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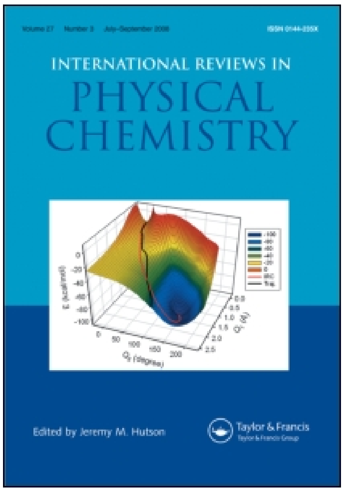

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Variational and perturbative descriptions of highly vibrationally excited molecules

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Variational and perturbative descriptions of highly vibrationally excited molecules

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Two theoretical approaches to the calculation of the highly excited vibrational states are reviewed. Particular emphasis is placed on the choice of coordinates, and the ramification this choice has on the quality of the ensuing calculations. The essential ingredients of variational calculations are highlighted via four illustrative calculations. The standard approach of using a product basis of harmonic oscillators based on a rectilinear normal mode framework is discussed using the work of Maessen and Wolfsberg. The improvements to this basis are presented within the context of the calculation of Romanowski *et al.* in which a self-consistent-field basis is employed. Bond-angle coordinates and the advantages they provide are demonstrated. This discussion focuses on the efficient algorithms which Carter and Handy developed for evaluating eigenvalues and eigenvectors of tri- and tetra-atomic molecules. For yet larger amplitude motion, associated with 'floppy' molecules, the combination of Jacobi coordinates and the discrete variable representation are reviewed in the context of a study of the eigenstates of HCN/HNC by Bačić and Light. Perturbative approaches are also considered. In particular, the application of canonical Van Vleck perturbation theory in a superoperator framework using curvilinear coordinates is reviewed. This section draws chiefly from the work of Sibert, McCoy, and Fried and Ezra.

1. Introduction

The accurate description of highly excited vibrational states is an essential step towards furthering the chemist's ability to model theoretically the dynamics and spectroscopy of polyatomic molecules as well as to elucidate the properties of potential energy surfaces, the features of which control dynamics and spectroscopy. Some important examples for which the nature of highly excited states is relevant include the Rice–Ramsberger–Kassel–Marcus (RRKM) theory of kinetics (Robinson and Holbrook 1972), multiphoton excitation (King 1982, Quack 1982), overtone-induced reactions (Crim 1984), mode-selective effects (Bloembergen and Zewail 1984, Butler *et al.* 1986, McIlroy and Nesbitt 1989) and collisional energy transfer (Haub and Orr 1987, Parson 1989). For this reason a great deal of interest is and has been directed towards developing new methods of obtaining vibrational eigenvalues and eigenfunctions. The objective of this review is to bring together some of the novel theoretical advances which have been achieved in this area of research.

Almost all of the early investigations of molecular rotation–vibration spectra were made within the normal mode framework. This is not a surprising result, given the computational tools available during the first half of this century. Normal modes provide an excellent description of semi-rigid molecules at low levels of excitation. In this energy regime the molecular vibrations behave as weakly coupled harmonic oscillators; hence the perturbative analyses, based on a zero-order picture of uncoupled

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harmonic oscillators, such as those found in the early work of Darling and Dennison (1940), produce relatively accurate expressions for the eigenvalues,

$$E=\sum_i \hbar\omega_i(n_i+\tfrac{1}{2})+\sum_{i\geqslant j}\chi_{ij}(n_i+\tfrac{1}{2})(n_j+\tfrac{1}{2}), \tag{1}$$

as a function of the vibrational quantum numbers, with a minimal amount of computation.

At higher levels of excitation, the accuracy of these expressions breaks down. The perturbative approach must be pushed to higher order in order to remedy this shortcoming. One practical problem in this regard is the vast amount of tedious algebra required for the higher order perturbative expansions. Algebraic manipulation routines such as MACYSMA, have proven to be very effective tools in this regard (Swimm and Delos 1979, Jaffe and Reinhardt 1979, 1982, Shirts and Reinhardt 1982, Sage and Child 1989); so too have C (Fried and Ezra 1987, 1989) and FORTRAN (Sibert 1986, 1988a) codes. Another difficulty with perturbative approaches is that an expansion of the potential in a Taylor series about the equilibrium configuration has an unsatisfactory radius of convergence, this leading to asymptotic behaviour in the perturbative expansions. This difficulty can in part be overcome through the use of curvilinear coordinates rather than the rectilinear normal coordinates which have been traditionally used in perturbative calculations. Two alternatives for the bond extension coordinate, ΔR_i, are either Simons–Parr–Finlan (SPF) coordinates, $\rho_i=\Delta R_i/R_i$, (Simons *et al.* 1973, Carney *et al.* 1978), where R_i is the bond length, or Morse coordinates, $y_i=[1-\exp(-a_i\,\Delta R_i)]$ (Coolidge *et al.* 1938, Efremov and Zhirnov 1980, Sage and Williams 1983, Halonen and Carrington 1988). Not only can the potential be expressed in these coordinates as a low-order Taylor series expansion, but the full Hamiltonian can be expressed as a low-order expansion of these coordinates and conjugate momenta (Cooper 1987); hence these coordinates provide an attractive alternative representation in which to formulate perturbation theory, as shown by Baggot (1987) and McCoy and Sibert (1989). Although the latter part of this review will address some recent progress which has extended the applicability of perturbation theory, the larger fraction of it focuses on some of the other methods which have been developed in order to overcome the difficulties of perturbation theory.

A partial list of alternative methods includes semiclassical quantization, Monte Carlo, and linear variational methods. Of the semiclassical methods, two of the most promising have recently been reviewed and hence will not be considered here. They are adiabatic switching, reviewed by Skodje and Cary (1988) and Reinhardt (1989), and spectral quantization, reviewed by Ezra *et al.* (1987). From scaling arguments, Monte Carlo methods have the brightest outlook for extensions to many degrees of freedom. For tri- and tetra-atomic molecules, however, this method (Caffarel *et al.* 1989) does not achieve the level of accuracy provided by variational calculations, for a given amount of computational effort. For these reasons this review focuses on the linear variational method.

The structure of the review is as follows. We begin with a description of variational approaches in normal coordinates, bond-angle coordinates, and Jacobi coordinates. For each of these coordinates, we focus on the relative advantages offered by each representation as well as the quality of the various approximations that are often applied. Our discussion of the normal coordinates borrows both from the excellent review of Carney *et al.* (1978) and a study by Maessen and Wolfsberg (1984) in which many of the ideas presented in the review of Carney *et al.* are applied to H_2CO

vibrations. The work of Maessen and Wolfsberg is then contrasted to the more recent study of Romanowski *et al.* (1985) who employ a more sophisticated, iteratively obtained self-consistent-field basis (SCF) set.

The discussion of variational calculations is extended to bond-angle coordinates, which are more appropriate for describing the large-amplitude vibrations associated with CH and OH stretches which are currently receiving considerable experimental attention (Crim 1984). The discussion here draws from the work of Carter and Handy (1986) who have determined some very efficient means of evaluating the eigenvalues of tri-atomic molecules. The extensions of these ideas to larger systems is also presented. These approaches are then compared to the discrete variable representation (DVR). Bačić and Light (1986, 1987) have used the DVR in their studies of 'floppy' molecules which possess more than one minimum on the potential energy surface. The results of these studies are extremely encouraging.

As stated above, the final section of this paper reviews perturbative approaches of obtaining eigenvalues and spectroscopic Hamiltonians. The work of Sibert (1988b, 1989), Sibert and McCoy (1989), and Fried and Ezra (1988, 1989) is reviewed. Here the discussion focuses on the way in which canonical Van Vleck perturbation theory is used to transform to Hamiltonians for which the eigenvalues can be readily obtained.

2. Variational approaches

There are six central steps in most variational calculations. They are the following.

1. Choose a coordinate system.
2. Determine the kinetic energy contribution to the Hamiltonian.
3. Obtain the Born–Oppenheimer potential energy.
4. Decide on a set of basis functions so that the Hamiltonian can be represented as a matrix.
5. Evaluate the matrix elements.
6. Diagonalize the matrix.

There are many options for each of the above steps, all of which are dependent on each other. We shall consider in detail some specific choices that recent researchers have made, as well as the rationale for these choices. There are, however, two steps we will not address. The first of these, the determination of Born–Oppenheimer potential energy surface, is perhaps the most difficult of the six. These calculations constitute a very active area of research among *ab initio* quantum chemists. It should be noted that many of the methods employed today in vibrational variational calculations, including the basic method itself, have originated from this field of research. Throughout the remainder of this review, we assume that the potential energy surface is a given quantity. We will also not review the advances that have been made in the sixth step, as this is more of a numerical problem. Partly for this reason and partly due to the very recent review we will not discuss the progress made by Wyatt and co-workers (1989) in developing the Lanczos algorithm. Iung and Leforestier (1989) recently demonstrated the power of this technique in their study of the determination of a potential energy surface for CD_3H.

The organization of this section is based on the choice of coordinate systems, the first of the above six steps. We will consider three of the many possible options, these being normal coordinates, bond-angle coordinates, and finally Jacobi coordinates. Although the inclusion of rotational degrees of freedom is not stressed in this review, high-lying rotational states provide a wealth of information; moreover, full rotation–vibration calculations have been performed in all three of these coordinate systems.

2.1. *Normal coordinates*

Owing to the success of normal coordinates in perturbative approaches, these coordinates were first used in variational calculations of molecular vibrations. Although the inclusion of rotations is beyond the scope of this review, the normal mode description has the additional advantage of allowing for a simple embedding of the body-fixed coordinate system. Eckart (1935) has given a prescription for this embedding which provides an excellent separation of the rotational and vibrational degrees of freedom for semirigid molecules that spend most of their time near the equilibrium configuration. The utility of the Eckart condition derives from the fact that both it and the normal coordinates are conveniently expressed as linear combinations of the Cartesian coordinates.

Wilson and Howard (1936) and Darling and Dennison (1940), with further simplifications by Watson (1968), made use of this linear relation in their derivation of the full rotation–vibration Hamiltonian for a nonlinear molecule. The pure vibrational contribution to the kinetic energy operator has the form

$$\hat{T}_{\mathrm{W}} = \frac{1}{2}\sum_{\alpha,\beta} \pi_\alpha \mu_{\alpha\beta} \pi_\beta + \frac{1}{2}\sum_k \hat{P}_k^2 + U_{\mathrm{W}}. \tag{2}$$

In equation (2) $\mu_{\alpha\beta}$ is an effective reciprocal inertia tensor and μ is its determinant. Both these terms depend on the instantaneous molecular geometry. The 'vibrational angular momentum', π_α, is a bilinear function of the normal coordinates, Q_i, and their conjugate momenta, $\hat{P}_i$. Its precise functional form depends on the molecular equilibrium configuration and the quadratic force constants. The final term in equation (2), which depends only on the coordinates, is the Watson term,

$$U_{\mathrm{W}} = -\frac{\hbar^2}{8}\sum_\alpha \mu_{\alpha\alpha}. \tag{3}$$

This term may be thought of as a mass-dependent contribution to the potential energy function.

The variational evaluation of the eigenfunctions entails rewriting the kinetic energy operator of equation (2) plus the potential operator as a matrix using a suitable basis. Much of the research here has followed the early work of Whitehead and Handy (1975, 1976) in which the basis functions have the following production form:

$$\chi_{n_1 n_2 n_3 \ldots n_N} = \prod_k^N \theta_{n_k}(\bar{Q}_k). \tag{4}$$

Here the $\theta_{n_k}(\bar{Q}_k)$ are the well known solutions to the harmonic oscillator associated with the kth degree of freedom. These functions are conveniently expressed as a function of the dimensionless coordinates

$$\bar{Q}_k = (2\pi\omega_k/\hbar)^{1/2} Q_k. \tag{5}$$

Having chosen a basis, the task of setting up the Hamiltonian matrix is reduced to evaluating the elements of this matrix by means of either numerical or analytical integration. Although the second term of $\hat{T}_{\mathrm{W}}$ can be evaluated exactly, the remaining two as well as the potential contribution, require the calculation of N-dimensional integrals corresponding to the N internal degrees of freedom. In the approach of Whitehead and Handy (1976) these integrals are evaluated using Gauss–Hermite quadrature. Each of the N-dimensional integrals can be expressed as a product of one-dimensional integrals each of which have the following form

$$\int_{-\infty}^{\infty} \mathrm{d}\bar{Q}_k \exp\{-\bar{Q}_k^2\}\, f(Q_k) \approx \sum_{i=1}^{M} A_i f(\bar{Q}_{k_i}), \tag{6}$$

where A_i are the points and $\bar{Q}_{k_i}$ are the weights. The second expression indicates that $f(\bar{Q}_k)$ is evaluated at the M points $\bar{Q}_{k_i}$.

It is instructive to consider the number of points required for an accurate representation of the above integral. The numerical quadrature of equation (6) is exact if $f(\bar{Q}_k)$ can be written as a polynomial in $\bar{Q}_k$ of degree less than or equal to $2M-1$. In evaluating the one-dimensional potential matrix between the states with quantum numbers n_k and m_k, $f(\bar{Q}_k)$ is the product of three terms, the potential and two Hermite polynomials of order n_k and m_k; hence, equation (6) will be accurate if the potential can be expressed as a polynomial of order $(2M-1)-(n_k+m_k)$.

The advantage of the above quadrature method is that it obviates the need to express the potential explicitly as a function of the normal coordinates. This is expedient, since potentials often are represented as functions of the internal bond-angle coordinates, either as a Taylor series expansion about an equilibrium configuration or as a more sophisticated global fit (Murrell 1984). With equation (6), one only needs to evaluate the potential at specific values of the normal coordinates. Using the linear transformation between normal and Cartesian coordinates, the values of these latter coordinates are readily determined for any value of the normal coordinates. The analytic expressions of Hoy *et al.* (1972) are then applied to determine the values of the bond-angle coordinates for a given value of the Cartesian coordinates. Hence it is straightforward to evaluate numerically the potential at the quadrature points.

Maessen and Wolfsberg (1984) have clearly demonstrated both the utility and the limitations of the quadrature scheme in their calculations of the vibrational states of H_2CO. This work carefully demonstrated the sensitivity of the eigenvalues on both the number of quadrature points and the number of basis functions used in the full diagonalization. One must be careful with regard to these issues, since both the size of the basis and the number of quadrature points for a molecule with six degrees of freedom is intractable unless some approximations are made.

Using the quartic, internal coordinate force field of Tanaka and Machida (1977) and using a relatively small basis set consisting of states whose harmonic contribution to the vibrational Hamiltonian was less than 6000 cm^{-1} above the zero-point energy, these workers showed that at least 6–8 quadrature points were required for each of the degrees of freedom in order to obtain eigenvalues to within 4 cm^{-1} of what they would be if an exact numerical integration scheme were used to obtain the Hamiltonian matrix. If a bigger basis has been chosen, more quadrature points would have been required.

In choosing their basis set, Maessen and Wolfsberg considered two criteria which a basis function had to satisfy in order to be included in the basis set. They first set an upper limit on the total number of quanta, $N_{\mathrm{MAX}} = \Sigma_i n_i$ of the product wavefunction of equation (4). Secondly, they set an upper limit on the energy above the zero point, E_{MAX}, as calculated in the normal mode limit. Although similar results were obtained, the second criterion was found to be superior. This is evident from the results of table 1, in

Table 1. Influence of choice of basis set on the A_1 energies (cm^{-1}).

(N_A)	Set I†	Set II‡	Set III§
0	5803·2	5816·4	5803·2
3_1	7332·7	7332·0	7328·3
2_1	7579·4	7582·3	7576·2
4_2	8155·3	8154·4	8154·1
6_2	8322·6	8321·8	8321·7
1_1	8671·4	8674·2	8671·4
3_2	8850·8	8850·1	8849·7
2_13_1	9092·7	9118·8	9091·5
2_2	9347·1	9372·3	9345·6
3_14_2	9808·2	9668·1	9664·7
3_16_2	9893·4	9857·4	9842·7
2_14_2	10013·6	19923·2	19917·0
5_16_1	10022·6	10039·9	19998·5
2_16_2	10243·4	10076·1	10104·5
1_13_1	10190·0	10505·4	10187·7
3_3	10452·5	10379·8	10426·6
1_12_1	10458·0	10797·4	10453·8
4_26_2	...	10575·3	10574·0
4_4	...	10697·6	10697·5
2_13_2	10766·2	10725·2	10743·9
6_4	...	10859·1	10859·0
2_23_1	11131·6	11115·7	11109·1
1_14_2	11068·6	11204·4	11168·7
1_16_2	11348·8	11378·1	11369·0
3_24_2	...	11438·6	11433·7
3_26_2	...	11492·5	11490·4
2_3	11571·0	11553·7	11549·7

† Set I has 36 basis functions chosen by the excitation criterion $N_{MAX}=3$.
‡ Set II has 36 basis functions chosen by the energy criterion $E_{MAX} \simeq 6000\,cm^{-1}$.
§ Set III combines set I and II and has 45 basis functions.

which the results of these two calculations are compared to the results of a diagonalization for which a basis function was included in the basis set if either of the two criteria was satisfied.

In their largest calculation, six quadrature points were used for each of the modes, except the out-of-plane bend, Q_4, and asymmetric bend, Q_6, where 8 quadrature points were used. States were included in the basis set if either $N_{MAX}=5$ or $E_{MAX}=9000\,cm^{-1}$, this providing a relatively small basis of 196 functions by today's standards. With this basis only the lowest four or five states of the A_1 symmetry block appeared to be converged to within 0·5 cm^{-1}. Apparently, one must go to extremely large basis sets in order to obtain accurate energies for highly excited states, if one chooses to use basis functions of harmonic oscillators.

These authors also examined the contributions to the eigenvalues of various components of the vibrational Hamiltonian associated with equation (2). For example, they numerically showed that the leading contribution of the Watson term is an overall shift of 3 cm^{-1} to the energy levels. This result also indicates that the normal coordinate dependence of $\mu_{\alpha\beta}$ in equation (2) makes at most a minor contribution to the overall eigenvalues.

Using these ideas, Romanowski *et al.* (1985), hereafter referred to as RBH, also calculated eigenvalues of the highly excited states of H_2CO using a modified *ab initio* potential of Harding and Ermler (1985). This potential is a full quartic expansion. The bends are described with the usual bend extension coordinates, but the stretches are modelled with SPF coordinates. RBH used a superior basis in their calculations, whose development we now describe. Before doing so, it should be noted that this more sophisticated treatment of the wavefunctions is made tractable only through some simplifying assumptions as to the form of the Hamiltonian operator. The first of these is to neglect the functional dependence of $\mu_{\alpha\beta}$ on the normal coordinates. This obviates the need of a quadrature scheme for the kinetic energy matrix elements, since the $\hat{T}_W$ can readily be expressed as a sum of separable terms, each of which can be evaluated as a product of at most four one-dimensional integrals. Furthermore, the solutions to these integrals are analytic. The evaluation of the potential matrix elements was simplified by expressing the potential as a Taylor series expansion in the normal coordinates through fourth order,

$$V(Q)=\sum_i f_{ii}Q_i^2+\sum_{i\leqslant j\leqslant k} f_{ijk}Q_iQ_jQ_k+\sum_{i\leqslant j\leqslant k\leqslant l} f_{ijkl}Q_iQ_jQ_kQ_l. \qquad (7)$$

In this form, the potential is also expressed as a sum of separable terms. Although the second of these approximations is not as good as the first (Sibert 1989), combined they simplify the evaluation of the Hamiltonian matrix to the extent that more flexible forms of the product basis functions may be considered.

RBH consider two forms of the vibrational basis functions both of which have the product form of equation (4). The first of these options follows the work of Carney and Porter (1974), where the θ_{n_k} are eigenfunctions of the uncoupled anharmonic oscillator (UAO) Hamiltonian

$$h_k^0=\tfrac{1}{2}\hat{P}_k^2+f_{kk}Q_k^2+f_{kkk}Q_k^3+f_{kkkk}Q_k^4, \qquad (8)$$

which includes those contributions to the full Hamiltonian consisting of the one-body terms and not just the quadratic contributions to h_k^0, as in the Whitehead and Handy approach (1975, 1976). In order to distinguish this basis from that used by Maessen and Wolfsberg, we use the notation of RBH and denote this basis $\theta_{n_k}^{\mathrm{UAO}}$. The basis can be further improved by using self-consistent field (SCF) wavefunctions, $\theta_{n_k}^{\mathrm{SCF}}$, which are iteratively obtained solutions to

$$h_k^{\mathrm{SCF}}=h_k^0+\left\langle \prod_{j\neq k}\theta_{n_j}^{\mathrm{SCF}}|V'|\prod_{j\neq k}\theta_{n_j}^{\mathrm{SCF}}\right\rangle, \qquad (9)$$

where h_k^{SCF} is a function of the quantum numbers n_j. The additional contribution to this Hamiltonian is obtained by averaging V', which includes all the terms in the full Hamiltonian other than the one-body terms, over the remaining five degrees of freedom. Both the SCF wavefunctions and the UAO wavefunctions are conveniently expressed as linear combinations of the previously defined harmonic oscillator functions θ_{n_k}. For example,

$$\theta_{n_k}^{\mathrm{UAO}}=\sum_{m_k=0}^{N_p} c_{m_kn_k}\theta_{m_k}, \qquad (10)$$

where the equality holds only in the limit that N_p approaches ∞. The method developed by RBH for setting up the full Hamiltonian matrix, using both the UAO and SCF wavefunctions, follows the standard approaches as discussed by these authors.

The difficult steps were deriving the SCF wavefunctions (i.e. carrying out the necessary integration to derive h_k^{SCF}) and, secondly, evaluating the matrix elements of the Hamiltonian matrix. The integration required in both these steps was made tractable by expressing the Hamiltonian as a sum of separable terms. As an elegant alternative, Ratner and Gerber (1986) incorporate semiclassical ideas in order to evaluate the expectation value of equation (9) without ever explicitly determining the wavefunctions, $\theta_{n_j}^{\mathrm{SCF}}$.

There were several noteworthy results found by RBH. The first of these, shown in table 2, is that if configuration interaction is neglected (i.e. the eigenvalues are approximated as the diagonal elements of the full Hamiltonian matrix), then the SCF wavefunctions provide a superior representation, giving a zero point energy 100 cm^{-1} lower than that found using the UAO wavefunctions. The differences between these two representations were, however, noticeably diminished when configuration interaction was included. This is evident from a comparison of the UAO–CI and SCF–

Table 2. Convergence of the UAO–CI and SCF–CI energies (cm^{-1}) for adjusted potential for H_2CO.

State	Symmetry	UAO†	UAO–CI‡	UAO–CI§	SCF†	SCF–CI‡
0	A_1	5880·1	5777·2	5777·1	5796·3	5777·2
1_1	A_1	8756·2	8558·9	8558·4	8610·5	8558·8
2_1	A_1	7643·8	7524·5	7524·2	7546·8	7524·5
3_1	A_1	7424·5	7277·6	7277·2	7303·0	7277·5
4_1	B_1	7085·3	6937·8	6937·5	6947·8	6937·8
5_1	B_2	8960·4	8634·9	8634·0	8640·1	8635·0
6_1	B_2	7161·5	7022·9	7022·6	7044·7	7022·9
1_2	A_1	11581·5	11278·8	11270·0	11370·8	11274·9
$1_1 2_1$	A_2	10519·8	10307·5	10306·1	10358·3	10306·7
$1_1 3_1$	A_1	10300·5	10048·5	10045·5	10082·5	10048·2
$1_1 4_1$	B_1	9961·3	9693·3	9690·9	9716·0	9692·0
$1_1 5_1$	B_2	11836·4	11366·8	11354·3	11459·7	11366·8
$1_1 6_1$	B_2	10037·5	9785·3	9781·6	9824·8	9783·7
2_2	A_1	9395·4	9256·4	9255·8	9281·9	9256·2
$2_1 3_1$	A_1	9188·1	9017·7	9016·7	9050·3	9017·3
$2_1 4_1$	B_1	8849·0	8676·9	8676·0	8690·4	8676·5
$2_1 5_1$	B_2	10724·0	10361·9	10358·1	10386·1	10362·2
$2_1 6_1$	B_2	8925·1	8780·4	8779·6	8790·3	8780·5
3_2	A_1	8969·2	8775·4	8774·4	8807·0	8774·8
$3_1 4_1$	B_1	8629·6	8433·0	8432·0	8449·4	8432·6
$3_1 5_1$	B_2	10504·7	10128·6	10123·9	10099·2	10128·9
$3_1 6_1$	B_2	8705·8	8478·8	8477·2	8558·5	8478·3
4_2	A_1	8306·9	8093·0	8092·0	8107·1	8092·3
$4_1 5_1$	A_2	10165·5	9776·8	9772·3	9732·4	9777·5
$4_1 6_1$	A_2	8366·6	8193·5	8192·5	8201·1	8193·0
5_2	A_1	12105·7	11472·1	11457·5	11408·7	11476·6
$5_1 6_1$	A_1	10241·7	9864·0	9860·5	9847·0	9864·1
6_1	A_1	8454·5	8266·9	8265·9	8299·0	8266·4

† The UAO and SCF results were obtained using a simplified form for the kinetic energy operator, $\hat{T}_{\mathrm{W}} = \frac{1}{2}\Sigma_k P_k^2$ (cf. equation (2)).

‡ The basis functions were chosen by the excitation criterion $N_{\mathrm{MAX}} = 5$.

§ The basis functions were chosen by the excitation criterion $N_{\mathrm{MAX}} = 8$ with the exception that n_5 and n_6 were only considered up to 5.

CI results of table 2 which were obtained from a diagonalization with a moderate size basis. These results are displayed in columns four and seven. This basis included those products states for which $N_{\mathrm{MAX}}=6$, yielding 313, 140, 169 and 266 basis states of A_1, A_2, B_1, and B_2 symmetry respectively. Also shown in table 2 in the fifth column are the results of a larger UAO–CI calculation where 827, 488, 526 and 794 basis states were included in each of the above symmetry groups. Here $N_{\mathrm{MAX}}=8$, with the exception that n_5 and n_6 were considered up to 5 (for states of A_2 and B_2 symmetry). The close similarity of the moderate size UAO–CI and SCF–CI results relative to the larger size UAO–CI calculation lead RBH to conclude that for a given size basis set, the energies obtained in these two representations are of roughly equal accuracy.

Table 2 includes states with a total of two or less quanta of excitation. Of the 14 states of A_1 symmetry, which are shown there, eight of them appear to be converged to within $0{\cdot}5\,\mathrm{cm}^{-1}$ of the exact eigenvalues for the SCF basis set. This is a marked improvement over the four or five similarly converged states that Maessen and Wolfsberg obtained with a basis set of 196 harmonic oscillator functions.

Another important result of this study was that the first overtones of the states corresponding to large amplitude CH stretches required at least $N_p=10$ in order to obtain the eigenvalues of equation (8) to within $1\,\mathrm{cm}^{-1}$ accuracy. The ability to describe the stretches as linear combinations of harmonic oscillator functions rapidly deteriorates as one goes to yet more highly excited stretching states. Fortunately, there exists an alternative description, bond-angle coordinates, which is ideally suited for just this type of motion.

2.2. *Bond-angle coordinates*

In recent years, researchers have found that there exists a very attractive alternative framework for describing and modelling vibrational dynamics and spectroscopy. This perspective has the localized stretching and bending oscillators as the zero-order modes (Sage and Jortner 1981, Crim 1984, Child and Halonen 1984). These ideas were motivated early on by noting that, whereas the expression for the eigenvalues of equation (1) often fails at high energies, for high-frequency vibrations such as CH and OH stretches the energy levels can still be fitted with the relatively simple expression

$$E=\sum_i \hbar\omega_i(n_i+\tfrac{1}{2})+\sum_i \chi_{ii}(n_i+\tfrac{1}{2})^2. \tag{11}$$

The surprising feature here is that this expression is appropriate for describing the vibrations of an isolated, diatomic molecule, this implying that the high-frequency CH and OH stretches are vibrating independently of each other and therefore can be treated as localized oscillations.

There are two reasons for this localization. The normal modes arise as a result of the off-diagonal quadratic coupling terms between the local modes. These coupling terms, which are normally responsible for the strong mixing of the local modes, have little effect in coupling oscillators with disparate frequencies (Wilson *et al.* 1955). Consequently, in molecules such as HDO, where the three local modes have distinctly different frequencies, the normal and local modes are similar. Of more interest are situations where the normal and local modes are different, as in H_2O. Here the two local OH oscillators have the same frequency; hence, to a good approximation they strongly mix to form the symmetric and antisymmetric normal modes, despite the relatively small magnitude of the quadratic coupling terms. It turns out, however, that because OH oscillators are so anharmonic, an OH stretch with three quanta of excitation has a frequency which is sufficiently diminished from the frequency associated with the zero-point energy that the quadratic coupling no longer leads to mixing of the OH oscillators. As a consequence of this detuning, the OH stretches provide a good zero-order description for highly excited states. Conversely, the anharmonicity of the OH oscillators leads to extensive mixing of the normal modes. For states with most of the excitation in a single OH bond, the local mode provides a superior representation.

The emergence of the local mode picture has been enhanced by the additional fact that these modes are the ones most commonly observed with the thermal lensing and photoacoustic techniques (Sage and Jortner 1981) which are commonly used to probe highly excited states. Not only do these states carry considerable oscillator strength in these experiments, they are also reasonably uncoupled to the remaining states, as the spectral energy level pattern of equation (11) suggests. Levine and Berry (1989) have argued that these relatively unmixed, localized states are more visible spectroscopically than their strong mixed counterparts whose spectral signatures are often washed out due to the mixing and sharing of oscillator strength with other background states. Consequently local modes have been the subjects of considerable experimental scrutiny (Crim 1984).

The ramifications of these observations encouraged workers to develop variational calculations in these alternative coordinates. As before, the first step in this process is the derivation of the kinetic energy operator. One route to doing this is to use the Podolsky transformation (1928). Meyer and Günthard (1968) and Pickett (1972) derived the rotation–vibration Hamiltonian in generalized curvilinear coordinates. The pure vibrational contribution to the kinetic energy operator is

$$\hat{T}_{\mathrm{MGP}}=\tfrac{1}{2}\mathbf{P}^{\mathrm{T}}\mathbf{G}\mathbf{P}+V'(\mathbf{S}). \tag{12}$$

It has been written in terms of the momenta, $\hat{P}_i=-i\hbar\,\partial/\partial S_i$ and the **G**-matrix elements. If the internal coordinates, S_i, are the bond-angle extension coordinates, ΔR_i, then the G_{ij} are just the well known Wilson **G**-matrix elements (Wilson *et al.* 1955). The second term, $V'(\mathbf{S})$ is a potential energy term which results from transforming the kinetic portion of the Hamiltonian from Cartesian into internal coordinates. It has the form

$$V'=\frac{\hbar^2}{8}\sum_{t,t'}\left[\frac{\partial G_{tt'}}{\partial S_t}\frac{\partial(\ln g)}{\partial S_{t'}}+G_{tt'}\left(\frac{\partial^2(\ln g)}{\partial S_t\,\partial S_{t'}}+\frac{1}{4}\frac{\partial(\ln g)}{\partial S_t}\frac{\partial(\ln g)}{\partial S_{t'}}\right)\right], \tag{13}$$

where

$$g=\frac{|\mathbf{I}|}{|\mathbf{G}|} \tag{14}$$

is the ratio of the determinants of the **G**-matrix and the moment of inertia matrix. The appropriate volume element for integration over the internal coordinates of the above Hamiltonian is $\mathrm{d}V=\mathrm{d}S_1\,\mathrm{d}S_2\ldots\mathrm{d}S_N$.

The $V'(\mathbf{S})$ term is usually small relative to the other potential energy terms, and can often be neglected. If this approximation is made, the Hamiltonian for a specific system may be obtained trivially by looking up the appropriate functional form of the G-matrix elements (Wilson *et al.* 1955).

The somewhat awkward form of equation (13) is a result of using the Podolski transformation. Handy (1987) and Sutcliffe (1982) have shown that analytic expressions for the kinetic energy operator can be derived in a more straightforward fashion. They start with the well known form for the kinetic energy operator expressed in Cartesian coordinates and then apply the chain rule in order to re-express this operator in the internal coordinates. All that is needed in order to carry out this step is to express both the Euler angles and the internal coordinates as function of the Cartesian coordinates and *vice versa*. Although the algebra which is required for these transformations is cumbersome, it can be readily handled using algebraic manipulation routines (Handy 1987).

Wallace (1975) was one of the first researchers to take advantage of the above bond-angle Hamiltonian in his investigations of the stretching dynamics of H_2O and C_6H_6. In this early work the effects of the bending motions were neglected. The zero-order Hamiltonian consisted of N uncoupled Morse oscillators, and the primitive product basis was defined accordingly. The exciting result of these studies was that, despite the complete neglect of all potential coupling between the stretches (i.e. the stretches were only kinetically coupled), the resulting eigenvalues agreed closely with the observed transition frequencies. Since that time, this model and more sophisticated versions of it have been applied to a large number of molecular systems, leading to novel insights into the nature of highly excited polyatomic molecules.

Before discussing some of the approximations that have been made, however, we first review an 'exact' method of obtaining the eigenvalues of an ABA triatonic molecule. The vibrational Hamiltonian for this molecule is

$$H=\frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3}\hat{P}_iG_{ij}\hat{P}_j+V'(R_1,R_2,\theta)+V(R_1,R_2,\theta), \tag{15}$$

where

$$\hat{P}_1=-i\hbar\frac{\partial}{\partial R_1},\qquad \hat{P}_2=-i\hbar\frac{\partial}{\partial R_2},\qquad \hat{P}_3\equiv\hat{P}_\theta=-i\hbar\frac{\partial}{\partial\theta}. \tag{16}$$

The G_{ij} elements are functions of the internal coordinates and the atomic masses. Introducing the notation, $\tau_i=(R_i)^{-1}$ and $\mu_{AB}=m_Am_B/(m_A+m_B)$, one obtains the following expressions:

$$\begin{aligned} &G_{11}=G_{22}=\frac{1}{\mu_{AB}}; \quad G_{33}=\frac{\tau_1^2+\tau_2^2}{\mu_{AB}}-\frac{2\tau_1\tau_2\cos\theta}{m_B};\\ &G_{12}=\frac{\cos\theta}{m_B}; \quad G_{13}=-\frac{\tau_2\sin\theta}{m_B}; \quad G_{23}=-\frac{\tau_1\sin\theta}{m_B}. \end{aligned} \tag{17}$$

After considerable algebraic manipulation, V' simplifies to

$$V'(R_1,R_2,\theta)=\frac{\hbar^2}{2m_B}\tau_2\tau_2\cos\theta-\frac{\hbar^2}{8}G_{33}[1+\operatorname{cosec}^2\theta]. \tag{18}$$

The reader will note that, whereas V' is generally small, it diverges at $\theta=\pi$. If one is considering systems with large-amplitude bending motion, this singularity must be removed. Sutcliffe (1983) showed that this could be achieved by rewriting the above Hamiltonian as a function of $z=\cos\theta$ and choosing $dR_1\,dR_2\,dz$ rather than $dR_1\,dR_2\,d\theta$ as the volume element.

Having obtained the Hamiltonian, the next step is to choose a set of basis functions. There are many ways to proceed at this juncture, and only a few of them will be considered here. It should be emphasized that all these approaches have a common goal, to minimize the number of basis functions used in the full matrix diagonalization without making the evaluation of the Hamiltonian matrix unduly difficult or time-consuming. The diagonalization should be the time intensive part of the variational procedure. The work of Carter and Handy (1986) provides a nice illustration of these concepts.

Carter and Handy, building on the earlier ideas of Lai and Hagstrom (1975), optimized their product basis functions by considering the full vibrational Hamiltonian as consisting of three zero-order anharmonic oscillators whose Hamiltonians are

$$H_{\text{bend}}=\frac{-1}{R_e^2}\left\{\frac{1}{\mu_{AB}}-\frac{\cos\theta_e}{m_B}\right\}\frac{\partial}{\partial z}(1-z^2)\frac{\partial}{\partial z}+V(z), \tag{19}$$

$$H_{\text{stretch}}=\frac{\hat{p}_i^2}{2\mu_{AB}}+V(R_i), \tag{20}$$

where R_e is the equilibrium bond length and $i=1$ or 2. The eigenfunctions of the above one-dimensional Hamiltonians are then used as a basis in the full calculation. This approach is the local mode equivalent of RBH using basis functions which are products of the $\theta_{n_k}^{\text{UAO}}$. To obtain these eigenfunctions or so-called pre-diagonalized functions, Carter and Handy diagonalized the above Hamiltonians in a basis of 'primitive' functions. The choice of these functions is not central to this procedure, since they are only used for diagonalizing the one-dimensional bend and stretch Hamiltonians. A convenient choice for these functions is Legendre polynomials for the bend and Morse functions for the stretches. If the barrier for the bending Hamiltonian is particularly high, the more flexible Jacobi basis used by Johnson and Reinhardt (1986) is an attractive alternative. Hamilton and Light (1986) have used multicentred expansions consisting of distributed Gaussian basis functions,

$$\phi_k(R_i)=(2A_k/\pi)^{1/4}\exp\left[-A_k(R_i-R_{i_k})^2\right], \tag{21}$$

centred at the points R_{i_k}. The evaluation of matrix elements is rapid since this localized basis requires very few quadrature points. Finally with some modifications, the above equations can also be solved by direct numerical integration as in the work of Cropek and Carney (1984).

The eigenfunctions $\phi_m^{(i)}$ (where $i=1,2$ corresponds to the two stretches and $i=3$ corresponds to the bend) of H_{stretch} and H_{bend} may then be further improved by carrying out the first step of an SCF iteration. Here the new one-dimensional bend Hamiltonian is

$$\int_0^\infty\int_0^\infty \mathrm{d}R_1\,\mathrm{d}R_2\,\phi_0^{(1)}\phi_0^{(2)}\hat{H}\phi_0^{(1)}\phi_0^{(2)}, \tag{22}$$

and the stretch functions are calculated similarly. For simplicity of notation we refer to these further-improved functions using the same notation. It should also be noted that, for molecules with C_{2v} symmetry, there is an additional important step in minimizing the size of the Hamiltonian matrix, which is to symmetrize the stretching wavefunctions by taking the appropriate plus and minus linear combinations.

Having obtained the pre-diagonalized basis, the matrix elements for the kinetic energy operator are easily calculated, since these terms may be written without approximation as the sum of product terms. The more difficult quantities to calculate are potential energy matrix elements,

$$\langle \Psi_m | V | \Psi_n \rangle = \langle \phi^{(1)}_{m_1}(R_1)\phi^{(2)}_{m_2}(R_2)\phi^{(3)}_{m_3}(\theta) | V | \phi^{(1)}_{n_1}(R_1)\phi^{(2)}_{n_2}(R_2)\phi^{(3)}_{n_3}(\theta)\rangle . \tag{23}$$

These were evaluated with the Harris–Engerholm–Gwinn (HEG) quadrature scheme (Harris *et al.* 1965) combined with the more recent work of Schwenke and Truhlar (1984). The first step in this scheme is the evaluation of the points. These are obtained by diagonalizing the $(N_3+1)\times(N_3+1)$ bend position matrix $\mathbf{\Theta}$, whose elements are

$$\Theta_{mn} = \int_{-1}^{1} \mathrm{d}z\, \phi^{(3)}_m \theta \phi^{(3)}_n, \quad m,n=0,1,\ldots,N_3 \tag{24}$$

and the matrices $\mathbf{R}_i$ $(i=1,2)$ with elements

$$(R_i)_{mn} = \int_{0}^{\infty} \mathrm{d}R_i\, \phi^{(1)}_m(R_i) R_i \phi^{(1)}_n(R_i), \quad m,n=0,1,\ldots,N_i. \tag{25}$$

The resulting eigenvalues of $\mathbf{\Theta}$ and $\mathbf{R}_i$ are the quadrature points. The weights corresponding to these points are obtained using the method of Schwenke and Truhlar (1984) in which the weights $w^{l_3}_{mn}$, as the notation suggests, depend on the particular matrix element being calculated. The weights for the bend are solutions to the following simultaneous equations,

$$\langle \phi^{(3)}_m | (\theta-\theta_e)^k | \phi^{(3)}_n \rangle = \sum_{l=0}^{N_3} w^{l_3}_{mn}(\theta_{l_3}-\theta_e)^k, \quad k=0,1,\ldots,N_3. \tag{26}$$

The weights for the stretches are calculated similarly.

This scheme leads to the powerful result that the matrix elements may be expressed exactly as

$$\langle \Psi_m | V | \Psi_n \rangle = \sum_{l_1=0}^{N_1}\sum_{l_2=0}^{N_2}\sum_{l_3=0}^{N_3} w^{l_1}_{m_1n_1} w^{l_2}_{m_2n_2} w^{l_3}_{m_3n_3} V(R_{l_1}, R_{l_2}, \theta_{l_3}), \tag{27}$$

if the potential can be also exactly represented as a Taylor series expansion of the form

$$V(R_1,R_2,\theta) = \sum_{l=0}^{N_1}\sum_{m=0}^{N_2}\sum_{n=0}^{N_3} c_{lmn}(R_1-R_{1e})^l (R_2-R_{2e})^m (\theta-\theta_e)^n. \tag{28}$$

Clearly, fewer points are required for this quadrature scheme than for the Gauss–Hermite quadrature of equation (6). Using these ideas, as well as some more sophisticated basis sets, Carter and Handy have shown that these methods provide a very efficient route to calculating the highly excited vibrational states of tri-atomic molecules.

The use of bond-angle coordinates has been applied successfully to larger systems. This has been made possible by the decoupling of high-frequency CH and OH variations relative to the lower frequency bending modes, so that undercomplete bases still provide accurate descriptions of the highly excited states. Following the early work of Wallace (1975), Halonen (1989) has recently reviewed the use of these ideas to model a wide variety of local mode molecules.

One of the distinct advantages of the bond-angle representation is that, unlike the normal coordinates, the potential may often be accurately expressed as a sum of separable terms. The key to doing this is to express the potential not as a Taylor series expansion of the internal extension coordinates, but rather to introduce some alternative definitions. Two well known examples for alternative stretching coordinates are the Simons–Parr–Finlan (SPF) coordinates (1973), $\rho_i = \Delta R_i/R_i$, where ΔR_i is a bond extension coordinate, and the Morse coordinates, $y_i = [1 - \exp(-a_i \Delta R_i)]$. These coordinates (Halonen and Carrington 1988) contain an additional fitting parameter, a_i, referred to as the Morse parameter. Insomuch as the Morse potential has been shown to describe accurately the stretching potentials for many molecules, and since this potential expanded in a Taylor series in y_i has the trivial form, $D_e y_i^2$, (D_e is the dissociation energy) it is expected that one-dimensional stretching potentials can, in general, be written as low-order polynomial expansions in these coordinates. Recent progress has also been made in regard to bending degrees of freedom. In particular, Carter and Handy (1987) have introduced the coordinate,

$$\bar{\theta} = \Delta\theta + \beta_2(\Delta\theta)^2 + \beta_3(\Delta\theta)^3, \tag{29}$$

where $\Delta\theta = \theta - \theta_e$ is the bending extension coordinate of an ABC triatomic molecule. These workers showed that the bending contributions to the potential can be written accurately as a quartic expansion in $\bar{\theta}$. In order that the potential has the correct boundary conditions, there is a single constraint between the two additional parameters, β_i (i.e. $\partial V/\partial\theta|_{\theta=\pi} = 0$). This leads to the requirement that $\partial\bar{\theta}/\partial\theta|_{\theta=\pi} = 0$. An alternative approach which will also insure the correct boundary conditions is to expand the potential in a Taylor series in $\Delta z = z - z_e = \cos\theta - \cos\theta_e$.

Expressing the potential energy as a low-order Taylor series expansion in these alternative coordinates has provided accurate representations of realistic potential energy surfaces; these methods are often adopted by *ab initio* quantum chemists as the most convenient way to parameterize the potential. This approximation obviates the need for numerical quadrature and allows for very rapid evaluation of the potential energy matrix elements. Halonen and Carrington (1988) have recently applied these ideas to an investigation of the highly excited states of H_2O, as have Carter and Handy (1988) in their studies of acetylene. In an earlier work Carter and Handy (1984) used a six-dimensional quadrature scheme to evalute the potential matrix elements, but found this to be an extremely slow process. In the more recent work, the quartic force field was used in order to avoid the slow quadrature step. It should be noted that Carter and Handy employed the exact form for the kinetic energy operator as opposed to neglecting various contributions to it as in the work of Gribov and Khovrin (1975). Although the form of this operator is quite complicated, it too can be written as a sum of separable terms.

Finally it should be mentioned that the use of bond-angle coordinates in no way precludes an embedding of a body-fixed reference frame in order to study rotations. Although it is not easy to employ the Eckart frame, several other options for the embedding have been put to practical use by Tennyson and Sutcliffe (1986), Sutcliffe *et al.* (1987) and Carter and Handy (1987). In addition to showing clearly the utility of the bond-angle coordinates for studying rotations, one of the important features of these studies has been to demonstrate that one should be careful to construct a basis set which avoids any singularities that are often present in the rotation–vibration Hamiltonian.

2.3. *Jacobi coordinates and the discrete variable representation*

Although the method of Carter and Handy (1986) provides an efficient method for calculating highly excited states of many tri-atomic molecules, difficulties are confronted when there is more than a single minimum on the potential energy surface, such as is found for the HCN molecule. For 'floppy' systems such as this, the bond-angle coordinates, appropriate for describing HCN vibrations, are inappropriate for describing HNC vibrations. Jacobi coordinates, originally developed in the context of scattering theory, provide an attractive alternative. This is not only due to the simplicity of the kinetic energy operator,

$$\hat{T}_J = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2}\left(\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2}\right)\frac{\partial}{\partial z}(1-z^2)\frac{\partial}{\partial z}, \tag{30}$$

where $\mu_1 = M_A M_{BC}/(M_A + M_{BC})$ and $\mu_2 = M_B M_C/(M_B + M_C)$; it is also a consequence of the fact that the vibrational wavefunctions are more separable in these coordinates. These are the BC (CN) bond length, r, the distance between the A (H) atom and the centre of mass of the BC diatom, R, and the angle, θ, between the diatom axis and the vector connecting the H atom to the centre of mass of the diatom.

The new choice of coordinates does not preclude the use of the diagonalization scheme discussed above. One can define three one-dimensional Hamiltonians as above in order to define the pre-diagonalized basis functions $\phi_k^{(i)}$ where $i = 1$–3 corresponds to the R, r and θ degrees of freedom respectively. If the potential contribution to the Hamiltonian is sufficiently small, as it is for many van der Waals molecules, then the contraction of the size of total basis set achieved by using pre-diagonalized bend functions rather than Legendre polynomials is minimal. In this situation it is easier to follow the standard approaches of scattering theory and simply to use the Legendre polynomials as the bend basis. In contrast, if there is an appreciable barrier to rotation, and if there exists more than one minimum on the potential energy surface such as there is in HCN/HNC, then some modifications must be made in order to contract the size of the overall basis. These changes result from the fact that the bend functions may be localized in different regions of configuration space. Some of these functions, denoted $\phi_{m'}^{(3)}$, are localized about $\theta = \pi$, and others, denoted $\phi_m^{(3)}$ are localized about $\theta = 0$; finally other bend functions, which are above the barrier to isomerization, are, as expected, delocalized. Consequently, if the stretch basis functions, $\phi_l^{(1)}$, are defined as the eigenfunctions of the one-dimensional stretching Hamiltonian,

$$\int_0^\infty \mathrm{d}R \int_{-1}^{1} \mathrm{d}z\, \phi_0^{(2)}\phi_m^{(3)}\hat{H}\phi_0^{(2)}\phi_m^{(3)}, \tag{31}$$

then this basis will accurately describe the CH stretches, but will do a poorer job in describing the NH stretches. Conversely, if the stretch basis is chosen to be eigenfunctions of

$$\int_0^\infty \mathrm{d}R \int_{-1}^{1} \mathrm{d}z\, \phi_0^{(2)}\phi_{m'}^{(3)}\hat{H}\phi_0^{(2)}\phi_{m'}^{(3)}, \tag{32}$$

then this basis will describe accurately the NH stretches.

In situations such as this it is fruitful to further improve the stretching basis by means of a self-consistent field (SCF) procedure, such as that of RBH or Bačić *et al.* (1986). Another alternative is to use an adiabatic basis set, where the bend is treated as the slowly moving variable as Johnson and Reinhardt (1986), Romanowski and Bowman (1984), and Certain and Moiseyev (1987) have done. Bačić and Light (1986, 1987) have advanced another powerful method for the solution of 'floppy' molecules, which has many of the advantages of the SCF and adiabatic wavefunctions while retaining the advantages of an extremely rapid quadrature scheme.

The key difference between this approach and that of Handy and Carter (1986) is that it uses a discrete variable representation (DVR) in contrast to the so called finite basis representations (FBR) with which this review has so far been concerned. An example of these two representations has already been provided in the discussion of the HEG quadrature scheme. The functions $\phi_m^{(3)}$ constitute a FBR for the bend, whereas the eigenfunctions of the $\boldsymbol{\Theta}$ matrix provide a DVR. In order to illustrate the beauty of this technique we briefly review the essential ideas, and then compare the form of the Hamiltonian matrix derived from this method to that which would be obtained for the same problem in a FBR.

The vibrational Hamiltonian in Jacobi coordinates (cf. equation (30)) may be expressed in the general form

$$H=h(R,r)+G(R,r)j^2+V(R,r,\theta). \tag{33}$$

In the traditional coupled channel approach to scattering theory the eigenfunctions of this Hamiltonian are expressed in the form

$$\Psi(R,r,\theta)=\sum_{j=0}^{j_{\max}} f_j(R,r)P_j(\cos\theta). \tag{34}$$

Rather than follow this approach using the Legendre basis, these functions are transformed to a representation labelled by a discrete set of angles, namely the discrete variable representation. This basis is obtained from the Legendre basis using the orthogonal transformation

$$T_{j\alpha}=[(2j+1)/2]^{1/2}\omega_\alpha^{1/2}P_j(z_\alpha), \tag{35}$$

where $z_\alpha=\cos\theta_\alpha$ are the points and ω_α are the weights of the $(j_{\max}+1)$-point Gauss–Legendre quadrature. This basis leads to $j_{\max}+1$ coupled equations in the DVR:

$$[h(R,r)\mathbf{I}+G(R,r)\mathbf{T}^\dagger\mathbf{j}^2\mathbf{T}+\mathbf{T}^\dagger\mathbf{V}(R,r,\theta)\mathbf{T}-E\mathbf{I}]\mathbf{f}(R,r)=0. \tag{36}$$

Here the matrices $\mathbf{I}$ and $\mathbf{j}^2$ are the $(j_{\max}+1)\times(j_{\max}+1)$ identity matrix and the diagonal matrix of eigenvalues $[j(j+1)]$ respectively. The matrix $\mathbf{T}^\dagger\mathbf{V}(R,r,\theta)\mathbf{T}$ is block diagonal in the DVR; its elements have the form

$$[\mathbf{T}^\dagger\mathbf{V}(R,r,\theta)\mathbf{T}]_{\alpha'\alpha}=\delta_{\alpha'\alpha}V(R,r,z_\alpha). \tag{37}$$

With this simplification, each of the $j_{\max}+1$ equations constitutes a set of effective two-dimensional oscillators describing the stretches, where the effective stretch Schrödinger equation is

$$[h(R,r)+V(R,r,z_\alpha)-\epsilon_\alpha]f_\alpha(R,r)=0. \tag{38}$$

The two-dimensional stretching potential is found by taking a slice through the full potential at an angle z_α. The solution of equation (38) for each channel may be obtained in any number of ways. Light and Hamilton (1986) have found that the DGB basis provides an excellent choice of primitive functions in which to express the $f_\alpha(R,r)$. Having obtained these radial basis functions, the full pre-diagonalized product wavefunctions have been determined.

As in the approach of Maessen and Wolfsberg (1984) where the E_{MAX} criterion was used to decide whether to include a product wavefunction in the basis set, a similar approach is employed in the DVR approach (Bačić and Light 1986, 1987, Whitnell and

Light 1989). Here the number of stretching functions is tailored to the associated bend function. This is neatly achieved in the DVR by including only those stretching functions whose energies are less than some specified energy, E_{RAY}.

An advantage of the DVR representation is in setting up the Hamiltonian matrix. The coupling between the different α channels (i.e. the coupling between states with different bend quanta) is entirely due to the kinetic term, $G(R, r)\mathbf{T}^{\dagger}\mathbf{j}^2\mathbf{T}$. Furthermore, the simple product form of this coupling term facilitates the evaluation of the coupling matrix elements.

Using the DVR approach, Bačić and Light accurately calculated the lowest 110 levels HCN/HNC using 652 basis functions. The basis included 45 DVR quadrature points and $E_{\mathrm{RAY}} = 20\,000\,\mathrm{cm}^{-1}$. Most of these 110 levels were converted to 1–3 cm^{-1}.

It is worthwhile to compare the above equations to the FBR equivalent. An excellent set of basis functions can be obtained with the bend functions, $\phi_m^{(3)}$, whose derivation was discussed above. Using these functions, a set of coupled equations analogous to those of the DVR (cf. equation (36)) is obtained where now the **T** matrix is the matrix which transforms between the primitive, Legendre polynomials and the $\phi_m^{(3)}$. The stretching Hamiltonians are quite different from those of the DVR. The FBR leads to an effective stretch Schrödinger equation for each channel which is obtained by averaging the full Hamiltonian over the bend function associated with that channel. In contrast, in the DVR the stretch basis has the same form as it would for an adiabatic basis set. This strongly suggests that, for systems where the bending motion is significantly lower frequency than the stretches, the DVR will provide a superior stretch basis. From a quadrature point of view, the set of coupled equations obtained in the FBR has the disadvantage that $\mathbf{T}^{\dagger}\mathbf{V}(R, r, \theta)\mathbf{T}$ is no longer block diagonal; hence obtaining the stretch Hamiltonian will require a more complicated quadrature scheme than is needed in the DVR.

It should be noted, however, that the FBR representation does have the possible advantage that there will be fewer overall coupled equations in the FBR, since the $\phi_m^{(3)}$ are obtained from the full one-dimensional bend Hamiltonian, whereas the DVR basis is chosen to diagonalize only the potential contribution to the pure bend Hamiltonian.

To summarize, the DVR representation provides a powerful variational technique for studying the dynamics of 'floppy' molecules. One central advantage of the DVR approach is that the basis is the product of the adiabatic stretch states, evaluated at the Gauss–Legendre quadrature points, and the DVR bend functions. A second advantage is that the coupling in the DVR representation is through the kinetic energy operator which has a simple product form, so that at most a two-dimensional quadrature scheme is required in order to evaluate the Hamiltonian matrix. Recently these ideas have been extended to include rotations (Tennyson and Henderson 1989, Moiseyev and Certain 1989).

Normal coordinates, bond-angle coordinates and Jacobi coordinates each have their range of applicability. The organization of this section may be thought of as a progression from semi-rigid to floppy molecules. Therefore, to conclude this section, it is appropriate to briefly mention the work of Hutson and Jain (1989), who have very recently developed a method for calculating bound state energies within the framework of hyperspherical coordinates. These coordinates are particularly well suited for weakly bound van der Waals trimers, where one must consider the full permutation–inversion symmetry of the molecule (i.e. all the atom–diatom configurations are energetically accessible). The advantage of the hyperspherical coordinates is that they give equal emphasis to each of the members of the trimer under particle permutation.

Hutson and Jain have used hyperspherical harmonics to obtain a set of coupled second-order differential equations in the hyper-radius, which is then solved exactly using coupled channel techniques.

3. Perturbative calculations

We have seen above that the exact quantum mechanical solutions to highly excited vibrational states, using standard variational methods, provide accurate results for triatomic molecules. For tetra-atomic molecules, however, the enhanced basis sets make the calculations of all but the lowest states considerably more difficult; hence alternative routes to their solutions are currently being explored and developed. One route that Sibert *et al.* (1988b, 1989) and Fried and Ezra (1987, 1988, 1989) have been developing is the application of high-order quantum mechanical canonical Van Vleck perturbation theory (hereafter referred to as CVPT). This theory has been applied to many polyatomic molecules and has been found to be an important technique for the determination of eigenvalues and spectroscopic Hamiltonians (Nielsen 1951). Fried and Ezra (1987) have also taken advantage of the similar forms of CVPT and classical Dragt–Finn perturbation theory (Dragt and Finn 1976, 1983) in order to elucidate the connections between quantum mechanical and semiclassical perturbation theory.

Computationally it is convenient to apply this theory in a framework which uses harmonic oscillators as the zero-order Hamiltonian. This approach has the obvious drawback that the perturbative expansions diverge quite rapidly for very large amplitude motion. Hence, its use is not recommended for floppy molecules. Nevertheless, CVPT works surprisingly well in energy regimes for which perturbation theory is not expected to be useful (Sibert 1988b, McCoy and Sibert 1989). In this section, we focus primarily on the work of Sibert, and Sibert and McCoy, who have studied the vibrations of H_2O, SO_2, and H_2CO using CVPT. The complementary work of Fried and Ezra (1989) will also be discussed. We begin by reviewing the goals of the perturbation theory.

3.1. *Spectroscopic Hamiltonians*

For many molecular species, the vibrational energy levels have been parameterized as a function of quantum numbers using expressions of the form of equation (1). From a perturbative point of view, it is surprising that both this expression, which is based on second-order perturbation theory, and more generalized versions of it, have such a wide range of applicability, extending to energy regimes well beyond those for which second-order perturbation theory is expected to give practical results.

The Hamiltonian, corresponding to equation (1), which is often referred to as a spectroscopic Hamiltonian, evidently is

$$\hat{H} = \sum_i \hbar\omega_i(\hat{n} + \tfrac{1}{2}) + \sum_{i \geq j} \chi_{ij}(\hat{n}_i + \tfrac{1}{2})(\hat{n}_j + \tfrac{1}{2}). \qquad (39)$$

It is written explicitly as a function of the number operators, $\hat{n}_i|\mathbf{n}\rangle \equiv a_i^\dagger a_i|\mathbf{n}\rangle = n_i|\mathbf{n}\rangle$, where $|\mathbf{n}\rangle \equiv |n_1, n_2, \ldots, n_N\rangle$ is a product wavefunction for the N degrees of freedom, and n_i is the number of quanta in the ith oscillator. Equation (39) is correct through second order; in general there are additional cubic, quartic, and yet higher order terms in $\hat{n}_i$. The objective of CVPT is to transform a vibrational Hamiltonian, expressed in either normal coordinates or curvilinear coordinates, via a series of similarity transformations so that the transformed Hamiltonian has the form of equation (39). Before discussing the details of these transformations, it should be noted that this latter form is appropriate only if there is no significant configuration interaction between any of the zero-order states. Roughly speaking, this implies that for equation (39) to be valid, no coupling matrix elements between two zero-order states can be comparable to the energy difference between the two states. If there is significant configuration interaction between groups of zero-order states then one must use perturbation theory to transform to more general forms than that of equation (39).

The water molecule provides a simple example of a system for which it is appropriate to use degenerate perturbation theory. Here the bend frequency, ω_2, is roughly half the symmetric stretch frequency ω_1, which in turn is approximately equal to the antisymmetric stretch frequency ω_3. Consequently, if the eigenfunctions of the full vibrational Hamiltonian are expressed as a linear superposition of the zero-order harmonic oscillator basis states $|n_1, n_2, n_3\rangle$, one expects that these eigenstates will contain significant admixtures of the nearly degenerate, zero-order states $|n_1, n_2, n_3\rangle$, $|n_1 \pm 1, n_2 \mp 2, n_3\rangle$, and $|n_1 \pm 2, n_2, n_3 \mp 2\rangle$, rather than consisting of a single leading component. One therefore constructs a spectroscopic Hamiltonian with a form which explicitly allows these sets of states to couple, rather than try to decouple them perturbatively.

Following the work of Benedict *et al.* (1956), the appropriate form for the spectroscopic Hamiltonian of H_2O, through second order in perturbation theory, is

$$\hat{H} = \sum_i \hbar\omega_i(\hat{n}_i + \tfrac{1}{2}) + \sum_{i \geq j} \chi_{ij}(\hat{n}_i + \tfrac{1}{2})(\hat{n}_j + \tfrac{1}{2}) + k_{122}(a_1^\dagger a_2 a_2 + a_1 a_2^\dagger a_2^\dagger) + k_{1133}(a_1^\dagger a_1^\dagger a_3 a_3 + a_1 a_1 a_3^\dagger a_3^\dagger). \qquad (40)$$

The first two terms, which also appeared in equation (39), are purely diagonal contributions. Off-diagonal couplings are present in order to allow for the admixture of states discussed above. This coupling results from the last two terms in equation (40): the k_{122} term represents the 2:1 Fermi resonance interaction between the symmetric stretch and the bend, and the k_{1133} term leads to the 2:2 Darling–Dennison resonance coupling between the symmetric and antisymmetric stretches. In contrast to the Hamiltonian matrix associated with equation (39), which is diagonal, equation (40) expressed in matrix form is block diagonal, and each block is defined by $n_t = 2(n_1 + n_3) + n_2$. Equivalently, the operator, $\hat{n}_t = 2(\hat{n}_1 + \hat{n}_3) + \hat{n}_2$, commutes with the Hamiltonian of equation (40).

In general, CVPT is applied in order to transform canonically the Hamiltonian to a representation where the solutions may be obtained using a significantly smaller basis set than is needed in the original representation. In the previous example, we indicated one such form, the essential feature of which is the transformation to a Hamiltonian which is block diagonal through a given order in perturbation theory. Descriptions of alternative forms of the transformed Hamiltonian may be found elsewhere (Sibert 1988a, b Fried and Ezra 1987). There are several features of the transformations which facilitate the usage of CVPT. The first of these is the choice of an appropriate set of coordinates, the second is the use of a super-operator framework.

3.2. *Curvilinear coordinates*

In order to apply CVPT in a super-operator framework it is essential that the Hamiltonian be expressed as a polynomial expansion of the raising and lowering operators. The most convenient route to doing this is to expand the potential V, the G-matrix elements, and V' of equation (12) in a Taylor series about the equilibrium configuration is a given set of coordinates. The Taylor series expansion coefficients may be obtained using algebraic computer language programmes (Handy 1987), finite difference techniques (Sibert 1989), or in terms of the elements of the nonlinear transformation matrix between the rectilinear normal coordinates and the internal coordinates (Green *et al.* 1987). The zero-order contribution to this Hamiltonian, $\hat{H}^{(0)}$, is chosen to consist of N uncoupled harmonic oscillators. If the cubic terms and quadratic coupling terms are grouped into $\hat{H}^{(1)}$, the quartic terms into $\hat{H}^{(2)}$, and so forth, then the Hamiltonian has the form

$$\hat{H}=\hat{H}^{(0)}+\lambda\hat{H}^{(1)}+\lambda^2\hat{H}^{(2)}+\dots. \tag{41}$$

The harmonic oscillators of $\hat{H}^{(0)}$ are then used to define raising and lowering operators, which, when substituted, lead to a Hamiltonian of the form

$$\hat{H}(\mathbf{a}^\dagger,\mathbf{a})=\sum_{j=1}^{N}\hbar\omega_j(a_j^\dagger a_j+\tfrac{1}{2})+V_c(\mathbf{a}^\dagger,\mathbf{a}). \tag{42}$$

Here V_c contains all the higher-order contributions to the full Hamiltonian of equation (41).

For a given order of Taylor series expansion, the quality of the potential energy fit depends sensitively on the choice of coordinates. This is also true for the **G**-matrix elements and V'. To illustrate this, consider the one-dimensional stretch Hamiltonians in the bond, Morse and SPF coordinates, denoted R, y, and ρ respectively:

$$\hat{H}_R=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}+V(R), \tag{43}$$

$$\hat{H}_y=-\frac{(\hbar a)^2}{2m}\left(\frac{\partial}{\partial y}(1-y)^2\frac{\partial}{\partial y}\right)+V(y)-\frac{(\hbar a)^2}{8m}, \tag{44}$$

$$\hat{H}_\rho=-\frac{\hbar^2}{2mR_e^2}\left(\frac{\partial}{\partial\rho}(1-\rho)^4\frac{\partial}{\partial\rho}\right)+V(\rho)-\frac{\hbar^2(1-\rho)^2}{mR_e^2}. \tag{45}$$

The bottom two Hamiltonians were obtained from the first by a straightforward application of the chain rule. The volume elements for these Hamiltonians are $\mathrm{d}R$, $\mathrm{d}y$ and $\mathrm{d}\rho$ respectively, as is required with a zero-order picture consisting of harmonic oscillators. Although the kinetic energy operators are more complicated for the SPF and Morse coordinates, as can be seen in the coordinate dependence of the **G**-matrix elements, this dependence can be expressed as a low-order polynomial expansion. The fact that the Morse oscillator may be represented as a low-order polynomial in the form of equation (44) was first noted by Cooper (1987).

Both the Morse coordinates and SPF coordinates have better limiting behaviour than do the bond-stretching coordinates for expressing the **G**-matrix elements as low-order polynomial expansions. For a tri-atomic molecule, all the **G**-matrix elements (cf. equation (17)) may be expanded exactly using at most a quartic expansion in the SPF coordinates. The alternative coordinates for the bending motion offer some of the advantages that have been found for the stretching coordinate. The previously mentioned coordinate, Δz, has the advantage of removing singularities (at $\theta=\pi$) in V', so that this contribution may accurately be represented as a low-order polynomial expansion. Additionally, the **G**-matrix elements can often be accurately written as a low-order polynomial expansion in Δz.

Sibert and McCoy found that the quality of the CVPT results differed markedly for the above Hamiltonians of equations (43)–(45) only if they are expanded to a given order, and the remaining terms were neglected. If, however, the Hamiltonian is expanded to sufficient order, so that no terms in the Hamiltonian are neglected, then the results are very insensitive to the particular choice of coordinates. For example, an nth-order perturbative transformation requires that the potential be expanded to at least $n+2$ order if one is using bond-angle coordinates. The central advantage of the SPF and Morse coordinates, therefore, is that it is computationally easier to expand the initial Hamiltonian in terms of them.

Finally, given a choice of coordinates in which to expand the Hamiltonian in a Taylor series, any linear combination of these coordinates will provide equally accurate expansions. In light of the recent advances with respect to the bond-angle coordinates, one might consider using coordinates, which to lowest order, are linearly related to them (i.e. using the SPF coordinates or the Morse coordinates themselves). However, Lehmann (1983), Kellman (1985), and Mills and Robiette (1985) have shown that there is an algebraic equivalence between the local mode and normal mode representations; hence, in contrast to a variational calculation, there is little to be gained by using bond-angle coordinates. In fact, since all the quadratic terms can be included in $\hat{H}^{(0)}$, normal modes generally have been found to converge faster (Sibert and McCoy 1989, Baggot 1987) using CVPT.

3.3. *Canonical Van Vleck perturbation theory*

The transformations to the spectroscopic Hamiltonian are implemented by a series of canonical transformations of the form

$$\exp\{i\lambda^n[S^{(n)},]\}\dots\exp\{i\lambda^2[S^{(2)},]\}\exp\{i\lambda[S^{(1)},]\}\,\hat{H}=\hat{K}. \tag{46}$$

As the form of these transformation implies, first

$$\exp\{i\lambda[S^{(1)},]\}\,\hat{H}=\hat{K}_1 \tag{47}$$

is calculated through nth order, than $\hat{K}_2$ is likewise calculated as

$$\exp\{i\lambda^2[S^{(2)},]\}\,\hat{K}_1=\hat{K}_2. \tag{48}$$

This process continues n times until the spectroscopic Hamiltonian is obtained from

$$\exp\{i\lambda^n[S^{(n)},]\}\,\hat{K}_{n-1}=\hat{K}_n. \tag{49}$$

The computations which are needed for each of these transformations are very similar, so only the first (cf. equation (47)) is considered. $\hat{K}_1$ is determined by expanding the exponential in equation (47) using the well known Campbell–Hausdorff formula,

$$\hat{K}_1=\exp\{i\lambda[S^{(1)},]\}\,\hat{H}=\hat{H}+i\lambda[S^{(1)},\hat{H}]-\frac{\lambda^2}{2!}[S^{(1)},[S^{(1)},\hat{H}]]+\dots, \tag{50}$$

and then expanding $\hat{H}$ and $\hat{K}_1$ in powers of λ as in equation (41). Equating powers of λ, the standard expressions (Kemble 1937) are obtained

$$\left.\begin{aligned} \hat{K}_1^{(0)} &= \hat{H}^{(0)}, \\ \hat{K}_1^{(1)} &= \hat{H}^{(1)} + [S^{(1)}, \hat{H}^{(0)}], \\ \hat{K}_1^{(2)} &= \hat{H}^{(2)} + [S^{(1)}, \hat{H}^{(1)}] - \frac{\lambda^2}{2!}[S^{(1)}, [S^{(1)}, \hat{H}^{(0)}]], \end{aligned}\right\} \tag{51}$$

and so forth. For the general case of $\hat{H}^{(1)}$ expressed in normal form,

$$\hat{H}^{(1)} = \sum_{\mathbf{m}} \sum_{\mathbf{n}} C_{\mathbf{m},\mathbf{n}} \prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{n_j}, \tag{52}$$

a choice of

$$S^{(1)} = \sum_{\mathbf{m}}{}' \sum_{\mathbf{n}}{}' C_{\mathbf{m},\mathbf{n}} \frac{\prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{n_j}}{\sum_{j=1}^{N} (m_j - n_j)\hbar\omega_j} \tag{53}$$

leads to

$$\hat{K}_1^{(1)} = \sum_{\mathbf{m}}{}'' \sum_{\mathbf{n}}{}'' C_{\mathbf{m},\mathbf{n}} \prod_{j=1}^{N} (a_j^\dagger)^{m_j} (a_j)^{n_j}. \tag{54}$$

The primes and double primes refer to restricted summations, where $\Sigma_{\mathbf{m}} = \Sigma'_{\mathbf{m}} + \Sigma''_{\mathbf{m}}$. Equivalently, the terms in $\hat{K}_1^{(1)}$ include a subset of the terms in $\hat{H}^{(1)}$.

The form of $\hat{K}$ is predicted by the choice of terms to be included in $S^{(1)}$. This choice is very flexible; a usual option is, if there are no degeneracies in $\hat{H}^{(0)}$, to include in $S^{(1)}$ all the terms in $\hat{H}^{(1)}$. Consequently $\hat{K}_1^{(1)} = 0$. If there are degenerate or nearly degenerate states, then the coupling between them is included in $\hat{K}_1^{(1)}$. In the example of H_2O discussed above, the 2:1 Fermi resonance term was included in $\hat{K}_1^{(1)}$ while all other terms were transformed away. In general, it is desirable to transform away as many of the terms as possible while avoiding a divergent perturbative expansion.

Recently Fried and Ezra (1989) have implemented a useful alternative to the above methods for constructing the transformed Hamiltonian. In their work all the coupling terms except those which can be expressed entirely as functions of the number operators are transformed away. As a result their transformed Hamiltonian is diagonal. If there are resonances, this expansion in the number operators diverges. To put the Hamiltonian in a useful form it must be 'reconstructed'. To illustrate this process, Fried and Ezra presented the following simple example involving two coupled states.

Consider two zero-order states whose energies are $a \pm \delta$. If the interaction matrix between these two states is λ, then the exact eigenvalues, $E_\pm$, may be readily determined by solving the secular equation,

$$(E - a)^2 = \lambda^2 + \delta^2 \tag{55}$$

to obtain

$$E_\pm = a \pm [\delta^2 + \lambda^2]^{1/2}. \tag{56}$$

This expression can be contrasted to the result of Rayleigh–Schrödinger perturbation theory, where the form of the perturbative solution is equivalent to that which is obtained by expanding the exact expression for the energy in powers of λ,

$$E_{\pm}=a\pm\delta\left[1+\frac{\lambda^2}{2\delta^2}-\frac{\lambda^4}{8\delta^4}\cdots\right]. \tag{57}$$

The radius of convergence of this perturbative series is found by considering the singularity structure of the eigenvalues in the complex λ plane. There are two branch points for the square root, located at $\lambda=\pm i\delta$. This implies that, for values of λ with absolute value greater than δ, the perturbation series will diverge.

The key to reconstruction is to note that the secular equation (55) is an entire function of λ; it has no singularities anywhere in the complex λ plane. Hence, if the secular equation is rewritten as

$$(E-E_+)(E-E_-)=0, \tag{58}$$

and the polynomial expansion, equation (57), is inserted for $E_{\pm}$, then this expansion will no longer diverge. In fact, since this expression is quadratic in λ, all the higher order terms must cancel exactly.

For more complicated systems where M states are nearly degenerate the simple product of equation (58) is replaced with the secular equation

$$\prod_{i=1}^{M}[E-E_i(\lambda)]=0, \tag{59}$$

where E_i is the ith root of the secular equation, and λ is again the perturbation parameter. Using the CVPT algorithms discussed above, the E_i are obtained as a series expansion in λ to a given order, n. The product of equation (59) will contain terms up to $n\times M$; however, only the terms up to order n are retained. Fried and Ezra have applied this method to several vibrational problems, comparing their result to Padé approximations and almost degenerate perturbation theory results. Reconstruction is found to be more accurate than the former and almost equivalent to the latter. This method does have the distinct advantage that, whereas Sibert (1988) must entirely re-do the perturbative expansion if the final form of the transformed Hamiltonian is found to be divergent, only the reconstruction must be re-done in the approach of Fried and Ezra.

Both Sibert and McCoy (1989) and Fried and Ezra (1987) have applied CVPT to study the vibrations of SO_2. The former workers used a Hamiltonian, where the G-matrix elements, the potential, and V' were expanded through quartic terms using SPF coordinates for the stretches and Δz to describe the bends. The latter workers used the rectilinear normal modes with a potential expanded as a quartic expansion in these coordinates. Both calculations yielded eigenvalues to within 0·1 cm^{-1} of the exact variational energies for energies as high as those equivalent to having ten quanta of excitation in the bend.

Although CVPT might be expected to provide excellent results for the semi-rigid SO_2 molecule, it is less likely to be expected to do so for the H_2O molecule. McCoy and Sibert (1989) modelled the vibrations of H_2O using the force field of Halonen and Carrington (1988) which is expressed as a restricted quartic expansion in terms of the Morse coordinates for the stretches and the traditional bend extension coordinate for the bend. CVPT was carried out using normal coordinates constructed as linear combinations of these coordinates. The eigenvalues $E(n)$ of nth-order block diagonal spectroscopic Hamiltonians (n_t is a constant of the motion) are compared to the results of a fully converged variational calculation in table 3. For high levels of perturbation theory, the agreement with the exact variational calculation is extremely good, the exceptions occurring for those states with large bend excitation. It should be noted that a state with eight quanta of excitation in the bend has an energy about that of the barrier height found at the linear molecular configuration. Both the SO_2 and H_2O calculations are extremely fast. The sixth- and eighth-order perturbative results took a total of 2·5 and 6·0 min on a VAX 8650.

Sibert (1989) has applied CVPT to study the vibrations of H_2CO. This study used the quartic force field of RBH, where the stretches were modelled using SPF coordinates. In this study both the internal coordinates and rectilinear normal coordinates were used. Selected eigenvalues of block diagonal spectroscopic Hamiltonians are shown in table 4 for various levels of perturbation theory. Here each block was defined by the constant of motion, $n_t = 2(n_1 + n_5) + n_2 + n_3 + n_4 + n_6$, where n_1

Table 3. Differences (cm^{-1}) between results of normal mode CVPT calculations on H_2O and results from a variational calculation.

State†	n_t	ΔE‡(2)	ΔE(4)	ΔE(6)	ΔE(8)	ε§
$(0,0)1$	1	−1·85	−0·26	−0·05	−0·03	1595·07
$(0,0)2$	2	−6·57	−1·31	−0·33	−0·17	3151·45
$(1,0)^+0$	2	−1·26	−0·01	0·00	0·00	3657·12
$(1,0)^-0$	2	−0·29	−0·01	0·00	0·01	3754·98
$(0,0)3$	3	−17·30	−4·47	−1·45	−0·75	4666·41
$(0,0)4$	4	−38·86	−12·44	−4·96	−2·74	6135·44
$(0,0)5$	5	−79·04	−30·78	−14·80	−9·07	7550·94
$(1,0)^+3$	5	−20·97	−4·12	−1·71	−0·88	8268·40
$(1,0)^-3$	5	−13·64	−3·02	−0·93	−0·49	8365·33
$(2,0)^+1$	5	−9·80	−0·60	−0·20	−0·08	8761·31
$(2,0)^-1$	5	−8·44	−0·51	−0·18	−0·07	8810·22
$(0,0)6$	6	−105·80	−71·37	−40·72	−27·89	8898·84
$(1,1)1$	5	−50·46	−0·50	−0·06	0·00	9000·43
$(3,0)^+4$	10	−39·46	−6·97	−3·46	−0·75	16522·22
$(3,0)^-4$	10	−36·59	−6·49	−3·30	−0·73	16536·83
$(2,1)^+4$	10	−39·81	−5·91	−2·44	−0·54	16790·79
$(4,0)^+2$	10	−22·07	−5·90	−3·23	−1·74	16830·83
$(4,0)^-2$	10	−21·81	−5·27	−2·84	−1·59	16832·16
$(5,0)^+0$	10	−50·56	−0·54	0·20	−0·14	16893·01
$(5,0)^-0$	10	−51·06	−0·56	0·19	−0·16	16893·49
$(2,1)^-4$	10	−24·34	−4·30	−1·06	−0·13	16947·46
$(3,1)^+2$	10	−37·60	−4·56	−1·10	−0·29	17225·11
$(3,1)^-2$	10	−29·71	−4·36	−1·37	−0·30	17322·18
$(4,1)^+0$	10	−33·79	−2·14	0·03	0·13	17458·01
$(4,1)^-0$	10	−35·42	−2·33	0·07	0·17	17497·70
$(2,2)2$	10	−17·49	−4·27	−0·84	0·12	17531·40
$(3,2)^+0$	10	−36·65	−2·66	−0·02	0·19	17751·03
$(3,2)^-0$	10	−26·98	−4·55	−0·51	0·06	17936·34

† We use local mode notation to assign the states.
‡ $\Delta E(n) = \varepsilon - n$th-order perturbative energy.
§ ε = result of variational calculation.

Table 4. Comparison of select rectilinear, E_r and curvilinear, E_c, eigenvalues (cm^{-1}) of H_2CO obtained using CVPT.

State	n_t	Symmetry	$E_r(4)$‡	$E_r(6)$	$E_c(2)$	$E_c(4)$
4_1	1	B_1	1166·1	1166·1	1166·4	1166·1
6_1	1	B_2	1250·5	1250·5	1250·2	1250·5
3_1	1	A_1	1505·7	1505·7	1505·5	1505·7
2_1	1	A_1	1747·4	1747·4	1747·4	1747·4
4_2	2	A_1	2323·4	2323·2	2325·0	2323·3
4_16_1	2	A_2	2426·2	2426·2	2426·2	2426·2
6_2	2	A_1	2497·8	2497·7	2496·3	2497·7
3_14_1	2	B_1	2667·8	2667·7	2667·4	2667·9
$3_16_1+5_1$	2	B_2	2727·1	2726·6	2723·6	2726·9
1_1	2	A_1	2780·4	2780·6	2778·8	2780·6
$5_1-3_16_1$	2	B_2	2845·1	2845·3	2843·1	2845·3
2_14_1	2	B_1	2905·9	2905·8	2906·3	2905·9
2_16_1	2	B_2	3001·7	3001·9	3002·8	3001·8
3_2	2	A_1	3009·8	3009·8	3010·2	3009·9
2_13_1	2	A_1	3245·8	3245·8	3245·9	3245·9
2_2	2	A_1	3475·9	3476·0	3476·1	3476·1
†	6	A_1	8011·3	8008·9	8003·6	8010·3
†	6	A_1	8019·2	8021·5	8012·2	8021·5
†	6	A_1	8029·1	8026·3	8026·0	8028·0
†	6	A_1	8027·5	8027·4	8037·7	8029·1
†	6	A_1	8078·9	8077·2	8063·2	8078·3
†	6	A_1	8115·4	8114·8	8109·2	8114·9
†	6	A_1	8130·7	8128·9	8123·6	8129·3
†	6	A_1	8139·8	8141·6	8132·3	8140·9
†	6	A_1	8220·1	8220·7	8211·4	8220·9
†	6	A_1	8277·3	8278·1	8272·0	8278·2
†	6	A_1	8280·7	8281·4	8282·3	8281·1

† States have not been assigned, due to the large degree of mixing.

‡ $E(n)$—nth-order perturbative result.

and n_5 correspond to the high-frequency CH stretches. The agreement between the two coordinate systems is quite good, as is the agreement between higher orders of perturbation theory.

4. Concluding remarks

This review has considered both variational and perturbative treatments of highly vibrationally excited states. The choice of coordinates was seen to be a central ingredient of these calculations. Since the time required for a matrix diagonalization of an $N \times N$ matrix scales as N^3, there is a strong impetus to make judicious choices for coordinate systems and basis functions in order to minimize the size of the basis set. This review has considered several of these choices.

In all the variational approaches discussed in this review, product basis sets were used. This need not be the case (Carter and Handy 1986), but it is computationally very convenient for the evaluation of the Hamiltonian. In the quest for a minimal product basis set representation for a vibrational system, it should always be recalled that the matrix diagonalization should be the time intensive part of the total calculation and not the setting up of the Hamiltonian matrix. Quadrature schemes as well as the form of the kinetic and potential energy operators play a key role in this context.

As in electronic structure calculations, the quality of the product basis can be dramatically improved by using SCF functions rather than some primitive basis function. There is an additional dimension, however, in vibrational problems. Here there is a great deal of flexibility in choosing a coordinate system in which to construct the product basis for the SCF calculation. Although this review was by no means complete in this regard, normal coordinates, bond-angle coordinates, and Jacobi coordinates were discussed.

Recent advances in the use of CVPT to calculate the eigenvalues of highly excited states were also reviewed. The use of curvilinear coordinates, such as SPF and Morse coordinates, was found to be a very efficient way to express the vibrational Hamiltonian as a low-order polynomial expansion in the coordinates and conjugate momenta. This fact, combined with a super-operator approach, which obviates the need to evaluate large Hamiltonian matrices, provides an efficient way of carrying out perturbation to high order. Several examples were included to illustrate the accuracy of this method.

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