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Variational calculations of vibrational energy levels for XY_4 molecules:
2. Bending states of methane

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A variational method for calculating excited bending states of symmetric tetrahedral penta-atomic molecules is presented based on the use of Radau coordinates and Jacobi polynomials as the basis functions. Symmetry is used both to reduce the size of secular matrix to be diagonalized and to calculate potential energy matrix elements over a reduced grid of quadrature points. Methods of treating the redundant coordinate are investigated and fitting is found to be more effective than the use of Taylor expansions. Test results are presented for methane, for which stretch–bend coupling and the contribution due to the redundant coordinate are found to be significant. Converged results are obtained for bending states significantly higher than considered in previous calculations. These states will be used as a basis for bending motions in a fully coupled stretch–bend calculation.

1. Introduction

The vibration–rotation spectroscopy of tetrahedral XY_4 molecules is of considerable interest but is difficult to treat theoretically in regimes where the assumption of small amplitude vibrational motion is not reliable. We are interested in developing a systematic procedure for studying these systems using internal coordinates and variational procedures that have proved very successful for highly excited states of smaller molecules [1]. However, the nine degrees of vibrational freedom mean that complete variational calculations on five-atom systems present a considerable computational challenge.

In the first paper [2] in this series we presented a formalism for treating the stretching motions in XY_4 molecules and applied it to a number of hydrides. In the present paper we address the problem of the bending motions in such systems. The approximate separation of low frequency bends from high frequency stretches in molecules such as hydrocarbons has long been considered [3]. Our main reason for performing this separation is not so much to get results for the bend-only problem but to use the solutions of this problem to tackle the full stretch–bend problem.

The bend-only problem presents more of a challenge than the stretch-only one for a number of reasons. Most obviously there are five bending degrees of freedom rather than the four stretching modes. Furthermore, the bending modes are coupled in ways that make them unsuitable for treatment using discrete variable representation (DVR) methods [5] which have proved highly successful in other circumstances [4]. Bending excitations generally lie at considerably lower energies than the stretches with the same number of quanta, meaning that for a given total vibrational energy in the molecule many more bending states have to be considered. Finally there is a well known problem with the redundant coordinate [6–10], which makes the use of symmetrized coordinates in the bending problem technically much more difficult than in the stretching case.

2. Theory

2.1. *The Hamiltonian*

As detailed in [2], the Hamiltonian for the vibrational motions of an XY_4 system in Radau coordinates can be written conveniently as

$$H = T_{\mathrm{str}} + T_{\mathrm{ang}} + V, \tag{1}$$

with

$$T_{\mathrm{str}} = -\frac{\hbar^2}{2\mu}\sum_{\alpha=1}^{4}\frac{\partial^2}{\partial r_\alpha^2}, \tag{2}$$

and

$$T_{\mathrm{ang}} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j>i}^{4}\left(\frac{1}{r_i^2}+\frac{1}{r_j^2}\right)\frac{\partial}{\sin\alpha_{ij}\partial\alpha_{ij}}\sin\alpha_{ij}\frac{\partial}{\partial\alpha_{ij}}$$

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$$-\frac{\hbar^2}{\mu}\sum_{i=1}^{4}\frac{1}{r_i^2}\sum_{j\neq i}^{4}\sum_{k\neq ij}^{4}\operatorname{csec}\alpha_{ij}\operatorname{csec}\alpha_{ik}$$
$$\times(\cos\alpha_{jk}-\cos\alpha_{ij}\cos\alpha_{ik})\frac{\partial^2}{\partial\alpha_{ij}\,\partial\alpha_{ik}}. \quad (3)$$

Here μ is the mass of atom Y, r_i is the Radau radial vector, and α_{ij} is the angle between the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$. In practice it is more convenient to transform the angular kinetic energy operator to a representation in cosines of the angles using $\omega_{ij}=\cos\alpha_{ij}$. This gives

$$T_{\text{ang}}=-\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j>i}^{4}\left(\frac{1}{r_i^2}+\frac{1}{r_j^2}\right)\frac{\partial}{\omega_{ij}}(1-\omega_{ij}^2)\frac{\partial}{\partial\omega_{ij}}$$
$$-\frac{\hbar^2}{\mu}\sum_{i=1}^{4}\frac{1}{r_i^2}\sum_{j\neq i}^{4}\sum_{k\neq ij}^{4}(\omega_{jk}-\omega_{ij}\omega_{ik})\frac{\partial^2}{\partial\omega_{ij}\partial\omega_{ik}}. \quad (4)$$

The bending kinetic energy operator (equation (3) or (4)) is defined in terms of six tetrahedral angles, α_{ij}. Only five of these angles are linearly independent; this leads to the well known redundancy condition that must be obeyed by the Hamiltonian. The redundancy condition in internal coordinates [6–9] can be expressed conveniently as

$$\begin{vmatrix} 1 & \omega_{12} & \omega_{13} & \omega_{14} \\ \omega_{12} & 1 & \omega_{23} & \omega_{24} \\ \omega_{13} & \omega_{23} & 1 & \omega_{34} \\ \omega_{14} & \omega_{24} & \omega_{34} & 1 \end{vmatrix}=0. \quad (5)$$

To utilize symmetry, we transform the Radau internal angular coordinate variables ω_{ij}, to the Radau symmetry coordinates. The symmetrized Radau angular coordinates and the redundancy coordinate s_r are defined as

$$s_{2a}=\frac{1}{\sqrt{12}}(2\omega_{12}-\omega_{13}-\omega_{14}-\omega_{23}-\omega_{24}+2\omega_{34}),$$
$$s_{2b}=\tfrac{1}{2}(\omega_{13}-\omega_{14}-\omega_{23}+\omega_{24}),$$
$$s_{4x}=\frac{1}{\sqrt{2}}(\omega_{24}-\omega_{13}),$$
$$s_{4y}=\frac{1}{\sqrt{2}}(\omega_{23}-\omega_{14}),$$
$$s_{4z}=\frac{1}{\sqrt{2}}(\omega_{34}-\omega_{12}),$$
$$s_r=\frac{1}{\sqrt{6}}(\omega_{12}+\omega_{13}+\omega_{14}+\omega_{23}+\omega_{24}+\omega_{34}), \quad (6)$$

where the redundancy coordinate is entirely determined by the other five symmetric variables, i.e. s_r is a function of $s_r(s_{2a},s_{2b},s_{4x},s_{4y},s_{4z})$. Using transformation (6), we can expand redundancy condition (5) and obtain the redundancy equation in symmetrized coordinates. An expression for s_r can be determined by solving the redundancy equation,

$$s_r=A_0+A_1s_r+A_2s_r^2+A_3s_r^3+A_4s_r^4, \quad (7)$$

where the coefficients A_0, A_1, A_2, A_3 and A_4 are functions of the other five symmetric coordinates $s_{2a}, s_{2b}, s_{4x}, s_{4y}$, and s_{4z}.

$$\begin{aligned}A_0=&\frac{s_{4x}^2}{8}+\frac{\sqrt{3}s_{2a}s_{4x}^2}{32}-\frac{3s_{2a}^2s_{4x}^2}{64}-\frac{3s_{2b}s_{4x}^2}{32}\\&-\frac{3\sqrt{3}s_{2a}\,s_{2b}s_{4x}^2}{64}-\frac{9s_{4x}^4}{256}+\frac{s_{4y}^2}{8}\\&+\frac{\sqrt{3}s_{2a}s_{4y}^2}{32}-\frac{3s_{2a}^2s_{4y}^2}{64}+\frac{3s_{2b}s_{4y}^2}{32}\\&+\frac{3\sqrt{3}s_{2a}\,s_{2b}s_{4y}^2}{64}\\&+\frac{9s_{4x}^2s_{4y}^2}{128}-\frac{9s_{4y}^4}{256}-\frac{9\,s_{4x}\,s_{4y}\,s_{4z}}{16\sqrt{2}}\\&+\frac{s_{4z}^2}{8}-\frac{\sqrt{3}s_{2a}s_{4z}^2}{16}\\&+\frac{3s_{2a}^2s_{4z}^2}{128}-\frac{9s_{2b}^2\,s_{4z}^2}{128}+\frac{9s_{4x}^2s_{4z}^2}{128}\\&+\frac{9s_{4y}^2s_{4z}^2}{128}-\frac{9s_{4z}^4}{256},\end{aligned} \quad (8)$$

$$\begin{aligned}A_1=&\frac{9s_{2a}^2}{16}-\frac{3\sqrt{3}s_{2a}^3}{32}+\frac{9s_{2b}^2}{16}\\&+\frac{9\sqrt{3}s_{2a}s_{2b}^2}{32}+\frac{3s_{4x}^2}{32}-\frac{3\sqrt{3}s_{2a}s_{4x}^2}{32}\\&+\frac{9s_{2b}s_{4x}^2}{32}+\frac{3s_{4y}^2}{32}-\frac{3\sqrt{3}s_{2a}s_{4y}^2}{32}\\&-\frac{9s_{2b}s_{4y}^2}{32}+\frac{3s_{4z}^2}{32}+\frac{3\sqrt{3}s_{2a}s_{4z}^2}{16},\end{aligned} \quad (9)$$

$$A_2=\frac{9}{4}-\frac{27s_{2a}^2}{64}-\frac{27s_{2b}^2}{64}-\frac{9s_{4x}^2}{64}-\frac{9s_{4y}^2}{64}-\frac{9s_{4z}^2}{64}, \quad (10)$$

$$A_3=-\frac{27}{16}, \quad (11)$$

$$A_4=\frac{27}{64}. \quad (12)$$

Using ‘Mathematica’ to solve this equation yields an exact solution of the redundancy problem for the bending motion in XY_4 systems in Radau coordinates. Because equation (7) is a quartic equation, it actually has four solutions. However, inspection of these shows that only one solution is real,

$$s_r = 1 + \frac{1}{2}\left(C_3 - C_4 + \frac{B_3}{4C_3}\right)^{1/2} \tag{13}$$

where

$$\begin{aligned}
B_0 &= \frac{256}{9}(A_0 + A_1) + \frac{4096}{729},\\
B_1 &= 1024A_0 + \frac{4096}{27}A_1^2 + \frac{32768}{81}(A_1 - 2A_0)A_2\\
&\quad + \frac{524\,288}{19\,683}A_2^3,\\
B_2 &= 4 - \frac{128}{81}A_2,\\
B_3 &= 64 - \frac{512}{27}A_1 - \frac{1024}{27}A_2,\\
C_1 &= \frac{1}{3}\left(\frac{B_1 + (-4B_0^3 + B_1^2)^{1/2}}{2}\right)^{1/3}\\
C_2 &= \frac{2^{1/3}B_0}{3C_1}\\
C_3 &= (B_2 + C_1 + C_2)^{1/2}\\
C_4 &= 2B_2 - C_1 - C_2
\end{aligned} \tag{14}$$

It should be noted that this solution does not correspond to the one given by Mladenović [10], which is complex for much of coordinate space apart from a region near the equilibrium configuration. Our final expression for s_r is fairly complicated but can be evaluated readily numerically. These numerical evaluations will be used below to obtain an approximation formula to represent the redundancy coordinate through fitting to an exact solution.

Considering the redundancy, the expression for the bending kinetic energy operator can be obtained with 'Mathematica' using the chain rule as

$$T_a \Big/ \left(-\frac{\hbar^2}{2\mu}\right) = \sum_{ij} t_{ij}\frac{\partial^2}{\partial q_i \partial q_j} + \sum_i t_i \frac{\partial}{\partial q_i}, \tag{15}$$

where $q_i = s_{2a}, s_{2b}, s_{4x}, s_{4y}, s_{4z}$. The terms t_{ij} and t_i are given by

$$\begin{aligned}
t_{2a2a} &= \left(\frac{1}{2} + \frac{s_{2a}}{2\sqrt{3}} - \frac{s_{2a}^2}{4} - \frac{s_{4x}^2}{24} - \frac{s_{4y}^2}{24} - \frac{s_{4z}^2}{6} - \frac{s_r}{2\sqrt{6}}\right)\mu_a\\
&\quad + \left(\frac{-s_{4x}}{3\sqrt{2}} - \frac{s_{2a}s_{4x}}{2\sqrt{6}} + \frac{s_{4y}s_{4z}}{6}\right)\mu_x\\
&\quad + \left(\frac{-s_{4y}}{3\sqrt{2}} - \frac{s_{2a}s_{4y}}{2\sqrt{6}} + \frac{s_{4x}s_{4z}}{6}\right)\mu_y\\
&\quad + \left(\frac{-(s_{4x}s_{4y})}{12} + \frac{s_{4z}}{6\sqrt{2}} + \frac{\sqrt{\frac{2}{3}}s_{2a}s_{4z}}{3} + \frac{s_{2a}s_{4z}}{3\sqrt{6}}\right)\mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2b2b} &= \left(\frac{1}{2} - \frac{s_{2a}}{2\sqrt{3}} - \frac{s_{2b}^2}{4} - \frac{s_{4x}^2}{8} - \frac{s_{4y}^2}{8} + \frac{s_r}{2\sqrt{6}}\right)\mu_a\\
&\quad + \frac{s_{2b}s_{4x}\mu_x}{2\sqrt{2}} - \frac{s_{2b}s_{4y}\mu_y}{2\sqrt{2}} + \left(\frac{s_{4x}s_{4y}}{4} - \frac{s_{4z}}{2\sqrt{2}}\right)\mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{4x4x} &= \left(\frac{1}{2} - \frac{s_{2a}^2}{24} + \frac{s_{2a}s_{2b}}{4\sqrt{3}} - \frac{s_{2b}^2}{8} - \frac{s_{4x}^2}{4}\right.\\
&\quad \left. + \frac{s_{2a}s_r}{6\sqrt{2}} - \frac{s_{2b}s_r}{2\sqrt{6}} - \frac{s_r^2}{12}\right)\mu_a\\
&\quad + \left(\frac{-(s_{2a}s_{4x})}{2\sqrt{6}} + \frac{s_{2b}s_{4x}}{2\sqrt{2}} + \frac{s_{4x}s_r}{2\sqrt{3}}\right)\mu_x,
\end{aligned}$$

$$\begin{aligned}
t_{4y4y} &= \left(\frac{1}{2} - \frac{s_{2a}^2}{24} - \frac{s_{2a}s_{2b}}{4\sqrt{3}} - \frac{{s_{2b}}^2}{8} - \frac{s_{4y}^2}{4}\right.\\
&\quad \left. + \frac{s_{2a}s_r}{6\sqrt{2}} + \frac{s_{2b}s_r}{2\sqrt{6}} - \frac{s_r^2}{12}\right)\mu_a\\
&\quad + \left(\frac{-(s_{2a}s_{4y})}{2\sqrt{6}} - \frac{s_{2b}s_{4y}}{2\sqrt{2}} + \frac{s_{4y}s_r}{2\sqrt{3}}\right)\mu_y,
\end{aligned}$$

$$\begin{aligned}
t_{4z4z} &= \left(\frac{1}{2} - \frac{s_{2a}^2}{6} - \frac{s_{4z}^2}{4} - \frac{s_{2a}s_r}{3\sqrt{2}} - \frac{s_r^2}{12}\right)\mu_a\\
&\quad + \left(\frac{s_{2a}s_{4z}}{\sqrt{6}} + \frac{s_{4z}s_r}{2\sqrt{3}}\right)\mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2a2b} &= \left(-\left(\frac{s_{2b}}{\sqrt{3}}\right) - \frac{s_{2a}s_{2b}}{2} + \frac{s_{4x}^2}{4\sqrt{3}} - \frac{s_{4y}^2}{4\sqrt{3}}\right)\mu_a\\
&\quad + \left(-\left(\frac{s_{4x}}{\sqrt{6}}\right) + \frac{s_{2a}s_{4x}}{2\sqrt{2}} - \frac{s_{2b}s_{4x}}{2\sqrt{6}} + \frac{s_{4y}s_{4z}}{2\sqrt{3}}\right)\mu_x\\
&\quad + \left(\frac{s_{4y}}{\sqrt{6}} - \frac{s_{2a}s_{4y}}{2\sqrt{2}} - \frac{s_{2b}s_{4y}}{2\sqrt{6}} - \frac{s_{4x}s_{4z}}{2\sqrt{3}}\right)\mu_y + \frac{s_{2b}s_{4z}\mu_z}{\sqrt{6}},
\end{aligned}$$

$$\begin{aligned}
t_{2a4x} &= \left(\frac{-7s_{2a}s_{4x}}{12} + \frac{s_{2b}s_{4x}}{4\sqrt{3}} + \frac{s_{4x}s_r}{6\sqrt{2}}\right)\mu_a\\
&\quad + \left(\frac{1}{\sqrt{6}} + \frac{\sqrt{2}s_{2a}}{3} - \frac{s_{2a}^2}{2\sqrt{6}} + \frac{s_{2b}}{\sqrt{6}} + \frac{s_{2a}s_{2b}}{2\sqrt{2}}\right.\\
&\quad \left. - \frac{s_{4x}^2}{2\sqrt{6}} - \frac{s_r}{6} + \frac{s_{2a}s_r}{2\sqrt{3}}\right)\mu_x\\
&\quad + \left(\frac{-(s_{4x}s_{4y})}{2\sqrt{6}} + \frac{s_{4z}}{2\sqrt{3}} + \frac{s_{2a}s_{4z}}{6} - \frac{s_{2b}s_{4z}}{2\sqrt{3}} - \frac{s_{4z}s_r}{3\sqrt{2}}\right)\mu_y\\
&\quad + \left(-\left(\frac{s_{4y}}{\sqrt{3}}\right) - \frac{s_{2a}s_{4y}}{12} + \frac{s_{2b}s_{4y}}{4\sqrt{3}} + \frac{s_{4x}s_{4z}}{\sqrt{6}} + \frac{s_{4y}s_r}{6\sqrt{2}}\right)\mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2a4y} = {} & \left(\frac{-7 s_{2a} s_{4y}}{12} - \frac{s_{2b} s_{4y}}{4\sqrt{3}} + \frac{s_{4y} s_r}{6\sqrt{2}} \right) \mu_a \\
& + \left(\frac{-(s_{4x} s_{4y})}{2\sqrt{6}} + \frac{s_{4z}}{2\sqrt{3}} + \frac{s_{2a} s_{4z}}{6} + \frac{s_{2b} s_{4z}}{2\sqrt{3}} - \frac{s_{4z} s_r}{3\sqrt{2}} \right) \mu_x \\
& + \Bigg(\frac{1}{\sqrt{6}} + \frac{\sqrt{2} s_{2a}}{3} - \frac{s_{2a}^2}{2\sqrt{6}} - \frac{s_{2b}}{\sqrt{6}} - \frac{s_{2a} s_{2b}}{2\sqrt{2}} \\
& - \frac{{s_{4y}}^2}{2\sqrt{6}} - \frac{s_r}{6} + \frac{s_{2a} s_r}{2\sqrt{3}} \Bigg) \mu_y \\
& - \left(-\left(\frac{s_{4x}}{\sqrt{3}} \right) - \frac{s_{2a} s_{4x}}{12} - \frac{s_{2b} s_{4x}}{4\sqrt{3}} + \frac{s_{4y} s_{4z}}{\sqrt{6}} + \frac{s_{4x} s_r}{6\sqrt{2}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2a4z} = {} & \left(\frac{-5 s_{2a} s_{4z}}{6} - \frac{s_{4z} s_r}{3\sqrt{2}} \right) \mu_a \\
& + \left(\frac{s_{4y}}{2\sqrt{3}} + \frac{s_{2a} s_{4y}}{6} - \frac{s_{4x} s_{4z}}{2\sqrt{6}} + \frac{s_{4y} s_r}{6\sqrt{2}} \right) \mu_x \\
& + \left(\frac{s_{4x}}{2\sqrt{3}} + \frac{s_{2a} s_{4x}}{6} - \frac{s_{4y} s_{4z}}{2\sqrt{6}} + \frac{s_{4x} s_r}{6\sqrt{2}} \right) \mu_y \\
& + \left(-\sqrt{\frac{2}{3}} - \frac{s_{2a}}{3\sqrt{2}} + \frac{s_{2a}^2}{\sqrt{6}} + \frac{s_{4z}^2}{\sqrt{6}} + \frac{s_r}{3} + \frac{s_{2a} s_r}{2\sqrt{3}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2b4x} = {} & \left(\frac{s_{2a} s_{4x}}{4\sqrt{3}} - \frac{3 s_{2b} s_{4x}}{4} - \frac{s_{4x} s_r}{2\sqrt{6}} \right) \mu_a \\
& + \Bigg(-\left(\frac{1}{\sqrt{2}} \right) + \frac{s_{2a}}{\sqrt{6}} - \frac{s_{2a} s_{2b}}{2\sqrt{6}} + \frac{{s_{2b}}^2}{2\sqrt{2}} + \frac{{s_{4x}}^2}{2\sqrt{2}} \\
& + \frac{s_r}{2\sqrt{3}} + \frac{s_{2b} s_r}{2\sqrt{3}} \Bigg) \mu_x + \left(\frac{-(s_{4x} s_{4y})}{2\sqrt{2}} + \frac{s_{4z}}{2} \right) \mu_y \\
& + \left(\frac{-(s_{2a} s_{4y})}{4\sqrt{3}} + \frac{s_{2b} s_{4y}}{4} + \frac{s_{4y} s_r}{2\sqrt{6}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2b4y} = {} & \left(\frac{-(s_{2a} s_{4y})}{4\sqrt{3}} - \frac{3 s_{2b} s_{4y}}{4} + \frac{s_{4y} s_r}{2\sqrt{6}} \right) \mu_a \\
& + \left(\frac{s_{4x} s_{4y}}{2\sqrt{2}} - \frac{s_{4z}}{2} \right) \mu_x \\
& + \Bigg(\frac{1}{\sqrt{2}} - \frac{s_{2a}}{\sqrt{6}} - \frac{s_{2a} s_{2b}}{2\sqrt{6}} - \frac{s_{2b}^2}{2\sqrt{2}} \\
& - \frac{s_{4y}^2}{2\sqrt{2}} - \frac{s_r}{2\sqrt{3}} + \frac{s_{2b} s_r}{2\sqrt{3}} \Bigg) \mu_y \\
& + \left(\frac{s_{2a} s_{4x}}{4\sqrt{3}} + \frac{s_{2b} s_{4x}}{4} - \frac{s_{4x} s_r}{2\sqrt{6}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{2b4z} = {} & \frac{-(s_{2b} s_{4z} \mu_a)}{2} + \left(\frac{-s_{4y}}{2} + \frac{s_{2a} s_{4y}}{2\sqrt{3}} + \frac{s_{4x} s_{4z}}{2\sqrt{2}} + \frac{s_{4y} s_r}{2\sqrt{6}} \right) \mu_x \\
& + \left(\frac{s_{4x}}{2} - \frac{s_{2a} s_{4x}}{2\sqrt{3}} - \frac{s_{4y} s_{4z}}{2\sqrt{2}} - \frac{s_{4x} s_r}{2\sqrt{6}} \right) \mu_y \\
& + \left(\frac{s_{2b}}{\sqrt{2}} + \frac{s_{2a} s_{2b}}{\sqrt{6}} + \frac{s_{2b} s_r}{2\sqrt{3}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{4x4y} = {} & \left(\frac{-(s_{4x} s_{4y})}{2} + \frac{s_{4z}}{\sqrt{2}} \right) \mu_a \\
& + \left(\frac{-(s_{2a} s_{4y})}{2\sqrt{6}} + \frac{s_{2b} s_{4y}}{2\sqrt{2}} + \frac{s_{4y} s_r}{2\sqrt{3}} \right) \mu_x \\
& + \left(\frac{-(s_{2a} s_{4x})}{2\sqrt{6}} - \frac{s_{2b} s_{4x}}{2\sqrt{2}} + \frac{s_{4x} s_r}{2\sqrt{3}} \right) \mu_y \\
& + \left(\frac{s_{2a}}{\sqrt{3}} - \frac{s_{2a}^2}{12} + \frac{{s_{2b}}^2}{4} + \frac{s_r}{\sqrt{6}} + \frac{s_{2a} s_r}{3\sqrt{2}} - \frac{s_r^2}{6} \right) \mu_z
\end{aligned}$$

$$\begin{aligned}
t_{4x4z} = {} & \left(\frac{s_{4y}}{\sqrt{2}} - \frac{s_{4x} s_{4z}}{2} \right) \mu_a \\
& + \left(\frac{-(s_{2a} s_{4z})}{2\sqrt{6}} + \frac{s_{2b} s_{4z}}{2\sqrt{2}} + \frac{s_{4z} s_r}{2\sqrt{3}} \right) \mu_x \\
& + \Bigg(\frac{-s_{2a}}{2\sqrt{3}} + \frac{s_{2a}^2}{6} - \frac{s_{2b}}{2} - \frac{s_{2a} s_{2b}}{2\sqrt{3}} \\
& + \frac{s_r}{\sqrt{6}} - \frac{s_{2a} s_r}{6\sqrt{2}} - \frac{s_{2b} s_r}{2\sqrt{6}} - \frac{s_r^2}{6} \Bigg) \mu_y \\
& + \left(\frac{s_{2a} s_{4x}}{\sqrt{6}} + \frac{s_{4x} s_r}{2\sqrt{3}} \right) \mu_z,
\end{aligned}$$

$$\begin{aligned}
t_{4y4z} = {} & \left(\frac{s_{4x}}{\sqrt{2}} - \frac{s_{4y} s_{4z}}{2} \right) \mu_a \\
& + \Bigg(\frac{-s_{2a}}{2\sqrt{3}} + \frac{s_{2a}^2}{6} + \frac{s_{2b}}{2} + \frac{s_{2a} s_{2b}}{2\sqrt{3}} \\
& + \frac{s_r}{\sqrt{6}} - \frac{s_{2a} s_r}{6\sqrt{2}} + \frac{s_{2b} s_r}{2\sqrt{6}} - \frac{s_r^2}{6} \Bigg) \mu_x \\
& + \left(\frac{-(s_{2a} s_{4z})}{2\sqrt{6}} - \frac{s_{2b} s_{4z}}{2\sqrt{2}} + \frac{s_{4z} s_r}{2\sqrt{3}} \right) \mu_y \\
& + \left(\frac{s_{2a} s_{4y}}{\sqrt{6}} + \frac{s_{4y} s_r}{2\sqrt{3}} \right) \mu_z,
\end{aligned}$$

$$t_{2a} = -s_{2a} \mu_a - \frac{s_{4x} \mu_x}{\sqrt{6}} - \frac{s_{4y} \mu_y}{\sqrt{6}} + \sqrt{\frac{2}{3}} s_{4z} \mu_z,$$

$$t_{2b} = -s_{2b} \mu_a + \frac{s_{4x} \mu_x}{\sqrt{2}} - \frac{s_{4y} \mu_y}{\sqrt{2}},$$

$$t_{4x} = -s_{4x} \mu_a + \left(-\frac{s_{2a}}{\sqrt{6}} + \frac{s_{2b}}{\sqrt{2}} + \frac{s_r}{\sqrt{3}} \right) \mu_x,$$

$$t_{4y} = -s_{4y}\mu_a + \left(-\frac{s_{2a}}{\sqrt{6}} - \frac{s_{2b}}{\sqrt{2}} + \frac{s_r}{\sqrt{3}}\right)\mu_y,$$

$$t_{4z} = -s_{4z}\mu_a + \left(\sqrt{\frac{2}{3}}s_{2a} + \frac{s_r}{\sqrt{3}}\right)\mu_z, \qquad (16)$$

where

$$\mu_a = 1/\mu(r_1^2 + r_2^2 + r_3^2 + r_4^2),$$

$$\mu_x = 1/\mu(r_1^2 - r_2^2 + r_3^2 - r_4^2),$$

$$\mu_y = 1/\mu(r_1^2 - r_2^2 - r_3^2 + r_4^2),$$

$$\mu_z = 1/\mu(r_1^2 + r_2^2 - r_3^2 - r_4^2). \qquad (17)$$

This expression for the bending kinetic energy operator is exact, but difficult to work with since the redundancy coordinate s_r appears regularly. To evaluate matrix elements involving this coordinate without approximation would require performing many numerical quadratures each as expensive as the integral over the potential. As discussed below, we therefore chose to approximate the contribution of this term.

2.2. *Symmetry and basis functions*

For the bending problem, we evaluate the kinetic energy matrix elements for each of five possible total symmetry types, denoted in standard point group notation A_1, A_2, E, F_1, F_2. For a symmetrized basis set it is necessary to consider basis functions that satisfy the rules of Hougen ([11], table 9). As in [2] symmetrized functions can be divided into different types. There are three cases for the ν_2 mode and four for the ν_4 mode. As the angular basis is a product of the basis in each mode this gives 12 different basis types.

Table 1 illustrates the three cases for the ν_2 vibrations. The cases are classified by their value of the mode function of the quantum numbers $m = \mathrm{mod}(a - b, 3)$, where $|ab\rangle$ means a and b are the number of quanta in modes s_{2a} and s_{2b}, respectively, and we take $a \geqslant b$. It is simpler to define the four cases for the ν_4 mode, for which $|def\rangle$ defines a basis state d quanta in s_{4x}, e in s_{4y} and f in s_{4z}, and $d \geqslant e \geqslant f$.

$$\begin{array}{ll} \text{Case A} & |ddd\rangle \\ \text{Case B} & |dee\rangle \\ \text{Case C} & |ddf\rangle \\ \text{Case D} & |edf\rangle \end{array} \qquad (18)$$

The total angular wavefunction is a sum over symmetry products of the basis function in ν_2 and ν_4 [11]. For example, considering ν_2 case I and ν_4 case B, the total wavefunction with A_1 total symmetry is given in terms of the vector coupling coefficient of Halonen [7] as

$$\frac{1}{\sqrt{3}}|ab\rangle(|dee\rangle + |ede\rangle + |eed\rangle). \qquad (19)$$

Table 1. Basis sets for ν_2 angular motions.

Basis functions	Label		Case
$\|ab\rangle$	A_1	$m = 0, a = b$	I
$\frac{1}{\sqrt{2}}(\|ab\rangle + \|ba\rangle)$	A_1	$m = 0, a \neq b$	II
$\frac{1}{\sqrt{2}}(\|ab\rangle - \|ba\rangle)$	A_2	$m = 0, a \neq b$	II
$\|ab\rangle$	E_a	$m \neq 0$	III
$\|ba\rangle$	E_b	$m \neq 0$	III

In this work we employ Jacobi polynomials to represent the angular motions.

$$|i\rangle = N_i(1 - x)^{\alpha/2}(1 + x)^{\beta/2}P_i^{(\alpha,\beta)}(x). \qquad (20)$$

where N_i is a normalization constant, and α and β are variational parameters, which are determined for the system investigated. $P_{\nu_i}^{(\alpha,\beta)}(x)$ is a standard Jacobi polynomial. These polynomials are orthogonal with respect to the weight function $(1 - x)^\alpha(1 + x)^\beta$ on the domain $[-1, 1]$. The variable x is related to symmetry coordinate q via $x = q/L$, where the scale factor L maps the symmetry coordinate domains into $[-1, 1]$. $L = 4/\sqrt{3}$, 2, $\sqrt{2}, \sqrt{2}$ and $\sqrt{2}$ for $q = s_{2a}, s_{2b}, s_{4x}, s_{4y}$ and s_{4z}, respectively.

2.3. *The kinetic matrix elements*

In the domain $[-1, 1]$ of the Jacobi polynomial, the matrix elements of the angular kinetic operators can be computed exactly using quadrature. A complete matrix element expression for the kinetic operator with symmetrized basis functions can be constructed by computing the matrix elements of the three operators considered in turn below. In each case matrix elements can be computed exactly, to within the limits of rounding errors, using an appropriate Gauss–Jacobi quadrature scheme.

$$\langle\nu|\frac{\partial}{\partial x}(1 - x^2)\frac{\partial}{\partial x}|\nu'\rangle = N_\nu N_{\nu'}\sum_{i=1}^{M}\omega_i D_\nu^{(\alpha,\beta)}(x_i)D_{\nu'}^{(\alpha,\beta)}(x_i), \qquad (21)$$

where

$$D_\nu^{(\alpha,\beta)}(x) = P_\nu^{(\alpha,\beta)}(x)[(\alpha + \tfrac{1}{2})(1 + x) - (\beta + \tfrac{1}{2})(1 - x)] - 2(1 - x^2)P_\nu^{(\alpha,\beta)}. \qquad (22)$$

x_i and ω_i are the points and weights of M-point Gauss–Jacobi quadrature based on $P_M^{(\alpha-1,\beta-1)}$ with $M > \max(\nu, \nu') + 2$ [12].

Using the same quadrature scheme, the matrix elements of $x^n(\partial/\partial x)$ can be obtained by

$$\langle \nu | x^n \frac{\partial}{\partial x} | \nu' \rangle = N_\nu N_{\nu'} \sum_{i=1}^{M} \omega_i B_\nu^{(\alpha,\beta)}(x_i) D_{\nu'}^{(\alpha,\beta)}(x_i), \qquad (23)$$

where

$$B_\nu^{(\alpha,\beta)}(x) = x^n P_\nu^{(\alpha,\beta)}(x) \qquad (24)$$

$$D_{\nu'}^{(\alpha,\beta)}(x) = P_{\nu'}^{(\alpha,\beta)}(x)[(\alpha + \tfrac{1}{2})(1+x) - (\beta + \tfrac{1}{2})(1-x)] - 2(1-x^2)P_{\nu'}^{(\alpha,\beta)}. \qquad (25)$$

Finally, the matrix elements of $x^n(\partial^2/\partial x^2)$ can be computed using M-point Gauss–Jacobi quadrature based on $P_M^{(\alpha-2,\beta-2)}$ with $M > \max(\nu, \nu') + 4$ using the expressions

$$\nu | x^n \frac{\partial^2}{\partial x^2} | \nu' \rangle = N_\nu N_{\nu'} \sum_{i=1}^{N} \omega_i D_\nu^{(\alpha,\beta)}(x_i) D_{\nu'}^{(\alpha,\beta)}(x_i), \qquad (26)$$

where

$$D_\nu^{(\alpha,\beta)}(x) = P_\nu^{(\alpha,\beta)}(x)[(\alpha + \tfrac{1}{2})(1+x) - (\beta + \tfrac{1}{2})(1-x)] - 2(1-x^2)P_\nu^{(\alpha,\beta)}(x)x^n. \qquad (27)$$

2.4. *The potential matrix elements*

There are two ways to evaluate the matrix elements of the different potential functions. The computationally more efficient method, as employed by Carter and Bowman in the normal coordinate programs 'multimode' [13] and by others, is to expand the potential energy function as a power series in the internal coordinates used in the calculation. For Radau symmetrized coordinate variables this means

$$V(s_{2a}, s_{2b}, s_{4x}, s_{4y}, s_{4z}) = \sum_{ijklm} C_{ijklm} s_{2a}^i s_{2b}^j s_{4x}^k s_{4y}^l s_{4z}^m. \qquad (28)$$

With this form of V, the matrix elements are separable and can be computed by the Gaussian quadrature in each dimension using standard Gauss–Jacobi quadrature based on $P_M^{(\alpha,\beta)}$ with $M > \max(\nu, \nu')$. This method is simple and quick but necessarily approximate.

To obtain a complete expression for the matrix elements it is necessary to use multidimensional quadratures. The full matrix elements over an arbitrary angular potential energy function can be evaluated using 5-dimensional quadrature. Taking advantage of the symmetry of the basis but not the quadrature this gives an expression

$$\langle abdef, \Gamma | V | a'b'd'e'f', \Gamma' \rangle = \sum_{\alpha=1}^{M_2} \sum_{\beta=1}^{M_2} \sum_{\gamma=1}^{M_4} \sum_{\delta=1}^{M_4} \sum_{\epsilon=1}^{M_4} \omega_{\alpha\beta\gamma\delta\epsilon} \Psi_{abdef}^{\Gamma}(\alpha\beta\gamma\delta\epsilon) \times \Psi_{a'b'd'e'f'}^{\Gamma'}(\alpha\beta\gamma\delta\epsilon) V(\alpha\beta\gamma\delta\epsilon) \qquad (29)$$

where $\alpha\beta$ and $\gamma\delta\epsilon$ represent points in quadrature of s_2 and s_4, respectively, and $\omega_{\alpha\beta\gamma\delta\epsilon}$ is the corresponding product of weights. This approach is very demanding on both memory and CPU time. As in [2], we therefore derived formulae for symmetrized quadrature that require only evaluation of the potential function at the reduced set of unique points given by $M_2 \geqslant \alpha \geqslant \beta \geqslant 1$ and $M_4 \geqslant \gamma \geqslant \delta \geqslant \epsilon \geqslant 1$. This complicates the expression for the potential matrix elements as this symmetriation mixes different components (denoted Γ_i below) for degenerate representations. The new expression is:

$$\langle abdef, \Gamma | V | a'b'd'e'f', \Gamma' \rangle = \frac{1}{h} \sum_{\alpha=1}^{M_2} \sum_{\beta=1}^{\alpha} \sum_{\gamma=1}^{M_4} \sum_{\delta=1}^{\gamma} \sum_{\epsilon=1}^{\delta} \omega'_{\alpha\beta\gamma\delta\epsilon} V(\alpha\beta\gamma\delta\epsilon) \times \sum_{i}^{h} \Psi_{abdef}^{\Gamma_i}(\alpha\beta\gamma\delta\epsilon) \Psi_{a'b'd'e'f'}^{\Gamma'_i}(\alpha\beta\gamma\delta\epsilon), \qquad (30)$$

where h, the degree of degeneracy, is 1, 2, 3 for A, E and F representations, respectively. The new weight $\omega'_{\alpha\beta\gamma\delta\epsilon}$ is related to the standard weight $\omega_{\alpha\beta\gamma\delta\epsilon}$ by a factor W, that depends on the number of symmetry related occurrences of the given geometry (see table 2).

The new algorithm is not only more efficient in computer time, since it significantly reduces the number of potential evaluations, but also it uses much less memory because fewer wavefunctions are stored in memory at the integration points. In practice the speed-up is a factor of between 3 and 12, depending on the details of the problem under investigation, and the overall memory requirement is reduced by a factor of more than 10.

Table 2. Weighting factor W for the possible combination of symmetrized angular grid points.

ν_2 case	ν_4 case	Grid points	W
1	1	$\alpha\alpha\gamma\gamma\gamma$	1
1	2	$\alpha\alpha\gamma\gamma\epsilon$	3
1	3	$\alpha\alpha\gamma\delta\delta$	3
1	4	$\alpha\alpha\gamma\delta\epsilon$	6
2	1	$\alpha\beta\gamma\gamma\gamma$	2
2	2	$\alpha\beta\gamma\gamma\epsilon$	6
2	3	$\alpha\beta\gamma\delta\delta$	6
2	4	$\alpha\beta\gamma\delta\epsilon$	12

Besides taking the maximum advantage of symmetry in the computation, our program also provides a way of fully treating the redundancy problem for XY_4 systems. We have coded both methods of computing potential energy matrix elements. The more approximate, expansion based, method was used for most of our test calculations to save time, but the final answers presented below are based on the evaluation of the complete angular potential of Schwenke and Partridge [14]. For testing purposes, we used an approximate Radau angular potential obtained as a fitting from the global methane potential function given by Schwenke and Partridge [14] in the form

$$V(s_{2a}, s_{2b}, s_{4x}, s_{4y}, s_{4z}) = C_{20000}(s_{2a}^2 + s_{2b}^2) + C_{00200}(s_{4x}^2 + s_{4y}^2 + s_{4z}^2). \tag{31}$$

3. Computational details

3.1. *Redundancy*

Redundancies in angular coordinates can occur whenever an atom is bonded to more than three other atoms (or more than two in a plane). XY_4 molecules are prototypes for the redundancy problem that arises because only three independent vectors can be defined in ordinary 3 dimensional space, so that one bond vector may always be written as a linear combination of the other three.

For tetrahedral molecules the relation between the internal vectors can be written using the determinant equation (5). The six linear combinations of the six ω_{ij} define the five symmetrized coordinate variables $(s_{2a}, s_{2b}, s_{4x}, s_{4y}, s_{4z})$ and a redundancy coordinate variable s_r. The redundancy coordinate is determined entirely by the other five, i.e. s_r is a function $s_r(s_{2a}, s_{2b}, s_{4x}, s_{4y}$ and $s_{4z})$, and it must transform with A_1 symmetry.

There are a number of different approximate approaches to treating the redundancy problem for XY_4 molecules. Halonen [7] expressed the six bond angles as a second-order power series expansion in the five symmetrized coordinates. Raynes *et al.* [8], derived an analytical approximation for s_r using a Taylor expansion in terms of the symmetrized coordinate variables. These two approaches have so far been employed only for low lying vibrational states in XY_4 molecules, for which no exact solution of the redundancy problem has been employed. Here we test the Taylor expansion method and a new procedure based on fitting expansion coefficient of s_r.

Through sixth order, the Taylor expansion for s_r can be written as

$$s_r = \sum_{n=1}^{15} A_n f_n,$$

with

$$\begin{aligned}
f_1 &= s_{4x}^2 + s_{4y}^2 + s_{4z}^2,\\
f_2 &= s_{4x}s_{4y}s_{4z},\\
f_3 &= s_{4x}^4 + s_{4y}^4 + s_{4z}^4,\\
f_4 &= (s_{2a}^2 + s_{2b}^2)(s_{4x}^2 + s_{4y}^2 + s_{4z}^2),\\
f_5 &= s_{4x}^2 s_{4y}^2 + s_{4x}^2 s_{4z}^2 + s_{4y}^2 s_{4z}^2,\\
f_6 &= (s_{2a}^3 - 3s_{2a}s_{2b}^2)(s_{4x}^2 + s_{4y}^2 + s_{4z}^2),\\
f_7 &= (s_{2a}^2 + s_{2b}^2)s_{4x}s_{4y}s_{4z},\\
f_8 &= s_{4x}s_{4y}s_{4z}(s_{4x}^2 + s_{4y}^2 + s_{4z}^2),\\
f_9 &= s_{4x}^2 s_{4y}^2 s_{4z}^2,\\
f_{10} &= (s_{4x}^2 + s_{4y}^2 + s_{4z}^2)(s_{4x}^4 + s_{4y}^4 + s_{4z}^4),\\
f_{11} &= (s_{2a}^2 + s_{2b}^2)(s_{4x}^4 + s_{4y}^4 + s_{4z}^4),\\
f_{12} &= (s_{2a}^2 + s_{2b}^2)(s_{4x}^2 s_{4y}^2 + s_{4x}^2 s_{4z}^2 + s_{4y}^2 s_{4z}^2),\\
f_{13} &= (s_{2a}^4 + s_{2b}^4 + 2s_{2a}^2 s_{2b}^2)(s_{4x}^2 + s_{4y}^2 + s_{4z}^2),\\
f_{14} &= s_{2a}(s_{2a}^2 - 3s_{2b}^2)(s_{2a}^2 + s_{2b}^2)(s_{4x}^2 + s_{4y}^2 + s_{4z}^2),\\
f_{15} &= s_{4x}^6 + s_{4y}^6 + s_{4z}^6.
\end{aligned} \tag{32}$$

Here A_n are the coefficients of the expansion and f_n are basis functions that must have A_1 symmetry. These expressions can be compared with those of Raynes *et al.* [8], whose fourth-order Taylor expansion contained ten terms. Through fourth order our expression contains only five terms, i.e. $n \leqslant 5$ in equation (32), since the other lower order terms presented by Raynes *et al.* can be shown to make a zero contribution [16].

Table 3 gives numerical values for the coefficients obtained using Taylor expansions up to second, fourth and sixth order. We actually tested Taylor expansions through tenth order, but found little sign of convergence in this series or our results obtained using them. An alternative approach was therefore adopted and it was decided to fit the coefficients A_n to computed values of our redundancy coordinate at the points defined by our numerical integration procedure. Table 3 also gives coefficients for our best fit, defined as the one that reproduced s_r with the smallest standard deviation σ, for 1000 integration points located about the minimum of the potential. We tested a number of other fits but found our results to be fairly insensitive to the fit employed, providing that it was reliable. It should be noted that the expansion coefficients given in table 3 are molecule inde-

Table 3. Coefficients A_n of the expansion of the redundancy coordinates (see equation (32)).

	Taylor expansion			Fit
Order	2	4	6	6
A_1	0.088 388	0.088 388	0.088 388	0.089 289
A_2		0.353 553	0.353 553	−0.438 848
A_3		−0.005 064	−0.005 064	0.023 515
A_4		0.008 286	0.008 286	0.014 551
A_5		0.174 015	0.174 015	0.004 119
A_6			0.004 510	−0.153 037
A_7			0.198 874	−0.138 866
A_8			0.287 262	0.225 502
A_9			0.720 486	0.065 709
A_{10}			0.106 242	−0.072 155
A_{11}			0.003 639	0.040 529
A_{12}			0.116 614	−0.062 144
A_{13}			0.004 714	0.547 565
A_{14}			0.027 063	−0.360 509
A_{15}			−0.008 703	−0.008 703
σ	0.121 91	0.084 142	0.091 25	0.019 341

Table 4. Absolute energies of the A_1 bending vibrational state number I (in cm^{-1}) as a function of the expansion used for the redundancy coordinate s_r. Energies are given relative to the $s_r = 0$ calculation, which neglects the redundancy condition.

		Taylor expantion			Fit
Order	$s_r = 0$	2	4	6	6
$I = 1$	3 431.274	0.140	0.274	0.306	0.343
2	5 984.535	0.454	0.916	1.177	1.039
3	6 440.637	0.255	0.283	0.302	0.401
4	7 222.189	1.112	1.610	1.942	2.137
5	7 445.158	0.568	0.916	0.902	1.205
6	7 896.552	0.210	0.281	0.303	0.302
7	8 409.484	1.526	2.414	2.358	3.638
8	8 489.778	1.236	2.245	3.269	2.339
9	8 886.749	0.573	0.898	1.079	1.113
10	8 955.060	0.668	0.952	1.191	1.175
11	9 380.661	0.301	0.304	0.267	0.532
21	10 949.659	2.883	4.832	7.928	4.499
31	11 969.963	5.922	7.424	7.976	12.498
41	12 789.834	1.318	2.843	2.491	3.827
51	13 366.135	5.905	9.527	17.469	7.710
61	13 982.622	2.891	4.417	4.089	6.366
71	14 459.499	1.581	1.892	1.939	2.320
81	14 743.727	5.818	7.348	11.539	8.779
91	15 138.463	4.621	6.344	6.927	7.970
101	15 463.334	2.802	4.199	5.867	4.930
121	16 023.862	5.270	9.086	14.585	10.359
141	16 610.863	5.325	4.525	5.983	5.194
161	17 053.193	2.947	6.751	7.869	4.988
181	17 468.922	1.299	6.444	8.723	7.754
201	17 872.361	5.234	5.013	21.564	18.944
221	18 176.821	12.735	16.334	18.637	21.182
241	18 529.023	3.327	2.753	3.159	3.414
261	18 867.521	17.947	20.188	19.422	20.635
281	19 192.338	14.180	20.614	25.141	27.550
301	19 396.017	12.982	16.545	21.171	24.859
321	19 664.849	3.042	5.658	3.921	7.641
341	19 891.067	−0.298	4.169	3.221	3.602
360	20 145.897	3.860	19.458	15.191	22.465

pendent: although we explicitly consider methane here they should be appropriate for other XY$_4$ tetrahedral molecules.

We have used the approximate expression of s_r in our equation for the symmetrized Radau angular kinetic operator (13), and tested the various approximations. Table 4 gives A$_1$ symmetry energy levels for methane computed using the approximate expansion coefficients for s_r given in table 3. The results show that in all cases the effect of the redundancy condition increases significantly with vibrational excitation. For states up to 6000 cm^{-1} above the ground state, the redundancy condition has a rather minor ($\sim$0.1 cm^{-1}) effect on the band origins. For higher states this effect can reach 30 cm^{-1}. Again the results obtained for the lower vibrational levels are fairly insensitive to the method of representing s_r, but for higher levels significant differences (up to 10 cm^{-1}) occur between different methods. In general the sixth-order Taylor expansion appears to overestimate the contribution of s_r. We consider results obtained by fitting s_r to be the most reliable because this expansion reproduces s_r much more accurately.

3.2. *Basis set convergence*

Table 5 shows the convergence of our calculations with increasing basis set size for an A$_1$ symmetry calculation on methane. The energy levels of other symmetries show similar behaviour on the size of the highest Jacobi polynomial used in each 1-dimensional bending basis set N. The results were computed using the $M = N + 3$ rule [15] for numerical quadrature, (meaning that for $N = 20$ we used 23 quadrature points per coordinate), and using the fitted expression for s_r. Table 5 shows that N should be at least 20 to obtain converged results for the higher bending states. With $N = 20$, the dimension of the A$_1$ secular matrix is 2405. Comparing the $N = 20$ and $N = 18$ calculations shows that most energies below 15 500 cm^{-1}, the lowest 100 A$_1$ bending states, are converged to within 0.3 cm^{-1}. There are 4 exceptions to this, all of which are shown in table 5 ($I = 66, 70, 72$ and 74), whose energies are converged to only within 3 cm^{-1}. For the lowest 60 states, which lie up 10 000 cm^{-1} above the ground state, $N = 18$

Table 5. A_1 bending vibrational state number I as a function of 1-dimensional basis set size N, based on the expansion used for the redundancy coordinate s_r. Absolute energies in cm^{-1} are given for $N = 20$; for $N < 20$ the results are given as the difference from the $N = 20$ result.

I	20	18	17	16	15
1	3430.93	0.00	0.00	0.00	0.00
11	9380.13	0.00	0.00	0.00	0.00
21	10945.11	0.01	0.04	0.05	0.14
31	11956.91	0.12	0.44	0.59	1.03
41	12785.98	0.00	0.02	0.03	0.07
51	13357.46	0.17	0.79	0.81	1.35
61	13976.08	0.03	0.15	0.18	0.65
66	14215.41	2.87	6.91	1.35	0.42
70	14317.19	2.17	7.71	6.61	12.38
71	14457.15	0.00	0.02	0.03	0.14
72	14463.83	1.65	4.78	3.95	10.37
75	14551.37	1.39	4.47	4.64	10.49
81	14732.99	0.39	1.56	1.81	4.51
91	15129.37	0.22	0.91	1.32	2.55
94	15232.15	0.08	0.41	0.36	2.34

is sufficient to get good convergence. Tests showed similar convergence behaviour for calculations with A_2, E, F_1 and F_2 symmetry.

4. Results

Using a Jacobi polynomial basis set defined by $N = 18$ gives secular problems of dimension 1550, 1355, 2898, 4063 and 4235 for A_1, A_2, E, F_1 and F_2 symmetries, respectively. This basis is sufficient to converge the results presented to within $0.3\,\mathrm{cm}^{-1}$. These calculations used a fully coupled angular potential function, and as a result they took 1 week on one processor of a 250 MHz DEC alpha DS20 workstation. It should be noted that potential evaluations were performed only for the A_1 calculations and then reused for the other symmetries since they shared the same quadrature grid. The calculations were performed using the *ab initio* methane potential calculated by Schwenke and Partridge [14]. Table 6 considers only pure bending states whose experimental band origins are known; a full set of calculated bending vibrational band origins for methane, covering all 5 symmetries, has been placed in the journal archive.

Schwenke and Partridge's calculations [14], also given in table 6, include full bend–stretch coupling. This is undoubtedly the major difference between their results and ours. It can be seen that for methane, as already concluded from our stretch-only calculations presented in [2], bend–stretch coupling produces significant shifts in the vibrational band origins. The importance of these stretch–bend coupling effects for methane means that little is to be gained from a direct comparison of our results with the experimental data. However, we note that our method is capable of getting converged results over the entire range of energies for which experimental data are available, which extends to over $25\,000\,\mathrm{cm}^{-1}$. This suggests that with the inclusion of stretch–bend coupling this procedure should be capable of addressing problems that cannot be tackled by other variational approaches.

Table 6. Band origins, (in cm^{-1}), of the bending vibrational states of methane using the potential energy surface of Schwenke and Partridge [14].

$\nu_1\nu_2\nu_3\nu_4$	Observed	[14]	This work
0001	1310.76 [17]	1311.76	1288.59
0100	1533.33 [17]	1533.26	1443.12
0002	2587.04 [17]	2589.92	2451.29
0002	2614.26 [17]	2616.30	2542.08
0002	2624.62 [17]	2627.40	2720.34
0101	2830.32 [17]	2831.77	2792.49
0101	2846.08 [17]	2847.04	2868.45
0200	3063.65 [17]	3063.74	2916.06
0200	3065.14 [17]	3065.74	3255.06
0003	3870.49 [18]	3878.34	3726.43
0003	3909.18 [18]	3917.83	3927.77
0003	3920.50 [18]	3929.98	3773.67
0003	3930.50 [18]	3940.98	3836.44
0102	4104.61 [18]	4109.08	4065.97
0102	4128.72 [18]	4136.63	3894.45
0102	4133.02 [18]	4140.19	4205.02
0102	4142.86 [18]	4150.21	3987.77
0102	4151.22 [18]	4159.19	4126.59
0102	4161.87 [18]	4169.73	3947.02
0201	4348.70 [18]	4355.27	4374.71
0201	4363.59 [18]	4369.53	4395.11
0300	4592.00 [18]	4599.15	4649.99
0300	4595.27 [18]	4599.15	4640.74
0300	4595.45 [18]	4599.45	4696.99

5. Conclusion

We have developed a fully symmetrized, general variational method for treating the bend-only vibrational motions of XY_4 systems. Particularly important for computational efficiency is our procedure for computing matrix elements over the potential energy surface by considering only the unique points on the surface. Our method includes explicit consideration of the redundancy coordinates, albeit with some approximation. We find that for methane including this redundancy condition accurately is essential for bending vibrational states lying 6000 cm^{-1} or more above the ground state.

Test calculations performed on methane extend very considerably the range of bending states for which converged variational results have been obtained. A comparison of our results with previous low energy studies confirms our previous conclusion [2] that stretch–bend coupling is strong in methane. The results reported here for the bending motions, and in part 1 [2] for the stretching motion represent the first steps in our development of a general fully coupled, symmetrized, variational procedure for XY_4 systems appropriate for treating much higher levels of vibrational excitation than have been considered so far. We are presently working on a general computer program to use these stretching and bending results as a basis for fully coupled, 9-dimensional calculations.

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