.

THEORETICAL METHODS FOR ROVIBRATIONAL STATES OF FLOPPY MOLECULES

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INTRODUCTION

Theoretical calculation of rotation-vibration energy levels of polyatomic molecules is a topic with a long history, characterized by a close, symbiotic relationship with molecular spectroscopy on one side and quantum chemistry on the other. What brings them together is the notion of the potential energy surface, which plays a central role in our understanding of the molecular structure and dynamics. In the case of polyatomic molecules, the experimental spectra cannot be inverted directly to yield potential surfaces [see Ref. (1) for some recent efforts within the semiclassical SCF approach], but they do provide a stringent test for the theoretically obtained potential surfaces and observables derived from them. These surfaces, usually from ab initio calculations, seldom meet the standards of spectroscopic accuracy, especially if more extended, high-energy regions are of interest. The only practical way available to test and improve them is by comparing the calculated and the experimental spectra, and minimizing the difference between the two.

The subject of the theoretical treatment of coupled molecular vibrations has undergone a real renaissance in the past decade. Significant conceptual advances have been made, particularly concerning highly vibrationally and

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rotationally excited states, and a variety of new computational approaches have been developed. The recent thematic issues of *Computer Physics Communication* (2) and *Faraday Transactions II* (3) testify to the vitality of this research area.

The resurgence of interest in molecular eigenstates owes a great deal to the extraordinary progress in the experimental techniques such as laser spectroscopy and supersonic molecular beams. This has made possible direct probing, in both time and frequency domains, of entirely new classes of molecules and regimes of rovibrational excitation previously beyond reach.

Floppy molecules, i.e. molecules having one or more large amplitude motion (LAM) vibrations, have attracted an exceptional amount of attention from experimentalists and theorists alike. Most of the effort has been focused on the weakly bound, van der Waals and hydrogen-bonded molecular complexes. Reviews by Nesbitt (4) and Miller (5, 6) summarize the experimental methods, notably the high-resolution infrared (IR) spectroscopy, used to study the weakly bound complexes, as well as the wealth of spectroscopic data concerning their structure and vibrational predissociation dynamics. Weakly bound complexes are by no means the only ones having LAM vibrations. In his review on the IR laser spectroscopy of molecular ions (7), Saykally discusses a number of intriguing polyatomic cations that exhibit a complicated interplay of LAM vibrations and tunneling.

LAM vibrations can be found in the more conventional, strongly bound molecules as well, provided that their vibrational modes are sufficiently highly excited, so that significant portions of the potential surface far from the equilibrium are accessible. Preparation and probing of well-defined highly excited vibrational states can now be achieved with many techniques, such as overtone vibration excitation and IR multiphoton excitation (8), proton energy loss spectroscopy (9), IR spectroscopy of molecular species (in particular H_3^+ and its isotopomers) in ion beams (10), stimulated emission pumping (11), and others (12).

The reasons for the exceptional interest in highly vibrationally and rotationally excited molecules and their large amplitude motions are many. The LAM vibrational states, because of the delocalized nature of their wave functions, contain detailed information about large regions of the potential surface beyond the global minimum. Moreover, while executing LAM vibrations, molecules can populate high-energy local minima inaccessible at lower energies, thus permitting detection of new isomers with strange structures and dynamics. In the case of weakly bound complexes, given their shallow minima and low isomerization barriers, all of this can be achieved by exciting the low-frequency van der Waals modes.

On a more fundamental level, studying excited floppy molecules is challenging and rewarding because it forces us to reexamine, modify, and often abandon many of the basic concepts, formalisms, and computational methods applicable to low-energy, small amplitude vibrations (13) but that become inappropriate with increasing excitation energy and amplitudes of vibrational motions. For example, assigning quantum numbers to vibrational eigenstates—a task that is at the heart of the traditional spectroscopic analysis and depends on some approximate mode separability—becomes increasingly difficult and eventually impossible. It is in this regime that experiments 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 decade [for excellent overviews see Refs. (14, 14a, 15)]. As discussed by Hamilton, Kinsey & Field (11) in their review article on stimulated emission pumping (SEP), highly vibrationally excited molecules, especially ones with LAM vibrations, offer one of the best opportunities for finding experimental manifestations of quantum chaos in molecular spectroscopy or dynamics (11, 16, 17).

Finally, the high-lying LAM vibrational states in many ways fall on the borderline between spectroscopy and chemical dynamics. The energy range in which they lie and the parts of potential surfaces over which they extend are relevant for unimolecular reactions, intramolecular vibrational redistribution (IVR), multiphoton excitation, and laser-molecule interactions in general. Accurate characterization and computation of the LAM rovibrational eigenstates is essential for the quantitative understanding of these and related processes.

The distinct features of the excited LAM vibrational states that make them so interesting and important, like the delocalization over large, anharmonic regions of the potential surfaces and strong coupling to other modes, make the task of calculating their energies and wave functions very difficult. The problem becomes even more complicated if one wants to compute a large number (50–100 or more) of highly excited LAM vibrational states, especially for potential surfaces with several minima separated by isomerization barriers. Approaches based on Watson's normal mode Hamiltonians for bent (18) and linear molecules (19), perhaps best exemplified by the variational method of Whitehead & Handy (20), have been widely used for calculating the low-lying rovibrational states of triatomic molecules. However, the first applications of this method to floppy molecules like CH_2^+ (21, 22) suffered from extremely slow convergence, and even divergence, of the bending energy levels with increasing basis, thus demonstrating clearly that normal coordinates are not appropriate for describing LAM vibrations. Since then, a large amount of

effort has been devoted to devising faster and more accurate methods for determining the rovibrational eigenstates of molecules with LAM vibrations.

This review focuses exclusively on excited large amplitude vibrations. We cover only those advances made in the past couple of years which have been aimed at and tested on floppy polyatomic molecules or weakly bound complexes. Consequently, this is not a comprehensive review of all theoretical methods for finding molecular eigenstates. Also, we do not discuss here the (non-, semi-) rigid bender method of Bunker and co-workers, the first approach designed specifically for large amplitude vibrations. This important work has been thoroughly reviewed by Bunker (23) and Jensen (24). Information about the current status of this method can be found in some recent references (25). The present review is largely, though not exclusively, devoted to triatomic molecules, reflecting the fact that most of the methodological advances and the vast majority of applications have dealt with systems of this size.

Preparation of this article has been made much easier by the existence of two excellent earlier reviews, devoted to topics closely related to our own. The first one, by Carter & Handy (26), reviews in broad terms the status of the variational method for calculating the rovibrational levels of molecules, up to 1986. Emphasis is on the techniques that should work best for the potentials with a deep, single minimum, allowing small to medium amplitude motions. The second review, by Tennyson (27), concentrates on the variational method developed by him and Sutcliffe for calculating the rovibrational spectra of floppy triatomics using the scattering coordinates. Many developments discussed in the present review use some aspects of this work. Since both reviews appear in 1986, we confine ourselves to the literature published since then.

COORDINATE SYSTEMS

The first step in formulating any theoretical treatment of the bound state problem is choosing between space-fixed and body-fixed coordinates. Although the space-fixed coordinates were used in some of the early work on floppy molecules (28, 29), all currently used methods employ body-fixed frames. The body-fixed representation, as recognized long ago in the theory of molecular collisions (30, 31), leads to a description that is simpler than in the space-fixed frame, and allows introduction of several decoupling approximations.

Having decided on the body-fixed frame, one then faces the problem that there is no unique way of fixing the coordinate axes to the molecule. Considerable attention has been given to this issue. For lack of space we

do not address it here but refer the reader to the review by Tennyson (27) and the papers by Tennyson, Sutcliffe and co-workers, who have considered various coordinate embeddings for triatomic (32, 33) and general polyatomic molecules (34).

After elimination of the center-of-mass coordinates and settling on some definition of the body-fixed axes, 3N-6 internal, purely vibrational degrees of freedom remain for a N atom molecule. For the low-lying, small amplitude vibrations, where the normal mode description (13, 18, 19) is adequate, there is no ambiguity concerning the choice of coordinates in which to perform the energy level calculations. The presence of LAM vibrations changes the situation profoundly. There, one realizes soon that the choice of optimal (or at least good) coordinates depends very much on the particular molecule considered, and that there is no single coordinate system that would be satisfactory for all triatomics, let alone larger molecules. Experience has shown that for any given molecule, the convergence rates and the overall quality of the results, whether obtained by the variational or some approximate method, depend strongly on the coordinates used in the calculation. Therefore, we discuss this problem in some length, for the case of triatomic molecules.

Which criteria should an optimal set of coordinates satisfy? First of all, it must span all of configuration space accessible to the system of interest, regardless of the amplitude of nuclear motion. Second, the coordinates should allow taking advantage, in a simple way, of the highest symmetry present in the system. Third, it is desirable that the coordinates be orthogonal, since that minimizes the number of cross terms in the kinetic energy operator, thus making the Hamiltonian simpler to evaluate. In addition, orthogonal coordinates facilitate partitioning of the full Hamiltonian into Hamiltonians of lower dimensionality, which plays an important role in some of the computational strategies discussed below. Finally, the coordinates should be chosen so as to minimize the mode-mode interaction, i.e. make the Hamiltonian as separable as possible. For more discussion of optimal coordinates we recommend the papers by Wallace (35, 36).

Several coordinate systems have been used in the calculations of the rovibrational energy levels of floppy triatomic molecules:

1. *Jacobi, or scattering coordinates*, R, r *and* θ: For a triatomic molecule A–BC, r is the length of BC diatomic bond, R is the distance of atom A to the center of mass of BC, whereas θ is the angle between R and r. Jacobi coordinates are suitable for describing atom-diatom complexes with two LAM vibrations, and for isomerizing systems. For this reason, they have dominated the calculations of floppy molecules. A mass-scaled version of Jacobi coordinates has existed for a long time (37) and has been extensively

used in molecular scattering (e.g. 38). It has only recently been used in (variational) bound state calculations (39, 40). A disadvantage of Jacobi coordinates is that with them it is difficult to take into account symmetries higher than C_{2v}, e.g. D_{3h}, present in A_3 systems.

2. *Hyperspherical coordinates*: A number of related hyperspherical coordinate systems have been developed. The one we mention here is by Pack (41, 42). It consists of a hyper-radius ρ, which defines the overall size of the system, and two hyper-angles, θ and χ, which describe its shape. This coordinate system and its relationship to Jacobi and other hyperspherical coordinates are discussed in detail by Pack & Parker (42). Papers by Johnson (43–45) are also highly recommended. Slightly different hyperspherical coordinates have been used by Frey & Howard (45a) to calculate the ground state energy of some van der Waals trimers. Hyperspherical coordinates, in contrast to Jacobi, do allow use of the full D_{3h} symmetry. Consequently, they are probably the coordinates of choice for highly symmetric systems, such as H_3^+.

3. *Internal, bond coordinates*, R_1, R_2 *and* θ: Here, R_1 and R_2 are the distances from the central atom to the other two atoms, and θ is the angle between the two bond lengths R_1 and R_2. No bound state calculations of floppy molecules have been reported by using these coordinates. But, since there is nothing that would a priori preclude their applications to LAM vibrations, we include them in this list. The internal coordinates are not orthogonal. They are not suitable for atom-diatom complexes or surfaces with multiple minima. Carter & Handy (26) review their variational procedure based on the R_1, R_2, θ coordinates, and numerous applications to the more rigid, strongly bound triatomics.

4. *Radau coordinates*: The two radial, stretching coordinates R_1 and R_2 measure the distance of the two light atoms from the so-called canonical point, which for a light-heavy-light system (e.g. H_2O) lies very close to the center of the heavy atom. The third coordinate θ represents the angle between R_1 and R_2. For the precise definition, the history, and other aspects of Radau coordinates, the paper by Johnson & Reinhardt (46) should be consulted. Radau coordinates are orthogonal; they may be loosely thought of as the orthogonal version of the bond coordinates, especially when light-heavy-light triatomics are considered.

In addition to the coordinate systems discussed above, we mention that Sutcliffe & Tennyson (47) have formulated a generalized coordinate system for triatomic molecules, which includes both Jacobi and bond coordinates as limiting cases. Also, an alternative set of internal coordinates and the corresponding Hamiltonian, applicable to floppy molecules, have been derived by Secrest and co-workers (48, 49).

HAMILTONIANS

For any chosen set of internal coordinates $\{Q_i\}$, the molecular Hamiltonian H can be written in the form (26, 27)

$$H = T_V + T_{VR} + V(\mathbf{Q}),\qquad\qquad 1.$$

where T_V is the purely vibrational kinetic energy operator, T_{VR} is the vibration-rotation kinetic energy operator, and $V(\mathbf{Q})$ represents the potential. For a nonrotating ($J = 0$) molecule, T_{VR} is zero. Derivation of the kinetic energy operators T_V and T_{VR} appearing in Eq. 1, in any coordinate system, is in principle straightforward. It is accomplished by the well-known Podolsky transformation (50). Alternatively, one can use the recently developed and increasingly popular method of Sutcliffe (51). Both approaches involve a lot of tedious algebra. To avoid errors in the derivation, especially for tetratomic and larger molecules, computer codes for symbolic, algebraic manipulation are beginning to be used (52).

Expressions for the full rotation-vibration polyatomic Hamiltonians tend to be quite long, so we prefer not to give them here. The review by Carter & Handy (26) contains detailed derivations of triatomic Hamiltonians in normal and internal (bond) coordinates. Tennyson (27) derives the Hamiltonian in Jacobi coordinates; it is also given by Carter & Handy (26). The triatomic $J = 0$ Hamiltonian in Radau coordinates is presented in the paper by Johnson & Reinhardt (46). Those interested in the Hamiltonian in hyperspherical coordinates are referred to Pack & Parker (42) and Johnson (43-45).

We give here only the $J = 0$ portion of the full triatomic rotation-vibration Hamiltonian in Jacobi coordinates, derived by Tennyson & Sutcliffe (32), since it is essential for our discussion in the later sections. Also, by far the largest number of calculations on floppy molecules, by any of the methods discussed in the present review, have been performed with the Hamiltonian in Jacobi coordinates. For a triatomic molecule A–BC, the $J = 0$ Hamiltonian in Jacobi coordinates can be written as

$$H = -\frac{\hbar^2}{2\mu_1 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2\mu_2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

$$-\frac{\hbar^2}{2}\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + V(R, r, \theta),\qquad 2.$$

where R is the distance from atom A to the BC center-of-mass, r is the BC bond length, and θ is the angle enclosed by R and r. The reduced masses are

$$\mu_1 = m_A m_{BC}/(m_A + m_{BC}), \qquad \mu_2 = m_B m_C/(m_B + m_C). \hspace{2em} 3.$$

The volume element for this Hamiltonian is $d\tau = R^2 r^2 \sin\theta \times dR\,dr\,d\theta$.

For the purpose of later discussion, we find it convenient to partition the Hamiltonian in Eq. 2 as

$$H = h(R, r) + G(R, r) j^2 + V(R, r, \theta), \hspace{2em} 4.$$

where $h(R, r)$ stands for the first two partial derivatives in R and r in Eq. 2, $G(R, r) = (\hbar^2/2)\,(1/\mu_1 R^2 + 1/\mu_2 r^2)$, and j^2 is the angular momentum operator multiplying $G(R, r)$.

Theoretical investigations of floppy molecules with more than three atoms are just beginning. Brocks et al (34) have formulated a Hamiltonian for two interacting polyatomic fragments, as yet not used in any calculation. Treatments of dimers consisting of diatomic molecules (treated as rigid rotors) have been reported (53–55). Hamiltonians appropriate for van der Waals complexes consisting of an atom and a polyatomic molecule (whose vibrational modes are frozen) have been developed (56, 57). Handy (52) has developed Hamiltonians in the internal, bond coordinates for the formaldehyde- and acetylene-like tetratomic molecules.

THE COUPLED-CHANNEL METHOD

Rotation-vibration energy levels of polyatomic molecules can be calculated accurately, without making any simplifying assumptions, by methods that belong to two basic categories. Methods in the first category, which are the subject of the following section, use L^2 basis set representation for all internal degrees of freedom. The desired eigenstates are usually obtained by diagonalizing the Hamiltonian matrix constructed in this basis.

In this section we review the second general approach, which relies on scattering theory. Here, one coordinate is identified as the scattering coordinate R; the remaining degrees of freedom are expanded in a L^2 basis. The Schrödinger equation can then be written as a set of coupled differential equations in R. These are solved with standard techniques of scattering theory, but are subject to the bound state boundary conditions. We illustrate this approach by considering, for simplicity, the $J = 0$ triatomic Hamiltonian in Eq. 2. We rewrite it as

$$H = -\frac{\hbar^2}{2\mu_1 R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial}{\partial R}\right) + U(R, \mathbf{X}), \hspace{2em} 5.$$

where $U(R, \mathbf{X})$ contains all of the terms of Eq. 2 except for the partial derivative in R, and $\mathbf{X}$ stands for the r and θ coordinates. We want to find the bound state solutions of the Schrödinger equation

$$(H - E_i)\Psi_i = 0. \qquad\qquad 6.$$

The wave function Ψ_i is expanded as

$$\Psi_i(R, \mathbf{X}) = R^{-1} \sum_n g_n^i(R)\Phi_n(\mathbf{X}). \qquad\qquad 7.$$

The functions $\{\Phi_n(\mathbf{X})\}$ represent a basis set for the r, θ degrees of freedom, labelled by the collective index n. Substitution of Eq. 7 into Eq. 6, followed by premultiplication by $\Phi_{n'}(\mathbf{X})^*$ and integration over $\mathbf{X}$, results in the standard set of coupled equations. They can be written in matrix form as

$$\left[-\frac{\hbar^2}{2\mu_1} \frac{d^2}{dR^2} I + W(R) - E_i I \right] \mathbf{g}(R) = 0. \qquad\qquad 8.$$

Here, I is the unit matrix and

$$[W(R)]_{n',n} = \int \Phi_{n'}(\mathbf{X})^* U(R, \mathbf{X})\Phi_n(\mathbf{X})\, d\mathbf{X}. \qquad\qquad 9.$$

The coupled-channel equations, such as these in Eq. 8, can be integrated numerically by a variety of methods (54, 58–62), mostly developed for scattering calculations, subject to the boundary conditions $\mathbf{g}(R) \sim 0$ for $R \to 0$ and $R \to \infty$. Usually, the trial eigenvalue, E_i, is varied until the two solutions satisfying boundary conditions at $R \to 0$ and $R \to \infty$ match satisfactorily at some intermediate R, defining E_i and Ψ_i. In the more general $J > 0$ case, the coupled equations in Eq. 8 become more complicated (30, 31), but the methods for solving them remain the same.

In spite of its ability to provide accurate energy levels, the coupled-channel method has been used in but a few bound state calculations of polyatomic molecules (61, 62). Its applications to the rovibrational spectra of floppy molecules have so far been limited to the H_2–H_2 dimer (55), with frozen H_2 bond lengths, and atom-diatom van der Waals complexes (54, 63, 64) in which the diatom has been treated as a rigid rotor. We draw attention to Hutson's calculation of the rovibrational spectrum of Ar–HCl (63). It led, by means of least-squares fitting to far-infrared laser (65) and microwave spectra (66) of Ar–HCl, to the determination of a new intermolecular potential surface for this complex.

No coupled-channel calculations have been reported involving highly excited vibrational states of triatomic molecules with LAM vibrations (whether van der Waals complexes or isomerizing, strongly bound molecules), with all modes included. Therefore, the performance of the coupled-channel method relative to some of the variational methods remains to be established.

OUTLINE OF THE VARIATIONAL APPROACH

The variational method (26, 27, 67) in its basic form is readily defined. For a given rotation-vibration Hamiltonian H and suitably chosen expansion functions $\{\Xi_i\}$, a set of algebraic equations

$$\sum_{j=1}^{N} \langle \Xi_i | H - E | \Xi_j \rangle c_j = 0 \quad i = 1, 2, \ldots, N \qquad 10.$$

is solved by diagonalization yielding the desired eigenvalues and eigenvectors. MacDonald's theorem (68) assures us that the eigenvalues obtained in this way are upper bounds to the corresponding exact eigenvalues.

The size of the rovibrational Hamiltonian matrix grows linearly with J. To prevent the calculation from becoming prohibitively time-consuming, variational treatments have generally been confined to low values of J. Recently, Tennyson & Sutcliffe (27, 69) have implemented a promising two-step procedure, which has already extended considerably the range of Js for which variational calculations are practical. In the first step, they generate eigenstates of the Hamiltonian in which only the off-diagonal Coriolis couplings are neglected (69). Due to the presence of the centrifugal distortion term in the first step, the resulting eigenstates provide a well-adapted and compact basis in which, in the second step, the full rovibrational Hamiltonian matrix is constructed and diagonalized (69).

The dimension of the Hamiltonian matrix to be diagonalized ultimately decides whether a certain rotation-vibration problem is amenable to variational treatment. The factor of crucial importance in determining the size of the Hamiltonian matrix is the choice of basis functions for expanding the internal degrees of freedom. When using Jacobi, bond or Radau coordinates mentioned above, the basis set typically consists of product functions of the form

$$H_m(R_1)F_n(R_2)\Theta_{jk}(\theta)D^J_{Mk}(\alpha, \beta, \gamma). \qquad 11.$$

In Equation 11, $H_m(R_1)$ and $F_n(R_2)$ represent some convenient one-dimensional (single-center), orthogonal functions of the radial coordinates, $\Theta_{jk}(\theta)$ is usually the associated Legendre polynomial, and D^J_{Mk} is the rotational (symmetric top) wave function. We denote this representation in terms of orthonormal L^2 basis functions as the finite basis representation, FBR. In many calculations dealing with low-lying, small amplitude vibrational states, the FBR proved satisfactory (26, 27). However, applications to the excited states of floppy molecules revealed serious deficiencies of the FBR in describing LAM vibrations. This prompted the development of a very different, pointwise representation of the internal degrees

of freedom, the discrete variable representation, DVR (70). Several demanding calculations have demonstrated that the DVR is well suited for molecules with LAM vibrations. In the following two sections we focus on the methodology and applications of the variational approaches to floppy molecules in FBR and DVR, respectively.

VARIATIONAL CALCULATIONS IN THE FINITE BASIS REPRESENTATION

Before reviewing the applications of the variational approach in the FBR to floppy molecules, and the problems encountered, we discuss briefly various choices of angular and radial basis functions.

Angular Basis Functions

By far the most common choice for angular basis functions $\Theta_{jk}(\theta)$ in Eq. 11 are the associated Legendre polynomials or, for $J = 0$, the Legendre polynomials $P_j(\cos\theta)$ (26, 27). With this basis and the expansion of the potential in Legendre polynomials

$$V(R, r, \theta) = \sum_i V_i(R, r) P_i(\cos\theta), \qquad\qquad 12.$$

which is common in both molecular scattering (30, 31) and bound state calculations (26, 27), the angular integration required in evaluating potential matrix elements can be done analytically.

Legendre polynomials have some drawbacks as angular basis sets for general molecular potentials. One problem is that Legendre polynomials provide a "uniform" basis on $(0, \pi)$ and cannot be tailored or optimized easily for any given angular potential. One procedure often used to alleviate this problem is to diagonalize the Hamiltonian in Eq. 2 with the radial coordinates R and r set to their equilibrium values in the Legendre polynomial basis. The resulting eigenstates are used as the new angular (hindered rotor) basis, better adapted to the particular potential (26, 61, 62, 71). An alternative, implemented by Johnson & Reinhardt (46), was to use Jacobi polynomials (of which Legendre polynomials are a special case) as the angular basis. By a judicious choice of their parameters, Jacobi polynomials can be made to emphasize various regions of the angular coordinate (46).

Radial Basis Functions

The one-dimensional basis functions, denoted in Eq. 11 as $H_m(R_1)$ and $F_n(R_2)$, used for representing the radial degrees of freedom fall into two

categories. Basis functions in the first category are numerical functions, obtained by numerical integration of a model (pseudo)diatomic radial Schrödinger equation. The model potential used in such calculations has often been defined by the first, isotropic term of the potential expansion in Eq. 12 (with $r = r_e$) (29, 72), or by choosing a particular angular cut through the potential surface $V(R,\theta)$ (setting θ to some fixed value θ_f) (73). In calculations on anisotropic atom-diatom complexes, both approaches have been found to be rather unsatisfactory, since neither could generate a sufficiently accurate and compact representation for the full problem.

In the second, at present much more popular, category are orthogonal polynomial basis functions, which are analytic solutions of model one-dimensional vibrational problems. Most commonly used are the Morse oscillator wave functions (26, 27). They are defined by the well-known Morse potential, whose parameters r_e, D_e, and ω_e can be optimized to produce a reasonably compact representation for a particular calculation. For molecules such as CH_2^+, for which the linear $R = 0$ structure is accessible, spherical oscillator-like functions have been used for the R coordinate (27, 49). Harmonic oscillator wave functions, although less suitable for excited, anharmonic vibrations, have also been employed in calculating the rovibrational spectra of triatomic van der Waals complexes (74).

Applications

Variational FBR calculations on floppy molecules up to 1986 have been reviewed by Tennyson (27) and, to a lesser extent, by Carter & Handy (26). We therefore confine our attention to the relevant work published since 1985.

The rovibrational spectrum of the H_3^+ molecule and its isotopomers has figured prominently in the work of Tennyson, Sutcliffe and co-workers. They have been particularly concerned with the highly rotationally excited states, as evidenced by the calculations on H_2D^+ for $J = 30$ (75) and $J = 11, 15$ (76), and also on H_3^+ and H_2D^+ for $J = 46$ and $J = 54$, respectively (77). These high J calculations, all performed with the two-step procedure (69), are important because they probe, for the first time, the regime of strong rotation-vibration coupling, where the level spacing within the rotational manifold becomes comparable to typical vibrational excitation. In addition, this group has reported rovibrational calculations of the overtone bands of H_3^+ (78) as well as calculations of the rovibrational transition frequencies and line strengths for H_3^+ (79) and H_2D^+ and D_2H^+ (80). Apart from H_3^+, rovibrational states of HeN_2^+ (frozen N_2^+ bond length) (81), and energy levels and transition intensities for Li_3^+ have been calculated (82).

Lee & Secrest have reported two calculations. In the first (82a), they have obtained the rovibrational states of He_2H^+ and have also investigated the possibility for vibrational bonding in this system. Their second paper (49) deals with the rotation-vibration states of CH_2^+.

Reid, Janda & Halberstadt (74), using model potential surfaces, have calculated the rovibrational energy levels and wave functions of the van der Waals complexes $X–Cl_2$ (X = He, Ne, Ar) (with frozen Cl_2), and compared them with the results of some simple models.

We are aware of only a few papers dealing with the rovibrational spectra of tetratomic and larger floppy molecules that have been published during the period covered by this review. In addition to the difficulty of handling a large number of internal degrees of freedom, a major obstacle to more widespread variational treatment of polyatomic complexes is the lack of potentials accurate enough to justify the effort. Brocks & Huygen (56), using an empirical intermolecular potential and employing many of the computational techniques developed for the triatomic systems, have calculated the low-lying van der Waals modes of the atom-molecule complexes Ar-benzene and Ar-tetrazine. Brocks & van Koeven (57) have introduced a method for calculating vibrational and rotational van der Waals states of atom-large molecule complexes, and have tested it on Ar-fluorene.

Leutwyler & Boesiger (57a) have investigated the microsolvent clusters MR_n, consisting of a large aromatic molecule M such as perylene, tetracene, or pentacene, and n rare gas atoms R. The potential used in this study was represented in terms of pair-wise atom-atom interactions between C and H atoms of M and the rare gas atoms. M was treated as a rigid body with no internal degrees of freedom. The energy levels of the intermolecular, van der Waals modes were mostly calculated by solving 1D vibrational Schrödinger equations separately along x, y, and z coordinates.

Problems

Introduction of novel coordinate systems, basis sets, and innovative computational strategies has made new classes of rotationally and vibrationally excited polyatomic molecules amenable to rigorous, variational treatment. At the same time, extensive applications to floppy molecules have shown that the finite basis representation has several shortcomings. One is slow convergence of the excited LAM vibrational states with respect to the FBR consisting of 1D basis functions given in Eq. 11. It has been noted elsewhere (83) that in representative FBR calculations dealing with excited two-mode (fixed diatom bond length) floppy systems such as LiCN/LiNC (84), HCN/HNC (85), KCN (86), Ar–HCl (87), and HeN_2^+ (81) and three-mode

systems like HCO/HOC (88) and H_3^+ (89–91), the basis set size was typically a factor 10–40 times the number of converged (to ~ 0.5–1 cm^{-1}) vibrational states.

Such convergence rates make straightforward extension of these methods to higher vibrational states and/or higher dimensional systems very problematic. In fact, in most FBR calculations on floppy triatomics to date, one of the vibrations has been frozen, thus reducing the (vibrational) problem to only two dimensions. In the relatively few cases (H_3^+, Li_3^+, CH_2^+) in which all three modes have been considered, FBR calculations have typically converged (to ~ 1 cm^{-1}) for about the ten lowest vibrational states. In addition, evaluation of potential matrix elements, which involves two- or three-dimensional integration, has required a large number, 10–20, of Gauss quadrature points per dimension, thus making such evaluation computationally very demanding.

The origins of the above problems have been traced (83) to the FBR itself. The variational methods discussed so far have invariably employed products of 1D Morse, harmonic, or numerical oscillator functions to represent the radial coordinates (26, 27). To understand the reasons for their inadequacy when dealing with anisotropic systems having LAM vibrations, it is useful to take a look at Figures 1 and 2. Figure 1 shows a contour plot of the HCN/HNC potential surface (92), while Figure 2 shows three 2D (R, r) cuts made at different angles through the same surface. Strong potential anisotropy is evident in both figures. It is also clear from Figure 2 that radial functions optimized for any one of the 2D (R, r) cuts will provide a poor basis for the cuts at other angles. To compensate for that, a large radial basis is needed. High-order polynomial functions present in a large FBR basis cause the integrands in the potential matrix element integrals to be highly oscillatory, thus making necessary the use of many quadrature points for their evaluation.

The problems just discussed are inherent to the FBR. This suggests that the FBR, although adequate for small amplitude vibrational states, is not the optimal choice for describing delocalized, LAM vibrational states of anisotropic systems. An alternative approach, in which the single-center oscillator basis is abandoned altogether, is described below.

VARIATIONAL AND ADIABATIC CALCULATIONS IN THE DISCRETE VARIABLE REPRESENTATION

The discrete variable representation, DVR (70), is a basis consisting of N discrete points. It is related by a unitary transformation to a set of N L^2 basis functions that constitute the familiar finite basis representation, FBR. The DVR appeared first as a strictly numerical technique for evaluating
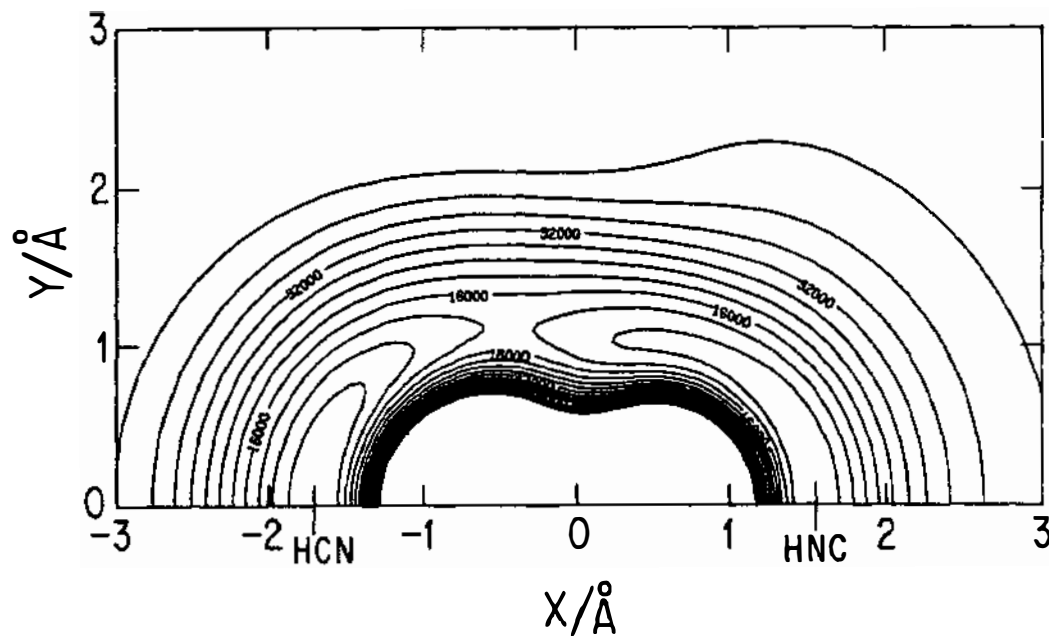
Figure 1 Contour map of the HCN/HNC potential surface by Murrell et al (92) for $r_{CN} = 1.16$ Å (roughly the average of CN bond lengths in the equilibrium HCN and HNC). Contour interval is 4000 cm^{-1}. Reproduced with permission from the *Journal of Chemical Physics*.
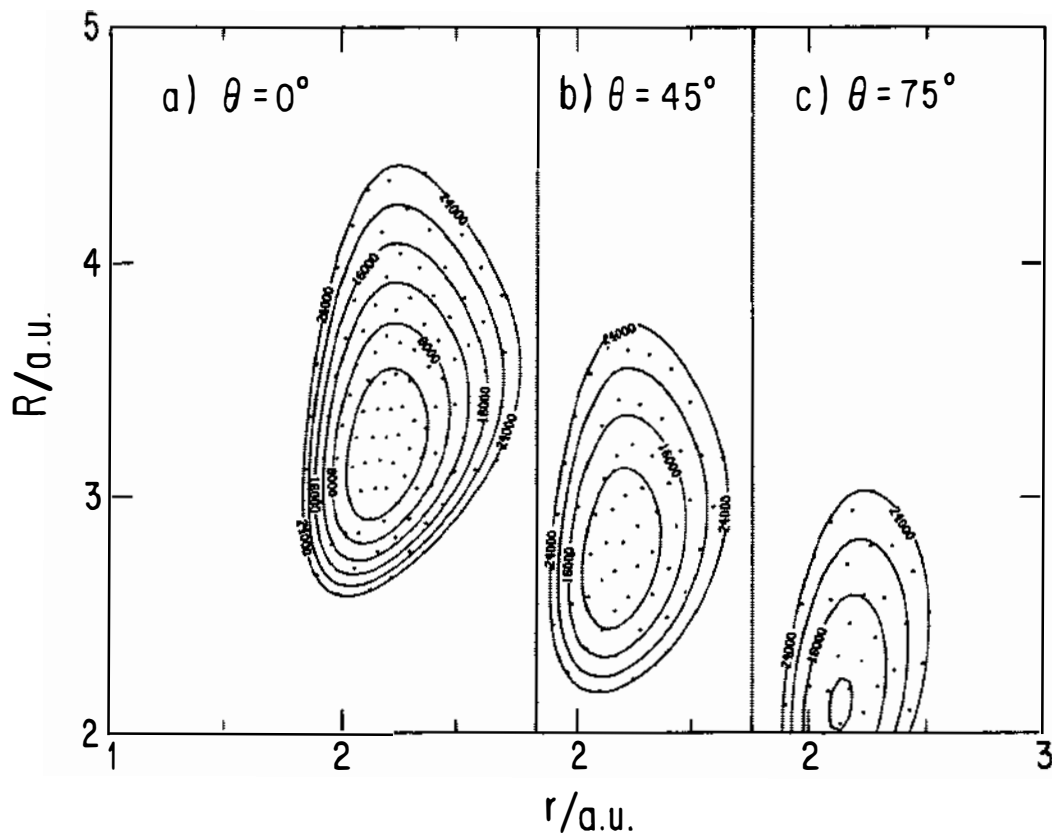
Figure 2   Three typical 2D (R, r) cuts through the HCN/HNC potential surface of Murrell et al (92). Notice how the shapes of the cuts and the positions of the 2D minima vary strongly as a function of angle θ. Also shown are the centers (●) of the 2D distributed Gaussian bases on these cuts [from Ref. (100)]. Reproduced with permission from the *Journal of Chemical Physics*.

potential matrix elements (93). Dickinson & Certain (94) provided the formal basis for the technique, and proved that the discrete points of the DVR were in fact the points of the Gaussian quadrature defined by the corresponding FBR. It has been established only recently that the DVR (70, 83, 95–97), or the equivalent discrete ordinate method (98, 99), can be the representation of choice for formulating and solving more easily a wide range of quantum mechanical problems. Since the basic formalism of the DVR for one dimension has been presented in several papers (70, 98, 99), we state here only two results that are useful for later discussion.

It has been shown (94) that the matrix T of the orthogonal transformation between representations in N Gaussian quadrature points $\{\chi_\alpha\}$ (DVR) and representations in N orthogonal polynomials $\{\phi_i(\chi)\}$ times their weight functions $\{\omega_\alpha\}$ is given by

$$T_{i\alpha} = \omega_\alpha^{1/2} \phi_i(\chi_\alpha).$$ 13.

Also, provided that the elements of the potential matrix in the FBR, V^{FBR}, have been evaluated using the appropriate N point Gaussian quadrature, one can show that

$$(T^T V^{FBR} T)_{\alpha\beta} = V(\chi_\alpha)\delta_{\alpha\beta} = (V^{DVR})_{\alpha\beta},$$ 14.

i.e. that the potential matrix in the DVR, V^{DVR}, is *diagonal* on the Gaussian quadrature points constituting that DVR. The matrix T appearing in Eq. 14 is defined in Eq. 13. In one dimension, the greater efficiency of the DVR relative to the FBR is largely due to this property of the DVR. In higher dimensions, other advantages appear, as described below.

Within the DVR-based formulation of the bound state problem, a number of complementary computational schemes have been developed (83, 100–104). They can be implemented in any coordinate system in which suitable orthogonal polynomials are defined, so that the DVR transformation in Eq. 13 can be defined. Consequently, it is possible to choose a combination of strategies and coordinate systems that would be most appropriate for a particular molecule. All of the applications to date have involved triatomic molecules, but the same DVR techniques should be applicable to, and perhaps even more important for, larger molecules. Concerning triatomics, there is the possibility of treating one, two, or all three internal coordinates in the DVR. Strategies for doing this are discussed below.

If only one or two internal coordinates are discretized via the DVR, then another basis is needed for the remaining degrees of freedom. We have chosen the distributed (real) Gaussian basis, DGB (105), one- or two-dimensional, depending on the number of coordinates to be represented

by the DGB (83, 100–102). The 2D DGB, used in several studies (83, 100–102, 106) to expand the radial r, R coordinates is given by

$$\phi_i = (1/S_{ii})^{1/2}(2A_i/\pi)^{1/4}(2a_i/\pi)^{1/4}\exp[-A_i(R-R_i)^2-a_i(r-r_i)^2], \qquad 15.$$

where S_{ij} is the overlap between any two Gaussians (83, 100). R_i and r_i define the center of the ith Gaussian, whereas A_i and a_i are the Gaussian exponents. Having defined the necessary ingredients, we now proceed to describe several DVR-based schemes.

DVR–DGB Approach

In this approach, thus far implemented in Jacobi (83, 100, 106) and Radau coordinates (101), the usual set of $j_{max}+1$ coupled-channel equations in the FBR (j_{max} refers to the highest order term in the Legendre polynomial expansion of the angular coordinate) is transformed to the DVR appropriate to Legendre polynomials (83, 100). The LAM angular, bending coordinate χ ($\chi = \cos\theta$) is thereby discretized on a set of points χ_α defined by the $(j_{max}+1)$-point Gauss-Legendre quadrature. On the 3D potential surface $V(R,r,\theta)$, each of the discrete angles χ_α defines a 2D (R,r) cut $V(R,r,\chi_\alpha)$, shown in Figure 2. A two-dimensional DGB, defined in Eq. 15, is distributed on the (R,r) cuts. The Gaussians are placed according to some simple rules regarding the overlap and the exponents A_i and a_i in Eq. 15 (83, 100), resulting in a semiclassical distribution of Gaussian centers, which can be seen in Figure 2. Combining the DVR with the 2D DGB produces a very flexible basis that, in contrast to the FBR, handles easily even strongly anisotropic potentials with multiple minima. It may also be noticed that the DGB is readily tailored to the potential, i.e. it can be distributed *only* over the *relevant* regions of the potential surface, defined by the maximum energy of interest.

At each χ_α, separate matrix representations of the operators $h(R,r)$, $G(R,r)$ and $V(R,r,\chi_\alpha)$, which appear in Eq. 2, are formed in the 2D DGB. The corresponding matrices h and V are block-diagonal in χ_α (V because of Eq. 14); we denote their respective diagonal blocks as h^α and V^α. In the DVR-DGB triatomic Hamiltonian, different χ_αs are coupled only by the transformed angular momentum matrix $T^T j^2 T$ (83, 100).

At this point, the DVR formalism provides a unique way to truncate the DGB, thus decreasing drastically the size of the final Hamiltonian matrix (83, 100, 101). For each of the $j_{max}+1$ χ_αs of the Legendre DVR, a 2D Hamiltonian (which depends on R, r only) is defined

$$H^\alpha - h^\alpha + V^\alpha, \quad (a - 1, 2, \ldots, j_{max}+1), \qquad 16.$$

and diagonalized. A subset of eigenvectors of H^αs, whose eigenvalues lie below a certain energy cutoff (related to the maximum energy of interest),

serves as the final, much reduced radial basis in which the full Hamiltonian matrix is formed and diagonalized, thus yielding the desired molecular eigenstates. Experience has shown that including only a small fraction of the total number of eigenvectors of H^*s is sufficient for obtaining converged and accurate final results (83, 100, 101).

An additional benefit of treating the angular coordinate in the DVR is that, as a consequence of Eq. 14, no angular integration is required to evaluate the potential matrix elements. Besides lowering the dimensionality of the integrals, this also eliminates the need for potential surface expansion in Legendre polynomials, given in Eq. 12, which is commonly done in the FBR in order to facilitate integral evaluation and which, in the case of anisotropic potentials, can be a difficult task in itself.

Multidimensional DVR Approach

We have already mentioned the possibility that not only one, but two, or all three internal coordinates (for a triatomic molecule) can be treated in the DVR. At the present time, multidimensional DVRs are really direct product DVRs, based on direct product FBRs consisting of 1D basis functions. Therefore, the multidimensional FBR-to-DVR transformation matrix is a direct product of 1D transformation matrices in Eq. 13 (102, 104, 107).

The multidimensional DVR has several attractive features (102, 104, 107). In the 3D DVR, which is a completely pointwise representation, only those DVR points lying in the relevant, energetically accessible part of the potential surface need to be retained; the rest can be removed from the basis. In addition, there are no numerical integrals to be calculated in the 3D DVR. In order to evaluate potential matrix elements, only the values of the potential at the DVR points are needed. This feature is also shared by the recently proposed collocation method for solving bound state problems (108, 108a, 108b).

In the DVR-DGB procedure described above, the DVR allowed an initial partitioning of the full 3D Hamiltonian into a set of 2D Hamiltonians. If two or three coordinates are treated in the DVR, this process can be carried one step further. By applying the second DVR, each of the 2D Hamiltonians can be decomposed into a set of 1D vibrational problems. A truncated set of 1D eigenvectors is then used as the basis for the 2D Hamiltonians. As in the DVR-DGB approach, these 2D Hamiltonians are diagonalized; a truncated set of their eigenvectors is then recoupled exactly to generate the final, full Hamiltonian matrix. This successive diagonalization-truncation procedure, which has two levels of truncation, is very effective in decreasing the size of the final basis (102, 104, 107). The extra work needed to generate the 1D and 2D eigenvectors

is compensated by an impressive reduction of the final Hamiltonian matrix. We note also that the 2D or 3D DVR makes the initial Hamiltonian very sparse, since only "one-dimensional" kinetic energy coupling is present for each of the two or three dimensions.

Adiabatic Approximation in the DVR

In addition to the novel variational techniques described above, the DVR permits a definition of the adiabatic approximation (106), which has several important advantages over the usual formulation in the FBR (109).

The development begins with the realization that the 2D Hamiltonian H^α in Eq. 16 is in fact the adiabatic two-mode stretching Hamiltonian for a particular angle χ_α (100). Consequently, its eigenvalues represent the energies of the stretching vibrations of the triatomic system, at that χ_α, in the adiabatic bend approximation. As a function of χ ($\chi = \cos\theta$), these eigenvalues in turn provide effective angular potentials for the bending motion.

In the DVR approaches discussed above, the entire matrix formed in the 2D eigenvector basis was diagonalized to provide variational estimate to the vibrational eigenstates. We have shown (106) that an adiabatic rearrangement of this full Hamiltonian matrix can be defined, such that the diagonal blocks (labelled by the eigenvalues of the 2D Hamiltonians in Eq. 16) provide the rigorous matrix representation of the adiabatic bend Hamiltonian. Their diagonalization yields progressions of bending levels corresponding to various stretching states.

The off-diagonal blocks of the adiabatically rearranged full Hamiltonian matrix contain all nonadiabatic coupling matrix elements. The non-adiabatic correction to the adiabatic vibrational levels can be readily, and very effectively, taken into account via second-order perturbation theory (106). In this approach, the vibrationally nonadiabatic matrix elements are calculated just as easily as the adiabatic ones. This is not the case with the adiabatic approximation in the FBR (109). There, the presence of derivatives of the radial wave function with respect to the angular coordinate makes the evaluation of nonadiabatic corrections difficult, and is seldom done.

Applications

The DVR-based bound state methods are just a few years old (83), and the number of their applications has not been particularly large. However, almost every one of them has addressed a problem that would be extremely difficult, or even intractable, for the FBR variational or adiabatic methods.

Bačić & Light (100), using the DVR-DGB method (83), have performed the first full three-mode variational calculation of the highly excited, LAM

vibrational ($J = 0$) states of HCN/HNC, including states above the isomerization barrier, which show varying degrees of delocalization over both potential minima. Jacobi coordinates and a model, empirical surface by Murrell, Carter & Halonen (92), shown in Figure 1, were employed. Previously, the LAM vibrational spectrum in this energy range important for isomerization could be studied only by approximate methods (23, 24). In addition to producing well over 100 accurate energy levels and wavefunctions, this study has shown that the onset of extensive delocalization over the isomerization barrier is determined by the height of the effective, adiabatic potential, which is more than 2000 cm^{-1} higher than the "bare" potential barrier (100).

The adiabatic approximation has been formulated in the DVR and applied to the two-mode LiCN/LiNC (frozen CN) and three-mode HCN/HNC (106). The accuracy of the adiabatic calculation on LiCN/LiNC relative to the variational DVR-DGB results (83), and the striking improvement caused by including the nonadiabatic correction, can be seen in Figure 3. It is evident that after including perturbatively the nonadiabatic correction, this approach can provide accurate characterization and quantum number assignment for a significant fraction of highly excited LAM states, including the localized states above the isomerization barrier (106).

Bačić, Watt & Light (101) have calculated variationally, in Radau coordinates, the vibrational levels of the (three-mode) water molecule up to $\sim 27{,}000$ cm^{-1} relative to the potential energy minimum. The DVR adiabatic-plus-perturbation treatment (106) has permitted reliable level assignment up to $\sim 18{,}000$–$20{,}000$ cm^{-1}.

HCN/HNC (100) and H$_2$O (101) are the first realistic three-mode systems for which the number of accurately calculated energy levels (> 100) was large enough to allow their analysis in terms of the level spacings distributions. This statistical measure figures prominently in the theories of classical and quantum ergodicity (11, 15).

Converged energy levels of $J = 0$ H$_3^+$ up to 20,000 cm^{-1} above the potential energy minimum (higher than in any previous H$_3^+$ calculation) have been reported by Whitnell & Light (104). Their calculation was performed in the hyperspherical coordinates of Pack (41, 42) with the 3D DVR and the successive diagonalization-truncation technique (102, 104, 107).

The 3D DVR employed in the above H$_3^+$ calculation was adapted for the full D_{3h} symmetry of this molecule by the procedure for constructing symmetry-adapted DVRs developed by Whitnell & Light (103). This allowed separate calculations for each of the three irreducible representations of H$_3^+$ and automatic, unambiguous symmetry assignment for all the calculated levels.
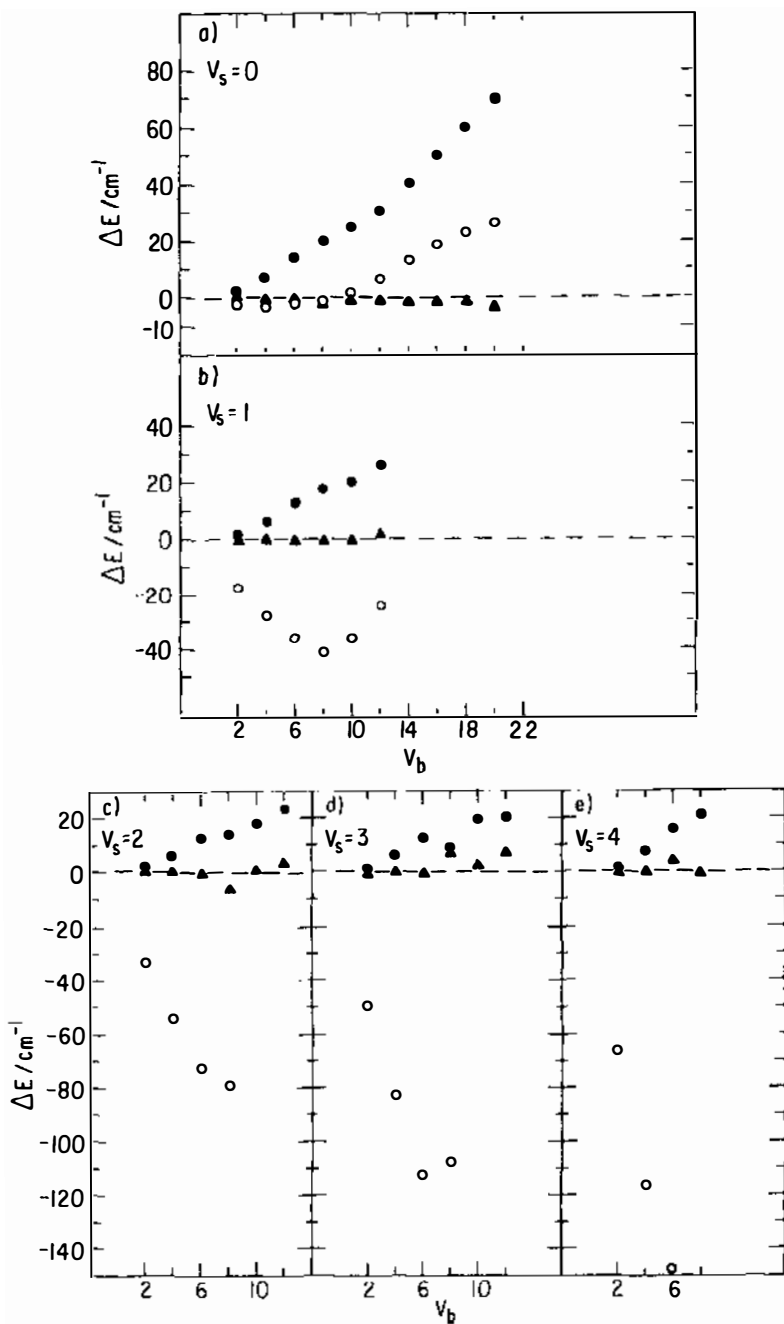
The DVR calculations described here, carried out in several coordinate systems and using different computational schemes, testify to the versatility and power of the DVR-based bound state methods when dealing with highly excited, LAM vibrations in strongly anisotropic, isomerizing, and other floppy molecules.

OTHER METHODS

Recursive Residue Generation Method

The absorption spectrum $I(\omega)$ from an initial state $|0\rangle$ is given by

$$I(\omega) = \sum_{\alpha} |\langle 0|\mu|\alpha\rangle|^2 \delta(\omega - \omega_{\alpha}), \qquad 17.$$

where μ is the dipole operator, and $\{|\alpha\rangle\}$ and $\{\omega_{\alpha}\}$ are the eigenvectors and eigenfrequencies, respectively, of the molecular Hamiltonian. The recursive residue generation method (RRGM), is a quantum mechanical method for calculating eigenvalues and residues $|\langle 0|\mu|\alpha\rangle|^2$ of the propagator associated with the time-independent Hamiltonian (111). It is based on the Lanczos algorithm (112) for finding the eigenvalues of sparse matrices. The computational power of the RRGM comes largely from its ability to focus on one row of the eigenvector matrix, consisting of the projections of the initial state onto the eigenvectors, rather than on the whole eigenvector matrix (111). An important feature of the RRGM calculations of spectra is that the most intense transitions are determined quite accurately after relatively few Lanczos recursion steps. Calculation of weaker lines requires many more recursions and is much more time consuming (113).

Very recently, Brunet et al (113), in the first RRGM calculation of the IR absorption spectrum of a realistic three-mode system, calculated vibrational ($J = 0$) eigenvalues and transition intensities of HCN, using the potential surface of Murrell, Carter & Halonen (92) and the ab initio calculated dipole surface of Jørgensen et al (114). Their calculation extended up to $\sim 12,000$ cm^{-1} relative to the zero point energy of HCN. This energy range has also been covered by the variational DVR-DGB calculation (100) on the same potential surface, so that the results of the two calculations can be compared directly. Most energy levels agree to

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Figure 3 Differences between the adiabatic (●) and adiabatic-plus-perturbation (▲) calculations of the vibrational levels of LiCN (106) and the accurate variational results (83). Results of the adiabatic calculations in the finite basis representation (110) are shown for comparison (○). Symbols V_s and V_b label the stretch and the bend quantum numbers, respectively. Reproduced with permission from the *Journal of Chemical Physics.*

within 2–3 cm^{-1}. Energies of some 15 RRGM-calculated states (out of 93 reported) do differ by 3–10 cm^{-1} from the levels calculated with the DVR-DGB method (100). The reasons for these differences are not clear at this point. They could be caused by some slight inadequacy of the (radial) basis used in the RRGM calculation. Expansion of the highly anisotropic HCN potential surface in terms of Legendre polynomials, done by Brunet et al (113) but not in the DVR-DGB calculation, could conceivably contribute to the differences.

Because the RRGM focused on determining the excitation spectrum from the ground state, the number of vibrational states that the two calculations find below 11,907 cm^{-1}, the energy of the highest state reported by Brunet et al, differs substantially. There are 114 variationally calculated excited states in this energy range (100), whereas Brunet et al (113) find transitions to only 93. The majority of the states not found by the RRGM are in the high-energy part of the calculated spectrum. From the group of 33 variational states $n = 82$–114, only 14 are found in the RRGM calculation. This means that the RRGM, at least for this choice of the initial state, fails to locate a significant fraction of the LAM vibrational states below and above the isomerization barrier (including the $n = 93$ state, the first to be extensively delocalized over both minima). Choice of a different initial state, perhaps one prepared by SEP (11), which would overlap better with highly excited LAM states, may lead to their detection by the RRGM.

Thus, the fact that the effort required from the RRGM to calculate a transition depends primarily on the intensity of the line and not its energy, represents both its strength and weakness. Strong, high-frequency transitions that, because of their energies, may be difficult to calculate variationally, are readily determined by the RRGM. On the other hand, the RRGM may miss entirely the weak lines, even at lower frequencies, that would be easily calculated variationally.

These differences notwithstanding, the RRGM is undoubtedly a promising new method for calculating molecular spectra and should be developed and tested further. It may be especially useful for the high energy portion of the spectrum, which may stretch the limits of the variational approach.

Semiclassical Quantization

In recent years there has been a great deal of interest in developing semiclassical quantization techniques for calculating bound states of multimode systems (115). In spite of such interest, few attempts have been made to calculate vibrational eigenvalues of polyatomic molecules with LAM vibrations by means of semiclassical quantization. One reason may be that

the current semiclassical methods of quantization are restricted to regular, quasiperiodic regions of phase space (115). Vibrational states of floppy molecules are very anharmonic, and the mode coupling is strong, characteristics that tend to make the underlying classical mechanics chaotic and hence make floppy molecules rather poor candidates for successful semiclassical quantization.

Smith & Shirts (116), using the semiclassical technique of adiabatic switching, have calculated some vibrational eigenvalues of the three-mode HCN/HNC for the surface by Murrell, Carter & Halonen (92). This has allowed comparison with the variational DVR-DGB calculation (100), which employed the same surface. Judging from the limited number of eigenstates reported by Smith & Shirts (116), the agreement is semiquantitative at best. The differences grow fairly rapidly with increasing excitation of the LAM bending mode. With two quanta in the bend mode, the difference is $\sim 10 \text{ cm}^{-1}$, rising to $\sim 16 \text{ cm}^{-1}$ with four quanta. Since there are many HCN and HNC states below the top of the isomerization barrier with 8, 10, or more quanta in the bending mode (100, 106), semiclassical quantization via adiabatic switching does not appear to provide an accurate description of the most interesting LAM vibrational states near the top or above the isomerization barrier.

Applicability of semiclassical quantization methods to floppy molecules in general cannot be judged from the results of one application. More studies on systems with LAM vibrations that employed a variety of quantization schemes would be of interest.

Optimal-Coordinates Vibrational Self-Consistent Field Method

In applications to realistic multimode systems, additional approximations are often introduced in the rigorous semiclassical quantization approach. The self-consistent field (SCF) approximation (117–119) has been among the more successful and widely used ones. In this approach, each vibrational mode moves in an effective potential that is the average of the full potential over the states of the other modes, all modes being treated self-consistently. The assumption central to the SCF approximation is separability, i.e. that the total vibrational wave function can be written in the Hartree form, as a single product of single-mode functions. This leads to a set of coupled single-mode SCF equations (117–119), which can be solved either quantum mechanically (117) or, in the semiclassical (SC) limit, by applying the Bohr-Sommerfeld quantization condition to the single-mode energies (118, 119). Here, we are concerned with the latter, SC-SCF method.

The quantitative success of the SCF method in any particular application

depends on the choice of coordinates (118). Nowhere has this dependence
been found to be so strong as in the case of excited LAM vibrations. The
SC-SCF study by Bačić, Gerber & Ratner (120) of the coupled bending-
stretching energy levels of HCN (frozen CN) represented the first appli-
cation of the SCF approximation to highly excited LAM vibrations. The
focus was on high excitation of the bending mode, because of its association
with HCN/HNC isomerization. Physical intuition suggested that in the
case of highly excited bending vibrations, a good choice of coordinates
might be the one providing good description of the motion along the
minimum energy path (MEP) for isomerization. Inspection of the potential
surface used in the calculation (92), shown in Figure 1, revealed that the
MEP can be roughly described by an ellipse.

This finding suggested the use of ellipsoidal (or spheroidal) coordinates
for the HCN calculation, in which the position of the H atom is determined
by two distances, r_1 and r_2, from the two foci on the CN axis (120).
The interfocal distance provided a parameter a that could be varied to
determine ellipsoidal coordinates optimal for a particular stretching-bend-
ing state. The importance of coordinate optimization in the SC-SCF ap-
proach is evident from Figure 4, in which several energy levels are plotted
versus a. Clearly, coordinate optimization always improves the SCF re-
sults, but in highly excited bending states, the improvement due to optimiza-
tion is quite dramatic, and the use of optimal coordinates appears to be essen-
tial. Moreover, the optical value of a varies considerably from one state to
another. Thus, the choice of optimal coordinates depends not only on the
molecule studied, but also on the degree of vibrational excitation (120).

Ellipsoidal coordinates have been found to be the most suitable for SC-
SCF calculations on I_2He (121) as well, where the large amplitude motion
of the He atom is similar to that of the hydrogen atom in HCN. The
ellipsoidal SCF energy levels were within ~ 1 cm^{-1} of the levels from
converged CI calculations. In the same paper, a very floppy system $XeHe_2$
was also studied. In this case, hyperspherical coordinates proved to be the
optimal choice (121).

It is clear that consideration of factors such as mass ratios and topology
of the potential surfaces can provide valuable guidance in selecting optimal
coordinates for specific applications. Nevertheless, there is a need for a
general algorithm for finding optimal coordinates that would not rely on
intuition.

CONCLUDING REMARKS

Significant advances have been made in recent years in the theoreti-
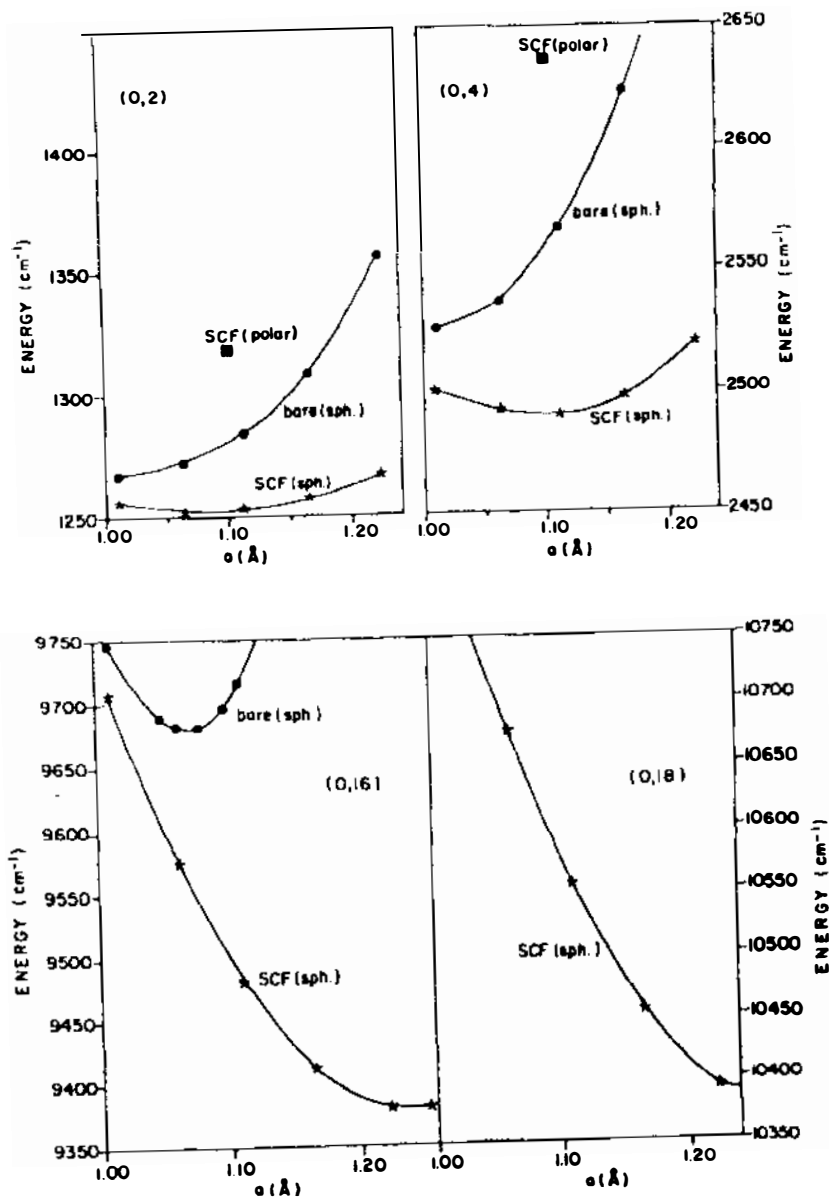cal treatment of rotation-vibration spectra of floppy molecules. Novel

Figure 4   Optimal-coordinate behavior of the SC-SCF energies of the $(0, 2)$ and $(0, 4)$ states (*top*), and the $(0, 16)$ and $(0, 18)$ states (*bottom*). The spheroidal results are plotted versus a, the spheroidal coordinates parameter (half of the interfocal distance). Also shown are the bare-mode results versus the same parameter, and the polar coordinates SCF results (*top*). From Ref. (120).

distributed, pointwise representations have been developed that are more appropriate for delocalized wave functions of large amplitude vibrational states than the usual bases. In the case of floppy triatomic molecules, a large number of excited vibrational states, including those delocalized over multiple minima that may be present on the potential surface, can now be calculated variationally with modest computational effort.

New computational procedures have also allowed variational calculations of rovibrational energy levels of floppy triatomics with very high values of the total angular momentum, where rovibrational interaction is strong and rotational manifolds from many vibrational states overlap. Methodology for dealing with bound states of tetratomic and larger floppy molecules is in the early stages of development but will undoubtedly be an important direction of future efforts. The theoretical treatment of large amplitude vibrations should be generalized to include electronically non-adiabatic bound states, which are receiving increasing attention from experimentalists.

The progress in theoretical methods has coincided with the emergence of several new spectroscopic techniques with unprecedented power to probe directly highly excited, large amplitude vibrational states of molecules and weakly bound clusters. Combined advances in theory and experiment will enable a determination of accurate potential surfaces, including regions far from the equilibrium configuration.

ACKNOWLEDGMENTS

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