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Extensions and tests of “multimode”: a code to obtain accurate vibration/rotation energies of many-mode molecules*

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Abstract. We describe extensions and tests of the code “multimode” which does vibrational self-consistent field method (VSCF) and two types of state-mixing (denoted VSCF-CI and V-CI) for rovibrational energies of many-mode systems. The extensions include an exact treatment of rotation, flexible approaches to perform the CI calculations, and the inclusion of a Davidson diagonalization routine to find low-lying eigenvalues of large matrices. The code is tested against previous exact variational calculations for non-rotating H_2CN, and $J = 0$ and $J = 1$ rovibrational states of H_2CS. The code represents the full potential by a hierarchical n-mode representation, where n is the number of normal coordinates that are coupled together. Tests are presented for the convergence and accuracy of this representation for n equal to 3 and 4, where 4 is the current maximum value. These tests are done at the VSCF and V-CI level, with very encouraging results.

Key words: Vibration-rotation energies – H_2CN – N_2CS – Vibrational self-consistent field

1 Introduction

The accurate calculation of rovibrational energies of many-mode molecular systems is a goal of computational chemistry that is as challenging as it is important. While this goal has essentially been realized for triatomic molecules up to and even above dissociation, and for low-lying states of tetraatomics, there are well-known bottlenecks that prevent facile scale-up of methods that are accurate and efficient for these size molecules. These include the $N^2 - N^3$ dependence on finding eigenvalues and eigenvectors of the Hamiltonian matrix of order N (the size of which grows exponentially with the number of degrees of freedom), the exponential increase in the number of grid points with the number of degrees of freedom, etc. This has meant that for systems with more than four atoms, and certainly for systems with say 10 or more atoms, the frequent method of choice, normal-mode analysis, is also the method of necessity.

Clearly, there is a large gap in accuracy and realism between a normal-mode analysis and an “exact” calculation. For example, one obvious limitation of a normal-mode analysis is the lack of coupling among modes. This precludes a description of line shapes, frequency shifts, energy transfer, relaxation, etc. A very viable approach to fill this gap is the vibrational self-consistent field (VSCF) method (see [1] for reviews). This method has been scaled up by two groups to address the vibrations of many-mode systems [2–4]. In our first code [3] and the code of Gerber and co-workers [2] the Watson Hamiltonian [6] is used; however, coriolis coupling constants are neglected. In a newer code, which we have named “multimode ”, the exact Watson Hamiltonian for zero total angular momentum, i.e., including coriolis coupling constants, is used in both VSCF and two types of configuration interaction (CI) calculations [4]. An approximate treatment of overall rotation, termed the adiabatic rotation approximation (ARA), was also used in that code to obtain vibration/rotation energies. This code was tested against previous exact calculations for non-rotating HCO [4b], and non-rotating and rotating HO_2 and H_2O [4c]. In the non-rotating cases, $J = 0$, the CI energies obtained with “multimode” were in excellent agreement with the other earlier ones. For the rotating cases, $J > 0$, the CI energies using the ARA were in excellent agreement with exact calculations for HO_2, which is a near prolate symmetric top, but only in good to very good agreement with exact calculations for H_2O, which is a strongly asymmetric top.

The application of the Watson Hamiltonian to a molecule/molecular system of any size is conceptually straightforward; however, the implementation for many-mode systems is severely hampered by the apparent large dimensionality of the potential, which is in principle of

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* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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dimension N, where N is the number of vibrational degrees of freedom. Thus, any exact approach, which in principle scales very non-linearly with this dimension, would be unfeasible for large molecules. Historically, this large dimensionality problem was circumvented by expanding the potential in a Taylor series in normal coordinates about an equilibrium geometry. In practice this has only been done for relatively small molecules, and even then there are a number of possible pitfalls with the approach. The first is the uncertainty in the radius of convergence of such an expansion. (The expansion in rectilinear normal coordinates typically requires more and higher order terms than the expansion in bond lengths and bond angles.) A second pitfall is the unphysical behavior of the expansion in the limit of large values of the normal coordinates, i.e., the potential is virtually guaranteed to diverge to infinity.

With these limitations of the Taylor series expansion in mind, we suggested the following hierarchical representation of the N-mode potential [4]:

$$\begin{aligned} V(Q_1, Q_2, \ldots, Q_N) = & \sum_i V_i^{(1)}(Q_i) + \sum_{ij} V_{ij}^{(2)}(Q_i, Q_j) \\ & + \sum_{ijk} V_{ijk}^{(3)}(Q_i, Q_j, Q_k) \\ & + \sum_{ijkl} V_{ijkl}^{(4)}(Q_i, Q_j, Q_k, Q_l) \end{aligned} \tag{1}$$

where the one-mode representation of the potential contains only $V_i^{(1)}(Q_i)$ terms, the two-mode representation contains those terms plus the $V_{ij}^{(2)}(Q_i, Q_j)$ terms, etc. Thus, explicit coupling of up to a maximum of four modes can be done. Note that Jung and Gerber [2c] have used a similar representation in their recent work on water dimers; however, they considered a maximum of two-mode coupling.

As mentioned above, the tests we reported previously were for triatomic molecules, which have three vibrational modes, and so the above representation of the potential is exact at just the three-mode level. In this paper we report tests of the three- and four-mode representations of the potential for two tetraatomic molecules, H_2CN and H_2CS, which have six vibrational degrees of freedom. In addition, we have made several extensions to "multimode", the most significant one of which is a full treatment of overall rotation, which is exact for triatomics. Thus, we report the results of CI and VSCF calculations using three- and four-mode representations of the potential for both non-rotating and rotating cases for the above tetraatomics against accurate variational calculations. Another extension we have made to "multimode" is the incorporation of an iterative diagonalization algorithm which is very similar to the Davidson method [5]. Finally, we discuss some new features to CI calculations, both for $J = 0$ and $J > 0$. All of these new features of the code are demonstrated in this paper.

In the next section we review the theoretical basis of the code and describe the extensions of the code. Tests of the code are presented in Sect. 3, along with new results for highly rotating H_2CS.

2 Theory and extensions to "multimode"

The complete Watson Hamiltonian in normal coordinates (and in atomic units) is given by [6]:

$$\begin{aligned} \hat{H} = & \frac{1}{2}\sum_{\alpha\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) \\ & - \frac{1}{2}\sum_k \frac{\partial^2}{\partial Q_k^2} - \frac{1}{8}\sum_\alpha \mu_{\alpha\alpha} + V(\boldsymbol{Q}) \end{aligned} \tag{2}$$

where $\hat{J}_\alpha$ and $\hat{\pi}_\alpha$ are the components of the total and vibrational angular momentum operators, respectively, μ is the effective reciprocal inertia tensor, and $V(\boldsymbol{Q})$ is the potential, which depends on the normal coordinates, denoted collectively by $\boldsymbol{Q}$.

The procedure to find the eigenvalues and eigenfunctions of $\hat{H}$ using a direct-product of harmonic-oscillator functions has been given in detail by Whitehead and Handy [7]. We follow many of the details given by them in setting up our CI for $J > 0$; however, we begin from a VSCF Hamiltonian, as described previously [4, 8]. In addition, and as already noted, we represent the many-mode potential in the hierarchical expansion given above. This reduces the computational effort in doing numerical quadratures enormously, and makes it possible to extend the Watson Hamiltonian to many-mode systems at the VSCF and CI levels of theory. To go beyond the VSCF level of accuracy we have implemented two types of "CI", as described in detail previously [4].

Our method of calculation in "multimode" for $J = 0$ is exact, providing the following conditions are met: first, integration over the potential and inverse moment of inertia μ is converged for coupling of no more than four normal coordinates; and second, that sufficient VSCF functions are included in either of the CI procedures so as to converge the resulting vibrational energies. The first condition is, of course, exactly met for triatomic molecules, where the total number of modes is three. We have confirmed in earlier work that exact vibrational energies are obtained in this case for HCO [4b], and HO_2 and H_2O [4c]. This was demonstrated using both CI options, one in which a non-orthogonal basis of VSCF functions is mixed, and the other where an orthogonal basis of eigenfunctions of a given VSCF Hamiltonian is mixed.

One goal of the present paper is to test the code for $J = 0$ for tetraatomic molecules. In this case, where there are six normal modes, the convergence and accuracy of the three- and four-mode representations of the potential and μ is the primary focus of inquiry. We have chosen two tetraatomic molecules for this and subsequent test purposes. These are H_2CN, for which we have recently published a new potential together with $J = 0$ results from our VSCF method and also from exact variational calculations [4a], and H_2CS, for which we have recently refined the potential energy surface to experimental spectroscopic data for $J = 0$ and $J = 1$ using an exact variational procedure [9]. Of course, an unambiguous test also requires convergence of the CI energies, and in going from a triatomic to a tetraatomic the size of the CI matrix can grow dramatically. One way to reduce the size of the matrix is to use symmetry (where applicable), and we have incorporated this into our CI procedures, although currently for C_{2v} symmetry only. The procedure is quite general even for molecules whose fundamental vibrations span differing numbers of C_{2v} irreducible representations (H_2O: A_1, B_2; H_2CO: A_1, B_2, B_1; $Fe(CO)_4XY$: A_1, B_2, B_1, A_2). Note that reduction of symmetry must take place for point groups with symmetries higher than C_{2v} (in the latter case C_{4v}), but this is quite straightforward from inspection of the normal-mode vectors.

Even when symmetry can be exploited, additional methods of reducing the matrix size are desired. Several effective methods exist for this purpose. One, which we use in a variational procedure for tetraatomic molecules, is to use successive contraction schemes in the pure stretch and bend/out-of-plane vibrations [10]. (Note that this procedure also requires an expansion of the potential in bond lengths and angles so that the multidimensional integrals can be done efficiently.)

In the current version of "multimode" a simple direct-product representation of the wavefunction is used. Since we allow a maximum of four modes to couple in the potential and inverse moment of inertia μ, we assume that a good approximation to the CI matrix will also allow a maximum of four modes to be simultaneously excited, since in our model, non-zero matrix elements can only exist between functions which differ in up to a maximum of four modes only. Our current CI algorithm is as follows: we allow all single-mode excitations to a maximum of N_1 quanta, two-mode excitations to a maximum of N_2 quanta each, three-mode excitations to a maximum of N_3 quanta each, and all four-mode excitations to a maximum of N_4 quanta each, respectively. Coupled with this, we constrain the sum of all quanta to be $M_1 (= N_1)$ for all one-mode bases (trivial), M_2 for all two-mode bases, M_3 for all three-mode bases, and M_4 for all four-mode bases. For each of the normal modes k in the system, we also define individual maximum quanta $n_j(k)$ for the $j = 1$–4 mode coupling schemes $[n_j(k) \leq N_j]$ as extra flexibility in forming the CI basis. For very large molecules, this scheme will be useful in forming a CI matrix which concentrates on a subset of vibrations; however, in tetraatomics, we do not use the full flexibility, but rather we form basis sets such as $N_1 = 7$, $N_2 = 6$, $N_3 = 5$ $N_4 = 4$; $M_1 = M_2 = M_3 = M_4 = 7$; $[n_1(k) = 7,\ n_2(k) = 6,\ n_3(k) = 5,\ n_4(k) = 4,\ k = 1,$ NMODE]. In this work, we use this particular basis, and those obtained by increasing each of N_j, $M_j, n_j(k)$ by one and two. We will refer to these bases as VCI(7), VCI(8), and VCI(9), respectively, and we will give the details of the size of the CI matrix in the next section.

Of course, any CI scheme can benefit from an efficient matrix diagonalization routine, and we describe an iterative routine, based on the Davidson method [5], at the end of this section.

2.1 Full treatment of rotation

We have coded the complete (exact) Whitehead-Handy implementation of Watson's rovibrational kinetic energy operator for non-linear molecules [7]. The algorithm follows very closely that adopted in our variational procedure, which was established in valence coordinates [10]. Briefly, we carry out $(2J + 1)$ "vibrational" calculations for each pair of quantum numbers K_a, K_c in turn, to form the $(2J + 1)$ diagonal blocks of the rovibrational matrix, and then fill in the remaining non-zero blocks as appropriate. To achieve this, we use the same primitive VCI vibrational basis for each K_a–K_c block, multiplied by the appropriate Wang combination of the usual symmetric-top rotational functions.

Our rotational functions are ordered according to the series

$$D^J_{00},\ iD^J_{01}(+),\ D^J_{01}(-),\ iD^J_{02}(-),\ D^J_{02}(+),\ldots \tag{3}$$

and these correspond, in turn to $K_a = 0$, $K_c = J$; $K_a = 1$, $K_c = J - 1$; $K_a = 1$, $K_c = JK_a = 2$, $k_c = J - 2$; $K_a = 2$, $K_c = J - 1, \ldots$, which is the most convenient way to order them since they then correspond to the series $\cos(0\gamma)$, $\sin(1\gamma)$, $\cos(1\gamma)$, $\sin(2\gamma)$, $\cos(2\gamma), \ldots$, where γ is the euler angle about the principal molecular-fixed z-axis. This series follows from the definition of the symmetric-top rotational functions. These are defined by

$$D^J_{0K_a} = d^J_{0K_a}(\beta)\exp(\mathrm{i}K_a\gamma) \tag{4}$$

where

$$d^J_{0-K_a}(\beta) = (-1)^{K_a} d^J_{0K_a}(\beta) \tag{5}$$

Inclusion of "i" in Eq. (3) completes the derivation. Rotational matrix elements exist for $\Delta K = 0$, $\Delta K = \pm 1$, and $\Delta K = \pm 2$, where we have dropped the subscript "a" from K_a, and refer to it hereafter as K. There is typographical error in Eq. (30) of the original Whitehead-Handy paper [7], and also a sign error in Eq. (13) of our ARA paper [4c]. We therefore give the complete set of non-zero rotational matrix elements again here. They are:

$$\langle JK|\hat{J}_z|JK\rangle = K\langle JK|JK\rangle = K \tag{6}$$

$$\langle JK|\hat{J}_z^2|JK\rangle = K^2 \tag{7}$$

$$\begin{aligned}\langle JK|\hat{J}_x^2|JK\rangle &= \langle JK|\hat{J}_y^2|JK\rangle \\ &= (1/2)[J(J+1) - K^2]\end{aligned} \tag{8}$$

$$\begin{aligned}\langle JK \pm 1|\hat{J}_x|JK\rangle &= \mp i\langle JK \pm 1|\hat{J}_y|JK\rangle \\ &= \mp(i/2)[(J \mp K)(J \pm K + 1)]^{\frac{1}{2}}\end{aligned} \tag{9}$$

$$\begin{aligned}\langle JK \pm 2|\hat{J}_x^2|JK\rangle &= -\langle JK \pm 2|\hat{J}_y^2|JK\rangle \\ &= -(1/4)[(J \pm K + 1)(J \pm K + 2) \\ &\quad \times (J \mp K)(J \mp K - 1)]^{\frac{1}{2}}\end{aligned} \tag{10}$$

$$\langle JK|\hat{J}_x\hat{J}_y|JK\rangle = -\langle JK|\hat{J}_y\hat{J}_x|JK\rangle = -(iK/2) \tag{11}$$

$$\begin{aligned}\langle JK \pm 2|\hat{J}_z\hat{J}_x|JK\rangle &= \mp i\langle JK \pm 1|\hat{J}_z\hat{J}_y|JK\rangle \\ &= (K \pm 1)\langle JK \pm 1|\hat{J}_x|JK\rangle\end{aligned} \tag{12}$$

$$\begin{aligned}\langle JK \pm 2|\hat{J}_x\hat{J}_z|JK\rangle &= \mp i\langle JK \pm 1|\hat{J}_y\hat{J}_z|JK\rangle \\ &= K\langle JK \pm 1|\hat{J}_x|JK\rangle \end{aligned} \tag{13}$$

$$\begin{aligned}\langle JK \pm 2|\hat{J}_x\hat{J}_y|JK\rangle &= \langle JK \pm 2|\hat{J}_y\hat{J}_x|JK\rangle \\ &= \mp(i/4)[(J \mp K - 1)(J \pm K + 2) \\ &\quad \times (J \mp K)(J \pm K + 1)]^{\frac{1}{2}} \end{aligned} \tag{14}$$

If we expand the complete Watson kinetic energy operator given in Eq. (2), we can see that there are four distinct types of terms. Terms in $\hat{J}_x^2, \hat{J}_y^2, \hat{J}_z^2$ appear in the K-diagonal blocks of the full matrix. Terms in $\hat{J}_z$ mix the two blocks with equal K. Terms in $\hat{J}_x, \hat{J}_y$, $[\hat{J}_x\hat{J}_z]_+$, $[\hat{J}_y\hat{J}_z]_+$ mix blocks where K differs by one, and terms in $\hat{J}_x^2, \hat{J}_y^2$, $[\hat{J}_x\hat{J}_y]_+$ mix blocks where K differs by two. Each of these terms also involves an element of the inverse moment of inertia tensor μ, and the operators $\hat{J}_x, \hat{J}_y, \hat{J}_z$ also involve the vibrational angular momentum operators $\hat{\pi}_\alpha$. Careful inspection of the definition of the operator $\hat{\pi}_\alpha$ in Eq. (2), together with the choice of rotational basis in Eq. (3) shows that all elements in the complete rovibrational matrix are real.

Since C_{2v} symmetry exists for the molecules under discussion, we make use of this in constructing the four discrete symmetry blocks for $J > 0$. In summary, the complete rovibrational matrices comprise the following vibration-rotation basis functions:

$$\begin{aligned} A_1: \quad & A_1 \cdot D^J_{00};\; B_1 \cdot iD^J_{01}(+);\; B_2 \cdot D^J_{01}(-); \\ & A_2 \cdot iD^J_{02}(-);\; A_1 \cdot D^J_{02}(+);\; \ldots \end{aligned} \tag{15}$$

$$\begin{aligned} B_2: \quad & B_2 \cdot D^J_{00};\; A_2 \cdot iD^J_{01}(+);\; A_1 \cdot D^J_{01}(-); \\ & B_1 \cdot iD^J_{02}(-);\; B_2 \cdot D^J_{02}(+);\; \ldots \end{aligned} \tag{16}$$

$$\begin{aligned} B_1: \quad & B_1 \cdot D^J_{00};\; A_1 \cdot iD^J_{01}(+);\; A_2 \cdot D^J_{01}(-); \\ & B_2 \cdot iD^J_{02}(-);\; B_1 \cdot D^J_{02}(+);\; \ldots \end{aligned} \tag{17}$$

$$\begin{aligned} A_2: \quad & A_2 \cdot D^J_{00};\; B_2 \cdot iD^J_{01}(+);\; B_1 \cdot D^J_{01}(-); \\ & A_1 \cdot iD^J_{02}(-);\; A_2 \cdot D^J_{02}(+);\; \ldots \end{aligned} \tag{18}$$

where the overall symmetry is for even J. For odd J, A must be interchanged with $B(A_1 \to B_1$, etc.). For reduction of symmetry to C_s, A_1 and B_2 merge to form A', and A_2 and B_1 merge to form A''. In C_1, all functions are A.

As we have already noted, all terms in the Watson Hamiltonian involving the J-operators contain some contribution from the inverse moment of inertia μ; some of them also contain contributions from the operators $\hat{\pi}_\alpha$. Because our vibrational basis is the same for all K-blocks, we can evaluate the matrix elements as functions of the vibrational coordinates once only, and repeatedly multiply each matrix element by an appropriate pure rotational matrix element to form the complete Hamiltonian matrix. There are nine such sets required, for $\hat{J}_x^2$, $\hat{J}_y^2$, $\hat{J}_z^2$, $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$, $[\hat{J}_x\hat{J}_z]_+$, $[\hat{J}_y\hat{J}_z]_+$, $[\hat{J}_x\hat{J}_y]_+$, and these are stored on disk for repeated use over the K-blocks.

2.2 Iterative diagonalization of large Hamiltonian matrices

Even with the ways of reducing the size of the Hamiltonian matrix outlined above in operation, it is unavoidable that extremely large VCI matrices will be encountered as the size of the molecule is increased. In many such cases, for example, in high-J analyses, only a fraction of the total number of eigenvalues will ever be required. For matrices of the order of around 5000 we use an efficient Givens diagonalization routine. For much larger matrices, the memory requirements of such a procedure become prohibitive, and we have therefore incorporated a Davidson-Lanczos-like diagonalization procedure.

Starting from a primitive VCI product basis ϕ_k of size M, we evaluate the diagonal Hamiltonian matrix elements H_{kk}. If we wish to calculate the lowest N eigenvalues E_i, we scan the matrix elements H_{kk} until we locate the N lowest values, and note the corresponding positions $k(i), i = 1,\ 2, \ldots, N$. We then define a set of starting functions

$$Y_0(i) = \sum_{k=1}^{M} C_0^k(i)\phi_k, \quad I = 1,\ 2, \ldots, N \tag{19}$$

where, for each of the N functions, all $C_0^k(i)$ are zero except for position $k(I)$ which is given the value 1. These starting functions $Y_0(i)$ are therefore single-term products of orthonormal VCI functions and are represented by the starting basis vectors $\underline{X}_0(i) = \underline{C}_0(i)$. Corresponding to each of these starting functions are the starting eigenvalues $E_0(i) = H_{k(i),k(i)}$.

We now wish to form the improved functions:

$$Y_1(i) = Y_0(i) + y_0(i), \quad i = 1,\ 2, \ldots, N \tag{20}$$

where

$$y_0(i) = \sum_{k=1}^{M} w_0^k(i)\phi_k, \quad i = 1,\ 2, \ldots, N \tag{21}$$

Assuming that the expansion coefficients $w_0^k(i)$ are small, i.e., treating $y_0(i)$ as a first-order correction to the wavefunction, leads to the following equation for the determination of $w_0^k(i)$:

$$\langle \phi_k|\hat{H} - E_0(i)|Y_0(i) + y_0(i)\rangle = 0, \quad i = 1,\ 2, \ldots, N \tag{22}$$

Note that in deriving Eq. (22), changes in the eigenvalues, which are second-order in $w_0^k(i)$, have been ignored. Direct substitution of Eq. (21) into (22) and assuming the Hamiltonian matrix is diagonally dominant leads to

$$\begin{aligned} w_0^k(i) &= -\left(\tau_0^k(i) - E_0(i)C_0^k(i)\right)/(H_{kk} - E_0(i)), \\ & \quad i = 1,\ 2, \ldots, N \end{aligned} \tag{23}$$

where $\tau_0(i)$ is a vector given by the product $\underline{H}\,\underline{X}_0(i)$ where $\underline{H}$ is the Hamiltonian matrix.

Substitution of $w_0^k(i)$, obtained from Eq. (23), into (21) gives the correction function $y_0(i)$. This function is orthogonalized to the $Y_0(i)$, i.e., the vectors $\underline{W}_0(i)$ are Schmidt-orthogonalized to the set of vectors $\underline{X}_0(i)$ to form an additional set of basis vectors, denoted $\underline{X}_1(i)$.

We now form the Hamiltonian matrix in the $\underline{X}_0(i)$ and $\underline{X}_1(i)$ basis functions (of order $2N$) and diagonalize it. This gives us two sets of coefficients for $\underline{X}_0(i)$ and $\underline{X}_1(i)$ which we designate by $\underline{D}_0(i)$ and $\underline{D}_1(i)$, respectively. The new (orthonormal) set of functions can therefore be constructed from

$$\underline{C}(i) = \underline{D}_0(i)\underline{X}_0(i) + \underline{D}_1(i)\underline{X}_1(i), \quad i = 1,\ 2, \ldots, N \tag{24}$$

and these in turn yield the improved functions

$$Y_1(i) = \sum_k^M C_1^k(i)\phi_k, \quad i = 1,\ 2, \ldots, N \tag{25}$$

in terms of the original primitive basis. The corresponding eigenvalues are denoted $E_1(i)$.

This process is repeated, i.e., first-order corrections to $Y_1(i)$ are obtained using Eq. (23) with the subscript "0" replaced by "1" and then the entire basis is orthogonalized, the new $3N \times 3N$ Hamiltonian matrix constructed and diagonalized, and so on to convergence. When a particular eigenvector is converged, it is "tagged" and further improvements of this eigenvector are excluded. Therefore, the size of matrices to be diagonalized, whilst initially increasing in steps of N, ultimately increase in much smaller steps.

In our current implementation in "multimode", the complete Hamiltonian matrix $\underline{H}$ is written to disk in full rows and read in as required. Other efficiencies taking account of available memory are also implemented. We typically expect this procedure to work efficiently when the lowest 5% of the eigenvectors are required.

We are fully aware that this approach is similar if not identical to other procedures for determining the lowest eigensolutions of large matrices. We have spelt out our implemented algorithm here because in this paper we are giving full details of the new version of "multimode".

Table 1. Rovibrational energies of the fundamentals of H_2CS (cm^{-1}) for $J = 0$ and 1, using the internal coordinate potential of [9]. The full Watson Hamiltonian is used in these calculations except for those headed "ARA". The exact calculations are from [9]. See text for an explanation of the VCI basis sets

Assignment	Exact	VCI(4, 7)	VCI(3, 7)	VCI(3, 8)	VCI(3, 9)	VSCF(4)
$J = 0$						
Zero point	5347.15	5347.11	5346.96	5346.93	5346.92	5375.40
Symmetry A_1						
0 1 0 0 0 0	1058.86	1059.54	1059.12	1059.08	1059.07	1060.07
0 0 1 0 0 0	1457.42	1457.72	1456.97	1456.78	1456.69	1490.93
1 0 0 0 0 0	2970.72	2971.90	2962.38	2961.69	2961.42	2970.07
Symmetry B_2						
0 0 0 0 0 1	990.94	991.77	990.99	990.88	990.83	1005.74
0 0 0 0 1 0	3024.58	3025.40	3033.61	3033.23	3033.07	3016.91
Symmetry B_1						
0 0 0 1 0 0	990.51	990.96	990.61	990.33	990.19	1004.73

	Exact	VCI(4, 7) Full	VCI(3, 7) Full	VCI(3, 8) Full	VCI(3, 9) Full	VCI(3, 9) ARA	VSCF(4) ARA
$J = 1$							
Symmetry B_1							
0 0 0 0 0 0	1.14	1.14	1.14	1.14	1.14	1.14	1.14
0 0 0 1 0 0	0.63	0.78	0.55	0.64	0.68	10.28	10.26
0 0 0 0 0 1	19.85	19.60	19.81	19.73	19.68	10.36	10.36
0 1 0 0 0 0	1.13	1.14	1.14	1.14	1.14	1.14	1.13
0 0 1 0 0 0	1.14	1.14	1.14	1.14	1.14	1.15	1.14
1 0 0 0 0 0	1.14	1.14	1.14	1.14	1.14	1.14	1.14
0 0 0 0 1 0	10.17	10.17	10.30	10.24	10.19	10.19	10.11
Symmetry A_2							
0 0 0 0 0 0	10.27	10.26	10.28	10.28	10.28	10.30	10.29
0 0 0 0 0 1	1.14	1.14	1.14	1.14	1.14	1.15	1.14
0 1 0 0 0 0	10.26	10.26	10.27	10.27	10.27	10.30	10.28
0 0 1 0 0 0	10.36	10.31	10.29	10.29	10.29	10.36	10.35
1 0 0 0 0 0	10.16	10.21	10.24	10.23	10.23	10.29	10.18
0 0 0 0 1 0	1.14	1.14	1.14	1.14	1.14	1.14	1.14
Symmetry A_1							
0 0 0 0 0 0	10.30	10.30	10.31	10.31	10.31	10.33	10.32
0 0 0 1 0 0	1.14	1.14	1.14	1.14	1.14	1.15	1.14
0 1 0 0 0 0	10.29	10.29	10.30	10.30	10.30	10.33	10.31
0 0 1 0 0 0	10.39	10.35	10.33	10.33	10.33	10.39	10.38
1 0 0 0 0 0	10.20	10.25	10.28	10.27	10.26	10.32	10.22
Symmetry B_2							
0 0 0 1 0 0	0.63	0.78	0.55	0.64	0.68	10.24	10.23
0 0 0 0 0 1	19.86	19.61	19.82	19.73	19.69	10.39	10.39
0 0 0 0 1 0	10.20	10.21	10.34	10.27	10.22	10.23	10.15

Table 2. Rovibrational energies of the fundamentals of H_2CN (cm^{-1}) for $J = 0$ and 1 using the internal coordinate potential of [4a]. Exact calculations are also from [4a] and see Table 1 and the text for the meaning of the other acronyms

Assignment	Exact	VCI(4, 7)	VCI(3, 7)	VCI(3, 8)	VCI(3, 9)	VSCF(4)	
$J = 0$							
Zero point	5496.85	5496.83	5496.73	5496.71	5496.71	5519.91	
Symmetry A_1							
0 0 1 0 0 0	1363.13	1363.22	1362.47	1362.41	1362.39	1373.18	
0 1 0 0 0 0	1657.43	1657.82	1657.15	1657.09	1657.08	1662.56	
1 0 0 0 0 0	2877.08	2877.03	2875.77	2875.51	2875.42	2913.26	
Symmetry B_2							
0 0 0 0 0 1	934.95	934.97	934.91	934.82	934.79	946.16	
0 0 0 0 1 0	2934.09	2934.11	2941.68	2941.44	2941.34	2939.50	
Symmetry B_1							
0 0 0 1 0 0	972.67	973.41	972.65	972.55	972.52	978.53	
	Exact	VCI(4, 7) Full	VCI(3, 7) Full	VCI(3, 8) Full	VCI(3, 9) Full	VCI(3, 9) ARA	VSCF(4) ARA
$J = 1$							
Symmetry B_1							
0 0 0 0 0 0	2.43	2.43	2.43	2.43	2.43	2.43	2.42
0 0 0 0 0 1	8.09	8.04	7.96	7.97	7.96	10.71	10.65
0 0 0 1 0 0	13.38	13.23	13.26	13.26	13.26	10.77	10.66
0 0 1 0 0 0	2.44	2.44	2.44	2.44	2.44	2.43	2.43
0 1 0 0 0 0	2.42	2.42	2.42	2.43	2.42	2.42	2.41
1 0 0 0 0 0	2.43	2.43	2.43	2.43	2.44	2.43	2.42
0 0 0 0 1 0	11.57	11.53	11.48	11.28	11.23	10.53	10.40
Symmetry A_2							
0 0 0 0 0 0	10.64	10.61	10.61	10.61	10.61	10.64	10.58
0 0 0 0 0 1	2.44	2.43	2.43	2.44	2.43	2.43	2.42
0 0 1 0 0 0	10.73	10.67	10.66	10.65	10.65	10.68	10.64
0 1 0 0 0 0	10.64	10.61	10.60	10.61	10.60	10.64	10.59
1 0 0 0 0 0	10.49	10.54	10.56	10.56	10.57	10.57	10.48
0 0 0 0 1 0	2.43	2.43	2.43	2.44	2.43	2.42	2.42
Symmetry A_1							
0 0 0 0 0 0	10.80	10.77	10.77	10.77	10.77	10.79	10.73
0 0 0 1 0 0	2.43	2.42	2.42	2.42	2.42	2.43	2.43
0 0 1 0 0 0	10.90	10.84	10.83	10.82	10.82	10.84	10.80
0 1 0 0 0 0	10.80	10.77	10.76	10.77	10.76	10.80	10.74
1 0 0 0 0 0	10.66	10.70	10.72	10.72	10.73	10.73	10.64
Symmetry B_2							
0 0 0 0 0 1	8.24	8.19	8.11	8.11	8.11	10.87	10.80
0 0 0 1 0 0	13.25	13.11	13.13	13.14	13.13	10.62	10.51
0 0 0 0 1 0	11.70	11.59	11.62	11.43	11.38	10.69	10.56

3 Results and discussion

For both H_2CS and H_2CN, we carried out a variety of calculations using the new code, and results for $J = 0$ and 1 are given in Tables 1 and 2, respectively, and compared with exact results obtained from converged variational calculations [4a, 9]. Some new results for $J = 20$ and 50 for H_2CS are given in Table 3. In these tables, VSCF(4) means VSCF calculations for four-mode coupling of the potential and inverse moment of inertia μ, and VCI(n, m) means a CI basis VCI(m), described in the previous section, together with an n-mode representation of the potential and inverse moment of inertia μ. The purpose of VCI(3, n) results is to track the convergence of the results with respect to the CI basis size, while the VCI(4, 7) results give an indication of the error in the three-mode and four-mode representation of the potential. The VSCF(4) results are given to assess the accuracy of pure VSCF levels.

First consider the results in Tables 1 and 2 for $J = 0$. Two important aspects emerge from these tables. First, the VCI results are seen to converge for sufficiently large CI basis sets. [The basis sizes for VCI(4, 7) and VCI(3, 7) are 563, 496, 288, 236, for the four vibrational symmetries, and the corresponding sizes for VCI(3, 9) are 1450, 1310, 765, and 640]. Second, and more importantly, residual errors in the three-mode coupling are largely eliminated in going to four-mode coupling of the potential and inverse moment of inertia μ. This is particularly true for the symmetric and asymmetric CH-stretching vibrations in both molecules (ν_1 and ν_5). Note that the four-mode VSCF results are of the expected, semi-quantitative, level of accuracy.

Next consider the $J = 1$ rovibrational energies, which are presented relative to the $J = 0$ energies discussed above. For VSCF(4) and VCI(3, 9) we also present ARA results. (This approximation was tested recently by us for HO_2 and H_2O [4c] and found to be quantitatively

Table 3. H_2CS rovibrational energies (cm^{-1}) for $J = 20$ and $J = 50$

$J = 20$	Assignment	K_a	K_c	Givens (K)	Iterdiag (K)	Givens (0)	Iterdiag (0)
1:	0 0 0 0 0 0	0	20	239.8958	239.8960	239.8958	239.8957
2:	0 0 0 0 0 0	2	19	277.7546	277.7541	277.7548	277.7547
3:	0 0 0 0 0 0	4	17	386.9786	386.9780	386.9788	386.9782
4:	0 0 0 0 0 0	6	15	569.7428	569.7415	569.7424	569.7412
5:	0 0 0 0 0 0	8	13	825.3872	825.3845	825.3864	825.3843
6:	0 0 0 0 0 0	0	11	1153.6512	1153.6478	1153.6494	1153.6465
7:	0 0 0 0 0 1	1	20	1229.2163	1229.2165	1229.2165	1229.2164
8:	0 0 0 1 0 0	1	19	1249.6897	1249.6899	1249.6902	1249.6901
9:	0 0 0 1 0 0	3	17	1283.0128	1283.0131	1283.0126	1283.0125
10:	0 1 0 0 0 0	0	20	1298.5943	1298.5941	1298.5945	1298.5945
11:	0 1 0 0 0 0	2	19	1335.1284	1335.1286	1335.1287	1335.1285
12:	0 0 0 0 0 1	3	18	1343.0294	1343.0298	1343.0292	1343.0293
13:	0 0 0 1 0 0	5	15	1407.8193	1407.8198	1407.8173	1407.8175
14:	0 1 0 0 0 0	4	17	1445.3238	1445.3237	1445.3234	1445.3236
15:	0 0 0 0 0 1	5	16	1506.0402	1506.0413	1506.0385	1506.0393
16:	0 0 0 0 0 0	2	9	1554.2173	1554.2120	1554.2127	1554.2093
17:	0 0 0 1 0 0	7	13	1604.8359	1604.8367	1604.8281	1604.8286
18:	0 1 0 0 0 0	6	15	1628.1061	1628.1055	1628.1056	1628.1055
19:	0 0 1 0 0 0	0	20	1697.0682	1697.0682	1697.0682	1697.0688
20:	0 0 1 0 0 0	2	19	1734.7951	1734.7958	1734.7953	1734.7960

$J = 50$	Assignment	K_a	K_c	Iterdiag (0)	$J = 50$	Assignment	K_a	K_c	Iterdiag (0)
1:	0 0 0 0 0 0	0	50	1441.6694	11:	0 0 0 1 0 0	3	47	2556.8249
2:	0 0 0 0 0 0	2	49	1510.1424	12:	0 1 0 0 0 0	2	49	2570.4320
3:	0 0 0 0 0 0	4	47	1607.9454	13:	0 0 0 1 0 0	5	45	2626.1622
4:	0 0 0 0 0 0	6	45	1789.4601	14:	0 1 0 0 0 0	4	47	2662.6337
5:	0 0 0 0 0 0	8	43	2044.5547	15:	0 0 0 0 0 1	5	46	2724.6879
6:	0 0 0 0 0 0	10	41	2372.3671	16:	0 0 0 0 0 0	12	39	2772.4644
7:	0 0 0 0 0 1	1	50	2426.8575	17:	0 0 0 1 0 0	7	43	2822.0401
8:	0 0 0 1 0 0	1	49	2468.1004	18:	0 1 0 0 0 0	6	45	2844.5292
9:	0 1 0 0 0 0	0	50	2496.8692	19:	0 0 1 0 0 0	0	50	2901.8882
10:	0 0 0 0 0 1	3	48	2506.5290	20:	0 0 0 0 0 1	7	44	2959.6572

accurate for HO_2 which is a near symmetric top, but of less accuracy for H_2O which is a strongly asymmetric top.) For both H_2CN and H_2CS it can be seen that the agreement with the exact variational results is very good, with the noticeable exception of the coriolis resonance between ν_4 and ν_6. This is particularly strong for H_2CS, where the fundamentals are only separated by 0.43 cm^{-1}. Since the adiabatic rotational levels are obtained by first diagonalizing the rigid-rotor rotational matrix, this effect can never be reproduced. However, as seen, the more exact algorithm implemented in the new version of "multimode", is able to reproduce the effect of the coriolis coupling on the nearly degenerate ν_4 and ν_6 modes.

In Table 3 we give the energies of the first 20 rovibrational levels of A_1 symmetry for H_2CS, calculated for $J = 20$ and $J = 50$. For $J = 20$, we compare results for both the Givens method and the iterative diagonalization method described above. In this case, we collect 100 functions from each K-block to give a matrix size of $(2J + 1)*100 = 4100$. These results are denoted (K) for both the Givens and iterative method (denoted "Iterdiag") in the table. The iterative results are converged to 0.001 cm^{-1} in less than 10 cycles. (In fact the iterative diagonalization procedure gave the lowest 100 eigenvalues to this level of convergence for $J = 20$ and 50.) The comparison is, in principle, exact, but there are slight differences due to the fact that we have used a disk input/output option of REAL*4. The time required to calculate rovibrational energies for very large values of J becomes dominated by the calculation of the "vibrational" K-diagonal blocks, of which there are $2J + 1$.

We are working on a new algorithm suggested to one of us (S.C.) by W. Meyer. In this approach the K-diagonal blocks are calculated once every ΔK times, and use the same contracted basis for all K from K to $K + \Delta K - 1$. As a preliminary to this, we have reevaluated the $J = 20$ rovibrational energies using a pure $J = 0$ basis throughout. These are denoted (0) in Table 3. It can be seen that excellent agreement is obtained between both sets of (K) and (0) results, given the inaccuracies introduced by the disk input/output REAL*4 option at all stages of the calculation. Although not in the table, we have confirmed that the $J = 0$ basis is good to about $K_a = 10$, when the typical error is about 0.01 cm^{-1} using the 100 functions/block matrix. Of these levels, only a single assignment is in error. This suggests that when the refined algorithm of Meyer is fully operational, these small errors will be corrected.

The results for $J = 50$ are only calculated using the iterative algorithm, with the $J = 0$ basis throughout. The levels are again converged to 0.001 cm^{-1} in 10 cycles, as above. The size of this matrix is 10100, which is too large for our Givens procedure, and thus the iterative algorithm is the only procedure we can apply to this large case.

4 Conclusions

In this paper we have presented details and tests of extensions to our "multimode" program for the calculation of rovibrational energy levels of many-mode molecules using the Watson Hamiltonian. These extensions include an exact treatment of rotation and several options to perform "CI" calculations. The heart of the method, which makes is feasible for many-mode systems, is the hierarchical representation of the potential and inverse moment of inertia tensor. Currently this representation is limited to a maximum of four-mode coupling. Within this restriction, "multimode" can be used to calculate rovibrational energies of many-mode molecules using an exact procedure. An iterative diagonalization method has also been implemented into the new code. This method is essential when dealing with large Hamiltonian matrices (of the order of 10^4).

We reported test calculations for the fundamental rovibrational energies of two tetraatomic molecules, H_2CS and H_2CN, for which previous accurate variational results are available for $J = 0$ and 1. For the former molecule we also reported rovibrational energies for $J = 20$ and 50. In both cases the three-mode mode coupling was shown to be accurate for these six-mode molecules, with the exception of the symmetric and antisymmetric CH stretches, where errors between 2 and 9 cm^{-1} were found. The four-mode representation of the potential did, however, yield rovibrational energies in excellent agreement with the accurate six-mode results. The ARA was also tested and found to be quite accurate except for the near-degenerate v_4 and v_6 modes of H_2CS, which are significantly perturbed by coriolis coupling for $J > 0$.

This code is available in source form. If interested in obtaining it please contact either S.C. (email: s.carter@reading.ac.uk) or J.M.B. (email: bowman@euch3g.chem.emory.edu).

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References

1. (a) Bowman JM (1986) Acc Chem Res 19:202; (b) Ratner MA, Gerber RB (1986) J Phys Chem 90:20
2. (a) Roitberg A, Gerber RB, Elber R, Ratner MA (1995) Science 268:1319; (b) Norris L, Ratner MA, Roitberg AE, Gerber RB (1996) J Chem Phys 105:11261; (c) Jung JO, Gerber RB (1996) J Chem Phys 105:10332; (d) Roitberg A, Gerber RB, Elber R, Ratner MA (1997) J Phys Chem B 101:1700
3. (a) Jelski D, Haley RH, Bowman JM (1996) J Comput Chem 17:1645; (b) Park SC, Bowman JM, Jelski DA (1996) J Chem Phys 104:2457
4. (a) Carter S, Bowman JM, Harding LB (1997) Spectrochim Acta A 53:1179; (b) Carter S, Culik S, Bowman JM (1997) J Chem Phys 107:10458; (c) Carter S, Bowman JM (1998) J Chem Phys 108:4397; (d) Culik S (1997) MS Thesis, Emory University
5. (a) Davidson ER (1975) J Comput Phys 17:87; (b) Davidson ER (1989) Comput Phys Commun 53:49; (c) Bramley MJ, Carrington T Jr (1993) J Chem Phys 99:8519; (d) Nauts A, Wyatt RE (1983) Phys Rev Lett 81:2238; (e) Iung C, Leforestier C (1989) J Chem Phys 90:3198; (f) Aoyagi M, Gray SK (1991) J Chem Phys 94:195; (g) Balint-Kurti GG, Pulay P (1995) J Struct Chem 341:1
6. Watson JKG (1968) Mol Phys 15:479
7. Whitehead RJ, Handy NC (1975) J Mol Spectrosc 55:356
8. Romanowski H, Bowman JM, Harding L (1985) J Chem Phys 82:4155
9. Carter S, Handy NC J Mol Spectrosc (in press)
10. Carter S, Pinnavaia N, Handy NC (1995) Chem Phys Lett 240:400