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APPLICATION OF *U*(2) ALGEBRAIC MODEL IN THE STUDY OF STRETCHING VIBRATIONAL SPECTRA OF C_{50} AND C_{84} FULLERENES

Ashim Kalyan[a*], **Rupam Sen**[a], **Joydeep Choudhury**[c],
Nirmal Kumar Sarkar[b], **Ramendu Bhattacharjee**[c]

[a]*Department of Physics, S. S. College, Hailakandi- 788151, INDIA*

[b]*Department of Physics, Karimganj College, Karimganj-788710, INDIA*

[c]*Department of Physics, Assam University, Silchar-788011, INDIA*

[*]*E-mail:* ashimkalyan@yahoo.com

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Abstract–The Hamiltonian describing the stretching vibrational spectra of polyatomic molecules is calculated within the framework of vibron model by using the dynamical U(2) Lie algebra. Here every C-C bond of the molecule is replaced by a corresponding Lie algebra and finally the Hamiltonian is constructed considering the interacting Casimir and Majorana operators. The fundamental stretching vibrational energy levels of the carbon C_{50} and C_{84} clusters are then calculated using this Hamiltonian to fit the experimental results.

Keywords: Lie algebra; vibrational spectra; C_{50}, C_{84}

1. Introduction

Since the discovery of fullerenes in carbon soot [1], many spectroscopic techniques have been utilized to identify the cage-like carbon structures. These identification techniques include infrared spectroscopy (IR) [2–8], nuclear magnetic resonance (NMR) [9-10], mass spectrometry (MS) [11–13], ultraviolet–visible spectroscopy (UV–VIS) [14], or a combination of these techniques [15, 16]. To analyse these experimental data, there are many theoretical approaches for calculation of vibrational frequencies, which belong to quantum mechanical potential approach and Dunham expansion method [17–26]. Despite intense effort and significant progress, the accuracy and reliability of theoretical calculations is still lagging far behind especially in the region of high overtones. To improve this situation, in recent years, algebraic models, such as Lie algebraic methods [27, 28] and the boson-realization model [29], have been proposed for descriptions of vibrations, rotations, and rotation-vibration interactions in polyatomic molecules. Lie algebraic methods for diatomic molecules have been modified by the corresponding quantum algebra [30, 31], and the boson-realization model has been developed for the higher vibrational states of polyatomic molecules in terms of q-deformed oscillators [32, 33]. In this study we use only the Lie algebraic approach. The basic element of this approach is the introduction of a set of bosons, referred to as vibrons, in terms of which the space of states of the molecule can be built. In Lie algebraic approaches, *U*(4) and *U*(2) algebraic models have been extensively used. The *U*(4) model took the rotation and the vibration into account simultaneously, but became quite complicated when the number of atoms in a molecule increased to larger than four. The *U*(2) model was particularly successful in explaining stretching vibrations of polyatomic molecules such as benzene-like and octahedral systems [34, 35]. This model was extended to deal with both stretching and bending vibrations in triatomic molecules [36]. Using this approach Sarkar et al. [37] recently reported better results for the vibrational energy levels of HCN, OCS, HCP, HCCF, HCCD than those reported earlier. Moreover, the *U*(2) algebraic model was particularly successful in explaining stretching vibrations of polyatomic molecules such as octahedral, benzene and pyrrole-like molecules [38–40]. But yet, there is no such paper has been reported so far, describing the large carbon cluster like fullerenes by this method. As such, we applied the Lie algebraic method to describe the vibrational frequencies of C_{50} and C_{84}.

The C_{50} and C_{84} molecules belong to class of spheroidal carbon clusters (fullerenes). These molecules have significantly lower symmetry as compared to C_{60}. As a result, there are a large number of allowed infrared and Raman modes for these molecules. The vibrational frequencies of C_{50} and C_{84} have been reported by several groups with different quantum mechanical approaches [41–43]. Bakowies et al. [41] calculated the vibrational frequencies of C_{50} by MNDO (Modified Neglect of Differential Overlap) method, which is a semi-empirical method for the quantum calculation of molecular electronic structure in computational chemistry. Negri et al. [42] calculated vibrational frequencies of C_{84} by QCFF/PI (Quantum-mechanical Consistent Force Field Method for Pi-Electron Systems) approach, but yet there have been no sophisticated experimental investigations on vibrational spectrum of these molecules. In this paper, we also attempted the Lie algebraic approach to study the vibrational stretching modes of C_{50} and C_{84} in one dimensional framework comparing with the other theoretical approaches.

2. The algebraic theory

In this study we apply the one-dimensional algebraic model consisting of formal replacement of the interaction bond coordinate with unitary algebra *U*(2). With this algebraic formulation, one can attain algebraic expressions of eigen values and eigen vectors even for a complex Hamiltonian operator, including intermode coupling terms as well as expectation values of any operator. Moreover, this algebraic approach has the following advantages over the conventional Dunham like expansions [39]:

(i) The algebraic models lead to a local Hamiltonian formulation of the physical problem.

(ii) Its expansions are intrinsically anharmonic at their zero-order approximation.

These two factors reduce drastically the number of arbitrary parameters in comparison to the harmonic series for medium and large size molecules. However, in the local Hamiltonian formulations, the actual eigen vectors of the physical system cannot be directly accessed through diagonalization of the Hamiltonian operators. Beside this disadvantage, the local Hamiltonian formulation can be used in the systematic study of highly excited overtones of the polyatomic molecules.

The motivation for the construction of this algebraic model is the isomorphism of the one-dimensional Lie algebra, *U*(2), with that of the one-dimensional Morse oscillator, which is a good description of a stretching vibration of a molecule. The Hamiltonian of the one-dimensional Schrödinger equation with Morse potential is

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

which can be put into one-to-one correspondence with the representation of the algebra $U\left(2\right)\supset O\left(2\right)$ characterized by the quantum numbers $\left|N,m\right\rangle$ with the provision that one takes only the positive branch of *m*, i.e., $m=N,N-1,N-2,\ldots,1$ or 0 for odd or even *N* (*N* = integer). Thus the Hamiltonian corresponding to the Morse potential on the basis of *U*(2) algebra is given by

$$H=\varepsilon_0+AC, \tag{2}$$

where *C* is the invariant operator of O(2), with eigen values $\left(m^2-N^2\right)$. So, the eigen values of *H* are

$$E=\varepsilon_0+A\left(m^2-N^2\right). \tag{3}$$

Introducing the vibrational quantum number $v=\left(n-m\right)/2,$ one can write the eigen value as

$$E=\varepsilon_0-4A\left(Nv-v^2\right) \tag{4}$$

with $v=0,1,\ldots,N/2$ or $\left(N-1\right)/2$ (for even or odd *N*).

According to the algebraic theory [27], polyatomic molecules consist of the separate quantization of rotations and vibrations in terms of vector coordinates $r_1,\ r_2,\ r_3,\ldots$ quantized by the algebra

$$G\equiv U_1\left(2\right)\otimes U_2\left(2\right)\otimes U_3\left(2\right)\cdots\cdots.$$

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

$$U^1\left(2\right)\otimes\ldots\otimes-U^n\left(2\right)\supset O^1\left(2\right)\otimes\ldots\otimes O^n\left(2\right)\supset O\left(2\right), \tag{5}$$

$$U^1\left(2\right)\otimes\ldots\otimes U^n\left(2\right)\supset U\left(2\right)\supset O\left(2\right), \tag{6}$$

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 $O^{ij}\left(2\right)$ and the second chain arises from all the possible couplings of $U^i\left(2\right)$ groups to obtain a total *U*(2) group, which in turn contains the final *O*(2) group [40]. 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 [37]

$$H = E_0 + \sum_{i=1}^{n} A_i C_i + \sum_{i/j}^{n} A_{ij} C_{ij} + \sum_{i/j}^{n} \lambda_{ij} M_{ij}, \tag{7}$$

where C_i, C_{ij} and M_{ij} are the algebraic operators. In the local basis the operators C_i 's are diagonal matrices with eigen values

$$\langle N_i, v_i \left| C_i \right| N_i, v_i \rangle = -4\left(N_i v_i - v_i^2\right). \tag{8}$$

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, whereas the Majorana operators have both diagonal and non-diagonal matrix elements, which are given by

$$\langle N_i, v_i; N_j, v_j \left| C_{ij} \right| N_i, v_i; N_j, v_j \rangle = -4\left[\left(v_i + v_j\right)\left(N_i + N_j\right) - \left(v_i + v_j\right)^2\right], \tag{9}$$

$$\langle N_i, v_i; N_j, v_j \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle = v_i N_j + v_j N_i - 2 v_i v_j, \tag{10}$$

$$\langle N_i, v_i + 1; N_j, v_j - 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle = -\sqrt{v_j \left(v_i + 1\right)\left(N_i - v_i\right) + \left(N_j - v_j + 1\right)}, \tag{11}$$

$$\langle N_i, v_i - 1; N_j, v_j + 1 \left| M_{ij} \right| N_i, v_i; N_j, v_j \rangle = -\sqrt{v_i \left(v_j + 1\right)\left(N_j - v_j\right) + \left(N_i - v_i + 1\right)}. \tag{12}$$

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

3. Result and Discussion

In the algebraic theory, we introduce the vibron number *N* which is directly related to the anharmonicity of the local C-C stretching bonds. Firstly, the value of vibron number *N* is determined by the relation [27]

$$N = \left(\omega_e / \omega_e x_e\right) - 1, \tag{13}$$

where, ω_e and $\omega_e x_e$ are the spectroscopic constants of diatomic 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*.

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

$$E\left(v = 1\right) = -4A\left(N - 1\right), \tag{14}$$

Lastly, in the third step 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. The value of these parameters can be calculated by considering the matrix structure of the molecules. 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' (whose initial value can be taken as zero) to fit the experimental results.

The fitting parameters used in the study of vibrational spectra of fullerene C_{70} is given in Table 1.

Table 1. Fitting parameters[a] of fullerene C_{50}.

Vibron number	Stretching parameters		
N	A	λ	λ'
140	–1.448	0.057	–0.0345

[a] A, λ, λ' all are in cm^{-1} whereas N is dimensionless

Table 2. Simulated and calculated energies (cm^{-1}) of fullerene C_{50} [42].

Normal level	I [42]	II Calculated	Δ (I–II)
v_1	776	776.108	–0.108
v_2	805	805.088	–0.088
v_3	821	821.048	–0.048
v_4	891	884.888	+6.112
v_5	1148	1143.792	+4.208
v_6	1257	1255.512	+1.488
v_7	1560	1562.296	–2.296
v_8	1600	1600.516	–0.516
v_9	1714	1712.236	+1.764

The fitting parameters used in the study of vibrational spectra of fullerene C_{84} is given in Table 3.

Table 3. Fitting parameters[b] of Fullerene C_{84}.

Vibron number	Stretching parameters		
N	A	λ	λ'
140	–0.624	0.678	–0.159

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

Table 4. Simulated and calculated energies (cm^{-1}) of fullerene C_{84} [41].

Normal level	I, [41]	II, Calculated	Δ(I–II)
v_1	346	347.00	- 1.00
v_2	480	480.56	- 0.56
v_3	536	536.84	- 0.84
v_4	722	719.96	+ 2.04
v_5	826	818.24	+ 7.76
v_6	896	888.80	+ 7.20

4. Conclusion

The algebraic model presented here is a model of coupled one-dimensional Morse oscillators describing the C-C stretching vibrations of the polyatomic molecules C_{50} and C_{84}. By this method, we overcome the hurdle of complicated integrations in the solution of coupled differential Schrödinger equations of polyatomic molecules. At the same time, the number of parameters in this case is also much less as compared to the traditional Dunham expansion calculations. Moreover by this method the hitherto unknown states can also be predicted which help enormously to detect the state experimentally. In this paper we presented only a few modes of vibrations of C_{50} and C_{84} which are in good agreement with other semi-empirical simulated result. Since the approach is very much successful in explaining the vibrational frequencies of the simple polyatomic molecules, so it is hoped that with the further advancement of this U(2) model, the higher order modes of vibrations of the molecules can also be explained.

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