

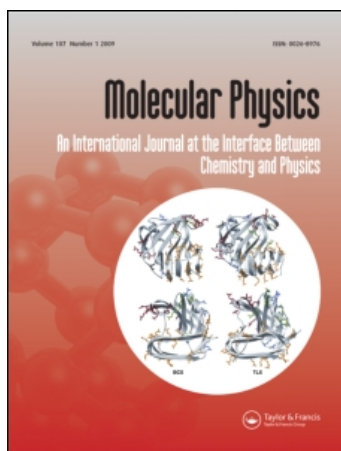
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## On the form of the exact quantum mechanical vibrational kinetic energy operator for penta-atomic molecules in internal coordinates

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Forms for the exact non-relativistic quantum mechanical vibrational ( $J = 0$ ) kinetic energy operators for sequentially bonded (A–B–C–D–E) and (A,B)–C–D–E-type penta-atomic molecules, expressed in valence internal coordinates, are presented. As advocated earlier (Handy, N. C., 1987, *Molec. Phys.*, **61**, 207), computer algebra has been employed during the derivation. The suggested use of these operators in calculations for vibrational energy levels of interesting penta-atomic molecules (e.g.,  $C_3O_2$ , and  $H_2CCO$ ) is outlined.

### 1. Introduction

During the last two decades, due partly to the emergence of efficient new methodologies (for recent reviews see [1–11]) and partly to the ever-increasing availability of computational resources, the accurate calculation of the rovibrational spectra of small molecules became very viable. For triatomic molecules efficient methods and computer programs have been developed employing different coordinate systems (e.g., normal, internal (simple valence or symmetry), Jacobi, Pekeris, Radau, and hyperspherical coordinates) and strategies (e.g., finite basis representation (FBR) [1, 2, 11], discrete variable representation (DVR) [3], semiclassical adiabatic switching [4] and spectral quantization [5, 9], Monte Carlo [6], and perturbative [7] methods). The successful application of these state-of-the-art methods to treat the rotational and vibrational motion of triatomics is too broad to cover here, but for a subjectively selected partial list of recent high-quality FBR and DVR results see [12].

Amongst the methodologies at one's disposal for determining rovibrational spectra *ab initio* the linear variational (sometimes called FBR) approaches have been playing a central role. It appears [7] that there are perhaps six central steps in most variational (or related nearly variational, such as DVR) calculations: (i) selection of a suitable coordinate system; (ii) derivation of the (exact) kinetic energy contribution ( $T$ ) to the total molecular Hamiltonian in the coordinate system selected; (iii) determination of the (Born–Oppenheimer) potential energy surface ( $V_N$ ) in the same coordinate system as selected for the representation of  $T$ ; (iv) choice of a set of appropriate expansion (basis) functions for the wavefunction allowing representation of the Hamiltonian as a matrix; (v) evaluation of the necessary matrix elements; and (vi) determination of the eigenvalues and eigenvectors of interest by (numerical) diagonalization of the Hamiltonian matrix.

Although the knowledge accumulated in the last two decades provides, in general, guidelines for the choices one has to make in all six steps, considerable difficulties will usually be encountered for any particular molecular system and any particular choice. The difficulties associated with the other areas notwithstanding, in this communication attention is focused on step (ii): more explicitly, on the derivation of the non-relativistically exact quantum mechanical vibrational kinetic energy operator in non-orthogonal internal coordinates.

The general form of  $T$  in normal coordinates was obtained by Watson [13, 14] quite a long time ago. However, it has since been realized [15–17] that internal coordinates are a considerably better choice than normal coordinates, especially if one tries to avoid: (a) the unfactorizability problem of Watson's rovibrational kinetic energy operator  $\hat{T}_{\text{VR}}$  (the inverse inertia tensor elements couple together all the rovibrational motions, necessitating a costly direct evaluation of multidimensional integrals in the case of strictly variational methods); (b) the problem of choosing a reference geometry (linear or nonlinear) to define the normal coordinates; and (c) the short convergence radius of normal coordinate expansions of the potential and an unnecessarily long and complicated form for the potential energy due to the rectilinear nature of the normal coordinates when dealing with high-energy and/or large-amplitude motions. Thus, derivation of the kinetic energy operator in carefully selected internal coordinates seems to be unavoidable. Considerable advances have been made along this line [18–29]. At this point, it should also be noted that (a) the actual form of  $T$  will be dependent always upon the choice of the internal coordinates and the normalization condition, suggesting that the extra effort needed to derive the necessary form of  $T$  should be modest so that it could be rederived and reprogrammed with relative ease if it became necessary, and (b) this derivation presented such a great challenge, for molecules larger than triatomic, that the correct form of  $\hat{T}_{\text{V}}$  and  $\hat{T}_{\text{VR}}$  even for tetra-atomic molecules has been obtained only recently [20b, 21, 26, 27]. This should be kept in mind and compared with the fact that, following some earlier work of Sutcliffe, Chapuisat and others [1, 2, 10, 19, 20a, 23a, 24a, 29], Handy presented in 1987 [21] a straightforward method, based on the application of computer algebra, for the derivation of kinetic energy operators in any well defined internal coordinate system for vibration–rotation problems of molecules of arbitrary size. Derivation of the vibrational kinetic energy operator ( $\hat{T}_{\text{V}}$ ) is especially simple in this scheme (*vide infra*) as it is derived by starting with the simple Laplacian form of the kinetic energy operator in Cartesian coordinates followed by a succession of straightforward transformations. Despite the apparent relative ease of carrying out the necessary transformations, no communications exist in the literature reporting the form of the exact quantum mechanical vibrational kinetic energy operator ( $\hat{T}_{\text{V}}$ ) for penta-atomic or larger molecules bonded non-sequentially. As a special tribute to modern computer algebra programming languages [30] we present below the full vibrational kinetic energy operator for a pair of selected penta-atomic molecules in internal coordinates.

## 2 Theoretical foundations

As mentioned above, the theory behind the derivation of the exact quantum mechanical vibrational kinetic energy operator in internal coordinates,  $\hat{T}_{\text{V}}$ , is rather

simple [19, 21, 26b]. Within the framework of the Born–Oppenheimer approximation one starts by defining the Cartesian coordinates  $\{x_{\alpha i}\}$  ( $\alpha = xyz, i = 1, 2, \dots, N$ ) of the  $N$  nuclei in a laboratory fixed frame of reference, for which the quantum mechanical kinetic energy operator  $\hat{T}$  is given by

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

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  $\partial/\partial x_{\alpha i} \mapsto \partial/\partial q_j$  one can write the exact  $J = 0$  kinetic energy operator as

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

where the definitions for the contravariant metric tensor  $g^{jk}$ , and for  $h^j$  are made evident. (Note that a set of vibrational coordinates, *a priori* curvilinear, are called internal if they depend explicitly on the (nuclear-fixed) Cartesian coordinates of the atoms, are rotationally invariant (i.e., invariant under rotation of the  $N$  nuclei about axes fixed in space), and are complete.) As expected, calculation of  $g^{jk}$  and  $h^j$  would require only the knowledge of the explicit dependence of the chosen internal coordinates on the Cartesians (requiring usually terms already familiar from transformations among different coordinate systems in theoretical vibrational spectroscopy [26c, 31–35]). Since calculation of this dependence and handling of the resulting complex expressions can sometimes be difficult, it seems most advantageous to define  $g^{jk}$  and  $h^j$  first in a set of internal coordinates for which this functional dependence is especially simple. Evidently, the simplest and most natural choice is a set of stretching-like interparticle distance coordinates. Unfortunately, the number  $N(N - 1)/2$  of interparticle distances for a general  $N$ -atomic molecule 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  $h^j$  for molecules having more than four atoms requires some additional effort, namely expressing the ‘extraneous’ interparticle distance(s) by those modes which define a ‘true’ set of internal coordinates. (This procedure results in the introduction of all (or most) internal coordinates into  $g^{jk}$  and  $h^j$  at an 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 differential operators.) Working towards expressions containing the final set of internal coordinates requires then some additional transformations. It is easy to show that changing from one set of internal coordinates  $\{q'_j\}$  to another set of internal coordinates  $\{q_j\}$  can be achieved by the use of the following expressions:

$$\left[ \sum_{\alpha i} \frac{1}{m_i} \frac{\partial q_j}{\partial x_{\alpha i}} \frac{\partial q_k}{\partial x_{\alpha i}} \right] = \sum_{lm} \left[ \sum_{\alpha i} \frac{1}{m_i} \frac{\partial q'_l}{\partial x_{\alpha i}} \frac{\partial q'_m}{\partial x_{\alpha i}} \right] \frac{\partial q_j}{\partial q'_l} \frac{\partial q_k}{\partial q'_m} \quad (3)$$

and

$$\left[ \sum_{xi} \frac{1}{m_i} \frac{\partial^2 q_j}{\partial x_{xi} \partial x_{xi}} \right] = \sum_k \left[ \sum_{xi} \frac{1}{m_i} \frac{\partial^2 q'_k}{\partial x_{xi} \partial x_{xi}} \right] \frac{\partial q_j}{\partial q'_k} + \sum_{kl} \left[ \sum_{xi} \frac{1}{m_i} \frac{\partial q'_k}{\partial x_{xi}} \frac{\partial q'_l}{\partial x_{xi}} \right] \frac{\partial^2 q_j}{\partial q'_k \partial q'_l} \quad (4)$$

Calculation of two new Jacobian tensors,  $\partial q_j / \partial q'_k$  and  $\partial^2 q_j / \partial q'_k \partial q'_l$  is therefore necessary. Computation of Jacobians of this type is a straightforward process if computer algebra languages are employed once the explicit dependence of  $\{q_j\}$  on  $\{q'_k\}$  has been determined. Note that this dependence also can be obtained most straightforwardly if  $\{q'_k\}$  are a set of stretching coordinates. Repeated application, if necessary, of equations (3) and (4) produces the desired quantities  $g^{jk}$  and  $h^j$ .

It is customary to employ a normalization condition which absorbs the stretching part of the full transformation Jacobian into  $\hat{T}_V$  [36]. This transformation,

$$\bar{\hat{T}}_V = s^{1/2} \hat{T}_V s^{-1/2}, \quad (5)$$

where  $s$  is the stretching part of the Jacobian for the transformation from  $\{x_{xi}\}$  to the final set of internal coordinates  $\{q_j\}$  (simply the square products of the bond lengths), yields a new Hermitian form for  $\hat{T}_V$  as follows:

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

Forms (5) and (6) have the usual Podolsky structure [36]. Note that since the internal coordinates used in this study are non-orthogonal,  $\bar{\hat{T}}_V$  has a considerably more complicated form in  $h^j$  than  $\hat{T}_V$ . To ease the notation, in the following  $\hat{T}_V$  will always be written instead of  $\bar{\hat{T}}_V$ .

### 3. Results and discussion

Application of the procedure detailed in the previous section to obtain the vibrational kinetic energy operator for tri- and tetra-atomic molecules (more explicitly, for those molecules shown in figure 1) is not new. For checking purposes we rederived and present the exact  $\hat{T}_V$ 's for sequentially bonded triatomic (A–B–C, such as H<sub>2</sub>O), sequentially bonded tetra-atomic (A–B–C–D, such as HCCH) and (A,B)–C–D-type tetra-atomic (such as H<sub>2</sub>CO) molecules in tables 1, 2 and 3. Tables 4–7 contain the new operators, where the terms forming  $\hat{T}_V$  are presented for the two penta-atomic molecules depicted in figure 2. Tables 2, 3, 5, and 7 are arranged in a form suggested by the contravariant metric tensor  $g^{jk}$ . (Note that all tables contain the full form of the respective  $\hat{T}_V / (-\frac{1}{2}\hbar^2)$ , i.e., off-diagonal  $g^{jk}$  elements have already been multiplied by two.) This form of presentation is especially useful for observing the general tendencies among the operator terms. For example, it is clear by simple inspection of tables 1–7 that those terms which do not involve new coordinates going from triatomic to penta-atomic molecules of similar arrangement, are basically the same, as required by the equivalence of the contravariant metric tensor  $g^{jk}$  and the appropriate analytic  $G$  matrix [22, 33, 37]. This fact provides a useful tool for checking the expressions derived for the different terms. As noted, it

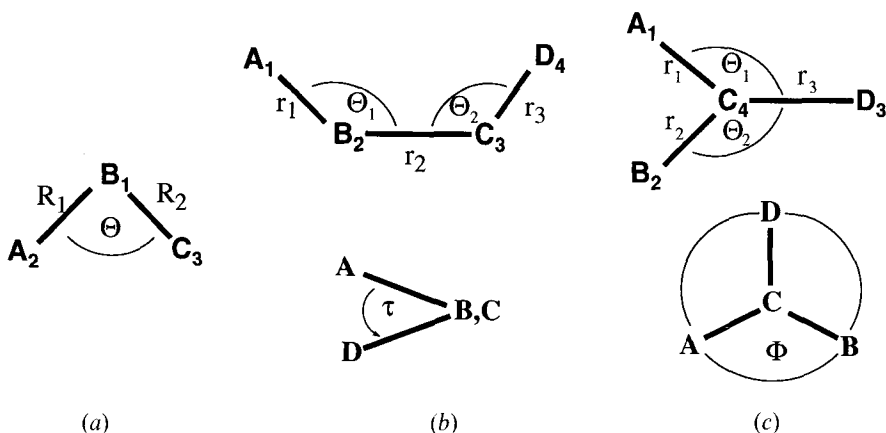


Figure 1. Atom numbering and definition of internal coordinates for triatomic and tetra-atomic molecules. In (b)  $\tau$  is the torsion angle between planes  $ABC$  and  $BCD$ , and in (c)  $\Phi$  is the book angle between planes  $ACD$  and  $BCD$ .

would be possible to write all first- and second-derivative operator terms using specific  $G$ -matrix expressions [37] (e.g., the coefficient of  $\partial^2/\partial r_1 \partial \tau_1$  in table 7 is the same as  $g_{r\tau}^1$  ( $\frac{1}{2}$ ) of table 2 of [37]), but at this stage, especially for programming purposes, we think it is useful to give the full formulae.

### 3.1. Use of computer algebra

As equations (1)–(6) exemplify, evaluation of kinetic energy operators in internal coordinates of any kind requires a lot of straightforward but tedious algebraic manipulations. As the complexity of the operator to be derived increases, the certainty that the operator actually determined by hand is correct gradually diminishes. Leaving all long and difficult manipulations to the powerful hardware and software available today is thus very appealing.

General purpose software enabling symbolic algebraic manipulations has been around for some time. From the several precursors (among them Macsyma [38], Reduce [39], Scratchpad [40], and Derive [41]) of modern symbolic computer algebra programs, Reduce was used by Handy to obtain kinetic energy operators for tri- and tetra-atomic molecules [21]. Since then a new generation of computer algebra packages enabling symbolic manipulation of considerably more complicated functions has been made commercially available. Among them probably Mathematica [30], Maple [42], and Axiom [43] are the most widespread and prominent. These software packages (a) include a highly functional programming language; (b) have numerous built-in functions which are easily applicable and extendable; and (c) allow symbolic determination and manipulation (differentiation, integration, expansion, simplification, etc.) of complicated functions and expressions.

The above capabilities of modern computer algebra systems (CASs) provide the necessary computing environment for the determination of kinetic energy operators in internal coordinates. Accordingly, determination of the exact quantum mechanical vibrational kinetic energy operator in internal coordinates, employing a program written, in the present case, in Mathematica [30], can be broken down into the following main steps: (a) setting up the necessary auxiliary functions, which form the

Table 1. Non-differential and first-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of sequentially bonded triatomic (A-B-C), and tetra-atomic A-B-C-D- and (A,B)-C-D-like molecules in internal coordinates  $\{R_1, R_2, \theta\}$ ,  $\{r_1, r_2, r_3, \theta_1, \theta_2, \tau\}$ , and  $\{r_1, r_2, r_3, \theta_1, \theta_2, \Phi\}$ , respectively (see figure 1).

	Non-differential term	$\partial/\partial R_1, \partial/\partial r_1$	$\partial/\partial R_2, \partial/\partial r_2$	$\partial/\partial \theta, \partial/\partial r_3$	$\partial/\partial \theta_1$	$\partial/\partial \theta_2$	$\partial/\partial \tau, \partial/\partial \Phi$	
3-atomic A-B-C	$\frac{2 \cos \theta}{m_1 R_1 R_2} + \frac{2 \cos \theta_2}{m_2 r_1 r_2} + \frac{2 \cos \theta_2}{m_3 r_2 r_3}$	$-\frac{2 \cos \theta}{m_1 R_2}$	$-\frac{2 \cos \theta}{m_1 R_1}$	$\left(\frac{1}{\mu_1 R_1^2} + \frac{1}{\mu_2 R_2^2}\right) \cot \theta$ $+ \frac{4 \sin \theta - 2 \operatorname{cosec} \theta}{m_1 R_1 R_2}$ $-\frac{2 \cos \theta_2}{m_3 r_2}$				
4-atomic A-B-C-D	$\frac{2 \cos \theta_1}{m_2 r_1 r_2} + \frac{2 \cos \theta_2}{m_3 r_2 r_3}$	$-\frac{2 \cos \theta_1}{m_2 r_2}$	$-\frac{2 \cos \theta_1}{m_2 r_1} - \frac{2 \cos \theta_2}{m_3 r_3}$	$\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) \cot \theta_1$ $+ \frac{4 \sin \theta_1 - 2 \operatorname{cosec} \theta_1}{m_2 r_1 r_2}$ $-\frac{2 \cos \theta_2}{m_3 r_3}$	$\left(\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2}\right) \cot \theta_2$ $+ \frac{4 \sin \theta_2 - 2 \operatorname{cosec} \theta_2}{m_3 r_2 r_3}$ $-\frac{2 \cos \tau \sin \theta_2}{m_2 r_1 r_2}$	$2 \sin \tau \left(\frac{\cot \theta_1 \sin \theta_2}{m_3 r_2 r_3} + \frac{\sin \theta_1 \cot \theta_2}{m_2 r_1 r_2}\right)$		
4-atomic (A,B)-C-D	$\frac{2 \cos \theta_1}{m_4} \left(\frac{\cos \theta_1}{r_1 r_3} + \frac{\cos \theta_2}{r_2 r_3}\right) + \frac{\cos \theta_1 \cos \theta_2}{r_2} + \frac{\cos \theta_2}{r_3}$	$-\frac{2 \cos \theta_1 \sin \theta_1 \sin \theta_2}{m_4} \left(\frac{\cos \theta_1}{r_1} + \frac{\cos \theta_2}{r_2}\right) + \frac{\cos \theta_1 \cos \theta_2}{r_2} + \frac{\cos \theta_2}{r_3}$	$-\frac{2 \cos \theta_1 \sin \theta_1 \sin \theta_2}{m_4} \left(\frac{\cos \theta_1}{r_1} + \frac{\cos \theta_2}{r_2}\right) + \frac{\cos \theta_1 \cos \theta_2}{r_2} + \frac{\cos \theta_2}{r_3}$	$-\frac{2 \cos \theta_1}{m_4} \left(\frac{\cos \theta_1}{r_1} + \frac{\cos \theta_2}{r_2}\right) + \frac{2 \cos \theta_1 \cos \theta_2}{m_4 r_1 r_2} + \frac{2 \cos \theta_2 \sin \theta_2}{m_4 r_2 r_3}$	$\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_3 r_3^2}\right) \cot \theta_1$ $+ \frac{4 \sin \theta_1 - 2 \operatorname{cosec} \theta_1}{m_4 r_1 r_3}$ $-\frac{2 \cos \tau \sin \theta_2}{m_2 r_1 r_2}$	$\left(\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2}\right) \cot \theta_2$ $+ \frac{4 \sin \theta_2 - 2 \operatorname{cosec} \theta_2}{m_4 r_2 r_3}$ $-\frac{2 \cos \tau \sin \theta_2}{m_2 r_1 r_2}$	$2 \sin \theta_1 \left(\frac{\cot \theta_1 \sin \theta_2}{m_4 r_2 r_3} - \frac{\sin \theta_1 \cot \theta_2}{r_1 r_3}\right) + \frac{2 \sin \theta_1 \cos \theta_2}{m_4 r_1 r_2} + \frac{2 \cos \theta_1 \sin \theta_2}{m_4 r_2 r_3}$	

Table 2. Second-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of sequentially bonded triatomic (A-B-C) and tetra-atomic (A-B-C-D) molecules in internal coordinates  $\{R_1, R_2, \theta\}$  and  $\{r_1, r_2, r_3, \theta_1, \theta_2, \tau\}$  respectively (see figure 1). Note that there were typographical errors in Appendix B of [21] in terms denoted below by  $\partial^2/\partial\tau\partial\theta_1$  and  $\partial^2/\partial\tau\partial\theta_2$ .

	$r_1$	$r_2$	$r_3$	$\theta_1/R_1$	$\theta_2/R_2$	$\tau/\theta$	
$r_1$	$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_2}$			$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_2}$	$\frac{2 \cos \theta}{m_1}$	$-\frac{2 \sin \theta}{m_1 R_2}$	$R_1$
$r_2$	$\frac{2 \cos \theta_1}{m_2}$	$\frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3}$			$\frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3}$	$-\frac{2 \sin \theta}{m_1 R_1}$	$R_2$
$r_3$	0	$\frac{2 \cos \theta_2}{m_3}$	$\frac{1}{\mu_3} = \frac{1}{m_3} + \frac{1}{m_4}$			$\frac{1}{\mu_1 R_1^2} + \frac{1}{\mu_2 R_2^2} - \frac{2 \cos \theta}{m_1 R_1 R_2}$	$\theta$
$\theta_1$	$-\frac{2 \sin \theta_1}{m_2 r_2}$	$-\frac{2 \sin \theta_1}{m_2 r_1}$	$\frac{2 \cos \tau \sin \theta_2}{m_3 r_2}$	$\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2 \cos \theta_1}{m_2 r_1 r_2}$			
$\theta_2$	$\frac{2 \cos \tau \sin \theta_1}{m_2 r_2}$	$\frac{2 \sin \theta_2}{m_3 r_3}$	$-\frac{2 \sin \theta_2}{m_3 r_2}$	$2 \cos \tau \left( \frac{\cos \theta_1}{m_2 r_1 r_2} + \frac{\cos \theta_2}{m_3 r_2 r_3} - \frac{1}{\mu_2 r_2^2} \right)$	$\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2} - \frac{2 \cos \theta_2}{m_3 r_2 r_3}$		
$\tau$	$-\frac{2 \sin \tau \sin \theta_1 \cot \theta_2}{m_2 r_2}$	0	$-\frac{2 \sin \tau \cot \theta_1 \sin \theta_2}{m_3 r_2}$	$2 \sin \tau \left( \frac{\cot \theta_2}{\mu_2 r_2^2} + \frac{\cot \theta_1}{\mu_3 r_3^2} - \frac{\cot \theta_1 \cot \theta_2}{m_2 r_1 r_2} - \frac{\text{cosec } \theta_2}{m_3 r_2 r_3} \right)$	$2 \sin \tau \left( \frac{\cot \theta_1}{\mu_2 r_2^2} - \frac{\cot \theta_1 \cos \theta_2}{m_3 r_2 r_3} - \frac{\text{cosec } \theta_1}{m_2 r_1 r_2} \right)$	$\frac{\text{cosec}^2 \theta_1}{\mu_1 r_1^2} + \frac{\cot^2 \theta_1}{\mu_2 r_2^2} + \frac{\cot^2 \theta_2}{\mu_2 r_2^2} + \frac{\text{cosec}^2 \theta_2}{\mu_3 r_3^2}$ + $\frac{2 \cos \tau \cot \theta_1 \cot \theta_2}{\mu_2 r_2^2} - \frac{2 \cos \tau \cot \theta_1 \text{cosec } \theta_2}{m_3 r_2 r_3}$	
						$\frac{2 \cos \tau \text{cosec } \theta_1 \cot \theta_2}{m_2 r_1 r_2} - \frac{2 \cot \theta_1 \text{cosec } \theta_1}{m_2 r_1 r_2}$ - $\frac{2 \cot \theta_2 \text{cosec } \theta_2}{m_3 r_2 r_3}$	



Table 3. Second-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of tetra-atomic (A,B)-C-D-like molecules in internal coordinates  $\{r_1, r_2, r_3, \theta_1, \theta_2, \phi\}$  (see figure 1). Note that a trivial simplification was made here for  $\partial^2/\partial\phi\partial\phi$  as compared with Appendix A of [21].

	$r_1$	$r_2$	$r_3$	$\theta_1$	$\theta_2$	$\phi$
$r_1$	$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_4}$					
$r_2$	$\frac{2}{m_4} (\cos \theta_1 \cos \theta_2 + \cos \phi \sin \theta_1 \sin \theta_2)$	$\frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_4}$				
$r_3$	$\frac{2 \cos \theta_1}{m_4}$	$\frac{2 \cos \theta_2}{m_4}$	$\frac{1}{\mu_3} = \frac{1}{m_3} + \frac{1}{m_4}$			
$\theta_1$	$\frac{2 \sin \theta_1}{m_4 r_3}$	$\frac{2 \cos \phi \cos \theta_1 \sin \theta_2}{m_4 r_1}$	$-\frac{2 \sin \theta_1}{m_4 r_1}$	$\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_3 r_3^2}$		
		$\frac{2 \cos \phi \sin \theta_2}{m_4 r_3} - \frac{2 \sin \theta_1 \cos \theta_2}{m_4 r_1}$		$-\frac{2 \cos \theta_1}{m_4 r_1 r_3}$		
$\theta_2$	$\frac{2 \cos \phi \sin \theta_1 \cos \theta_2}{m_4 r_2}$	$\frac{2 \sin \theta_2}{m_4 r_3}$	$-\frac{2 \sin \theta_2}{m_4 r_2}$	$2 \cos \phi \left( \frac{1}{\mu_3 r_3^2} + \frac{\cos \theta_1 \cos \theta_2}{m_4 r_1 r_2} \right)$	$\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2}$	
	$\frac{2 \cos \phi \sin \theta_1}{m_4 r_3} - \frac{2 \cos \theta_1 \sin \theta_2}{m_4 r_2}$			$-\frac{\cos \theta_1 \cos \theta_2}{m_4 r_1 r_3} - \frac{2 \sin \theta_1 \sin \theta_2}{m_4 r_1 r_2}$	$-\frac{2 \cos \theta_2}{m_4 r_2 r_3}$	
$\phi$	$\frac{2 \sin \phi \sin \theta_1}{m_4} \times \left( \frac{\cot \theta_2}{r_3} - \frac{\operatorname{cosec} \theta_2}{r_2} \right)$	$\frac{2 \sin \phi \sin \theta_2}{m_4} \times \left( \frac{\cot \theta_1}{r_3} - \frac{\operatorname{cosec} \theta_1}{r_1} \right)$	0	$2 \sin \phi \left( -\frac{\cot \theta_2}{\mu_3 r_3^2} + \frac{\operatorname{cosec} \theta_2}{m_4 r_2 r_3} \right)$	$2 \sin \phi \left( \frac{\cot \theta_1}{\mu_3 r_3^2} - \frac{\operatorname{cosec} \theta_1}{m_4 r_1 r_3} \right)$	$\operatorname{cosec}^2 \theta_1 + \frac{\cot^2 \theta_1}{\mu_3 r_3^2}$
				$+\frac{\cos \theta_1 \cot \theta_2}{m_4 r_1 r_3} + \frac{\cos \theta_2 \cot \theta_1}{m_4 r_2 r_3}$	$+\frac{\operatorname{cosec} \theta_1}{m_4 r_1 r_3} + \frac{\cos \theta_2 \cot \theta_1}{m_4 r_2 r_3}$	$+\frac{\cot^2 \theta_2}{\mu_3 r_3^2} + \frac{\operatorname{cosec}^2 \theta_2}{\mu_3 r_3^2}$
				$-\frac{\cos \theta_1 \operatorname{cosec} \theta_2}{m_4 r_1 r_2}$	$+\frac{\cos \theta_2 \cot \theta_1}{m_4 r_2 r_3}$	$-\frac{2 \cos \phi \cot \theta_1 \cot \theta_2}{\mu_3 r_3^2}$
				$-\frac{\cos \theta_2 \operatorname{cosec} \theta_1}{m_4 r_1 r_2}$	$-\frac{\cos \theta_2 \operatorname{cosec} \theta_1}{m_4 r_1 r_2}$	$-\frac{2 \cos \phi \operatorname{cosec} \theta_1 \operatorname{cosec} \theta_2}{m_4 r_1 r_2}$
					$+\frac{2 \operatorname{cosec} \theta_1 (\cos \phi \cot \theta_2 - \cot \theta_1)}{m_4 r_1 r_3}$	
					$+\frac{2 \operatorname{cosec} \theta_2 (\cos \phi \cot \theta_1 - \cot \theta_2)}{m_4 r_2 r_3}$	

Table 4. Non-differential and first-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of sequentially bonded penta-atomic molecules in internal coordinates  $\{r_1, r_2, r_3, r_4, \theta_1, \theta_2, \theta_3, \tau_1, \tau_2\}$  (see figure 2).

Non-differential term	$\partial/\partial r_1$	$\partial/\partial r_2$	$\partial/\partial r_3$	$\partial/\partial r_4$
$\frac{2 \cos \theta_1}{m_2 r_1 r_2} + \frac{2 \cos \theta_2}{m_3 r_2 r_3} + \frac{2 \cos \theta_3}{m_4 r_3 r_4}$	$-\frac{2 \cos \theta_1}{m_2 r_2}$	$-\frac{2 \cos \theta_1}{m_2 r_1} - \frac{2 \cos \theta_2}{m_3 r_3}$	$-\frac{2 \cos \theta_2}{m_3 r_2} - \frac{2 \cos \theta_3}{m_4 r_4}$	$-\frac{2 \cos \theta_3}{m_4 r_3}$
$\partial/\partial \theta_1$	$\partial/\partial \theta_2$	$\partial/\partial \theta_3$	$\partial/\partial \tau_1$	$\partial/\partial \tau_2$
$\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) \cot \theta_1$	$\left(\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2}\right) \cot \theta_2$	$\left(\frac{1}{\mu_3 r_3^2} + \frac{1}{\mu_4 r_4^2}\right) \cot \theta_3$	$\frac{2 \sin \tau_1 \sin \theta_1 \cot \theta_2}{m_2 r_1 r_2}$	$\frac{2 \sin \tau_2 \sin \theta_3 \cot \theta_2}{m_4 r_3 r_4}$
$+\frac{4 \sin \theta_1 - 2 \operatorname{cosec} \theta_1}{m_2 r_1 r_2}$	$+\frac{4 \sin \theta_2 - 2 \operatorname{cosec} \theta_2}{m_3 r_2 r_3}$	$+\frac{4 \sin \theta_3 - 2 \operatorname{cosec} \theta_3}{m_4 r_3 r_4}$	$+\frac{2 \sin \tau_1 \cot \theta_1 \sin \theta_2}{m_3 r_2 r_3}$	$+\frac{2 \sin \tau_2 \cot \theta_3 \sin \theta_2}{m_3 r_2 r_3}$
$\frac{2 \cos \tau_1 \sin \theta_2}{m_3 r_2 r_3}$	$\frac{2 \cos \tau_1 \sin \theta_1}{m_2 r_1 r_2} - \frac{2 \cos \tau_2 \sin \theta_2}{m_3 r_2 r_3}$	$\frac{2 \cos \tau_2 \sin \theta_2}{m_3 r_2 r_3}$	$\frac{2 \sin \tau_2 \operatorname{cosec} \theta_2 \sin \theta_3}{m_4 r_3 r_4}$	$+\frac{2 \sin \tau_1 \operatorname{cosec} \theta_2 \sin \theta_1}{m_2 r_1 r_2}$

Table 5. Second-derivative terms in the exact quantum mechanical kinetic energy operator for sequentially bonded penta-atomic molecules in internal coordinates  $\{r_1, r_2, r_3, r_4, \theta_1, \theta_2, \theta_3, \tau_1, \tau_2\}$  (see figure 2).

	$r_1$	$r_2$	$r_3$	$r_4$	$\theta_1$
$r_1$	$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_2}$				
$r_2$	$\frac{2 \cos \theta_1}{m_2}$	$\frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3}$			
$r_3$	0	$\frac{2 \cos \theta_2}{m_3}$	$\frac{1}{\mu_3} = \frac{1}{m_3} + \frac{1}{m_4}$		
$r_4$	0	0	$\frac{2 \cos \theta_3}{m_4}$	$\frac{1}{\mu_4} = \frac{1}{m_4} + \frac{1}{m_5}$	
$\theta_1$	$-\frac{2 \sin \theta_1}{m_2 r_2}$	$-\frac{2 \sin \theta_1}{m_2 r_1}$	$\frac{2 \sin \theta_2 \cos \tau_1}{m_3 r_2}$	0	$\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} - \frac{2 \cos \theta_1}{m_2 r_1 r_2}$
$\theta_2$	$\frac{2 \sin \theta_1 \cos \tau_1}{m_2 r_2}$	$-\frac{2 \sin \theta_2}{m_3 r_3}$	$-\frac{2 \sin \theta_2}{m_3 r_2}$	$\frac{2 \sin \theta_3 \cos \tau_2}{m_4 r_3}$	$2 \cos \tau_1 \left( -\frac{1}{\mu_2 r_2^2} + \frac{\cos \theta_1}{m_2 r_1 r_2} + \frac{\cos \theta_2}{m_3 r_2 r_3} \right)$
$\theta_3$	0	$\frac{2 \sin \theta_2 \cos \tau_2}{m_3 r_3}$	$-\frac{2 \sin \theta_3}{m_4 r_4}$	$-\frac{2 \sin \theta_3}{m_4 r_3}$	$\frac{2 \sin \tau_1 \sin \tau_2}{m_3 r_2 r_3} - \frac{2 \cos \theta_2 \cos \tau_1 \cos \tau_2}{m_3 r_2 r_3}$
$\tau_1$	$-\frac{2 \sin \tau_1 \sin \theta_1 \cot \theta_2}{m_2 r_2}$	0	$-\frac{2 \sin \tau_1 \cot \theta_1 \sin \theta_2}{m_3 r_2}$	$-\frac{2 \sin \tau_2 \operatorname{cosec} \theta_2 \sin \theta_3}{m_4 r_3}$	$2 \sin \tau_1 \left( -\frac{\cos \theta_1 \cot \theta_2}{m_2 r_1 r_2} + \frac{\cot \theta_2}{\mu_2 r_2^2} - \frac{\operatorname{cosec} \theta_2}{m_3 r_2 r_3} \right)$
$\tau_2$	$-\frac{2 \sin \tau_1 \sin \theta_1 \operatorname{cosec} \theta_2}{m_2 r_2}$	$-\frac{2 \sin \tau_2 \sin \theta_2 \cot \theta_3}{m_3 r_3}$	0	$-\frac{2 \sin \tau_2 \cot \theta_2 \sin \theta_3}{m_4 r_3}$	$-2 \sin \tau_1 \operatorname{cosec} \theta_2 \left( -\frac{1}{\mu_2 r_2^2} + \frac{\cos \theta_1}{m_2 r_1 r_2} + \frac{\cos \theta_2}{m_3 r_2 r_3} \right) + \frac{2 \cot \theta_3}{m_3 r_2 r_3} (-\sin \tau_1 \cos \tau_2 + \cos \tau_1 \sin \tau_2 \cos \theta_2)$

	$\theta_2$	$\theta_3$	$\tau_1$	$\tau_2$
$\nu_2$	$\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2} - \frac{2 \cos \theta_2}{m_3 r_2 r_3}$			
$\nu_3$	$2 \cos \tau_2 \left( -\frac{1}{\mu_3 r_3^2} + \frac{\cos \theta_2}{m_3 r_2 r_3} + \frac{\cos \theta_3}{m_4 r_3 r_4} \right)$	$\frac{1}{\mu_3 r_3^2} + \frac{1}{\mu_4 r_4^2} - \frac{2 \cos \theta_3}{m_4 r_3 r_4}$		
$\nu_1$	$2 \sin \tau_1 \left( -\frac{\cot \theta_1 \cos \theta_2}{m_3 r_2 r_3} + \frac{\cot \theta_1}{\mu_2 r_2^2} - \frac{\operatorname{cosec} \theta_1}{m_2 r_1 r_2} \right)$	$-2 \sin \tau_2 \operatorname{cosec} \theta_2 \left( -\frac{1}{\mu_3 r_3^2} + \frac{\cos \theta_2}{m_3 r_2 r_3} + \frac{\cos \theta_3}{m_4 r_3 r_4} \right) + \frac{2 \cot \theta_1}{m_3 r_2 r_3} (-\sin \tau_2 \cos \tau_1 + \cos \tau_2 \sin \tau_1 \cos \theta_2)$	$\frac{\operatorname{cosec}^2 \theta_1}{\mu_1 r_1^2} + \frac{\cot^2 \theta_1}{\mu_2 r_2^2} + \frac{\cot^2 \theta_2}{\mu_2 r_2^2} + \frac{\operatorname{cosec}^2 \theta_2}{\mu_3 r_3^2} + \frac{2 \cos \tau_1 \cot \theta_1 \cot \theta_2}{\mu_2 r_2^2} - \frac{2 \cos \tau_1 \operatorname{cosec} \theta_1 \cot \theta_2}{m_2 r_1 r_2} - \frac{2 \operatorname{cosec} \theta_1 \cot \theta_1}{m_2 r_1 r_2} - \frac{2 \cos \tau_1 \cot \theta_1 \operatorname{cosec} \theta_2}{m_3 r_2 r_3} - \frac{2 \operatorname{cosec} \theta_2 \cot \theta_2}{m_3 r_2 r_3}$	
$\nu_2$	$2 \sin \tau_2 \left( \frac{\cot \theta_1}{\mu_3 r_3^2} - \frac{\operatorname{cosec} \theta_3}{m_4 r_3 r_4} - \frac{\cos \theta_2 \cot \theta_3}{m_3 r_2 r_3} \right)$	$2 \sin \tau_2 \left( \frac{\cot \theta_2}{\mu_3 r_3^2} - \frac{\operatorname{cosec} \theta_2}{m_3 r_2 r_3} - \frac{\cot \theta_2 \cos \theta_3}{m_4 r_3 r_4} \right)$	$2 \operatorname{cosec} \theta_2 \left( \frac{\cos \tau_1 \cot \theta_1 + \cot \theta_2}{\mu_2 r_2^2} + \frac{\cos \tau_2 \cot \theta_3 + \cot \theta_2}{\mu_3 r_3^2} - \frac{2 \cos \tau_1 \operatorname{cosec} \theta_1}{m_2 r_1 r_2} - \frac{2 \cos \tau_2 \operatorname{cosec} \theta_3}{m_4 r_3 r_4} \right) - \frac{2}{m_3 r_2 r_3} [\cot^2 \theta_2 + \operatorname{cosec}^2 \theta_2] + \cos \tau_1 \cot \theta_1 \cot \theta_2 + \cos \tau_2 \cot \theta_2 \cot \theta_3 + \cot \theta_1 \cot \theta_3 (\cos \tau_1 \cos \tau_2 + \sin \tau_1 \sin \tau_2 \cos \theta_2)$	$\frac{\operatorname{cosec}^2 \theta_3}{\mu_4 r_4^2} + \frac{\cot^2 \theta_3}{\mu_3 r_3^2} + \frac{\cot^2 \theta_2}{\mu_3 r_3^2} + \frac{\operatorname{cosec}^2 \theta_2}{\mu_3 r_3^2} + \frac{2 \cos \tau_2 \cot \theta_3 \cot \theta_2}{\mu_3 r_3^2} + \frac{2 \cos \tau_2 \operatorname{cosec} \theta_3 \cot \theta_2}{m_4 r_3 r_4} - \frac{2 \operatorname{cosec} \theta_3 \cot \theta_3}{m_4 r_3 r_4} - \frac{2 \cos \tau_2 \cot \theta_3 \operatorname{cosec} \theta_2}{m_3 r_2 r_3} - \frac{2 \operatorname{cosec} \theta_2 \cot \theta_2}{m_3 r_2 r_3}$

Table 6. Non-differential and first-derivative terms in the exact quantum mechanical vibrational kinetic energy operator of (A,B)-C-D-E-like penta-atomic molecules in internal coordinates  $\{r_1, r_2, r_3, r_4, \theta_1, \theta_2, \theta_3, \tau_1, \tau_2\}$  (see figure 2).

Non-differential term	$\partial/\partial r_1$	$\partial/\partial r_2$	$\partial/\partial r_3$	$\partial/\partial r_4$
$2 \cos \theta_1 + \frac{2 \cos \theta_2}{m_4 r_1 r_3} + \frac{2 \cos \theta_3}{m_3 r_1 r_4}$	$\frac{2 \cos \theta_1}{m_4 r_3}$	$\frac{2 \cos \theta_2}{m_4 r_3}$	$\frac{2 \cos \theta_1}{m_4 r_1} \frac{2 \cos \theta_2}{m_4 r_2} \frac{2 \cos \theta_3}{m_3 r_4}$	$\frac{2 \cos \theta_3}{m_3 r_3}$
$+ \frac{2 \cos \theta_1 \cos \theta_2}{m_4 r_1 r_2}$	$\frac{2 \sin \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_2}$	$\frac{2 \sin \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_1}$		
$+ \frac{2 \sin \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_2}$				
$\partial/\partial \theta_1$	$\partial/\partial \theta_2$	$\partial/\partial \theta_3$	$\partial/\partial \tau_1$	$\partial/\partial \tau_2$
$\left( \frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_3 r_3^2} \right) \cot \theta_1$	$\left( \frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2} \right) \cot \theta_2$	$\left( \frac{1}{\mu_3 r_3^2} + \frac{1}{\mu_4 r_4^2} \right) \cot \theta_3$	$\frac{2 \sin \tau_1 \cot \theta_2 \sin \theta_3}{m_3 r_3 r_4}$	$\frac{2 \sin \tau_2 \sin \theta_1 \cot \theta_3}{m_4 r_1 r_3}$
$+ \frac{4 \sin \theta_1 - 2 \operatorname{cosec} \theta_1}{m_4 r_1 r_3}$	$+ \frac{4 \sin \theta_2 - 2 \operatorname{cosec} \theta_2}{m_4 r_2 r_3}$	$+ \frac{4 \sin \theta_3 - 2 \operatorname{cosec} \theta_3}{m_3 r_3 r_4}$	$+ \frac{2 \sin \tau_1 \sin \theta_2 \cot \theta_3}{m_4 r_2 r_3}$	$+ \frac{2 \sin \tau_2 \cot \theta_1 \sin \theta_3}{m_3 r_1 r_4}$
$+ \frac{2 \sin \theta_1 \cos \theta_2}{m_4 r_1 r_2} - \frac{2 \sin \theta_3 \cos \tau_2}{m_3 r_3 r_4}$	$+ \frac{2 \cos \theta_1 \sin \theta_2}{m_4 r_1 r_2} - \frac{2 \sin \theta_3 \cos \tau_1}{m_4 r_3 r_4}$	$- \frac{2 \sin \theta_1 \cos \tau_2}{m_4 r_1 r_3} - \frac{2 \sin \theta_2 \cos \tau_1}{m_4 r_2 r_3}$	$+ \frac{2 \sin(\tau_1 - \tau_2) \sin \theta_1 \operatorname{cosec} \theta_2}{m_4 r_1 r_2}$	$- \frac{2 \sin(\tau_1 - \tau_2) \operatorname{cosec} \theta_1 \sin \theta_2}{m_4 r_1 r_2}$
$- \frac{2 \cos \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_2}$	$- \frac{2 \sin \theta_1 \cos \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_2}$		$+ \frac{2 \sin \theta_1}{m_4 r_1 r_3} [\sin \tau_2 \cot \theta_3]$	$+ \frac{2 \sin \theta_2}{m_4 r_2 r_3} [\sin \tau_1 \cot \theta_3]$
$+ \frac{2 \sin \theta_2 \cos(\tau_1 - \tau_2)}{m_3 r_2 r_3}$	$+ \frac{2 \sin \theta_1 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_3}$		$- \sin(\tau_1 - \tau_2) \cot \theta_2]$	$+ \sin(\tau_1 - \tau_2) \cot \theta_1]$

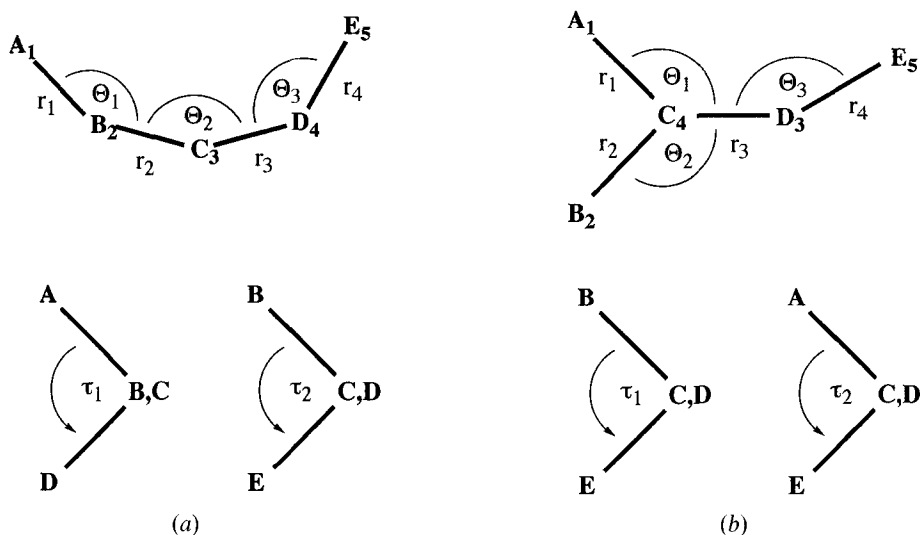


Figure 2. Atom numbering and definition of internal coordinates for penta-atomic molecules. In (a)  $\tau_1$  is the torsion angle between planes ABC and BCD, and  $\tau_2$  is the torsion angle between planes BCD and CDE, while in (b)  $\tau_1$  is the torsion angle between planes BCD and CDE, and  $\tau_2$  is the torsion angle between planes ACD and CDE.

basis of the general purpose CAS program developed, for subsequent use; (b) definition of masses, Cartesian coordinates, and  $3N - 6$  interparticle distances as internal coordinates; (c) transformation from Cartesian coordinates to the  $3N - 6$  stretching-type interparticle distances, thus forming  $g^{jk}$  and  $h^j$  in these coordinates via equation (2); (d) elimination, if necessary, of the Cartesians left in  $g^{jk}$  due to the 'extraneous' interparticle distance(s); (e) successive transformations, via equations (3) and (4), from the stretching coordinates to the final set of internal coordinates after the explicit dependence of the new coordinates upon the old ones is provided; (f) inclusion of the stretching part of the Jacobian into  $\hat{T}_V$  through equation (6); and (g) simplification of the resulting  $g^{jk}$  and  $h^j$  expressions.

There are several stages during the calculation of the  $g^{jk}$  and  $h^j$  arrays where one relies on the capabilities of modern computer algebra languages. For example, all the required  $\partial q_j / \partial x_{ai}$ ,  $\partial^2 q_j / \partial x_{ai} \partial x_{ai}$ ,  $\partial q_j / \partial q'_k$ ,  $\partial^2 q_j / \partial q'_k \partial q'_l$ ,  $\partial s^{-1/2} / \partial q_j$ , and  $\partial^2 s^{-1/2} / \partial q_j \partial q_k$  Jacobian derivative tensors can be computed symbolically using simple built-in 'differentiate' functions. Furthermore, when the necessary matrix multiplications and summations appearing in the relevant equations, i.e., (2)–(4), and (6), are performed one can take advantage of the functions and programming language provided with CAS programs so that, for example, no reference is made to the size of the problem, resulting in a general code applicable to molecules of any size and complexity. One warning, however, is necessary at this point: the forms derived for  $g^{jk}$  and  $h^j$ , obtained through the straightforward use of equations (1)–(6), might contain an excessive number of terms. For example, for certain derivative terms expressions containing a few hundred terms have been obtained. As [37] and tables 1–7 show, however, the final expressions contain only a few terms. Thus, simplification of these complicated expressions is necessary. As emphasized, not only the derivations but also these simplifications should be done with as little human intervention as possible. In Mathematica, for example, judicious use of built-in

Table 7. Second-derivative parts in the exact quantum mechanical vibrational kinetic energy operator for (A,B)–C–D–E-like penta-atomic molecules in internal coordinates  $\{r_1, r_2, r_3, r_4, \theta_1, \theta_2, \theta_3, \tau_1, \tau_2\}$  (see figure 2).

	$r_1$	$r_2$	$r_3$	$r_4$	$\theta_1$
$r_1$	$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_4}$				
$r_2$	$\frac{2}{m_4} [\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)]$	$\frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_4}$			
$r_3$	$\frac{2 \cos \theta_1}{m_4}$	$\frac{2 \cos \theta_2}{m_4}$	$\frac{1}{\mu_3} = \frac{1}{m_3} + \frac{1}{m_4}$		
$r_4$	0	0	$\frac{2 \cos \theta_3}{m_3}$	$\frac{1}{\mu_4} = \frac{1}{m_3} + \frac{1}{m_5}$	
$\theta_1$	$-\frac{2 \sin \theta_1}{m_4 r_3}$	$\frac{2}{m_4} \left[ \frac{\cos \theta_1 \sin \theta_2 \cos(\tau_1 - \tau_2)}{r_1} - \frac{\sin \theta_2 \cos(\tau_1 - \tau_2)}{r_3} - \frac{\sin \theta_1 \cos \theta_2}{r_1} \right]$	$-\frac{2 \sin \theta_1}{m_4 r_1}$	$\frac{2 \sin \theta_3 \cos \tau_2}{m_3 r_3}$	$\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_3 r_3^2} - \frac{2 \cos \theta_1}{m_4 r_1 r_3}$
$\theta_2$	$\frac{2 \sin \theta_1 \cos \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_2} - \frac{2 \sin \theta_1 \cos(\tau_1 - \tau_2)}{m_4 r_3} - \frac{2 \cos \theta_1 \sin \theta_2}{m_4 r_2}$	$-\frac{2 \sin \theta_2}{m_4 r_3}$	$-\frac{2 \sin \theta_2}{m_4 r_2}$	$\frac{2 \sin \theta_3 \cos \tau_1}{m_3 r_3}$	$\frac{2 \cos(\tau_1 - \tau_2)}{\mu_3 r_3^2} - \frac{2 \cos \theta_1 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_3} + \frac{2 \cos \theta_1 \cos \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_1 r_2} + \frac{2 \sin \theta_1 \sin \theta_2 - 2 \cos \theta_2 \cos(\tau_1 - \tau_2)}{m_4 r_2 r_3}$
$\theta_3$	$\frac{2 \sin \theta_1 \cos \tau_2}{m_4 r_3}$	$\frac{2 \sin \theta_2 \cos \tau_1}{m_4 r_3}$	$-\frac{2 \sin \theta_3}{m_3 r_4}$	$-\frac{2 \sin \theta_3}{m_3 r_3}$	$2 \cos \tau_2 \left( -\frac{1}{\mu_3 r_3^2} + \frac{\cos \theta_1}{m_4 r_1 r_3} + \frac{\cos \theta_3}{m_3 r_3 r_4} \right)$
$\tau_1$	$\frac{2 \sin \theta_1 \cot \theta_2 \sin(\tau_1 - \tau_2)}{m_4 r_3} - \frac{2 \sin \theta_1 \operatorname{cosec} \theta_2 \sin(\tau_1 - \tau_2)}{m_4 r_2} - \frac{2 \sin \theta_1 \cot \theta_3 \sin \tau_2}{m_4 r_3}$	$\frac{2 \sin \tau_1 \sin \theta_2 \cot \theta_3}{m_4 r_3}$	0	$-\frac{2 \sin \tau_1 \cot \theta_2 \sin \theta_3}{m_3 r_3}$	$\frac{2 \cot \theta_3 \sin \tau_2}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_3 \sin \tau_2}{m_3 r_3 r_4} - \frac{2 \cot \theta_2 \sin(\tau_1 - \tau_2)}{\mu_3 r_3^2} + \frac{2 \operatorname{cosec} \theta_2 \sin(\tau_1 - \tau_2)}{m_3 r_3 r_4} - \frac{2 \cos \theta_1 \cot \theta_3 \sin \tau_2}{m_3 r_1 r_4} + \frac{2 \cos \theta_1 \cot \theta_2 \sin(\tau_1 - \tau_2)}{m_4 r_1 r_3} - \frac{2 \cos \theta_1 \operatorname{cosec} \theta_2 \sin(\tau_1 - \tau_2)}{m_4 r_1 r_2}$
$\tau_2$	$-\frac{2 \sin \tau_2 \sin \theta_1 \cot \theta_3}{m_4 r_3}$	$-\frac{2 \sin \theta_2 \cot \theta_1 \sin(\tau_1 - \tau_2)}{m_4 r_3} + \frac{2 \sin \theta_2 \operatorname{cosec} \theta_1 \sin(\tau_1 - \tau_2)}{m_4 r_1} - \frac{2 \sin \theta_2 \cot \theta_3 \sin \tau_1}{m_4 r_3}$	0	$-\frac{2 \sin \tau_2 \cot \theta_1 \sin \theta_3}{m_3 r_3}$	$\frac{2 \cot \theta_3 \sin \tau_2}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_3 \sin \tau_2}{m_3 r_3 r_4} - \frac{\cos \theta_1 \cot \theta_3 \sin \tau_2}{m_4 r_1 r_3}$

	$\theta_2$	$\theta_3$	$\tau_1$	$\tau_2$
$\theta_2$	$\frac{1}{\mu_2 r_2^2} + \frac{1}{\mu_3 r_3^2} - \frac{2 \cos \theta_2}{m_4 r_2 r_3}$			
$\theta_3$	$2 \cos \tau_1 \left( -\frac{1}{\mu_3 r_3^2} + \frac{\cos \theta_2}{m_4 r_2 r_3} + \frac{\cos \theta_3}{m_3 r_3 r_4} \right)$	$\frac{1}{\mu_3 r_3^2} + \frac{1}{\mu_4 r_4^2} - \frac{2 \cos \theta_3}{m_3 r_3 r_4}$		
$\tau_1$	$\frac{2 \cot \theta_3 \sin \tau_1}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_3 \sin \tau_1}{m_3 r_3 r_4} - \frac{\cos \theta_2 \cot \theta_3 \sin \tau_1}{m_4 r_2 r_3}$	$\frac{2 \cot \theta_2 \sin \tau_1}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_2 \sin \tau_1}{m_4 r_2 r_3} - \frac{2 \cot \theta_2 \cos \theta_3 \sin \tau_1}{m_3 r_3 r_4}$	$\frac{\operatorname{cosec}^2 \theta_2 + \cot^2 \theta_2}{\mu_2 r_2^2 + \mu_3 r_3^2} + \frac{\cot^2 \theta_3 + \operatorname{cosec}^2 \theta_3}{\mu_3 r_3^2 + \mu_4 r_4^2} + \frac{2 \cos \tau_1 \cot \theta_2 \cot \theta_3}{\mu_3 r_3^2} - \frac{2 \cos \tau_1 \operatorname{cosec} \theta_2 \cot \theta_3}{m_4 r_2 r_3} - \frac{2 \operatorname{cosec} \theta_2 \cot \theta_2}{m_4 r_2 r_3} - \frac{2 \cos \tau_1 \cot \theta_2 \operatorname{cosec} \theta_3}{m_3 r_3 r_4} - \frac{2 \operatorname{cosec} \theta_3 \cot \theta_3}{m_3 r_3 r_4}$	
$\tau_2$	$\frac{2 \cot \theta_3 \sin \tau_1}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_3 \sin \tau_1}{m_3 r_3 r_4} - \frac{2 \cot \theta_1 \sin (\tau_1 - \tau_2)}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_1 \sin (\tau_1 - \tau_2)}{m_4 r_1 r_3} - \frac{2 \cos \theta_2 \cot \theta_3 \sin \tau_1}{m_4 r_2 r_3} - \frac{2 \cot \theta_1 \cos \theta_2 \sin (\tau_1 - \tau_2)}{m_4 r_2 r_3} + \frac{2 \operatorname{cosec} \theta_1 \cos \theta_2 \sin (\tau_1 - \tau_2)}{m_4 r_1 r_2}$	$\frac{2 \cot \theta_1 \sin \tau_2}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_1 \sin \tau_2}{m_4 r_1 r_3} - \frac{2 \cot \theta_1 \cos \theta_3 \sin \tau_2}{m_3 r_3 r_4}$	$\frac{2 \cot^2 \theta_3 + 2 \operatorname{cosec}^2 \theta_3}{\mu_3 r_3^2 + \mu_4 r_4^2} + \frac{2 \cos \tau_1 \cot \theta_2 \cot \theta_3}{\mu_3 r_3^2} + \frac{2 \cos \tau_2 \cot \theta_1 \cot \theta_3}{\mu_3 r_3^2} + \frac{2 \cot \theta_1 \cot \theta_2 \cos (\tau_1 - \tau_2)}{\mu_3 r_3^2} - \frac{2 \operatorname{cosec} \theta_1 (\cos (\tau_1 - \tau_2) \cot \theta_2 + \cos \tau_2 \cot \theta_3)}{m_4 r_1 r_3} - \frac{2 \operatorname{cosec} \theta_2 (\cos (\tau_1 - \tau_2) \cot \theta_1 + \cos \tau_1 \cot \theta_3)}{m_4 r_2 r_3} - \frac{2 \cos \tau_1 \cot \theta_2 \operatorname{cosec} \theta_3}{m_3 r_3 r_4} - \frac{2 \cos \tau_2 \cot \theta_1 \operatorname{cosec} \theta_3}{m_3 r_3 r_4} - \frac{2 \cot \theta_3 \operatorname{cosec} \theta_3}{m_4 r_1 r_3} - \frac{2 \cot \theta_3 \operatorname{cosec} \theta_3}{m_3 r_3 r_4} - \frac{2 \cot \theta_1 \operatorname{cosec} \theta_1}{m_4 r_1 r_3} - \frac{2 \cot \theta_1 \operatorname{cosec} \theta_1}{m_3 r_3 r_4}$	$\frac{\operatorname{cosec}^2 \theta_1 + \cot^2 \theta_1}{\mu_1 r_1^2 + \mu_3 r_3^2} + \frac{\cot^2 \theta_3 + \operatorname{cosec}^2 \theta_3}{\mu_3 r_3^2 + \mu_4 r_4^2} + \frac{2 \cos \tau_2 \cot \theta_1 \cot \theta_3}{\mu_3 r_3^2} - \frac{2 \cos \tau_2 \operatorname{cosec} \theta_3 \cot \theta_1}{m_3 r_3 r_4} - \frac{2 \operatorname{cosec} \theta_3 \cot \theta_3}{m_3 r_3 r_4} - \frac{2 \cos \tau_2 \cot \theta_3 \operatorname{cosec} \theta_1}{m_4 r_1 r_3} - \frac{2 \operatorname{cosec} \theta_1 \cot \theta_1}{m_4 r_1 r_3}$



functions like Simplify, Substitute, Expand, Together, and Collect, together with several explicit, user-defined trigonometric simplification rules and the occasional collection of terms with common denominators can effectively reduce the number of terms to those presented in tables 1–7.

### 3.2. Choice of internal coordinates

When choosing the internal coordinates  $\{q_i\}$  in which the exact quantum mechanical vibrational 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 (note in this context that in the case of multidimensional quadratic Hamiltonians rectilinear normal coordinates, linear combinations of mass-weighted Cartesians, provide complete separation both in the kinetic and potential energy terms); (b) certain transformations [some or all of equations (1)–(6)] may need to be carried out repeatedly; and (c) the choice of  $\{q_i\}$  not only determines the actual form of  $\hat{T}_v$  but also it in turn affects the choice of the basis set for the expansion of the wavefunction through occurrences of unavoidable singularities in the Hamiltonian  $\hat{H}_v$ . It is extremely important to emphasize this last point, as to facilitate efficient practical calculations of vibrational spectra  $\hat{H}_v$  should be separable and factorizable [26b]. It should also be noted that the use of curvilinear internal coordinates ensures that no difficulties arise at special nuclear arrangements (e.g., at linear configurations).

Combined consideration of the above factors dictate the use of simple, elementary internal coordinates in the derivation of  $\hat{T}_v$ . This means that simple, unsymmetrized stretching and angle bending coordinates should be used as often as possible for coordinates involving two and three atoms. In the case of four-atomic molecules, for the remaining coordinates (usually involving out-of-plane- and torsional-type motions) it was found advantageous to use the usual torsional coordinate for HCCH and HOOH [26], and the book-angle coordinate for H<sub>2</sub>CO [21]. Use of these internal coordinates seems to ensure both the relative ease of transformations and the required properties of  $\hat{T}_v$ , while their dependence on simple stretch and angle bend coordinates can either be obtained from textbooks [33] or derived. At the same time, these coordinates are usually appropriate for the expansion of the potential energy for semi-rigid molecules [44]. For the penta-atomic molecules presented in this paper use of the regular torsional coordinates proved to be also desirable. For example, use of two torsions for the (A,B)–C–D–E-type penta-atomic molecules provides a symmetric kinetic energy operator (see tables 6 and 7), which means that application of the derived operator to symmetric molecules, such as ketene (H<sub>2</sub>CCO, of C<sub>2v</sub> symmetry), is straightforward. Note, however, that the introduction of novel internal coordinates might be advisable and/or unavoidable for other (especially larger) molecular systems.

One particularly important advantage of special internal coordinate systems would be if they greatly reduced the number of terms in the exact kinetic energy operator. It is noted that while in the valence internal coordinates employed in this study the exact quantum mechanical vibrational kinetic energy operator for a sequentially bonded triatomic molecule contains only 15 individual terms (see tables 1 and 2), the exact vibrational kinetic energy operator for an (A,B)–C–D–E-type penta-atomic molecule is composed of 160 terms (tables 6 and 7), though many of

them are not distinct. To reduce the number of terms in the kinetic energy expression has particular importance in certain numerical algorithms used to solve the rovibrational Schrödinger equation. (For example, the Lanczos algorithm [45] will gain considerable efficiency if the product of the Hamiltonian and the trial vector can be formed easily [12g].) In this respect orthogonal internal coordinate systems (e.g., Jacobi [46], Radau [47], and hyperspherical [48] coordinates) may have a lot to offer, as  $\hat{T}_V$  expressed in these coordinates contains no mixed second derivatives. Indeed, orthogonal coordinates have been used routinely for triatomic and tetra-atomic systems having the required molecular arrangement. Note, however, that in those regions of the potential energy surface where bond making or breaking does not occur, and especially around equilibrium,  $\hat{V}_N$  is usually more separable in valence internal coordinates than in orthogonal coordinates.

### 3.3. Reduction in the size of the variational problem

Although the kinetic energy operators presented in this communication would, in principle, allow the determination of a great number of vibrational eigenvalues and eigenvectors for interesting penta-atomic molecules like  $\text{H}_2\text{CCO}$ ,  $\text{HCOCN}$ ,  $\text{C}_3\text{O}_2$ ,  $\text{HC}_4$ , etc., it is obviously not practical to carry out FBR calculations in all nine dimensions due to the excessive cost of the required computations. Therefore, attempts to reduce the dimensionality of the variational problem are of considerable importance. At this point it should be noted that reduction in the size of the rovibrational problem of a general penta-atomic molecule has already been achieved, when the kinetic energy operator was restricted to be rotationless (i.e., having total angular momentum zero), thus reducing the complete 12-dimensional problem by the three rotational degrees of freedom. This reduction was achieved by effectively setting all angular momentum components appearing in the full exact rovibrational kinetic energy operator to zero. In other words, by taking the wavefunction to be independent of the Euler angles a projection of the full vibration-rotation  $\hat{T}_{VR}$  onto the rotationless  $J = 0$  state has been achieved. As required, this simple procedure yields a Hermitian kinetic energy operator  $\hat{T}_V$ .

One possible method for reduction of the size of the variational problem, documented and rationalized a long time ago within the framework of normal modes [33], is the adiabatic separation of vibrations of considerably differing frequencies [23g, 33, 49–52]. The adiabatic approach, when extended beyond the normal mode picture, seems to have found experimental justification in at least two important and complementary cases: (a) the local mode picture for X–H stretching overtones [53]; and (b) the bender models for low-frequency motions [54–57]. Despite these apparent successes it must be noted that adiabatic methods will break down, or require special treatment, if resonances are present, and that they do not give a bound to the true energy. In practical applications of the adiabatic approach one usually separates the stretching and bending modes of vibration, as for many molecular systems this is a very natural separation. (As illustrated by Reinhardt and co-workers [50] there are not one but two adiabatic ('slow' versus 'fast') separations for stretch-bend Hamiltonians. The traditional adiabatic bend (AB) method considers the bends to be adiabatic ('slow') with respect to stretchings, while the counterintuitive adiabatic stretch (AS) method assumes just the opposite. See, furthermore, the comments of Ojha and Berry [51c] concerning these methods and, in particular, flaws in the treatment of Reinhardt.) Such adiabatic approaches, in the context of theoretical

rovibrational spectroscopy, offer considerable advantages, as they allow (a) rovibrational calculations to be carried out to considerably higher energies than traditionally seemed practical; and (b) studies of (ro)vibrational states of molecules of medium size given that the number of active coordinates is kept less than about 6 or 7. Note also that a postulated near adiabatic approximation between certain degrees of freedom has been used successfully to contract multidimensional basis sets in rovibrational studies of tri- and tetra-atomic molecules [3, 26].

In practice, therefore, one way forward in the reduction of the size of the variational problem is to use the exact  $\hat{T}_v$  operator in all  $3N - 6$  coordinates and to use expansion functions of the form

$$\Phi_r = \prod_{i=1}^p f_i(q_i) \prod_{j=p+1}^{3N-6} f_{rj}(q_j). \quad (7)$$

In other words, fixed forms are used for some of the internal coordinate expansion functions. For example, all of the stretch coordinates could be associated with fixed (possibly optimized SCF) harmonic or Morse-oscillator functions. In such a case the secular matrix would determine the bending-only spectrum, the stretching motions being only zero point. In the case of the sequentially bonded penta-atomic molecules, there would be essentially five active bending and torsion modes. Such a calculation is very feasible. (The bending/torsion motions of some molecules, such as  $C_3O_2$ , are extremely anharmonic, and the only way forward towards a complete understanding of such motions will be through a solution of the secular equations for the problem.) Of course, extensions to the inclusions of a small number of stretching configurations to look after major resonances are also possible. At this stage we stress that the relatively large number of terms in  $\hat{T}_v$  will not present any problem if the FBR method is used for the variational calculation. (For the discrete variable representations of complicated kinetic energy operators see [58].) By its nature, all matrix elements will be products of prestored one-dimensional integrals. It is also probable that the number of terms in the potential will also be of the same order. Of course, all the methodology of successive contractions [26d], which has made the FBR approach a success, must be employed.

A simpler approach, which finds less favour with us but may be more practical is to ignore some internal coordinates completely. For example, one may use expansion functions which depend only upon bending and torsion coordinates. In this case all terms making differentiation with respect to stretching coordinates in the Lagrangian form of  $\hat{T}_v$  [28, 33, 59] are deleted, and bond lengths are given their equilibrium values. Furthermore, because no integrations are carried out in 'stretch' space, it is not appropriate to carry out transformation (5). In an approach such as this one must be careful that one has, after deletion, a Hermitian operator. It is always possible to write the full  $\hat{T}_v$  writing products of Hermitian and anti-Hermitian form [26b], and therefore it must be possible to write any reduced  $\hat{T}_v$  similarly. Note also that in certain molecules the bending-type vibrational motions might be strongly coupled to the overall rotation of the molecule. In these species discarding these effects can be only a first step towards understanding their complete motion.

#### 4. Conclusion

Distinct features of modern computer algebra systems (e.g., their highly functional programming language, numerous, easily applicable and extendable built-in func-

tions, and their capability of performing symbolic determination and manipulation of complex functions and expressions) provide the necessary computing environment for the determination of kinetic energy operators in internal coordinates. As a practical application of the general-purpose CAS package developed, forms for the exact (within the Born–Oppenheimer approximation) non-relativistic quantum mechanical vibrational ( $J = 0$ ) kinetic energy operators for sequentially bonded (A–B–C–D–E) and (A,B)–C–D–E-type penta-atomic molecules, expressed in valence internal coordinates are presented. Based on the equivalence of the contravariant metric tensor,  $g^{jk}$  with the inverse kinetic energy matrix  $G_{jk}$  there are obvious similarities to previously defined operators for tri- and tetra-atomic molecules based on the same elementary internal coordinates. Although the kinetic energy operators presented in this communication would, in principle, allow determination of a great number of vibrational eigenvalues and eigenvectors for interesting penta-atomic molecules like  $\text{H}_2\text{CCO}$ ,  $\text{C}_3\text{O}_2$ ,  $\text{HCOCN}$ ,  $\text{HC}_4$ , etc., it is obviously not practical to carry out variational calculations in all nine dimensions due to the excessive cost of the required computations. Therefore it is suggested that, while retaining the full exact vibrational kinetic energy operator, a fixed form should be used for some of the internal coordinate expansion functions (e.g., for the stretch coordinates if the bend-only spectrum is to be calculated). Naturally, reduction in the dimension of the kinetic energy operator by appropriate constraints is also possible, but this approach finds less favour with us.

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