J. Chem. Soc., Faraday Trans. 2, 1987, **83**(9), 1663-1674

Variational Methods for the Calculation of Rovibrational Energy Levels of Small Molecules

Brian T. Sutcliffe
Chemistry Department, University of York, Heslington, York Y01 5DD

Jonathan Tennyson
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT

Variational rovibrational calculations performed on the molecules H_2O and CH_2^+ are discussed with a view to pin-pointing the best solution strategy for each system. While all the methods discussed appeared to be reliable for the low-lying levels of water, CH_2^+ has proved a more testing system. A recently proposed method for calculating highly rotationally excited states is applied to the $J = 10$ levels of CH_2^+. Comparison of these calculations with those of Carter and Handy suggests that at this level of rotational excitation it will be necessary to consider full rovibronic coupling effects in the characterisation of any spectra of this floppy system.

It is nearly twenty years since Watson[1] derived what is now widely accepted[2] as the simplest and most elegant quantum-mechanical form of Eckart's[3] classical vibration–rotation Hamiltonian. Watson's Hamiltonian differed by one term (the so-called 'Watson term') from that which had become commonly used on experimental grounds.[4] That Watson's Hamiltonian is correct is now beyond doubt and it has been widely used. However, as was noted by Sayvetz[5] in 1939, this formalism needs to be adapted for the case of large amplitude vibrational motion, and, as shown by Watson himself,[6] it is not appropriate for linear molecules for which the Watson term becomes singular.

Although a variety of Hamiltonians have been used for variational calculations,[2] in many ways the derivation by Watson marks the start of variational calculations on the vibration–rotation spectra of polyatomic molecules. In the past two decades several significant steps have been made on the path to accurate variational calculations on polyatomic systems. As Handy has been involved in many of these stages, this would appear to be an appropriate time and place to survey past work and point to what the immediate future would appear to hold in the increasingly rich area of bound state nuclear motion calculations. In discussing previous calculations we will not attempt to be comprehensive, but will instead focus on two contrasting triatomic molecular systems, water and CH_2^+. Between them these systems have formed the testing ground for many ideas on how best to calculate the rovibrational spectra predicated by a given potential.

In the development of *ab initio* bound-state nuclear motion techniques, water has often been used as the prototype, near-rigid molecule for which the Eckart conditions are undoubtedly valid. It has a high barrier to linearity, *ca.* 11 000 cm^{-1},[7-9] and its few electrons have made it the subject of many state-of-the-art electronic structure calculations.[9-15] Experimental data on its low-lying rovibrational states are also widely available[16-20] and have yielded several (semi-) empirical potential-energy surfaces.[8,21-24]

In contrast, CH_2^+ is a Renner–Teller system whose ground electronic state has a barrier to linearity of less than 1000 cm^{-1}.[25] This means that the system is not only highly anharmonic with a large-amplitude bending motion, but also displays non-Born–Oppenheimer effects due to coupling with the vibrational levels of the other Renner–Teller component.[26] As yet there is no recorded spectrum of CH_2^+, although the ion is known to be an important constituent of some interstellar clouds.[27]

Theory

Within the Born–Oppenheimer approximation, the Hamiltonian for the motion of the nuclei in an N-atomic molecule is given by

$$\hat{H}_{\text{full}} = -\frac{\hbar^2}{2}\sum_{i=1}^{3N}\frac{1}{m_i}\nabla_i^2 + V(\boldsymbol{q}) \tag{1}$$

where the potential depends only on $\boldsymbol{q}$, the $3N-6$ internal coordinates of the system. This Hamiltonian suffers from the strong disadvantage that it still contains the continuous spectrum given by the centre of mass motion of the whole system. There is also no distinction between motions that are usually associated with vibrations and those commonly ascribed to rotations. These problems, besides making direct calculation with $\hat{H}_{\text{full}}$ cumbersome, also lead to considerable difficulties in the interpretation of results.

The translational part of the Hamiltonian can be separated off by defining the centre-of-mass motion coordinate

$$\boldsymbol{X} = \frac{1}{M}\sum_i \frac{1}{m_i}\boldsymbol{x}_i, \qquad M = \sum_i m_i. \tag{2}$$

Of the remaining $3N-3$ degrees of freedom, 3 (or 2 for a linear system) can be associated with the overall rotation. These rotational coordinates can be defined in terms of the Euler angles required to rotate the laboratory fixed axes into the frame of the molecule, whose remaining $3N-6$ $(3N-5)$ internal coordinates carry the vibrational motion. Formally one is free to choose any coordinate set and system of axes and transform $\hat{H}_{\text{full}}$ into the appropriate body-fixed form.

An example of such an embedding are the two conditions proposed by Eckart[3] which are the basis of Watson's Hamiltonian[1]

$$\hat{H}_{\text{W}} = \tfrac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}(\Pi_\alpha - \pi_\alpha)(\Pi_\beta - \pi_\beta) + \tfrac{1}{2}\sum_k \frac{\partial^2}{\partial Q_k^2} - \frac{\hbar^2}{8}\sum_\alpha \mu_{\alpha\alpha} + V(\boldsymbol{Q}). \tag{3}$$

$\hat{H}_{\text{W}}$ is expressed in normal coordinates, Q_k, which are mass-weighted displacements from some fixed (equilibrium) geometry. In the above, π_α are the cartesian components of the Coriolis terms, Π_α are the components of the total angular momentum with respect to the body-fixed axes and the matrix $\boldsymbol{\mu}$ is closely related to the inverse inertia tensor. A more detailed discussion of these terms can be found in ref. (1).

A procedure for embedding an arbitrary set of internal coordinates and axes has been given by Sutcliffe.[28] Application of this procedure is not without its problems. The algebra is usually lengthy and complicated, resulting in at least one acknowledged failure[29] and other incorrect results. Recently, however, Handy[30] has adapted Sutcliffe's procedure so that the algebraic language REDUCE can be used to perform the transformation. Additionally, some care must be taken in choosing the internal coordinates, as the domain for which the resulting body-fixed Hamiltonian is well behaved may not encompass the physical domain of the problem.[31]

Recently, we have used Sutcliffe's procedure to derive a body-fixed Hamiltonian for triatomic systems in terms of the distance between atoms 2 and 3, r_1, the distance, r_2, from an arbitrary point on $\boldsymbol{r}_1$ to atom 1, and the angle, θ, between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.[32] Once integration has been performed over the rotational coordinates, whose motion is carried by rotation matrices $|Jk\rangle$, the Hamiltonian for the internal coordinates can be written

$$\hat{H}_{\mathrm{ST}}=\hat{K}_{\mathrm{V}}^{(1)}+\hat{K}_{\mathrm{V}}^{(2)}+\hat{K}_{\mathrm{VR}}^{(1)}+\hat{K}_{\mathrm{VR}}^{(2)}+V(r_1,r_2,\theta) \tag{4}$$

with

$$\begin{aligned}\hat{K}_{\mathrm{V}}^{(1)}=-\frac{\hbar^2}{2}\bigg[&\frac{1}{\mu_1 r_1^2}\left(\frac{\partial}{\partial r_1}r_1^2\frac{\partial}{\partial r_1}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\\&+\frac{1}{\mu_2 r_2^2}\left(\frac{\partial}{\partial r_2}r_2^2\frac{\partial}{\partial r_2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\bigg]\end{aligned} \tag{5}$$

$$\begin{aligned}\hat{K}_{\mathrm{V}}^{(2)}=\frac{\hbar^2}{\mu_{12}}\bigg[&-\cos\theta\frac{\partial^2}{\partial r_1\partial r_2}+\frac{\cos\theta}{r_1r_2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\\&+\sin\theta\left(\frac{1}{r_1}\frac{\partial}{\partial r_2}+\frac{1}{r_2}\frac{\partial}{\partial r_1}+\frac{1}{r_1r_2}\right)\frac{\partial}{\partial\theta}\bigg]\end{aligned} \tag{6}$$

$$\begin{aligned}\hat{K}_{\mathrm{VR}}^{(1)}=\delta_{k'k}\hbar^2&\left[\frac{[J(J+1)-2k^2]}{2\mu_1r_1^2}+\frac{k^2}{2}\operatorname{cosec}^2\theta\left(\frac{1}{\mu_1r_1^2}+\frac{1}{\mu_2r_2^2}-\frac{2\cos\theta}{\mu_{12}r_1r_2}\right)\right]\\&+\delta_{k'k\pm1}\frac{\hbar^2}{2\mu_1r_1^2}C_{Jk}^{\pm}\left(\mp\frac{\partial}{\partial\theta}+k\cot\theta\right)\end{aligned} \tag{7}$$

$$\hat{K}_{\mathrm{VR}}^{(2)}=\delta_{k'k\pm1}\frac{\hbar^2C_{Jk}^{\pm}}{2\mu_{12}r_1r_2}\left[\pm\cos\theta\left(\frac{\partial}{\partial\theta}\mp k\cot\theta\right)\pm\left(r_2\frac{\partial}{\partial r_2}\mp k\right)\sin\theta\right]. \tag{8}$$

The form given above is appropriate for the z-axis embedded along $\boldsymbol{r}_1$. The embedding along $\boldsymbol{r}_2$ is obtained simply by making the exchanges $r_1\leftrightarrow r_2$ and $\mu_1\leftrightarrow\mu_2$. In using the operator in this form any integral over the internal coordinates must be performed with the volume element $r_1^2r_2^2\sin\theta\,\mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}\theta$. The range of r_i is $(0,\infty)$ and that of θ $(0,\pi)$. The coefficients $C_{Jk}^{\pm}$ are the usual step-up and -down coefficients

$$C_{Jk}^{\pm}=[J(J+1)-k(k\pm1)]^{1/2} \tag{9}$$

and the reduced masses are given by

$$\begin{aligned}\mu_1^{-1}&=m_2^{-1}+m_3^{-1}\\\mu_{12}^{-1}&=g(m_2^{-1}+m_3^{-1})-m_3^{-1}\\\mu_2^{-1}&=m_1^{-1}+g^2m_2^{-1}+(1-g)^2m_3^{-1}\end{aligned} \tag{10}$$

with

$$g=(r_2-v)/r_2 \tag{11}$$

where v is the distance from atom 2 to the point at which $\boldsymbol{r}_2$ cuts $\boldsymbol{r}_1$.

$\hat{H}_{\mathrm{ST}}$ generalises a number of previously known Hamiltonians. In particular, when $\boldsymbol{r}_2$ links atoms 1 and 3 ($g=1$), the resulting bond length-bond angle Hamiltonian is in the form of Lai and Hagstrom.[33-35] When $\boldsymbol{r}_2$ cuts $\boldsymbol{r}_1$ at the centre of diatomic mass [$g=m_2/(m_2+m_3)$], the resulting Hamiltonian, in which $\mu_{12}^{-1}=\hat{K}_{\mathrm{V}}^{(2)}=\hat{K}_{\mathrm{VR}}^{(2)}=0$, is well known from atom-diatom scattering calculations.[36,37] A discussion of other coordinate choices with this Hamiltonian can be found in ref. (38). $\hat{H}_{\mathrm{ST}}$ also provides a choice of axis embedding as the z-axis can lie along either $\boldsymbol{r}_1$ or $\boldsymbol{r}_2$; a further generalisation which allows the z-axis to be embedded along any line between these has just been proposed,[39] but difficulties remain over its application.

Until recently, fully coupled, variational rovibrational calculations were limited to problems with low angular momentum, $J \leqslant 4$. This restriction was caused by the rapid increase in the size of the secular matrix with J. However, recently the use of a two-variational step has been proposed[40] as a means to obviate this problem. Essentially this involves using the solutions of a Hamiltonian in the form

$$\hat{H}^{1}_{\mathrm{ST}} = \hat{K}^{(1)}_{\mathrm{V}} + \hat{K}^{(2)}_{\mathrm{V}} + \delta_{kk'}\hat{K}^{(1)}_{\mathrm{VR}} + V(r_1, r_2, \theta) \tag{12}$$

to solve the full problem. The saving arises because not all solutions of eqn (12) are required to give converged solutions of eqn (4), and because the resulting secular matrix has a sparse structure which can be utilised computationally.[40] Chen *et al.*[41] have developed a similar procedure based on Watson's Hamiltonian.

Calculations on the Water Molecule

Standard Variational Treatments

The earliest fully variational calculation on the low-lying rovibrational levels of the water molecule, indeed on any triatomic, was by Bucknell and Handy.[42] The calculations were performed on a number of surfaces using a Hamiltonian derived by Handy and coworkers,[43] which was later[44] shown to be equivalent to, but more cumbersome than, Watson's Hamiltonian of eqn (1).

Another notable early variational calculation was performed by Lai[33] using the bond angle–bond length coordinates discussed above. Unfortunately this work, though widely referred to [see ref. (24) and (41) for example], was never published. However, Lai's work does appear to be the first fully variational vibrational calculation which did not rely on the Eckart conditions and the concept of an equilibrium geometry.

The early work based on the Eckart approach by Bucknell and Handy was consolidated in two papers by Whitehead and Handy (WH),[44,45] both of which considered water. These works presented and applied an efficient variational algorithm which employs a basis set of harmonic oscillator functions (weighted Hermite polynomials) and constructs the matrix elements using Gauss–Hermite quadrature. This method is still the one of choice for solving the Watson Hamiltonian for non-linear molecules [see for example ref. (8), (15), (41), (46) and (47)] and provides the benchmark against which alternative variational techniques must be calibrated.

Calculations on the water molecules similar to those of WH were also performed in the mid-seventies by Carney *et al.*[24] (CCL) and Sorbie and Murrell.[8] Both these works used the potential derived from a perturbation theory based fit to experiment due to Hoy *et al.*[22] (HMS) as a starting point to providing improved potentials. Table 1 compares the results of a number of calculations on this potential.

The WH method essentially settled the argument over how to perform variational calculations on the low-lying levels of a fairly rigid molecule such as water (see later for a discussion of less orthodox solution strategies). This method was used by Sexton and Handy[15] in an extensive *ab initio* study on the fundamentals of water. More recently Chen *et al.*[41] (CMW) have used the WH method to solve the $J = 0$ problem as the first step in a two-step variational study of the rotational states of water with $J \leqslant 10$.

In order for a direct comparison of variational rovibrational methods to be meaningful, it is necessary for the methods to be applied to the same potential-energy surface. In the case of water such a comparison is difficult because of the variety of surfaces that have been studied. The most frequently used potential is that of HMS; table 1 compares calculations performed on this surface. The most obvious conclusion to be drawn from table 1 is that all theoretical results are in good agreement, with the major differences still attributable to small changes in the potential. For example the two most extensive calculations on the same surface, by Lai[33] and CCL,[24] agree to within 1 cm^{-1}

Table 1. Comparison of variational calculations[a] on the HMS potential:[22] (*a*) potential expansion in displacement coordinates and (*b*) potential expansions in SPF coordinates.[24,50]

			(*a*)				(*b*)			
			Lai	CCL	WH[b]	BQ	CCL	CC	CMW	exptl
ν_1	ν_2	ν_3 ref.:	31	24	44	49	24	48	41	20
0	0	0	4652	4652		4652	4639	4639		
0	1	0	1597	1597	1598	1597	1596	1595	1596	1595
0	2	0	3159	3159	3160	3160	3156	3154	3156	3152
1	0	0	3717	3717	3717	3716	3659	3659	3659	3657
0	0	1	3821	3821	3821	3820	3758	3758	3759	3756
0	3	0	4683	4684			4679	4677		4667
1	1	0	5299	5300		5300	5237	5236		5235
0	1	1	5403	5403		5402	5335	5334		5331
0	4	0	6168	6176			6169	6159		6136
1	2	0	6895	6846		6842	6777	6775		6775
0	2	1	6950	6950		6951	6877	6875		6872
2	0	0	7419	7420			7211	7210		7201
1	0	1	7520	7521			7261	7259		7250
0	0	2	7626	7626			7453	7452		7445

[a] All frequencies in cm^{-1} are relative to the (0, 0, 0) ground state. [b] Corrected results reported as a personal communication by Huber,[51] whose own calculations agree with WH's to within 1 cm^{-1}.

for the lowest eight states. Thereafter Lai's results are variationally slightly superior, due to the use of a relatively large basis. Murrell and Sorbie's calculation[8] on the HMS potential is not included in table 1 because they appeared to have an incorrect sign in one of the potential coefficients.[24] The results of Cropek and Carney[48] (CC), which used the bond length-bond angle coordinates of Lai, are variationally the best for the second version of the potential.

The sensitivity of the results to the potential is illustrated by comparing the results listed under headings (*a*) and (*b*) of table 1. Those in column (*a*) used the Taylor series derived by HMS in its original displacement form, while column (*b*) gives results obtained using the same coefficients but with Simons-Parr-Finlan (SPF) coordinates.[50] The results computed with the latter version of the HMS potential are clearly much closer to experiment. Recent calculations by CMW[41] suggest that the best force field is that due to Lai and Hagstrom.[33]

Table 2 surveys *ab initio* calculations of the fundamental vibrations of water. The table contains a number of interesting features. The first is the great improvement over the last decade or so in the quality of electronic structure calculations that it has become possible to do. While it is apparent that the accuracy of this step in the calculation is of paramount importance in obtaining good results, analysis of the results of Kraemer *et al.*[12] (KRS) illustrate the importance of including good nuclear motion calculations. Their published fundamentals, based upon harmonic frequencies with anharmonic corrections, suggest that their results are fairly poor with two fundamental frequencies more than 30 cm^{-1} in error. However, variational calculations performed on their surface by Sexton and Handy[12] (SH) suggest that the KRS surface actually gives the best current *ab initio* values for the fundamental frequency of water.[15]

When comparing the errors in the fundamentals, it should be remembered that even the best of the variational electronic structure calculations on water give energies many thousands of wavenumbers above the true energy. This means that the calculation of a surface well above, but parallel to, the actual surface is being attempted. In this

Table 2. Comparison of *ab initio* calculations of the vibrational fundamentals of the water molecule[a]

workers	ref.	type of surface	year	fundamental/cm^{-1} ν_1	ν_2	ν_3
BH	42	SCF	1974	1728	4045	4139
WH	45	SDCI	1976	1629	3720	3807
RES[b]	10	SDQ	1976	1633	3689	3798
HKD	9	SDQ	1978	1649	3619	3753
BSP[c]	11	MBPT	1979	1610	3702	3789
KSH	14	CASSCF	1982	1645	3691	3794
KRS	12	MRDCI	1982	1647	3662	3787
KRS[d]	12	MRDCI	1982	1613	3654	3757
SH	15	MRDCI	1984	1623	3667	3752
exptl	20			1595	3657	3756

[a] The year and type refer to the data of and method used for solving the electronic structure problem. [b] Vibrational analysis by KSH.[14] [c] Vibrational analysis of Romanowski and Bowman.[52] [d] Vibrational analysis by SH.[15]

context it is interesting to note that although the properties of the various electronic structure methods with respect to dissociation has been the subject of much debate, it is the non-dissociating bending coordinate whose fundamental has proved the most difficult to calculate accurately.

Another source of error in these calculations is the ability analytically to continue (or fit) the calculated grid of points to produce a potential-energy surface. Typical fitting errors are *ca.* 2 cm^{-1},[15] which is significant if highly accurate results are desired.[53] WH side-stepped this problem by performing electronic structure calculations at the grid of points required for their Gauss-Hermite quadrature, but for reasons discussed later in the section on CH_2^+, this method has not found general favour.

The development of sophisticated procedures for finding (analytic) derivatives[54] suggests that one might be able substantially to reduce the number of grid points required to characterise an *ab initio* potential if these points were supplemented with the additional information available from derivative calculations. However, this leads to two problems which so far remain unresolved. How should this reduced grid be distributed for maximum efficiency[15] and what relative weighting should be given to energy points as against derivatives?

An alternative strategy for using these derivative techniques has been pioneered by Gaw and Handy.[55] Their approach is to calculate directly, from the derivatives of the molecule at its equilibrium geometry, the constants commonly used by spectroscopists to represent their data. This method, which of course is not variational, relies on the validity of the perturbed harmonic oscillator-rigid rotor model from which the parameters are derived. The approach has shown that high-order parameters (force constants *etc.*) can be calculated for molecules such as water with surprising accuracy using relatively crude theoretical techniques.

Alternative Methodologies

Besides the standard variational techniques discussed above, the nuclear motions of the water molecule have been the subject of a large number of other calculations. If we are to say anything about the future of *ab initio* rovibrational spectroscopy it is interesting also to consider some of these. The method with, perhaps, the longest pedigree as far as rovibrational calculations on water are concerned is the (non-)rigid bender method as employed by Bunker and co-workers.[7,23,56] This technique does a full treatment for the bending and rotational coordinates, with a perturbative treatment of the more rigid stretches. Perhaps the most interesting recent result of this work is the conclusion by Beardsworth *et al.*[56] that the standard spectroscopic approach of using perturbation theory to treat the effects of anharmonicity, Coriolis coupling and centrifugal distortion will be 'unsatisfactory very often'. This emphasises the desirability of using variational approaches to treat the nuclear motion problem.

An approach in direct contrast to the non-rigid bender method has been employed by Lawton and Child[57] to study the highly excited stretching states of water. Their local modes analysis gave quantum, semi-classical and classical results into the region (above 30 000 cm^{-1}) where classical calculations found many chaotic trajectories. If the barrier to linearity in water is only *ca.* 11 000 cm^{-1}, analysis of other triatomics suggests[58] that the onset of chaos would be considerably lowered by including the bending motion. Semi-classical studies which include the bending mode are rare, a notable exception being the work of Colwell and Handy.[59] Work using local modes for water, studying for example the effects of high rotational excitation,[60] is still continuing.

A number of authors[50,52,61] have used an SCF approach to calculate the vibrational levels of the water molecule. As in electronic structure calculations, it is necessary to follow this step with a configuration interaction calculation if accurate reuslts are to be achieved. Romanowski and Bowman[52] compared SCF CI calculations with an approximation which made an adiabatic separation between the stretching and bending modes. We note, however, that they omitted the Watson term from the Hamiltonian and considered no more than three quanta of vibrational excitation. Even at this relatively low level of excitation some of the levels were found to be up to 100 cm^{-1} too low in the adiabatic model. This is in line with calculations which suggest that such adiabatic separations are of limited accuracy for highly excited bending modes.[62] Recent analysis by Johnson and Reinhardt[63]† suggests that the reverse adiabatic approximation shows more promise for water in highly excited states.

Burden and Quiney[49] (BQ) utilised the SCF CI method, but with a numerical SCF procedure, on the HMS water potential. Their results compare favourably with the other variational treatments of this potential shown in table 1, suggesting that this SCF CI procedure can indeed give a compact and accurate representation of the nuclear motion problem. We note, however, that BQ's results for the HCN problem were less satisfactory. In a second work, Burden[64] used hyperspherical coordinates to treat problems ranging from e_3^+ to water and ArHCl using the same algorithm. High accuracy was not aimed for in these calculations.

Finally, mention must be made of the recent use by Handy,[65] following a proposal by Coker and Watts,[66] of the quantum Monte Carlo method for a vibrational calculation on water. He demonstrates that this procedure, which is not variational but rather aims at a direct solution of the nuclear motion Schrödinger equation, can be made viable for calculating zero-point energies. However, at this time it is unclear how the method can be adapted to deal routinely with vibrational excitation and hence transition frequencies.

Calculations on the CH_2^+ Radical

In the absence of an observed spectrum of the CH_2^+ radical, the discussion of this system will concentrate solely on *ab initio* calculations. The original calculations were performed by Bartholomae *et al.*[67] (BMS) who performed electronic CI calculations at the grid points required for Gauss–Hermite integration along their vibrational coordinates. They used this surface for vibrational calculations performed with Watson's Hamiltonian,

---

† The reader is referred to this work for a more complete list of non-variational vibrational calculations on water.

eqn (1). It was soon apparent that while the equilibrium structure of CH_2^+ is bent, the large-amplitude bending mode samples linear geometries. BMS suppressed the resulting singularities in the Watson term by weighting the vibrational wavefunctions so as not to sample linear geometries.

The challenge of this system was taken up by Carter and Handy[25] (HC) who used Watson's isomorphic Hamiltonian[6] for linear molecules. In order to perform these calculations HC refitted BMS's surface to the form of Sorbie and Murrell.[8] This illustrates a drawback of performing *ab initio* calculations at a set of grid points (as originally proposed by Whitehead and Handy[45]) from the point of view of comparing calculations. Although performing calculations only at a set of grid points implicitly assumes a fit to the surface, namely in terms of the orthogonal polynomials used in the quadrature process, that fit is not an explicit one. Thus there is no potential-energy surface that can be used for a comparative calculation and the vibrational calculations cannot be unambiguously reproduced by an alternative method. This has meant that this method of eliminating the explicit representation of the potential has fallen from favour.

The HC potential was utilized by us (TS)[68] to perform fully coupled rovibrational calculations on CH_2^+ using scattering coordinates. These calculations also explored the efficiency of neglecting Coriolis interactions in the two embeddings of $\hat{H}_{ST}$ discussed above. In turn, these calculations were used by Carter *et al.*,[69]† (CHS) to test their calculations, which used a bond length–bond angle Hamiltonian similar to $\hat{H}_{ST}$, but with the z-axis placed symmetrically along the bisector of the HCH angle. Further calculations by us (ST)[32] confirmed that the bond length–bond angle coordinates give a much more efficient representation for this system than the scattering coordinates used previously by us. Finally, Carter and Handy (HC2)[26] augmented BMS's electronic calculations on the ground state with calculations on the first excited state and used these for variational non-Born–Oppenheimer calculations which included (in some parts approximately) the vibrational coupling between the two surfaces.

Table 3 summarizes the results of the various vibrational ($J = 0$) calculations. It is apparent from this table that most of the results show a fair measure of agreement. Besides the HC2 vibronic results, the exception to this are the results of BMS. Their calculations appear superior, in a variational sense, to the others because of the lower absolute energies they obtained. However, it would appear that this improvement is an artifact of the Whitehead–Handy method[44,45] and in particular the Watson Hamiltonian. This uses an embedding which is valid in only the small amplitude limit, but can fail for larger amplitude motion as the coordinates can leave the true domain of the problem. In particular, it is possible for the bending coordinate to pass through linear geometries and to sample regions which should be related to the true problem by a rotation and not a vibration. This difficulty was even encountered for the low-lying states of water by Chen *et al.*[41] It probably gives as severe a restriction on the utility of the Whitehead–Handy method as does the singularity for linear geometries encountered in $\hat{H}_W$.

It was just this problem which prompted Carter and Handy to treat CH_2^+ (and CH_2) as a quasi-linear molecule.[25] As the comparison of results shows, this method gives reliable results, but suffers from the disadvantage that the bending coordinate is being represented by a basis set expanded about the incorrect equilibrium structure. The resulting inefficiency makes this method unattractive for other 'quasi-linear' systems and to our knowledge it has not been used subsequently.

Similarly, our (TS) scattering coordinate calculations gave a reliable representation of the lowest 11 vibrational states of CH_2^+, but the system is not naturally represented as a collision complex between C^+ and H_2. This meant that a relatively large number of basis functions (432 for each symmetry) were required to converge the higher states. Although this basis set is larger than those used in the corresponding calculations, it

---

† We note that a term $-(\hbar^2/m_B)\cos\theta(\partial^2/\partial R_1\,\partial R_2)$ was omitted from $\hat{H}_V$ in this reference.

Table 3. Comparison of vibrational calculations [a] on CH_2^+

				BMS	HC	TS	CHS	ST	HC2
ν_1	ν_2	ν_3	ref.:	67	25	68	69	32	26
0	0^0	0		−70 519.6	−70 398.7	−70 400.6	−70 400.6	−70 400.6	
0	2^0	0		908	718	718.3	718.3	718.4	938.1
0	4^0	0				1611.0	1610.9	1611.4	2021.8
0	6^0	0				2770.7	2770.2	2772.7	3293.6
1	0^0	0		2935	2999	2998.8	2998.8	2998.9	2998.8
0	0^0	1		3162	3271	3270.6	3270.6	3270.7	3268.9
1	2^0	0				3678.6	3678.4	3678.6	3898.1
0	2^0	1				3966.8	3966.7	3966.9	4181.7
0	8^0	0				4117.4	4115.4		4717.1
1	4^0	0				4551.1	4550.1		4952.8
0	4^0	1				4839.4	4839.2		5240.0
0	10^0	0				5598.5	5587.6		

[a] The vibrational band origins, in cm^{-1}, are relative to the $(0, 0^0, 0)$ ground state. The labelling is as for a linear triatomic; for further details see text.

should be noted that in our methodology[70] diagonalisation is the rate-limiting step, due in part to reduction in integration times achieved by taking advantage of the properties of orthogonal polynomial expansions.[71] In contrast, the speed of the then current algorithms of Carter and Handy was very much determined by integration times.[72] We note, however, that Carter and Handy have since implemented an algorithm[35] based upon the optimised choice of integration points suggested by Schwenke and Truhlar[73] in which diagonalisation is also the rate-limiting step.

The CH_2^+ vibrational calculations labelled CHS and ST both used the same Hamiltonian ($\hat{H}_{ST}$ in its bond length-bond angle form) but differed in their choice of basis functions and integration procedures. In particular, several of the angular integrals which CHS evaluated using Gauss-Legendre integration were shown to have analytic forms by ST. However, the small differences between the predicted band origins is almost certainly attributable to the smaller basis set used by ST, which contained at least 40% fewer functions than any of the other calculations presented in table 3, with the exception of the anomalous BMS calculations.

Finally, the column labelled HC2 presents the results of Carter and Handy's Renner-Teller calculations. It is clear from these results that for CH_2^+ the bending mode is very severely perturbed by non-Born-Oppenheimer effects, even at very low levels of excitation. This calculation consistuted the first fully mode coupled vibronic calculation and will almost certainly be a prelude to similar investigations of other systems with more than one low-lying electronic state.

All the calculations discussed above considered only low-lying rotational levels with $J \leqslant 2$. However, CH_2^+ is a light molecule and thus does not need much rotational excitation for the separation between rotational and vibrational levels to become comparable. Table 4 gives the results of a two-step variational calculation on the $J = 10$ levels of CH_2^+, a calculation that would require a secular matrix of dimension 7382 if it were performed in a single variational step. As can be seen, convergence to better than 0.1 cm^{-1} can be achieved using a matrix of dimension only 880.

The rapidity of this convergence, which is much better than found in H_2D^+,[40] is due in part to the fact that k, the projection of the angular momentum along the body-fixed z-axis, which was placed along one C—H bond in these calculations, is a nearly good quantum number. This can be seen from the pairs of nearly degenerate levels with differing parity. Levels 3, 4 and 6 with e parity are nearly degenerate with levels 2, 3

Table 4. Low-lying levels of CH_2^+ with $J = 10$ calculated using a two-step variational procedure and bond length-bond angle coordinates.[a]

		$J = 10^e$				$J = 10^f$
level	$N =$	40	80	120	160	100
1		801.912	801.858	801.856	801.855	937.846
2		889.952	889.820	889.815	889.815	1131.861
3		1133.466	1133.346	1133.358	1133.357	1423.289
4		1423.303	1423.221	1423.203	1423.202	1769.770
5		1512.006	1511.793	1511.760	1511.759	1872.147
6		1769.905	1769.834	1769.830	1769.829	2160.891
7		1822.397	1821.719	1821.682	1821.680	2232.713
8		2160.965	2160.907	2160.904	2160.903	2588.819
9		2227.890	2226.636	2226.564	2226.555	2658.085
10		2422.275	2421.267	2421.242	2421.222	2968.003

[a] Frequencies, in cm^{-1}, are relative to the $J = 0$ ground state.

and 4 of the *f* stack and correspond to *k*s of *ca.* 2, 3 and 4 respectively. States with *k* equal to 0 occur only for the *e* stack and thus levels 1, 5 and 10 can be assigned as the lowest members of the rotational manifold of the $(0, 0^0, 0)$, $(0, 2^0, 0)$ and $(0, 4^0, 0)$ vibrational states. As the $J = 10$ rotational manifold for each of these states has 11 *e* and 10 *f* members, this means there is a large degree of overlap between the manifolds belonging to different vibrational states. As HC2's calculations showed that the bending excitations of CH_2^+ were strongly perturbed by vibronic interactions, a complete determination of these levels would require a fully coupled rovibronic treatment.

Conclusions

The calculations considered above on water and CH_2^+ suggest that, for triatomics at least, reliable variational methods are now available for obtaining rovibrational wavefunctions. This is certainly true for relatively low degrees of vibrational excitation and new methods[40,41] have opened an exciting new world of high rotational excitation to accurate calculation. However, there is still much work to be done on highly excited vibrational states. For example, the observation of *ca.* 27 000 lines in a small region of the near dissociating spectrum of H_3^+ by Carrington and Kennedy[74] has highlighted the inadequacy of our knowledge in this spectral region and provided a tantalising target for the theoretician to aim at. So far only very approximate quantum-mechanical calculations have been possible on this problem.[75]

Some promising work in this direction is now becoming available, mostly on simplified or model systems. Amongst these the use of the discrete variable techniques by Light and co-workers[76] (which have already been used for the low-lying levels of water[51]), the attempt to stabilise highly excited states outside the variational approach by Chang *et al.*[77] and the use of dynamical basis sets as suggested by Blanco and Heller[78] perhaps show the most promise for the future. Carter and Handy[79] have recently demonstrated, again using CH_2^+, how to consider higher excited states, in the fashion of Chang *et al.*,[77] and still obtain variational results.

References

1 J. K. G. Watson, *Mol. Phys.*, 1968, **15**, 479.

2 G. D. Carney, L. L. Sprandel and C. W. Kern, *Adv. Chem. Phys.*, 1978, **37**, 305.

3 C. Eckart, *Phys. Rev.*, 1935, **47**, 552.

4 R. Wertheimer, *Mol. Phys.*, 1974, **27**, 1673.

5 A. Sayvetz, *J. Chem. Phys.*, 1939, **6**, 383.

6 J. K. G. Watson, *Mol. Phys.*, 1970, **19**, 465.

7 P. R. Bunker and J. M. R. Stone, *J. Mol. Spectrosc.*, 1972, **41**, 310.

8 K. S. Sorbie and J. N. Murrell, *Mol. Phys.*, 1975, **29**, 1387.

9 P. Hennig, W. P. Kramer, G. H. F. Diercksen and G. Strey, *Theoret. Chim. Acta*, 1978, **47**, 233.

10 B. J. Rosenberg, W. C. Ermler and I. Shavitt, *J. Chem. Phys.*, 1976, **65**, 4072.

11 R. J. Bartlett, I. Shavitt and G. D. Purvis III, *J. Chem. Phys.*, 1979, **71**, 281.

12 W. P. Kraemer, B. O. Roos and P. E. M. Siegbahn, *Chem. Phys.*, 1982, **69**, 305.

13 P. Saxe, H. F. Schaefer III and N. C. Handy, *Chem. Phys. Lett.*, 1981, **79**, 202.

14 P. J. Knowles, G. J. Sexton and N. C. Handy, *Chem. Phys.*, 1982, **48**, 157.

15 G. J. Sexton and N. C. Handy, *Mol. Phys.*, 1984, **51**, 1321.

16 W. S. Benedict, N. Gailar and E. K. Plyler, *J. Chem. Phys.*, 1956, **24**, 1139.

17 G. Steenbeckeliers and J. Bellet, *J. Mol. Spectrosc.*, 1973, **45**, 10; J. Bellet, W. J. Laffertyy and G. Steenbeckeliers, *J. Mol. Spectrosc.*, 1973, **47**, 388.

18 L. A. Pugh and K. N. Rao, *J. Mol. Spectrosc.*, 1973, **47**, 403.

19 J. M. Flaud and C. Camy-Peyret, *Mol. Phys.*, 1973, **26**, 811; *J. Mol. Spectrosc.*, 1974, **51**, 142; J. M. Flaud, C. Camy-Peyret and J. P. Maillard, *Mol. Phys.*, 1976, **32**, 499; C. Camy-Peyret, J. M. Flaud, J. P. Maillard and G. Guelachvili, *Mol. Phys.*, 1977, **33**, 1641.

20 J. S. Garing and R. A. McClatchey, *Appl. Opt.*, 1973, **12**, 2525; C. C. Ferriso and C. B. Ludwig, *J. Chem. Phys.*, 1964, **41**, 1668.

21 D. F. Smith Jr and J. Overend, *Spectrochim. Acta, Part A*, 1972, **28**, 471.

22 A. R. Hoy, I. M. Mills and G. Strey, *Mol. Phys.*, 1972, **24**, 1265.

23 A. R. Hoy and P. R. Bunker, *J. Mol. Spectrosc.*, 1974, **52**, 439; 1979, **74**, 1.

24 G. D. Carney, L. A. Curtiss and R. S. Langhoff, *J. Mol. Spectrosc.*, 1976, **61**, 371.

25 S. Carter and N. C. Handy, *J. Mol. Spectrosc.*, 1982, **95**, 9.

26 S. Carter and N. C. Handy, *Mol. Phys.*, 1984, **52**, 1367.

27 G. Pineau des Forets, D. R. Flower, T. W. Hartquist and A. Dalgarno, *Mon. Nat. R. Astr. Soc.*, 1986, **24**, 801.

28 B. T. Sutcliffe, in *Current Aspects of Quantum Chemistry*, ed. R. Carbo (*Studies in Theoretical Chemistry*, Elsevier, Amsterdam, 1982) vol. 21, p. 99.

29 S. Carter and N. C. Handy, *Mol. Phys.*, 1984, **53**, 1033.

30 N. C. Handy, *Mol. Phys.*, 1987, **61**, 207.

31 B. T. Sutcliffe, *Mol. Phys.*, 1983, **48**, 561.

32 B. T. Sutcliffe and J. Tennyson, *Mol. Phys.*, 1986, **58**, 1053.

33 E. C. K. Lai, *Master's Thesis* (Indiana University, 1975).

34 S. Carter and N. C. Handy, *Mol. Phys.*, 1982, **47**, 1445.

35 S. Carter and N. C. Handy, *Mol. Phys.*, 1986, **57**, 175.

36 J. Tennyson and B. T. Sutcliffe, *J. Chem. Phys.*, 1982, 77, 4061.

37 G. Brocks, A. van der Avoird, B. T. Sutcliffe and J. Tennyson, *Mol. Phys.*, 1983, **50**, 1025.

38 B. T. Sutcliffe and J. Tennyson, in *Molecules in Physics, Chemistry and Biology*, ed. I. Csizmadia and J. Maruani (Reidel, Dordrecht, 1987).

39 B. T. Sutcliffe, to be published.

40 J. Tennyson and B. T. Sutcliffe, *Mol. Phys.*, 1986, **58**, 1067.

41 C-L. Chen, B. Maessen and M. Wolfsberg, *J. Chem. Phys.*, 1985, **83**, 1795.

42 M. G. Bucknell and N. C. Handy, *Mol. Phys.*, 1974, **28**, 777.

43 M. G. Bucknell, N. C. Handy and S. F. Boys, *Mol. Phys.*, 1974, **28**, 759.

44 R. J. Whitehead and N. C. Handy, *J. Mol. Spectrosc.*, 1975, **55**, 356.

45 R. J. Whitehead and N. C. Handy, *J. Mol. Spectrosc.*, 1976, **59**, 459.

46 N. C. Handy and S. Carter, *Chem. Phys. Lett.*, 1981, **79**, 118.

47 B. Maessen and M. Wolfsberg, *J. Chem. Phys.*, 1984, **60**, 4651; B. Maessen, M. Wolfsberg and L. B. Harding, *J. Chem. Phys.*, 1985, **89**, 3324.

48 D. Cropek and G. D. Carney, *J. Chem. Phys.*, 1984, **80**, 4280.

49 F. R. Burden and H. M. Quiney, *Mol. Phys.*, 1984, **53**, 917.

50 J. M. Simons, R. G. Parr and J. M. Finlan, *J. Chem. Phys.*, 1973, **59**, 3229.

51 D. Huber, *Mol. Phys.*, 1986, **59**, 1007; *Int. J. Quantum Chem.*, 1985, **28**, 245.

52 H. Romanowski and J. M. Bowman, *Chem. Phys. Lett.*, 1984, **110**, 235.

53 J. Tennyson and B. T. Sutcliffe, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 1151.

54 *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, ed. P. Jorgensen and J. Simons (Reidel, Dordrecht, 1986).

55 J. F. Gaw and N. C. Handy, *Chem. Phys. Lett.*, 1985, **121**, 321; 1986, **128**, 182; J. F. Gaw, Y. Yamaguchi, H. F. Schaefer III and N. C. Handy, *J. Chem. Phys.*, 1986, **85**, 5132.

56 R. Beardsworth, P. R. Bunker, P. Jensen and W. P. Kraemer, *J. Mol. Spectrosc.*, 1986, **118**, 50.

57 R. T. Lawton and M. S. Child, *Mol. Phys.*, 1981, **44**, 709.

58 J. Tennyson and S. C. Farantos, *Chem. Phys.*, 1985, **93**, 237.
59 S. M. Colwell and N. C. Handy, *Mol. Phys.*, 1978, **35**, 1183.
60 R. B. Shirts, *J. Chem. Phys.*, 1986, **85**, 4949; W. B. Clodius and R. B. Shirts, *J. Chem. Phys.*, 1986, **84**, 6224; R. B. Shirts and K. M. Holbrook, *Int. J. Quantum Chem.*, 1987, **85**, 6210.
61 T. C. Thompson and D. G. Truhlar, *J. Chem. Phys.*, 1982, **77**, 3031.
62 S. C. Farantos and J. Tennyson, *J. Chem. Phys.*, 1986, **84**, 6210.
63 B. R. Johnson and W. P. Reinhardt, *J. Chem. Phys.*, 1986, **85**, 4538.
64 F. R. Burden, *J. Phys. B*, 1986, **19**, 1397.
65 N. C. Handy, *Commun. Phys. Chem.*, 1987, **1**, 1.
66 D. F. Coker and R. O. Watts, *Mol. Phys.*, 1986, **58**, 1113.
67 R. Bartholomae, D. Martin and B. T. Sutcliffe, *J. Mol. Spectrosc.*, 1982, **87**, 367.
68 J. Tennyson and B. T. Sutcliffe, *J. Mol. Spectrosc.*, 1983, **101**, 71.
69 S. Carter, N. C. Handy and B. T. Sutcliffe, *Mol. Phys.*, 1983, **49**, 745.
70 J. Tennyson, *Comput. Phys. Rep.*, 1986, **4**, 1.
71 J. Tennyson, *Comput. Phys. Commun.*, 1985, **38**, 39.
72 S. Carter, personal communication, 1983.
73 D. W. Schwenke and D. G. Truhlar, *Comput. Phys. Commun.*, 1984, **34**, 57.
74 A. Carrington and R. A. Kennedy, *J. Chem. Phys.*, 1984, **81**, 91.
75 R. Pfeiffer and M. S. Child, *Mol. Phys.*, 1987, **60**, 1367.
76 J. C. Light, I. P. Hamilton and J. V. Lill, *J. Chem. Phys.*, 1985, **82**, 1400; Z. Bacic and J. C. Light, *J. Chem. Phys.*, 1986, **85**, 4594; 1987, **86**, 3065.
77 J. Chang, N. Moiseyev and R. E. Wyatt, *J. Chem. Phys.*, 1986, **84**, 4997.
78 M. Blanco and E. J. Heller, *J. Chem. Phys.*, 1985, **83**, 1149.
79 S. Carter and N. C. Handy, *Comput. Phys. Commun.*, 1987, **44**, 1.

Paper 7/111; *Received* 22*nd January*, 1987