A finite basis representation Lanczos calculation of the bend energy levels of methane

Xiao-Gang Wang\textsuperscript{a)} and Tucker Carrington, Jr.\textsuperscript{b)}

Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-ville, Montréal (Québec) H3C 3J7, Canada

(Received 5 November 2002; accepted 2 January 2003)

We present a method for computing bend energy levels of a five-atom molecule. We use polyspherical coordinates in terms of which both the kinetic energy operator and its associated volume element are simple. The basis functions we use are new. They are parity-adapted combinations of products of spherical harmonics and an associated Legendre function. We show that in the parity-adapted basis it is possible to evaluate matrix-vector products efficiently, despite the fact that the parity-adapted functions are not products of functions of a single variable. The method is applied to compute bend levels of methane. Within each parity block we use the symmetry-adapted Lanczos algorithm to compute levels labeled by irreps of a four-member group that contains the parity operator and the permutation of two of the four hydrogen atoms. In a future publication we shall use the bend wave functions as contracted basis functions to compute numerically exact vibrational levels of methane. © 2003 American Institute of Physics. [DOI: 10.1063/1.1554735]

I. INTRODUCTION

To calculate energy levels accurately and to assign them with confidence one must compute eigenvectors and eigenvalues of a matrix representation of the Hamiltonian. This variational approach has been used to study many three-atom and a few four-atom molecules.\textsuperscript{1–6} Variational methods have been used to compute vibrational levels of three-atom molecules for more than two decades.\textsuperscript{1} The first such calculations for four-atom molecules appeared a little less than 10 years ago.\textsuperscript{7–10} Very recently the first calculations for a molecule with five atoms (methane) have appeared in the literature.\textsuperscript{11,12} Progress is slow because both the CPU time and the in-core memory required to compute energy levels grow dramatically as the number of atoms is increased.

It is now possible to calculate vibrational energy levels of five-atom molecules for three reasons: (1) computers have become much more powerful; (2) theorists have learned that it is possible to write kinetic energy operators (KEOs) in a simple and compact fashion; (3) new techniques have been developed for choosing good basis functions and computing eigenvalues of very large vibrational Hamiltonian matrices. All of these reasons are important but theoretical chemists have clearly contributed only to (2) and (3).

Two strategies for computing energy levels, once the KEO has been chosen, are in common use. Either one uses product basis functions and an iterative method that exploits the simplicity of the product structure\textsuperscript{6,7,13,14–20} or contracted basis functions and a direct method that exploits the small size of the contracted basis.\textsuperscript{4,5,21–23} If one wishes to compute a small number of levels of a five-atom molecule it is possible to use product basis functions and an iterative method, but to make this approach feasible it is necessary to remove some basis functions from the basis; the resultant basis is no longer a direct product basis.\textsuperscript{12} A very advantageous option, that is not yet popular, combines the advantages of an iterative method for computing eigenvalues and the advantages of a contracted basis for representing wave functions.\textsuperscript{24–27} At the present time it seems that the only way to compute more than a few vibrational levels of a five-atom molecule is to use this sort of combination. In a forthcoming paper we shall use the combined iterative eigensolver/contracted basis we proposed in Ref. 26 to calculate vibrational levels of methane.\textsuperscript{28} To do this calculation we must first compute the bend energy levels of methane (with stretch coordinates set equal to their equilibrium values).

In this paper we present the results of the bend calculation. As coordinates we use the polyspherical angles between Radau vectors.\textsuperscript{29,30} To compute energy levels we use the Lanczos algorithm.\textsuperscript{31} As basis functions we use a new set of parity adapted combinations of products of associated Legendre polynomials and plane wave functions. The basis functions we use are similar to the bend functions commonly used for four-atom molecules.\textsuperscript{32,33} To the best of our knowledge, we are the first to do a five-dimensional nondirect product basis calculation of this kind to compute five-dimensional (5-d) bend levels. There are two dihedral angles ranging from 0 to 2\(\pi\) and three planar angles ranging from 0 to \(\pi\).

Matrix elements of the KEO in our finite basis representation (FBR) are extremely simple. Matrix elements of the potential are computed using Gauss quadrature.\textsuperscript{34} Our coordinates have the important advantage that they simplify the KEO and the volume element but they make exploiting the full symmetry of methane impossible. Our computed energy levels and those of Xie and Tennyson (XT)\textsuperscript{35} are quite different. For example, their \(\nu_3\) fundamental (1288.59 cm\(^{-1}\)) is about 50 cm\(^{-1}\) lower than the value we compute. Their fundamental bands are all below the experimental values. Our
fundamental bands are all above the experimental values. To check our results we have also done discrete variable representation (DVR) calculations using the DVR functions that correspond to \((m = 0)\) Legendre polynomials and plane wave functions. Our DVR and FBR energy levels are essentially identical.

The discrepancy between our results and those of Xie and Tennyson may be due in part to deficiencies of the symmetrized coordinates they use. Their five symmetrized coordinates are linear combinations of the cosines of six inter-Radau vector angles. They do not always uniquely specify the shape of the methane molecule (see the Appendix). The ranges of the symmetrized coordinates are interdependent. The KEO of XT appears to be derived from a KEO in six (redundant) coordinates that is itself not a valid KEO. The discrepancy may also be due to the failure of XT to consider the complicated volume element associated with their KEO.

It should be stressed that it is meaningless to compare the reduced-dimension bend levels with experimental results. To interpret and understand the experimental results one must consider both the stretches and the bends. Nonetheless the bend calculation that is the subject of this paper is an essential component of the contracted/iterative calculation for the full problem.

The vibrational spectrum of methane is of considerable interest. Several full dimensional calculations have been reported. Wang and Sibert have done a high order perturbation theory calculation. Carter and Bowman have done vibrational self-consistent field and vibrational configuration interaction calculations. The methods used in these studies are approximate. Impressive variational calculations were reported by Schwenke (details should be forthcoming). Recently Yu did a DVR calculation (removing some basis functions) and reported results for the four fundamental bands. Convergence of the stretch fundamental is however poor. It is important to have good variational methods for tetrahedral \(XY_4\) molecules.

II. THEORY

A. Kinetic energy operator and parity-adapted basis

It is possible to choose coordinates to take advantage of the full symmetry of methane. However, if one uses such coordinates one faces two difficulties. First, the most natural set of symmetry coordinates, the six angles between the four Radau vectors, is redundant. Instead, one imposes a redundancy condition and defines five nonredundant symmetrized coordinates. Xie and Tennyson have derived a KEO in terms of these coordinates. Their KEO is complicated but certainly usable. The second difficulty is more important: the volume element associated with the symmetrized coordinate KEO is so complicated that it makes using these coordinates extremely difficult. Xie and Tennyson appear to have used a unit volume element with their symmetrized KEO but this is incorrect.

Rather than using symmetrized coordinates we use 4 + 1 Radau vectors and their associated polyspherical coordinates. See Fig. 1. In these “orthogonal coordinates,” the kinetic energy operator has the important advantage that it does not have momentum stretch-bend coupling terms. The \(J=0\) bend KEO is written (we use atomic units) as

\[
T_b = -\left[\frac{1}{2\mu_1 r_1^2} + \frac{1}{2\mu_0 r_0^2}\right] \left[\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \theta_1 \frac{\partial}{\partial \theta_1}\right] - \frac{1}{\sin \theta_2} (l_{2z} + l_{3z})^2 + \left[\frac{1}{2\mu_2 r_2^2} + \frac{1}{2\mu_0 r_0^2}\right] l_2^2 + \frac{1}{\mu_0 r_0^2} l_3^2 - (l_{2z} + l_{3z})^2
- i(l_{2z} + l_{3z}) \frac{\partial}{\partial \theta_1} + \cot \theta_1 (l_{2z} + l_{3z}) (l_{2z} + l_{3z}) \right].
\]

FIG. 1. 4 + 1 Radau vectors where \(B\) is the canonical point associated with carbon atom (not shown). The polyspherical angles are also defined in this diagram.

In the case of methane, \(\mu_i, i = 0,1,2,3\) is the mass of the hydrogen atom. The operators \(l_{2k}, l_{3k}\), and \(l_{ik}\) are angular momentum operators in terms of \(\theta_k, \phi_k, k = 2,3\). All the stretch coordinates take their equilibrium values for the 5D bend calculation. This KEO must be used with the volume element \(\sin \theta_1 \sin \theta_2 \sin \theta_3 \sin \theta_4 d\theta_1 d\theta_2 d\theta_3 d\theta_4 d\phi_1 d\phi_2 d\phi_3 d\phi_4\).

We use parity adapted basis functions that are linear combinations of the product functions,

\[
|l_1, l_2 m_2, l_3 m_3\rangle = \Theta_i^{m_1}(\theta_1) Y_i^{m_2}(\theta_2, \phi_2) Y_i^{m_3}(\theta_3, \phi_3)
\]

with

\[
Y_i^m(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \Theta_i^m(\theta) e^{im\phi},
\]

where \(\Theta_i^m(\theta)\) are normalized associated Legendre function with the \((-1)^m\) Condon–Shortley phase factor. An auxiliary quantum number \(m_1 \equiv -(m_2 + m_3)\) is used in all the matrix elements in this paper.

The effect of the parity operator on a function of \((\theta_1, \theta_2, \phi_2, \theta_3, \phi_3)\) is \(\hat{P}(\theta_1, \theta_2, \phi_2, \theta_3, \phi_3) = f(\theta_1, \theta_2, 2\pi - \phi_2, \theta_3, 2\pi - \phi_3)\). In particular, for the product basis in Eq. (2), we have \(\hat{P}|l_1, l_2 m_2 l_3 m_3\rangle = |l_1, l_2 m_2 l_3 m_3\rangle\). We have deliberately chosen the phase of the basis functions in Eq. (2) so that they transform without a prefactor under the parity operation. The basis functions we used in Ref. 26 were chosen similarly. Because there is no prefactor, the parity-adapted basis can be easily written as...
with

$$N_{m_2,m_3} = \frac{1}{\sqrt{1 + \delta_{m_2,0}\delta_{m_3,0}}} \quad \text{where } \bar{m} = -m, m_3 \geq 0, \text{ and } P = 0 \text{ and } 1 \text{ correspond to even and odd parity, respectively.}$$

The quantum number \( m_2 \) assumes the values:

\[
m_2 \in [0, m_{\text{max}}] \quad (m = 0),
\]

\[
m_2 \in [-m_{\text{max}}, m_{\text{max}}] \quad (m > 0),
\]

and the combination \( P = 1 \) and \( m_2 = m_3 = 0 \) is not allowed. \( m_{\text{max}} \) is the maximum value of \( m_2, m_3, \) and \( m_1 \). These restrictions apply to all the matrix-vector products involving parity-adapted basis functions. An even parity-adapted basis function is

\[
u_{l_{12},m_2,m_3}^{0} = \frac{1}{\sqrt{2\pi}} \Theta_{l_{1}}^{m_{1}}(\theta_{1}) \Theta_{l_{2}}^{m_{2}}(\theta_{2}) \Theta_{l_{3}}^{m_{3}}(\theta_{3}) \cos(m_2\phi_2 + m_3\phi_3)
\]

and an odd parity-adapted basis function is (after removing the factor \( i \))

\[
u_{l_{12},m_2,m_3}^{1} = \frac{1}{\sqrt{2\pi}} \Theta_{l_{1}}^{m_{1}}(\theta_{1}) \Theta_{l_{2}}^{m_{2}}(\theta_{2}) \Theta_{l_{3}}^{m_{3}}(\theta_{3}) \sin(m_2\phi_2 + m_3\phi_3)
\]

This parity-adapted basis is new.

The FBR basis we use has two important advantages. First, in the nondirect product FBR basis all matrix elements of the KEO are formally finite. This is not the case if one uses a direct product FBR basis (or the equivalent DVR) composed of \((m = 0)\) Legendre polynomials. The infinite matrix elements do not cause a problem if \( \theta \) quadrature points near 0 and \( \pi \) can be discarded (because close to these points the potential is large and the wave functions are small). This is the case (at least for low-lying states) for methane. Second, matrix elements of the KEO in the FBR basis are very simple.

**B. Kinetic matrix elements**

In the non-parity-adapted product basis, the bend kinetic terms have simple matrix elements,

\[
\langle l_{1},l_{2},m_{2},l_{3},m_{3}\mid T_{b}\mid l_{1},l_{2},m_{2},l_{3},m_{3}\rangle = \frac{1}{2\mu_{0}r_{0}^{2}} \delta_{m_{2},0} \delta_{m_{3},0}
\]

\[
\langle l_{1},l_{2},m_{2}+1,l_{3},m_{3}\mid T_{b}\mid l_{1},l_{2},m_{2},l_{3},m_{3}\rangle = \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},1}^{-} \lambda_{l_{2},m_{2}}^{+}
\]

\[
\langle l_{1},l_{2},m_{2},l_{3},m_{3}+1\mid T_{b}\mid l_{1},l_{2},m_{2},l_{3},m_{3}\rangle = \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},m_{3}}^{+}
\]

\[
\langle l_{1},l_{2},m_{2},l_{3},m_{3}+1\mid T_{b}\mid l_{1},l_{2},m_{2},l_{3},m_{3}\rangle = \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},m_{3}}^{+}
\]

where

\[
\lambda_{l,m}^{\pm} = \sqrt{i(l+1) - m(m \pm 1)}.
\]

In the parity-adapted basis the diagonal matrix elements of the KEO are obtained from the right-hand side of Eq. (8). The off-diagonal matrix elements are

\[
\langle u_{l_{1},l_{2},m_{2}+1,l_{3},m_{3}}^{P} \mid T_{b} \mid u_{l_{1},l_{2},m_{2},l_{3},m_{3}}^{P} \rangle
\]

\[
= \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},m_{3}}^{+}
\]

\[
\langle u_{l_{1},l_{2},m_{2}+1,l_{3},m_{3}}^{P} \mid T_{b} \mid u_{l_{1},l_{2},m_{2},l_{3},m_{3}}^{P} \rangle
\]

\[
= \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},m_{3}}^{+}
\]

where

\[
f_{m_{2},m_{3}} = \frac{1 + (-1)^{P} \delta_{m_{2},0}\delta_{m_{3},0}}{\sqrt{1 + \delta_{m_{2},0}\delta_{m_{3},0}}}.
\]

Whenever a parity-adapted basis is used one must be careful to ensure that matrix elements for basis functions with values of the restricted \( m \) index close to zero are correct. For the parity-adapted basis we use in this paper one must use the following equations for matrix elements with basis functions with \( m_{3} = 0 \):

\[
\langle u_{l_{1},l_{2},-m_{2},l_{3},m_{3}}^{P} \mid T_{b} \mid u_{l_{1},l_{2},m_{2},l_{3},m_{3}}^{P} \rangle
\]

\[
= (-1)^{P} \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},0}^{+} \quad (m_{2} > 0),
\]

\[
\langle u_{l_{1},l_{2},-m_{2},-l_{3},m_{3}}^{P} \mid T_{b} \mid u_{l_{1},l_{2},m_{2},l_{3},m_{3}}^{P} \rangle
\]

\[
= (-1)^{P} \frac{1}{2\mu_{0}r_{0}^{2}} \lambda_{l_{1},m_{1}}^{-} \lambda_{l_{2},m_{2}}^{+} \lambda_{l_{3},0}^{+} \quad (m_{2} > 0).
\]

Using Eqs. (8), (10), and (11) for the nonzero parity-adapted matrix elements of the KEO we can now evaluate kinetic matrix-vector products. Because of the simplicity of the kinetic energy matrix the cost of the matrix-vector products scales as \( N \) (the size of the complete basis).
C. Potential matrix elements and matrix-vector products

We use Gauss quadrature to calculate the potential matrix elements in the parity-adapted basis. We present a detailed explanation only for the odd parity case (an equation for the even parity basis is given at the end of this subsection). The potential matrix elements are

$$
\langle x_{l'} | \mathcal{V} | x_{l}, m'_{l}, m_{l} \rangle = \sum_{a_1, a_2, a_3} T_{a_1}^{(m_1)} T_{a_2}^{(m_2)} T_{a_3}^{(m_3)} \int_{0}^{\pi} d\phi_2 \int_{0}^{\pi} d\phi_3 \sin(m'_2 \phi_2 + m'_3 \phi_3) 
\times \sin(m_2 \phi_2 + m_3 \phi_3) V(\theta_{a_1}, \theta_{a_2}, \theta_{a_3}, \phi_2, \phi_3).
$$

(12)

The integrals over \( \phi_2 \) and \( \phi_3 \) are done using a trapezoidal rule with quadrature points and weights

$$
\phi_{\beta} = \frac{2 \pi}{n_{\phi}}, \quad w_{\beta} = \frac{2 \pi}{n_{\phi}},
$$

where \( n_{\phi} \) is even, \( \beta = 1, \ldots, n_{\phi} \) for \( \phi_2 \), and \( \beta = 1, \ldots, n_{\phi}/2 \) for \( \phi_3 \). We introduce two sets of transformation matrices for the above-given quadrature:

$$
T_{m}^{\beta_{\phi}} = \left( \frac{1}{2 \pi} \right)^{1/4} \sqrt{w_{\phi}} \cos(m \phi_{\beta}),
$$

$$
T_{m}^{\beta_{\theta}} = \left( \frac{1}{2 \pi} \right)^{1/4} \sqrt{w_{\theta}} \sin(m \phi_{\beta}),
$$

(17)

where \((\beta, m) = (\beta_2, m_2)\), or \((\beta_3, m_3)\). Now we can evaluate the integral as (we drop the \( a_1 a_2 a_3 \) indices from \( I_{m_2 m_2', m_{m_3}}^{a_1 a_2 a_3} \) and \( V_{\beta_2 \beta_3}^{a_1 a_2 a_3} \) hereafter for brevity)

$$
I_{m_2 m_2', m_{m_3}}^{a_1 a_2 a_3} = \sum_{l_1} T_{a_1}^{(l_1)} T_{a_2}^{(m_2)} T_{a_3}^{(m_3)} \sum_{l_2} \sum_{l_3} \sum_{l_3'} T_{l_1}^{(m_1)} T_{l_2}^{(m_2)} T_{l_3}^{(m_3)} x_{l_1}, l_2, m_2, l_3, m_3.
$$

(15)

This technique of doing sums sequentially is used in many papers.

The parity-adapted basis enables us to calculate even and odd states separately (of course one expects the even and odd states to be very nearly degenerate because the inversion barrier separating the two equivalent forms of methane is very high). Not surprisingly, to calculate only the odd (or only the even) states one needs a basis half as large as the basis that would be required to calculate both the even and the odd states. However, the odd wave functions are nonzero in both methane wells and it might therefore appear that even to calculate only the odd wave functions one will need twice as many quadrature points as would be required to calculate wave functions localized in only one well. In fact, the number of required quadrature points can be reduced by about a factor of 2 by exploiting the property,

$$
V_{\beta_2 \beta_3}^{a_1 a_2 a_3} = V(\theta_{a_1}, \theta_{a_2}, \theta_{a_3}, \phi_{\beta_2}, \phi_{\beta_3})
= V(\theta_{a_1}, \theta_{a_2}, \theta_{a_3}, 2\pi - \phi_{\beta_2}, 2\pi - \phi_{\beta_3}).
$$

This is done by rewriting Eq. (13),

$$
I_{m_2 m_2', m_{m_3}}^{a_1 a_2 a_3} = \frac{1}{2 \pi} \int_{0}^{\pi} d\phi_2 \int_{0}^{\pi} d\phi_3 \sin(m_2 \phi_2 + m_3 \phi_3) \sin(m'_2 \phi_2 + m'_3 \phi_3)
\times \sin(m_2 \phi_2 + m_3 \phi_3) V(\theta_{a_1}, \theta_{a_2}, \theta_{a_3}, \phi_2, \phi_3).
$$

(16)

Hereafter the limits of all sums over \( \beta_2 \) and \( \beta_3 \) are as indicated in Eq. (18).

We choose an even (instead of an odd) number of trapezoidal points because we divide the integration range into [0, \( \pi \)] and [\( \pi, 2 \pi \)] and use Gauss–Chebychev quadrature of the first kind in each interval. Using the same points for \( \phi_2 \) and \( \phi_3 \) facilitates exploiting exchange symmetry (see Sec. II C and Ref. 28).

The overlap integral

$$
1 \int_{0}^{\pi} d\phi_2 \int_{0}^{\pi} d\phi_3 \sin(m_2 \phi_2 + m_3 \phi_3) \sin(m'_2 \phi_2 + m'_3 \phi_3)
$$

(19)

is evaluated exactly by the Gauss–Chebychev quadrature with \( n_{\phi} = 2(m_{\text{max}} + 1) \) points. The total number of quadrature points is \( 2(l_{\text{max}} + 1)^2(m_{\text{max}} + 1)^2 \). Note that the spherical harmonic basis requires \( l_{\text{max}} = m_{\text{max}} \).
We now discuss evaluating potential matrix-vector products. As indicated in Eq. (15) the sums over \( l_1, l_2, \) and \( l_3 \) are done sequentially. We demonstrate that it is also possible to do the sums over \( m_2 \) and \( m_3 \) and over \( \beta_2 \) and \( \beta_3 \) sequentially. After evaluating sums over \( l_1, l_2, \) and \( l_3 \) and dropping the \( \alpha_1, \alpha_2, \alpha_3 \) indices, the central sum of Eq. (15) becomes:

\[
\begin{align*}
\mathbf{u}^{\prime}_{m_2^l m_3^l} &= 2 \left( \sum_{\beta_2} T^{e}_{m_2^l, \beta_2} \sum_{\beta_3} T^{c}_{m_3^l, \beta_2} \sum_{\beta_3} T^{c}_{m_3^l, \beta_3} + \sum_{\beta_2} T^{e}_{m_2^l, \beta_2} \sum_{\beta_3} T^{c}_{m_3^l, \beta_2} \sum_{\beta_3} T^{e}_{m_3^l, \beta_3} \right) \\
& \times V\beta_2 \beta_3 \times \left( \sum_{m_3} T^{c}_{m_3, \beta_2} \sum_{m_2} \sum_{m_2} T^{c}_{m_3, \beta_2} \right) u_{m_2 m_3} \tag{20}
\end{align*}
\]

The cost of this sum scales as \( 4n^2 m^2 + 4n \rho_n m^2 \). If instead one used the transformation matrix \( T_{m_2 m_3, \beta_2 \beta_3} = 1/(\sqrt{2}) \sqrt{w}_{\beta_2} \sqrt{w}_{\beta_3} \sin(m_2 \beta_2 + m_3 \beta_3) \) and did the sums over \( m_2 \) and \( m_3 \) simultaneously and the sums over \( \beta_2 \) and \( \beta_3 \) simultaneously then the cost would scale as \( 2n^2 \rho_n^2 \). If the integral \( I_{m_2^l m_3^l, m_2 m_3} \) were stored and none of the sums were done sequentially, the cost would scale as \( n^3 \). Comparing these options makes the advantage of Eq. (20) obvious. Note that in all of these summations the constraints of Eq. (5) on \( m_2 \) and \( m_3 \) are applied. As a result, the order of all the sums of Eq. (20) must be as presented.

The matrix-vector product in the even parity basis is:

\[
\begin{align*}
\mathbf{u}^{\prime}_{m_2^l m_3^l} &= \sum_{m_2 m_3} I_{m_2^l m_3^l, m_2 m_3} u_{m_2 m_3} \\
&= 2N_{m_2 m_3} \left( \sum_{\beta_2} T^{c}_{m_2^l, \beta_2} \sum_{\beta_3} T^{e}_{m_3^l, \beta_3} + \sum_{\beta_2} T^{c}_{m_2^l, \beta_2} \sum_{\beta_3} T^{e}_{m_3^l, \beta_2} \right) \\
& \times V\beta_2 \beta_3 \times \left( \sum_{m_3} T^{c}_{m_3, \beta_2} \sum_{m_2} \sum_{m_2} T^{e}_{m_3, \beta_2} \right) u_{m_2 m_3} \tag{21}
\end{align*}
\]

The prefactor \( N_{m_2 m_3} \) can be incorporated into the matrix-vector product without jeopardizing the sequential summation algorithm.

### **D. Use of exchange symmetry**

The most obvious way to exploit symmetry when computing energy levels is to introduce symmetry-adapted basis functions. Unfortunately, symmetry adapted basis functions and efficient matrix-vector products are usually mutually incompatible. This is due to the fact that symmetry-adapted basis functions are, in general, not products of functions of a single variable and one needs to exploit product structure to do matrix-vector products efficiently.\(^7\) It has been known for many years that for a four-atom molecule it is possible to use parity-adapted basis functions without sacrificing the favorable scaling of product-basis matrix-vector products.\(^7\) In Sec. II C we demonstrate that this is also true for a five-atom molecule. It is important that we be able to exploit parity, but it would be nice to take advantage of more of the symmetry of methane. If symmetry-adapted basis functions and efficient matrix-vector products are incompatible one can use the symmetry adapted Lanczos (SAL) algorithm.\(^47,48\) The SAL enables one to calculate levels labeled by different irreducible representations as efficiently as if they were computed separately (but it does not decrease the size of vectors).

Using the parity-adapted basis we have divided the levels into even and odd groups. In this subsection we show that it is possible, within each of these groups, to use the SAL to calculate levels that are symmetric and antisymmetric with respect to the exchange of \( H \) atom 2 and \( H \) atom 3. The Radau coordinates we use have the advantage that they simplify the KEO but using Radau coordinates it is impossible to exploit the full symmetry of methane. The complete nuclear permutation inversion group of methane is \( G_{48} \) (Ref. 49) which is a direct product of \( (E,E^*) \) and a group, \( G_{24} \), that is isomorphic to \( T_d \). The coordinates and basis functions we use allow us to label levels with irreps of a symmetry group \( G_4 \) composed of \( (E,E^*,(23),(23)^*) \). Our choice for the names of the irreps of \( G_4 \) is presented in Table I. We choose the names so that \( A^- \) and \( B^- \) correlate with \( A_1^- \) and \( A_2^- \) of \( G_{48} \).\(^49\) The group \( G_4 = \{E,E^*\} \otimes (E,(23)^*) \). We denote \( (E,(23)^*) \) as \( G_2 \). Because our basis is parity-adapted, we can work with the subgroup \( G_2 \). Under the \( (23)^* \) operation the basis functions transform as:

\[
(23)^* u_{l_1 l_2 l_3} = (-1)^P u_{l_1 l_2 l_3} \quad \text{for } m_2 \geq 0
\]

\[
(23)^* u_{l_1 l_2 l_3} = u_{l_1 l_2 l_3} \quad \text{for } m_2 < 0.
\]

It is now easy to write down projection operators for the \( G_2 \) group. This enables us to use the SAL to calculate \( A \) and \( B \) levels using as few matrix-vector products as would be required to calculate them separately. We have used the five-vector SAL algorithm of Ref. 46 to obtain the \( A \) and \( B \) symmetry levels from one set of matrix-vector products.

Fortunately, being able to label the even and odd parity levels with the irreps \( A \) and \( B \) of \( G_2 \) enables us to unambiguously assign each of the even and odd levels to one of the irreps of \( G_{24} \). From the correlation of the \( G_2 \) and \( T_d (G_{24}) \) groups it can be shown that the \( A \) symmetry of \( G_2 \) correlates with the following \( T_d \) group symmetry species: \( A_1 \), \( E_a \), one \( F_1 \) component, and two \( F_2 \) components; and that the \( B \) symmetry of \( G_2 \) correlates with the following \( T_d \) group symmetry species: \( A_2 \), \( E_b \), two \( F_1 \) components, and one \( F_2 \) component. Using these correlations the symmetry labeling can be done unambiguously. If a doubly degenerate pair of levels appears in the \( A \) block of our calculation, we know the levels have \( F_2 \) symmetry (and we know that the third equal level in the \( B \) block also has \( F_2 \) symmetry). If a nondegenerate level appears in both the \( A \) and \( B \) blocks, we know that the levels have \( E \) symmetry. If a doubly degenerate pair of levels appears in the \( B \) block of our calculation, we know the levels have \( F_1 \) symmetry (and that the equal level in the \( A \) block also has \( F_1 \) symmetry). Levels that are not degenerate and only in the \( A \) block are \( A_1 \) levels and that are not degenerate and only in the \( B \) block are \( A_2 \). An example is given in Table
II to show how the $G_2$ symmetry enables one to unambiguously assign $T_d$ symmetry labels. For Table II we have deliberately chosen a relatively small basis so that two types of splittings (discussed in Sec. III) are discernible.

Exploiting symmetry enables us to calculate levels more efficiently, to assign a $T_d$ symmetry label to each level, and it also helps us to assign zeroth-order quantum numbers to the levels we calculate. For each zeroth-order level, labeled by $(n_2, n_4)$, where $n_2$ is the total number of quanta with $\nu_2$ and $n_4$ is the total number of quanta with $\nu_4$, one can obtain its symmetry components by decomposing $E^{n_2} \otimes F^{n_4}$ into constituent irreps. In a harmonic uncoupled picture the levels labeled by the different irreps are all degenerate. In reality they are very close. To make assignments we start with the lowest level and work up matching the irrep labels obtained by decomposing the irrep labels of our computed levels. Owing to the fact that methane has only two distinct bend normal mode frequencies, the assignment (at least for the lower levels) is rather easy.

**E. DVR test calculations**

Any calculation of the bend energy levels of methane is very complex. Even if the KEO and the corresponding volume element are correct there are many places where an error might occur. Errors can easily be made in the calculation of the KEO matrix elements, the quadratures used to obtain potential matrix elements, and the loop structure employed to calculate matrix-vector products. Due to the fact that the KEO has very few terms the method we used is quite simple. The simplicity clearly makes it easier to write an error free program. Nonetheless it is very sure that the program does not have errors we have also calculated the first few levels of methane using a pure DVR approach. The results of the DVR calculation clearly confirm that our FBR program is free of errors. For example, the DVR and FBR zero point energies agree to more than 10 digits! In this subsection we briefly describe the DVR calculation.

For the DVR calculation one needs to rearrange the KEO so that each term is a product of Hermitian and anti-Hermitian factors.\(^7\) We have found a very simple method to do this. We simply write the vibrational angular momentum operators, which appear in Eq. (1), in terms of anti-Hermitian momentum operators:

$$l_x = i(\sin \phi p_\phi + \cot \theta p_\theta),$$

$$l_y = i(- \cos \phi p_\phi + \cot \theta p_\theta),$$

$$l_z = -i \rho_\phi,$$

where

$$p_\phi = \frac{\partial}{\partial \theta} + \frac{1}{2} \cot \theta,$$

$$p_\phi^c = \cos \phi \frac{\partial}{\partial \phi} - \frac{1}{2} \sin \phi,$$

$$p_\phi^s = \sin \phi \frac{\partial}{\partial \phi} + \frac{1}{2} \cos \phi, \quad (23)$$

$$p_\phi = \frac{\partial}{\partial \phi}.$$

The resulting KEO has been given by Yu.\(^\text{12}\) It has 25 terms and is much more complicated than the operator of Eq. (1). The FBR basis has the advantage that despite the singularities of the KEO ($\theta = 0, \pi$) all KEO matrix elements are rigorously finite. For methane the singularities are probably unimportant (at least for the low-lying levels): it is semirigid and its equilibrium structure is far from the points of singularity. This implies that a direct product basis is probably adequate. For the $\theta$ angles we use the PO-DVR basis\(^\text{30,51}\) obtained from a DVR that corresponds to $(m = 0)$ Legendre polynomials. For the $\phi$ angles we use Meyer’s DVR.\(^5\) This sort of approach was recently taken by Yu.\(^\text{12}\) Note, however, that for $\theta$ he uses DVR, rather than PODVR, functions, and that he discards basis functions. Because we want very accurate DVR levels (to compare them with our FBR levels) we do not discard DVR functions. We use the same potential ceiling value as in the FBR calculation (see Sec. III).

It is not only the KEO employed for the FBR calculation that is compact, the FBR basis itself is also compact. Let us compare a FBR basis with $m_{\text{max}} = l_{\text{max}}$, and a direct product DVR (after parity-adaptation) with $l_{\text{max}}+1$ functions for each of the $\theta$ angles and $2l_{\text{max}}+1$ functions for each of the $\phi$ angles. The FBR basis size for the 5-D calculation is about a factor of 8 smaller than the DVR basis size (it is 3 times smaller for the three angles of a four-atom molecule and 2 times smaller for a pair of spherical polars). The size of

**TABLE I.** Character table and definition of irreducible presentations of $G_4$.\(^a\)

<table>
<thead>
<tr>
<th>irrep.</th>
<th>$E$</th>
<th>$(23)^*$</th>
<th>$E^*$</th>
<th>$(23)^*$</th>
</tr>
</thead>
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<tr>
<td>$A^+$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B^+$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
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<tr>
<td>$A^-$</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
</tr>
<tr>
<td>$B^-$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$Irreducible representation names based on effects of $E$ and $(23)^*$.

**TABLE II.** Demonstration of how the $G_2$ symmetry label (A or B) is used to assign $T_d$ symmetry labels (for an $l_{\text{max}}=m_{\text{max}}=25$ basis).

<table>
<thead>
<tr>
<th>$A$ block</th>
<th>$n_2n_4;T_d$ sym</th>
<th>$B$ block</th>
<th>$n_2n_4;T_d$ sym</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>00:A$_1$</td>
<td>1342.6313</td>
<td>01:F$_2$</td>
</tr>
<tr>
<td>1342.6313</td>
<td>01:F$_2$</td>
<td>1572.5488</td>
<td>10:E</td>
</tr>
<tr>
<td>1342.6315</td>
<td>01:F$_2$</td>
<td>2683.3738</td>
<td>02:F$_2$</td>
</tr>
<tr>
<td>1572.5488</td>
<td>10:E</td>
<td>2690.6454</td>
<td>11:F$_2$</td>
</tr>
<tr>
<td>2660.8619</td>
<td>02:A$_1$</td>
<td>2911.9767</td>
<td>11:F$_1$</td>
</tr>
<tr>
<td>2683.3738</td>
<td>02:F$_2$</td>
<td>2919.1175</td>
<td>11:F$_1$</td>
</tr>
<tr>
<td>2683.3739</td>
<td>02:F$_2$</td>
<td>2919.1180</td>
<td>11:F$_1$</td>
</tr>
<tr>
<td>2690.6454</td>
<td>02:E</td>
<td>3147.8273</td>
<td>20:E</td>
</tr>
<tr>
<td>2911.9750</td>
<td>11:F$_2$</td>
<td>3987.2151</td>
<td>03:F$_2$</td>
</tr>
<tr>
<td>2911.9767</td>
<td>11:F$_2$</td>
<td>4029.3979</td>
<td>03:F$_1$</td>
</tr>
<tr>
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<td>11:F$_1$</td>
<td>4029.3998</td>
<td>03:F$_1$</td>
</tr>
<tr>
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<td>4036.4170</td>
<td>03:F$_2$</td>
</tr>
<tr>
<td>3147.8273</td>
<td>20:E</td>
<td>4036.4170</td>
<td>03:F$_2$</td>
</tr>
<tr>
<td>3987.2151</td>
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<td>4036.4150</td>
<td>03:F$_2$</td>
</tr>
<tr>
<td>3987.2226</td>
<td>03:F$_3$</td>
<td>4036.4150</td>
<td>03:F$_2$</td>
</tr>
<tr>
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<tr>
<td>4029.3998</td>
<td>03:F$_1$</td>
<td>4036.4150</td>
<td>03:F$_2$</td>
</tr>
<tr>
<td>4036.4150</td>
<td>03:F$_2$</td>
<td>4036.4170</td>
<td>03:F$_2$</td>
</tr>
</tbody>
</table>
the parity-adapted DVR basis is nearly equal to the number of quadrature points (after using the inversion symmetry to reduce their number by a factor of 2) used in our FBR calculation. Although the DVR basis is much larger the levels computed using the FBR and DVR basis sets are of comparable accuracy. The DVR basis is a direct product basis and does not satisfy the right boundary conditions.

III. RESULTS

We use the T8 potential surface of Schwenke described in Ref. 11. It is an accurate \textit{ab initio} global surface and has been used for some previous vibrational calculation.\textsuperscript{11,35} On this surface, the equilibrium bond length is 2.05791 \textit{a}_0. The potential energy surface is a function of Radau coordinates defined using nuclear masses. In our KEO we use atomic masses. This slight inconsistency has a very small effect on our results. To limit the spectral range of the Hamiltonian potential energy surface is a function of Radau coordinates.

It is important to assess the extent to which the energy levels are converged. If the number of basis functions and quadrature points is insufficient two types of spurious splittings occur: (1) levels within an \textit{A} or a \textit{B} block that should be exactly degenerate (\textit{F}, \textit{A} levels in the \textit{A} block and \textit{F}, \textit{B} levels in the \textit{B} block) will be split (type I); (2) levels in the \textit{A} and \textit{B} blocks that should be degenerate (\textit{E}, \textit{F}, or \textit{A} \textit{B} levels) will be split (type II). We find that as the size of the basis is increased splittings of type \textit{II} decrease very rapidly. For example, for the \nu_4 level for which two of the \textit{F} levels are in the \textit{A} block and one of the \textit{F} levels is in the \textit{B} block, the splitting between one of the \textit{A} levels and the \textit{B} level is as small as 7 \times 10^{-5} \textit{cm}^{-1} for a modest basis with \textit{l}_\text{max} = m_\text{max} = 19. Splittings of type \textit{I} are always larger than splittings of type \textit{II}. In Fig. 2 we plot, for the \nu_4 state, and as a function of the basis size, the splitting (type \textit{I}) of the \textit{F} levels in the \textit{A} block, and the difference between an \textit{F} level and the value we deem converged (computed with \textit{l}_\text{max} = m_\text{max} = 30). For all the levels in Table I we find that the splitting error is always less than the convergence error but that both errors are on the same order of magnitude and decrease exponentially as the basis size increases. This demonstrates that our basis is very efficient. For the \nu_4 level in Fig. 2, we find that the splitting error is about a factor of 2 smaller than the convergence error. It is useful to know that the splitting error and convergence error tend to zero at the same rate because this enables one to estimate the convergence error without doing calculations with larger basis sets. Note that in almost all cases the splitting of type \textit{I} is large enough that it is clear that two \textit{F} (\textit{F}) levels in the \textit{B} (\textit{A}) block are not numerical copies generated by the (nonorthogonalized) Lanczos algorithm.

In Table III we present odd levels up to those in the \textit{n}_2 \textit{n}_4=5 polyad and in addition the (0,6) band. We use a basis with \textit{l}_\text{max} = m_\text{max} = 29 and about 10 000 SAL iterations. We have also calculated even levels with this basis. The odd–even splitting for the ground state is on the order of 10^{-7} \textit{cm}^{-1}, which is very close to zero, in accordance with the high inversion barrier. For all but a few levels the difference between our reported levels and those computed with \textit{l}_\text{max} = m_\text{max} = 30 is less than 0.001 \textit{cm}^{-1}. The difference is largest for the lowest (23;\textit{F}) level for which it is about 0.005 \textit{cm}^{-1}. The same level also has the largest type \textit{I} splitting of 0.0018 \textit{cm}^{-1}. In fact, for the \textit{l}_\text{max} = m_\text{max} = 29 basis, the splitting of the \textit{A} pair of low-lying \textit{F} levels is so small (smaller than 10^{-6} \textit{cm}^{-1}, see Fig. 2) that they are actually taken as copies of one level by our Lanczos code.

The convergence tests we have discussed and the results of Table III are all computed with \textit{l}_\text{max} = m_\text{max}. We have also done calculations with basis sets with \textit{m}_\text{max} < \textit{l}_\text{max}. Whether or not it is necessary to take \textit{m}_\text{max} = \textit{l}_\text{max} depends on the \phi dependence of the potential. For some molecules \textit{m}_\text{max} < \textit{l}_\text{max} is sufficient (see, e.g., Refs. 53, 33, 26). For methane we find that using \textit{m}_\text{max} = \textit{l}_\text{max} is necessary. Note that changing \textit{m}_\text{max} affects the basis size less than changing \textit{l}_\text{max}. For example, a basis set with \textit{l}_\text{max} = 29 and \textit{m}_\text{max} = 10 is of about the same size as a basis set with \textit{l}_\text{max} = m_\text{max} = 25. The latter basis set converge levels much better.
anharmonicity difference, when the initial vector is 49
found to occur at \(n_4\) (in \(\text{cm}^{-1}\)). The size of basis is 6.7
full-dimensional calculation of methane vibrational levels.28
will be discussed in our next paper where we shall present a
assignment procedure exploits knowledge of the
symmetry coordinates. The energy levels of methane may be divided into dif-
fine groups labeled by zeroth-order quantum numbers \((n_2,n_4)\). Our assignment procedure exploits knowledge of the
symmetry of each level but also relies on being able to
distinguish the groups. Our results demonstrate that for the
low-lying levels these groups are well separated. As one
moves up in the spectrum one expects the \((n_2,n_4)\) groups to
begin to overlap. The groups merge because they spread and
because the centers of the groups increase at unequal rates as
n_2 and n_4 are increased. If there were no anharmonicity and
no coupling each group would be a single level and the energy
difference between neighboring groups would be the
same for all groups (it would depend only on the difference
between \(\nu_2\) and \(\nu_4\)). The scalar anharmonicity of the \(\nu_4\)
mode is larger than the scalar anharmonicity of the \(\nu_2\) mode:
\(x_{22} = -2.98 \text{ cm}^{-1}\) and \(x_{44} = -15.63 \text{ cm}^{-1}.\)44 Because of the
anharmonicity difference, when \(n_2\) is increased, the energy
of a group \((n_2,n_4)\) will increase more slowly than when \(n_4\)
is increased. For this reason, as \(n_4\) increases the pure \(\nu_4\)
overtone \((0,n_4)\) could be overtaken by \((n_4-1,0)\). This is
found to occur at \(n_4 = 6\). Indeed, the energy gap \(E_{(n_4-1,0)}
- E_{(n_4-1,0)}\) decreases monotonically from 1088 cm\(^{-1}\) at \(n_4 = 2\) to 290 cm\(^{-1}\) at \(n_4 = 5\), as seen from Table II.

We have two \(A_1\) levels (at 7866.5 and 7882.1 cm\(^{-1}\)) in
the vicinity of the \((5,0)\) group. One of these is an intruder
from the \((0,6)\) group. We tentatively assign the higher level
to the \((0,6)\) group because there is a \((5,0;A_2)\) level (from the
\(B\) block) at 7865.3 cm\(^{-1}\) and we expect the \(A_1\) and \(A_2\) levels
of the \((0,5)\) group to be close to each other. This is the only
level in Table III for which we are not able to establish a
definite assignment based on symmetry alone. This tentative
assignment is confirmed by examining the wave functions
shown in Fig. 3. The calculation of the bend wave function
will be discussed in our next paper where we shall present a
full-dimensional calculation of methane vibrational levels.28
See the Appendix for details on how we solve the redund-
cy relation in order to project the wave function onto
symmetry coordinates.

It is reassuring that we can compute many bend levels of
methane very accurately. However, the bend levels (5-D) are
not physically meaningful. Our main purpose in calculating
the bend levels is obtaining a compact basis that we can use
to solve the full 9-D problem. We find that even with a
\(l_{\text{max}} = m_{\text{max}} = 25\) basis, the largest convergence error for levels
in Table I is 1.0 \text{ cm}^{-1}, which again occurs for the lowest
\((23)F_2\) level. With \(l_{\text{max}} = m_{\text{max}} = 25\), the size of basis is 3.3
\times 10^6 and each SAL iteration takes only 40 s.

### Table III. Bend levels calculated from a basis with \(l_{\text{max}} = m_{\text{max}} = 29\) (in cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>((n_2,n_4;\text{sym}))</th>
<th>Energy</th>
<th>((n_2,n_4;\text{sym}))</th>
<th>Energy</th>
<th>((n_2,n_4;\text{sym}))</th>
<th>Energy</th>
</tr>
</thead>
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<td>04;F1</td>
<td>5380.991</td>
<td>05;F1</td>
<td>6728.536</td>
</tr>
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<td>01;F2</td>
<td>1342.631</td>
<td>04;A1</td>
<td>5387.650</td>
<td>05;F2</td>
<td>6734.804</td>
</tr>
<tr>
<td>10;E</td>
<td>1572.548</td>
<td>13;F2</td>
<td>5552.887</td>
<td>14;E</td>
<td>6855.940</td>
</tr>
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</tr>
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<td>04;F2</td>
<td>5326.244</td>
<td>05;F2</td>
<td>6657.339</td>
<td>32;A1</td>
<td>7375.168</td>
</tr>
<tr>
<td>04;F1</td>
<td>5367.433</td>
<td>05;F2</td>
<td>6713.276</td>
<td>32;A2</td>
<td>7380.528</td>
</tr>
<tr>
<td>04;E</td>
<td>5379.716</td>
<td>05;E</td>
<td>6713.409</td>
<td>32;F1</td>
<td>7390.770</td>
</tr>
</tbody>
</table>
IV. CONCLUSION

We have developed a reliable, numerically exact method for calculating the bend levels of methane. Our method does not enable us to exploit the full symmetry of methane but it has the important advantage of simplicity. We choose coordinates in terms of which the KEO is quite simple. We use angular momentum operators to write the KEO so that most of the kinetic matrix elements are zero and those that are nonzero can be computed from simple closed-form expressions. Potential matrix elements are computed by quadrature.

Our coordinates and KEO are simple. Perhaps the simplest method for calculating the bend levels of methane would entail using the KEO of Eq. (1) and the basis of Eq. (2) and making no attempt to exploit symmetry. Instead, we use the KEO of Eq. (1) and exploit the symmetry in two steps. First, we parity adapt the basis. Second, we use the SAL to exploit the (23) exchange symmetry. We are not taking advantage of the full symmetry of methane. Rather, we exploit as much symmetry as we can without rendering the equations and the program overly complicated. The method we propose is ideal for calculating levels for CXYZ₂ or CX₂Y₂ molecules. It is also very good for CXY₃ molecules, for which none of the levels within a block of the G₂ group are degenerate.

Another strategy has been employed by Xie and Tennyson (XT), who have also recently calculated the bend levels of methane using the same potential surface. Their levels and ours differ significantly. As coordinates they use five symmetrized linear combinations of the six cosines of the the angles between the 4 + 1 Radau vectors. XT appear to have assumed that the volume element is unity. Because the five symmetrized coordinates do not uniquely specify the shape of the molecule (this was noted by Schwenke) they are not good coordinates. Any set of five inter-Radau vector angles also fails to uniquely specify the shape of the molecule. If one can establish a rule that enables one to unambiguously associate a set of five symmetrized coordinate values and a set of five inter-Radau vector angles with a single shape, then it is possible to use both sets of coordinates. The rule we propose is: associate a set of coordinates with the shape with the lowest sₖ (see XT for the definition of sₖ). If such a rule is applied the correct volume element could be obtained from the volume element we use (given after Eq. (1)) by using the chain rule (see Ref. 56)

\[ J = \sin \theta_1 \sin \theta_2 \sin \theta_3 \frac{\partial \phi_2}{\partial \theta_4} \frac{\partial \phi_3}{\partial \theta_5} \frac{\partial (s_{2n}, s_{2b}, s_{3a}, s_{3b}, s_{3c})}{\partial (\theta_1, \theta_2, \theta_3, \theta_4, \theta_5)} \]

where \( \theta_1 \) and \( \theta_5 \) are the Radau angles corresponding to the dihedral angles \( \phi_2 \) and \( \phi_3 \), respectively, and \( \theta_1 \), \( \theta_2 \), and \( \theta_3 \) are as defined in this paper. This volume element is so complicated that it can only be evaluated numerically at points (see Ref. 56). Although it would be possible to absorb the volume element into the wave functions and introduce a pseudopotential term (this has been done for another complicated volume element) doing numerically exact calculations with the symmetrized coordinates of XT would be very difficult. We conclude that for methane and probably for many molecules with high symmetry it is better not to attempt to exploit all of the symmetry but instead to exploit only some of it while maintaining a simple KEO and volume element.

Because we write the KEO in terms of angular momentum operators it is natural to use products of spherical harmonics as basis functions. An obvious disadvantage of such a basis set is the fact that its functions are nonzero for all possible configurations of the methane molecule. In effect, the basis of Eq. (2) includes enough basis functions to represent wave functions of two different methane molecules: one with hydrogen atoms 1, 2, and 3 clockwise and another with hydrogen atoms 1, 2, and 3 counterclockwise. Since we know that the inversion barrier is very high this seems wasteful. Although the parity-adapted basis functions we use are nonzero for all possible configurations of the methane molecule they allow us to calculate only even or only odd wave functions. This means that we require as few basis functions as we would need if we had basis functions that only had nonzero amplitude in a single methane well. This enables us to maintain the simplicity of an approach based on angular momentum operators and spherical harmonics without using
more basis functions than would be necessary if we were computing levels for only one of the two forms of methane.

ACKNOWLEDGMENTS

We are grateful for David Schwenke for providing his potential energy surface. This work has been supported by the Natural Sciences and Engineering Research Council of Canada.

APPENDIX: OBTAINING POLYSPERHAL COORDINATES FROM SYMMETRY COORDINATES

To plot wave functions (Fig. 3) as functions of symmetrized coordinates defined as linear combinations of cosines we must know how to transform from \((s_a, s_b, s_c, s_y, s_z)\) to \((\theta_1, \theta_2, \phi_2, \phi_3)\) (this is also necessary in order to do variational calculation using the symmetrized coordinates, e.g., for evaluating the potential at the quadrature points). In this Appendix we discuss this transformation. To obtain \((\theta_1, \theta_2, \phi_2, \phi_3)\) from \((s_a, s_b, s_c, s_y, s_z)\) we proceed as follows: (1) we compute \(s_i(s_a, s_b, s_c, s_y, s_z)\); (2) we compute six cosines of the inter-Radau vector angles by a linear transformation from the five symmetry coordinates plus \(s_i\); (3) from the six cosines we calculate five of the six \((\theta_1, \theta_2, \phi_2, \phi_3)\). The equation for \(s_i(s_a, s_b, s_c, s_y, s_z)\) is obtained from the redundancy condition. We find

\[
A_0 + A_1 s_r + A_2 s_r^2 + A_3 s_r^3 + A_4 s_r^4 = 0, \tag{A1}
\]

where

\[
A_0 = 1 - (s_a^2 + s_b^2) - (s_c^2 + s_y^2 + s_z^2) + \frac{2}{3} s_a(s_c^2 - 3s_b^2) + \frac{2\sqrt{2}}{3} s_a s_c(s_y^2 - s_z^2) + \frac{1}{3} s_a(s_c^2 + s_y^2) + \frac{1}{3} s_b(s_a^2 - s_z^2) + \frac{1}{3} s_c(s_a^2 + s_y^2 + s_z^2),
\]

\[
A_1 = -\sqrt{\frac{6}{5}} (s_c^2 + s_a^2) + \frac{\sqrt{2}}{3} s_a(s_a^2 - 3s_b^2) + \frac{\sqrt{2}}{3} s_a s_c(s_y^2 - s_z^2) + \frac{6}{5} s_a(s_y^2 - s_z^2),
\]

\[
A_2 = -1 + \frac{1}{2} (s_a^2 + s_b^2) + \frac{1}{2} (s_a^2 + s_y^2 + s_z^2),
\]

\[
A_3 = \frac{2\sqrt{3}}{9},
\]

\[
A_4 = -\frac{1}{12}.
\]

This does not appear to be the same as the equation given by XT. This equation is solved numerically for \(s_r\). We find that depending on the values of \(s_a, s_b, s_c, s_y, s_z\) there are either one or two physical solutions. This means that the five symmetry coordinates do not uniquely determine the shape of the methane molecule. To complete step 1 we need a rule for determining which solution to choose (when there are two). We choose the solution for which \(s_r\) is smaller. This solution has lower energy.

Mladenovic discussed using the five inter-Radau vector angles for variational calculations. But these coordinates also fail to uniquely determine the shape of the molecule. This is because there are almost always two possible (physical) solutions for the sixth angle. Only one solution is given in Eq. (43) of Ref. 43. In this case one could apply the same rule, i.e., choose the solution with lower \(s_r\).

\[\text{References}\]

44. R. N. Zare, Angular Momentum (Wiley, New York 1998).


