

9 VARIATIONAL CALCULATIONS OF ROTATION-VIBRATION SPECTRA

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9.1 Introduction

Perturbation theory, as described by Sarka and Demaison in this volume, has for a long time been the theoretical bedrock of high resolution molecular spectroscopy. However, there are many problems for which perturbation theory struggles to find accurate solutions. Most standard perturbative treatments of the rotational and vibrational spectra of chemically bound molecules are based on the assumption of small amplitude vibrational motion. There are many situations where this is a

poor assumption: molecules containing hydrogen or multiple symmetry related minima in their potential energy surface and associated tunnelling splittings are typical examples. Furthermore, as a molecule approaches dissociation it must always undergo large amplitude motion. It follows that it is not a question of if, but when, perturbation theory will break down.

Variational methods have been developed over the last twenty years to address directly cases for which perturbation theory is not reliable. These methods are more complete in the sense that they aim at a direct and full solution of the nuclear motion problem. Variational methods can usually solve both the vibrational and rotational problems within the same framework which adds considerably to their scope and flexibility. However these advantages also carry a price: except

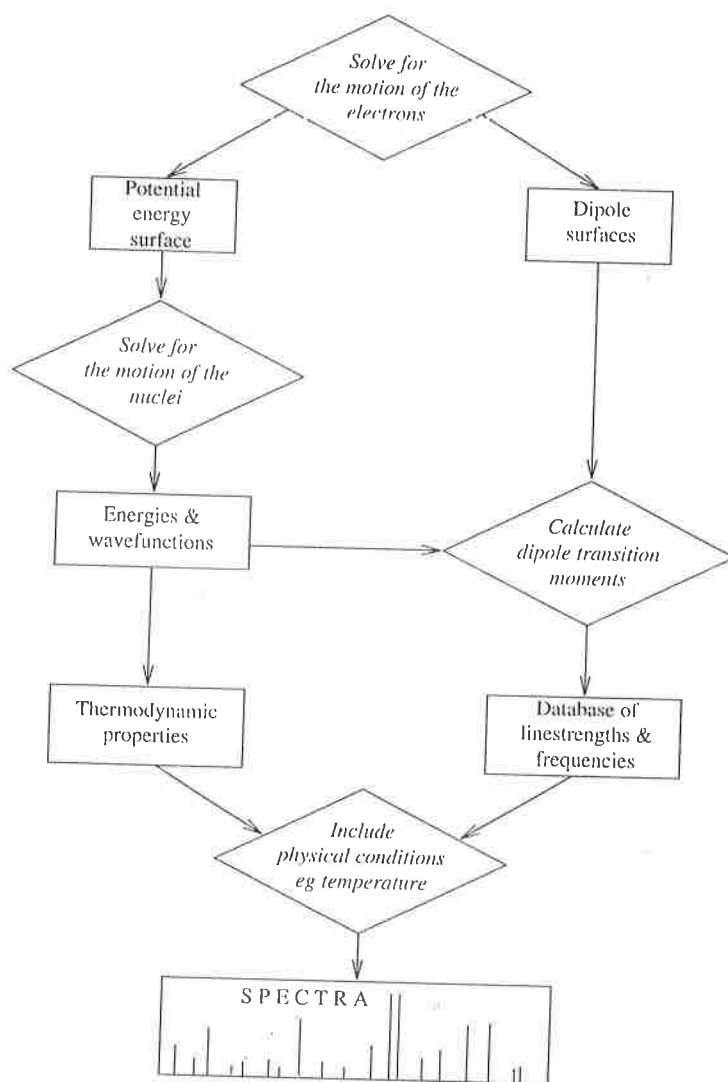


Figure 9.1. Flow diagram depicting the steps involved in generating the rotation-vibration spectrum of a molecule from first principles. Diamonds represent different steps in the calculation, while rectangles represent data transfers.

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for diatomic systems for which rotation-vibration energy levels and spectra can be computed essentially exactly for a given potential by direct integration of the Schrödinger equation [Le Roy (1996)], variational calculations are much more computationally intensive than calculations based on perturbation theory. This computational expense also scales rapidly with the number of vibrational modes of the molecule being studied.

For this reason most of the work using variational methods has concentrated on triatomic molecules, although calculations on tetra-atomics are becoming more common and the first attempts at treating penta-atomic systems are beginning to appear [Dunn, Boggs and Pulay (1987), Jung and Leforestier (1992), and Carter, Shnyder and Bowman (1999)]. As it is not possible to do justice to all methods here, I will concentrate on methods developed for triatomics and point to possible extensions to larger systems. Similarly there are many methods which have been used only to study the vibrational states of rotationless molecules. These will largely be neglected as not being suitable for generating actual spectra.

There are a number of steps involved in generating the vibration-rotation spectrum of a molecule from first principles. These steps are summarized in Figure 9.1, which assumes a complete *ab initio* procedure. This includes a series of electronic structure calculations to generate the potential energy (and dipole) surface used as the basis for the nuclear motion calculations. In practice, with the sole exception of H_3^+ [Polyansky and Tennyson (1999)], *ab initio* potentials for polyatomic molecules are not accurate enough to give results whose accuracy is even close to that obtained in a typical high resolution spectroscopy experiment. Many calculations therefore replace the *ab initio* stage of the calculation with potentials determined by other means such as by fitting to experimental data.

Given a potential energy surface, the major step in Figure 9.1 is determining the energy levels and associated wavefunctions for that surface. This is the main topic of this chapter, although there will also be some discussion of use of these wavefunctions to give electric dipole transition intensities and hence to generate complete synthetic spectra.

9.2 Hamiltonians

Unlike the electronic structure problems discussed elsewhere in this volume, there is no unique Hamiltonian for studying the nuclear motion problem. This arises from the need to identify and separate out the centre-of-mass motion of the molecule, which gives a continuous spectrum, prior to attempting to determine any rotation-vibration energy levels.

For an N -atomic molecule, there are $3N$ coordinates specifying the position of each atom relative to some arbitrary laboratory-fixed origin. Removal of the three centre-of-mass motion coordinates leaves $3N - 3$ coordinates. These coordinates, which are usually described as space fixed, are widely used for calculations on Van der Waals complexes [Le Roy and Carley (1980), and Hutson (1991)]. Space-fixed coordinates have the disadvantage that they do not distinguish between vibrational and rotational motion of the system. To do this requires a second transformation to body-fixed coordinates. This transformation involves fixing or embedding a rotational axis system within the framework of the molecule. To do this requires defining three rotational angles, two for linear molecules, which link the space-fixed axes to the body-fixed ones. In fact there are situations where even for non-linear molecules it can be advantageous to define less than three rotation angles [see Brocks *et al.* (1983) for example], but these will not be pursued here.

Sutcliffe (1982) gave a general prescription for developing body-fixed Hamiltonians for various choices of internal coordinates based upon application of the chain rule. In principle this prescription is easy to follow but in practice there are two pitfalls. Firstly, the algebra can get very messy. This problem has been alleviated by the use of computer algebra programs [Handy (1987), and Colwell and Handy (1997)]. Secondly, the act of embedding the body-fixed axes *always* leads

to regions of the Hamiltonian where it is singular. This is an unavoidable consequence of the mathematical procedure involved. Singularities arise whenever the value of one coordinate causes the Hamiltonian not to depend on some other coordinate. For example, in polar coordinates a vector of length zero is the same for all orientations.

How serious any singularity is depends on the coordinates and embedding chosen, and the nature of the problem to be tackled. For example many of the Hamiltonians discussed below are singular as an atom-atom distance, or something similar to it, approaches zero. Such singularities are usually not important as the potential is very strongly repulsive in this region. Conversely bent molecule Hamiltonians are usually singular for geometries in which the molecule goes linear. As many bent molecules, such as water, sample linear geometries at relatively low energy, such a singularity can be important. In this case strategies have been developed to deal with this problem [Hougen, Bunker and Johns (1970), Tennyson and Sutcliffe (1982), and Jensen 1983].

As the detailed form for the different Hamiltonians used for variational studies of nuclear motion all differ, it is not possible, or desirable, to give them all here. However within the Born-Oppenheimer approximation these Hamiltonians all have the same basic structure:

$$\hat{H} = \hat{K}_V + \hat{K}_{VR} + V, \quad (1)$$

where \hat{K}_V is the vibrational kinetic energy operator, and \hat{K}_{VR} is the vibration-rotation kinetic energy, which is null unless the molecule is rotationally excited. V is the potential energy surface. Both the potential and the vibrational kinetic energy operator are functions of the $3N - 6$ internal coordinates only. This means that the rotationless ($J = 0$) Hamiltonian depends on the internal coordinate system chosen, but is independent of the various ways of defining the body-fixed axis system discussed below. This represents a significant simplification for vibration only calculations.

9.3 Coordinate systems

The computer requirements of a variational calculation are largely determined by the size of the basis set required, which in turn depends on the coordinate system chosen. Although the choice of coordinate is perhaps not quite as crucial as it is for the SCF methods described by Gerber and Jung in this volume, they are still important for the efficiency of a calculation. Even for triatomics it is possible to define unlimited different sets of coordinates [Zúñiga, Bastida and Requena (1997)], so it is helpful to break these into different classes.

9.3.1 NORMAL COORDINATES

Perhaps the most obvious coordinates for treating the vibrational motion, and the ones which were used for the earliest variational calculations [see Carney, Sprandel and Kern (1978)], are normal coordinates. These coordinates are those obtained from diagonalizing the standard harmonic force field problem for the molecule about its equilibrium geometry [Wilson, Decius and Cross (1955)]. The body-fixed Hamiltonian expressed in these coordinates was originally derived, in its simplest form, by Watson (1968), who showed that the Hamiltonian contained terms dependent directly on the inverse of the moment-of-inertia tensor. This term, generally called the Watson term, is singular for linear geometries.

Even more serious than problems with the Watson term was the realization that for large amplitude motion, standard straight line extrapolations of normal coordinates often leave the true domain of the problem. This means that these coordinates are now rarely used for triatomic problems. However, the use of normal coordinates for larger systems is actively being pursued [Carter, Bowman and Handy (1998)]. One advantage in this case is that it is often possible to calculate all the matrix elements for these coordinates analytically [see Dunn, Boggs and Pulay (1987), for example].

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9.3.2 INTERNAL COORDINATES: STRETCHES ONLY

One of the conceptually simplest ways of representing the internal structure of a molecule is via atom-atom distances or related stretching coordinates. For three- or four-atom molecules these coordinates might seem natural since the number of interatomic distances coincides with the number of vibrational degrees of freedom. However, there is a severe technical problem with the use of coordinates based directly on atom-atom distances to do with integration ranges. The fact that one atom-atom distance alone cannot go to infinity leads to coupled integration ranges. The coupling of these ranges makes it hard to design efficient algorithms for evaluating matrix elements in these coordinates, although Watson (1995) performed successful calculations on the H_3^+ molecule using these coordinates in a grid representation, which he simply truncated at linear geometries.

One set of stretching only coordinates, used originally by Pekeris (1958), have been proposed which avoid the coupling of integration ranges. These are so-called perimetric coordinates. For a three-atom system perimetric coordinates transform atom-atom distances (r_1, r_2, r_3) into a set defined by $q_1 = -r_1 + r_2 + r_3$, and cyclic permutations thereof. This transformation decouples the integration ranges but thus far use of perimetric coordinates for rotation-vibration calculations has been limited [Sutcliffe (1992)].

9.3.3 INTERNAL COORDINATES: ONE DISTANCE PLUS ANGLES

As it is not possible to define a structure using only angles, any coordinate system must contain at least one radial coordinate. Hyperspherical coordinates [see Manz and Schor (1986), for example] use a single radial coordinate, generally known as the hyperradius, which represents the size of the molecule as a whole. The different structures for a given hyperradius are represented by two angles for a triatomic, five for a tetratomic and so forth.

There has been a considerable amount of theoretical work on hyperspherical coordinates. However these coordinates have often proved difficult to use in actual numerical applications, particularly those with rotational excitation or well-localized motions. This means that even for systems such as H_3^+ , whose symmetry is naturally represented in these coordinates [Whitnell and Light (1989), Carter and Meyer (1994), and Wolniewicz and Hinze (1994)], other less symmetric coordinate systems have been widely favoured.

9.3.4 INTERNAL COORDINATES: DISTANCES AND ANGLES

Most successful methods have used a mixture of angular and radial coordinates. For triatomic systems this means two radial coordinates and one angle or (r_1, r_2, θ) . A natural form of these coordinates, which have been widely exploited by Carter, Handy and co-workers [Carter and Handy (1986a, 1986b)] are bond length, bond angle coordinates. For a molecule such as water these correspond to normal parameters used to represent the bonding pattern in the molecule.

Bond length, bond angle coordinates suffer from the disadvantage that they are not orthogonal. Orthogonal coordinates are ones for which the kinetic energy operator is diagonal, i.e. contain no terms with mixed differential operators. Hamiltonians expressed in orthogonal coordinates are therefore considerably simpler. This is an important consideration for discrete variable representations (DVRs) where the kinetic energy operator provides the off-diagonal coupling, but is less important in basis set approaches [Carter and Handy (1986a, 1986b)].

The most widely used orthogonal coordinate systems are Jacobi and Radau; these are illustrated in Figure 9.2. Jacobi coordinates are also called atom-diatom scattering coordinates and are appropriate for Van der Waals dimers such as $Ar-H_2$. However, they have proved robust and have been widely used for other systems less obvious systems, such as H_3^+ .

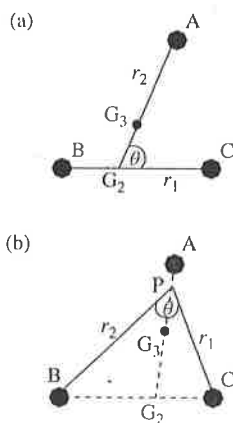


Figure 9.2. Orthogonal coordinates for the ABC triatomic molecule involving two stretches (r_1, r_2) and one angle (θ): (a) Jacobi or atom-diatom scattering coordinates; (b) Radau coordinates. G_2 and G_3 are the diatom (BC) and triatom centres-of-masses respectively. In Radau coordinates the canonical point, P, is defined such that $(PG_2)^2 = AG_3 \times AG_2$ [Hutson (1994)].

Radau coordinates are close to bond length, bond angle coordinates when the central atom is heavy. They were originally proposed for the planetary three-body problem [Radau (1868)] but have been widely used for molecules, such as water, which have a heavy central atom.

A number of workers [Sutcliffe and Tennyson (1991), and Zúñiga, Bastida and Requena (1997)] have developed very general methods of generating (r_1, r_2, θ) coordinate systems. Schwenke (1996) has also shown how orthogonal coordinates and the corresponding Hamiltonians can be derived in a relatively straightforward manner by successive addition of Jacobi or Radau coordinates or even mixtures of the two. Colwell and Handy (1997) extended their bond length, bond angle approach to tetra-atomic systems for which they have derived a number of different Hamiltonians depending on the bonding of the molecule in question: linear, as in acetylene, or branched, as in formaldehyde, for example.

9.3.5 BODY-FIXED AXES

Within the normal coordinate Hamiltonian discussed above it is usual to define the body-fixed axes using the second Eckart (1935) condition. This condition minimizes the interaction between vibrational and rotational motion, the Coriolis coupling, for each geometry. This condition is thus the optimal one for defining rotational motion. Unfortunately, the use of the Eckart embedding in conjunction with the standard normal coordinate Hamiltonian, for which it was originally proposed, suffers from the problems involved with using normal coordinates and discussed above.

While considerable effort has been expended on exploring suitable internal coordinate systems for vibrational calculations, less work has been done exploring possible axis embeddings. Indeed for some time the only general scheme was due to Sutcliffe and Tennyson (1991). Recently, however, Wei and Carrington (1997a, 1997b) have proposed a method of combining the virtues of the Eckart (1935) embedding of the axes, which minimize the Coriolis coupling between vibrational and rotational motion, with the advantages of the orthogonal internal coordinates discussed above. It is too early to say how Wei and Carrington's Hamiltonians perform in practical calculations.

Figure 9.3 illustrates some of the axes embeddings possible with Jacobi and Radau coordinates. Hamiltonians have been derived for other possible orientations of the axes [Sutcliffe and Tennyson (1991)] but most of these suffer from profound problems with singularities which have so far prevented their use. It should be noted that an inappropriate axis embedding will not only lead to greatly increased coupling between the vibrational and rotational motions of the system, but can also lead to loss of symmetry in the system. Furthermore, calculation of vibrational band

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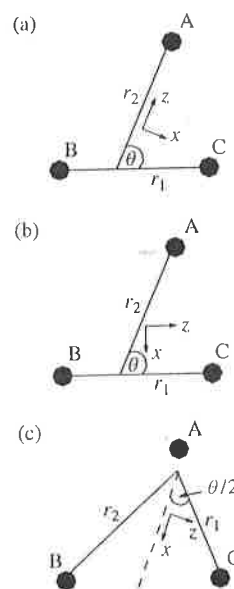


Figure 9.3. Some possible axis embeddings for orthogonal triatomic coordinates. (a) Jacobi coordinates, r_2 embedding; (b) Jacobi coordinates, r_1 embedding; (c) Radau coordinates, bisector embedding. In all cases the y -axis is perpendicular to the plane of the diagram.

intensities using rotationless wavefunctions, a useful method for obtaining intensity estimates cheaply, also depends on the axis system used. Since vibrational band intensities are an approximation which rely on separation of vibrational and rotational motion, they should be calculated using Eckart axes which minimize these interactions [Le Sueur *et al.* (1992)].

9.4 Vibrational motion

For diatomic molecules the vibrational Schrödinger equation can be solved by direct integration [Le Roy (1996)]. For larger molecules, however, there is no single procedure appropriate for all cases. Accurate, non-perturbative methods of solving the vibrational problem for both triatomic and larger molecules have received considerable attention. Not all these methods are based upon the variational principle. One example, direct solution of the problem using quantum Monte Carlo (QMC) procedures, is discussed by Wales elsewhere in this volume.

Another class of methods used for both vibration and rotation-vibration problems are based on generalization of the close coupled equations of Arthurs and Dalgarno (1960). These methods, as encapsulated in the program BOUND [Hutson (1993)], use standard basis set expansions to reduce the problem to solving for one, key interaction coordinate which is attacked using numerical integration procedures adapted from those used for diatomics. These procedures find particular application for Van der Waals dimers [Hutson (1991)] where the interaction coordinate clearly operates on a different energy scale to the internal coordinate(s) of the interacting molecules.

In some ways similar in spirit to the close-coupling methods are the various non-rigid or semi-rigid bender approaches developed by Bunker and co-workers [for a review see Jensen (1983)]. These approaches focus on the coupling between a large amplitude bending motion and rotation, for which very accurate solutions are obtained. In these approaches the other coordinates are treated in a less complete manner. The MORBID (Morse-oscillator rigid bender internal dynamics) method of Jensen (1988), described in more detail in Sections 15.4.7 and 15.4.8 of Bunker and Jensen (1998), can be thought of as the natural successor of the non-rigid bender approach for triatomic systems. The MORBID method has many similarities to the variational approaches discussed below but differs in that there is some approximation in the nuclear motion

kinetic energy used. For this reason the more standard variational procedures have sometimes been dubbed exact kinetic energy or EKE methods.

What can be thought of as the standard method for performing a variational calculations has a number of ingredients. In particular it requires:

- A potential energy surface for the system under consideration. In most cases the accuracy of this surface determines the accuracy of the final calculation.
- A choice of coordinates which then defines the Schrödinger equation to be solved.
- A choice of basis functions to be used to represent the vibrational motions in each coordinate.

Given these ingredients, the computational strategy involves the following steps.

- (1) Construction of matrix elements for various terms in the Hamiltonian. Depending on the choice of basis functions, some of these matrix elements may be evaluated analytically although it is usually necessary to use numerical procedures to compute matrix elements over the potential.
- (2) Construction of the Hamiltonian matrix from the individual matrix elements.
- (3) Diagonalization of the Hamiltonian matrix.

For triatomics there are public domain programs which use this strategy to solve the nuclear motion problem and, if required, generate rotation-vibration spectra [Tennyson, Miller and Le Sueur (1993), and Tennyson, Henderson and Fulton (1995)]. For triatomics the computer time required is usually dominated by the final matrix diagonalization. For this reason various strategies have been developed to reduce the size of this matrix. The most common of these involves preconditioning or contracting the final basis by constructing and diagonalizing reduced dimension problems. The idea of such procedures is that fewer basis functions are then required to give converged results.

For molecules with more than three atoms, numerical quadrature can become a computationally very demanding problem. It is in evaluating the potential energy matrix element that this problem is the worst: this involves simultaneous numerical quadrature in all $3N - 6$ vibrational coordinates for an N -atomic problem. With M (typically 10–30) quadrature points in each coordinate this leads to M^{3N-6} evaluations of the potential energy surface. One strategy to avoid this problem is to write the potential as a separable or multinomial expansion [Romanowski, Bowman and Harding (1985), Carter and Handy (1996), and Rosenstock *et al.* (1998), for example]. In this form the numerical integrals can all be expressed as products of one-dimensional quadratures. However, this procedure clearly constrains the form of the potential energy surface and the range of any calculation that can be performed using it.

9.4.1 BASIS SET VERSUS GRID METHODS

A number of groups have worked on variational procedures to solve the vibrational problem. Broadly these procedures divide into two camps: those employing (polynomial) basis functions and those employing grid-based procedures. The procedures are closely related but have some subtle differences.

For a triatomic problem in (r_1, r_2, θ) coordinates a basis set representation of the wavefunction of the i th state might be:

$$|i\rangle = \sum_{j,m,n} c_{j,m,n}^i P_j(\theta) Q_m(r_1) R_n(r_2), \quad (2)$$

where, for example, the angular motion might be expanded in terms of Legendre polynomials, and the stretching motion might be represented by Morse or harmonic oscillator functions, which

in turn can be expressed in terms of Laguerre and Hermite polynomials, respectively. With preconditioned basis sets, the functions used in equation (2) may be some predetermined linear combination of these polynomials. The calculation involves determining the expansion coefficient matrix, c , for each wavefunction. This is done by diagonalizing the real symmetric ('secular') matrix given by:

$$H_{s,s'} = \langle P_j Q_m R_n | \hat{H} | P_{j'} Q_{m'} R_{n'} \rangle, \quad (3)$$

where s is a compound index running over the basis functions used in the expansion; \hat{H} is the Hamiltonian operator whose derivation is discussed above and the integration runs over the vibrational coordinates. These integrals are often referred to as matrix elements.

The variational principle is often stated in a form which deals only with the upper bound to the lowest energy level of a given system. However, it has long been known [MacDonald (1933)] that the matrix formulation of the problem gives an upper bound for excited states of the problem as well. In fact the i th eigenvalue of the problem represents an upper bound to the i th exact solution to the problem. This property is clearly important for rotation-vibration calculations, where one is usually interested in many states of a given system.

Of course knowing something is an upper bound to a desired solution does not mean that it is close to that solution. To be confident that one has obtained a reliable solution to a given problem it is necessary to demonstrate variational convergence. The usual way to do this is to increase the number of terms in the expansion (2) until the results do not change by more than the desired accuracy. It is usually found that lower lying energy levels converge more rapidly than more highly excited ones but one has to be careful because, particularly in multidimensional problems, different levels often converge at markedly different rates. A further complication is that it is sometimes not computationally feasible to perform calculations which conclusively demonstrate convergence.

Procedures which employ basis functions are sometimes labelled FBR for finite basis representation. This name is a tacit acknowledgement that, at least in principle, basis set expansions for vibrational motion involve truncating infinite series of functions. FBR procedures also require a means of evaluating matrix elements numerically. If the basis sets employed are polynomials then it is usual to use Gaussian quadrature schemes based upon these polynomials [Stroud and Secrest (1966)]. Within this method it is possible to perform the numerical integrals to arbitrary accuracy, within the usual limitations of a finite precision computer. For a given potential energy surface and an EKE Hamiltonian, the FBR yields results which are strictly variational upper bounds to the various states of the system. FBR procedures are particularly efficient at obtaining high accuracy results for a few low-lying rotation-vibration states of a molecule.

The most commonly used grid-based method is the so-called discrete variable representation (DVR) [Bačić and Light (1989)]. Formally the DVR is obtained as a transformation from a corresponding FBR,

$$\begin{aligned} H_{t,t'}^{\text{DVR}} &= H_{\alpha,\beta,\gamma,\alpha',\beta',\gamma'} \\ &= \sum_{j,j'} \sum_{m,m'} \sum_{n,n'} T_j^\alpha T_{j'}^{\alpha'} T_m^\beta T_{m'}^{\beta'} T_n^\gamma T_{n'}^{\gamma'} \langle P_j Q_m R_n | \hat{H} | P_{j'} Q_{m'} R_{n'} \rangle, \end{aligned} \quad (4)$$

where the transformation matrices T are defined in terms of the Gaussian quadrature points and weights of the (polynomial) basis functions. For an M -point Gaussian quadrature the quadrature points, $\{\alpha\}$, are defined as the zeroes of M^{th} order function P_M and the transformation is given by:

$$T_j^\alpha = \sqrt{w_\alpha} P_j(\alpha), \quad (5)$$

where w_α is the weight associated with quadrature point α .

Equation (4) demonstrates the close similarity between the FBR and DVR methods. However, the two methods are only identical in the case where the number of basis functions used to represent the vibrational motions in a particular coordinate is equal to the number of Gaussian quadrature points used for evaluating numerical integrals in that coordinate. In practice one would not usually choose to use this few quadrature points in an FBR calculation: it is half the number that can, by the theorems of Gaussian quadrature, be shown to yield exact integrals in most practical applications [Stroud and Secrest (1966)]. This compromise on the accuracy of the integrals used in DVR procedures mean that DVR-based methods, although they often behave variationally, are not actually strictly variational [Wei (1997)].

The loss of strict variational character is a disadvantage, so what advantages does the DVR have? By the so-called quadrature approximation DVR methods are diagonal in the matrix elements of the potential energy operator [Dickinson and Certain (1968)]:

$$\sum_{j,j'} \sum_{m,m'} \sum_{n,n'} T_j^\alpha T_{j'}^{\alpha'} T_m^\beta T_{m'}^{\beta'} T_n^\gamma T_{n'}^{\gamma'} \langle P_j Q_m R_n | V | P_{j'} Q_{m'} R_{n'} \rangle \simeq \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma,\gamma'} V(\alpha, \beta, \gamma). \quad (6)$$

The potential diagonal property makes the Hamiltonian matrix very sparse. It is possible to take advantage of this sparseness directly by using iterative matrix diagonalization procedures to obtain the desired solutions of the Hamiltonian matrix [Bramley and Carrington (1993)]. It is also possible to exploit this property to adapt a DVR grid to a particular potential using a so-called potential-optimized DVR [Echave and Clary (1992)].

Conversely the potential diagonal property makes the DVR particularly good, possibly optimally good, for designing diagonalization and truncation procedures [Bačić and Light (1989)]; these result in a Hamiltonian matrix containing a representation of a much higher fraction of well-converged states than can usually be obtained with an FBR-based procedure. This means that the DVR is particularly effective for problems where a large number of states are of interest. It would appear that which of the two DVR procedures is most effective is dependent on the system under study, and in particular how good the coordinates used are at representing the vibrational motions of this system. With a good match, the diagonalization and truncation procedure performs best, but with a poor match direct diagonalization is computationally more efficient [Bramley and Carrington (1994)].

Finally a grid-based procedure can be used as a means of avoiding singularities in the Hamiltonian by simply dropping the region in the vicinity of the singularity from the calculation [Tennyson and Sutcliffe (1992)]. Of course, this is only useful if the singular regions lie at high enough energy not to effect the energy levels of interest.

9.4.2 DIAGONALIZATION

Diagonalizing the final Hamiltonian (or secular) matrix is a crucial computational step in the above procedures. It is the ability to diagonalize this matrix which usually dictates the level at which it is possible to tackle a problem. Indeed the rapid growth in the application of variational methods at the expense of methods based on perturbation theory is a direct consequence of the increase in computer power which has made such diagonalizations feasible even for fairly challenging systems on standard desktop computers.

In all cases discussed above the matrices that need to be diagonalized are real and symmetric. Usually one is only interested in the k lowest solutions of an N -dimensional matrix. The ratio between k and N is important for determining which diagonalization procedure to use.

Standard real symmetric matrix diagonalization procedures which yield either all eigenvalues or all eigenvalues and eigenvectors have a memory requirement which scales as N^2 and computer time requirement proportional to N^3 .

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The time requirement of iterative procedures, such as Lanczos diagonalizers, scale as $k \times N^2$ for matrices with few zero elements. However, if the matrix is sparse, it is not necessary either to store or to process the entire matrix. This can lead to considerable saving in computer resources, although, as discussed above, it would appear that this situation is somewhat case dependent. It is even possible to formulate these iterative procedures using a so-called direct approach which means that the Hamiltonian matrix is never actually explicitly constructed [Roy and Carrington (1996)]. Such procedures have been used to diagonalize to obtain the lowest few, $k = 50$, eigenvalues from a very large matrices, $N > 2 \times 10^6$ [Lehoucq *et al.* (1998)].

The diagonalization procedures, discussed above, implicitly assume that one is interested in obtaining k energy levels from the lowest upwards. This assumption is compatible with the behaviour of variational procedures, which generally converge the lowest energy levels first. However, for many applications one is only interested in certain high-lying states of system. A number of methods have been proposed for obtaining only a few results of interest from a large matrix [Roy and Carrington (1995)]. The most successful of these appear to be filter diagonalization which uses semi-classical procedures to project out energy levels in the energy region of interest [Mandelsham and Taylor (1997)] and the pseudo-spectral method [Antikainen, Friesner and Leforestier (1995)] which replaces the direct diagonalization of the matrix with consideration of a matrix element similar to that used to compute linestrengths, see equation (10) below.

9.5 Rotational motion

There are many variational procedures available for treating the purely vibrational problem. Only a fraction of these procedures have been adapted to treat rotationally excited molecules. This is perhaps somewhat surprising as it is not possible to model nuclear motion spectra correctly without the explicit treatment of rotational excitation.

In some ways the rotational excitation problem is simpler than the vibrational one. In body-fixed coordinates, the rotational motion is a function of the three Euler angles, (α, β, γ) , which link the space-fixed axis system to the body-fixed one. Using these coordinates, the rotation matrices, $D_{kM}^J(\alpha, \beta, \gamma)$ [Brink and Satchler (1993), and Zare (1988)] form a complete and finite representation for the rotational motion. In the rotation matrices, k represents the projection of J onto the space-fixed z -axis and M is the projection of J onto the body-fixed z -axis. In the absence of a magnetic field, the dependence on M can be ignored. This means that the rotational motion of a molecule with total angular momentum quantum number J can be entirely represented by $2J + 1$ of these functions with $k = -J, -J + 1, \dots, 0, \dots, J - 1, J$. Further simplification can be achieved by use of symmetry:

$$|J, k, p\rangle = \frac{1}{\sqrt{2}}(|J, k, M\rangle + (-1)^p |J, -k, M\rangle), \quad k > 0, p = 0, 1, \quad (7)$$

$$|J, k, p\rangle = |J, k = 0, M\rangle, \quad p = 0,$$

where $|J, k, M\rangle$ are the wavefunctions of a rotating rigid symmetric top. These symmetric top functions are closely related to the rotation matrices, [see Zare (1988), equation (3.125)], but have the advantage that they are normalized. In equation (7), p is the Wang symmetry which gives the parity of the rotational functions under spatial inversion symmetry as $(-1)^{J+p}$. Use of this symmetry means that it is possible to separate the rotational basis into two non-interacting portions of dimension J (for $p = 1$) and $J + 1$ (for $p = 0$).

This much is common to all variational treatments of rotational motion. Difficulties arise because it is necessary to treat rotational motion at the same time as vibrational motion, significantly increasing what is often already a large vibrational problem. Superficially it might appear

that the addition of rotational motion would result in problems whose usage of computer time would scale as $(J + 1)^3 \times N^3$.

The solution to the problem is to solve the vibrational problem first and then use these solutions as the vibrational part of the basis to solve the rotational problem. The simplest way of doing this is to use the solutions of the rotationless ($J = 0$) vibrational problem for this purpose [Chen, Maessen and Wolfsberg (1985)]. However, this method fails for molecules for which a smooth transition from bent to linear geometries is important. There are many examples of these including Van der Waals dimers and floppy but strongly bound systems such as water and H_3^+ .

For such molecules it is necessary to solve 'vibrational' problems which include the diagonal part of the rotational kinetic energy operator. In this step of the calculation the projection of J onto the body-fixed z -axis, k , is assumed to be a good quantum number. The second step of the calculation relaxes this assumption but produces a Hamiltonian matrix with a particularly simple block off-diagonal structure [Tennyson and Sutcliffe (1986)]. It should be noted that this two-step procedure places much more importance on a suitable choice of body-fixed axes than direct solution of the full rotation-vibration problem: with a good choice of axes rather few solutions to the 'vibrational' problem are needed to converge the results of the full rotation-vibration problem. The reduction in the number of 'vibrational' states needed is of course equivalent to minimizing the Coriolis interaction between the vibrational states. This is exactly what the Eckart embedding, discussed above, strives to do.

The structure of the Hamiltonian matrix inherent in these two-step procedures can be directly exploited using iterative diagonalization procedures which also lead to a substantial (approximately J -fold) reduction in the memory requirement for the calculation. These two-step procedures have been used to obtain reliable results for highly rotationally excited molecules [Miller and Tennyson (1988)].

Of course the standard spectroscopic method of representing rotational motion is via rotational constants. Although there are well-documented cases where such methods based on perturbation theory do not work [Polyansky (1985)], this representation is compact and reliable for many systems, particularly those undergoing only small amplitude vibrational motion. There are two methods of obtaining rotational constants from a variational calculation. The first is to determine the constants using energy levels obtained from the procedures discussed above. The second is to recognize that, at least in principle, the rotational constants represent the expectation values of various operators. It is straightforward to use vibrational wavefunctions, determined from variational calculations, to evaluate these expectation values as a function of vibrational state.

Table 9.1 compares results obtained with the two methods for the molecule HO_2 , which is sufficiently floppy to be regarded as a poor candidate for such a treatment. It is clear that the two

Table 9.1. Comparison of rotational constants, in cm^{-1} , for several vibrational states of HO_2 computed from expectation values of the $J = 0$ vibrational wavefunctions or from the $J = 1$ and $J = 0$ calculated energy levels [Brandão, Rio and Tennyson (1999)].

State	From expectation values			From energy levels		
	A	B	C	A	B	C
(000)	19.75	1.113	1.053	19.74	1.117	1.053
(001)	19.71	1.099	1.039	19.70	1.103	1.039
(010)	20.37	1.107	1.048	20.36	1.117	1.049
(100)	19.02	1.115	1.049	19.02	1.119	1.053
(200)	18.32	1.115	1.045	18.31	1.122	1.052

methods give reasonably similar results. On balance, the expectation value method of evaluating rotational constants is probably the method of choice because (a) it is computationally cheaper as it does not require solving any problems for rotationally excited molecules and (b) the results are more stable, as they are less likely to be distorted by accidental resonances caused by interactions between rotational levels belonging to different vibrational states.

9.6 Symmetry considerations

For a molecule containing no like atoms, the only rigorous symmetry that needs to be considered for the rotation-vibration problem is the total rotational quantum number J and the parity p , defined above. One secular matrix needs to be constructed and diagonalized for each (J, p) of interest.

For molecules containing identical atoms it is also necessary to consider the effects of permutation symmetry [Bunker and Jensen (1998)]. It is desirable to include this symmetry explicitly in the nuclear motion calculation for a number of reasons. Inclusion of a symmetry block factorizes the secular matrix into a number of smaller matrices which can be diagonalized separately resulting in a considerable saving of computational resources. Furthermore the results of these separate diagonalizations are automatically symmetry labelled. This helps not only with identifying vibrational states, but is particularly important when generating synthetic spectra, as transitions involving different symmetry species are weighted by different statistical weights, g_{ns} , due to the effects of nuclear spin. In particularly extreme examples, such as H_3^+ or CO_2 , statistical weights of zero may occur resulting in the complete absence of certain lines from the spectrum.

Although it is desirable to include the full permutation symmetry of the molecule under consideration in the calculation, this is not always achieved in practice because of other technical and computational considerations. Thus the majority of published variational rotation-vibration calculations on H_3^+ , for example, have used Jacobi coordinates despite the fact that it is not possible to represent the full symmetry of H_3^+ using these coordinates.

To exploit the symmetry of a particular molecule it is necessary to use coordinates in which it is possible to represent the effects of the various symmetry operations. Thus for an AB_2 molecule, interchanging the two identical atoms involves changing θ to $-\theta$ in Jacobi coordinates but involves interchanging r_1 and r_2 in Radau coordinates. It is possible to represent this symmetry in both these coordinate systems.

The next step is to define basis functions for the relevant coordinate(s), which can be separated according to symmetry type. Thus for the AB_2 molecule in Jacobi coordinate Legendre polynomials, $P_j(\cos \theta)$ might make an appropriate choice, since functions with even j represent symmetries which are even with respect to interchange of the identical atoms and odd j are odd with respect to this interchange. The secular problem can thus be split according to the parity of j .

When the symmetry operation mixes coordinates, as in the AB_2 system in Radau coordinates example, there are two possible approaches. One option is to redefine the coordinates so that the symmetry behaviour depends only on a single coordinate [Whitnell and Light (1988)]. In the Radau case, or indeed bond length, bond angle coordinates, this transformation is:

$$\begin{aligned} r &= \frac{1}{\sqrt{2}}(r_1 + r_2), \\ q &= r_1 - r_2, \end{aligned} \quad (8)$$

and the symmetry is now carried by the parity of coordinate q .

An alternative approach is to symmetrize the functions (or grid points) directly:

$$|m, n, s\rangle = \frac{1}{\sqrt{2}} (H_m(r_1)H_n(r_2) + (-1)^s H_n(r_1)H_m(r_2)), \quad m \geq n + s, s = 0, 1; \quad (9)$$

$$|m, n, s\rangle = H_m(r_1)H_n(r_2), \quad m = n, s = 0.$$

In this approach, functions $|m, n, s\rangle$ with $s = 0$ are even and those with $s = 1$ are odd. The two approaches both work although there are some subtle differences over their domains of validity [Polyansky, Tennyson and Zobov (1999)].

9.7 Transition intensities

In nearly all cases of interest, transitions involving changes in rotational and/or vibrational state are driven by electric dipoles. To calculate the probability of such a transition occurring using the wavefunctions derived from variational calculations, it is also necessary to have information on the dipole of the molecule as a function of its internal coordinates. These dipole surfaces can be computed by most *ab initio* electronic structure packages. Usually the dipole is represented by a separate surface for each of its (Cartesian) components. This is necessary as the dipole, unlike the potential, is a vector property, with both a magnitude and a direction.

The computation of rotation-vibration dipole transition intensities is relatively straightforward, if in some cases quite expensive, given a suitable set of rotation-vibration wavefunctions and appropriate dipole surfaces. However the topic has not received a great deal of attention and there are relatively few program suites which include calculation of transition intensities as a routine part of the calculation. This situation perhaps arises because many experiments are not suitable for measuring either absolute or relative intensities and therefore do not yield information for comparison with theory. However, nearly all actual applications of spectroscopy rely on detailed knowledge of transition intensities (see below). Furthermore, as experimental measurements of transition intensities are often only accurate to about 10%, there are grounds for believing that for simple systems it is often possible to calculate both absolute and relative transition intensities more accurately than they have been measured. Indeed in some cases, such as the spectra of molecular ions, theory remains the only source of transition intensity data.

The line strength of a dipole transition linking state $|i\rangle$ to state $|f\rangle$ is given by Bunker and Jensen (1998) [equation (14-7)] as:

$$S(f-i) = \sum_{a,b} \sum_{\lambda=-1}^{+1} |\langle f_b | \mu_\lambda | i_a \rangle|^2, \quad (10)$$

where μ_λ is one of the three components of the space-fixed electric dipole expressed at the molecular centre of mass. The first summation in equation (10) runs over not only any degeneracy in the vibrational wavefunctions but also the projection of the rotational functions onto the space-fixed axes, M_i and M_f . Summing over these leads to factors of $(2J_i + 1)(2J_f + 1)$ in the final expression [Bunker and Jensen (1998)].

The Einstein A_{if} coefficient for spontaneous emission can be obtained from the line strength:

$$A_{if} = \frac{1}{(2J_f + 1)} \frac{64\pi^4 \omega_{if}^3}{3h} S(f-i), \quad (11)$$

where $\omega_{if} = E_f - E_i$ is the transition frequency between the states. A_{if} can be used to generate both emission and adsorption intensities, although certain applications may also require further information to characterize the line profile of a particular transition.

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The matrix element in equation (10) involves integration only over the vibrational (or internal) and rotational coordinates [Miller, Tennyson and Sutcliffe (1989), and Schwenke (1996)]. These matrix elements contain all the rigorous dipole selection rules for the system. From analysis of the rotational wavefunctions one finds that electric dipole transitions are strictly forbidden unless:

$$\begin{aligned} \Delta J = J_f - J_i = \pm 1, & \quad p_i = p_f; \\ \Delta J = J_f - J_i = 0, & \quad p_i \neq p_f. \end{aligned} \quad (12)$$

Unless the molecule contains identical atoms there are no further selection rules; however, for molecules with permutation symmetry the additional selection rules can be summarized by saying that transitions only occur between states with the same nuclear spin. Thus in the case of water para ($g_{\text{ns}} = 1$) states undergo transitions to para states and ortho ($g_{\text{ns}} = 3$) to ortho only.

Any other 'rules' governing transitions such as those obtained from the analysis of harmonic oscillators which suggest that overtone bands, combination bands or difference bands should all be forbidden, are not given by analysing equation (10). These rules are therefore approximate and indicate which will be the strong transitions. Indeed the weak forbidden transitions play an important role in spectroscopy.

9.8 Applications

There are a large number of studies which have used variational methods to compute rotation-vibration. Therefore it is only possible to consider here illustrative examples which give the range of problems that variational calculations can be used for. For this purpose only calculations on the single molecule water (H_2^{16}O) will be considered, and only a very selective subset of these.

One of the original motivations for developing variational methods was to test potential energy surfaces derived from *ab initio* electronic structure calculations [see Whitehead and Handy (1976), for example]. This motivation remains [Partridge and Schwenke (1997), and Kedziora and Shavitt (1997)], although the accuracy of modern electronic structure calculations has led to studies investigating where the 'standard' non-relativistic, Born-Oppenheimer models fails. For example, studies have analysed the failure of the Born-Oppenheimer approximation [Zobov *et al.* (1996)] and the contribution of electronic relativistic effects [Czaszar *et al.* (1998)]. In all these studies, data from high resolution spectroscopy experiments such as the compilation available from the atmospheric database HITRAN [Rothman *et al.* (1998)], are used as the arbiter of accuracy of the underlying (effective) potential energy surface. This match is made via high accuracy nuclear motion calculations.

The realization that it is not possible to calculate *ab initio* potential energy surfaces of many electron molecules to spectroscopic accuracy has led to an alternative strategy. Comparisons between the calculations and experimental data, usually either transition frequencies or energy levels derived from transition frequencies, are used to refine the potential energy surface. This procedure, which results in a spectroscopically determined, effective potential energy surface, is summarized in Figure 9.4. Spectroscopically determined potentials usually rely on high accuracy *ab initio* calculations as a starting point. Of course these calculations only give the potential energy surface at a grid of points, so these are normally interpolated by fitting to some suitable function [see Murrell *et al.* (1984), for example]. This fitted potential is then used as a basis for variational calculations, the results of which can be compared with experiment. The potential is then adjusted and the procedure repeated until convergence is achieved.

The usual technique used to optimize the potential is least-squares fitting for which sophisticated packages are available [Law and Hutson (1997)]. In practice it is desirable for the fitting procedure not to take too many iterations, as each step is fairly computationally expensive. This

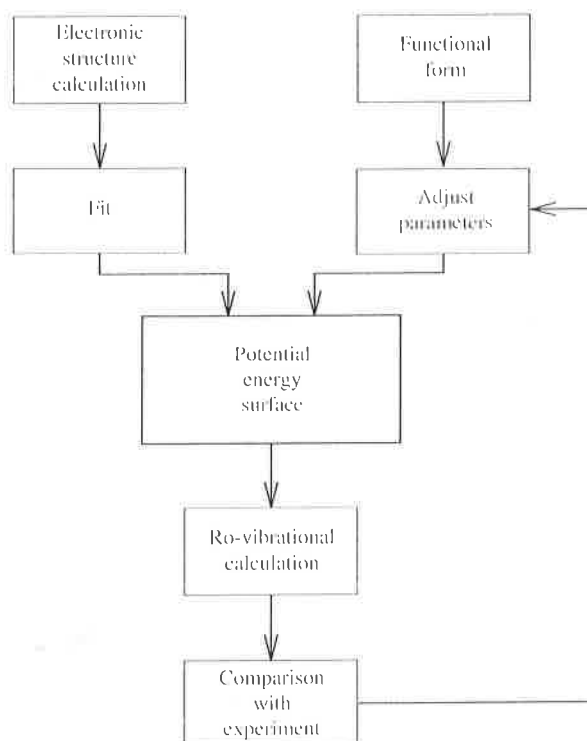


Figure 9.4. Flow diagram depicting the steps involved in fitting an (effective) potential energy surface to experimental data, usually rotation–vibration spectra or energy levels derived from such spectra.

is achieved because the derivatives of the potential, with respect to changing all the various constants that are used to parameterize it, can be obtained at only modest computation cost using the Hellmann–Feynman theorem. This is done by evaluating the expectation value:

$$\frac{\partial}{\partial c} \langle i | \hat{H} | i \rangle = \langle i | \frac{\partial V}{\partial c} | i \rangle \quad (13)$$

for each state of interest, where V is the present approximation to the potential and c is any parameter that one might wish to vary. In equation (13), the derivative of the kinetic energy operator with respect to c is assumed to be zero since, in the EKE approach, the kinetic energy operators are parameter free.

This method of potential optimization has proved highly effective and a number of high accuracy, spectroscopically determined potentials have been derived in this manner for water. The best presently available is due to Partridge and Schwenke (1997) which reproduces a wide range of vibrational and rotational experimental data with a standard deviation of only 0.25 cm^{-1} . It should be noted, however, that a potential energy surface derived in this manner will not correspond to the results of an exact, Born–Oppenheimer electronic structure calculation, as the process of fitting will always attempt to compensate for any effect which influences the spectrum, such as Born–Oppenheimer breakdown, which is not included in the calculation by any other means.

A major reason for performing electronic structure and nuclear motion calculations is to predict molecular spectra, to aid their observation or to help interpret observations of difficult spectra. Traditionally, spectral analysis, the assignment of quantum numbers to observed transitions, has

relied heavily on perturbation theory. This situation is changing as variational calculations are able to address problems not amenable to perturbative analysis. A recent example is the assignment of a highly congested spectrum of water recorded in sunspots [Polyansky *et al.* (1997)].

As has already been mentioned, it is sometimes difficult to measure transition intensities even for situations where transition frequencies can be measured to high accuracy. However, applications of high resolution spectroscopy, whether it be the monitoring of a combustion process via infrared emission, modeling the transmission of sunlight through our atmosphere or the study of a species in the interstellar medium, rely heavily on a knowledge of the intensity and temperature dependence of individual transitions. A match of one or more line frequencies may provide proof that a particular molecule is present in the object being studied, but it is only via the intensity that information on the amount present and the physical conditions such the (effective) temperature can be obtained. Furthermore, unlike frequencies which are routinely measured with an accuracy much better than 1 part in a million, even good intensity measurements are often only reliable to around 10%.

Variational calculations can therefore act as a provider of intensity information even when the frequencies have been measured. One interesting finding is that while spectroscopically determined potential energy surfaces yield much more accurate results than *ab initio* ones for a molecule such as water, the reverse is true for dipole surfaces [Lynas-Gray, Miller and Tennyson (1995)].

Some studies require huge quantities of spectral data. For example, many millions of water transitions are required to model the transport of radiation through super-heated steam. This data is important for modeling situations as diverse as the atmospheres of cool stars and the exhausts of hydrogen burning rockets. In the case of water, many years of laboratory measurements have yielded only a very small fraction of the number of the lines required. For instance the database HITRAN [Rothman *et al.* (1998)] contains just over 30 000 water transitions, sufficient for room temperature models but completely inadequate at high temperature. A number of groups have used variational calculations to compute water linelists appropriate for high temperature studies. The most extensive of these [Partridge and Schwenke (1997)] contains 300 million transitions, the individual measurement of which is clearly beyond any reasonable laboratory campaign.

The radiative transport problems are not the only ones which can benefit from the large quantity of data that can be obtained from variational rotation-vibration calculations. Partition functions, which can be used to determine thermodynamic properties such as specific heats and entropies, can be determined by explicit summation of energy levels. Particularly for hot species, large numbers of energy levels may be required for an accurate computation of the partition function. Variational calculations can be used to compute these properties up to temperatures where other methods fail [Harris *et al.* (1998)].

Calculations, such as those used to compute partition functions at high temperatures, require information on essentially all the bound states of the molecule. Studying bound states up to dissociation naturally links into studies of behaviour just above the dissociation limit. This is, of course, the natural domain of chemical reaction theory, but processes such as photodissociation



or the chemical reaction



can occur on the same (ground state) potential energy surface as that used for studying the spectroscopy of water. Furthermore at low energy and high resolution, these continuum processes often show pronounced structures as a function of energy. These structures are due to quasi-bound states (or resonances) lying in the continuum. It is necessary to adapt the variational methods

used here to study these states which do not have an exact energy but are characterized by an energy plus a width or natural lifetime.

A final example of the application of variational calculations has a motivation somewhat different from those discussed above. Chaos theory has seen a major rise in the latter half of the twentieth century. However, this theory only rigorously applies to systems obeying classical mechanics. There has been considerable work in the area of quantum chaology---the study of quantal systems in energy regimes where their classical counterparts are chaotic. Molecular vibrations form a particularly good paradigm for the study of quantum chaology. Anharmonically coupled oscillators are well known to be one of the simplest classically chaotic systems and of course molecular vibrations are generally represented as anharmonically coupled oscillations. So far studies of highly excited states of water have concentrated only on the coupling between the stretching modes [Cho and Child (1994)]. Variational calculations, particularly ones which produce both energy levels and wavefunctions, can provide a rich source of data for testing out ideas on possible manifestations of quantum chaos.

9.9 References

- Arthur, A. M., and Dalgarno, A., 1960, *Proc. R. Soc. London, Ser. A* **256**, 540-551.
- Antikainen, J., Friesner, R., and Leforestier, C., 1985, *J. Chem. Phys.*, **102**, 1270-1279.
- Bačić, Z., and Light, J. C., 1989, *Annu. Rev. Phys. Chem.*, **40**, 469-498.
- Bramley, M. J., and Carrington, T., Jr., 1993, *J. Chem. Phys.*, **99**, 8519-8541.
- Bramley, M. J., and Carrington, T., Jr., 1994, *J. Chem. Phys.*, **101**, 8494-8507.
- Brandão, J., Rio, C. M. A., and Tennyson, J., 1999, unpublished.
- Brink, D. M., and Satehler, G. R., 1993, *Angular Momentum*, 3rd edition; Clarendon Press: Oxford.
- Brooks, G., van der Avoird, A., Sutcliffe, B. T., and Tennyson, J., 1983, *Mol. Phys.*, **50**, 1025-1043.
- Bunker, P. R., and Jensen, P., 1998, *Molecular Symmetry and Spectroscopy*, 2nd edition; NRC Research Press: Ottawa.
- Carney, G. D., Sprandel, L. L., and Kern, C. W., 1978, *Adv. Chem. Phys.*, **37**, 305-79.
- Carter, S., Bowman, J. M., and Handy, N. C., 1998, *Theor. Chem. Accounts*, **100**, 191.
- Carter, S., Shneider, H. M., and Bowman, J. M., 1999, *J. Chem. Phys.*, **110**, 8417-8423.
- Carter, S., and Handy, N. C., 1986a, *Mol. Phys.*, **57**, 175-185.
- Carter, S., and Handy, N. C., 1986b, *Comput. Phys. Commun.*, **5**, 115-172.
- Carter, S., and Handy, N. C., 1996, *J. Mol. Spectrosc.*, **179**, 65-72.
- Carter, S., and Meyer, W., 1994, *J. Chem. Phys.*, **100**, 2104-2117.
- Chen, C.-L., Maessen, B., and Wolfsberg, M., 1985, *J. Chem. Phys.*, **83**, 1795-1807.
- Cho, S. W., and Child, M. S., 1994, *Mol. Phys.*, **81**, 447-465.
- Colwell, S. M., and Handy, N. C., 1997, *Mol. Phys.*, **92**, 317-330.
- Csaszar, A. G., Kain, J. S., Polyansky, O. L., Zobov, N. F., and Tennyson, J., *Chem. Phys. Lett.*, **293**, 317-323.
- Dickinson, A. S., and Certain, P. R., 1968, *J. Chem. Phys.*, **49**, 4209-4211.
- Dunn, K. M., Boggs, J. E., and Pulay, P., 1987, *J. Chem. Phys.*, **86**, 5088-5093.
- Echave, J., and Clary, D. C., 1992, *Chem. Phys. Lett.*, **190**, 339-349.
- Eckart, C., 1935, *Phys. Rev.*, **47**, 552.
- Handy, N. C., 1987, *Mol. Phys.*, **61**, 207-223.
- Harris, G. J., Viti, S., Mussa, H. Y., and Tennyson, J., 1998, *J. Chem. Phys.*, **109**, 7197-7204.
- Hougen, J. T., Bunker, P. R., and Johns, J. W. C., 1970, *J. Mol. Spectrosc.*, **34**, 136-172.
- Hutson, J. M., 1991, *Adv. Molecular Vibrations and Collision Dynamics*, **1A**, 1-45.
- Hutson, J. M., 1993, BOUND: A program for calculating bound-state energies for weakly bound molecular complexes, version 5, Distributed via Collaborative Computational Project No. 6 of the Science and Engineering Research Council, on Heavy Particle Dynamics.
- Hutson, J. M., 1994, *Comput. Phys. Commun.*, **84**, 1-18.
- Jung, C., and Leforestier, C., 1992, *J. Chem. Phys.*, **97**, 2481-2489.
- Jensen, P., 1983, *Comput. Phys. Commun.*, **1**, 1-55.
- Jensen, P., 1988, *J. Mol. Spectrosc.*, **128**, 478-501.
- Kedziora, G. S., and Sharvitt, I., 1997, *J. Chem. Phys.*, **106**, 8733-8745.
- Law, M. M., and Hutson, J. M., 1997, *Comput. Phys. Commun.*, **102**, 252-268.
- Lehoucq, R. B., Gray, S. K., Zhang, D.-H., and Light, J. C., 1998, *Comput. Phys. Commun.*, **109**, 15-26.
- Le Roy, R. J., 1996, University of Waterloo Chemical Physics Research Report CP-555R, 1.
- Le Roy, R. J., and Carley, J. S., 1980, in *Potential Energy Surfaces*, Lawley, K. P., Ed.; Wiley: New York, pp. 353-420.

Le Sueur
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- Le Sueur, C. R., Miller, S., Tennyson, J., and Sutcliffe, B. T., 1992, *Mol. Phys.*, **76**, 1147-1156.
- Lynas-Gray, A. E., Miller, S., and Tennyson, J., 1995, *J. Mol. Spectrosc.*, **169**, 458-467.
- MacDonald, J. K. L., 1933, *Phys. Rev.*, **43**, 830.
- Mandelstam, V. A., and Taylor, H. S., 1997, *J. Chem. Phys.*, **106**, 5085-5090.
- Manz, J., and Schor, H. H. R., 1986, *J. Phys. Chem.*, **91**, 1813.
- Miller, S., and Tennyson, J., 1988, *Chem. Phys. Lett.*, **145**, 117-120.
- Miller, S., Tennyson, J., and Sutcliffe, B. T., 1989, *Mol. Phys.*, **66**, 429-456.
- Murrell, J. N., Carter, S., Farantos, S. C., Huxley, P., and Varandas, A. J. C., 1984, *Molecular Potential Energy Functions*; Wiley: Chichester.
- Partridge, H., and Schwenke, D. W., 1997, *J. Chem. Phys.*, **106**, 4618-4639.
- Pekeris, C. L., 1958, *Phys. Rev.*, **112**, 1649.
- Polyansky, O. L., 1985, *J. Mol. Spectrosc.*, **112**, 79-87.
- Polyansky, O. L., and Tennyson, J., 1999, *J. Chem. Phys.*, **110**, 5056-5064.
- Polyansky, O. L., Tennyson, J., and Zobov, N. F., 1999, *Spectrochim. Acta A*, **55**, 659-693.
- Polyansky, O. L., Zobov, N. F., Viti, S., Tennyson, J., Bernath, P. F., and Wallace, L., 1997, *Science*, **277**, 346-349.
- Radau, R., 1868, *Ann. Sci. Ecole Normale Superior*, **3**, 311.
- Rosenstock, M., Rosmus, P., Reinsch, E. A., Treutler, O., Carter, S., and Handy, N. C., 1998, *Mol. Phys.*, **93**, 853-865.
- Romanowski, H., Bowman, J. M., and Harding, L., 1985, *J. Chem. Phys.*, **82**, 4155-4165.
- Rothman, L. S., Rinsland, C. P., Goldman, A., Massie, S. T., Edwards, D. P., Flaud, J.-M., Perrin, A., Camy-Peyret, C., Dana, V., Mandin, J.-Y., Schroeder, J., McCann, A., Gamache, R. R., Wattson, R. B., Yoshino, K., Chance, K. V., Jucks, K. W., Brown, L. R., Nemtchinov, V., and Varanasi, P., 1998, *J. Quant. Spectrosc. Radiat. Transfer*, **60**, 665-710.
- Roy, P. N., and Carrington, T. Jr., 1995, *J. Chem. Phys.*, **103**, 5600-5612.
- Roy, P. N., and Carrington, T. Jr., 1996, *Chem. Phys. Lett.*, **257**, 98-104.
- Schwenke, D. W., 1996, *J. Phys. Chem.*, **100**, 2867-2884.
- Stroud, A. H., and Secrest, D., 1966, *Gaussian Quadrature Formulas*; Prentice-Hall: London.
- Sutcliffe, B. T., 1982, in *Current Aspects of Quantum Chemistry*, Carbo, R., Ed., Vol. 21; Elsevier: Amsterdam, p. 9.
- Sutcliffe, B. T., 1992, *Mol. Phys.*, **75**, 1233-1236.
- Sutcliffe, B. T., and Tennyson, J., 1991, *Int. J. Quant. Chem.*, **39**, 183-196.
- Tennyson, J., Henderson, J. R., and Fulton, N. G., 1995, *Comput. Phys. Commun.*, **86**, 175-198.
- Tennyson, J., Miller, S., and Le Sueur, C. R., 1993, *Comput. Phys. Commun.*, **1993**, **75**, 339-364.
- Tennyson, J., and Sutcliffe, B. T., 1982, *J. Chem. Phys.*, **77**, 4061-4072.
- Tennyson, J., and Sutcliffe, B. T., 1986, *Mol. Phys.*, **58**, 1067-1085.
- Tennyson, J., and Sutcliffe, B. T., 1992, *Int. J. Quant. Chem.*, **42**, 941-952.
- Watson, J. K. G., 1968, *Mol. Phys.*, **15**, 479-490.
- Watson, J. K. G., 1995, *Chem. Phys.*, **190**, 291-300.
- Wei, H., 1997, *J. Chem. Phys.*, **106**, 6885-6900.
- Wei, H., and Carrington, T. Jr., 1997a, *J. Chem. Phys.*, **107**, 2813-2818.
- Wei, H., and Carrington, T. Jr., 1997b, *J. Chem. Phys.*, **107**, 9493-9501.
- Whitehead, R. J., and Handy, N. C., 1976, *J. Mol. Spectrosc.*, **59**, 459-469.
- Whitnell, R. M., and Light, J. C., 1988, *J. Chem. Phys.*, **89**, 3674-3680.
- Whitnell, R. M., and Light, J. C., 1989, *J. Chem. Phys.*, **90**, 1774-1786.
- Wilson, E. B., Jr., Decius, J. C., and Cross, P. C., 1955, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*, Dover Publications: New York.
- Wolniewicz, L., and Hinze, J., 1994, *J. Chem. Phys.*, **101**, 9817-9829.
- Zare, R. N., 1988, *Angular Momentum*; Wiley: New York.
- Zobov, N. F., Polyansky, O. L., Le Sueur, C. R., and Tennyson, J., 1996, *Chem. Phys. Lett.*, **260**, 381-387.
- Zúñiga, J., Bastida, A., and Requena, A., 1997, *J. Chem. Soc., Faraday Trans.*, **93**, 1681-1690.