Vibrational kinetic energy operator for the AB_4-type molecules

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The vibrational kinetic energy operator is constructed for the AB_4-type molecules in different orthogonal nonsymmetrized and symmetrized coordinates. Different forms of the vibrational kinetic energy operator are analyzed from the viewpoint of convenience of its use in solving the vibrational problem.

Introduction

Determination of the energy levels of pentatomic molecules from the potential energy surface is now an urgent problem of molecular spectroscopy.[1–3] In contrast to the cases of triatomic and tetratomic molecules, no accurate calculations for pentatomic molecules have been so far available. The accuracy of calculations of the energy levels is still as low as 1 cm^{-1}. Methane is the simplest pentatomic molecule from the viewpoint of making *ab initio* calculations. High symmetry of the methane molecule allows the space of basis functions to be decreased by several times. However, by now there are no convenient internal coordinates to employ the molecular symmetry most efficiently. Let us take the following names for the systems of internal coordinates: $4R5Q$, $4R3Q2T$, $4RX2Q2T$. In all the cases, $4R$ means four radial coordinates r_1, r_2, r_3, r_4 (see Fig. 1).

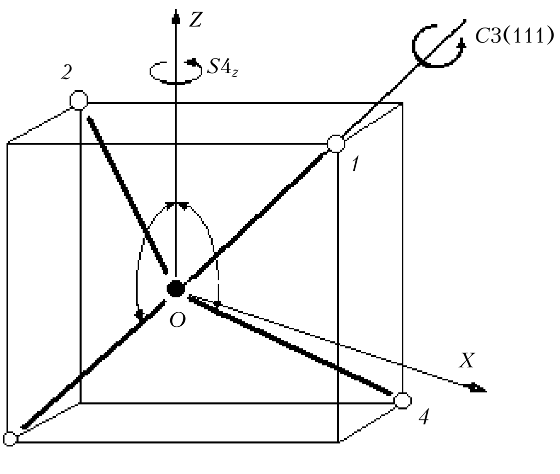

Fig. 1. The $4RX2Q2T$ coordinate system (hydrogen atoms *1–4*).

As angular coordinates, the system $4R5Q$ uses five angles between mass-dependent coordinates: $\cos(q_{12})$, $\cos(q_{13})$, $\cos(q_{14})$, $\cos(q_{23})$, and $\cos(q_{24})$. The system $4R3Q2T$ differs from $4R5Q$ in that the angles $\cos(q_{23})$, $\cos(q_{24})$ are replaced with the torsion angles t_{23} and t_{24} in the system, where the axis Z is directed along the coordinate $\tilde{\mathbf{r}}_1$ and $\tilde{\mathbf{r}}_2$ belongs to the plane XOZ. Definition of the coordinate system $4RX2Q2T$ and symmetrized coordinates is given below. Since the radial part is the same for all the above systems of internal coordinates, it is mentioned only once, when considering the system $4R5Q$. Besides, all the off-diagonal radial-angular coefficients of the g matrix are zero.

Mass-dependent orthogonal coordinates

Assume that the Hamiltonian is constructed in the internal mass-dependent coordinates:

$$\tilde{\mathbf{r}}_i = (\mathbf{r}_{B_i} - \mathbf{r}_A) + \alpha \sum_{j=1}^{4} (\mathbf{r}_{B_j} - \mathbf{r}_A),$$

where

$$\alpha = -\frac{1}{4} + \frac{1}{4}\left(1 + \frac{4m_B}{m_A}\right)^{-1/2} = -\frac{1-\sqrt{\mu_A}}{4}.$$

Let us express, using the designations from Ref. 4, the internal coordinates as follows

$$\tilde{\mathbf{r}}_i = (\mathbf{r}_{B_i} - \mathbf{r}_{cm}) + t_n \sum_{j=1}^{4} (\mathbf{r}_{B_j} - \mathbf{r}_{cm}),$$

where

$$t_n = -\frac{1}{4} + \frac{1}{4\sqrt{1-4\mu_B}}; \qquad \mathbf{r}_{cm} = \mu_A \mathbf{r}_A + \mu_B \sum_{j=1}^{4} \mathbf{r}_{B_j}$$

(μ is the relative mass of an atom). In the mass-dependent Cartesian coordinates $\tilde{\mathbf{r}}$, the kinetic energy operator has the orthogonal form

$$T = -\frac{\hbar}{2m_B} \sum_{i=1}^{4} \frac{\partial^2}{\partial \tilde{\mathbf{r}}_i^{\,2}} - \frac{\hbar}{2M} \frac{\partial^2}{\partial \tilde{\mathbf{r}}_{cm}^{\,2}}.$$

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Kinetic energy $J = 0$ in the internal coordinates

Let us use the designations of Ref. 5:

$$T_V / (-\frac{1}{2}h^2) = \sum_{jk}^{3N-6} g^{jk} \frac{\partial^2}{\partial q_j \partial q_k} + \sum_{j}^{3N-6} h^j \frac{\partial}{\partial q_j},$$

where

$$g^{jk} = \sum_{\alpha}^{xyz} \sum_{i}^{N} \frac{1}{m_i} \left(\frac{\partial q_i}{\partial x_{\alpha i}}\right) \left(\frac{\partial q_k}{\partial x_{\alpha k}}\right);$$

$$h^{jk} = \sum_{\alpha}^{xyz} \sum_{i}^{N} \frac{1}{m_i} \left(\frac{\partial^2 q_i}{\partial x_{\alpha i} \partial x_{\alpha k}}\right).$$

Thus, to find the kinetic energy operator in the internal coordinates, it is sufficient to find the coefficients g and h. Then we will need some equations for transformation of the coefficients g and h at transformation of the internal coordinates:

$$\tilde{g}^{ij} = \sum_{kl} g^{kl} \frac{\partial \tilde{q}_i}{\partial q_k} \frac{\partial \tilde{q}'_j}{\partial q_l};$$

$$\tilde{h}^i = \sum_{k} h^k \frac{\partial \tilde{q}_i}{\partial q_k} + \sum_{kl} g^{kl} \frac{\partial^2 \tilde{q}_i}{\partial q_k \partial q_l}. \quad (1)$$

The $4R5Q$ coordinates

Using explicit equations for r_i and $\cos(q_{ij})$, through the Cartesian coordinates, we can easily obtain the following result. The radial coefficients are $g^{ij} = \delta_{ij}/m_i$. The angular diagonal coefficients of the g matrix are equal to

$$\sin^2(q_{ij}) \left(\frac{1}{m_i r_i^2} + \frac{1}{m_j r_j^2}\right) \frac{\partial^2}{\partial^2 \cos(q_{ij})}.$$

The angular off-diagonal coefficients of the g matrix are nonzero with one coinciding index $(ij)(lk)$ in a couple of angles $q_{ij} q_{lk}$:

$$g^{\cos(q_{ij}),\cos(q_{jk})} = \frac{-\cos(q_{ij})\cos(q_{jk}) + \cos(q_{ik})}{m_j r_j^2} \times$$

$$\times \frac{\partial^2}{\partial \cos(q_{ij}) \, \partial \cos(q_{jk})}$$

and zero, if all the four indices are different. All the off-diagonal radial-angular coefficients of the g matrix are equal to zero. The radial coefficients $h^i = 2/(m_i r_i)$, i.e., the angular elements of the h matrix, are

$$h^{\cos(q_{ij})} = -2\cos(q_{ij}) \left(\frac{1}{m_i r_i^2} + \frac{1}{m_j r_j^2}\right) \frac{\partial}{\partial \cos(q_{ij})}.$$

From the coordinates $4r5\cos(q_{ij})$, using Eq. (1) we can easily obtain the coefficients of the g and h matrices in the $4R3Q2T$ coordinates.

The $4RX2Q2T$ coordinates

Let the plane ZOX contain the points *12O* (see Fig. 1). The axis OZ is directed normally, and the axis OX is parallel to the straight line *12*. The axis Z is directed along the vector

$$\mathbf{e}_z = \frac{\tilde{\mathbf{r}}_1}{2\tilde{r}_1} + \frac{\tilde{\mathbf{r}}_2}{2\tilde{r}_2},$$

and the X axis is directed along the vector

$$\mathbf{e}_x = \frac{\tilde{\mathbf{r}}_1}{2\tilde{r}_1} - \frac{\tilde{\mathbf{r}}_2}{2\tilde{r}_2}.$$

As coordinates, take $\chi_{12} = q_{12}/2$ and polar angles of the third and fourth atoms:

$$\cos(qZ_3) = \frac{1}{2r_3 \cos(\chi_{12})} \left[\frac{(\mathbf{r}_1\mathbf{r}_3)}{r_1} + \frac{(\mathbf{r}_2\mathbf{r}_3)}{r_2}\right],$$

$$\cos(t_3) = \frac{1}{2r_3 \sin(\chi_{12})} \left[\frac{(\mathbf{r}_1\mathbf{r}_3)}{r_1} - \frac{(\mathbf{r}_2\mathbf{r}_3)}{r_2}\right],$$

$$\cos(qZ_4) = \frac{1}{2r_4 \cos(\chi_{12})} \left[\frac{(\mathbf{r}_1\mathbf{r}_4)}{r_1} + \frac{(\mathbf{r}_2\mathbf{r}_4)}{r_2}\right],$$

$$\cos(t_4) = \frac{1}{2r_4 \sin(\chi_{12})} \left[\frac{(\mathbf{r}_1\mathbf{r}_4)}{r_1} - \frac{(\mathbf{r}_2\mathbf{r}_4)}{r_2}\right].$$

Let us use the designations

$$m_+ = \frac{1}{m_1 r_1^2} + \frac{1}{m_2 r_2^2}, \qquad m_- = \frac{1}{m_1 r_1^2} - \frac{1}{m_2 r_2^2}$$

and number the internal coordinates from 1 to 9 as follows: r_1, r_2, r_3, r_4, χ_{12}, qZ_3, t_3, qZ_4, t_4. Then the angular tensors g and h have the following forms:

$$g^{55} = \frac{m_+}{4}, \quad g^{65} = -\frac{m_-}{4}\cos(t_3),$$

$$g^{66} = \frac{m_3}{r_3^2} + \frac{1}{4} m_+ \left[\cos^2(t_3) + \frac{\sin^2(t_3)}{\cos^2(\chi_{12})}\right],$$

$$g^{75} = \frac{m_-}{4} \sin(t_3)\cot(qZ_3),$$

$$g^{76} = \frac{m_+}{4} \sin(t_3)\cos(t_3)\cot(qZ_3)\tan^2(\chi_{12}) +$$

$$+ \frac{m_-}{4\cos(\chi_{12})\sin(\chi_{12})} \sin(t_3),$$

$$g^{77}=\frac{m_3}{r_3^2\sin^2(qZ_3)}+$$

$$+\frac{m_+}{4}\cot^2(qZ_3)\left[\sin^2(t_3)+\frac{\cos^2(t_3)}{\cos^2(\chi_{12})}\right]+$$

$$+\frac{m_+}{4\sin^2(\chi_{12})}+\frac{m_-\cos(t_3)\cot(qZ_3)}{2\cos(\chi_{12})\sin(\chi_{12})},$$

$$g^{85}=-\frac{m_-}{4}\cos(t_4),$$

$$g^{86}=\frac{m_+}{4}\left[\cos(t_3)\cos(t_4)+\frac{\sin(t_3)\sin(t_4)}{\cos^2(\chi_{12})}\right],$$

$$g^{87}=-\frac{m_+}{4}\cot(qZ_3)\left[\sin(t_3)\cos(t_4)-\frac{\cos(t_3)\sin(t_4)}{\cos^2(\chi_{12})}\right]+$$

$$+\frac{m_-\sin(t_4)}{4\cos(\chi_{12})\sin(\chi_{12})},$$

$$g^{88}=\frac{m_4}{r_4^2}+\frac{1}{4}m_+\left[\cos^2(t_4)+\frac{\sin^2(t_4)}{\cos^2(\chi_{12})}\right],$$

$$g^{95}=\frac{m_-}{4}\sin(t_4)\cot(qZ_4),$$

$$g^{96}=-\frac{m_+}{4}\cot(qZ_4)\left[\sin(t_4)\cos(t_3)-\frac{\cos(t_4)\sin(t_3)}{\cos^2(\chi_{12})}\right]+$$

$$+\frac{m_-\sin(t_3)}{4\cos(\chi_{12})\sin(\chi_{12})},$$

$$g^{97}=\frac{m_+}{4}\cot(qZ_3)\cot(qZ_4)\times$$

$$\times\left[\sin(t_3)\sin(t_4)+\frac{\cos(t_3)\cos(t_4)}{\cos^2(\chi_{12})}\right]+\frac{m_+}{4\sin^2(\chi_{12})}+$$

$$+\frac{m_-}{4\sin(\chi_{12})\cos(\chi_{12})}[\cos(t_3)\cot(qZ_3)+$$

$$+\cos(t_4)\cot(qZ_4)],$$

$$g^{98}=\frac{m_+}{4}\sin(t_4)\cos(t_4)\cot(qZ_4)\tan^2(\chi_{12})+$$

$$+\frac{m_-}{4\cos(\chi_{12})\sin(\chi_{12})}\sin(t_4),$$

$$g^{99}=\frac{m_4}{r_4^2\sin^2(qZ_4)}+\frac{m_+}{4}\cot^2(qZ_4)\times$$

$$\times\left[\sin^2(t_4)+\frac{\cos^2(t_4)}{\cos^2(\chi_{12})}\right]+\frac{m_+}{4\sin^2(\chi_{12})}+$$

$$+\frac{m_-\cos(t_4)\cot(qZ_4)}{2\cos(\chi_{12})\sin(\chi_{12})};$$

$$h^5=\frac{m_+\left[2\cos^2(\chi_{12})-1\right]}{4\sin(\chi_{12})\cos(\chi_{12})}=\frac{m_+\cot(2\chi_{12})}{2},$$

$$h^6=\frac{m_+}{4}\cot(qZ_3)\left[\sin^2(t_3)+\frac{\cos^2(t_3)}{\cos^2(\chi_{12})}\right]+$$

$$+\frac{m_-}{2}\tan(\chi_{12})\cos(t_3),$$

$$h^7=-\frac{m_+\sin(t_3)\cos(t_3)\tan^2(\chi_{12})[1+\cos^2(qZ_3)]}{4\sin^2(qZ_3)}-$$

$$-\frac{m_-\sin(t_3)\tan(\chi_{12})\cot(qZ_3)}{2},$$

$$h^8=\frac{m_+}{4}\cot(qZ_4)\left[\sin^2(t_4)+\frac{\cos^2(t_4)}{\cos^2(\chi_{12})}\right]+$$

$$+\frac{m_-}{2}\tan(\chi_{12})\cos(t_4),$$

$$h^9=-\frac{m_+\sin(t_4)\cos(t_4)\tan^2(\chi_{12})[1+\cos^2(qZ_4)]}{4\sin^2(qZ_4)}-$$

$$-\frac{m_-\sin(t_4)\tan(\chi_{12})\cot(qZ_4)}{2}.$$

Symmetrized coordinates

Define the symmetrized coordinates as follows[6]:

$$S_{E_a}=\frac{1}{\sqrt{12}}[2\cos(q_{12})-\cos(q_{13})-\cos(q_{14})-$$

$$-\cos(q_{23})-\cos(q_{24})+2\cos(q_{34})],$$

$$S_{E_b}=\frac{1}{2}[\cos(q_{13})-\cos(q_{14})-\cos(q_{23})+\cos(q_{24})],$$

$$S_{F_{2x}}=\frac{1}{\sqrt{2}}[\cos(q_{24})-\cos(q_{13})],$$

$$S_{F_{2y}}=\frac{1}{\sqrt{2}}[\cos(q_{23})-\cos(q_{14})],$$

$$S_{F_{2z}}=\frac{1}{\sqrt{2}}[\cos(q_{34})-\cos(q_{12})].$$

The kinetic energy operator in the symmetrized coordinates can be derived in several ways. The main difficulty in this case is too complicated dependence of the cosine of the sixth coordinate, for example $\cos(q_{34})$, on the rest five angles.[1] We can overcome this complexity by using, for example, the tensor g in the coordinates $4R3Q2T$ and parameterizing the symmetrized coordinates through the $3q2t$ coordinates. Let us use, in what follows a simpler approach.

It should be noted that the symmetrized coordinates E_b, F_{2x}, and F_{2y} are independent of q_{34}, and, consequently, the g and h tensors for these coordinates can be obtained from the g and h tensors in the $4R5Q$ coordinates by Eqs. (1). For the AB_4 molecules, all the five coordinates are transformed differently, therefore g^{ij} and h^j can correspondingly be presented as tensors of the first and second rank transformable as S_iS_j and S_i.

Taking the symmetry properties into account, we can easily find g^{ij} and h^j for the coordinates E_a and F_{2z}. Below, we will use definitions from Ref. 7, in particular, permutation (234) = (23)(24). For example, using h^x, we can obtain h^z = (234) h^x and h^y = (234) h^z:

$$h^x = \left(\frac{1}{m_1 r_1^2} + \frac{1}{m_3 r_3^2}\right)\cos(q_{13}) - \left(\frac{1}{m_2 r_2^2} + \frac{1}{m_4 r_4^2}\right)\cos(q_{24}),$$

$$h^y = \left(\frac{1}{m_1 r_1^2} + \frac{1}{m_4 r_4^2}\right)\cos(q_{14}) - \left(\frac{1}{m_2 r_2^2} + \frac{1}{m_3 r_3^2}\right)\cos(q_{23}),$$

$$h^z = \left(\frac{1}{m_1 r_1^2} + \frac{1}{m_2 r_2^2}\right)\cos(q_{12}) - \left(\frac{1}{m_3 r_3^2} + \frac{1}{m_4 r_4^2}\right)\cos(q_{34}),$$

$$h^{E_b} = \frac{\cos(q_{14}) - \cos(q_{13})}{m_1 r_1^2} + \frac{\cos(q_{23}) - \cos(q_{24})}{m_2 r_2^2} + \frac{\cos(q_{14}) - \cos(q_{24})}{m_3 r_3^2} + \frac{\cos(q_{23}) - \cos(q_{13})}{m_4 r_4^2}.$$

From the equation

$$h^{E_a} = \frac{2}{\sqrt{3}}\left[(234)h^{E_b} + \frac{1}{2}h^{E_b}\right]$$

we can obtain h^{E_a}. Similarly, we can construct the g matrix in the symmetrized coordinates. Calculation of the 3×3 g matrix for the coordinates E_b, F_{2x}, F_{2y} is trivial. The rest elements of the symmetric g matrix can be calculated in series using the permutation operators:

$$\begin{aligned}
&g^{zz} = (234)g^{xx}, \quad g^{xz} = (234)g^{yx}, \quad g^{yz} = (234)g^{xy}, \\
&g^{aa} = \frac{2}{3}\left[(234) + (243) - \frac{1}{2}\right]g^{bb}, \\
&g^{ab} = \frac{2}{\sqrt{3}}\left[(234)g^{bb} - \frac{3}{4}g^{aa} - \frac{1}{4}g^{bb}\right], \\
&g^{ax} = \frac{2}{\sqrt{3}}\left[(234)g^{by} + \frac{1}{2}g^{bx}\right], \\
&g^{ay} = 2(243)g^{ax} + \sqrt{3}g^{by}, \\
&g^{az} = (243)\left(-\frac{\sqrt{3}}{2}g^{by} - \frac{1}{2}g^{ay}\right).
\end{aligned} \tag{2}$$

By Eq. (1) from the $4R5Q$ coordinates, we derive:

$$g^{bb} = \frac{1}{4m_1 r_1^2}[2 - \cos^2(q_{13}) - \cos^2(q_{14}) - \cos(q_{34}) + \cos(q_{13})\cos(q_{14})] + \frac{1}{4m_2 r_2^2}[2 - \cos^2(q_{23}) - \cos^2(q_{24}) - \cos(q_{34}) + \cos(q_{23})\cos(q_{24})] + \frac{1}{4m_3 r_3^2}[2 - \cos^2(q_{13}) - \cos^2(q_{23}) - \cos(q_{12}) + \cos(q_{13})\cos(q_{23})] + \frac{1}{4m_4 r_4^2}[2 - \cos^2(q_{14}) - \cos^2(q_{24}) - \cos(q_{12}) + \cos(q_{14})\cos(q_{24})],$$

$$g^{bx} = \frac{\sqrt{2}}{4m_1 r_1^2}[-1 + \cos^2(q_{13}) + \cos(q_{34}) - \cos(q_{13})\cos(q_{14})] + \frac{\sqrt{2}}{4m_2 r_2^2}[1 - \cos^2(q_{24}) - \cos(q_{34}) + \cos(q_{23})\cos(q_{24})] + \frac{\sqrt{2}}{4m_3 r_3^2}[-1 + \cos^2(q_{13}) + \cos(q_{12}) - \cos(q_{13})\cos(q_{23})] + \frac{\sqrt{2}}{4m_4 r_4^2}[1 - \cos^2(q_{24}) - \cos(q_{12}) + \cos(q_{14})\cos(q_{24})],$$

$$g^{by} = \frac{\sqrt{2}}{4m_1 r_1^2}[1 - \cos^2(q_{14}) - \cos(q_{34}) - \cos(q_{13})\cos(q_{14})] + \frac{\sqrt{2}}{4m_2 r_2^2}[-1 + \cos^2(q_{23}) + \cos(q_{34}) - \cos(q_{23})\cos(q_{24})] + \frac{\sqrt{2}}{4m_3 r_3^2}[-1 - \cos^2(q_{23}) + \cos(q_{12}) - \cos(q_{13})\cos(q_{23})] + \frac{\sqrt{2}}{4m_4 r_4^2}[1 - \cos^2(q_{14}) - \cos(q_{12}) + \cos(q_{14})\cos(q_{24})],$$

$$g^{xy} = \frac{\cos(q_{34}) - \cos(q_{13})\cos(q_{14})}{2m_1 r_1^2} + \frac{\cos(q_{34}) - \cos(q_{23})\cos(q_{24})}{2m_2 r_2^2} + \frac{\cos(q_{13})\cos(q_{23}) - \cos(q_{12})}{2m_3 r_3^2} + \frac{\cos(q_{14})\cos(q_{24}) - \cos(q_{12})}{2m_4 r_4^2},$$

$$g^{yy} = \frac{1}{2}\sin^2(q_{14})\left(\frac{1}{m_1 r_1^2} + \frac{1}{m_4 r_4^2}\right) + \frac{1}{2}\sin^2(q_{23})\left(\frac{1}{m_2 r_2^2} + \frac{1}{m_3 r_3^2}\right).$$

Using permutations of six g elements we can easily obtain all 15 elements of the g matrix, for example:

$$g^{zz} = (234)g^{xx} = \frac{1}{2}\sin^2(q_{12})\left(\frac{1}{m_1 r_1^2} + \frac{1}{m_2 r_2^2}\right) + \frac{1}{2}\sin^2(q_{34})\left(\frac{1}{m_3 r_3^2} + \frac{1}{m_4 r_4^2}\right).$$

Expressing six angles $\cos(q_{ij})$ through five symmetrized coordinates S and the sixth coordinate

$$S_{A_1} = \frac{1}{\sqrt{6}}[\cos(q_{12}) + \cos(q_{13}) + \cos(q_{14}) + \cos(q_{23}) + \cos(q_{24}) + \cos(q_{34})],$$

we obtain g^{ij} as a quadratic form of the six symmetrized coordinates. It is an important property of thus obtained kinetic energy that it has no singularities.

Conclusion

The equations presented for the kinetic energy operator are planned to be used for determination of the energy levels of the methane molecule. Different systems of the internal coordinates differ by the degree they make use of the symmetry and by complications of the integral calculations.

The efficiency of making use of the symmetry in solving the angular problem can be understood in the following example. The use of the permutation (34) in the coordinates $3Q2T$ allows the space of wave functions to be divided into the subspaces of symmetric and antisymmetric (about the permutation (34)) wave functions.

In the $X2Q2T$ coordinates, the space of wave functions breaks into four subspaces by permutations. From the viewpoint of the symmetry use, the coordinates described in Ref. 2 are twice as efficient as the $X2Q2T$ coordinates. The symmetrized coordinates use the symmetry completely.

It should be noted that the higher is the symmetry of the internal coordinates, the more compact is usually the PES representation. The main problem arising in using the symmetrized coordinates is the need for applying approximate integration. Nevertheless, in my opinion, the use of the symmetrized coordinates is promising.

Acknowledgments

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