

Algebraic methods in quantum mechanics: from molecules to polymers

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Abstract. We present a brief review of algebraic techniques developed and applied in molecular spectroscopy in the last five years. We also outline perspectives for new applications of the Lie algebraic method in the first decade of the new century.

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1 Introduction

Lie algebraic methods have been useful in the study of problems in physics ever since Lie algebras were introduced by Sophus Lie at the end of the 19th century, especially after the development of quantum mechanics in the first part of the 20th century. This is because quantum mechanics makes use of commutators $[x, p_x] = \hbar$ which are the defining ingredients of Lie algebras. 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 one of the authors (F.I.) and Arima in the study of spectra of atomic nuclei (interacting boson model) [1,2]. In 1981, one of the authors (F.I.) introduced Lie algebraic methods in the systematic study of spectra of molecules (vibron model) [3]. This introduction was based on the second quantization of the Schrödinger equation with a three dimensional Morse potential and described rotation-vibration spectra of diatomic molecules [4]. Soon afterwards the algebraic method was extended to rotation-vibration spectra of polyatomic molecules [5]. In the intervening years much work was done. Most notable advances were the extension to two coupled one-dimensional oscillators [6] and its generalization to many coupled one-dimensional oscillators [7], which led to a simpler treatment of vibrational modes in polyatomic molecules, and the extension to two-dimensional oscillators [8] which allowed a simpler description of bending modes in linear molecules. The situation up to 1995 was reviewed in ref-

erence [9]. This article presents a brief review of the work done in the last five years and, most importantly, provides perspectives for the *algebraic method* in the first decade of the new century.

2 Algebraic methods

In order to place the algebraic method within the context of molecular spectroscopy, we begin with a brief description of it.

The essence of the algebraic method can be traced to the Heisenberg formulation of quantum mechanics [10]. Consider a quantum problem in one-dimension with Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x).$$

Rather than solving the differential equation $H\Psi(x) = E\Psi(x)$ directly, consider the case of a harmonic oscillator potential

$$V(x) = kx^2/2$$

and introduce creation and annihilation operators

$$a^\dagger = \frac{1}{\sqrt{2}} \left(x - \frac{d}{dx} \right),$$
$$a = \frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right)$$

together with a vacuum state $|0\rangle$. The Hamiltonian for the harmonic oscillator can be written as

$$H = \hbar\omega(a^\dagger a + 1/2)$$

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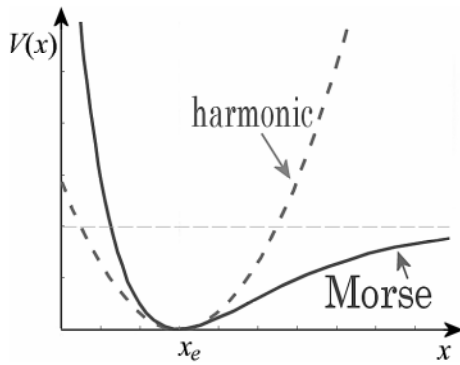


Fig. 1. The Morse potential and its approximation with a harmonic oscillator potential.

with eigenvalues

$$E(n) = \hbar\omega(n + 1/2), \quad n = 0, 1, \dots, \infty$$

and eigenstates

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle.$$

The harmonic frequency is $\omega = (k/m)^{1/2}$. For a generic potential, expand $V(x)$ in powers of x

$$V(x) = \sum_{i=2} k_i x^i$$

i.e. in powers of a^\dagger , a , $a^\dagger a$ and diagonalize it in the space $n = 0, \dots, N$.

The set of four operators a^\dagger , a , $a^\dagger a$, 1 forms an algebra with commutation relations

$$[a, a^\dagger] = 1; \quad [a, a^\dagger a] = a; \quad [a^\dagger, a^\dagger a] = a^\dagger$$

called the Heisenberg-Weyl algebra $H(2)$ (the identity 1 commutes with all operators). Hence the method wherein the Hamiltonian operator is expanded in powers of operators of $H(2)$ is called *algebraic harmonic analysis* [11]. The advantage of the method is that all manipulations are done algebraically rather than using differential operators. The key ingredients in these algebraic manipulations are the matrix elements of the operators, a^\dagger , a (called step up and step down operators) given by

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle; \quad a |n\rangle = \sqrt{n} |n-1\rangle.$$

It is all one needs to calculate any observable within the framework of harmonic analysis. However, molecular potentials often deviate considerably from harmonic (Fig. 1). As a result, the expansion of $V(x)$ contains many parameters and/or the basis in which the diagonalization is done needs to be taken very large, $N \rightarrow \infty$.

This difficulty can be overcome by considering other solvable potential functions which contain from the beginning anharmonicity. One such a function is the Morse function

$$V(x) = V_0 [1 - \exp(-a(x - x_0))]^2.$$

With a series of transformations, the Schrödinger equation with a Morse potential can be written in terms of an algebra composed of four operators F_+ , F_- , F_z , N satisfying commutation relations

$$[F_+, F_-] = 2F_z; \quad [F_\pm, F_z] = \pm F_\pm.$$

(The operator N commutes with all elements.) The four operators form a Lie algebra, called $U(2)$, while the three operators F_+ , F_- , F_z form a Lie algebra, called $SU(2)$, isomorphic to the angular momentum algebra and hence called quasi-spin algebra. The Hamiltonian for the Morse oscillator, when written in terms of these operators takes the simple form

$$H = E_0 + AF_z^2.$$

Introducing the vibrational quantum number v related to the eigenvalue M of F_z by $v = (N - M)/2$, the eigenvalues of H can be written as

$$E(v) = E_0 + AN^2 - 4A(Nv - v^2), \\ v = 0, 1, \dots, N/2 \text{ or } (N-1)/2 \text{ (} N \text{ even or odd)}$$

and the eigenfunctions as $|N, v\rangle$. The expression for the energy levels can be cast in the familiar form

$$E(v) = \hbar\omega_e \left(v + \frac{1}{2} \right) - \hbar\omega_e x_e \left(v + \frac{1}{2} \right)^2$$

which represents an anharmonic oscillator with quadratic anharmonicities. The algebra of $U(2)$ provides then a framework for performing *algebraic anharmonic analysis*. A generic potential can be expanded in terms of quasi-spin operators F_+ , F_- , F_z . All one needs are the matrix elements of the step up and step down operators of $SU(2)$ given by

$$F_- |N, v\rangle = \sqrt{v(N-v+1)} |N, v-1\rangle, \\ F_+ |N, v\rangle = \sqrt{(N-v)(v+1)} |N, v+1\rangle.$$

The anharmonic analysis based on the Lie algebra $U(2)$ shares with the harmonic oscillator analysis its simplicity while at the same providing a basis in which anharmonicities are built in from the very beginning. Furthermore, for molecular potentials that are not very different from Morse, the expansion converges very quickly, *i.e.* very few terms are needed to obtain an accurate description. Also the harmonic limit can be easily recovered from $U(2)$ using a mathematical procedure called contraction ($1/N \rightarrow 0$). It is easy to see that, by renormalizing the operators F_+ and F_- with $N^{1/2}$, their matrix elements go over those of the harmonic oscillator in the limit $N \rightarrow \infty$.

The Morse function is not the only one that can be used to provide a basis for anharmonic analysis. Another function of interest in molecular physics, especially for bending vibrations, is the Poeschl-Teller function (Fig. 2),

$$V(x) = -\frac{V_0}{\cosh^2 ax},$$

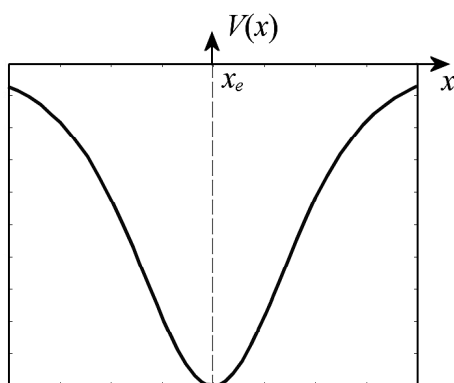


Fig. 2. The Poeschl-Teller potential.

This function is also associated with the Lie algebra $U(2)$. The potential functions for which a connection with the algebra of $U(2)$ is possible have been completely enumerated.

The algebraic method can be applied to problems in any number of dimensions, in particular two and three dimensions where harmonic analysis is done in terms of the Weyl-Heisenberg algebras $H(3)$ and $H(4)$, and anharmonic analysis in terms of the Lie algebras $U(3)$ [8] and $U(4)$ [3]. Indeed the original suggestion to use algebraic methods in molecular physics was in terms of the Lie algebra $U(4)$ within which it is possible to describe the eigenstates and eigenvalues of the Morse potential in three dimensions. In general for a quantum mechanical problem in v dimension anharmonic analysis can be done in terms of the Lie algebra $U(v+1)$ [12].

3 The role of algebraic methods

The algebraic formulation of quantum mechanics outlined above can be used to attack problems of relevance in physics and chemistry. In particular, in molecules it can be used to analyze rotational and vibrational spectra. For the treatment of electronic spectra, additional ingredients, describing the electron spin, are needed. An algebraic model of electronic spectra was introduced in 1989 [13] but it has not been exploited much up to this point. Instead the field in which the algebraic method has had most impact is that of *vibrational* spectroscopy. The reason is that the main advantages of the algebraic method 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.

4 Vibrational spectroscopy

Vibrational spectroscopy can be studied with a variety of experimental tools. Infrared and Raman spectroscopy provide information on the vibrational modes built on the ground state electronic configuration. Franck-Condon spectroscopy provides information on the vibrational modes built on two electronic manifolds. For the sake of discussion in this article it is convenient to divide molecules according to their size. We shall denote molecules with $n = 2-4$ atoms “small molecules”, molecules with $n = 5-100$ atoms “medium-size molecules” and molecules with $n > 100$ “macro-molecules”.

4.1 Small molecules

When dealing with molecules an important aspect is what coordinate system is chosen. For small molecules the best set for vibrational analysis is provided by the internal coordinates. If A is the number of atoms, the number of internal coordinates is $3A - 6$. If the molecule is linear there are $3A - 5$ internal coordinates. The algebraic method as applied to the vibrational spectroscopy of small molecules consists in quantizing each internal degree of freedom with the algebra of $U(2)$. The Hamiltonian for a set of n coupled one-dimensional degrees of freedom is then written in terms of the quasi-spin operators $F_{+,i}, F_{-,i}, F_{z,i}$ for each degree of freedom i . A Hamiltonian often used is [7]

$$H = E_0 + \sum_{i=1}^n A_i F_{z,i}^2 + \sum_{i<j=1}^n B'_{ij} F_{z,i} F_{z,j} + \sum_{i<j=1}^n B_{ij} (F_{+,i} F_{-,j} + F_{-,i} F_{+,j}).$$

The first term in this Hamiltonian represents a set of n uncoupled anharmonic oscillators, while the additional terms represent coupling between the modes. Apart from some overall constant, this Hamiltonian is the anharmonic version of the coupled harmonic oscillator Hamiltonian

$$H = E_0 + \sum_{i=1}^n A_i a_i^\dagger a_i + \sum_{i \leq j=1}^n B'_{ij} a_i^\dagger a_i a_j^\dagger a_j + \sum_{i<j=1}^n B_{ij} (a_i^\dagger a_j + a_i a_j^\dagger).$$

In fact one can be obtained from the other by a simple substitution.

For bending vibrations of linear molecules the motion occurs in the plane perpendicular to the axis of the molecule (Fig. 3), that is in two dimensions. These vibrations are therefore quantized with the algebra of $U(3)$.

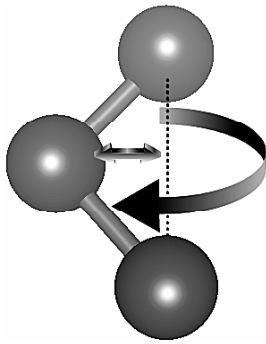


Fig. 3. Bending vibrations in linear polyatomic molecules.

The algebra of $U(3)$ is composed of nine operators. For linear molecules one thus has one $U(2)$ for each stretching vibration and one $U(3)$ for each bending vibration. The expansion of the Hamiltonian operator is done in terms of the four operators of $U(2)$ and the nine operators of $U(3)$.

This scheme has been used recently to study bent and linear molecules. In bent triatomic molecules (SO_2 , S_2O) there are three one-dimensional degrees of freedom, quantized with $U(2) \times U(2) \times U(2)$ while in linear triatomic molecules (CO_2) there are two one-dimensional stretching modes and one two-dimensional bending mode, $U(2) \times U(2) \times U(3)$. Similarly, in linear four-atomic molecules (C_2H_2) [14] one has $U(2) \times U(2) \times U(2) \times U(3) \times U(3)$. By fitting the experimental energy levels it has been possible to extract the algebraic parameters. These parameters play the role of the force-field constants in the usual harmonic analysis.

It is of importance to give a perspective on the results obtained so far. First and foremost on the usefulness of the Lie algebraic method and its comparison with usual harmonic analysis. This is shown in Figure 4. Here the r.m.s. deviation for CO_2 is shown against the number of basis states [15]. The curve “conventional” denotes the usual harmonic analysis, while the curve “algebraic” denotes the anharmonic analysis. The convergence properties are clearly displayed in this figure. One can note that for this molecule, for which there are strong Fermi resonances between the double bending vibration and the symmetric stretch, the conventional analysis requires at least 1500 basis states to converge to a good r.m.s. deviation, while the algebraic analysis has already converged with less than 1000 states. The second important point of the algebraic method is its ability to calculate vibrational energies to very high quantum numbers. This calculation is feasible because one starts from the beginning with an anharmonic basis. Perturbations and couplings in this basis are small. This situation is illustrated by the calculation of SO_2 where it has been possible to follow the vibrational states up to 20 quanta of vibration. The possibility to reliably calculate highly excited states of molecules permits several important questions to be answered, in particular the question on where and how the transition between normal modes and local modes occurs and whether or not

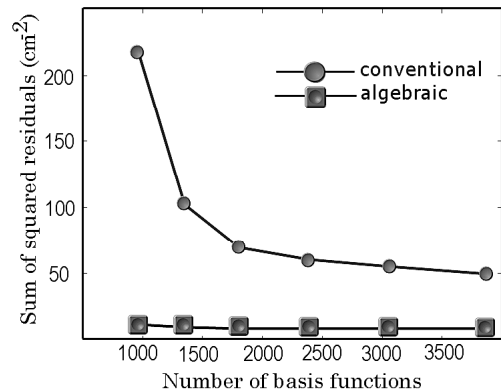


Fig. 4. Convergence properties of the algebraic method as compared with the conventional method. From reference [15].

chaotic properties emerge at some excitation energy. An analysis of SO_2 and H_2O reveals that the transition from normal to local occurs in SO_2 at $v \approx 18$, while it occurs in H_2O already at $v \approx 2$ [16]. Figure 5 depicts the probability density of vibrational eigenstates in SO_2 obtained by the algebraic method. The wave functions of the $(v_m, 0, 0)$ states bifurcate at $v = 18$. In general, most molecules with hydrogen bonds behave locally for $v \geq 2$, although a much more complex dynamics, equally well described in an algebraic framework [14], is observed in certain molecules such as acetylene, C_2H_2 [17].

As mentioned above one of the main advantages of the algebraic method is that it permits a calculation of transition intensities (infrared, Raman and Franck-Condon). Intensities of transitions have not been much used in molecular spectroscopy because absolute calibration is often difficult. However, recently experimental techniques have improved to such an extent as to be able to extract transition intensities. If so they provide an enormous amount of information on the structure of molecules. A recent example is the study of Franck-Condon intensities in S_2O [18]. In studying transitions in the algebraic approach, one needs a model of the transition operator. For infrared transitions one needs a dipole moment function. In the usual harmonic analysis in one-dimension this is often expanded in powers of the coordinate x

$$M(x) = \sum_{k=0} m_k x^k$$

or algebraically

$$M = \sum_{k=0} m_k (a + a^\dagger)^k.$$

This dipole moment function suffers from the same problems of the potential function, *i.e.* it is difficult to include anharmonicities. In the algebraic approach the dipole function is expanded in terms of algebraic operators

$$M = \sum_{k=0} m_k (F_+ + F_-)^k.$$

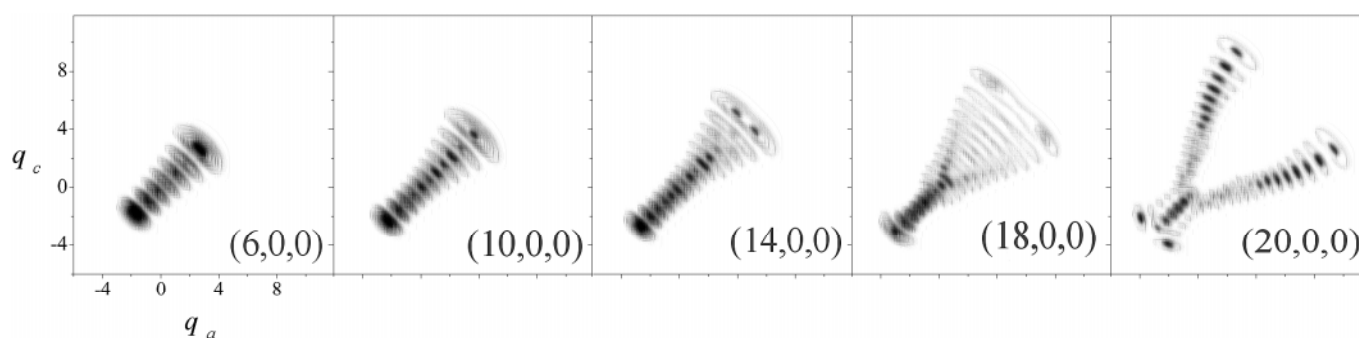


Fig. 5. The algebraic probability density of the vibrational eigenstates in the $(v_m, 0, 0)$ series of the fundamental electronic state of SO_2 . Adapted from reference [26].

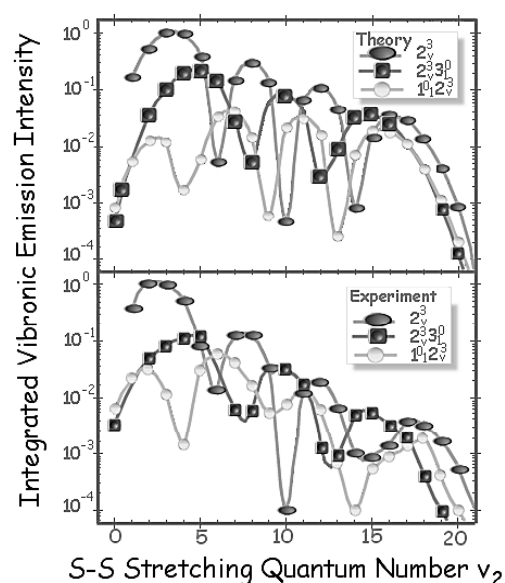


Fig. 6. Intensities of Franck-Condon transitions in the S_2O molecule. From reference [17].

A better form, often used, is

$$M = M_0 \exp[\alpha(F_+ + F_-)].$$

The algebraic approach provides a way to do calculations of transition intensities in which the anharmonicities are included from the beginning both in the potential function and in the transition moment function. The technique has given an excellent description of 1 000 Franck-Condon intensities in S_2O (Fig. 6). In addition, it has been possible to extract information on the wave functions of both the upper and the lower electronic manifold and information of the extent to which non-Condon effects play a role in these transitions [19].

Perspectives for the algebraic method in this area are:

- (i) the study of other normal to local transitions and onset of chaos if any;
- (ii) the study of Franck-Condon intensities in linear to bent transitions.

4.2 Medium-size molecules

In contrast to small molecules, for medium size molecules a convenient set of coordinates is provided by the local coordinates. Local coordinates have the advantage that it is possible to write down the Hamiltonian operator in a simple form. They have the disadvantage that the spurious coordinates associated with overall translations and rotations must be removed. Also, for mid-size molecules, discrete symmetries play a major role. In view of these two difficulties, mid-size molecules present a real challenge to any calculation. Several techniques have been devised to circumvent these difficulties. In order to circumvent the first one, a technique often used is that of adding to the Hamiltonian a term proportional to the center of mass coordinates and letting the coefficient of that term go to a large value. This removal of the center of mass motion is exact if the potential is harmonic. Otherwise it is only approximate and there is a small error in the calculation of the vibrational modes which are admixed with the center of mass motion. The technique has been used for the calculation of benzene C_6H_6 [20]. In order to circumvent the second problem, one can construct symmetry adapted states and operators. Several methods have been used to this end. One of the methods introduced by Frank, Lemus and others has been used to formulate algebraic models directly in terms of symmetry adapted operators [21]. Using another method, introduced by Chen, it has been possible to calculate vibrational states with up to $v = 10$ quanta of vibrations in octahedral molecules (UF_6) [22]. The algebraic method is particularly useful in this area since conventional methods are difficult to apply. Using this method, it has been possible to analyze several phenomena of particular importance, most importantly the question of vibrational energy redistribution in medium-size molecules.

Perspectives for the algebraic method in this area are:

- (i) the study of IVR in increasingly complex molecules;
- (ii) the study of molecules with substitutions and/or impurities, such as an atom at the center of the cage in C_{60} .

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 [23].

4.3 Macromolecules

For macromolecules local coordinates are the best choice and there is no problem in removing the spurious center of mass motion since its role is negligible when the overall mass of the molecule is large. Also the role of discrete symmetries is less prominent than in medium-size molecules. The area of macromolecules has not been attacked with algebraic methods so far. For this area thus the perspective is to an open field. Similarly the information on vibrational spectroscopy of these systems is not fully acquired. A combination of theoretical and experimental studies could be essential for a deep understanding of these structures.

5 Rotational spectroscopy

Although the main thrust of this article is on vibrational spectroscopy where anharmonicities play an important role, it is worthwhile discussing briefly the role of algebraic methods in rotational spectroscopy. Indeed algebraic methods were initially introduced in molecular physics in order to deal with both rotational and vibrational degrees of freedom [3]. The idea here is to quantize the bond variables (vectors) in three-dimensional space. For harmonic oscillators this leads to the introduction of vector creation and annihilation operators

$$\begin{aligned} \mathbf{a}^\dagger &= \frac{1}{\sqrt{2}} \left(\mathbf{r} - \frac{\partial}{\partial \mathbf{r}} \right) \\ \mathbf{a} &= \frac{1}{\sqrt{2}} \left(\mathbf{r} + \frac{\partial}{\partial \mathbf{r}} \right) \end{aligned}$$

and to the associated Heisenberg-Weyl algebra $H(4)$. For anharmonic oscillators this leads to the algebra of $U(4)$. The basis states of the three dimensional Morse oscillator are now characterized by the vibrational quantum number v and the rotational quantum number J . The algebra $U(4)$ describes diatomic molecules for which there is only a vector coordinate \mathbf{r} . Triatomic molecules can be described by introducing two vectors, \mathbf{r}_1 and \mathbf{r}_2 quantized with $U(4) \times U(4)$ and four atomic molecules introducing three vectors $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ [$U(4) \times U(4) \times U(4)$]. The advantage of this scheme is that one treats simultaneously rotations and vibrations and thus one can study situations in which there is coupling between rotations and vibrations. The disadvantages are that although results are obtained by algebraic manipulation, these manipulations increase in complexity as one goes from diatomic to triatomic to four atomic molecules. Beyond four atoms the method becomes intractable. Extensive calculations of linear and bent triatomic molecules [24] have been done as well as of some four atomic molecules [25]. Perspectives in this area are the further study of vibration-rotation interactions and their role in the spectroscopy of small molecules.

6 Perspectives for the algebraic method

In view of its generality, the algebraic method can be used in many circumstances of interest in *Chemical Physics*. There are two main direction for immediate development of the algebraic method.

6.1 Floppy molecules

The method has been used so far mostly for situations in which the potential has a sharp minimum as a function of some coordinate x . However, there is a increasing number of molecules where this condition is not met. The potential in the variable x may be rather flat. These situations are encountered in non-rigid molecules. 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 [26]). For very flat potentials this requires many terms in the expansion (harmonic or anharmonic Morse). 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. The situation in which the Hamiltonian operator is diagonal is called *dynamic* symmetry. The difficulty posed by flat potentials can be overcome by introducing Hamiltonian operators which are not diagonal in either basis harmonic or anharmonic Morse. These more general situations correspond to breaking of dynamic symmetries and have been investigated extensively in the study of atomic nuclei (interacting boson model). The area of non-rigid (van der Waals, quasi-linear, and the like) molecules is one of the main perspectives for the algebraic model in the next few years.

Another area of interest is that of potentials with many minima such as those occurring in torsional oscillations and to molecules with hindered rotations. Preliminary calculations for the latter have been done [27].

6.2 Polymers

A second perspective is provided by the wealth of new experimental information that is being obtained in macromolecules and polymers including biomolecules and biopolymers. The algebraic method here could be particularly useful for vibrational spectroscopy. For finite polymers, results could be obtained by a combination of analytical and numerical methods. For infinite dimensional polymers, $n \rightarrow \infty$, all results must be obtained analytically. A research program in this direction has started [28–30]. In view of its implications to practical applications and to biology, this program is the main perspective for the algebraic model in the 21st century. The algebraic method here could be useful in obtaining analytic expressions for polymer dispersion relations, for calculation of the response of the system to infrared and

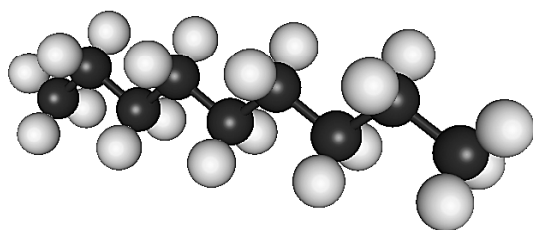


Fig. 7. Ball and stick view of the 9-paraffine molecule, C_9H_{20} .

Raman radiation, and for understanding mode-mode couplings. The preliminary work done so far has been for one-dimensional linear chains. This work has been applied to the study of paraffins [29] (Fig. 7), $CH_3-(CH_2)_{n-2}-CH_3$, and polyethylene. It needs 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). The modification in the spectroscopic information due to folding could also be investigated.

7 Long-range perspectives

Among the long range perspectives, there is the study of reactions between molecules. The algebraic method has been used up to now mostly to study bound state problems. An algebraic treatment of the continuum was suggested some time ago, but it has not been exploited much. There are several problems within reach of the algebraic method in this area:

- (i) the study of resonances in the continuum,
- (ii) the study of bound to free transitions in infrared absorption,
- (iii) the study of bound to free transitions in Franck-Condon processes,
- (iv) the study of molecule-molecule collisions and electron-molecule collisions.

The latter subject was in fact investigated in the early 1990's by a combination of traditional and algebraic methods (the collision process was described by traditional method while the structure was described algebraically). It would be of interest to develop a fully algebraic description.

8 Conclusions

Lie algebraic methods have provided a new tool to *systematically* study problems in *Chemical Physics*. In the last twenty years many molecular systems (small and medium-size molecules) have been analyzed. The perspective in the next few years is the analysis of larger, more complex systems (macromolecules, polymers). The main advantage of

the algebraic method is the introduction of anharmonicities. There are other physical systems where anharmonicities play a role. Among these liquids and surfaces. It would be of great interest to expand the applications of the algebraic method to cover these situations. The basic idea behind algebraic methods is a simplification of the analysis through the use of sophisticated mathematical methods. This simplification becomes more and more useful as the complexity of the system increases. For very complex systems, such as biomolecules and biopolymers another simplification could be brought in by the identification of some relevant degrees of freedom. One could then consider an algebraic description of the relevant degrees of freedom, much in the same way in which it has been done in the study of atomic nuclei [1].

In view of the many possible applications of the algebraic method it is hoped that the present article will stimulate further research, especially in the new areas of complex systems for which alternative methods of analysis are difficult to apply.

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