Vibrational Spectra of Polyatomic Molecules Using Lie Algebraic Method: (A Review)

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ABSTRACT

In this review paper, we have presented the Lie algebraic method for vibrational frequencies of polyatomic molecules.

Key words: Polyatomic molecules, Vibrational spectra, Lie algebraic method.

INTRODUCTION

Review of Lie algebraic Method

Lie algebraic theory can be defined as the framework that studies the problems in mathematics and molecular physics. In the last part of the 19th century, Marius Sophus Lie proposed Lie algebras. Nevertheless, these methods have been useful in the study of the problems in the beginning portion of the 20th century, after the evaluation of quantum mechanics. This is because quantum mechanics make use of commutators $[x, p_x] = i\hbar$, where $[x, p_x] = x\, p_x - p_x x$ which is the commutator of x and p_x (linear momentum operator in x direction) and $\hbar = h / 2\pi$, where h is the Planck's constant, which are the defining ingredients of Lie algebras. The framework of the Lie algebraic method has been used to trace the Heisenberg formulation of quantum mechanics[1, 2, 3, 4]. The systematic development of Lie algebraic method to physical systems (spectrum algebras) was introduced by Iachello and Arima in their pioneer work of spectra of atomic nuclei (interacting Boson model)[5, 6, 7, 8, 9, 10, 11]. Iachello (1981) presented Lie algebraic method (vibron model) for the study of vibrational spectra of molecules[12]. This method is based on the second quantization of the Schrodinger wave equation with a 3-Dimensional Morse potential function and is described as ro-vibration spectra of diatomic molecules[13]. This method was improved in subsequent works to study ro-vibrational spectra of polyatomic molecules[14, 15, 16, 17, 18]. Considerable interest has focused on the improvement of two coupled 1-Dimensional oscillators[19] and its generalization to many coupled 1-Dimensional oscillators[20, 21]. This is given a complete framework to analyze bending

vibrational modes in linear molecules[22]. These Lie algebraic methods were extended for some more molecules[23, 24, 25, 26, 27, 28]. There are two well-known approaches for the analysis of vibrational spectra of polyatomic molecules other than Lie algebraic methods.

The first approach is based on Dunham expansion[29]. It is a series of expansion of energy levels of rotational (J) and vibrational (v) quantum numbers. This approach is useful when the spectra can be expressed by a small number of parameters. The major drawbacks of this approach are that there is no Hamiltonian operator and it requires more number of parameters for large polyatomic molecules. This expansion does not give any information about the wave function of individual states of a molecule[25].

The second approach is potential approach. This approach is based on the Schrodinger wave equation. In this approach, the energy levels are computed by fitting the Schrodinger wave equation in terms of interatomic variables. The potential coefficients are evaluated by fitting the experimental data on energy levels. The basic drawback of this approach is that it is very difficult to fit potential coefficients if the number of atoms in the molecule increases[28].

In both approaches it can be very difficult to overcome such issues if the molecule contains more than three atoms. The present study is motivated by this difficulty. The basic idea of the Lie algebraic method is that series expansion of the Hamiltonian in terms of a set of operators (Boson operators) characterizes the local and normal modes of the system. The Lie algebraic method provides a framework that allows the analysis of experimental ro-vibrational spectrum of polyatomic molecules based on the idea of dynamical symmetry. This Lie algebraic method is used to generate Hamiltonian operator that provides the description of ro-vibrational degrees of freedom of the physical system[25]. There are two extensively used Lie algebraic methods such as $U(4)$ and $U(2)$. The advantage of $U(4)$ Lie algebraic method is that the vibrations and rotations are handled simultaneously. This method becomes more complicated when there are more than four atoms in the molecule[30]. Roosmalen et al., developed $SU(2)$ algebraic method for some molecules to describe

stretching modes by separating the vibrational degrees of freedom from the rotational[13]. In 1991, this method was extended by Iachello and Oss to deal with the stretching vibrations of polyatomic molecules[31]. In 1996, this method was expanded to include bending modes in XY_3 type molecules[22]. As alternative schemes, other Lie algebraic methods[25, 32, 33] have been presented for molecular spectroscopy. However, they are more complex than the $SU(2)$ method. In a different way, Ma *et al.*, using a set of Boson operators to describe the motion of each bond in polyatomic molecules, have recently proposed another algebraic method, where the stretching and bending interactions are described by a quadratic term or possible Fermi resonance terms [34, 35, 36]. The $U(2)$ Lie algebraic method was developed to describe the stretching vibrations of diatomic molecules and was successfully extended for benzene and octahedral molecules[9, 21, 25, 37, 38, 39, 40]. This method was improved further to deal with both stretching and bending vibrations of H_2O (up to first overtone), XH_3, PH_3 and NF_3 [42, 43, 44, 45, 46, 47]. Also in the last few years Lie algebraic methods have been used extensively by Ramendu Bhattacharjee and co-workers to study the vibrational spectra of different bio-molecules such as nickel metalloporphyrins[48, 49, 50, 51, 52], copper tetramesityl porphyrin[53], metallotetraphenyl porpyrins and its cation radicals[54, 55, 56], and copper and magnesium octaethyl porphyrin[54]. The framework of Lie algebraic method has been successfully applied to study vibrational spectra of fullerenes C_{50}, C_{60}, C_{70}, C_{80}, C_{84} [57, 58, 59, 60]. This framework was set up to be really well suited to integrate the underlying discrete symmetries. In particular, invariant interactions under the point group were made by using projection techniques on an expansion of the Hamiltonian in terms of invariant (Casimir) operators. Karumuri and co-authors used the process of symmetry adaptation to the generators of the algebras themselves, rather than by the Casimir operators[39, 40, 41]. This procedure leads to new interaction terms.

CONCLUSION

In this paper we have presented a review of the recent development in Lie algebraic method. We observed that the results by Lie algebraic method are accurate to the existing experimental or theoretical data.

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