Symmetrized form of kinetic energy operator of pentatomic molecules with three identical atoms in internal coordinates

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A symmetrized form of the vibrational kinetic energy for pentatomic molecules with three identical atoms in internal coordinates is presented. This form allows application of the Wigner–Eckart theorem, which can considerably facilitate calculation of the matrix elements.

Introduction

The total kinetic energy operator is transformed by the totally symmetric representation. In many cases the study of the symmetry properties of the kinetic energy operator is restricted to only this statement. Nevertheless, in the case that wave functions are presented as a sum of a large number of terms, representation of the kinetic energy operator in the symmetrized form allows some optimization of calculation of matrix elements. It should be noted that sophistication of the kinetic energy operator symmetrization strongly depends on the used internal coordinates.[1–4] We specify the internal coordinates by four vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, $\mathbf{r}_4$, each being the linear combination of radius vectors of a pentatomic molecule in some coordinate system.[1] Permutation of three vectors $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$ can be reduced to permutation of equivalent atoms. As internal coordinates, we use four separations r_1, r_2, r_3, r_4, three angles between the bonds q_{12}, q_{13}, q_{14}, and two torsion angles t_{23}, t_{24}.

Transformation of torsion coordinates at (23) and (34) permutations

Figure 1 demonstrates transformation of torsion coordinates at $(23)I$ permutations. The inversion I is needed to keep the right orientation of the coordinate axes. From the Figure we can obtain the transformation rules presented in the second row of the Table.

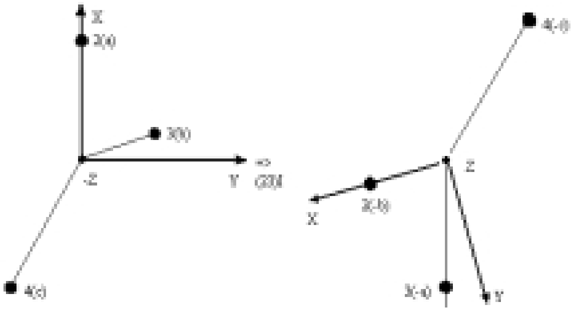

Fig. 1. Transformation of the coordinate system at $(23)I$ permutation, where I is inversion.

Transformation of torsion coordinates and their derivatives

Permutation	Permutation-induced transformation of torsion coordinates		$\frac{\partial}{\partial \tilde{t}} = \frac{\partial t_3}{\partial \tilde{t}}\frac{\partial}{\partial t_3} + \frac{\partial t_4}{\partial \tilde{t}}\frac{\partial}{\partial t_4}$	
$(23)I$	$\tilde{t}_3 = t_3$	$\tilde{t}_4 = t_3 - t_4$	$\frac{\partial}{\partial \tilde{t}_3} = \frac{\partial}{\partial t_3} + \frac{\partial}{\partial t_4}$	$\frac{\partial}{\partial \tilde{t}_4} = -\frac{\partial}{\partial t_4}$
$(34)I$	$\tilde{t}_3 = -t_4$	$\tilde{t}_4 = -t_3$	$\frac{\partial}{\partial \tilde{t}_3} = -\frac{\partial}{\partial t_4}$	$\frac{\partial}{\partial \tilde{t}_4} = -\frac{\partial}{\partial t_3}$
(234)=(34)(23)	$\tilde{t}_3 = -t_4$	$\tilde{t}_4 = t_3 - t_4$	$\frac{\partial}{\partial \tilde{t}_3} = -\frac{\partial}{\partial t_3} - \frac{\partial}{\partial t_4}$	$\frac{\partial}{\partial \tilde{t}_4} = \frac{\partial}{\partial t_3}$
(243)=(23)(34)	$\tilde{t}_3 = t_4 - t_3$	$\tilde{t}_4 = -t_3$	$\frac{\partial}{\partial \tilde{t}_3} = \frac{\partial}{\partial t_4}$	$\frac{\partial}{\partial \tilde{t}_4} = -\frac{\partial}{\partial t_3} - \frac{\partial}{\partial t_4}$
$(24)I$=(34)(234)	$\tilde{t}_3 = t_4 - t_3$	$\tilde{t}_4 = t_4$	$\frac{\partial}{\partial \tilde{t}_3} = -\frac{\partial}{\partial t_3}$	$\frac{\partial}{\partial \tilde{t}_4} = \frac{\partial}{\partial t_3} + \frac{\partial}{\partial t_4}$

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By similar reasoning, we can obtain the transformation rules for the torsion coordinates at the (34)I permutation, which are also presented in the Table. The transformation rules for the torsion coordinates at other permutations can be derived from those for (23)I and (34)I. Transformations of the torsion coordinates and their derivatives are summarized in the Table.

Construction of symmetrized functions

Using the Table, we can show that for any function $f()$ it is possible to construct three functions of two torsion angles t_3 and t_4 transformed according to the irreducible representations E and A_1. In the particular case $f(t) = t$, the function A_1 is zero:

$$E_a(t_3,t_4) = \frac{1}{\sqrt{6}}\left[f(-t_3) + f(t_4) - 2f(t_3 - t_4)\right],$$

$$E_b(t_3,t_4) = \frac{1}{\sqrt{2}}\left[f(t_4) - f(-t_3)\right],$$

$$A_1(t_3,t_4) = \frac{1}{\sqrt{3}}\left[f(t_3) + f(-t_4) + f(-t_3 + t_4)\right].$$

It is also possible to construct the following symmetrized functions of the first and second derivatives with respect to the torsion coordinates:

$$E_a\left(\frac{\partial}{\partial t_i}\right) = \frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial t_4} - \frac{\partial}{\partial t_3}\right),\ E_b\left(\frac{\partial}{\partial t_i}\right) = \sqrt{\frac{3}{2}}\left(\frac{\partial}{\partial t_4} + \frac{\partial}{\partial t_3}\right),$$

$$E_a\left(\frac{\partial^2}{\partial t_i^2}\right) = \frac{1}{\sqrt{6}}\left(\frac{\partial^2}{\partial t_3^2} + \frac{\partial^2}{\partial t_4^2} + 4\frac{\partial}{\partial t_3}\frac{\partial}{\partial t_4}\right),$$

$$E_b\left(\frac{\partial^2}{\partial t_i^2}\right) = \frac{1}{\sqrt{2}}\left(\frac{\partial^2}{\partial t_4^2} - \frac{\partial^2}{\partial t_3^2}\right),$$

$$A_1\left(\frac{\partial^2}{\partial t_i^2}\right) = \frac{1}{\sqrt{3}}\left(\frac{\partial^2}{\partial t_3^2} + \frac{\partial^2}{\partial t_4^2} + \frac{\partial}{\partial t_3}\frac{\partial}{\partial t_4}\right).$$

As a symmetrized functions for q, we use the standard symmetrized functions:

$$E_a\left[f(q_i)\right] = \frac{1}{\sqrt{6}}\left[2f(q_2) - f(q_3) - f(q_4)\right],$$

$$E_b\left[f(q_i)\right] = \frac{1}{\sqrt{2}}\left[-f(q_3) + f(q_4)\right];$$

$$A_1\left[f(q_i)\right] = \frac{1}{\sqrt{3}}\left[f(q_2) + f(q_3) + f(q_4)\right];$$

$$E_a\left[f(q_i)f(q_j)\right] = \\ = \frac{1}{\sqrt{6}}\left[f(q_2)f(q_3) + f(q_2)f(q_4) - 2f(q_3)f(q_4)\right],$$

$$E_b\left[f(q_i)f(q_j)\right] = \\ = \frac{1}{\sqrt{2}}\left[-f(q_2)f(q_3) + f(q_2)f(q_4)\right];$$

$$A_1\left[f(q_i)f(q_j)\right] = \\ = \frac{1}{\sqrt{3}}\left[f(q_2)f(q_3) + f(q_2)f(q_4) + f(q_3)f(q_4)\right].$$

Similar symmetrized functions can be used for the coordinates r_i and masses m_i.

Symmetrization of vibrational kinetic energy

Represent the total vibrational kinetic energy as a sum

$$H = H_1^{QQ} + H_2^{QQ} + H_3^{QQ} + H^{QT} + H_1^{TT} + H_2^{TT} + H_3^{TT},$$

where

$$H_1^{QQ} = \frac{1}{m_1 r_1^2}\sum_{i=2}^{4}\left(\frac{\partial^2}{\partial q_i^2} + \cot(q_i)\frac{\partial}{\partial q_i}\right),$$

$$H_2^{QQ} = \sum_{i=2}^{4}\frac{1}{m_i r_i^2}\left(\frac{\partial^2}{\partial q_i^2} + \cot(q_i)\frac{\partial}{\partial q_i}\right);$$

$$H_3^{QQ} = \frac{2}{m_1 r_1^2}\times \\ \times\left(\cos(t_3)\frac{\partial^2}{\partial q_2\partial q_3} + \cos(t_4)\frac{\partial^2}{\partial q_2\partial q_4} + \cos(t_3 - t_4)\frac{\partial^2}{\partial q_3\partial q_4}\right);$$

$$H^{QT} = \frac{2}{m_1 r_1^2}\left(-\sin(t_3)\cot(q_3)\frac{\partial^2}{\partial q_2\partial t_3} - \right. \\ \left. -\sin(t_4)\cot(q_4)\frac{\partial^2}{\partial q_2\partial t_4} + A^{QT} + B^{QT}\right);$$

$$A^{QT} = -\sin(t_3)\cot(q_2)\frac{\partial^2}{\partial q_3\partial t_3} + \\ +\sin(t_3 - t_4)\cot(q_4)\frac{\partial^2}{\partial q_4\partial t_4} - \sin(t_3)\cot(q_4)\frac{\partial^2}{\partial q_4\partial t_4};$$

$$B^{QT} = -\cot(q_3)\sin(t_3 - t_4)\frac{\partial^2}{\partial q_4\partial t_3} - \\ -\sin(t_4)\cot(q_2)\frac{\partial^2}{\partial q_4\partial t_3} - \sin(t_4)\cot(q_2)\frac{\partial^2}{\partial q_4\partial t_4};$$

$$H_1^{TT} = \frac{1}{m_2 r_2^2\sin^2(q_2)}\left(\frac{\partial^2}{\partial t_3^2} + \frac{\partial^2}{\partial t_4^2} + 2\frac{\partial^2}{\partial t_3\partial t_4}\right) + \\ + \frac{1}{m_3 r_3^2\sin^2(q_3)}\frac{\partial^2}{\partial t_3^2} + \frac{1}{m_4 r_4^2\sin^2(q_4)}\frac{\partial^2}{\partial t_4^2};$$

$$H_2^{TT} = \frac{-2}{m_1 r_1^2}\left(\cos(t_3)\cot(q_2)\cot(q_3)\frac{\partial^2}{\partial t_3^2} + \right.$$
$$\left. + \cos(t_4)\cot(q_2)\cot(q_4)\frac{\partial^2}{\partial t_4^2} + C^{TT}\right);$$

$$C^{TT} = [\cos(t_3)\cot(q_2)\cot(q_3) + \cos(t_3)\cot(q_2)\cot(q_3) -$$
$$- \cos(t_3 - t_4)\cot(q_3)\cot(q_4)]\frac{\partial^2}{\partial t_3 \partial t_4};$$

$$H_3^{TT} = \frac{1}{m_1 r_1^2}\left[\cot^2(q_2)\left(\frac{\partial^2}{\partial t_3^2} + \frac{\partial^2}{\partial t_3^2} + 2\frac{\partial^2}{\partial t_3 \partial t_4}\right) + \right.$$
$$\left. + \cot^2(q_3)\frac{\partial^2}{\partial t_3^2} + \cot^2(q_4)\frac{\partial^2}{\partial t_4^2}\right].$$

Each of seven terms (H_1^{QQ}, H_2^{QQ}, H_3^{QQ}, H^{QT}, H_1^{TT}, H_2^{TT}, H_3^{TT}) is transformed according to the representation A_1, which can be readily shown using the transformation rules for the coordinates and derivatives at the $(23)I$ and $(34)I$ permutations. We use the following definition for bound operators[5]:

$$(|G_a>|G_b>)_\sigma^G =$$
$$= \sqrt{|G|}\sum_{\sigma_a\sigma_b}\begin{pmatrix} G_a & G_b & G \\ \sigma_a & \sigma_b & \sigma \end{pmatrix} |G_a\sigma_a>|G_b\sigma_b>,$$

where

$$\begin{pmatrix} E & E & E \\ 1 & 1 & 1 \end{pmatrix} = -\frac{1}{2}, \quad \begin{pmatrix} E & E & E \\ 1 & 2 & 2 \end{pmatrix} = \frac{1}{2},$$
$$\begin{pmatrix} A_2 & E & E \\ 1 & 1 & 2 \end{pmatrix} = \frac{1}{\sqrt{2}}, \quad \begin{pmatrix} A_1 & E & E \\ 1 & 1 & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}.$$

In some cases, of interest is decomposition into the irreducible Q and T parts. For H_1^{QQ}, no transformation is needed:

$$H_2^{QQ} = \left\{A_1\left(\frac{1}{m_i r_i^2}\right)A_1\left(\frac{\partial^2}{\partial q_i^2} + \cot(q_i)\frac{\partial}{\partial q_i}\right) + \right.$$
$$\left. + \sqrt{2}\left[E\left(\frac{1}{m_i r_i^2}\right)E\left(\frac{\partial^2}{\partial q_i^2} + \cot(q_i)\frac{\partial}{\partial q_i}\right)\right]^{A_1}\right\},$$

$$H_3^{QQ} = \frac{2}{m_1 r_1^2}\times$$
$$\times\left[A_1[\cos(t_i)]A_1(\frac{\partial^2}{\partial q_i \partial q_j}) + \sqrt{2}\left(E[\cos(t_i)]E(\frac{\partial^2}{\partial q_i \partial q_j})\right)^{A_1}\right].$$

Represent the QT part of the vibrational kinetic energy as the sum

$$H^{QT,E} = 2\left\{\left[E[\cot(q_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^E - \right.$$
$$-\left[\left(E[\cot(q_i)]A_1\left(\frac{\partial}{\partial q_i}\right)\right)^E\right]\Bigg\}\left[E[\sin(t_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^{A_1} +$$
$$+2\left\{\left(\left[E[\cot(q_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^E + \left[A_1[\cot(q_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^E\right)\times\right.$$
$$\left.\times\left[A_1[\sin(t_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^E\right\}^{A_1},$$

$$H^{QT,A_1} = \left\{-\sqrt{2}\left[E[\cot(q_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^{A_1} - \right.$$
$$\left. -2\left[A_1[\cot(q_i)]A_1\left(\frac{\partial}{\partial q_i}\right)\right]^{A_1}\right\}\left[E[\sin(t_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^{A_1},$$

$$H^{QT,A_2} = \sqrt{2}\left\{\left((E[\cot(q_i)]E\left(\frac{\partial}{\partial q_i}\right)\right)^{A_2}\times\right.$$
$$\left.\times\left[E[\sin(t_i)]E\left(\frac{\partial}{\partial q_i}\right)\right]^{A_2}\right\}^{A_1}.$$

Represent the TT part of the vibrational kinetic energy as the sums:

$$H_1^{TT} = \frac{2}{\sqrt{6}}\left[E\left(\frac{1}{m_i r_i^2}\right)E\left(\frac{1}{\sin^2(q_i)}\right)E\left(\frac{\partial^2}{\partial t_i^2}\right)\right]^{A_1} +$$
$$+\frac{2\sqrt{2}}{\sqrt{3}}\left[E\left(\frac{1}{m_i r_i^2}\right)E\left(\frac{1}{\sin^2(q_i)}\right)\right]^{A_1} A_1\left(\frac{\partial^2}{\partial t_i^2}\right) +$$
$$+\frac{\sqrt{2}}{\sqrt{3}}A_1\left(\frac{1}{m_i r_i^2}\right)\left[E\left(\frac{1}{\sin^2(q_i)}\right)E\left(\frac{\partial^2}{\partial t_i^2}\right)\right]^{A_1} +$$
$$+\frac{\sqrt{2}}{\sqrt{3}}A_1\left(\frac{1}{\sin^2(q_i)}\right)\left[E\left(\frac{1}{m_i r_i^2}\right)E\left(\frac{\partial^2}{\partial t_i^2}\right)\right]^{A_1} +$$
$$+ \frac{2}{\sqrt{3}}A_1\left(\frac{1}{\sin^2(q_i)}\right)A_1\left(\frac{1}{m_i r_i^2}\right)A_1\left(\frac{\partial^2}{\partial t_i^2}\right);$$

$$H_2^{TT} = \frac{-2\sqrt{2}}{m_1 r_1^2\sqrt{3}}\times$$
$$\times\left\{\left[E[\cot(q_i)\cot(q_j)]E[\cos(t_i)]E\left(\frac{\partial^2}{\partial t_i^2}\right)\right]^{A_1} + \right.$$
$$+\frac{1}{\sqrt{2}}\left[A_1[\cot(q_i)\cot(q_j)]A_1[\cos(t_i)]A_1\left(\frac{\partial^2}{\partial t_i^2}\right)\right] +$$
$$+\left\{E[\cot(q_i)\cot(q_j)]E[\cos(t_i)]\right\}^{A_1} A_1\left(\frac{\partial^2}{\partial t_i^2}\right) +$$

$$+A_1\left[\cot(q_i)\cot(q_j)\right]\left\{E[\cos(t_i)]E\left(\frac{\partial^2}{\partial t_i^2}\right)\right\}^{A_1}+$$

$$+A_1\left[\cos(t_i)\right]\left\{E[\cot(q_i)\cot(q_j)]E\left(\frac{\partial^2}{\partial t_i^2}\right)\right\}\Bigg\},$$

$$H_3^{TT}=\frac{1}{m_1 r_1^2}\left\{2A_1[\cot^2(q_i)]A_1\left(\frac{\partial^2}{\partial t_i^2}\right)+\right.$$

$$\left.+\sqrt{2}\left[E[\cot^2(q_i)]E\left(\frac{\partial^2}{\partial t_i^2}\right)\right]^{A_1}\right\}.$$

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