



An Algebraic Approach to Study the Vibrational Spectra of fullerene C_{80}

Rupam Sen¹, Ashim Kalyan¹, Rajat Subhra Paul², Raghunandan Das³, Joydeep Choudhury⁴, Nirmal Kumar Sarkar², Ramendu Bhattacharjee⁴.

¹ Department of Physics, Srikishan Sarma College, Hailakandi-788151, India

² Department of Physics, Karimganj College, Karimganj-788710, India.

³ Department of Physics, Govt. Degree college, Dharmanagar-799251, India

⁴ Department of Physics, Assam University, Silchar – 788011, India

Correspondence; email: rupamsen@yahoo.com

Abstract

The vibrational energy levels of fullerene C_{80} are calculated considering the local Hamiltonian of Morse potential using the $U(2)$ algebra. Here each bond of the molecule is replaced by a corresponding Lie algebra and finally the Hamiltonian is constructed considering the interacting Casimir and Majorana operators. By constructing the model Hamiltonian, we calculated the local mode vibrational energy levels of the fullerene C_{80} .

Keywords: Lie algebra, vibrational energy level, Morse potential, Casimir and Majorana operators.

Introduction:

Molecular spectroscopy is an area of active interest from many standpoints. Due to its numerous connections with other scientific areas, this branch of modern physics is playing an essential role in both experimental and theoretical approaches to understanding a huge number of important problems. Presently, molecular spectroscopy is going through an exciting time of renewed interest, which, once again, is being fueled by the rapid development of sophisticated experimental approaches. Recent developments include the following: Tunable, stable, and powerful lasers are available to create complex excitation schemes, thus allowing for the study of fundamental as well as highly excited levels with unprecedented resolution.

To keep up with the vast production of experimental observations, theoretical physics is constantly being tested to provide a collection of satisfactory models that can account for the observations. However, it should be clear that molecular spectroscopy is undergoing a radical change not simply as a result of technical

advancements. One should also realize that as a consequence of new experimental results, an unprecedented effort toward constructing alternative theoretical models and formulating novel ideas has taken place in recent years.

A comprehensive theoretical treatment for most aspects of molecular spectroscopy necessarily has to rely on a Hamiltonian formulation. As a matter of fact, the typical theoretical procedure used to study a given molecule consists of (1) separating the electronic and nuclear motions (assuming the Born-Oppenheimer approximation) and (2) solving the Schrodinger equation in the potential surface for the rovibrating nuclei. If the molecule is larger than a diatomic, the potential energy surface is a very complex function, composed of a discouragingly large number of coordinates. A standard approach to this problem involves approximating the potential energy surface by convenient analytical functions [1]. A widely used procedure of this type is the force field method but this kind of approach, of course, encounters difficulties as soon as one considers highly excited

levels, and once more, a large number of parameters are needed to achieve meaningful results. The need for practical methods for computing molecular spectra is, in part, satisfied by introducing semiempirical expansions in powers [2] and products of rotational and vibrational quantum numbers. The preeminent expansion is provided by the Dunham series [1]. The most serious drawbacks of this approach are that (1) no Hamiltonian operator is available (not directly, at least), and (2) for large polyatomic molecules, one needs a correspondingly large number of parameters. These parameters, in turn, have to be adjusted by a fitting procedure over a conveniently large experimental database, which is not always available.

In the last part of the 20th century [3] a new theoretical concept, known as Vibron model (based on Lie algebra) was introduced by Levine & Iacchello to study the molecular spectra of polyatomic molecules. This new model seems to offer a concrete and complementary technique to the traditional approaches used in molecular spectroscopy. The algebraic model (Vibron model) was originally developed for diatomic and triatomic molecules [4]. U(4) and U(2) algebraic model been used so far in the analysis of experimental data. It is to be pointed out that the U(4) model becomes complicated when the number of atoms in a molecule increases more than four. Recently, Sarkar et al [5, 6] have been studied the algebraic U(4) and U(2) model to describe the vibrational spectra of different polyatomic molecules [1, 2] and obtained better results than earlier results. In this paper we use the U(2) algebraic model of coupled anharmonic oscillators based on the theory of Lie groups to study the vibrational stretching modes of C₈₀.

Since no extensive experimental study of the vibrational spectra of C₈₀ is reported yet, but is the only quantum mechanical approach of PM3 method [7] which comes forward to analyze the study of vibrational spectra of fullerene C₈₀ with its different energy bands. Recently it was found that Lie algebraic method was extremely successful and accurate in calculating the vibrational frequencies of polyatomic molecules compare to

the other conventional methods. So, by using the one-dimensional U(2) algebraic model we calculate the stretching vibrational energies of fullerene C₈₀ which is an excellent alternative mathematical treatment for determination of energy bands of fullerene C₈₀ in spectroscopic point of view.

Theory: An algebraic approach

The interpretation of experimental data by solving Schrödinger equation with interatomic potentials becomes increasingly difficult when the number of atoms in the molecule increases. Similarly, Dunham expansion contains large numbers of parameters [1] which cannot be determined from the few available data. The third approach is the algebraic model in which each bond is represented by unitary group algebra. For addressing quantum mechanical problems embedded in a group theoretical framework, a particularly powerful mathematical technique is that of continuous Lie groups and algebras. As a direct consequence, the matrix or algebraic formulation of quantum mechanics started to show its greater suitability compared with the differential or wave formulation, at least in regard to matters inherent in symmetry problems.

In Lie algebraic method, the U(2) model is very much successful in explaining the stretching and bending vibrational energies of medium size molecules. The algebraic Hamiltonian in the U(2) model can be constructed with the Casimir and Majorana operators and hence able to explain successfully the stretching vibrations of fullerene C₈₀.

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 eigen states of the one dimensional Schrödinger equation with Morse potential [9] is

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

can be put into one to one correspondence with the dynamical symmetry U(2) O(2)

characterized by the quantum numbers

with the provision that one takes only the positive branch of m , i.e., $m = N, N - 1, N - 2, \dots, 1$ or 0 for $N = \text{odd}$ or even ($N = \text{integer}$). Thus the Hamiltonian corresponding to the Morse potential on the basis of $U(2)$ algebra is given by

$$H = \hat{a}_0 + AC \quad (2)$$

Where C is the invariant operator of $O(2)$, with eigen values $(m^2 - N^2)$. So, the Eigen Values of H are

$$E = \varepsilon_0 + A(m^2 - N^2) \quad (3)$$

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

$$E = \varepsilon_0 - 4A(Nv - v^2) \quad (4)$$

with $v = 0, 1, \dots, N/2$ or $(N - 1)/2$ (for $N = \text{even}$ or odd)

Since the potential in coordinate can be taken to a good approximation, as a Morse potential, we can write the Hamiltonian of a polyatomic molecule in terms of Morse anharmonic oscillators by introducing an algebra $U(2)$ for each coordinate (C-C bonds).

The algebraic model Hamiltonian we consider is thus has the following form [5],

$$H = E_0 + \sum_{i=1}^n A_i C_i + \sum_{i \langle j} A_{ij} C_{ij} + \sum_{i \langle j} \lambda_{ij} M_{ij} \quad (5)$$

In the equation (5), C_i is an invariant operator with Eigen values $4(v_i^2 - N_i v_i)$ and the operator C_{ij} is diagonal with matrix elements.

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)] \quad (6)$$

while the operator M_{ij} has both diagonal and non-diagonal matrix element

$$(7)$$

Eq. (7) is a generalization of the two-bond model to n bonds [2].

The simplest basis to diagonalize the Hamiltonian is characterized by the representation of local mode chain .where below each group we have used quantum numbers characterizing the Eigen values of the corresponding invariant operator N is the number of bosons related to stretching physical modes. The quantum numbers v_i correspond to the number of quanta in each oscillator while V is the total vibrational quantum number given by

$$V = \sum_{i=1}^n v_i \quad (8)$$

For a particular polyad, the total vibrational quantum number is always conserved. The inclusion of M_{ij} in the local Hamiltonian operator cannot affect the conservation rule. In eq. (5), C_i is an invariant operator of uncoupled bond with Eigen values $4(v_i^2 - N_i v_i)$ and the operator C_{ij} for coupled bonds are diagonal with matrix elements.

Results and Discussion:

We use the four algebraic parameters $(E_0, A_i, A_{ij}, \lambda_{ij})$ and N_i, N_j, v_i, v_j to study the vibrational spectra of the C_n molecules where N is the vibron number.

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

$$(i = 1, 2, \dots) \quad (9)$$

Where ω_e and χ_e are the spectroscopic constants of polyatomic molecules of stretching interaction of the molecule considered. 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 vibrational frequencies of fullerene C_{80} , 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,

$$(10)$$

An Algebraic Approach to Study the.

Using the relation (10), \bar{A} can be obtained as,

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

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

$$(12)$$

To have better results a numerical fitting procedure (in a least-square sense) is required to obtain the parameters A , A' and starting from the values as given by Eq. (11) and Eq. (12). Initial guess for λ may be taken as zero.

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

Table 1: Fitting parameters* of Fullerene

Vibron number	Stretching parameters		
	A	λ	λ'
140	-2.181	0.3428	-0.0708

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

Table 2: Experimental and calculated energies (cm^{-1}) of fullerene

Normal level	I Ref.[11]*	II This Study	$\Delta(I - II)$
ν_1	1214.91	1213.10	+1.81
ν_2	1271.06	1272.57	-1.51
ν_3	1310.77	1309.08	+1.69
ν_4	1343.83	1345.31	-1.48
ν_5	1379.20	1382.11	-2.91
ν_6	1416.69	1418.61	-1.92
ν_7	1450.31	1455.12	-4.81
ν_8	1483.70	1491.63	-7.93

*Medhat Ibrahim et al. 2005.

Conclusion:

In this study, we presented a brief analysis of the vibrational spectra of C_{80} fullerene in the algebraic framework making use of the U(2) algebraic model. Using the U(2) algebraic model to study the higher excited vibrations of fullerene C_{80} & for the higher excited energy levels, the calculated stretching vibrational energy levels of C_{80} are found to be in good agreement with that of the results obtained from other models [8]. For the lower vibrational energy levels of C_{80} , results obtained using the U(2) algebraic model obviously will be in good agreement with that of the results obtained from other standard models. Hence it may be concluded that the U(2) algebraic model can also be used as an excellent alternative model in the study of the vibrational spectra of C_{80} .

References

- C_{80} , *J. Chem. Phys.* 100, 7196 (1994).
 F. Iachello and R. D. Levine (1995), Algebraic Theory of Molecules, Oxford University, Press.
 F. Iachello (1981), Chem. Phys. Lett. 78, 581.
 F. Iachello and R.D. Levine (1982), J. Chem. Phys. 77, 3046.
 N. K. Sarkar, J. Choudhury and R. Bhattacharjee (2006), Mol.Phys. 104,3051.
 N. K. Sarkar, J. Choudhury and R. Bhattacharjee (2008), Indian J. Phys. 82,767.
 Medhat Ibrahim (2005), Acta Chim. Slov., 52, 153–158.
 Medhat Ibrahim and Hanan El-Haes (2005), Chinese Journal of Physics, 43,915.
 O. S. Van Roosmalen, I. Benjamin and R.D. Levine (1984), J. Chem. Phys., 81,5986.