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MULTIMODE: A code to calculate rovibrational energies of polyatomic molecules

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MULTIMODE: a code to calculate rovibrational energies of polyatomic molecules

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This review focuses on the calculation of rovibrational energies of polyatomic molecules using the code MULTIMODE. This code, which uses normal coordinates and a hierarchical n -mode representation of the potential, aims to be applicable to a wide class of molecules and molecular complexes. The theoretical and computational methods used in this code are described, followed by a review of selected applications. These applications illustrate various features of the code and also point out some limitations of the current version of the code. The review concludes with some ideas about possible future directions in this area of research.

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1. Introduction

The accurate calculation of rovibrational energies, in full dimensionality, of polyatomic molecules is an important goal of computational chemistry. This goal has been largely realized for triatomic molecules, for which a variety of efficient spectral and grid methods have been developed. These methods generally make use of one of several choices of coordinates for which exact Hamiltonians have been derived. There is currently great activity and progress in extending these methods to

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tetraatomic and larger molecules [1–10]. This progress is being made in two areas. One is the extension of curvilinear coordinate systems to larger molecules and the derivation of the corresponding Hamiltonians. The other is in the development of basis sets and linear algebra methods that permit the calculation of eigenvalues and eigenfunctions of the Hamiltonian. The methods and coordinates currently used in most approaches are quite specific to the molecule of interest. This is a necessity given the great difficulty in obtaining ‘exact’ results for even tetraatomic systems.

An alternative approach taken by us [11] and Gerber and co-workers [12] has been to develop codes that can be applied generally to polyatomic molecules and molecular complexes. Both groups use as the basis of their programs the well-known Watson Hamiltonian [13]. This Hamiltonian, which is given in terms of rectilinear normal coordinates, is ‘universal’ for non-linear molecules. There are, however, well-known limitations with this approach, perhaps the most serious one being the great difficulty it has in describing very large amplitude motion, as occurs, for example, in isomerization. Thus, while it is a universal Hamiltonian it cannot in practice be readily applied universally.

This Hamiltonian was the basis of several codes written in the 1980s and 1990s [14–18]. In these codes the implementation was made with several approximations, e.g. approximate or no treatment of vibrational angular momentum terms, limitation to non-rotating cases, the use of second-order perturbation theory or limited variational methods. A critical approximation that was made in these codes was the representation of the potential as a fairly low-order multinomial in the normal coordinates. This representation greatly simplified the evaluation of matrix elements of the potential; however, it also severely limited the range of applicability of the codes and (along with other approximations) made calculations less than ‘exact’. For this and other reasons (e.g. interest in floppy motion) these approaches based on the Watson Hamiltonian fell out of favour during the 1990s, and indeed great progress has been made using other Hamiltonians that, however, are not as general as the Watson Hamiltonian.

In the past few years, we and Gerber and co-workers have re-examined the general approach to describe vibrations of molecules based on the Watson Hamiltonian. There are some significant differences between the codes developed by us and by Gerber and co-workers and we point these out as we give the details of our code. Our code, which we call MULTIMODE (MM) [11], is described in this review along with a selection of applications which illustrate the methods used in the code and some recent extensions of the code to describe moderately floppy motion.

The methods used in this code are described and verified in the next section. Following that we review several varied applications of the code to a number of interesting and challenging molecules and molecular complexes. We conclude with some comments on future directions in this field.

2. Methods

The code MM is based on the familiar Watson Hamiltonian, which is given in mass-scaled normal coordinates (and atomic units) by

$$\hat{H} = \frac{1}{2} \sum_{\alpha\beta} (\hat{J}_\alpha - \hat{\pi}_\alpha) \mu_{\alpha\beta} (\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha} + V(\mathbf{Q})_l, \quad (1)$$

where \hat{J}_α and $\hat{\pi}_\alpha$ ($\alpha = x, y, z$) are the total and vibrational angular momenta respectively, $\mu_{\alpha\beta}$ is the inverse of the effective moment of inertia and V is the full potential in terms of the N normal coordinates denoted collectively in this equation by \mathbf{Q} .

The potential is the major source of non-separability in this Hamiltonian and as mentioned above, with rare exceptions, it had been represented by a multinomial expansion (usually to fourth order) in the normal coordinates. This approach has obvious limitations, e.g. a limited and unknown range of applicability and accuracy. Further, for larger molecules the numerical determination of a full multinomial expansion can be quite difficult and cumbersome. The key approximation in MM is to represent the potential in a novel way that permits calculations for many-mode systems. This is done by making the following hierarchical n -mode representation of the potential:

$$V(Q_1, Q_2, \dots, Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{ij} V_{ij}^{(2)}(Q_i, Q_j) + \sum_{ijk} V_{ijk}^{(3)}(Q_i, Q_j, Q_k) \\ + \sum_{ijkl} V_{ijkl}^{(4)}(Q_i, Q_j, Q_k, Q_l) + \sum_{ijklm} V_{ijklm}^{(5)}(Q_i, Q_j, Q_k, Q_l, Q_m) + \dots \quad (2)$$

In this expression the one-mode representation of the potential contains only $V_i^{(1)}(Q_i)$ terms, that is cuts through the hyperspace of normal coordinates with just one coordinate varying at a time, the two-mode representation contains those terms plus the $V_{ij}^{(2)}(Q_i, Q_j)$ terms, etc. In one version of MM, which uses multidimensional quadratures (described in detail below), the current maximum number of coupled modes is 4. In a new version of the code, which does fits to the various n -mode terms in equation (2), the maximum number of coupled modes is 5. It will become clear below why this representation makes calculations for large molecules feasible. Also, this representation of the potential affords a systematic approach to test and increase the accuracy of a calculation. A test of the accuracy can be (and generally is) done by examining the convergence of eigenvalues with respect to the level of mode coupling. The accuracy of the code will increase as the level of mode coupling increases, and this can be increased as computational resources increase.

At this point we note that the code of Gerber and co-workers [12] uses this hierarchical representation but truncated at the two-mode representation, i.e.

$$V(Q_1, Q_2, \dots, Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{ij} V_{ij}^{(2)}(Q_i, Q_j).$$

It is also important to credit this group with suggesting this representation. We also note that the Watson Hamiltonian is used by Gerber and co-workers, but without vibrational angular momentum terms and also limited to zero total angular momentum. This approximation and limitation are not made in MM.

The theoretical approach used in MM and the Gerber group's code builds on a vibrational self-consistent field (VSCF) [19, 20] wavefunction for a given reference state labelled by a set of quantum numbers. This trial wavefunction is given by a simple Hartree product

$$\Psi_{m_1, n_2, \dots, n_N}^{VSCF}(Q_1, Q_2, \dots, Q_N) = \prod_{i=1}^N \phi_{n_i}^{(i)}(Q_i), \quad (3)$$

and the optimum modals wavefunctions $\phi_{n_i}^{(i)}(Q_i)$ are obtained from the solution of the VSCF equations for $J=0$

$$\left(T_l + \left\langle \prod_{i \neq l}^N \phi_{n_i}^{(i)} | V + T_c | \prod_{i \neq l}^N \phi_{n_i}^{(i)} \right\rangle - \epsilon_{n_l}^{(l)} \right) \phi_{n_l}^{(l)}(Q_l) = 0, \quad l = 1, N, \quad (4)$$

where

$$T_l \equiv -\frac{1}{2} \frac{\partial^2}{\partial Q_k^2}, \quad T_c \equiv \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - \frac{1}{8} \sum_{\alpha} \mu_{\alpha\alpha}$$

and the integration is over the coordinates of $N-1$ modals. These coupled equations are typically solved iteratively and for low-lying reference states the iteration procedure is usually quick, stable and efficient. (These modals are expanded in terms of a primitive harmonic oscillator basis, resulting in a procedure that is analogous to the Hartree–Fock–Roothan–Hall method in electronic structure calculations.) Once convergence is achieved a VSCF Hamiltonian can be defined as

$$H_{n_1, n_2, \dots, n_N}^{VSCF} \equiv \sum_{l=1}^N \left(T_l + \left\langle \prod_{i \neq l}^N \phi_{n_i}^{(i)} | V + T_c | \prod_{i \neq l}^N \phi_{n_i}^{(i)} \right\rangle \right), \quad (5)$$

and the eigenfunctions of this Hamiltonian form an orthonormal set. The eigenfunction $\Psi_{n_1, n_2, \dots, n_N}^{VSCF}(Q_1, Q_2, \dots, Q_N)$ is the VSCF state and all other eigenfunctions are termed ‘virtual states’, which we discuss further below.

It is clear that if N is larger than 4 or so the integration becomes extremely computer intensive. It is equally clear that the n -mode representation of the potential, given by equation (1), is a reasonable way to deal with this bottleneck. Thus, for the two-mode representation of the potential only one-dimensional integrals are required in these equations, and the method is extremely efficient with this representation. Unfortunately, as we demonstrate below, this level of coupling is not always sufficient to obtain accurate results, and thus we use a greater level of mode coupling in MM.

It is usually necessary to go beyond the VSCF description to obtain accurate energies. Gerber and co-workers have chosen to use second-order perturbation theory to correct VSCF energies [12(b)]. This approach uses the virtual states defined above to correct the VSCF expectation value of the Hamiltonian. The first-order correction vanishes and the second-order correction is used. This is analogous to second-order Möller–Plesset theory of electronic structure theory. Gerber and co-workers term the resulting theory ‘correlation-corrected VSCF’ or ‘cc-VSCF’ [12(c)]. As noted already, this approach also uses the two-mode representation of the potential and so at most two-dimensional integrals are needed in the cc-VSCF approach. The use of second-order perturbation theory together with the two-mode representation of the potential renders this method very efficient and thus feasible to apply to large molecules [12(b)].

In order to go beyond the VSCF level of accuracy, we use two ‘CI’ schemes in MM, which can give, in principle, exact results, for a given n -mode representation of the potential. In one scheme, denoted by ‘VSCF + CI’, the many-mode wavefunction is expanded in a basis of VSCF states. These states are not orthogonal and this results in a generalized eigenvalue problem. This problem is solved by standard methods. In the other scheme, denoted by ‘VCI’, the many-mode wavefunction is

expanded in terms of the virtual states of a given VSCF Hamiltonian. Usually the ground state VSCF Hamiltonian is used. This basis is orthonormal and results in a standard eigenvalue problem. Both schemes have been tested on triatomic molecules where three-mode coupling is exact and both produce variational results that converge to the correct energy eigenvalues [11(b)].

These CI schemes can result in very large Hamiltonian matrices and so a very flexible basis set selection method has been developed for the VCI scheme. The scheme divides the excitations into one-mode, two-mode, three-mode and four-mode excitations and limits the total number of quanta excited in these four classes of mode excitation. In addition, the maximum number of excitations in any mode can be further restricted. Thus, for example, a basis can be created in which excitations are restricted to a subset of modes, while other modes remain in their ground states. This could be very useful for large problems with a large number of 'spectator modes'. Another consideration in making this approach efficient is the numerical evaluation of matrix elements of the potential. (For a given n -mode representation of the potential, n -dimensional integration must be done.) In all versions of MM prior to version 5 these matrix elements are evaluated by optimized numerical quadrature. Finally, eigenvalues and eigenvectors of the final Hamiltonian matrix can be obtained using either standard routines, or an iterative diagonalization routine. Detailed descriptions of these methods can be found elsewhere [11(e)].

A new version of MM (version 5), avoids these n -dimensional quadratures by doing fits to all $(N!/n!(N-n)!)$ n -mode grids [21]. To illustrate this procedure consider the example $N=3$. In this case equation (2) reduces to

$$V(Q_1, Q_2, Q_3) = V^{(1)}(Q_1) + V^{(1)}(Q_2) + V^{(1)}(Q_3) + V^{(2)}(Q_1, Q_2) \\ + V^{(2)}(Q_1, Q_3) + V^{(2)}(Q_2, Q_3) + V^{(3)}(Q_1, Q_2, Q_3).$$

In this expression the intrinsic n -mode potentials, $V^{(n)}$, are fitted using a linear least-squares procedure in a direct-product polynomial basis in a scaled coordinate $y_i = \tanh(\gamma Q_i)$. The procedure begins by fitting the one-mode potentials $V^{(1)}$. Then two-mode potentials $V(Q_i, Q_j)$ are generated and the intrinsic two-mode potentials, given by

$$V^{(2)}(Q_i, Q_j) = V(Q_i, Q_j) - V^{(1)}(Q_i) - V^{(1)}(Q_j)$$

are fitted. This procedure continues and fitting is done up to current maximum of five-mode potentials. The advantage of using a direct-product basis for each of these fits is that the matrix elements of the potential can be written as sums of products of one-dimensional integrals. These integrals, which are evaluated using the usual basis of one-dimensional contracted primitive functions, need only be evaluated once and then stored for future use, thus avoiding the direct numerical integration of five-dimensional integrals.

Another advantage in fitting, or interpolating [22], these n -mode potential grids occurs when considering 'direct dynamics' implementations of MM. By this we mean directly calculating the potential at the quadrature grid points. This has been done extensively by Gerber and co-workers with, as noted already, the restriction to two-mode grids. This approach is certainly quite feasible for such grids since each grid requires $O(10^2)$ electronic structure calculations. This number is determined by the number of quadrature points in each n -mode grid. However, for our applications, where typically four-mode and more recently five-mode grids are used, the effort,

Table 1. A list of applications to date of the code MM and references.

Molecules	Transition states	Adsorbates	Complexes
HCO [11(a)], HO ₂ [11(c)]	H ₂ OH [11(f)]	CO–Cu [11(a)]	Cl [−] –H ₂ O [23]
H ₂ O [11(c)], HOCl [24]	HCO ₂ [11(h)]	(CO) ₂ –Cu [11(d)]	H ₃ O ₂ ⁺ [25]
H ₂ C [11(b)], H ₂ CS [11(e)]			
HOCO [11(g)], CH ₄ [26, 27]			
NH ₃ [28], H ₃ O ⁺ [21, 29, 30]			

which scales like $O(10^4)$ or $O(10^5)$, becomes very computer intensive. (Nevertheless, we did such a calculation for Cl[−]–H₂O [23] for four-mode grids.) By using fits, or interpolation of less dense grids, great savings in computational effort can be realized, with almost no loss in accuracy.

Another obvious point to be made about either interpolating or fitting these grids is that the full global potential is never required and relatively low-order fits are required, even for large molecules.

Numerous applications of MM have been made to date, and these are summarized in table 1. Tests of the code have been made for several triatomic [11(c)] and tetraatomic [11(e)] molecules, where it has been shown to reproduce ‘exact’ results to within 0.2 cm^{-1} or less for states with fairly high levels of excitation for triatomics (where three-mode coupling is exact) and to within several cm^{-1} or less for moderate levels of excitation for tetraatomics. Below we present selected tests of the code as well as some recent applications which illustrate some of the new features of the code. Before doing that, however, we present some new calculations which illustrate the importance of the vibrational angular momentum terms in the Watson Hamiltonian. We also present some tests of the accuracy of using a two-mode representation of the potential. These tests bear directly on the approach taken by the Gerber group, which neglects vibrational angular momentum terms and uses two-mode coupling.

3. Analysis of approximations

Here we examine the accuracy of approximations that are often made to the Watson Hamiltonian and/or the two-mode representation of the potential, for low-lying vibrational states of non-rotating H₂O. One approximation is to represent the potential with two-mode coupling, but to make no further approximations. Another is to make this approximation and also to ignore the vibrational angular momentum and Watson terms (denoted by ‘two-mode and neglect’) and the final one is to make no approximations to the potential but to neglect the vibrational angular momentum and Watson terms (denoted by ‘three-mode and neglect’). Converged VCI calculations were performed for H₂O using an accurate potential energy surface [31]. A comparison of the energies of low-lying states obtained with these various approximations against exact ones is shown in table 2. As seen, the two-mode results are quite accurate for some states, but for most errors are between 15 and 18 cm^{-1} . The errors in the ‘three-mode and neglect’ approximation are even larger for states involving bend excitation. This is not surprising because vibrational angular momentum terms are generally larger for a bending mode than a stretch mode.

Table 2. Comparison of energies (cm^{-1}) for a two-mode representation of the potential for H_2O with no other approximations and three-mode and two-mode representations of the potential neglecting vibrational angular momentum terms and the ‘Watson term’, denoted by ‘3-mode and neglect’ and ‘2-mode and neglect’, respectively, with exact energies. Excitation energies are relative to the zero-point energy (ZPE) and ν_b , ν_s , ν_a are the bend, symmetric and antisymmetric stretch quantum numbers.

ν_b, ν_s, ν_a	2 mode	3 mode and neglect	2 mode and neglect	Exact
ZPE	4636.9	4647.7	4647.6	4638.0
1, 0, 0	1593.3	1581.8	1599.3	1594.8
2, 0, 0	3167.2	3125.3	3141.7	3152.3
0, 1, 0	3655.9	3656.1	3656.7	3658.4
0, 0, 1	3742.85	3742.1	3744.7	3760.4
1, 1, 0	5222.4	5221.7	5268.7	5237.4

Table 3. Energies (cm^{-1}) of low-lying vibrational states of non-rotating CH_4 with respect to the level of n -mode representation of the potential and comparison with recent full-dimensional Lanczos calculations.

State	2 mode ^a	3 mode ^a	4 mode ^a	Lanczos ^b
ZPE	9693.1	9707.4	9707.2	—
$\nu_4(\text{F}_2)$	1311.7	1312.9	1313.3	1314.1
$\nu_2(\text{E})$	1531.1	1534.4	1534.5	1534.0
$\nu_1(\text{A}_1)$	2925.7	2948.3	2949.4	2955.8
$2\nu_4$	2626.1	2621.6	2623.9	2627.2
$\nu_2 + \nu_4$	2881.6	2831.5	2836.4	2838.1
$\nu_3(\text{F}_2)$	3004.3	3053.7	3053.1	3056.5
$2\nu_2$	3067.3	3067.2	3067.3	3069.0

^a Reference [26].

^b Reference [32].

The errors in the ‘two-mode and neglect’ calculations are in the range from -1.7 to 31.3 cm^{-1} with an average absolute error of 12.6 cm^{-1} for excitation energies.

Thus, all of these approximations produce errors that are outside the usual standard of ‘spectroscopic’ accuracy. However, it must be noted that they are all a vast improvement over the errors made using the harmonic approximation. The average error made in this approximation for the excitation energies shown in the table is 160 cm^{-1} . Finally, it should also be noted that because three-mode coupling is exact for H_2O the two-mode coupling approximation is not as severe as it would be in general for larger molecules. We have previously examined the convergence of VCI results using two-, three- and four-mode coupling for $\text{Cl}^- - \text{H}_2\text{O}$ [23] and CH_4 [26]. The results for $\text{Cl}^- - \text{H}_2\text{O}$ show large errors in the two-mode coupling approximation (of the order of 100 cm^{-1} or more). This is a fairly floppy complex and so errors of this magnitude are perhaps not surprising.

A detailed test of two-mode and also four-mode coupling for CH_4 , a strongly bound molecule, is shown in table 3. The test of four-mode coupling makes use of recent full-dimensional calculations of Yu [32], which are also given in this table. These calculations used a ‘two-layer’ Lanczos method and coordinates that are very suitable for this molecule. These calculations were done with the *ab initio* quartic

force field of Lee *et al.* [33]. First, note that the agreement between the four-mode and full-dimensional calculations is quite good for all of the states listed (the average difference is 2.5 cm^{-1}). (It will be important in the future to apply version 5 of MM which can do five-mode coupling to see whether the small differences with the presumed accurate full-dimensional calculations are reduced.) Second, the two-mode results are within 15 cm^{-1} of the three- and four-mode energies, with the exception of the two high frequency (degenerate) CH stretch modes $\nu_1(A_1)$ and $\nu_3(F_2)$. For these states the two-mode energies are in error by 23 and 49 cm^{-1} respectively. Thus, for CH_4 and for other cases we have examined two-mode coupling is not a reliable level of coupling to obtain accurate vibrational energies.

These MM calculations on CH_4 and the isotopomers, CH_2D_2 , CH_3D , CHD_3 and CD_4 , were the first reported variational calculations using a rigorous Hamiltonian for a nine-degree-of-freedom molecule. Since these were reported there has been a significant amount of progress in doing variational calculations on CH_4 [32, 34, 35], including those of Yu listed in table 3. These calculations have been for CH_4 only, and also for zero total angular momentum. They all used specialized coordinates that are highly suited for CH_4 . In addition, several potentials that are more realistic than the quartic force field have been developed [27, 34]. Our efforts in this direction have been to transform the quartic force field by replacing the stretch displacements with Morse variables and then to adjust slightly some of the force constants to improve agreement with experiment. The results of this work, which include calculations for the above isotopomers and for total angular momentum 0 and 1, have been reported [27].

4. Selected results for water systems

We have applied MM to several water systems, including rotating and non-rotating H_2O , H_3O^+ and H_5O_2^+ . This series of molecules, in addition to being of significant scientific interest, illustrates a number of the features and capabilities of MM.

4.1. H_2O

The low-lying vibrational states of H_2O were presented above for zero total angular momentum. Elsewhere [11(c)] a comparison with benchmark calculations was done for fairly highly excited states and the agreement with the benchmark results was excellent, except for very high excited bend states which sample the linear configuration, for which the Watson Hamiltonian has a well-known singularity. These calculations also exploited the C_{2v} symmetry of H_2O . Exploiting this level of symmetry is a feature of MM.

Calculations for non-zero total angular momentum, J , can also be done with MM. There are two options for such calculations. One is an 'exact' calculation and the other is based on the adiabatic rotation approximation [11(c)]. This approximation calculates the asymmetric top rotational energy at a given nuclear geometry and adds that energy to the potential to yield an effective potential. The approximation neglects Coriolis coupling, and so it is a very efficient method to obtain approximate rovibrational energies. In cases where Coriolis coupling is very small, e.g. HO_2 and HOCl , it is very accurate [11(c)]. For H_2O , for which Coriolis coupling is large, this approximation is not very accurate, e.g. energies relative to $J=0$ are of the order of

Table 4. Comparison of rovibrational energies of H_2O (cm^{-1}) for $J=3$ and low-lying vibrational states (ν_b, ν_s, ν_a), relative to the ZPE. The first column of energies contains exact calculations^a and the second column is from MM.

K_a	K_c			K_a	K_c		
0, 0, 0				1, 0, 0			
ZPE		4637.97 ^a	4637.97 ^b				
0	3	136.76 ^a	136.85 ^b	0	3	1731.92	1732.77
1	3	142.28	142.32	1	3	1739.52	1739.68
1	2	173.37	173.41	1	2	1772.44	1772.63
2	2	206.30	206.36	2	2	1813.82	1813.88
2	1	212.15	212.14	2	1	1819.36	1818.60
3	1	285.22	285.25	3	1	1907.48	1907.38
3	0	285.42	285.45	3	0	1907.64	1907.52
2, 0, 0				0, 1, 0			
0	3	3289.23	3290.64	0	3	3791.36	3791.45
1	3	3299.99	3300.25	1	3	3796.53	3796.59
1	2	3334.62	3334.93	1	2	3827.37	3827.44
2	2	3387.68	3387.74	2	2	3858.86	3858.98
2	1	3392.74	3391.43	2	1	3864.76	3864.83
3	1	3500.51	3500.30	3	1	3935.20	3935.37
3	0	3500.64	3500.39	3	0	3935.34	3935.57

^a Reference [31].

^b Reference [11(c)].

2% in error. However, the ‘exact’ treatment of rotation in MM does produce very accurate results, as shown in table 4.

4.2. H_3O^+

The addition of a proton to water produces the well-known hydronium ion (also known as oxonium) which is isoelectronic to NH_3 . Like NH_3 , H_3O^+ has two equivalent pyramidal geometries. The barrier to inversion in H_3O^+ has been calculated by us [21] and by Halonen and co-workers [36], using similar high-level *ab initio* calculations, to be 690 cm^{-1} . This is roughly half the value of the barrier in NH_3 , and this leads to much larger splittings in H_3O^+ than in NH_3 . We recently reported a full-dimensional, *ab initio* potential energy surface and full dimensionality calculations of the rovibrational energies of H_3O^+ and isotopomers, D_3O^+ , H_2DO^+ and HD_2O^+ [21]. The vibrational calculations were done using MM (versions 4 and the new version 5) and the exact code RVIB4. RVIB4 is a code specifically developed to describe ammonia and ammonia-like molecules [28, 37]. (Both MM and RVIB4 were also recently applied to obtain rovibrational energies and splittings of NH_3 [28]). We review the highlights of the modifications in MM that were necessary to perform accurate calculations of vibrational energies H_3O^+ .

The normal coordinates in the Watson Hamiltonian are obtained by diagonalizing the force-constant matrix at a reference stationary point, which usually is the global minimum of a potential. For molecules like NH_3 and H_3O^+ , where there are two symmetric minima, separated by a substantial barrier, and where tunnelling splittings are significant, this approach will obviously encounter serious difficulties. Nevertheless, this approach can be and was implemented by Wright and Gerber [12(e)], who chose one minimum as the reference geometry. Not only were the

vibrational energies obtained (with an interesting new ‘partially separable VSCF method’) not split by the inversion barrier but the degeneracy of the OH stretch modes was not well described.

Our solution to this symmetric double-well problem has been to choose the inversion saddle point (ISP) (of D_{3h} symmetry) as the reference geometry [29]. This choice treats the two C_{3v} minima equivalently, leading to a proper description of the tunnelling dynamics and overall symmetry of the wavefunction. The normal mode analysis at the ISP produced, as expected, one imaginary frequency normal mode, which we denote by Q_1 . Motion along this mode alone does approach the two minima; however, the energy at the minima of this cut in the full-dimensional potential is significantly above the global minima. This is not unexpected, since the other normal modes of the ISP are different from zero at the global minima. In figure 1 we show a contour plot of the potential energy surface in two ISP modes, Q_1 , the imaginary frequency normal mode, and the symmetric OH stretch, which we denote by Q_2 in this figure. It is interesting that the ‘reaction’ path connecting the two minima and the saddle point is highly curved. Also, because of symmetry considerations, these two modes are sufficient to describe the global minima. However, as we determined in calculations, this does not imply that two-mode coupling is sufficient to describe the vibrations. Certainly, the choice of ISP normal coordinates will not be ‘optimum’ for the two minima, and thus a fairly high level of mode coupling beyond two-mode coupling was expected and found.

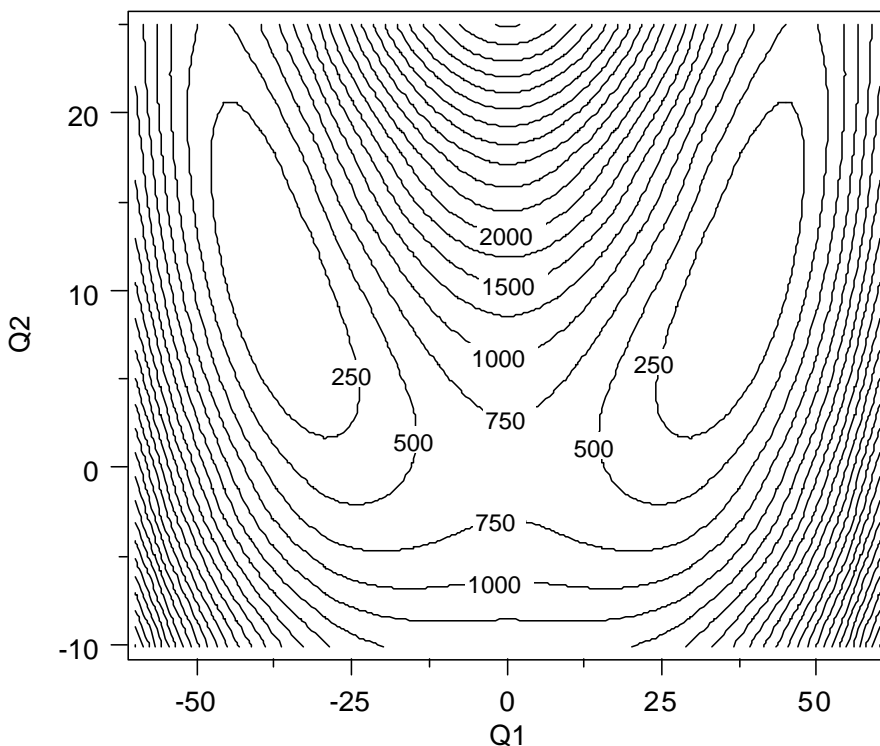


Figure 1. Equipotential contour plot (in cm^{-1}) of the full-dimensional *ab initio* potential of H_3O^+ in the two normal modes of the inversion saddle point described in detail in the text.

The details of the implementation of this approach have been given elsewhere [29, 30], so we omit them here. However, we do note that the numerical basis for the imaginary mode was obtained using a relatively large primitive harmonic oscillator basis and with a frequency that is user supplied. This numerical basis must be quite large so that it spans both minima and the saddle point region. We also included a simple optimization procedure to describe relaxation of the other normal coordinates as Q_1 varies. (It is important to note that another approach to this double-well problem is the very significant ‘reaction path’ extension of MM [38, 39], which we do not review here. In the last section of this review we describe this extension briefly.)

Results of these calculations are shown in table 5. There we compare vibrational energies and splittings obtained using MM version 4, which used four-mode coupling, MM version 5 (which does fits to the various n -mode potentials), which used 5-mode coupling, and the ‘exact’ results from the specialized code RVIB4. The quantum number labelling in this table is according to the normal modes of the ISP starting with the imaginary frequency ‘umbrella’ mode and increasing according to increasing harmonic frequency. The signs ‘+’ and ‘-’ in parentheses indicate the symmetry as symmetric and antisymmetric with respect to inversion through the barrier. To verify that MM version 5 calculations are reliable, four-mode results from that code are also given. First, as seen, there is excellent agreement between the four-mode calculations using versions 4 and 5 of MM. Second, note the general excellent agreement between the four-mode calculations and the ‘exact’ RVIB4 ones, with the exception of the states 000010(+) and 000010(-). The energies of these states should be rigorously degenerate with those of 000001(+) and 000001(-). The slight splitting of this degeneracy at the four-mode coupling level is essentially corrected using five-mode coupling, with a subsequent very good agreement with the RVIB4 results. Thus, it is very satisfying that MM can describe the vibrational splittings and energies of this challenging molecule accurately.

It remains only to compare these vibrational energies and splittings with experiment. This was done in detail previously [21]; here we summarize this

Table 5. Comparison of vibrational energies (cm^{-1}) of H_3O^+ obtained from MM version 4, version 5.0 and exact RVIB4 calculations. Excitation energies are relative to the ZPE.

State	4-mode MM_4	4-mode MM_5	5-mode MM_5	RVIB4
ZPE	7450.5	7450.9	7450.9	7450.6
000000(-)	46.7	46.7	46.6	46.4
100000(+)	580.5	580.5	580.5	580.4
100000(-)	934.0	934.0	934.0	933.6
010000(+)	1623.7	1623.7	1624.8	1623.7
010000(-)	1682.8	1682.8	1683.8	1681.2
001000(+)	1623.6	1623.5	1624.6	1623.7
001000(-)	1682.5	1682.4	1683.5	1681.2
000100(+)	3400.0	3399.9	3399.9	3399.7
000100(-)	3439.0	3439.0	3438.6	3437.5
000010(+)	3537.4	3537.5	3534.3	3533.3
000010(-)	3575.0	3575.1	3567.8	3565.3
000001(+)	3534.0	3533.9	3534.1	3533.3
000001(-)	3567.7	3567.8	3567.4	3565.3

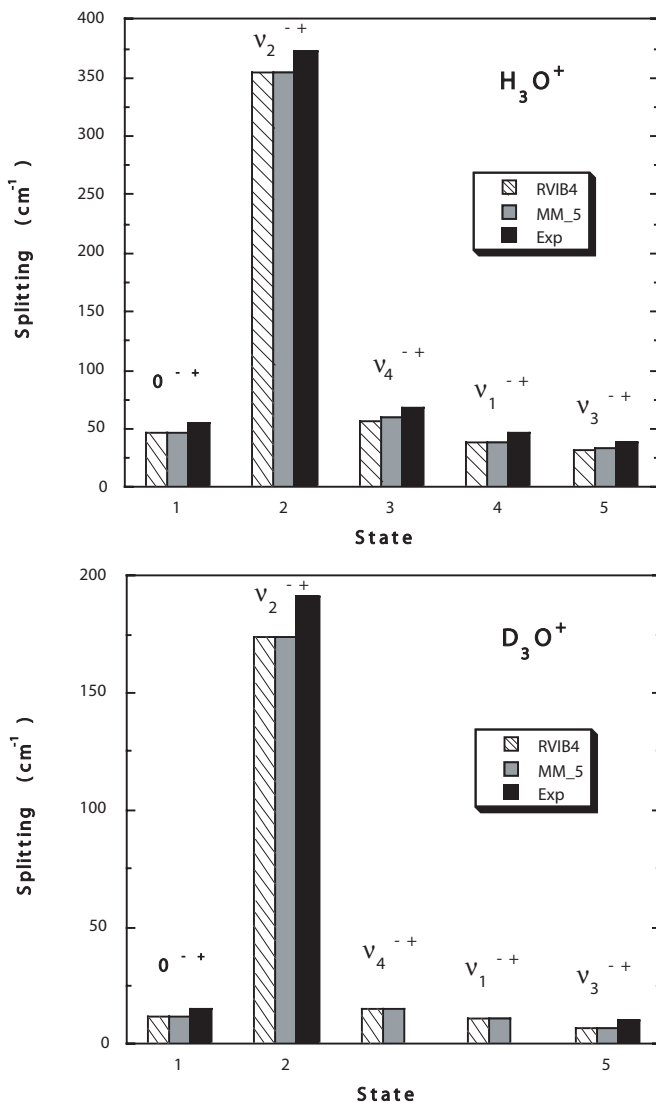
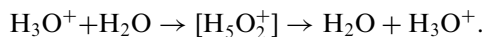


Figure 2. Calculated and experimental doublet splittings for the fundamental excitation in H_3O^+ and D_3O^+ .

comparison in figure 2. As seen there is very good agreement with experiment [40] and these completely *ab initio* calculations.

4.3. H_5O_2^+

The protonated water dimer, H_5O_2^+ , is almost certainly an important intermediate in the proton transfer reaction



Little is known experimentally about this ion. Several OH stretch fundamental energies have been reported in molecular beam experiments [41]. Very recently a low resolution, infrared multiphoton dissociation experiment was reported [42]. Assignments of the observed low-frequency intermolecular proton modes were made

on the basis of model calculations [43], which did not include any coupling of these modes to the inter- and intramolecular monomer modes. Calculations of vibrational energies of H_5O_2^+ have also been reported by Gerber and co-workers [44], but with two-mode coupling only. The experimental assignments mentioned above were not based on these calculations, which, although limited to two-mode coupling, do include the monomer modes.

An accurate, full-dimensional treatment of the vibrations of H_5O_2^+ is quite challenging, even beyond the problem of the high dimensionality (15 degrees of freedom), owing to a large degree of ‘floppiness’. Limited, although high quality *ab initio* calculations [45] indicate that the global minimum has a slightly bent $\text{O}-\text{H}^+-\text{O}$ geometry, with a small barrier, i.e. less than 100 cm^{-1} separating two mirror image minima.

Very recently we reported preliminary four-mode coupling calculations of the vibrational energies of H_5O_2^+ using MM (version 4) [25]. This report focused on the ZPE, which was also calculated by an elaborate and full-dimensionality diffusion Monte Carlo calculation. These calculations used the full-dimensional potential of Ojamäe *et al.* [46], denoted by OSS3(p), which was based on a fit to several thousand *ab initio* calculations at the MP2 level of theory. This potential is not of spectroscopic accuracy; however, it is quite realistic and currently the only full-dimensional potential which does describe the low barrier between the two slightly non-collinear minima mentioned above.

As in the case of H_3O^+ the reference geometry chosen for the MM calculations is a saddle point. Specifically, the reference geometry is for a collinear $\text{O}-\text{H}^+-\text{O}$ geometry with the proton midway between the two O atoms. On the OSS3(p) potential this is a second-order saddle point with two imaginary frequency modes. The potential in these two modes with the remaining 13 held fixed at zero is shown in figure 3. As seen, the potential is quite flat but with steep repulsive walls. Clearly the proton motion will be highly delocalized in these two degrees of freedom and, unlike H_3O^+ , which has a much larger barrier separating the two minima (roughly 700 cm^{-1}), doublet splittings are not expected in the spectrum as a result of this low barrier and were not found in the MM calculations. Further evidence for delocalization is that the lowest energy fundamental is at 310 cm^{-1} , which is well above the barrier separating the two equivalent minima. Definitive evidence of delocalization comes from the diffusion Monte Carlo calculation, which shows delocalization over the two minima of the zero-point wavefunction.

We conclude this section on H_5O_2^+ with an investigation of a four degree-of-freedom model of the proton and OO stretch modes. As mentioned above, such a reduced-dimensionality model was used to assign an experimental spectrum. This model calculation introduced an additional approximation, however, with an adiabatic separation of the four modes into two groups of two, the two bends, the OO stretch and the proton asymmetric stretch. In this model there are three Cartesian coordinates for the proton (with the origin at the centre of the OO bond) and a fourth degree of freedom, the OO stretch. These modes are present in the full-dimensional description of H_5O_2^+ (at least at the level of normal modes) and so it is possible to isolate these modes in an approximate MM calculation. This was done by using a large basis for mixing in these four modes, but restricting the basis in the remaining 11 modes to a single basis function (the ground vibrational state in each mode). This is not a perfect decoupling since there is some average interaction with the ground vibrational state of these other spectator modes. However, by comparing

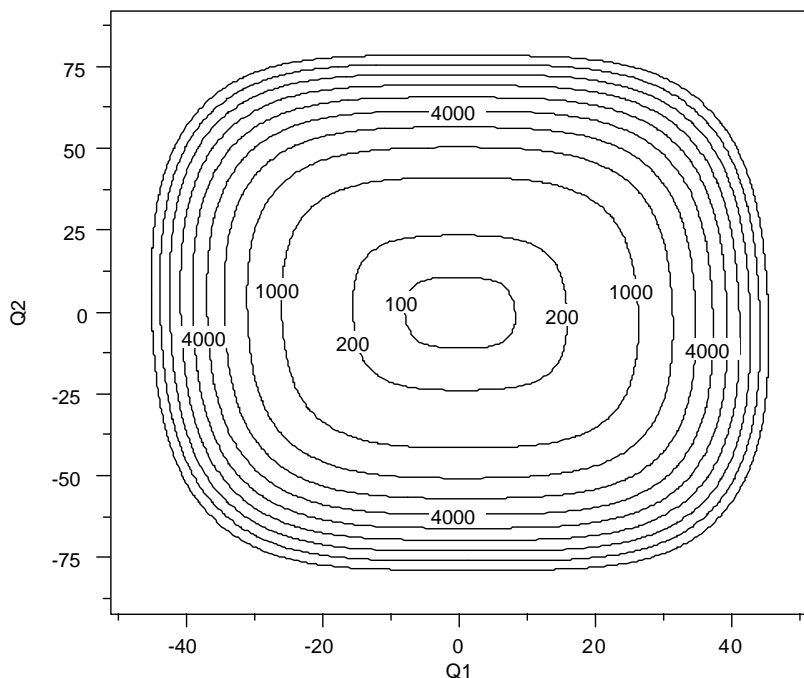


Figure 3. Equipotential contour plot (in cm^{-1}) of the full-dimensional *ab initio* potential of H_5O_2^+ in the two normal modes of the second-order saddle point described in detail in the text.

Table 6. Comparison of energies (in cm^{-1}) of fundamentals of H_5O_2^+ calculated using the reduced dimensionality (spectator) and coupled methods as explained in the text. Modes of interest are labelled.

Mode	4-mode spectator	4-mode coupled
1	—	516
2	—	310
3	—	583
4	—	590
5	—	569
OO stretch	646	564
O–H ⁺ –O asymmetric	1071	914
X bend	1354	1369
Y bend	1372	1380
10	—	1646
11	—	1809
12	—	3319
13	—	3427
14	—	3468
15	—	3472

the fundamental energies of the three proton modes plus the OO stretch with our previous calculations which use a large basis in all modes, we can determine the effect of dynamic mode coupling. This is done in table 6. As seen, there are significant differences between these two calculations for the OO stretch and proton asymmetric

stretch, but fairly good agreement for the two proton bend modes is found. This is understandable since the two bend modes are approximately orthogonal to the OO axis and thus motion in these modes is approximately orthogonal to the H₂O monomers. However, both the OO stretch and the asymmetric proton stretch are parallel to the OO axis and so these modes interact with the monomers, which allows for some relaxation of the energies.

5. Summary and prognosis

In summary, we have reviewed methods used and applications of two versions of the code MULTIMODE (MM), which does rovibrational energies of general polyatomic molecules. The code is based on the general Watson Hamiltonian and makes use of a hierarchical n -mode representation of the exact potential. The first version of the code makes direct use of the exact potential on grids determined by optimized quadrature points and is limited to a maximum of four-mode coupling. The newer version fits the potential on grids, which may be much sparser than the ones corresponding to quadrature points. These fits result in highly efficient evaluation of matrix elements and thus five-mode coupling is done in version 5 of MM. Both versions use two 'CI' schemes to obtain rovibrational energies. Both schemes begin with a VSCF procedure. The CI schemes use a non-orthogonal VSCF basis or an orthogonal virtual basis of the zero-point VSCF state. Both versions can utilize normal coordinates determined at a saddle point separating two minima on the global potential. This feature permits the calculation of tunnelling splittings in the case of a large barrier separating these minima.

Futures directions for development of MM will certainly include increasing the level of mode coupling. Also, further work on and applications with the reaction path version of MM [30, 38] is warranted. This code can describe internal rotation, for example in methanol and other large floppy molecules. A similar code, in spirit if not in practice, has been developed by Luckhaus and Quack and applied to cis–trans isomerization in H₂O₂ [47]. The determination of the potential will continue to present major challenges to all methods. The advantage of using an n -mode representation of the potential is that the full-dimensional potential is not required. This fact has been exploited to very good effect by Gerber and co-workers and by us, and this will continue to receive attention, especially in using 'direct' *ab initio* codes to obtain the potential on the n -mode grids.

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