Chapter 6

CONCLUSION AND PROLOGUE TO THE FUTURE

6.1 Conclusion:

In this chapter we conclude the whole findings of research work. Algebraic Theory is a powerful tool that unifies the whole of quantum mechanics. For addressing quantum mechanical problems embedded in a group theoretical framework, a particularly powerful mathematical technique is that of continuous Lie-Groups and algebras. The Lie algebraic methods were introduced for the first time by Marius Sophus Lie at the end of 19th century in the context of the new matrix mechanics. However the use of Lie algebras as a tool to systematically investigate physical systems did not 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 (Arima and Iachello, 1975, 1976, 1978, 1979; Iachello and Arima, 1987; Iachello and Isacker, 1991).

This kind of strategy was then exported to the world of molecules (Iachello and Levine, 1982, 1995; Iachello, 1981; Roosmalen *et al*., 1982, 1983a, 1983b, 1984; Frank and Isacker, 1994; Iachello *et al*., 1995; Frank *et al*., 1996; Lemus and Frank, 1991, 1994; Child and Lawton, 1982; Benjamin and Levine, 1983; Kellman, 1985; Child and Zhu, 1998; Iachello *et al*., 1991; Iachello and Oss, 1996; Wang, *et al*., 2000; Feng *et al*., 2007; Ding and Zheng, 1999; Sako *et al*., 2000). C. E. Wulfman played a great role in the introduction of the algebraic approach to molecular Spectroscopy (Wulfman, 1979; Levine and Wulfman, 1979). As a matter of fact, the only difference between nuclei and molecules from the viewpoint of the building blocks used is that when

dealing with molecules, one has to start with a diatomic unit. This is equivalent to considering boson operators related to the dipole character of the diatom. A comprehensive and up-to-date review of mathematical concepts, physical aspects, practical applications and numerical implementation of algebraic models in molecular spectroscopy was presented by S. Oss in 1996 (Oss, 1996). The brief review work of F. Iachello and S. Oss (Iachello and Oss, 2002) 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. A two-dimensional Lie algebraic technique has been recently introduced by F. Iachello and S. Oss (1996) and preliminarily applied to the vibrational analysis of pure bending modes of the acetylene molecule. Later in 1998 the two dimensional algebraic model with the study of infrared transition intensities has been done by S. Oss and M. A. Temsamani (1998).

The Lie algebraic methods up to now have focused essentially on the description of bound (Arima and Iachello, 1976, 1978; Iachello, 1981; Roosmalen *et al*., 1982; Iachello and Levine, 1982; Levine and Wulfman, 1979; Roy *et al*., 2010, 2011) and scattering states (Alhassid *et al*., 1983a, 1983b, 1986; Frank and Wolf, 1984; Alhassid and Wu, 1984; Alhassid *et al*., 1984). Also in the last few years Lie algebras have been used extensively by Ramendu Bhattacharjee and coworkers to illustrate the spectra of various polyatomic molecules including various bio-molecules like metalloporphyrins and nano particles like C_{60}, C_{70}, C_{80} (Choudhury *et al*., 2008a, 2008b, 2009a, 2009b, 2010; Das, 2010, 2011; Kalyan, 2011a, 2011b; Karumuri, 2008a, 2008b, 2009a, 2009b, 2009c, 2010a, 2010b; Sarkar, 2006, 2008, 2009).

The main advantages of the algebraic methods are as follows :

1. A very few number of algebraic parameters are involved which can be determined with the knowledge of symmetry of the molecules with a few number of available experimental data.
2. Anharmonicities in the energy spectra are put in from the very beginning.

3. Anharmonicities in the interactions between different modes are introduced automatically since they are already contained in the matrix elements of the step operators.
4. The method allows one to calculate wave functions and thus observables other than energies, such as intensities of transitions (infrared, Raman, Franck-Condon).
5. It can be generalized to cases where the Hamiltonian is specified in terms of the generators of the group rather than as a differential Schrödinger operator.

Since anharmonicities play a crucial role in vibrational spectroscopy, so it is here that U(2) algebraic methods have found their most useful applications for polyatomic molecules and hence we have chosen the problem – Analysis of vibrational spectra of Benzene and its derivaties using U(2) Lie Algebric Method.

Although extensive studies by several techniques (Mukharjee *et al*., 2008; 2009; 2010. Scotoni, *et al*., 1995. Bassi, *et al*., 1997. Tummanapelli, *et al*.,2013. Goodman, *et al*.,1991. Iachello and Oss, 1992; 1995 on the molecule have clarified several aspects many other aspects required for further theoretical explanations and there is enormous scope for improving the algebraic method for determining vibrational energy levels of benzene and its derivatives.

6.2 Prologue to the Future :

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 / Medium-size 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.
iii. The study of IVR in increasingly complex molecules.

In case of medium-size molecules another important point is to be noted. The spectroscopy of fullerene and its variants is an important goal of the algebraic method. It can be greatly helped by the development of symmetry adapted bases for the icosahedral group done by Chen and Ping (Chen and Ping, 1997).

(b) Macromolecules:

In the present study algebraic model is applied on few molecules but many more remain where the Lie algebraic methods have not been applied till this period. Thus, for this area the perspective of the algebraic methods is to open a new field.

(c) Floppy molecules:

Floppy molecules i.e. non rigid having one or more large amplititude (LAM) vibrations have attracted an exceptional amount of attention from experimentalists and theorists alike. These area is one of the main perspectives of the lie algebraic method in the next few years. 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 studied 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 Pöschl-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).

On a more fundamental level, studying excited floppy molecules is challenging and rewarding because it forces one to reexamine, modify an often abandon many of the basic concepts, formalisms and computational methods applicable to low energy, small amplitude vibrations (Wilson *et al*., 1955), but that become inappropriate with increasing excitation energy and amplitudes of vibrational motion. It is in this regime that experiments and theories come in contact with the question of classical and quantum chaos, which has certainly been one of the most visible and most intensely studied theoretical issues. In the past decades (Casati *et al*., 1995; Mukamel 1987; Stechel *et al*., 1984).

(d) 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 bio-molecules 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, $n \rightarrow \propto$, all results must be obtained analytically. In this direction, a research program already has been started (Lemus and Frank, 1994; Iachello and Truini, 1999). 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 couplings. So far, the preliminary work has been done for one dimensional linear chains. In the study of paraffins (Iachello and Truini, 1999), $CH_3 - (CH_2)_{n-2} - CH_3$, 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.

(e) Nano material studies:

Nano materials are cornerstones of nano science and nano technology. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is one of the most important perspectives for the Lie algebraic method in the next few years. Recently sen *et al*. (sen *et al,*2013) applied U(2) algebraic model and analyzed vibrational spectra of few nano materials but many fields remain where algebraic model can be applied as an viable alternative. We are hopeful that very soon the usefulness of the Lie algebraic methods can be seen in the study of various other nano materials.

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.

(e) The determination of energy bands of real crystals and thereby predicting various properties.

Thus we find that the Lie algebraic method of analysis of vibrational spectra of molecules is an essential tool. 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 (bio-molecules), Floppy molecules, Polymers, Nano material studies.