

# Exact quantum mechanical vibrational kinetic energy operator of sequentially bonded molecules in valence internal coordinates

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The full nonrelativistic quantum mechanical vibrational ( $J=0$ ) kinetic energy operator for sequentially bonded  $N$ -atom molecules, expressed in valence stretch, bend, and torsion internal coordinates, is explicitly given. Certain properties of the operator and its possible applications are discussed. © 1995 American Institute of Physics.

## I. INTRODUCTION

One of the principal difficulties which had to be overcome to allow accurate calculation of (ro)vibrational spectra of small molecules<sup>1-6</sup> was the derivation of the exact, in the nonrelativistic limit and within the framework of the Born–Oppenheimer approximation, quantum mechanical (ro)vibrational kinetic energy operator,  $\hat{T}$ . The general form, i.e., a form which applies to any  $N$ -atom molecule, of  $\hat{T}$  in normal coordinates was obtained by Watson<sup>7</sup> some 25 years ago. Following the first few calculations using this operator, however, it was realized<sup>8</sup> that valence internal coordinates are a considerably better choice than normal coordinates for but the lowest vibrational levels. The utility of (nonorthogonal) internal coordinates in practical calculations is related to at least four key factors: (i) their use avoids the unfactorizability problem<sup>9</sup> of Watson's rovibrational kinetic energy operator  $\hat{T}_{VR}$ ; (ii) normal coordinate expansions of the potential,  $\hat{V}$ , have a comparatively short convergence radii and the rectilinear nature of the normal coordinates results in unnecessarily long and complicated forms when dealing with high-energy and/or large-amplitude motions; (iii) it might, occasionally, be a problem to choose a reference geometry (linear or nonlinear) to define the normal coordinates, while the use of curvilinear internal coordinates ensures that no difficulties arise at special nuclear arrangements (e.g., at linear configurations); and (iv) while the normal coordinate-Hamiltonian may be more efficient than the one expressed in internal coordinates for the lowest-lying energy levels, it will always lead to convergence problems as the energy levels become more comparable with the barrier height. Thus, derivation of the kinetic energy operator in carefully selected internal coordinates, suitable for the molecule under consideration, seems to be unavoidable.

Derivation of the exact (ro)vibrational quantum mechanical kinetic energy operator of sequentially bonded ( $A-B-C$ ) triatomic molecules, in stretch–stretch–bend internal coordinates, dates back to at least 1966, when Freed and Lombardi,<sup>10</sup> building on an earlier form of  $\hat{T}$  expressed in three bond length coordinates,<sup>11</sup> derived a Hamiltonian in stretch–stretch–bend internal coordinates. However, the form they obtained does not appear to be hermitian.<sup>8c</sup> In 1974, Gribov and Khovrin<sup>12</sup> performed crude vibrational variational calculations on  $H_2O$ , using a stretch–stretch–bend  $\hat{T}_V$

not explicitly given but believed to be exact. Carney, Sprandel, and Kern<sup>13</sup> report that the exact  $\hat{T}_V$  was obtained by them at about the same time. However, it seems that the use of the exact triatomic  $\hat{T}_{VR}$  in valence coordinates started several years later with the work of Carter and Handy,<sup>8c</sup> and that derivation of  $\hat{T}_{VR}$  for tetra-atomic molecules was only attempted in the early 1980's.<sup>14</sup> The first complete, exact, detailed rovibrational kinetic energy operator for tetra-atomic molecules was derived in 1987.<sup>15</sup> Since then efficient computer programs to calculate the rovibrational spectra of triatomic and tetra-atomic molecules have been developed in several groups.<sup>1,2,16-18</sup> Recently, forms for the exact quantum mechanical vibrational kinetic energy operator,  $\hat{T}_V$ , of sequentially bonded ( $A-B-C-D-E$ ) and ( $A,B$ )– $C-D-E$ -type penta-atomic molecules have been reported by the present authors.<sup>19</sup> Hopefully the next few years will bring implementations of these operators for calculation of the vibrational spectra of interesting penta-atomic molecules, like ketene ( $CH_2CCO$ ), and carbon suboxide ( $C_3O_2$ ).

This communication builds on previous efforts of the authors<sup>15,19</sup> and reports the general form of the non-relativistically exact quantum mechanical vibrational kinetic energy operator,  $\hat{T}_V$ , for  $N$ -atom sequentially bonded molecules. After a brief discussion of the theory, which is employed to obtain the formulae all distinct nondifferential, first-derivative, and second-derivative terms in an  $N$ -atomic  $\hat{T}_V$  are presented and reviewed. Finally, possible uses of these operators are discussed.

## II. THEORETICAL FOUNDATIONS

In theoretical molecular spectroscopy, there seem to have been two approaches employed for the derivation of the exact quantum mechanical kinetic energy operator in internal coordinates.<sup>20</sup> The basic difference between the two approaches is in their starting point: while the first approach starts with the classical Lagrangian form of the kinetic energy operator,<sup>21</sup> the second approach<sup>15</sup> begins with the quantum mechanical kinetic energy operator in Cartesian coordinates.

The first, conventional approach writes the classical, Lagrangian form of the kinetic energy,  $T$ , of an  $N$ -atom molecule in terms of the velocities  $\dot{R}_i$  as

$$T = \frac{1}{2} \sum_{i=1}^N m_i \dot{R}_i \cdot \dot{R}_i, \quad (1)$$

where  $m_i$  is the mass of atom  $i$ . Using successive transformations,<sup>22,23</sup> one obtains the formula

$$T = \frac{1}{2} p_q^T G(q) p_q, \quad (2)$$

where  $p_q$  are the momenta conjugate to the internal coordinate  $q$  and  $G(q)$  is the well-known  $G$  matrix of molecular spectroscopy.<sup>23,24</sup> In the next step one employs a formalism, first formulated by Podolsky,<sup>21</sup> to obtain the quantum mechanical operator  $\hat{T}_V$  as

$$\hat{T}_V = -\frac{\hbar^2}{2} g^{1/4} \sum_{i,j} \frac{\partial}{\partial q_i} g^{-1/2} G_{ij} \frac{\partial}{\partial q_j} g^{1/4}, \quad (3)$$

where  $g = \det G$ . This approach leads to the following final form for  $\hat{T}_V$ :

$$\hat{T}_V(q) = \frac{1}{2} \sum_{i,j} p_i G_{ij}(q) p_j + V'(q), \quad (4)$$

where  $p_i = -i\hbar \partial / \partial q_i$  and

$$V'(q) = \frac{\hbar^2}{8} \sum_{i,j} \left( \frac{\partial}{\partial q_i} G_{ij} \frac{\partial \ln g}{\partial q_j} \right) + \frac{\hbar^2}{32} \sum_{ij} \left( G_{ij} \frac{\partial \ln g}{\partial q_i} \frac{\partial \ln g}{\partial q_j} \right). \quad (5)$$

In Eq. (4) the classical-like first term and the purely quantum-mechanical, nondifferential second term are clearly separated. It is important to note that the simple form of  $\hat{T}_V$ , as given in Eq. (4), follows from the choice of the volume element,  $dV = dq_1 dq_2 \dots dq_N$ . Note also that  $V'(q)$  can be regarded as a mass-dependent contribution to the potential energy function.

In this connection we wish to draw attention to a not fully recognized paper by Decius,<sup>24</sup> published in 1948. In that paper he derived (by hand!) all the possible  $G$  matrix elements for bond stretching, bending and torsional internal coordinates, for all 33 acyclic configurations. Decius used the fundamental formulas of Wilson<sup>23</sup> for  $G$  in terms of the  $s$  vectors. Given the appropriate normalization condition this then gives, using Eqs. (4) and (5) above, all  $\hat{T}_V$  operators for these problems. Note that Decius does not derive the messy term Eq. (5), which was not of interest to those who used Wilson's GF formalism. The algebra in the Decius paper is far from trivial; the approach which we now describe, besides obtaining the full  $\hat{T}_V$  operator, will also check the Decius formulae.

The second approach, advocated by Sutcliffe<sup>5</sup> and Handy<sup>15</sup> starts with the simple Laplacian form of the quantum mechanical kinetic energy operator written in Cartesian coordinates  $\{x_{\alpha i}\}$  ( $\alpha = xyz, i = 1, 2, \dots, N$ ) of the  $N$  nuclei in a laboratory fixed frame of reference

$$\hat{T} = -\frac{\hbar^2}{2} \sum_i^N \frac{\nabla_i^2}{m_i} = -\frac{\hbar^2}{2} \sum_i^N \frac{1}{m_i} \sum_{\alpha}^{xyz} \frac{\partial^2}{\partial x_{\alpha i} \partial x_{\alpha i}}. \quad (6)$$

Then, by choosing a set of suitable internal coordinates  $\{q_i\}$  ( $i = 1, 2, \dots, 3N - 6$ ) for the molecule considered and applying the chain rule twice to execute the transformation  $\partial / \partial x_{\alpha i} \rightarrow \partial / \partial q_j$  one can write the exact  $J=0$  kinetic energy operator as

$$\begin{aligned} \hat{T}_V / (-\frac{1}{2} \hbar^2) &= \sum_{jk}^{3N-6} g^{jk} \frac{\partial^2}{\partial q_j \partial q_k} + \sum_j^{3N-6} h^j \frac{\partial}{\partial q_j} \\ &:= \sum_{jk}^{3N-6} \left[ \sum_{\alpha}^{xyz} \sum_i^N \frac{1}{m_i} \left( \frac{\partial q_j}{\partial x_{\alpha i}} \frac{\partial q_k}{\partial x_{\alpha i}} \right) \right] \frac{\partial^2}{\partial q_j \partial q_k} \\ &+ \sum_j^{3N-6} \left( \sum_{\alpha}^{xyz} \sum_i^N \frac{1}{m_i} \frac{\partial^2 q_j}{\partial x_{\alpha i} \partial x_{\alpha i}} \right) \frac{\partial}{\partial q_j}, \quad (7) \end{aligned}$$

where the definitions for the contravariant metric tensor  $g^{jk}$ , and for  $h^j$ , are made evident. Note that, when comparing Eqs. (4) and (7),  $g^{jk} = G_{jk}$  and, of course, it has the same Wilson formula as used by Decius. Calculation of  $g^{jk}$  and  $h^j$  requires knowledge of the explicit dependence of the chosen internal coordinates on the Cartesians. Therefore, it seems most advantageous<sup>19</sup> to define  $g^{jk}$  and  $h^j$  first in a set of internal coordinates for which this functional dependence is especially simple, i.e., in a set of interparticle distance coordinates. However, the number of interparticle distances for a general  $N$ -atom molecule,  $[N \times (N - 1) / 2]$ , is different, apart from tri- and tetra-atomic molecules, from the number of independent internal coordinates,  $(3N - 6)$ . This means that elimination of all Cartesian terms from  $g^{jk}$  and  $h^j$  obtained using Eq. (7) and the interparticle distances as internal coordinates for molecules having more than four atoms requires additional effort, namely expressing the "extraneous" interparticle distance(s) by the selected set of internal coordinates. This step might require involved vector and algebraic manipulations but can be achieved rather easily if only stretch, bend, and torsion internal coordinates are selected to describe the internal motion. The key formula required is the vector position of a fourth atom,  $\mathbf{A}_{i-2}$ , in terms of the position of earlier atoms  $\mathbf{A}_{i-1}$ ,  $\mathbf{A}_i$ ,  $\mathbf{A}_{i+1}$  and the new internal coordinates  $r_{i-2}$ ,  $\Theta_{i-2}$ , and  $\tau_{i-2}$ , and is given as

$$\begin{aligned} \mathbf{A}_{i-2} &= \mathbf{A}_{i-1} - r_{i-2} \cos \Theta_{i-2} \mathbf{A}_i \mathbf{A}_{i-1} \\ &+ r_{i-2} \sin \Theta_{i-2} \sin \tau_{i-2} \frac{\mathbf{A}_i \mathbf{A}_{i-1} \times \mathbf{A}_i \mathbf{A}_{i+1}}{\sin \Theta_{i-1}} \\ &+ r_{i-2} \sin \Theta_{i-2} \cos \tau_{i-2} \frac{\mathbf{A}_i \mathbf{A}_{i+1} - \cos \Theta_{i-1} \mathbf{A}_i \mathbf{A}_{i-1}}{\sin \Theta_{i-1}}, \quad (8) \end{aligned}$$

where  $\mathbf{A}_i \mathbf{A}_{i-1}$  and  $\mathbf{A}_i \mathbf{A}_{i+1}$  are appropriate unit vectors pointing from the first toward the second atom, and definition of the atoms and the internal coordinates is as given in Fig. 1. All interparticle distances can then be calculated in terms of  $r$ ,  $\Theta$ , and  $\tau$ . This procedure results in the introduction of all

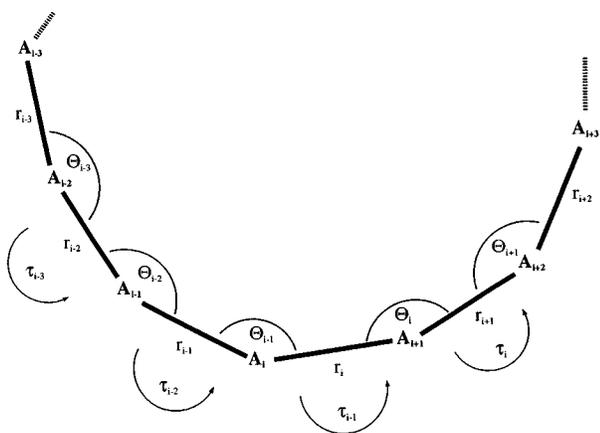


FIG. 1. Atom numbering and definition of ( $r$ ,  $\Theta$ ,  $\tau$ ) internal coordinates for  $N$ -atom molecules. Note that Eq. (8) is consistently used for the consecutively labeled atoms ensuring that the sense of  $\tau$  is always the same as one moves along the chain.

internal coordinates into  $g^{jk}$  and  $h^j$  at this early stage. This presents no difficulty during later algebraic manipulations as derivatives of  $g^{jk}$  and  $h^j$  are never formed, they appear simply as multiplicative terms of the differential operators. It is easy to show that changing from one set of internal coordi-

nates  $\{q'_j\}$  to another set of internal coordinates  $\{q_j\}$  can be achieved by the use of the following expressions:

$$\left( \sum_{\alpha i} \frac{1}{m_i} \frac{\partial q_j}{\partial x_{\alpha i}} \frac{\partial q_k}{\partial x_{\alpha i}} \right) = \sum_{lm} \left( \sum_{\alpha i} \frac{1}{m_i} \frac{\partial q'_l}{\partial x_{\alpha i}} \frac{\partial q'_m}{\partial x_{\alpha i}} \right) \frac{\partial q_j}{\partial q'_l} \frac{\partial q_k}{\partial q'_m} \quad (9a)$$

and

$$\left( \sum_{\alpha i} \frac{1}{m_i} \frac{\partial^2 q_j}{\partial x_{\alpha i} \partial x_{\alpha i}} \right) = \sum_k \left( \sum_{\alpha i} \frac{1}{m_i} \frac{\partial^2 q'_k}{\partial x_{\alpha i} \partial x_{\alpha i}} \right) \frac{\partial q_j}{\partial q'_k} + \sum_{kl} \left( \sum_{\alpha i} \frac{1}{m_i} \frac{\partial q'_k}{\partial x_{\alpha i}} \frac{\partial q'_l}{\partial x_{\alpha i}} \right) \frac{\partial^2 q_j}{\partial q'_k \partial q'_l}. \quad (9b)$$

Repeated application, if necessary, of Eq. (9) produces the desired quantities  $g^{jk} = G_{jk}$  and  $h^j$ . A final transformation, to include the stretching part of the full transformation Jacobian into  $\hat{T}_V$  is carried out as

$$\bar{\hat{T}}_V = s^{1/2} \hat{T}_V s^{-1/2}, \quad (10)$$

where  $s$  is the stretching part of the Jacobian for the transformation from  $\{x_{\alpha i}\}$  to the final set of internal coordinates  $\{q_j\}$  and is simply the square product of the bond lengths. This yields a new form for the operator as

$$\bar{\hat{T}}_V / (-\frac{1}{2} \hbar^2) = \sum_{jk}^{3N-6} g^{jk} \frac{\partial^2}{\partial q_j \partial q_k} + \sum_j^{3N-6} h^j \frac{\partial}{\partial q_j} + 2s^{1/2} \sum_{jk}^{3N-6} g^{jk} \frac{\partial s^{-1/2}}{\partial q_j} \frac{\partial}{\partial q_k} + s^{1/2} \left( \sum_{jk}^{3N-6} g^{jk} \frac{\partial^2 s^{-1/2}}{\partial q_j \partial q_k} + \sum_j^{3N-6} h^j \frac{\partial s^{-1/2}}{\partial q_j} \right). \quad (11)$$

Since here only the stretching part of the full transformation Jacobian has been absorbed into  $\hat{T}_V$ , the volume element is not the same as used during derivation of Eqs. (4) and (5). It then follows that although the coefficients of the second-order differential operators are the same ( $g^{jk} = G_{jk}$ ), the coefficients of the linear operators and the nondifferential term are different. Note that Eqs. (4) and (5) and (11) have the usual Podolsky structure.<sup>21</sup> To ease the notation, in the following  $\hat{T}_V$  will always be written instead of  $\bar{\hat{T}}_V$ .

The second approach was used by the authors to derive kinetic energy operators for sequentially bonded ( $A-B-C-D$ ) and ( $A,B$ )- $C-D$ -type tetra-atomic molecules,<sup>15</sup> and for sequentially bonded ( $A-B-C-D-E$ ) and ( $A,B$ )- $C-D-E$ -type penta-atomic molecules.<sup>19</sup> For actual derivation of the exact quantum mechanical kinetic energy operator, use of computer algebra systems (CAS) and the following scheme is advocated: (a) set up the necessary auxiliary functions, which form the basis of a general-purpose CAS program, for subsequent use; (b) define the masses, the Cartesian coordinates, and the  $(3N-6)$  interparticle distances used as internal coordinates; (c) transform, via Eq. (7), from Cartesian coordinates to the  $(3N-6)$  stretching-type interparticle distances;

(d) eliminate, if necessary, the Cartesians left in  $g^{jk}$  due to the “extraneous” interparticle distance(s) [using Eq. (8) or similar equations]; (e) apply successive transformations, via Eq. (9), from the interparticle coordinates to the final set of internal coordinates; (f) include the stretching part of the Jacobian into  $\hat{T}_V$  through Eq. (11); and (g) simplify the resulting operators.<sup>19</sup>

### III. RESULTS AND DISCUSSION

The derivation, using the CAS scheme<sup>19</sup> reiterated in Sec. II, of  $\hat{T}_V$  for sequentially bonded tetra- and penta-atomic molecules can simply be extended to sequentially bonded molecules of arbitrary size. This stems from the fact that the optimal choice of the internal coordinates is very clear for these molecules. When choosing the internal coordinates  $\{q_i\}$  in which the exact quantum mechanical kinetic energy operator is to be expressed, it is necessary to keep in mind that (a) practical calculations become easier and much insight into the physical nature of the system can be gained if one can find a set of optimal internal coordinates in which the system is nearly separable; (b) the choice of  $\{q_i\}$  not only determines the actual form of  $\hat{T}_V$ , however, it, in turn, affects

TABLE I. Nondifferential, first-derivative, and second-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of sequentially bonded molecules in internal coordinates  $\{r, \Theta, \tau\}$  (see Fig. 1).

Nondiff. term	$\sum_{i=1}^{N-2} \frac{2 \cos \Theta_i}{m_{i+1} R_i R_{i+1}}$	$\frac{\partial^2}{\partial \Theta_i \partial \Theta_i}$	$\frac{1}{\mu_i r_i^2} + \frac{1}{\mu_{i+1} r_{i+1}^2} - \frac{2 \cos \Theta_i}{m_{i+1} r_i r_{i+1}}$
$\frac{\partial}{\partial r_i}$	$-\frac{2 \cos \Theta_{i-1}}{m_i r_{i-1}} - \frac{2 \cos \Theta_i}{m_{i+1} r_{i+1}}$	$\frac{\partial^2}{\partial \Theta_i \partial \Theta_{i+1}}$	$2 \cos \tau_i \left( -\frac{1}{\mu_{i+1} r_{i+1}^2} + \frac{\cos \Theta_i}{m_{i+1} r_i r_{i+1}} + \frac{\cos \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} \right)$
$\frac{\partial}{\partial \Theta_i}$	$\left( \frac{1}{\mu_i r_i^2} + \frac{1}{\mu_{i+1} r_{i+1}^2} \right) \cot \Theta_i - \frac{2 \cos \tau_{i-1} \sin \Theta_{i-1}}{m_i r_{i-1} r_i}$ $+ \frac{4 \sin \Theta_i - 2 \operatorname{cosec} \Theta_i}{m_{i+1} r_i r_{i+1}} - \frac{2 \cos \tau_i \sin \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}}$	$\frac{\partial^2}{\partial \Theta_i \partial \Theta_{i+2}}$	$-\frac{2 \sin \tau_i \sin \tau_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} - \frac{2 \cos \tau_i \cos \tau_{i+1} \cos \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}}$
$\frac{\partial}{\partial \tau_i}$	$\frac{2 \sin \tau_i \sin \Theta_i \cot \Theta_{i+1}}{m_{i+1} r_i r_{i+1}} + \frac{2 \sin \tau_{i-1} \sin \Theta_{i-1} \operatorname{cosec} \Theta_i}{m_i r_{i-1} r_i}$ $+ \frac{2 \sin \tau_i \cot \Theta_i \sin \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} - \frac{2 \sin \tau_{i+1} \sin \Theta_{i+2} \operatorname{cosec} \Theta_{i+1}}{m_{i+3} r_{i+2} r_{i+3}}$	$\frac{\partial^2}{\partial \Theta_i \partial \tau_i}$	$2 \sin \tau_i \left( \frac{\cot \Theta_{i+1}}{\mu_{i+1} r_{i+1}^2} - \frac{\cos \Theta_i \cot \Theta_{i+1}}{m_{i+1} r_i r_{i+1}} - \frac{\operatorname{cosec} \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} \right)$
$\frac{\partial^2}{\partial r_i \partial r_i}$	$1/\mu_i = 1/m_i + 1/m_{i+1}$	$\frac{\partial^2}{\partial \Theta_i \partial \tau_{i+1}}$	$-2 \sin \tau_i \operatorname{cosec} \Theta_{i+1} \left( -\frac{1}{\mu_{i+1} r_{i+1}^2} + \frac{\cos \Theta_i}{m_{i+1} r_i r_{i+1}} + \frac{\cos \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} \right)$ $+ \frac{2 \cot \Theta_{i+2}}{m_{i+2} r_{i+1} r_{i+2}} (-\sin \tau_i \cos \tau_{i+1} + \cos \tau_i \sin \tau_{i+1} \cos \Theta_i)$
$\frac{\partial^2}{\partial r_i \partial r_{i+1}}$	$\frac{2 \cos \Theta_i}{m_{i+1}}$	$\frac{\partial^2}{\partial \Theta_i \partial \tau_{i+2}}$	$-\frac{2 \operatorname{cosec} \Theta_{i+2}}{m_{i+2} r_{i+1} r_{i+2}} (\sin \tau_i \cos \tau_{i+1} - \cos \tau_i \sin \tau_{i+1} \cos \Theta_{i+1})$
		$\frac{\partial^2}{\partial \tau_i \partial \tau_i}$	$\frac{\operatorname{cosec}^2 \Theta_i}{\mu_i r_i^2} + \frac{\cot^2 \Theta_i}{\mu_{i+1} r_{i+1}^2} + \frac{\cot^2 \Theta_{i+1}}{\mu_{i+1} r_{i+1}^2} + \frac{\operatorname{cosec}^2 \Theta_{i+1}}{\mu_{i+2} r_{i+2}^2}$ $+ \frac{2 \cos \tau_i \cot \Theta_i \cot \Theta_{i+1}}{\mu_{i+1} r_{i+1}^2}$
$\frac{\partial^2}{\partial r_i \partial \Theta_i}$	$-\frac{2 \sin \Theta_i}{m_{i+1} r_{i+1}}$		$-\frac{2 \operatorname{cosec} \Theta_i \cot \Theta_i}{m_{i+1} r_i r_{i+1}} - \frac{2 \cos \tau_i \operatorname{cosec} \Theta_i \cot \Theta_{i+1}}{m_{i+1} r_i r_{i+1}}$ $-\frac{2 \operatorname{cosec} \Theta_{i+1} \cot \Theta_{i+1}}{m_{i+2} r_{i+1} r_{i+2}} - \frac{2 \cos \tau_i \operatorname{cosec} \Theta_{i+1} \cot \Theta_i}{m_{i+2} r_{i+1} r_{i+2}}$
		$\frac{\partial^2}{\partial \tau_i \partial \tau_{i+1}}$	$2 \operatorname{cosec} \Theta_{i+1} \left( \frac{\cos \tau_i \cot \Theta_i + \cot \Theta_{i+1}}{\mu_{i+1} r_{i+1}^2} + \frac{\cos \tau_{i+1} \cot \Theta_{i+2} + \cot \Theta_{i+1}}{\mu_{i+2} r_{i+2}^2} \right)$ $- \frac{2 \cos \tau_i \operatorname{cosec} \Theta_i}{m_{i+1} r_i r_{i+1}} - \frac{2 \cos \tau_{i+1} \operatorname{cosec} \Theta_{i+2}}{m_{i+3} r_{i+2} r_{i+3}}$ $- \frac{2}{m_{i+2} r_{i+1} r_{i+2}} [\cot^2 \Theta_{i+1} + \operatorname{cosec}^2 \Theta_{i+1}$ $+ \cos \tau_i \cot \Theta_i \cot \Theta_{i+1} + \cos \tau_{i+1} \cot \Theta_{i+1} \cot \Theta_{i+2}$ $+ \cot \Theta_i \cot \Theta_{i+2} (\cos \tau_i \cos \tau_{i+1} + \sin \tau_i \sin \tau_{i+1} \cos \Theta_{i+1})]$
$\frac{\partial^2}{\partial r_i \partial \Theta_{i+1}}$	$\frac{2 \sin \Theta_i \cos \tau_i}{m_{i+1} r_{i+1}}$	$\frac{\partial^2}{\partial \tau_i \partial \tau_{i+2}}$	$\frac{\cos \tau_i \operatorname{cosec} \Theta_i \operatorname{cosec} \Theta_{i+1}}{\mu_{i+1} r_{i+1}^2} - \frac{\operatorname{cosec} \Theta_{i+1}}{m_{i+1} r_i r_{i+1}} [\cos \tau_i \cot \Theta_i$ $+ \cot \Theta_{i-1} (\cos \tau_{i-1} \cos \tau_i + \sin \tau_{i-1} \sin \tau_i \cos \Theta_i)]$ $- \frac{\operatorname{cosec} \Theta_i}{m_{i+2} r_{i+1} r_{i+2}} [\cos \tau_i \cot \Theta_{i+1} + \cot \Theta_{i+2} (\cos \tau_i \cos \tau_{i+1}$ $+ \sin \tau_i \sin \tau_{i+1} \cos \Theta_{i+1})]$
		$\frac{\partial^2}{\partial r_i \partial \tau_{i+1}}$	$\frac{\operatorname{cosec} \Theta_{i+1} \operatorname{cosec} \Theta_{i+3}}{m_{i+3} r_{i+2} r_{i+3}} (-\cos \tau_{i+1} \cos \tau_{i+2}$ $+ \sin \tau_{i+1} \sin \tau_{i+2} \cos \Theta_{i+2})$

the choice of the basis set for the expansion of the wave function through occurrences of unavoidable singularities in the Hamiltonian,  $\hat{H}_V$ . It is important to emphasize this last point, as to facilitate efficient practical calculations of vibra-

tional spectra  $\hat{H}_V$  should be separable and factorizable.<sup>9</sup> Combined consideration of these factors dictate the use of simple, elementary internal coordinates in the derivation of  $\hat{T}_V$ . In summary, for sequentially bonded molecules one

should use the simple, unsymmetrized stretching, angle bending, and torsion coordinates (see Fig. 1), as use of these coordinates ensures the required properties of  $\hat{T}_V$  and, at the same time, these coordinates are usually appropriate for the expansion of the potential energy for semirigid molecules.

Once the internal coordinate system is selected for a certain class of molecules, the appropriate  $G$ -matrix elements can be obtained<sup>23–24</sup> which, in turn, determine the form of the kinetic energy operator [see Eq. (4)]. It must be realized that even for an  $N$ -atom sequentially bonded molecule there are only a few distinct  $G$ -matrix elements<sup>24</sup> as coordinates having no common atom have zero off-diagonal  $G$  elements. This fact is exploited in the present case to derive the exact quantum mechanical kinetic energy operator for this class of compounds. In Fig. 1 a seven-atom molecule is depicted, which is the smallest sequentially bonded molecule having an arrangement which produces all the distinct  $\hat{T}_V$  terms, as only in this case would the first and last torsions have one and only one atom in common. As can easily be verified, there are only twenty distinct terms in the exact  $\hat{T}_V$  of sequentially bonded molecules and all of them are given in Table I. Note that while all terms which arise in the full  $\hat{T}_V$  of sequentially bonded molecules can be derived from the terms given in Table I, indexing of the masses, distances and angles may need special attention. For example, while the operator  $\partial^2/\partial r_i \partial \Theta_i$  should be premultiplied by  $-2 \sin \Theta_i/m_{i+1}r_{i+1}$  (see Table I), the operator  $\partial^2/\partial r_i \partial \Theta_{i-1}$  should be premultiplied by  $-2 \sin \Theta_i/m_i r_{i-1}$ . Note that the coefficients of the second derivative operators in Table I are, as required and emphasized in Sec. II, precisely the distinct  $G$ -matrix elements, first derived by Decius, of the problem.<sup>24,25</sup>

Finally, application of the elegant general operator form presented in Table I needs to be addressed. In principle, it could be used for variational evaluation of vibrational energy levels of  $N$ -atom molecules. However, since, at present, it seems practical to carry out full variational calculations in no more than seven dimensions, this puts a severe restriction on the size of the system which could be handled. Even if fixed expansion functions are used for certain internal coordinates, as suggested previously by the authors,<sup>19</sup> the largest system for which the bend-only spectrum could be obtained probably has only six atoms, while an eight-atom molecule seems to be the largest system for which calculation of the stretch-only vibrational spectrum seems to be feasible. If the full, exact form of the operator is too complicated, it is always possible to delete or to replace certain of the operators by some average of their values. Approximate kinetic energy operators for local vibrational modes<sup>26</sup> and bender models<sup>27</sup> are examples of this nature. Derivation of these operators for larger systems could possibly follow from the present exact results. Application of the exact (or simplified) operators is also envisioned in scattering theory or in quantum Monte Carlo methods.<sup>28</sup>

#### IV. CONCLUSIONS

Distinct features of modern computer algebra systems (e.g., their highly functional programming language, numerous, easily applicable and extendable built-in functions, and their capability to perform symbolic determination and ma-

nipulation of complex functions and expressions) provide the necessary computing environment for the determination of quantum mechanical kinetic energy operators in internal coordinates. However, as this communication shows, it might not always be necessary to carry out the tremendous amount of algebraic manipulations involved in these derivations, as simple analytic formulae can be devised for certain classes of molecules employing selected internal coordinates. The full form of  $\hat{T}_V$  of any  $N$ -atom sequentially bonded molecule in stretch, bend, and torsion internal coordinates and employing a customary normalization condition is elegantly presented in terms of only twenty distinct operator terms. Similar terms could be derived for other classes of compounds and other internal coordinate sets if desired. Use of the exact kinetic energy operators of  $N$ -atom molecules is envisioned in vibrational spectroscopy, scattering theory, and in quantum Monte Carlo calculations, for possibly less than eight-atom systems.

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