$$

To obtain an initial guess for the algebraic parameters λ whose role is to split the initially degenerate local modes is obtained by considering the relation,

$$\text{is } \lambda = \frac{E_3 - E_1}{2N} \tag{12}$$

and for hyperfine splitting of the spectrum, the corresponding algebraic parameter

$$\lambda' = \frac{E_2 - E_1}{6N} \tag{13}$$

For fundamental stretching of the concerned molecules, the exact relationships are

$$E_1 = \varepsilon = -4A\,(N-1) - 8A' \tag{14}$$

$$E_2 = \varepsilon + 6\lambda' N \tag{15}$$

$$E_3 = \varepsilon + 2\lambda N. \tag{16}$$

To have better results a numerical fitting procedure, it is required to obtain the parameters A, λ , λ' starting from the values as given by Eqs. (11, 12, 13). The Initial guess for A' may be taken as zero.

The algebraic parameters used in the study of vibrational spectra of fullerene dimers $C_{60}O$ and $C_{60}O_2$ are given in Table 1 and the calculated vibrational energy levels (in cm^{-1}) of both the dimers are shown in Table 2:

Table 1. Algebraic parameters of fullerene dimers $C_{60}O$ and $C_{60}O_2$*

Molecule	Vibron number	Stretching algebraic parameters		
	N	A	λ	λ'
$C_{60}O$	140	- 1.92	0.29	0.065
$C_{60}O_2$	140	- 1.95	0.31	0.071

*A, λ , λ' all are in cm^{-1} whereas N is dimensionless.

Table 2. Calculated energies (cm^{-1}) of fullerene dimers $C_{60}O$ and $C_{60}O_2$

Normal level	Dimmer $C_{60}O$	Dimmer $C_{60}O_2$
v_1	1067.5	1084.2
v_2	1122.1	1143.8
v_3	1148.7	1171.0
v_4	1167.4	1185.7
v_5	1176.5	1197.6
v_6	1193.9	1205.2
v_7	1199.7	1231.5
v_8	1209.6	1256.9
v_9	1234.2	1275.4
v_{10}	1245.8	1284.3
v_{11}	1264.2	1301.7

5. Conclusion

The algebraic model presented here is a model of coupled one dimensional Morse oscillators describing the C-C stretching vibrations of the fullerene dimers $C_{60}O$ and $C_{60}O_2$. 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. For the C-C stretching inter-bond interactions, this model can be used in a simple and straightforward way and reliable calculation of the stretching bonds can be explained in terms of the above fitting parameters. Moreover, the number of parameters in this case is also much less as compared to the traditional Dunham expansion calculations. In this paper, we have presented only a few fundamental modes of vibrations of the fullerene dimers $C_{60}O$ and $C_{60}O_2$ which leads to explore few fundamental hitherto unknown vibrational energy levels of both the fullerene dimmers. It is hoped that with the further advancement of the U(2) model, the higher order modes can also be obtained.

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