

A Simple Method for Derivation of the Rovibrational Hamiltonian: Application to Orthogonal Radau Coordinate Systems as Special Cases

H.P. Ebrahimi^a, M. Tafazzoli^{a,*} and R. Islampour^b

^aDepartment of Chemistry, Sharif University of Technology, Tehran, Iran

^bDepartment of Chemistry, University for Teacher Education, Tehran, Iran

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The molecular Hamiltonian of polyatomic molecules has been obtained. A general choice of internal coordinates depending on external parameters was considered. The rovibrational Hamiltonian for this set of coordinate system was derived in general terms as a function of the external parameters a and b . This procedure is also applicable to various kinds of internal coordinates in a straightforward way. The rovibrational Hamiltonian of triatomic molecules is considered as an application of this general formulation. In addition, orthogonal Radau coordinates are considered as cases of this new approach.

Keywords: Rovibrational Hamiltonian, Application, Generalized internal coordinates, Orthogonal coordinates

INTRODUCTION

An appropriate molecular Hamiltonian is essential for many concepts in the field of physics and chemistry [1]. To date, several methods have been applied for construction of a complete molecular Hamiltonian. Moreover, different scholars have reported an explicit, compact and simple rovibrational Hamiltonian [2-7]. Nonetheless, finding optimal coordinates to describe vibrational variables of polyatomic molecules is a difficult task. The best coordinates for a given molecule can be defined as those which properly combine mathematical simplicity. Besides, triatomic molecules are simple and useful models in the study of the optimal coordinates and appropriate Hamiltonian because they function well in the evaluation of the vibration-rotation terms in the Hamiltonian. Therefore, we apply an arbitrary triatomic molecule, which has quite different molecular point groups as appropriate to their different equilibrium geometries, but the same vibration-

rotation Hamiltonian.

Islampour *et al.* introduced a simple method for derivation of the molecular Hamiltonian based on tensor form [8]. This method has been extended to cover large amplitude motions by solving completely the vector ω'_f for various kinds of coordinate systems [9-11]. In this article, we have applied a general definition of internal coordinates and obtained the rovibrational Hamiltonian in this coordinate system. These definitions contain valence coordinates and the set of orthogonal coordinate systems such as Jacobi and Radau coordinates as particular cases.

THEORY OF MOLECULAR HAMILTONIAN

The method is based on the molecular Hamiltonian operator in tensor form which has obtained an expression for the translational-rovibronic Hamiltonian in terms of arbitrary vibrational variables. The general form of rovibrational Hamiltonian in internal coordinates is expressed as

$$\hat{H}_{RV} = \hat{T}_{vib} + \hat{T}_{rot} + \hat{T}_{rot-vib} + \hat{U}(\mathbf{q}) + \hat{V}(\mathbf{r}, \mathbf{q}) \quad (1)$$

*Corresponding author. E-mail: tafazzoli@sharif.edu

In this equation, the first two terms represent the vibrational and the rotational kinetic energy of the molecule, respectively. The third term is the contribution of the energy of interaction among the various types of molecular motion to the kinetic energy of the molecule. The so-called pseudo-potential $\hat{U}(\mathbf{q})$ is a function of the vibrational variables and originates from the kinetic energy transformation. Finally, $\hat{V}(\mathbf{r}, \mathbf{q})$ is the potential energy of the entire molecule and consists of all the coulomb interactions between all pairs of particles.

The transformation yields the following analytical expressions for the rovibrational Hamiltonian operator of the molecular systems [12]:

$$\hat{T}_{vib} = -\frac{1}{2}\hbar^2 \sum_{kl} \frac{\partial}{\partial q_k} \left(\sum_i m_i^{-1} \nabla_i q_k \cdot \nabla_i q_l \right) \frac{\partial}{\partial q_l} \quad (2)$$

$$\hat{T}_{rot} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \left\{ (\hat{J}_\alpha - \hat{L}_\alpha)(\hat{J}_\beta - \hat{L}_\beta) \right\} \quad (3)$$

$$\hat{T}_{rot-vib} = i\hbar \sum_{\alpha k} \left(\frac{1}{2} \frac{\partial(\mathbf{V}_1)_{\alpha k}}{\partial q_k} + (\mathbf{V}_1)_{\alpha k} \frac{\partial}{\partial q_k} \right) (\hat{J}_\alpha - \hat{L}_\alpha) \quad (4)$$

The pseudo-potential $\hat{U}(\mathbf{q})$ is given by

$$\hat{U}(\mathbf{q}) = \frac{\hbar^2}{8} g'^{-1} \sum_{kl} \left[\frac{\partial g^{kl}}{\partial q_k} \frac{\partial g'}{\partial q_l} - \frac{3}{4} g^{kl} g'^{-1} \frac{\partial g'}{\partial q_k} \frac{\partial g'}{\partial q_l} + g^{kl} \frac{\partial^2 g'}{\partial q_k \partial q_l} \right] \quad (5)$$

Here, the indices i, j refer to the nuclei, s, t refer to the electrons, k, l refer to the vibrational variables, f, g, h refer to a general direction of the LF frame axes, α, β, γ refer to a general direction of the BF frame axes, \mathbf{e}_f and \mathbf{e}_α are the orthogonal unit vectors along the LF and the BF frame axes, respectively. Finally, m_N is the total mass of the nuclei [13].

In the Eqs. (3)-(4), the 3×3 symmetric matrix $\mu_{\alpha\beta}$, and the $3 \times (3N - 6)$ matrix $(\mathbf{V}_1)_{\alpha k}$ are defined as

$$\mu_{\alpha\beta} = \sum_{fi} m_i^{-1} \omega_{f\alpha}^i \omega_{f\beta}^i \quad (6)$$

$$(\mathbf{V}_1)_{\alpha k} = \sum_{fi} m_i^{-1} \omega_{f\alpha}^i (\mathbf{e}_f \cdot \nabla_i q_k) \quad (7)$$

(The vector ω_f^i , a key vector quantity in our calculations, must be determined).

The α -component of the total angular momentum is defined by

$$\hat{J}_\alpha = i\hbar \sum_u (\mathbf{X}^{-1})_{\alpha u} \frac{\partial}{\partial u}$$

The so-called the electronic angular momentum is defined as

$$\hat{L}_\alpha = -i\hbar \sum_{\beta\gamma s} e_{\alpha\beta\gamma} r_{\beta s} \frac{\partial}{\partial r_{\gamma s}}$$

Also, we have $\mathbf{g}' = \det(\mu^{-1}) \det(\mathbf{G}^{-1})$ where

$$(\mathbf{G}^{-1})_{kl} = \sum_i m_i \left(\frac{\partial \mathbf{r}_i}{\partial q_k} \right) \cdot \left(\frac{\partial \mathbf{r}_i}{\partial q_l} \right) \quad (8)$$

(m_i the mass of nucleus i and the gradients are evaluated with respect to the BF frame, \mathbf{r}_i is the position vector of nucleus i with respect to the BF frame).

For large amplitude motions, the vector ω_f^i satisfies the following identities:

$$\sum_i \omega_{f\alpha}^i = 0 \quad (9a)$$

$$\sum_{\beta} \omega_{f\alpha}^i (\mathbf{e}_f \cdot \partial \mathbf{r}_i / \partial q_\beta) = 0 \quad (9b)$$

$$\sum_{\beta} \omega_{f\alpha}^i [\mathbf{e}_f \cdot (\mathbf{r}_i \times \boldsymbol{\varepsilon}_\beta)] = \delta_{\alpha\beta} \quad (9c)$$

The vector ω_f^i is obtained by Eqs. (9) after specifying the nature of the vibrational variables and the way we attach BF system on the molecule. We have chosen generalized internal coordinates and the calculations will be done in these coordinate systems.

GENERALIZED INTERNAL COORDINATES

The first step in the theoretical calculation of polyatomic molecules is choosing a set of coordinates. Many exact forms of Hamiltonian have been derived in terms of curvilinear internal coordinates, such as valence coordinates and orthogonal coordinates [14,15], and used for large molecular systems [16,17]. The internal coordinates are geometrically defined and span a curvilinear configuration space. Internal coordinates can be generalized by making arbitrary linear combinations of the internal vectors of the molecules. These coordinates are known by the magnitudes of vectors and their

angles expressed as linear combinations of the internal vectors which depend on external parameters. Sutcliffe has introduced the generalized internal coordinates depending only on two parameters [18]. Also, Makarewicz applied more general definitions of generalized internal coordinates and derived the rovibrational Hamiltonian [19]. The generalized internal vectors for a triatomic molecule, \mathbf{q}_1 and \mathbf{q}_2 , are defined as linear combinations of the internal valence vectors, \mathbf{r}_1 and \mathbf{r}_2 , which can be expressed as follows [20]:

$$\mathbf{q}_1 = (1-ab)^{-\frac{1}{2}} (\mathbf{r}_1 + a\mathbf{r}_2) \quad (10a)$$

$$\mathbf{q}_2 = (1-ab)^{-\frac{1}{2}} (b\mathbf{r}_1 + \mathbf{r}_2) \quad (10b)$$

where a and b are the external parameters and the scale factor $(1-ab)^{-1/2}$ is introduced to make the Jacobian of the transformation equal to unity.

DERIVATION OF THE ROVIBRATIONAL HAMILTONIAN

To proceed further, we must specify the BF frame axes system and a complete definition of the vibrational variables $\{q_k\}$. The BF frame is attached to arbitrary orientation with respect to the molecule and the position of vectors of the nuclei. In general form, different axis embedding is commonly used. In addition to bond embedding which is generally considered for the BF axes embedding, bisector embedding is commonly used. Here, we consider a nonlinear triatomic molecule where BF frame is defined as q_1 and q_2 span the xz plane of the BF frame system and x axis is in the direction of the bisector. In this frame, the position vectors are:

$$\begin{aligned} \mathbf{r}_1 &= \left(\frac{q_1}{m_N} (m_3 + (1+b)m_2) - \frac{q_2}{m_N} (am_3 + (1+a)m_2) \right) \cos \frac{\theta}{2} \mathbf{e}_x + \left(\frac{q_1}{m_N} (m_3 + (1+b)m_2) + \frac{q_2}{m_N} (am_3 + (1+a)m_2) \right) \sin \frac{\theta}{2} \mathbf{e}_z \\ \mathbf{r}_2 &= \left(-\frac{q_1}{m_N} (bm_3 + (1+b)m_1) + \frac{q_2}{m_N} (m_3 + (1+a)m_1) \right) \cos \frac{\theta}{2} \mathbf{e}_x + \left(-\frac{q_1}{m_N} (bm_3 + (1+b)m_1) - \frac{q_2}{m_N} (m_3 + (1+a)m_1) \right) \sin \frac{\theta}{2} \mathbf{e}_z \\ \mathbf{r}_3 &= \left(\frac{q_1}{m_N} (bm_2 - m_1) + \frac{q_2}{m_N} (am_1 - m_2) \right) \cos \frac{\theta}{2} \mathbf{e}_x + \left(\frac{q_1}{m_N} (bm_2 - m_1) - \frac{q_2}{m_N} (am_1 - m_2) \right) \sin \frac{\theta}{2} \mathbf{e}_z \end{aligned} \quad (11)$$

where atom 3 is the central atom of triatomic molecule and the above equation should be multiplied by $(1-ab)^{-1/2}$.

To calculate vector $\boldsymbol{\omega}_f^i$, which has to be determined *via* BF axes conventions, we calculated the gradients of the internal coordinates with respect to the BF system. The results are shown in Table 1, where \mathbf{e}_1 and \mathbf{e}_2 are unit vectors along the vectors \mathbf{q}_1 and \mathbf{q}_2 , respectively. The vector $\boldsymbol{\omega}_f^i$ can be determined by introducing the position vectors (Eq. (11)) into Eqs. (9b)-(9c) and making use of Eq. (9a) and related gradients from Table 1. The results are summarized in Table 2. Here $C_{fa} = \mathbf{e}_f \varepsilon_{\alpha}$, a function of three rotational variables u , is an element of direction cosine matrix \mathbf{C} , which determines the orientation of the BF frame axes with respect to the LF frame axes. To translate the results of Table 2 into Eq. (6), the elements of the symmetric matrix $\boldsymbol{\mu}$ is formed as follows:

$$\mu_{xx} = \frac{1}{4 \sin^2 \frac{\theta}{2}} \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} - \frac{2}{\mu_3 q_1 q_2} \right) \quad (12a)$$

$$\mu_{yy} = \frac{1}{4} \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} + \frac{2 \cos \theta}{\mu_3 q_1 q_2} \right) \quad (12b)$$

$$\mu_{zz} = \frac{1}{4 \cos^2 \frac{\theta}{2}} \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} + \frac{2}{\mu_3 q_1 q_2} \right) \quad (12c)$$

$$\mu_{xz} = \mu_{zx} = -\frac{1}{2 \sin \theta} \left(\frac{1}{\mu_1 q_1^2} - \frac{1}{\mu_2 q_2^2} \right) \quad (12d)$$

Here the reduced masses depend explicitly on the external parameters a and b as follows and all terms should be multiplied by $(1-ab)^{-1}$:

$$\frac{1}{\mu_i} = \frac{1}{m_i} + \frac{a^2}{m_2} + \frac{(1+a)^2}{m_3} \quad (13a)$$

Table 1. The Gradients of Generalized Internal Coordinates with Respect to BF Frame^a

i	Gradient	$\nabla_i q_1$	$\nabla_i q_2$	$\nabla_i \theta$
1		\mathbf{e}_1	$b\mathbf{e}_2$	$\csc \theta \left(\frac{\mathbf{e}_1 \cos \theta - \mathbf{e}_2}{q_1} + b \frac{\mathbf{e}_2 \cos \theta - \mathbf{e}_1}{q_2} \right)$
2		$a\mathbf{e}_1$	\mathbf{e}_2	$\csc \theta \left(a \frac{\mathbf{e}_1 \cos \theta - \mathbf{e}_2}{q_1} + \frac{\mathbf{e}_2 \cos \theta - \mathbf{e}_1}{q_2} \right)$
3		$-(1+a)\mathbf{e}_1$	$-(1+b)\mathbf{e}_2$	$\csc \theta \left((1+a) \frac{\mathbf{e}_2 - \mathbf{e}_1 \cos \theta}{q_1} + (1+b) \frac{\mathbf{e}_1 - \mathbf{e}_2 \cos \theta}{q_2} \right)$

^a i index refers to the nucleus i and all terms should be multiplied by $(1-ab)^{-1/2}$.

Table 2. BF Components of the Vector $\boldsymbol{\omega}_f^i$ ^a

i	ω_{fx}^i	ω_{fy}^i	ω_{fz}^i
1	$\frac{C_{fy}}{\sin \frac{\theta}{2}} \left(\frac{1}{q_1} - \frac{b}{q_2} \right)$	$\left(\frac{1}{q_1} + \frac{b}{q_2} \right) \cos \frac{\theta}{2} C_{fz} + \left(-\frac{1}{q_1} + \frac{b}{q_2} \right) \sin \frac{\theta}{2} C_{fx}$	$-\frac{C_{fy}}{\cos \frac{\theta}{2}} \left(\frac{1}{q_1} + \frac{b}{q_2} \right)$
2	$\frac{C_{fy}}{\sin \frac{\theta}{2}} \left(\frac{a}{q_1} - \frac{1}{q_2} \right)$	$\left(\frac{a}{q_1} + \frac{1}{q_2} \right) \cos \frac{\theta}{2} C_{fz} + \left(-\frac{a}{q_1} + \frac{1}{q_2} \right) \sin \frac{\theta}{2} C_{fx}$	$-\frac{C_{fy}}{\cos \frac{\theta}{2}} \left(\frac{a}{q_1} + \frac{1}{q_2} \right)$
3	$-(\omega_{fx}^1 + \omega_{fx}^2)$	$-(\omega_{fy}^1 + \omega_{fy}^2)$	$-(\omega_{fz}^1 + \omega_{fz}^2)$

^a i index refers to the nucleus i and all terms should be multiplied by $\frac{1}{2}(1-ab)^{-1/2}$.

$$\frac{1}{\mu_2} = \frac{b^2}{m_1} + \frac{1}{m_2} + \frac{(1+b)^2}{m_3} \quad (13b)$$

$$\frac{1}{\mu_3} = \frac{b}{m_1} + \frac{a}{m_2} + \frac{(1+a)(1+b)}{m_3} \quad (13c)$$

Also, the matrix \mathbf{V}_1 (Eq. (7)) takes the following form:

$$\mathbf{V}_1 = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 \\ \frac{\sin \theta}{\mu_3 q_2} & -\frac{\sin \theta}{\mu_3 q_1} & \left(\frac{1}{\mu_1 q_1^2} - \frac{1}{\mu_2 q_2^2} \right) \\ 0 & 0 & 0 \end{pmatrix} \quad (14)$$

the rows and columns are arranged in order of q_1 , q_2 and θ ,

respectively.

Finally, the pseudo-potential (defined as Eq. (5)) takes the following form:

$$\hat{U}(\mathbf{q}) = -\frac{\hbar^2}{2} \left\{ \frac{1}{4} (2 + \cot^2 \theta) \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} - \frac{2 \cos \theta}{\mu_3 q_1 q_2} \right) + \frac{\cos \theta}{\mu_3 q_1 q_2} \right\} \quad (15)$$

It should be emphasized that we obtain the corresponding Hamiltonian by making use of the transformation $(\sin \theta)^{-1/2} \hat{H}(\sin \theta)^{1/2}$ to remove pseudo-potential (Eq. (15)). Therefore, the rovibrational Hamiltonian is obtained in the following expression:

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$$\begin{aligned}
 \hat{H}_{RV} = & -\frac{\hbar^2}{2} \left\{ \frac{1}{\mu_1} \frac{\partial^2}{\partial q_1^2} + \frac{1}{\mu_2} \frac{\partial^2}{\partial q_2^2} + \frac{2 \cos \theta}{\mu_3} \frac{\partial^2}{\partial q_1 \partial q_2} \right. \\
 & + \frac{2}{\mu_3} \left[\left(-\frac{\sin \theta}{q_2} \right) \frac{\partial^2}{\partial q_1 \partial \theta} - \left(\frac{\sin \theta}{q_1} \right) \frac{\partial^2}{\partial q_2 \partial \theta} + \left(-\frac{\cos \theta}{q_2} \right) \frac{\partial}{\partial q_1} + \left(-\frac{\cos \theta}{q_1} \right) \frac{\partial}{\partial q_2} \right] \\
 & + \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} - \frac{2 \cos \theta}{\mu_3 q_1 q_2} \right) \frac{\partial^2}{\partial \theta^2} + \left(\cot \theta \left(\frac{1}{\mu_1 q_1^2} + \frac{1}{\mu_2 q_2^2} \right) + \frac{2(\sin^2 \theta - \cos^2 \theta)}{\mu_3 q_1 q_2 \sin \theta} \right) \frac{\partial}{\partial \theta} \left. \right\} \\
 & + \frac{1}{2} \left\{ \mu_{xx} (\hat{J}_x - \hat{L}_x)^2 + \mu_{yy} (\hat{J}_y - \hat{L}_y)^2 + \mu_{zz} (\hat{J}_z - \hat{L}_z)^2 + \mu_{xy} [(\hat{J}_x - \hat{L}_x)(\hat{J}_y - \hat{L}_y)]_+ \right\} \\
 & + \frac{i\hbar}{2} \left[\left(\frac{1}{\mu_1 q_1^2} - \frac{1}{\mu_1 q_2^2} \right) \left(\frac{1}{2} \cot \theta + \frac{\partial}{\partial \theta} \right) + \frac{\sin \theta}{\mu_3} \left(\frac{1}{q_2} \frac{\partial}{\partial q_1} - \frac{1}{q_1} \frac{\partial}{\partial q_2} \right) \right] (\hat{J}_y - \hat{L}_y) + \hat{V}(\mathbf{r}, \boldsymbol{\theta})
 \end{aligned}
 \tag{16}$$

The reduced masses, which depend on external parameters, form a number of known vibrational coordinate systems. These cases are obtained by attributing specific values to a and b . Several expressions for the external parameters and the reduced masses corresponding to a different set of internal coordinate systems are collected in Table 3. In the next section, we address Radau orthogonal coordinates and the calculation are done in this set of coordinates.

RADAU ORTHOGONAL COORDINATES

Orthogonal coordinates make a special set of coordinate systems. The term ‘‘orthogonal’’ is used for coordinates where the vibrational kinetic energy operator of triatomic molecules does not contain differential cross-coupling terms such as

Jacobi, Radau, and hyperspherical coordinates.

Radau coordinates are suitable for describing the vibrational motions of molecules with a heavy central atom [21-23]. Radau coordinates for triatomic molecules are defined as shown in Fig. 1. The point **D** is the centre of mass of the terminal atoms, the so-called the triatomic centre of mass **F** and **P** is the canonical point satisfying the condition of the geometrical mean of the distances \overline{OD} and \overline{FD} . Therefore,

$$\overline{PD}^2 = \overline{OD} \times \overline{FD}.$$

These coordinates are very similar to the widely used valence coordinates since mass of the central atom is much heavier than the masses of two terminal atoms. Radau coordinates have commonly been considered for molecules with heavy central atom in different applications [24-27].

By applying both $\frac{1}{\mu_3} = 0$ and $a = b = 0$ condition, we obtain

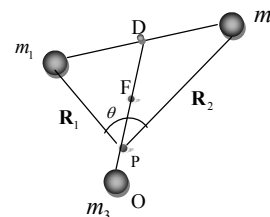


Fig. 1. Radau coordinates for triatomic molecules.

Table 3. The Analytical Expressions for the External Parameters and the Reduced Masses of Various Kinds of Internal Coordinate System^a

Coordinates	a	b	$\frac{1}{\mu_1}$	$\frac{1}{\mu_2}$	$\frac{1}{\mu_3}$	Ref.
Valence	0	0	$\frac{m_1 + m_3}{m_1 m_3}$	$\frac{m_2 + m_3}{m_2 m_3}$	$\frac{1}{m_3}$	[9]
Jacobi	-1	$\frac{m_1}{m_2}$	$\frac{m_1 + m_2}{m_1 m_2}$	$\frac{m_N}{m_3(m_1 + m_2)}$	0	[8]
Radau	$\frac{(t-1)m_2}{tm_1 + m_2}$	$\frac{(t-1)m_1}{tm_2 + m_1}$	$\frac{1}{tm_1}$	$\frac{1}{tm_2}$	0	[10]

^a $t = \left(\frac{m_3}{m_N} \right)^{\frac{1}{2}}$

a more symmetric rovibrational Hamiltonian for triatomic molecules in bisector Radau coordinates:

$$\begin{aligned} \hat{H}_{RV} = & -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial q_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial q_2^2} - \frac{\hbar^2}{2} \left(\frac{1}{m_1 q_1^2} + \frac{1}{m_2 q_2^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right) \\ & + \frac{1}{8} \left(\frac{1}{m_1 q_1^2} + \frac{1}{m_2 q_2^2} \right) \left(\frac{1}{\sin^2 \theta} (\hat{J}_x - \hat{L}_x)^2 + (\hat{J}_y - \hat{L}_y)^2 + \frac{1}{\cos^2 \theta} (\hat{J}_z - \hat{L}_z)^2 \right) \\ & - \frac{1}{4 \sin \theta} \left(\frac{1}{m_1 q_1^2} - \frac{1}{m_2 q_2^2} \right) [(\hat{J}_x - \hat{L}_x), (\hat{J}_z - \hat{L}_z)]_+ \\ & + \frac{i\hbar}{2} \left(\frac{1}{m_1 q_1^2} - \frac{1}{m_2 q_2^2} \right) (\hat{J}_y - \hat{L}_y) \left(\frac{\partial}{\partial \theta} + \frac{1}{2} \cot \theta \right) + \hat{V}(\mathbf{r}, \mathbf{q}) \end{aligned} \quad (17)$$

As a result, we apply the general rovibrational Hamiltonian (Eq. (16)) to symmetric triatomic molecules. Therefore, we consider an arbitrary symmetric triatomic molecule, *e.g.*, ABA systems. For these molecules, we apply $m_1 = m_2 = m$ and symmetrical generalized internal coordinates. The molecular Hamiltonian of C_{2v} molecules is specifically obtained in symmetricized Radau coordinates [28]. In bisector embedding, the rovibrational kinetic energy operator is simple and its coriolis term is zero at equilibrium for symmetric triatomic molecules, *e.g.*, ABA systems [29]. This Hamiltonian can be used for symmetric molecules such as H_2O , H_2S , SO_2 [28,30-32].

CONCLUSIONS

The derivation of the rovibrational Hamiltonian based on tensor form is now extended to generalized internal coordinates depending on external parameters. A simple rovibrational kinetic energy operator has been derived that is applicable to various kinds of vibrational coordinates. An explicit analytic expression for general triatomic molecules of arbitrary structures in generalized internal coordinates has been obtained. This derivation has been performed in bisector embedding.

Also, a detailed study of derivation of the rovibrational Hamiltonian in Radau coordinates as a special case of internal coordinates has been presented. In addition, our results include the symmetricized Radau coordinates as vibrational variables.

In this article, the flexibility of the Hamiltonian for large amplitude motions has been shown. The two main characteristics of our method are its simplicity and generality.

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