Chapter 6

Conclusion and Prologue to the Future

6.1 Conclusion

The Lie algebra was introduced by Marius Sophus Lie at the end of the 19th century. However, Lie algebraic methods have been useful in the study of problems in Physics after the development of quantum mechanics in the first part of the 20th 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, when it was introduced in a systematic fashion by A. Arima and F. Iachello in the study of spectra of atomic nuclei (interacting boson model). Wulfman played a great role in the introduction of the algebraic approach to molecules. He is the pioneer to publish the first paper on the algebraic approach to molecules in 1979 (Wulfman and Levine, 1979). Later, in 1981, F. Iachello used Lie algebraic methods in the systematic study of spectra of molecules (vibron model). After 1981, there was a rapid progress in the process. The brief review work of F. Iachello and S. Oss, reflects the progress of the field upto 2002 alongwith the perspectives for the algebraic method in the first decade of the 21st century.

The main advantages of the algebraic methods are:

(i) Anharmonicities in the energy spectra are put in from the very beginning.

(ii) Anharmonicities in the interactions between different modes are introduced automatically since they are already contained in the matrix elements of the step operators.
(iii) 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.

The present research work is organized in the form of different Chapters as follows:

**Chapter 1: Introduction:** In this chapter, we have introduced a brief discussion about the structure and dynamics of C\textsubscript{70} molecules. We have also introduced molecular spectroscopy, its principle & application and the different approaches used to study the vibrational spectroscopy.

**Chapter 2: Review of Literature and Formalism of Lie algebraic theory:** In this chapter, we have introduced the idea of group theory with special reference to Lie groups and Lie Algebra and its relationship with molecular spectroscopy. A brief review works on vibrational spectroscopy by the Lie algebraic method also have been discussed in this chapter.

**Chapter 3: Formalism of Lie algebraic theory of Fullerene molecules:** In this chapter, we formulated the stretching and bending Hamiltonian for the Fullerene molecules by using U(2) Lie algebra starting from diatomic molecules. These results have been used in Chapter-4 and Chapter-5. In this Chapter, we also present the isomorphism of U(2) Lie algebra with the one dimensional Morse potential.

**Chapter 4: Calculation of vibrational energy levels of Fullerene C\textsubscript{70} & C\textsubscript{70}O:** In this chapter, we presented the Calculations of the vibrational energy levels of C\textsubscript{70} and C\textsubscript{70}O using the Lie algebraic method. For C\textsubscript{70}, in this chapter we report a RMS deviation \( \Delta (r.m.s) = 8.44 \text{ cm}^{-1} \) for 31 vibrational bands in the strict local limit. In the strict local limit, also we report here RMS deviation for C\textsubscript{70}O as \( \Delta (r.m.s) = 0.534 \text{ cm}^{-1} \) against the available six experimental values.

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Chapter 5: Calculation of vibrational IR spectra of Fullerene $C_{70}C_8H_8$: In this chapter, we presented the calculations of the vibrational energy levels of Fullerene $C_{70}C_8H_8$. In this Chapter, it has been shown that RMS deviation obtained for Fullerene $C_{70}C_8H_8$ (for 22 vibrational bands) using the local Hamiltonian is $\Delta (r.m.s) = 0.466$ \text{cm}^{-1}, which is near about the experimental accuracy.

On the basis of the cited statement we may now have the conclusions of our study (Kalyan et al., 2011, 2012) as follows:

(i) The RMS deviation we have reported for $C_{70}$, $C_{70}O$ and $C_{70}C_8H_8$ in this study is the best result.

(ii) In Lie algebraic method, $C_{70}$, $C_{70}O$ and $C_{70}C_8H_8$ are well approximated in the strict local limit, the local Hamiltonian gives a much better fit to experimental results.

(iii) Even though the vibrational spectra of $C_{70}$, $C_{70}O$ and $C_{70}C_8H_8$ could be described using the local Hamiltonian to a first approximation, with the available experimental data base, but there is enormous scope to advance the algebraic model. With the help of this model, one can predict the hitherto unknown states of a molecule, which are not experimentally explored. However in this study we have calculated only the fundamental modes of vibration of the molecule. 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 greater interest of further experimental study. At the same time, the Raman Intensity of the molecules also can be studied with the help of this algebraic model.

6.2 Prologue to the future

6.2.1 Perspective in the next few years

On the basis of the results obtained so far, the perspective for the Lie algebraic methods in the next few years may be visualized as follows:
(a) **Small molecules**

(i) The study of normal to local transitions and onset of chaos if any for the molecules where the Lie algebraic methods have not been applied till this period.

(ii) The study of Franck-Condon intensities in linear to bent transitions.

(b) **Medium-size molecules**

The development of symmetry adapted bases for icosahedral group (Chen and Ping, 1997) greatly helped to study the vibrational states of fullerene molecules. Although in this study we have analysed the vibrational states of fullerene $C_{70}$ and some of its derivatives, but the spectroscopy of fullerene and its variants is still an important goal of the algebraic method.

(c) **Macromolecules**

The area of macromolecules has not been attacked with the algebraic methods so far. Thus, for this area the perspective of the algebraic methods is to open a field.

(d) **Floppy molecules**

The Lie algebraic method has been used so far mostly for situations in which the potential has a sharp minimum as a function of some coordinate $x$. It may be noted that there is an increasing number of molecules where this condition is not met. In the variable $x$, the potential may be rather flat. In non-rigid molecules, these situations are encountered. We note that the way in which these situations have been attacked so far has been that of expanding into a harmonic oscillator or Morse potential functions (algebraic force-field expansion (Sako et al., 1999). This requires, for very flat potentials, many terms in the expansion (harmonic or anharmonic Morse). It is seen that when the problem of expanding an anharmonic potential in the harmonic basis was encountered, the solution was that
of introducing the Lie algebraic approach with a Hamiltonian operator diagonal in the Morse (or Poeschl-Teller) basis. We know that the situation in which the Hamiltonian operator is diagonal is called dynamic symmetry. Here one can see that the difficulty posed by flat potentials can be overcome by introducing Hamiltonian operators which are not diagonal in either basis harmonic or anharmonic Morse. Here also one should note that these more general situations correspond to breaking of dynamic symmetries and have been investigated extensively in the study of atomic nuclei (interacting boson model). Thus we see that the area of non-rigid (vander Waals, quasi-linear and other like) molecules is one of the main perspectives for the Lie algebraic methods in the next few years.

Potentials with many minima such as those occurring in torsional oscillations and to molecules with hindered rotations are other areas of interest for floppy molecules (Champion et al., 1999).

(e) Polymers

Another important perspective for the Lie algebraic method is provided by the wealth of new experimental information that is being obtained in macromolecules and polymers including biomolecules and biopolymers. Here, the algebraic method could be particularly useful for vibrational spectroscopy. Results could be obtained by a combination of analytical and numerical methods for finite polymers. One should note here that for infinite dimensional polymers, \( n \to \infty \), all results must be obtained analytically. In this direction, a research program already has been started (Lemus and Frank, 1994; Iachello and Truini, 1999; Marinkovic and Oss, 2002). It may be noted that in view of its implications to practical applications and to biology, this program is an important perspective for the Lie algebraic methods in the 21st century. Here, the algebraic method could be useful in obtaining analytic expressions for polymer dispersion relations, for calculation of the response of the system to infrared and Raman
radiation, and for understanding mode-mode couplings. So far, the preliminary work has been done for one dimensional linear chains. In the study of paraffins (fig. 6.1), \( \text{CH}_3 - (\text{CH}_2)_{n-2} - \text{CH}_3 \), and polyethylene, this work has been applied. Now, it need to be extended to the full set of vibrational degrees of freedom (CH bending, torsion and CC skeletal modes), to more complex geometric structures, such as helicoidal structures and to more than one dimension (membranes). Here, the modification in the spectroscopic information due to folding could also be investigated.

![Ball and stick view of the 9-paraffine molecule, C₉H₂₀.](image)

**Fig. 6.1** Ball and stick view of the 9-paraffine molecule, C₉H₂₀.

(f) Nano material studies

It is one of the most important perspectives for the Lie algebraic method in the next few years. We are hopeful that very soon the usefulness of the Lie algebraic methods can be extended further in the study of nano materials.

6.2.2. Long-range perspectives

The study of reactions between molecules may be one important area among the long range perspectives. It may be noted that the algebraic method has been
used up to now mostly to study bound state problems. Even though an algebraic treatment of the continuum was suggested some years ago, it has not been exploited much. Thus we see that there are several problems within the reach of the algebraic method in this area. These are –

(a) The study of resonances in the continuum.

(b) The study of bound to free transitions in infrared absorption.

(c) The study of bound to free transitions in Franck-Condon processes.

(d) The study of molecule-molecule collisions and electron-molecule collisions.

Thus the Lie algebraic method can be one of the best alternate and essential tool for the analysis of vibrational spectra of molecules. Further, in view of the many possible applications of the algebraic method, it is hoped that the present study will stimulate further research, especially in the new areas of complex systems like Macromolecules, Floppy molecules, Polymers, Nano material studies.