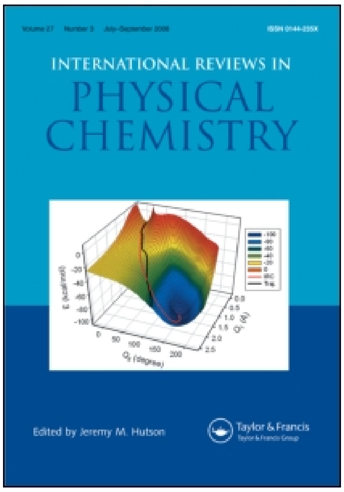
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

The calculation of vibrational energy levels by semiclassical and quantum methodology: A review

Nicholas C. Handy[a]
[a] University Chemical Laboratory, Cambridge, CB2 1EW, England

To cite this Article Handy, Nicholas C.(1989) 'The calculation of vibrational energy levels by semiclassical and quantum methodology: A review', International Reviews in Physical Chemistry, 8: 4, 275 — 288
To link to this Article: DOI: 10.1080/01442358909353231
URL: http://dx.doi.org/10.1080/01442358909353231

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Reviews in Physical Chemistry, 1989, Vol. 8, No. 4, 275–288

The calculation of vibrational energy levels by semiclassical and quantum methodology: a review

by NICHOLAS C. HANDY
University Chemical Laboratory, Lensfield Road,
Cambridge CB2 1EW, England

In this review the four best techniques that answer the question 'Given an analytical potential-energy surface, how does one calculate the ($J=0$) vibrational energy levels?' are discussed. The methods examined are (i) the fully variational matrix procedure, (ii) the semiclassical approaches relying on quantisation of the Einstein action integrals, (iii) the adiabatic switch-on method, and (iv) the quantum Monte Carlo method applied to vibrations. In particular, the usefulness of each procedure is examined with regard to the number of atoms ($N \geqslant 3$), and the calculation of highly excited vibrational levels.

1. Introduction

This review is an attempt to report on the best answers, to date, to the question 'Given an analytical potential-energy surface for a polyatomic molecule, how does one calculate the ($J=0$) vibrational energy levels?' This is an important question because it is argued that the potential surface lies behind the whole of chemistry, and hence we spend a considerable amount of time deriving analytic representations for such surfaces. One test of the acceptibility of such surfaces is the requirement that the vibrational levels derived from these surfaces give good agreement with experimental vibrational levels—we are therefore faced with the problem considered here. Such surfaces may have been derived indirectly from experimental work, or may result from *ab initio* computation. We may need to optimise parameters in such a surface by a non-linear least-squares fit of experimental values to these vibrational levels, and thus it is desirable to have methods that obtain these levels efficiently. It is also desirable to obtain many such levels and to have procedures that determine such levels for a general polyatomic molecule. With these points in mind, the sections that follow analyse the various methods that are available for solving this problem. We also note that typically experimentalists are able to observe frequencies to an accuracy of 0·01 cm^{-1} or better; it will never be possible for us to calculate to that accuracy, but as a guide an accuracy of 1 cm^{-1} in the vibrational levels of the potential is reasonable.

We concentrate in this review on vibrational eigenvalues (i.e. the total angular momentum J is taken to be zero). An accurate determination of vibrational–rotational energy levels is a very much larger problem. In principle this is because there are $2J+1$ rotational levels associated with each J, and these are usually determined by diagonalising an approximate $(2J+1)\times(2J+1)$ effective Hamiltonian matrix. This suffices in most cases. However, once J is large, say $J \approx 20$, there will be considerable interaction with vibrational levels; some work on this problem has been discussed by Tennyson and Sutcliffe (1986). We shall confine attention to molecular bound states with well defined minima; the determination of vibrational levels for weakly bound molecules requires different procedures, which are beyond the scope of this restricted review. It will be seen that the problem is complex enough for intramolecular

0144–235X/89 $3·00

vibrational energy levels anyway. We also observe that as the energy increases, the density of vibrational states increases enormously. The vibrational levels in which we are interested for a typical polyatomic may be such that on average the separation between levels is a few tens of wavenumbers.

We shall not discuss diatomic molecules in this review. This is because the potential surface of a diatomic molecule is represented in terms of only one coordinate, the internuclear distance. The Born–Oppenheimer equation for the nuclear motion is then a one-dimensional problem, which can be solved essentially exactly by numerical means, for any given form of the potential.

2. Analytical representation of the potential surface

There is an excellent book on this subject, by Murrell *et al.* (1984), to which the reader is referred. For diatomics, Murrell *et al.* recommend the extended Rydberg representation

$$V=D\left(1+\sum_i c_i\rho^i\right)\exp(-\alpha\rho), \tag{1}$$

where $\rho=r-r^0$, r is the diatomic separation and r^0 is some reference value (such as the equilibrium separation r_e). Such a representation is satisfactory for both bound and repulsive states, although it does not include long-range dispersion effects. The constants in (1) are available for many diatoms, and the accuracy of such representations far exceeds 1 cm^{-1} in vibrational levels.

For triatomics, it is desirable to represent V in terms of some internal coordinates. For example, for H_2O, the usual bond-length and bond-angle changes $\Delta r_1, \Delta r_2, \Delta\theta$ give the Dunham form (Dunham 1932), expressed normally up to quartic terms (or higher):

$$V=\sum c_{abc}(\Delta r_1)^a(\Delta r_2)^b(\Delta\theta)^c. \tag{2}$$

Any function V so represented will not be well described away from equilibrium, because the radius of convergence for Δr is $0\leqslant r\leqslant 2r_e$; Simons *et al.* (1973) suggested the alternative form

$$V=\sum d_{abc}\left(\frac{\Delta r_1}{r_1}\right)^a\left(\frac{\Delta r_2}{r_2}\right)^b(\Delta\theta)^c, \tag{3}$$

for which the radius of convergence is $1/2r_e\leqslant r\leqslant\infty$. More recently, Meyer *et al.* (1986) have suggested the representation

$$V=\sum e_{abc}[1-\exp(-\alpha_1\,\Delta r_1)]^a[1-\exp(-\alpha_2\,\Delta r_2)]^b(\Delta\theta)^c, \tag{4}$$

the functions $[1-\exp(-\alpha_1\Delta r_1)]^a$ being related to Morse-oscillator potential functions. The potentials (2)–(4) can be arranged to have the same Taylor expression through any order. They should give reasonable representations for V in the region of the equilibrium geometry. There are of course other sets of coordinates that could be used for a triatomic molecule:

(i) atom-diatomic coordinates R, r, θ (Tennyson and Sutcliffe 1985);
(ii) hyperspherical coordinates for the stretching motions r, φ, together with the bond angle θ (Frey and Howard 1985);
(iii) symmetry coordinates, for example $s_1=\rho_1+\rho_2$, $s_2=\rho_1-\rho_2$, $s_3=\rho_3$.

Which one is the best is debatable for the system under consideration, but current evidence is that, whichever set is chosen, they will be satisfactory provided that sufficient powers in the expansion are used; for example, it appears necessary to include some eighth-order terms if (2) is used (Botschwina *et al.* 1983), whereas quartic terms may be sufficient to obtain comparable accuracy from (3).

For a representation of the whole potential surface, Murrell *et al.* (1984) argue in favour of the analytical representation

$$V=\sum V^{(2)}_{\text{diatom}}+\sum V^{(3)}_{\text{triatom}}+\ldots, \tag{5}$$

where the $V^{(2)}$ are the extended Rydberg representations for the dissociated diatoms of the system, and

$$V^{(3)}=\prod_i\left[1-\tanh\left(\tfrac{1}{2}\gamma_i\rho_i\right)\right]\left[1+\sum c_i\rho_i+\sum c_{ij}\rho_i\rho_j+\ldots\right]. \tag{6}$$

It can be seen that $V^{(3)}$ is chosen so that it tends to zero as any one atom of the molecule moves to infinity. In this way the Murrell *et al.* representation guarantees that the surfaces have the correct dissociation products. There are problems with conical and avoided intersections, which are present in nearly all potential surfaces, but Murrell *et al.* show how it is possible to overcome these problems in principle. In practice, the greater difficulty is with the form of $V^{(3)}$, and in particular the determination of appropriate expansion coordinates ρ_i and the coefficients c_{ij}. The Murrell *et al.* form does have the advantage that it can be extended to tetratomics, but little work has been done to date on such systems. There are of course other analytical representations of potential surfaces in the literature, for example, the earlier LEPS (Tennyson 1986) and DIM (Ellison 1963) forms. For example, there are many such surfaces for H_3.

We must not neglect to observe that it is possible to derive quadratic representations for V in either bond-displacement or normal coordinates. For example, a full quadratic representation may be determined from *ab initio* computation for quite large molecules, now that analytic second-derivative methods have appeared (Pople *et al.* 1979, Handy *et al.* 1985). Although the associated force constants may not be too reliable, their accuracy can be somewhat systematically improved. One procedure is to amend the most unreliable constants (the bond stretches) by scaling or other procedures related to experiment (Botschwina 1979).

The *ab initio* approach is certainly the most straightforward for the determination of a quadratic force field. The success of analytic *ab initio* procedures means that it is now possible to produce cubic and quartic force constants, and evidence so far shows that these can be remarkably accurate (Gaw and Handy 1985).

If sufficient experimental information is available, so that harmonic frequencies ω_i and anharmonic constants x_{ij} are known, it is possible to use second-order perturbation theory to determine a quartic force field in mass-weighted normal coordinates, from which, by a nonlinear transformation, a Dunham representation may be obtained. This was the way that Hoy *et al.* (1972) determined their famous H_2O potential.

Therefore in concluding this discussion of analytic potential surfaces, we can point out that Dunham-type representations, through quartic terms, are becoming increasingly available as experimental and *ab initio* procedures become more sophisticated, but analytic forms that hold over the whole surface are very scarce, especially for any molecule with more than four atoms.

3. Forms for the kinetic-energy operator $\hat{T}$

In laboratory-fixed coordinates, $\hat{T}$ has the form (atomic units are used throughout, unless otherwise stated)

$$\hat{T}=-\frac{1}{2}\sum_{I}^{N}\frac{\nabla_I^2}{m_I}, \tag{7}$$

in the usual notation. It is desirable to derive forms for $\hat{T}$ in terms of internal or normal coordinates. Because internal coordinates (bond lengths, bond angles etc.) are defined independently of the laboratory frame, the simplest way to derive $\hat{T}$ in these coordinates is through the chain rule:

$$\frac{\partial}{\partial x_I}=\sum_{i}^{3N-6}\frac{\partial r_i}{\partial x_I}\frac{\partial}{\partial r_i}, \quad I=1,2\ldots,3N, \tag{8}$$

where r_i are the internal coordinates. A little algebra produces the following form for $\hat{T}$ for triatomic ABC molecules (Carter and Handy 1984):

$$\hat{T}=-\frac{1}{4}\left[\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}-\frac{2\cos\theta}{m_B r_1 r_2}\right),\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}\right)\right]_+$$
$$-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r_1^2}-\frac{1}{2\mu_2}\frac{\partial^2}{\partial r_2^2}-\frac{\cos\theta}{m_B}\frac{\partial^2}{\partial r_1\partial r_2}+\frac{1}{m_B}\left(\frac{1}{r_1}\frac{\partial}{\partial r_2}+\frac{1}{r_2}\frac{\partial}{\partial r_1}\right)\left(\sin\theta\frac{\partial}{\partial\theta}+\cos\theta\right), \tag{9}$$

where $\mu_1^{-1}=m_A^{-1}+m_B^{-1}$ and $\mu_2^{-1}=m_C^{-1}+m_B^{-1}$. Such ideas may be extended to larger systems, and, using algebraic computer programs, it is thus possible to derive $\hat{T}$ straightforwardly for any well defined internal coordinate system (Handy 1987).

There is one other form of $\hat{T}$ that is often used, namely the Watson form in normal coordinates (Watson 1968), which for nonlinear systems is

$$\hat{T}=-\frac{1}{2}\sum_{\alpha\beta}^{3}\mu_{\alpha\beta}\pi_\alpha\pi_\beta-\frac{1}{2}\sum_{k}^{3N-6}\frac{\partial^2}{\partial Q_k^2}-\frac{1}{8}\sum_{\alpha}^{3}\mu_{\alpha\alpha}, \tag{10}$$

where

$$\pi_\alpha=\sum\zeta_{kl}\frac{\partial}{\partial Q_l}$$

is called the Coriolis-coupling operator. This general form for $\hat{T}$ forms the basis of the second-order perturbation-theory analysis discussed in the previous section.

There are also in the literature forms for $\hat{T}$ that are combinations of the two forms referred to here, such as those used by Bunker and co-workers (Hougen *et al.* (1970); for a review see Jensen (1986)) under the names (semi) rigid-bender Hamiltonians, designed for use when one or more of the internal coordinates undergoes large distortions, the remainder being adequately described in terms of normal coordinates.

In conclusion, although in the past the derivation of $\hat{T}$ in particular coordinate systems has been the subject of many papers, there is now no real difficulty in this procedure.

4. The Variational Method†

This is the most natural way to proceed; suitable expansion functions are chosen for the vibrational wavefunctions, $\psi=\sum c_I\Phi_I$, and the secular matrix is diagonalised:

$$\langle\Phi_I|H-W|\sum c_J\Phi_J\rangle=0. \tag{11}$$

---

† Carney *et al.* (1978); see also for example Burden and Quiney (1984).

The Φ_I will be products of one-oscillator functions:

$$\Phi_I = \prod_i^{3N-6} \phi_{I,i}(s_i). \tag{12}$$

For triatomics this procedure is feasible, because the number of expansion functions Φ_I does not become excessive; each is a product of only three functions. For example, if coordinates r_1, r_2, θ are used then $\phi(r_1)$ may be a Morse-oscillator expansion function, and $\phi(\theta)$ may be a Legendre function. The form (9) for T shows how $\hat{T}\Phi$ is evaluated; its form also shows that the matrix elements $\langle \Phi_I|\hat{T}|\Phi_J\rangle$ may be evaluated as products of one-dimensional integrals. If one of the forms (2), (3) or (4) is used for V then the same is true for $\langle \Phi_I|V|\Phi_J\rangle$, and thus the evaluation of the secular matrix is a very efficient procedure. The limiting features in this approach will be the restriction of the size $N_c \times N_c$ of the secular matrix, and the time it takes to evaluate the required eigensolutions. Now that it is possible to consider $N_c = 1000$ or more, this method is practical for triatomics, and in one form or another it has been used by many workers. For example, numerical functions $\phi(s_i)$ may be used (Carney *et al.* (1978), and also different coordinate systems. Low-order approximations may be obtained through the use of self-consistent procedures (Carney *et al.* 1978). There are many examples in the literature. Early calculations (Whitehead and Handy 1975) used the Watson form for $\hat{T}$ with normal-coordinate harmonic-oscillator expansion functions $H_n(Q)$, but these have lost favour because such functions are poor representations of excited vibrational states, particularly those that take the local-mode form (Lawton and Child 1980).

The results of such calculations are many, and may be found in the literature. A few points may be made. One of the earliest results (Whitehead and Handy 1975) showed that the vibrational levels of the experimentally determined quartic Dunham form (2) for H_2O (Hoy *et al.* 1972) did not reproduce the original experimental input. For example the fundamental stretching frequencies were in error by 50 cm^{-1}. Carney *et al.* (1976) then went on to show that if an SPF potential (3) was derived from (2) (by expanding (3) in the form of (2) to obtain the coefficients) then almost perfect agreement (≈ 1 cm^{-1}) was obtained with the original data for many of the vibrational levels. This demonstrates that for H-containing systems a quartic Dunham potential is not a sufficient representation of the potential-energy surface around the minimum. More recently Carter and Handy (1987) have shown that if the Morse form (4) is used then agreement with all experimental H_2O and D_2O levels up to 10 000 cm^{-1}, to within 5 cm^{-1}, is achieved, which is promising.

Carter *et al.* (1982) have used this variational procedure to optimise some of the parameters in Murrell's potentials, for molecules such as SO_2.

Attempts to extend the variational procedure to systems with more than three atoms ($N > 3$) are fraught with problems. The number of expansion functions Φ rapidly becomes unmanageable, even for a small set of vibrational functions $\phi(s)$, because, for example, when $N = 4$, each Φ is a product of six such functions. Even so, there has been some work on H_2CO (Handy and Carter 1981, Maessen and Wolfsberg 1984) C_2H_2 and H_2O_2 (Willetts *et al.* 1989). The greatest difficulty lies in the choice of good expansion functions to represent bond-angle and twisting vibrations. However, the calculations on H_2O_2 show what is possible today; six low-lying torsional levels were obtained, together with the splittings of all the other fundamental vibrational levels. The *ab initio* surface, obtained with the MP2 *ab initio* method, gave remarkably good agreement with experiment in this instance.

All such calculations to date have relied on MacDonald's (1933) theorem: the *i*th eigenvalue is an upper bound on the *i*th exact eigenvalue. This has been the basis for the convergence of these approaches. For higher eigenvalues, increasingly large matrices have therefore been used.

Wyatt and co-workers have suggested that this may not be necessary (Chang *et al.* 1986): if the expansion functions Φ_I are ordered approximately in energy order then, instead of working with the whole secular matrix, they suggest working with smaller secular matrices, centred on the region where the eigensolutions are required. Convergence is examined by increasing the dimension of these smaller secular matrices. In some trial investigations they showed that the eigenvalues effectively converged before the full matrix was used, and for many of the eigenvalues only small matrices were required. Those that represented local modes rapidly converged; those that were a heavy mixture of normal mode oscillations needed more functions. Wyatt's approach opens up the possibility of using the vibrational method for both higher eigenvalues and larger molecules ($N > 3$).

The present author (with S. Carter) has investigated a similar procedure, which may be on a firmer theoretical (variational-theory) ground: (i) all the expansion functions are placed in some approximate energy ordering (e.g. $I < J$ if $\langle \Phi_I | H | \Phi_I \rangle < \langle \Phi_J | H | \Phi_J \rangle$); (ii) the first N functions are used to construct a secular matrix **H**, and it is diagonalised; (iii) these N eigenvectors and the next M expansion functions are used to construct a blocked $(N+M) \times (N+M)$ matrix **H**, which is diagonalised; (iv) the lowest eigenvalues of the two calculations, starting with the first eigenvalue, and those successive ones that agree within some tolerance are said to have converged. These eigenvectors (say M' of them) are removed, M new expansion functions are added, an $(N+M-M'+M) \times (N+M-M'+M)$ matrix is constructed and diagonalised and the lowest eigenvalues are compared with the previous diagonalisation. The lowest M'' will have converged, M new expansion functions are added, and so on.... Our experience with this method to date is that it is possible to keep matrix sizes down to an acceptable size, while converging on a very large number of eigenvalues. Efficient use may be made of the special structure of the matrix **H** at any stage in the iterative cycle.

The size difficulties associated with extending the variational procedure to molecules with $N > 3$ have motivated searches for other approaches to this problem. Some of these are outlined in the following sections.

5. Semiclassical methods

The undoubted success of the Rydberg–Klein–Rees procedure (Dickinson 1972) for the determination of potential-energy curves directly from experimental term values (using Bohr–Sommerfeld quantisation) for diatomic molecules has encouraged a lot of research into this topic. It will be recalled that the RKR procedure assumes knowledge of $G(n)$ and $B(n)$,

$$G(n) = \omega(n+\tfrac{1}{2}) - x\omega(n+\tfrac{1}{2})^2 + \dots, \tag{13}$$

$$B(n) = B + \alpha(n+\tfrac{1}{2}) + \dots, \tag{14}$$

with

$$E(n, J) = B(n)J(J+1) + G(n) + \dots, \tag{15}$$

and uses two Bohr–Sommerfeld 'semiclassical' quantisation conditions to derive

$$r_{\max}-r_{\min}=K_1\int_{-1/2}^{n}\frac{\mathrm{d}n'}{[G(n)-G(n')]^{1/2}},\tag{16}$$

$$\frac{r_{\max}-r_{\min}}{r_{\max}r_{\min}}=K_2\int_{-1/2}^{n}\frac{\mathrm{d}n'B(n')}{[G(n)-G(n')]^{1/2}}.\tag{17}$$

We note that to obtain the turning points $r_{\min}$ and $r_{\max}$, both vibrational and vibrational–rotational levels are required. However, in spite of valiant attempts by Percival and co-workers (Percival 1977), no successful procedure has been developed for the extension of the RKR procedure for $N>2$, namely to invert the rovibrational spectra of a polyatomic molecule to give a numerical potential surface.

Considerable progress has been made however, in the determination of semiclasssical vibrational eigenvalues for systems with $N>2$, and this has brought renewed interest in the old quantum theory—all scientists in this field should study Born's (1922) masterpiece *The Mechanics of the Atom.*

For separable systems such as those with Hamiltonians

$$H_0=\sum_i^N\frac{1}{2}\left(\frac{p_i^2}{m_i}+m_i\omega_i^2x_i^2\right),\tag{18}$$

motion in $\mathbf{x}$ space will not wander over all the allowed space given by $V=E$, but will be constrained because the energy in each oscillator is fixed. In phase space this means that motion wanders on an N-dimensional surface in $2N$-dimensional space. For $N=2$ therefore, motion is constrained to lie on a torus, or doughnut, in the four-dimensional phase space. These may be vividly seen in practice by constructing Poincaré surfaces of section, defined as (y, p_y) plots for points on the classical trajectories for which $x=0$, $p_x>0$; x and y are interchanged to give a second Poincaré section. These Poincaré sections are cross-sections of the torus. If the initial conditions for the trajectories are chosen so that the area of these two cross-sections obey

$$(n_1+\tfrac{1}{2})2\pi=\int_{C_1}p_y\,\mathrm{d}y,\quad (n_2+\tfrac{1}{2})2\pi=\int_{C_2}p_x\,\mathrm{d}x\tag{19}$$

then it follows that the energy of the system is given by

$$E=(n_1+\tfrac{1}{2})\omega_1+(n_2+\tfrac{1}{2})\omega_2.\tag{20}$$

The remarkable fact is that this situation also holds in many situations where the Hamiltonian is not separable, namely

$$H=H_0+H_1,\tag{21}$$

where for example $H_1=\varepsilon x^2y^2$ for an $N=2$ system. This follows from the Kolmogorov–Arnold–Moser theorem (Abraham 1967), which states, that 'provided H_1 is sufficiently small, classical motion proceeds as if there are N constants of the motion'. These constants of the motion, called adiabatic invariants, were first defined for toroids by Einstein (1917), and they are precisely the areas of the Poincaré sections defined above.

If this situation held in general then a lot of progress could be made, but the problem is that, as the energy increases, these tori have increasingly weird shapes. The other problem is that, above a certain initial energy, motion for an increasing number of starting conditions becomes ergodic or chaotic, there are no constants of the motion, and classical motion proceeds only under the one constraint that the total energy is constant.

For those energies and starting conditions where motion is non-ergodic (or regular), semiclassical eigenvalues are obtained by quantising the area of the Poincaré sections, namely

$$(n_i+\tfrac{1}{2})2\pi=\int_{C_i} p_i\,\mathrm{d}x_i, \tag{22}$$

and this procedure has formed the basis of many recent studies (Sorbie 1976). The earliest work was that by Marcus (1973), who used this approach to calculate the section areas numerically from the trajectory information. An examination of his results shows that good agreement is achieved between exact quantum eigenvalues and semiclassical eigenvalues. In particular, it appears that semiclassical frequencies agree with quantum frequencies to better than one wavenumber.

Much progress has been made recently with this semiclassical approach. One of the more interesting recent ideas is due to De Leon and Heller (1983), who showed how to remove the necessity of finding the precise trajectory that lies on the quantising torus. Their approach depends upon the following features, for a system with N degrees of freedom.

(*i*) For a given energy E, run the trajectory for a sufficiently long time so that it nearly returns to its starting point (see Sorbie and Handy (1977)), and time-average the accumulated phase

$$\phi=\sum_i\int \mathbf{p}_i\cdot\mathrm{d}\mathbf{s}_i.$$

This phase may also be written as $\phi=\boldsymbol{\omega}\cdot\mathbf{J}$, where $\mathbf{J}$ and $\boldsymbol{\omega}=\partial H/\partial\mathbf{J}$ are the actions and frequencies of this motion. The frequencies $\boldsymbol{\omega}$ of any given trajectory may be found from a Fourier analysis of any dynamical variable $A(t)$ (such as a coordinate) over the period of the motion:

$$A(t)=\sum_{\mathbf{l}} A_{\mathbf{l}}\exp(\mathrm{i}\mathbf{l}\cdot\boldsymbol{\omega}t). \tag{23}$$

By considering this given trajectory, and a set of N nearby trajectories so that a relation $\Phi=\boldsymbol{\omega}\cdot\mathbf{J}$ holds, each with the same energy, and finding their frequencies, $\mathbf{J}$ may be found from $\mathbf{J}=\boldsymbol{\omega}^{-1}\Phi$.

(ii) Having obtained the frequencies $\boldsymbol{\omega}$ for a trajectory with given energy E, and the associated $\mathbf{J}$, the formula for the semiclassical energy for a state with actions $\mathbf{n}+\frac{1}{2}$ is

$$E(\mathbf{n})=E+\boldsymbol{\omega}\cdot(\mathbf{n}+\tfrac{1}{2}-\mathbf{J})+O[(\mathbf{n}+\tfrac{1}{2}-\mathbf{J})^2]. \tag{24}$$

De Leon and Heller found by calculation that this method of procedure is capable of producing useful information; even when the percentage error in the actions is a few per cent, the percentage error in the energy is typically $\frac{1}{100}$ of this. It is therefore possible to find estimates for a range of eigenvalues from information derived from one trajectory.

In a subsequent paper Miller (1984) showed that it is not necessary to calculate the nearby trajectories referred to above, but that sufficient information is already available from the phase to derive formula equivalent to (24), namely

$$E(\mathbf{n})=E+\boldsymbol{\omega}\cdot(\mathbf{n}+\tfrac{1}{2})-\Phi/T.$$

De Leon and Heller underline the importance of this method in so far that it is coordinate-independent; the shape of the tori is no longer of consequence. There are some difficulties, but they argue that these can be overcome with more sophisticated Fourier-transform techniques. They believe that the method can be extended to systems with many degrees of freedom, and they state that there should be no difficulty with systems that exhibit resonance $\sum m_i\omega_i \approx 0$ (the ω_i are frequencies of the motion and the m_i are small positive or negative integers).

In this limited space it is not possible to refer to all of the large number of papers on this topic in the last ten years. There is much discussion on the interpretation to be attached to the chaotic, or non-quantisable, motions. There are many papers on reliable methods for the determination of semiclassical eigenvalues; see especially the work of Eastes and Marcus (1974), Sorbie (1976), Davis and Heller (1979) Shirts and Reinhardt (1982), Miller (1984) and Knudsen *et al.* (1986). If there are any criticisms to be made of such work, much of which has a high-quality original mathematical flavour, it is that some authors do not work with forms of H (T and V) that represent polyatomic vibrational motion. In the present author's view, too much is read into 'Hénon–Heiles'-like systems (Hénon and Heiles 1964). The number of papers in the literature that calculate semiclassical molecular vibrational levels is small (H_2O being the most complicated case; Colwell and Handy (1978)); there are of course many papers which discuss the stretching motions in isolation and analyse them in terms of local-mode vibrations.

The next section also discusses a semiclassical method, which is old in its origin, but is now attracting attention.

6. The method of adiabatic switching

The one-dimensional adiabatic theorem, a proof of which can be found in Landau and Lifshitz (1960), states that under a slowly time-varying perturbation, the action

$$\oint p\,\mathrm{d}x$$

is conserved provided that the frequency of the motion $\omega(t)$ is never zero during the motion. Johnson (1985) has proposed that this approach be used for multidimensional systems, although there can be no extension of the one-dimensional proof to these systems. The idea is very straightforward: at time $t=0$ the system is vibrating under a separable $H_0(\mathbf{p},\mathbf{r})$ with actions $\mathbf{n}+\frac{1}{2}$, the perturbation is then very slowly switched on under a Hamiltonian such as

$$H(t)=H_0+\left[\frac{t}{T}-\frac{\sin(2\pi t/T)}{2\pi}\right]H_1(\mathbf{p},\mathbf{r}), \tag{25}$$

so that at some large $t=T$ the system is vibrating under

$$H(\mathbf{p},\mathbf{r})=H_0+H_1. \tag{26}$$

The energy at $t=T$ will be the eigenvalue corresponding to actions $\mathbf{n}+\frac{1}{2}$ for the system $H(\mathbf{p},\mathbf{r})$.

There is an excellent article on this approach by Skodje *et al.* (1985), but unfortunately the results are much as one would anticipate. However, it has to be stressed that in this semiclassical approach there is no searching for a quantizing trajectories. Provided that the 'shape' of the toroid does not change suddenly during the motion, the method appears quite viable. Mathematically, this means that the system must not pass through a strong resonance; if $\omega_i(t)$ are the frequencies of the motion then if $|\sum m_i\omega_i|$ can become very small, a strong resonance occurs (in parallel to $\omega=0$ in the one-dimensional case), and the method fails. To overcome this problem, H_0 must be chosen such that this problem does not occur. Skodje *et al.* discussed examples that demonstrate good choices for H_0. The other case where the method fails is when the trajectories are chaotic, although Skodje *et al.* found that some states can be quantised, even though the trajectories are chaotic. They attributed this success to the 'adiabatic switching of a vague torus through chaotic phase space'.

Skodje *et al.* considered the stretching motions of HOD and HOH systems, using uncoupled Morse oscillators with $\cos\theta\, p_1 p_2$, (9), as the H_1 perturbation. For the HOD system the method works well and in a straightforward manner, giving typical semiclassical energies, but for HOH there is a severe problem because of the exact 1 : 1 resonance. For the local-mode states of HOH there is actually no problem, but for those trajectories that correspond to normal modes meaningless results are obtained. They solve this problem by analysing the motion in terms of a Morse oscillator and a hindered rotor, and then redefining H_0 so that its motion corresponds to the final motion of the system, that is a trapped rotor. This gives acceptable results for HOH for the 'normal-mode' oscillators.

Skodje *et al.* also applied this method to many levels of the standard Hénon–Heiles (1964) system. They also applied it to three-, four- and five-dimensional extensions of the Hénon–Heiles system. These latter results are important because, as they say, 'we cannot judge the absolute accuracy of the results obtained here because we do not have accurate quantum results for comparison'. This, of course, lies behind the whole study, so the present author's summary of this approach is that it is worthy of further study because it can be applied to higher-dimensional systems, but the problem remains that different H_0 may have to be designed for different vibrational levels, and this in the end may be the point where the method breaks down.

7. The quantum Monte Carlo procedure

Here we shall discuss the diffusion Monte Carlo method, with importance sampling but without nodal release as it may be applied to molecular vibrations. This is a full quantum-mechanical approach, and it has found favour recently as an alternative to the variational method because it does not depend upon expansion functions and integral evaluation.

In the diffusion Monte Carlo (DMC) method, the Schrödinger equation is written in imaginary time

$$-\frac{\partial\Phi}{\partial t}=\left[-\frac{1}{2}\sum_I\frac{\nabla_I^2}{m_I}+V-E_\mathrm{T}\right]\Phi, \tag{27}$$

where V is the potential surface, the first term on the right-hand side is the nuclear kinetic energy and E_T is an energy shift. If E_T is close to the eigenvalue E_0 then, after a long time,

$$\Phi(\mathbf{R},t)\simeq\exp\left[-(E_0-E_\mathrm{T})t\right]\phi_0(\mathbf{R}), \tag{28}$$

and so if E_T is adjusted to be E_0 then asymptotically the long-time solution will be the eigensolution $\phi_0(\mathbf{R})$. We note that equation (27) resembles a diffusion equation together with a growth (or decay) term.

In quantum chemistry, nearly all applications of DMC have been to the electronic Schrödinger equation, but recently Watts and co-workers have suggested its application to molecular vibrations (Coker *et al.* 1985). One follows the procedure outlined by Anderson (1975), but adjusts it for vibrations.

(i) A sample (N_c) of different positions $\mathbf{R}_I$ (configurations) of the nuclei is obtained.

(ii) For each time step τ, for all nuclei in each configuration, they are moved according to

$$\mathbf{R}_I \rightarrow \mathbf{R}_I + \chi_I, \tag{29}$$

where χ_I is a Gaussian random number with zero mean and a variance $2\tau/m_I$.

(iii) After all the nuclei in any one configuration have been moved, M copies of this configuration are entered into the sample,

$$M = \mathrm{int}\{\exp[-(V' - E_T)\tau] + \zeta\}, \tag{30}$$

where V' is the value of V for this new configuration and ζ is a random number in $[0, 1]$. This corresponds to the growth (or decay) term in (27).

After a reasonable number of time steps, E_T is updated to be a suitable average of the V calculated at all time steps so far.

The process is continued for a time sufficiently long for all initial effects to have disappeared, and ideally the final results are averaged over many different starting samples, and time steps and length of runs.

This approach appears to be very attractive for molecular vibrations, because in the simplest analysis, only eigenvalues are required. This is unlike the quantum chemistry application, where the principal objection must be that a potential surface calculated by this method cannot be smooth because of its statistical nature.

The present author first applied the method to the simple harmonic oscillator

$$H = -\frac{1}{2m}\frac{d^2}{dx^2} + \tfrac{1}{2}kx^2, \tag{31}$$

with $m = 1836$ and $k = 0{\cdot}25$, for which the exact lowest eigenvalue is 1807 cm^{-1}. Using $N_c = 100$ and $\tau = 0{\cdot}1$, values for E_T after successive blocks of 12 500 time steps were 1855, 1832, 1830, 1819, 1811, 1803, 1813 and 1816 cm^{-1}. Although reasonably successful, it is clear that very long runs would be required to obtain an eigenvalue estimated to be corrected to 1 cm^{-1}.

In DMC, as applied to a molecular vibration, it is probable that the fast-moving stretching vibration will take longer to settle than the slower-moving bending motions. However, for the stretching motions, we do have an excellent idea of the form of the wavefunction, namely harmonic-oscillator or Morse-oscillator functions. This leads to the idea of importance sampling (as applied to the electronic Schrödinger equation by Reynolds *et al.* 1982). If $f = \Phi(\mathbf{R}, t)\psi_T(\mathbf{R})$, where ψ_T is a well chosen trial function, the Schrödinger equation (27) becomes

$$-\frac{\partial f}{\partial t} = -\frac{1}{2}\sum_I \frac{\nabla_I^2 f}{m_I} + [E_L(\mathbf{R}) - E_T]\, f + \frac{1}{2}\sum_I \frac{\nabla_I \cdot (\mathbf{F}_I f)}{m_I}, \tag{32}$$

where $E_L = H\psi_T/\psi_T$ and $\mathbf{F}_I = 2\nabla_I\psi_T/\psi_T$. This DMC equation has the same form as (27), with V replaced by E_L, the local energy of ψ_T, and $\mathbf{F}_I$ plays the role of a drift term.

It was again applied to the harmonic oscillator, using a trial function $\psi_T = \exp(-0{\cdot}95\alpha x^2)$, where $\exp(-\alpha x^2)$ is the exact wavefunction. The old algorithm is changed in two places: V is replaced by E_L, and (29) is replaced by

$$\mathbf{R}_I \to \mathbf{R}_I + \chi_I + \frac{1}{2m_I}\mathbf{F}_I. \qquad (33)$$

Using the same values as before for N_c and τ, the values for E_T after successive blocks of 12 500 time steps were 1806·0, 1806·3, 1806·2, 1805·8 and 1806·1 cm^{-1}, an enormous improvement! With $N_c = 200$ and $\tau = 0{\cdot}5$ the results were 1807·8, 1807·8, 1807·6 and 1807·5 cm^{-1}, and with $N_c = 100$ and $\tau = 0{\cdot}5$ they were 1806·8, 1806·8, 1807·1 and 1807·2 cm^{-1}. These trial calculations show that the importance-sampling algorithm makes such calculations of great interest.

Finally, the method was applied to H_2O, using the potential

$$V = 0{\cdot}25(\Delta r_1^2 + \Delta r_2^2) + 0{\cdot}1\,\Delta\theta^2, \qquad (34)$$

with a trial function

$$\psi = \exp(-\alpha\,\Delta r_1^2 - \alpha\,\Delta r_2^2). \qquad (35)$$

The form of $\hat{T}$ in internal coordinates has already been given for H_2O, in (9). Writing the wavefunction ψ_T as $r_1 r_2 \psi$, then selecting only those terms that depend upon r_1 and r_2, it follows that

$$\frac{T\psi_T}{\psi_T} = -\frac{1}{\psi}\left[\frac{1}{2\mu_1 r_1}\frac{d^2}{dr_1^2}(r_1\psi) + \frac{1}{2\mu_2 r_2}\frac{d^2}{dr_2^2}(r_2\psi) + \frac{\cos\theta}{m_0}\frac{\partial^2\psi}{\partial r_1\,\partial r_2}\right]. \qquad (36)$$

α is chosen such that the first two terms of $\hat{T}\psi_T/\psi_T$ cancel the first two terms of V.

The approach continues exactly as for the harmonic oscillator; for each configuration each nucleus has coordinates (x, y, z) in a laboratory-fixed frame. Using $m_H = 1836$, $m_O = 16m_H$, $N_c = 400$ and $\tau = 0{\cdot}5$, values of E_T for successive blocks of 10 000 time steps were 4563, 4556, 4555, 4555, 4552, 4555 and 4555 cm^{-1}. The exact quantum eigenvalue obtained by the variational method is 4560 cm^{-1}. The approach therefore seems viable, and it is attractive because it can be applied to systems with more than three atoms.

All of the above holds for the lowest vibrational eigenvalue, namely the zero-point energy. This is very useful in itself. For example, Isaacson and Truhlar (1984) observe that one of the best ways to calculate vibrational partition functions is by the Pitzer–Gwinn method, and all that this method requires is the zero-point energy of the molecule.

For the lowest eigensolution, the wavefunction is everywhere-positive. To extend the approach to excited states is more difficult, because, for the approach to be successful, the probability distribution must be single-signed. This has been overcome by the electronic-structure DMC enthusiasts using a 'fixed-node' algorithm, the domain of the configurations being constrained to lie in a region where ψ_T is single-signed. In other words, one obtains, in principle, an upper bound on the exact eigenvalue, with the boundary conditions being that $\Phi = 0$ where $\psi_T = 0$.

There are methods in the literature that have overcome this fixed-mode constraint (Ceperley and Alder 1984), but whether in practice it is possible to pick up the energy change on nodal release from the underlying uncertainty in the results remains to be seen. Watts has, however, been successful in using the DMC approach to calculate accurate vibrational frequencies for the water dimer and trimer (Coker *et al.* 1985, Coker and Watts 1987) and small HF clusters (H. Sun and R. O. Watts, unpublished work).

8. Conclusion

This review has attempted to show that there is active research in the area of the determination of vibrational energy levels of molecular potential surfaces. It is hoped that the impression has been given that there are several alternative ways of proceeding for polyatomic molecules—variational, semiclassical or quantum Monte Carlo—but that each has major difficulties associated with it. At present there does not seem to be a way of accurately calculating the lowest vibrational energy levels of a molecule like formaldehyde or methane, for a simple (e.g. quartic) potential surface.

Acknowledgements

The author has worked over the years with many people on this problem: M. G. Bucknell, R. Whitehead, K. Sorbie, S. M. Colwell and S. Carter, from all of whom he has benefited.

This review was written and some calculations performed while the author was on sabbatical leave at the University of Sydney; the hospitality of Professor N. S. Hush is gratefully acknowledged. The author learnt much from discussions with J. R. Reimers, and the last section was stimulated by a discussion with Professor R. O. Watts (Canberra and Seattle).

Dr J. F. Gaw made useful comments on the manuscript.

References

Abraham, R., 1967, *Foundations of Mechanics* (New York: Benjamin).
Anderson, J. B., 1975, *J. chem. Phys.*, **63**, 1499; 1976, *Ibid.*, **65**, 4121.
Born, M., 1922, *The Mechanics of the Atom.* Reprinted 1960 (New York: Frederick Ungar).
Botschwina, P., 1979, *Chem. Phys.*, **40**, 33.
Botschwina, P., Rosmus, P., and Reinsch, E. A., 1983, *Chem. Phys. Lett.*, **102**, 299.
Burden, F. R., and Quiney, H. M., 1984, *Molec. Phys.*, **53**, 917.
Carney, G. D., Curtiss, L. A., and Langhoff, S. R., 1976, *J. molec. Spectrosc.*, **61**, 371.
Carney, G. D., Sprandel, L. L., and Kern, C. W., 1978, *Adv. Chem. Phys.*, **37**, 305.
Carter, S., and Handy, N. C., 1984, *Molec. Phys.*, **52**, 1367; 1987, *J. chem. Phys.*, **87**, 4294; 1988, *Comput. Phys. Commun.*, **51**, 49.
Carter, S., Mills, I. M., Murrell, J. N., and Varandas, A. J. C., 1982, *Molec. Phys.*, **45**, 1053.
Ceperley, D. M., and Alder, B. J., 1984, *J. chem. Phys.*, **81**, 5833.
Chang, J., Moiseyer, N., and Wyatt, R. E., 1986, *J. chem. Phys.*, **84**, 4997.
Coker, D. F., Miller, R. E., and Watts, R. O., 1985, *J. chem. Phys.*, **82**, 3554.
Coker, D. F., and Watts, R. O., 1987, *J. phys. Chem.*, **91**, 2513.
Colwell, S. M., and Handy, N. C., 1978, *Molec. Phys.*, **35**, 1183.
Davis, M. J., and Heller, E. J., 1979, *J. chem. Phys.*, **71**, 3383.
De Leon, N., and Heller, E. J., 1983, *J. chem. Phys.*, **78**, 4005.
Dickinson, A., 1972, *J. molec. Spectrosc.*, **44**, 183.
Dunham, J. L., 1932, *Phys. Rev.*, **41**, 721.
Eastes, W., and Marcus, R. A., 1974, *J. chem. Phys.*, **61**, 4301.
Einstein, A., 1917, *Verh. dt. phys. Ges.*, **19**, 82.
Ellison, F. O., 1963, *J. Am. Chem. Soc.*, **85**, 3540.
Frey, J. G., and Howard, B. J., 1985, *Chem. Phys.*, **99**, 427.
Gaw, J. F., and Handy, N. C., 1985, *Chem. Phys. Lett.*, **121**, 321.
Handy, N. C., 1987, *Molec. Phys.*, **61**, 207.
Handy, N. C., and Carter, S., 1981, *Chem. Phys. Lett.*, **79**, 118.
Handy, N. C., Amos, R. D., Gaw, J. F., Rice, J. E., and Simandiras, E. D., 1985, *Chem. Phys. Lett.*, **120**, 151.
Hénon, M., and Heiles, C., 1964, *Astron J.*, **69**, 73.
Hougen, J. T., Bunker, P. R., and Johns, J. W. C., 1970, *J. molec. Spectrosc.*, **34**, 136.
Hoy, A. R., Mills, I. M., and Strey, G., 1972, *Molec. Phys.*, **24**, 1265.

ISAACSON, A. D., and TRUHLAR, D. G., 1984, *J. chem. Phys.*, **80,** 2888.
JENSEN, P., 1986, *Comput. Phys. Rep.*, **1,** 1.
JOHNSON, B. R., 1985, *J. chem. Phys.*, **83,** 1204.
KNUDSON, S. K., DELOS, J. B., and NOID, D. W., 1986, *J. chem. Phys.*, **84,** 6886.
LANDAU, L. D., and LIFSHITZ, E. M., 1960, *Mechanics* (Oxford: Pergamon).
LAWTON, R. T., and CHILD, M. S., 1980, *Molec. Phys.*, **40,** 773.
MACDONALD, J. K. L., 1933, *Phys. Rev.*, **43,** 830.
MAESSEN, B., and WOLFSBERG, M., 1984, *J. chem. Phys.*, **80,** 4651.
MARCUS, R. A., 1973, *Faraday Discuss. chem. Soc.*, **55,** 34.
MEYER, W., BOTSCHWINA, P., and BURTON, P., 1986, *J. chem. Phys.*, **84,** 891.
MILLER, W. H., 1984, *J. chem. Phys.*, **81,** 3573.
MURRELL, J. N., CARTER, S., FARANTOS, S. C., HUXLEY, P., and VARANDAS, A. J. C., 1984, *Molecular Potential Energy Functions* (Chichester: Wiley).
PERCIVAL, I. C., 1977, *Adv. chem. Phys.*, **36,** 1.
POPLE, J. A., KRISHNAN, R., SCHLEGEL, H. B., and BINKLEY, J. S., 1979, *Int. J. quantum Chem. Symp.*, **13,** 225.
SHIRTS, R. B., and REINHARDT, W. P., 1982, *J. chem. Phys.*, **77,** 5204.
REYNOLDS, P. J., CEPERLEY, D. M., ALDER, B. J., and LESTER, W. A., *J. chem. Phys.*, **77,** 5593.
SIMONS, G., PARR, R. G., and FINLAN, J. M., 1973, *J. chem. Phys.*, **59,** 3229.
SKODJE, R. T., BORONDO, F., and REINHARDT, W. P., 1985, *J. chem. Phys.*, **82,** 4611.
SORBIE, K. S., 1976, *Molec. Phys.*, **32,** 1577.
SORBIE, K. S., and HANDY, N. C., 1977, *Molec. Phys.*, **33,** 1319.
TENNYSON, J., 1986, *Comput. Phys. Rep.*, **4,** 1.
TENNYSON, J., and SUTCLIFFE, B. T., 1985, *Molec. Phys.*, **56,** 1175; 1986, *Ibid.*, **58,** 1067.
WATSON, J. K. G., 1968, *Molec. Phys.*, **15,** 479.
WHITEHEAD, R. J., and HANDY, N. C., 1975, *J. molec. Spectrosc.*, **55,** 356.
WILLETTS, A., GAW, J. F., HANDY, N. C., and CARTER, S., 1989, *J. molec. Spectrosc.*, **135,** 370.