# Symmetry of the vibrational-rotational operator of the kinetic energy for pentatomic molecules with three and more identical atoms in the internal nonorthogonal coordinates

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Symmetry of the vibrational-rotational operator of the kinetic energy for pentatomic molecules with three and more identical atoms in the internal nonorthogonal coordinates is considered. The use of nonorthogonal coordinates can significantly simplify simultaneous description of several isotopic modifications of the same molecule.

## Introduction

In recent years, a considerable number of papers have appeared on the problem of constructing the kinetic energy quantum-mechanical operator for the polyatomic molecules in the internal coordinates.[1–5] In the Refs. 2 and 3, the kinetic energy quantum-mechanical operator has been constructed based on classical kinetic energy operator for the $n$-atomic molecules by replacing classical momentums and angular momentums by the corresponding quantum-mechanical operators, in addition, the formulas for calculation of the matrix elements are presented. In Ref. 4, the quantum-mechanical kinetic energy operator has been constructed by changing the variables (passing from laboratory coordinates to the internal polar coordinates and to the variables that describe rotational and translational motions of the molecule as a whole). In Ref. 5, the nonorthogonal terms of the kinetic energy operator have been considered in the general form for an arbitrary molecule.

In this paper, a symmetric form of the kinetic energy operator is presented in the internal nonorthogonal coordinates for the case of three and more atoms. Thus obtained form of the operator can make the calculation of matrix elements much easier, if the wave functions are presented in a symmetrized form. Besides, symmetry properties of the kinetic energy operator and angular momentums are considered at permutations of atoms. The symmetry of the kinetic energy quantum-mechanical operator in the internal nonorthogonal coordinates has been analyzed in Ref. 6.

Everywhere below, the internal coordinates are set by four vectors, $\mathbf{R}$, $\mathbf{d}_1$, $\mathbf{d}_2$, and $\mathbf{d}_3$, each of which is a linear combination of radius vectors of a pentatomic molecule in a certain coordinate system.[4] Permutation of three vectors, $\mathbf{d}_1$, $\mathbf{d}_2$, and $\mathbf{d}_3$, is reduced to permutation of equivalent atoms. As the internal coordinates, we use four distances, $R$, $d_1$, $d_2$, and $d_3$, three angles made by $\mathbf{R}$ with $\mathbf{d}_1$, $\mathbf{d}_2$, and $\mathbf{d}_3$ ($g_1$, $g_2$, and $g_3$), and two torsion angles, $\varphi_2$ and $\varphi_3$.

## Mass dependent coordinates

To exclude the translational motion of the $n$-atomic molecule from consideration, we shall make the $3n$ replacement of the laboratory coordinates $\mathbf{r}_i$ by $3(n-1)$ internal coordinates $\tilde{\mathbf{r}}_a = \sum_{i=1}^{n-1} t_{ai}(\mathbf{r}_i - \mathbf{r}_{cm})$ and the coordinates of center of mass $\mathbf{r}_{cm} = \sum_{j=1}^{n} \mu_j \mathbf{r}_j$ (here $t_{ai}$ depends on the atomic mass). Moreover, kinetic energy can be written[4] as follows:

$$T = T_{cm} - \frac{\hbar^2}{2M} \sum_{1}^{n-1} F_{ab} \frac{\partial^2}{\partial \tilde{r}_a \partial \tilde{r}_b}, \qquad (1)$$

where

$$F_{ab} = \sum_{i=1}^{n-1} \frac{1}{\mu_i} t_{ai} t_{bi} - \left( \sum_{i=1}^{n-1} t_{ai} \right)\left( \sum_{i=1}^{n-1} t_{bi} \right).$$

The internal coordinates are called orthogonal, if $F_{ab} = \delta_{ab}/\mu'_a$. It is advisable for the symmetric molecules that permutation of the $\tilde{\mathbf{r}}_a$ coordinates should correspond to the permutation of the $\mathbf{r}_i$ coordinates. Such a choice yields the symmetry of the $F_{ab}$ coefficients. For the $AB_4$ molecules, all the $F_{ab}$ coefficients are identical at $a \neq b$. For the $ABC_3$ molecules, it is possible to choose the $\tilde{\mathbf{r}}$; coordinates, for which $F_{12} = F_{13} = F_{14}$ and $F_{23} = F_{24} = F_{34}$. In case of considering several isotopic modifications of the same molecule, the use of orthogonal coordinates leads to the necessity of using their own coordinates

for each isotopic modification. The use of different coordinates makes it impossible to use the same potential energy surface for different isotopic modifications.

Alternative approach consists in using of nonorthogonal coordinates or the coordinates being orthogonal only for one isotopic modification. In this case, the form of kinetic energy gets complicated, since nondiagonal terms as $\dfrac{\partial^2}{\partial \tilde{r}_a \partial \tilde{r}_b}$ appear in it, when $a \neq b$.

## Symmetrical form of the kinetic energy operator in the internal nonorthogonal coordinates

Below we shall use definitions and designations from Refs. 4 and 5. The nonorthogonal addition can be presented in the following form[4]:

$$^{n}T^{\text{add}} = \frac{1}{2M} \sum_{i,j=0, i \neq j}^{3} F_{ij} (\mathfrak{R} + \mathfrak{I})_i (\mathfrak{R} + \mathfrak{I})_j, \qquad (2)$$

where

$$\mathfrak{R} = \mathfrak{R}_0 + \mathfrak{R}_1 + \mathfrak{R}_2 + \mathfrak{R}_3, \quad \mathfrak{I} = \mathfrak{I}_0 + \mathfrak{I}_1 + \mathfrak{I}_2 + \mathfrak{I}_3;$$

$$\mathfrak{R}_0 = i\hbar \mathbf{e}_z \frac{\partial}{\partial d_0};$$

$$\mathfrak{R}_i = i\hbar [\sin(\theta_i)\cos(\varphi_i), \sin(\theta_i)\sin(\varphi_i), \cos(\theta_i)] \frac{\partial}{\partial d_i}$$

for $i = 1, 2, 3$, and $\varphi_1 = 0$;

$$\mathfrak{I}_j = (A_j, B_j, C_j)\frac{1}{d_j} = [\mathbf{n}_j \times \mathbf{l}_j];$$

$n$ is the unit vector along the direction of $d$;

$$A_\alpha = \sin(\theta_\alpha)\sin(\varphi_\alpha)l_{\alpha z} - \cos(\theta_\alpha)l_{\alpha y};$$

$$B_\alpha = \cos(\theta_\alpha)l_{\alpha x} - \sin(\theta_\alpha)\cos(\varphi_\alpha)l_{\alpha z};$$

$$C_\alpha = -i\hbar \sin(\theta_\alpha)\frac{\partial}{\partial \theta_\alpha}; \quad A_1 = -\cos(\theta_1)l_{1y};$$

$$B_1 = -\frac{J_z - l_z}{\sin(\theta_1)}; \quad C_1 = -i\hbar \sin(\theta_1)\frac{\partial}{\partial \theta_1};$$

$$A_0 = -l_{0y}, \quad B_0 = l_{0x}, \quad C_0 = 0.$$

The angular momentum of the 2nd and the 3rd atom is determined in a standard way:

$$\hat{l}_{ix} = i h \left( \sin\varphi_i \frac{\partial}{\partial \theta_i} + \cot\theta_i \cos\varphi_i \frac{\partial}{\partial \varphi_i} \right),$$

$$\hat{l}_{iy} = i h \left( -\cos\varphi_i \frac{\partial}{\partial \theta_i} + \cot\theta_i \sin\varphi_i \frac{\partial}{\partial \varphi_i} \right),$$

$$\hat{l}_{iz} = -i h \left( \frac{\partial}{\partial \varphi_i} \right).$$

For a zero atom:

$$\mathbf{l}_0 = \mathbf{J} - \mathbf{l}_1 - \mathbf{l},$$

and for the atom 1:

$$\hat{l}_{1x} = -\cot\theta_1 (J_z - l_z), \quad \hat{l}_{1y} = -i\hbar \frac{\partial}{\partial \theta_1}, \quad \hat{l}_{1z} = J_z - l_z.$$

Obviously, only $\mathfrak{I}_0$ and $\mathfrak{I}_1$ depend on $J$. The $\mathfrak{R}_i$ includes only derivatives with respect to radial coordinates, and $\mathfrak{I}_j$ includes the derivatives with respect to angular coordinates and $J$. Reference 5 presents the form equivalent to the form (2), in which $\mathfrak{R}_i$ and $\mathfrak{I}_i$ are replaced by the explicit expressions.

## Transformation rules at atomic permutation

Table 1 demonstrates the transformations of torsion coordinates, their derivatives at atomic permutations (see Refs. 6 and 7), angular momentum operators $l$ and operators of the reduced angular momentum $\mathfrak{I}_j$.

**Table 1. Transformation of torsion coordinates, their derivatives and angular momentum operators at atomic permutations**

| Operator or coordinate | $(12)I$ | $(23)I$ |
|---|---|---|
| $\varphi_2$ | $\varphi_2$ | $-\varphi_3$ |
| $\varphi_3$ | $\varphi_2 - \varphi_3$ | $-\varphi_2$ |
| $\dfrac{\partial}{\partial \varphi_2}$ | $\dfrac{\partial}{\partial \varphi_2} + \dfrac{\partial}{\partial \varphi_3} - \dfrac{iJ_z}{\hbar}$ | $-\dfrac{\partial}{\partial \varphi_3}$ |
| $\dfrac{\partial}{\partial \varphi_3}$ | $-\dfrac{\partial}{\partial \varphi_3}$ | $-\dfrac{\partial}{\partial \varphi_2}$ |
| $\begin{pmatrix} l_{1x} \\ l_{1y} \end{pmatrix}$ | $\begin{pmatrix} -\cos(\varphi_2) & -\sin(\varphi_2) \\ -\sin(\varphi_2) & \cos(\varphi_2) \end{pmatrix}\begin{pmatrix} l_{2x} \\ l_{2y} \end{pmatrix}$ | $\begin{pmatrix} -l_{1x} \\ l_{1y} \end{pmatrix}$ |
| $l_{1z}$ | $-l_{2z}$ | $-l_{1z}$ |
| $\begin{pmatrix} l_{2x} \\ l_{2y} \end{pmatrix}$ | $\begin{pmatrix} -\cos(\varphi_2) & -\sin(\varphi_2) \\ -\sin(\varphi_2) & \cos(\varphi_2) \end{pmatrix}\begin{pmatrix} l_{1x} \\ l_{1y} \end{pmatrix}$ | $\begin{pmatrix} -l_{3x} \\ l_{3y} \end{pmatrix}$ |
| $l_{2z}$ | $l_{2z} + l_{3z} - J_z$ | $-l_{3z}$ |
| $\begin{pmatrix} l_{3x} \\ l_{3y} \end{pmatrix}$ | $\begin{pmatrix} -\cos(\varphi_2) & -\sin(\varphi_2) \\ -\sin(\varphi_2) & \cos(\varphi_2) \end{pmatrix}\begin{pmatrix} l_{3x} \\ l_{3y} \end{pmatrix}$ | $\begin{pmatrix} -l_{2x} \\ l_{2y} \end{pmatrix}$ |
| $l_{3z}$ | $-l_{3z}$ | $-l_{2z}$ |
| $\begin{pmatrix} A_1 \\ B_1 \end{pmatrix}$ | $\begin{pmatrix} \cos(\varphi_2) & \sin(\varphi_2) \\ \sin(\varphi_2) & -\cos(\varphi_2) \end{pmatrix}\begin{pmatrix} A_2 \\ B_2 \end{pmatrix}$ | $\begin{pmatrix} A_1 \\ -B_1 \end{pmatrix}$ |
| $C_1$ | $C_2$ | $C_1$ |
| $\begin{pmatrix} A_2 \\ B_2 \end{pmatrix}$ | $\begin{pmatrix} \cos(\varphi_2) & \sin(\varphi_2) \\ \sin(\varphi_2) & -\cos(\varphi_2) \end{pmatrix}\begin{pmatrix} A_1 \\ B_1 \end{pmatrix}$ | $\begin{pmatrix} A_3 \\ -B_3 \end{pmatrix}$ |
| $C_2$ | $C_1$ | $C_3$ |
| $\begin{pmatrix} A_3 \\ B_3 \end{pmatrix}$ | $\begin{pmatrix} \cos(\varphi_2) & \sin(\varphi_2) \\ \sin(\varphi_2) & -\cos(\varphi_2) \end{pmatrix}\begin{pmatrix} A_3 \\ B_3 \end{pmatrix}$ | $\begin{pmatrix} A_2 \\ -B_2 \end{pmatrix}$ |
| $C_3$ | $C_3$ | $C_2$ |
| $\begin{pmatrix} J_x \\ J_y \end{pmatrix}$ | $\begin{pmatrix} -\cos(\varphi_2) & -\sin(\varphi_2) \\ -\sin(\varphi_2) & \cos(\varphi_2) \end{pmatrix}\begin{pmatrix} J_x \\ J_y \end{pmatrix}$ | $\begin{pmatrix} -J_x \\ J_y \end{pmatrix}$ |
| $-J_z$ | $-J_z$ | $-J_z$ |

# Invariance of the nonorthogonal addition to the kinetic energy

Using data presented in Table 1, it is possible to show the invariance of nonorthogonal addition ${}^{n}T^{\mathrm{add}}$, proposed in Ref. 5. However it is much easier to show the invariance of the form (2). Having this in mind, we shall find the transformation rules for $\mathfrak{I}_0$. It follows from the definition $\mathbf{l}_0 = \mathbf{J} - (\mathbf{l}_1 + \mathbf{l}_2) - \mathbf{l}_3$ that it transforms at the permutation of *(12)I* as $\mathbf{J}$ or $\mathbf{l}_1$. Therefore, $\mathfrak{I}_0$ transforms at permutation of *(12)I*, as $\mathfrak{I}_3$. At the permutation *(23)I*, $\mathbf{l}_0 = \mathbf{J} - \mathbf{l}_1 - (\mathbf{l}_2 - \mathbf{l}_3)$ transforms as $\mathbf{J}$ or $\mathbf{l}_1$, and $\mathfrak{I}_0$ as $\mathfrak{I}_1$. Table 2 presents the transformation of $\mathbf{l}_0$ and $\mathfrak{I}_0$ at atomic permutations.

**Table 2. Transformation of $\mathbf{l}_0$ and $\mathfrak{I}_0$ at atomic permutations**

| Operator | (12)I | (23)I |
|---|---|---|
| $\begin{pmatrix} l_{0x} \\ l_{0y} \end{pmatrix}$ | $\begin{pmatrix} -\cos(\varphi_2) & -\sin(\varphi_2) \\ -\sin(\varphi_2) & \cos(\varphi_2) \end{pmatrix}\begin{pmatrix} l_{0x} \\ l_{0y} \end{pmatrix}$ | $\begin{pmatrix} -l_{0x} \\ l_{0y} \end{pmatrix}$ |
| $l_{0z}$ | $-l_{0z}$ | $-l_{0z}$ |
| $\begin{pmatrix} \mathfrak{I}_{0x} \\ \mathfrak{I}_{0y} \end{pmatrix}$ | $\begin{pmatrix} \cos(\varphi_2) & \sin(\varphi_2) \\ \sin(\varphi_2) & -\cos(\varphi_2) \end{pmatrix}\begin{pmatrix} \mathfrak{I}_{0x} \\ \mathfrak{I}_{0y} \end{pmatrix}$ | $\begin{pmatrix} \mathfrak{I}_{0x} \\ -\mathfrak{I}_{0y} \end{pmatrix}$ |
| $\mathfrak{I}_{0z}$ | $\mathfrak{I}_{0z}$ | $\mathfrak{I}_{0z}$ |

It is easy to show that expression (2) is invariant at the permutations *(12)I* and *(23)I*. Let us consider, for example, the angular part of the expression (2). At the *(12)I* permutation, $\mathfrak{I}_0(\mathfrak{I}_1 + \mathfrak{I}_2) + \mathfrak{I}_3$ and $(\mathfrak{I}_1 + \mathfrak{I}_2)\mathfrak{I}_3 + \mathfrak{I}_1\mathfrak{I}_2$ do not change, while at the permutation *(23)I*, we have that $\mathfrak{I}_0(\mathfrak{I}_1 + (\mathfrak{I}_2 + \mathfrak{I}_3))$ and $\mathfrak{I}_1(\mathfrak{I}_2 + \mathfrak{I}_3) + \mathfrak{I}_2\mathfrak{I}_3$ do not change. Therefore, the angular part of the expression (2) is invariant. Similarly $\mathfrak{R}_0(\mathfrak{I}_1 + \mathfrak{I}_2 + \mathfrak{I}_3)$ and $\mathfrak{R}_0\mathfrak{I}_0$ are also invariant because only $\mathfrak{R}_{0z}$ component differs from zero. Having in mind that $\mathfrak{R}_1$, $\mathfrak{R}_2$, and $\mathfrak{R}_3$ transform, correspondingly as $\mathfrak{I}_1$, $\mathfrak{I}_2$ and $\mathfrak{I}_3$, the invariance of $(\mathfrak{R}_1 + \mathfrak{R}_2 + \mathfrak{R}_3)(\mathfrak{I}_1 + \mathfrak{I}_2 + \mathfrak{I}_3)$ becomes quite obvious.

## Conclusion

The main difficulty in using the nonorthogonal coordinates is in a much complicated kinetic part. The transformation rules found above can make the programming calculations of the matrix elements much easier, if the symmetrized wave functions are used. For example, using such relations as $\mathfrak{I}_0\mathfrak{I}_1 = (12)^{*}\mathfrak{I}_0\mathfrak{I}_2$ and the fact that matrix elements do not change at simultaneous rotation of wave functions and of the operator, the calculations of a part of the kinetic energy terms can be simplified.

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