



On the construction of the non-adiabatic nuclear kinetic energy operator for diatomic and triatomic systems

Mykhaylo V. Khoma¹, Ralph Jaquet²

¹ Department of Theoretical Physics, Uzhhorod National University, Voloshyna 54, 8000 Uzhhorod, Ukraine

² Theoretical Chemistry, Siegen University, Siegen, Germany

Abstract

The kinetic energy operator for triatomic molecules with coordinate-dependent effective nuclear masses has been derived in the framework of perturbation theory with respect to the ratio of the electron and proton mass. We have demonstrated that a *ad-hoc* introduction of the coordinate-dependent nuclear masses in the Cartesian form of a trinuclear kinetic energy operator preserves the total rotational invariance of the problem. Obtained results can be used for analysis of the non-adiabatic effects in the rotation-vibration spectra of triatomic molecules.

1 Introduction

Non-adiabatic effects play a crucial role in the understanding of many phenomena in atomic and molecular physics. The account for non-adiabaticity is necessary for an adequate description of a quantum tunneling, dynamics of the Rydberg states, molecule dissociation and ionization, high-precision molecular spectroscopy and many others effects and properties of molecular systems. The variety of possible scenarios of the quantum evolution of the system is much broader if a trinuclear molecule is chosen as the object of study. In the present work, we derive an effective kinetic energy operator (KEO) for a triatomic system with coordinate-dependent effective nuclear masses. One of the purposes of such a KEO is to account for non-adiabatic effects related to coupling between the electronic and nuclear degrees of freedom.

Simulating non-adiabatic contributions to low lying ro-vibrational states by using different constant masses for rotational and vibrational motions had been already investigated in the past. It has been proven theoretically [1, 6, 7, 8, 9] that this assumption is reasonable as a first order correction. In the case of H_3^+ , earlier calculations [10, 11, 12, 13] have shown that for transition frequencies higher than the barrier of linearity the strategy with different constant masses for rotation and vibration does not improve in the average the deviation from experiment. The correct way would be to take into account that all nuclear masses or reduced nuclear masses used in the ro-vibrational Hamiltonian are distance-dependent: this can be done based on a rigorous theory [1, 12, 14, 15, 16, 17] or empirically [18]. The distance dependence means that the contribution of the electronic mass or the

coupling of the electronic motion to the nuclear motion changes with internuclear distance.

An elegant approach to account for the total contribution of non-adiabatic effects (for weak non-adiabatic interactions) to a given electronic state has been proposed by Herman and Asgharian [1] and consists of the construction of an effective KEO based on second-order perturbative analysis of the exact kinetic energy operator for nuclear motion. This leads to non-adiabatic picture using a single potential energy surface with distance-dependent effective nuclear masses within the different kinetic energy operator terms.

The practical realization of the Herman-Asgharian algorithm consists of the construction of a perturbation expansion for the intermediate nuclear KEO in the Cartesian body-fixed (BF) frame with subsequent representation of the obtained results in generalized molecular coordinates related to an arbitrarily oriented space-fixed (SF) frame. However, in this case the technical difficulties arise, because the differential operators which compose the intermediate Cartesian nuclear KEO are multiplied by mass-prefactors (coordinate-dependent effective masses), which are not only different for each single operator but also defined in a uniquely chosen BF frame. To demonstrate the rotational invariance of the problem one has to represent the final result in a arbitrarily oriented SF frame. Consequently, one has to deal with the transformation of each individual differential operator from the BF frame into the SF frame with further representation of the final result as a linear combination of the components of the total orbital momentum operator plus the pure vibrational part. This transformation constitutes the main difficulty in the application of the Herman-Asgharian approach for the construction of the effective nuclear KEO. Probably because of such complications of the theory the method of Herman and Asgharian, shown to be successful for diatomic molecules, was not utilized further for more complex systems.

First implementations and applications by the present authors have been published recently [2, 3, 4, 5].

2 Perturbation expansion for the non-adiabatic correction

The application of the method of distance-dependent corrections to nuclear masses imposes certain conditions on the usage of the coordinate frames, which we shall discuss here briefly. To construct the effective non-adiabatic nuclear kinetic energy operator we must first obtain the general expression for the corrections to the ro-vibrational energies within a perturbation expansion. Such expansion includes the matrix elements between the electronic wave functions [see equation (16) further in the text], which depends on the relative position of the nuclei and on the chosen directions of the coordinate axis. Therefore, to keep the meaning of these matrix elements unaltered during the molecular rotation we should use the body-fixed frame for their representation.

For the explicit representation of the rotational degrees of freedom of the molecule we use the space-fixed frame which is arbitrarily oriented with respect to the BF frame. The mutual orientation of the BF and SF frames is determined by

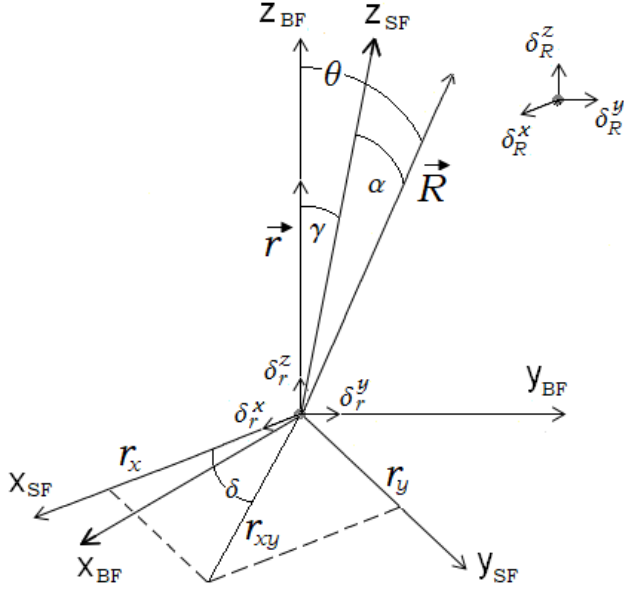


Figure 1: The geometry of the system and notations used. (α, β) and (γ, δ) denotes the polar angles of the vectors \vec{R} and \vec{r} in the SF frame. $\delta_R^{x,y,z}$ and $\delta_r^{x,y,z}$ indicates the variations of the Cartesian coordinates (in the BF frame) of the vectors \vec{R} and \vec{r} respectively.

three Euler angles $\Omega = \{\delta, \gamma, \varphi\}$. We employ the passive picture (see [19, 20]) for the definition of the rotation matrix, i.e. the molecular system is assumed in rest and rotation is described by the rotation of the SF frame (see [2]).

In the following we shall consider the molecular system which consists of the three nuclei and n electrons. The relative position of the nuclei is described through the Jacobi coordinates $\vec{Q} = \{r, R, \theta\}$. r represents the distance between two nuclei (diatomic fragment), and R is the distance from the center of mass of the diatomic fragment to the third nucleus; θ being the angle between the vectors \vec{r} and \vec{R} . We shall use the following relations for angles [21]:

$$\cos \theta = \cos \alpha \cos \gamma + \cos(\beta - \delta) \sin \alpha \sin \gamma, \quad (1)$$

$$\tan \varphi = \frac{\sin \alpha \sin(\beta - \delta)}{\sin \alpha \cos \gamma \cos(\beta - \delta) - \sin \gamma \cos \alpha}. \quad (2)$$

We shall denote the Cartesian coordinates of the vectors \vec{r} , \vec{R} in the BF frame as follows

$$\vec{R}(X, Y, Z), \quad \vec{r}(x, y, z). \quad (3)$$

The geometry of the molecular system and notations of the coordinate frames are shown in figure 1. Without loss of generality we can assume that the origins of the BF and SF frames are placed into the total center of mass of the molecule.

In the following we are going to generalize the ideas formulated in [1] to the case of three nuclei. For Jacobi coordinates (3) the nuclear reduced masses are given by

$$\mu_r^{-1} = m_1^{-1} + m_2^{-1}, \quad \mu_R^{-1} = (m_1 + m_2)^{-1} + m_3^{-1}, \quad (4)$$

where m_i ($i = 1, 2, 3$) is the mass of the i -th nucleus. After separation of the translational motion, the exact Schrödinger equation for the total wave function ψ of the molecular system has the following form

$$\left(T + V(\vec{Q}, \vec{q}) - E \right) \psi(\vec{Q}, \vec{q}) = 0, \quad (5)$$

where T is the complete translation-free kinetic energy operator of the whole system, \vec{q} denotes the complete set of electronic coordinates, $V(\vec{Q}, \vec{q})$ represents the potential of the Coulomb interaction of all particles in the molecule and E is the total energy.

We use for ψ the expansion over the complete orthonormal set of the product of electronic $\varphi_\lambda(\vec{q}|\vec{Q})$ and nuclear $v_\lambda^k(\vec{Q})$ wave functions

$$\psi(\vec{Q}, \vec{q}) = \sum_{\lambda k} C_{\lambda k} \varphi_\lambda(\vec{q}|\vec{Q}) v_\lambda^k(\vec{Q}) \equiv \sum_{\lambda k} C_{\lambda k} |\lambda k\rangle, \quad (6)$$

where the symbols λ denote the electronic and k the nuclear state, respectively. Substituting the expansion for ψ into the Schrödinger equation (5) we come to the standard adiabatic approximation for the nuclear motion

$$\left(T_0 + E_\lambda^{AD} - E \right) \varphi_\lambda v_\lambda^k + W \varphi_\lambda v_\lambda^k = 0, \quad (7)$$

where $E_\lambda^{AD} \equiv E_\lambda^{AD}(\vec{Q})$ is the adiabatic potential energy surface (PES), T_0 denotes the standard nuclear KEO

$$T_0 \equiv -\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_r} \nabla_r^2, \quad (8)$$

and W denotes the operator of non-adiabaticity

$$W = -\frac{\hbar^2}{\mu_R} \nabla_R^{(n)} \cdot \nabla_R^{(e)} - \frac{\hbar^2}{\mu_r} \nabla_r^{(n)} \cdot \nabla_r^{(e)}. \quad (9)$$

The superscript indicates that the given operator acts on the nuclear (n) or electronic (e) states only. If one neglects the operator W the Schrödinger equation for the nuclear motion reads

$$\left(-\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_r} \nabla_r^2 + E_\lambda^{AD}(\vec{Q}) - E_{\lambda k} \right) v_\lambda^k(\vec{Q}) = 0. \quad (10)$$

Considering the functions v_λ^k in (10) as a zero approximation, one may treat (7) in the framework of perturbation theory. The first-order correction to the energy $E_{\lambda k}$

of the state $|\lambda k\rangle$ with respect to the perturbation operator W vanishes. Therefore, the leading non-vanishing energy shift is represented by the second-order correction

$$E_{\lambda k}^{(2)} = - \sum_{a=r,R} \sum_{\lambda' k' \neq \lambda k} \left(\frac{\hbar^4}{\mu_a^2} \right) \frac{\langle \lambda k | \nabla_a^{(e)} \lambda' \cdot \nabla_a^{(n)} k' \rangle \langle \lambda' k' | \nabla_a^{(e)} \lambda \cdot \nabla_a^{(n)} k \rangle}{E_{\lambda' k'} - E_{\lambda k}}. \quad (11)$$

Representing the vectors \vec{r} and \vec{R} in (11) in Cartesian coordinates, we introduce the common symbols χ, η, ζ , which depend parametrically on a as follows

$$\chi, \eta, \zeta = \begin{cases} x, y, z, & a = r, \\ X, Y, Z, & a = R. \end{cases} \quad (12)$$

Denoting the Cartesian unit vectors as \vec{n}_i ($i = x, y, z$), we may write for an arbitrary scalar function ψ

$$\partial_\alpha (\vec{n}_i \psi) = \vec{n}_i \partial_\alpha \psi, \quad \alpha = \chi, \eta, \zeta, \quad (13)$$

leading to the short notation for the partial derivative: $\partial_\alpha \equiv \frac{\partial}{\partial \alpha}$. So, the matrix element $\langle \lambda k | \nabla_a^{(e)} \lambda' \cdot \nabla_a^{(n)} k' \rangle$ is represented as (see the definitions in (12))

$$\langle \lambda k | \nabla_a^{(e)} \lambda' \cdot \nabla_a^{(n)} k' \rangle = \sum_{\alpha=\chi,\eta,\zeta} \langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle \langle k | \partial_\alpha^{(n)} k' \rangle, \quad a = r, R. \quad (14)$$

Similar expressions can be given for the matrix elements $\langle \lambda' k' | \nabla_a^{(e)} \lambda \cdot \nabla_a^{(n)} k \rangle$. In the following, we neglect the 'smaller' nuclear ro-vibrational energies against the electronic energies in (11). Therefore, the difference $E_{\lambda' k'} - E_{\lambda k}$ can be approximated by $E_{\lambda'} - E_\lambda$, and (11) leads to

$$E_{\lambda k}^{(2)} = - \sum_{a=r,R} \frac{\hbar^4}{\mu_a^2} \times \left\langle k \left| \sum_{\lambda' \neq \lambda} \sum_{\alpha=\chi,\eta,\zeta} \frac{\langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle}{E_{\lambda'} - E_\lambda} \partial_\alpha^{(n)} \sum_{\beta=\chi,\eta,\zeta} \langle \lambda' | \partial_\beta^{(e)} \lambda \rangle \partial_\beta^{(n)} \right| k \right\rangle. \quad (15)$$

Let us to introduce the following abbreviations for the matrix element

$$\omega_\alpha^{\lambda \lambda'} = \langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle, \quad \alpha = \chi, \eta, \zeta. \quad (16)$$

Computing the sums in (15), by keeping the ordering of the operators $\partial_\alpha^{(n)}$, $\partial_\beta^{(n)}$, and taking into account that $\langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle = -\langle \lambda' | \partial_\alpha^{(e)} \lambda \rangle$, we come to the following expression for the energy corrections $E_{\lambda k}^{(2)}$ (keeping in mind definition in (12)):

$$E_{\lambda k}^{(2)} = \sum_{a=r,R} \frac{\hbar^2}{2\mu_a} \left\langle k \left| \frac{2\hbar^2}{\mu_a} \sum_{\lambda' \neq \lambda} \frac{1}{E_{\lambda'} - E_\lambda} \left[\omega_\chi^2 \frac{\partial^2}{\partial \chi^2} + \omega_\eta^2 \frac{\partial^2}{\partial \eta^2} + \omega_\zeta^2 \frac{\partial^2}{\partial \zeta^2} \right. \right. \right. \\ \left. \left. \left. + \omega_\chi \omega_\eta (\partial_\chi \partial_\eta + \partial_\eta \partial_\chi) + \omega_\chi \omega_\zeta (\partial_\chi \partial_\zeta + \partial_\zeta \partial_\chi) + \omega_\eta \omega_\zeta (\partial_\eta \partial_\zeta + \partial_\zeta \partial_\eta) \right] \right| k \right\rangle$$

$$\begin{aligned}
& + (\omega_\chi \partial_\chi \omega_\chi + \omega_\eta \partial_\eta \omega_\chi + \omega_\zeta \partial_\zeta \omega_\chi) \partial_\chi + (\omega_\chi \partial_\chi \omega_\eta + \omega_\eta \partial_\eta \omega_\eta + \omega_\zeta \partial_\zeta \omega_\eta) \partial_\eta \\
& + (\omega_\chi \partial_\chi \omega_\zeta + \omega_\eta \partial_\eta \omega_\zeta + \omega_\zeta \partial_\zeta \omega_\zeta) \partial_\zeta \Big| \Big| k \Big\rangle. \tag{17}
\end{aligned}$$

For the sake of compactness in (17), and in the following, we omit the superscripts in the notation for $\omega_\alpha^{\lambda\lambda'}$. Expression (17) represents the complete non-adiabatic contribution in the second order of perturbation theory.

3 Derivation of the non-adiabatic effective Hamiltonian

As said before, the main idea of [1] is to interpret the second-order correction $E_{\lambda k}^{(2)}$ of the exact nuclear KEO as the first-order correction of a new effective non-adiabatic nuclear KEO T_{na} , which can be deduced from (17) as

$$E_{\lambda k}^{(2)} = \langle k | T_{\text{na}} | k \rangle. \tag{18}$$

The electronic matrix elements $\omega_\alpha^{\lambda\lambda'}$, and therefore the correction $E_{\lambda k}^{(2)}$, are defined in the BF frame of coordinates. To introduce the rotational degrees of freedom (the Euler angles) we shall represent the $E_{\lambda k}^{(2)}$ in the SF frame, which is assumed arbitrarily oriented with respect to the BF frame, see figure 1. In the present work we use the molecular embedding with the diatom vector \vec{r} aligned along the z -axis of the BF frame and the vector \vec{R} in the xz -plane (we denote this embedding as $[\vec{r} || z]$). The operator T_{na}

$$T_{\text{na}} \equiv T_{\text{na}}^{(1)} + T_{\text{na}}^{(2)}, \tag{19}$$

can be written immediately by comparing (17) and (18):

$$\begin{aligned}
T_{\text{na}}^{(1)} &= -\frac{\hbar^2}{2\mu_r} \left[G_{xx}^{(r)} \frac{\partial^2}{\partial x^2} + G_{yy}^{(r)} \frac{\partial^2}{\partial y^2} + G_{zz}^{(r)} \frac{\partial^2}{\partial z^2} \right] \\
&\quad - \frac{\hbar^2}{2\mu_R} \left[G_{XX}^{(R)} \frac{\partial^2}{\partial X^2} + G_{YY}^{(R)} \frac{\partial^2}{\partial Y^2} + G_{ZZ}^{(R)} \frac{\partial^2}{\partial Z^2} \right], \tag{20}
\end{aligned}$$

and

$$\begin{aligned}
T_{\text{na}}^{(2)} &= -\frac{\hbar^2}{2\mu_r} \left[G_{xy}^{(r)} \mathcal{O}_{xy} + G_{xz}^{(r)} \mathcal{O}_{xz} + G_{yz}^{(r)} \mathcal{O}_{yz} + g_x^{(r)} \partial_x + g_y^{(r)} \partial_y + g_z^{(r)} \partial_z \right] \\
&\quad - \frac{\hbar^2}{2\mu_R} \left[G_{XY}^{(R)} \mathcal{O}_{XY} + G_{XZ}^{(R)} \mathcal{O}_{XZ} + G_{YZ}^{(R)} \mathcal{O}_{YZ} + g_X^{(R)} \partial_X + g_Y^{(R)} \partial_Y + g_Z^{(R)} \partial_Z \right], \tag{21}
\end{aligned}$$

with $\mathcal{O}_{\alpha\beta} = \partial_\alpha \partial_\beta + \partial_\beta \partial_\alpha$. $G_{\alpha\beta}^{(a)}$ and $g_\alpha^{(a)}$ are given by

$$G_{\alpha\beta}^{(a)} = -\frac{2\hbar^2}{\mu_a} \sum_{\lambda' \neq \lambda} \frac{\omega_\alpha \omega_\beta}{E_{\lambda'} - E_\lambda},$$

$$g_\alpha^{(a)} = -\frac{2\hbar^2}{\mu_\alpha} \sum_{\lambda' \neq \lambda} \frac{\omega_\chi \partial_\chi \omega_\alpha + \omega_\eta \partial_\eta \omega_\alpha + \omega_\zeta \partial_\zeta \omega_\alpha}{E_{\lambda'} - E_\lambda}, \quad \alpha, \beta = \chi, \eta, \zeta. \quad (22)$$

It has been shown (see [2]) that the leading non-adiabatic contribution comes from the term $T_{\text{na}}^{(1)}$. Therefore, further we shall assume that $T_{\text{na}} \approx T_{\text{na}}^{(1)}$ and neglect contribution of $T_{\text{na}}^{(2)}$. This assumption leads to the following form of the effective Schrödinger equation for nuclear motion

$$\left(T_0 + T_{\text{na}}^{(1)} + E_\lambda^{AD}(\vec{Q}) - E_{\lambda k} \right) v_\lambda^k(\vec{Q}) = 0. \quad (23)$$

Expression 20 can be interpreted as a kinetic energy operator in the BF frame with coordinate-dependent nuclear masses $\mu_{2,3}^{(\alpha,\beta)}$ defined in the following way

$$\frac{1}{\mu_2^{(\alpha)}} = \frac{1 + G_{\alpha\alpha}^{(r)}}{\mu_r}, \quad \frac{1}{\mu_3^{(\beta)}} = \frac{1 + G_{\beta\beta}^{(R)}}{\mu_R}, \quad \alpha = x, y, z; \quad \beta = X, Y, Z. \quad (24)$$

In order to transform the Cartesian (BF) form of the KEO 20 into the Jacobi (SF) coordinates we need to represent the derivatives $\partial^2/\partial\alpha^2$, ($\alpha = x, y, z, X, Y, Z$) through the combination of derivatives in Jacobi coordinates $\{u\}$, $\{u\} = \{\vec{Q}, \vec{\Omega}\} = \{r, R, \theta, \delta, \gamma, \varphi\}$. The problem of construction of the final nuclear KEO with coordinate-dependent nuclear masses is rather complicated, since terms with different mass-prefactors are not canceling each other (as it take place in case of conventional masses). To handle with this we employed the infinitesimal coordinate variations and compute derivatives analytically as a limit of corresponding finite difference scheme.

Namely, we write the second derivative of the arbitrary function f as a three-point finite difference

$$\partial_\alpha^2 f = \frac{1}{(\delta\alpha)^2} [\delta_2 f - 2\delta_1 f], \quad (25)$$

with $\delta_1 f = f(\alpha + \delta\alpha) - f_0$, and $\delta_2 f = f(\alpha + 2\delta\alpha) - f_0$. For the sake of brevity we write the variable α only as an argument of function f . The similar relation for the mixed derivatives $\partial_\alpha \partial_\beta$ reads

$$\partial_\alpha \partial_\beta f = \frac{1}{\delta\alpha \delta\beta} [\delta_2 f - \delta_1^{(\alpha)} f - \delta_1^{(\beta)} f], \quad (26)$$

with $\delta_1^{(\alpha)} f = f(\alpha + \delta\alpha) - f(\alpha)$, $\delta_1^{(\beta)} f = f(\beta + \delta\beta) - f(\beta)$ and $\delta_2 f = f(\alpha + \delta\alpha, \beta + \delta\beta) - f(\alpha, \beta)$. Note, that equations (25) and (26) are *exact* if we take the limit $\delta\alpha \rightarrow 0$, $\delta\beta \rightarrow 0$ analytically. For details of the computation of variations of the Jacobi coordinates and application of the equations (25), (26) for transformation of the derivatives from the BF to the SF frame we refer to publications [2] and [5]. We shall introduce the notation $K_V + K_{VR} = T_0 + T_{\text{na}}^{(1)}$, where K_V is the pure

vibrational and K_{VR} is the ro-vibrational part of the total KEO. Finally, we have

$$\begin{aligned}
\frac{K_V}{\hbar^2} = & -\frac{1}{2\mu_2^{(z)}} \frac{\partial^2}{\partial r^2} - \frac{1}{2} \left(\frac{\sin^2 \theta}{\mu_3^{(x)}} + \frac{\cos^2 \theta}{\mu_3^{(z)}} \right) \frac{\partial^2}{\partial R^2} \\
& - \frac{1}{2R} \left(\frac{\cos 2\theta}{2\mu_3^{(x)}} + \frac{\sin^2 \theta}{\mu_3^{(z)}} + \frac{1}{2\mu_3^{(x)}} + \frac{1}{\mu_3^{(y)}} \right) \frac{\partial}{\partial R} \\
& - \frac{1}{2r} \left(\frac{1}{\mu_2^{(x)}} + \frac{1}{\mu_2^{(y)}} \right) \frac{\partial}{\partial r} \\
& - \frac{1}{2} \left(\frac{\cot \theta}{r^2 \mu_2^{(y)}} + \frac{\cot \theta}{R^2 \mu_3^{(y)}} + \frac{\omega_{3zx} \sin 2\theta}{R^2} \right) \frac{\partial}{\partial \theta} \\
& - \frac{1}{2} \left(\frac{1}{r^2 \mu_2^{(x)}} + \frac{\cos^2 \theta}{R^2 \mu_3^{(x)}} + \frac{\sin^2 \theta}{R^2 \mu_3^{(z)}} \right) \frac{\partial^2}{\partial \theta^2} + \frac{\omega_{3zx} \sin 2\theta}{2R} \frac{\partial^2}{\partial R \partial \theta},
\end{aligned} \tag{27}$$

and

$$\begin{aligned}
\frac{K_{VR}}{\hbar^2} = & -\frac{\cot \gamma}{2r^2} \left(\frac{\sin^2 \varphi}{\mu_2^{(x)}} + \frac{\cos^2 \varphi}{\mu_2^{(y)}} \right) \frac{\partial}{\partial \gamma} - \frac{1}{r^2} \left(\frac{\cos^2 \varphi}{\mu_2^{(x)}} + \frac{\sin^2 \varphi}{\mu_2^{(y)}} \right) \frac{\partial^2}{\partial \gamma^2} \\
& + \frac{\sin \varphi}{r^2} \left(\frac{\cot \gamma \cos \varphi}{\mu_2^{(x)}} - \frac{\cot \gamma \cos \varphi}{\mu_2^{(y)}} - \frac{\cot \theta}{\mu_2^{(y)}} \right) \frac{\partial^2}{\partial \gamma \partial \varphi} \\
& + \frac{\omega_{2xy} \cot \gamma \sin 2\varphi}{2r^2 \sin \gamma} \frac{\partial}{\partial \delta} - \frac{\omega_{2xy} \sin 2\varphi}{2r^2 \sin \gamma} \frac{\partial}{\partial \delta} \frac{\partial^2}{\partial \delta \partial \gamma} \\
& + \frac{\csc \gamma}{r^2} \left(\frac{\cot \theta \cos \varphi}{\mu_2^{(y)}} + \frac{\cot \gamma \sin^2 \varphi}{\mu_2^{(x)}} + \frac{\cot \gamma \cos^2 \varphi}{\mu_2^{(y)}} \right) \frac{\partial^2}{\partial \delta \partial \varphi} \\
& + \frac{1}{r^2 \mu_2^{(x)}} \left(\cos \varphi \frac{\partial^2}{\partial \theta \partial \gamma} + \frac{\sin \varphi}{\sin \gamma} \frac{\partial^2}{\partial \theta \partial \delta} - \cot \gamma \sin \varphi \frac{\partial^2}{\partial \theta \partial \varphi} \right) \\
& + \frac{\omega_{2yx} \sin 2\varphi}{2r^2 \sin^2 \gamma} \left(\frac{\cos^2 \gamma + 1}{2} \right) \frac{\partial}{\partial \varphi} - \frac{\csc^2 \gamma}{2r^2} \left(\frac{\sin^2 \varphi}{\mu_2^{(x)}} + \frac{\cos^2 \varphi}{\mu_2^{(y)}} \right) \frac{\partial^2}{\partial \delta^2} \\
& - \frac{1}{2r^2} \left(\frac{2 \cot \gamma \cot \theta \cos \varphi}{\mu_2^{(y)}} + \frac{\cot^2 \gamma \sin^2 \varphi}{\mu_2^{(x)}} + \frac{\cot^2 \gamma \cos^2 \varphi}{\mu_2^{(y)}} \right. \\
& \left. + \frac{\cot^2 \theta}{\mu_2^{(y)}} \right) \frac{\partial^2}{\partial \varphi^2} - \frac{1}{2} \frac{\csc^2 \theta}{R^2 \mu_3^{(y)}} \frac{\partial^2}{\partial \varphi^2},
\end{aligned} \tag{28}$$

where $\omega_{n\alpha\beta}$ are given by

$$\omega_{n\alpha\beta} = \left(\mu_n^{(\alpha)} \right)^{-1} - \left(\mu_n^{(\beta)} \right)^{-1}, \quad n = 2, 3, \quad \alpha, \beta = x, y, z. \tag{29}$$

After some algebraic transformations we can represent the ro-vibrational part K_{VR} (28) through the projections Π_x , Π_y , and Π_z of the total angular momentum

operator, which depends on the Euler angles δ, γ, φ and defined as follows [20]:

$$\begin{aligned}\Pi_x &= i\hbar \left(\sin \varphi \frac{\partial}{\partial \gamma} - \frac{\cos \varphi}{\sin \gamma} \frac{\partial}{\partial \delta} + \cos \varphi \cot \gamma \frac{\partial}{\partial \varphi} \right), \\ \Pi_y &= i\hbar \left(\cos \varphi \frac{\partial}{\partial \gamma} + \frac{\sin \varphi}{\sin \gamma} \frac{\partial}{\partial \delta} - \sin \varphi \cot \gamma \frac{\partial}{\partial \varphi} \right), \quad \Pi_z = i\hbar \frac{\partial}{\partial \varphi}.\end{aligned}\tag{30}$$

Namely,

$$\begin{aligned}K_{VR} &= \frac{\csc^2 \theta}{2R^2 \mu_3^{(y)}} \Pi_z^2 + \frac{1}{2r^2} \left[\left(\frac{\Pi_x^2}{\mu_2^{(y)}} + \frac{\Pi_y^2}{\mu_2^{(x)}} \right) + \frac{\cot^2 \theta}{\mu_2^{(y)}} \Pi_z^2 \right. \\ &\quad \left. + \frac{\cot \theta}{\mu_2^{(y)}} (\Pi_x \Pi_z + \Pi_z \Pi_x) - i\hbar \left(\frac{2}{\mu_2^{(x)}} \frac{\partial}{\partial \theta} + \frac{\cot \theta}{\mu_2^{(y)}} \right) \Pi_y \right].\end{aligned}\tag{31}$$

Hence, we have constructed the effective nuclear KEO in Jacobi coordinates, which allows to write a Schrödinger equation (23) for the nuclear motion with account for non-adiabatic effects. Note, the representation (31) for K_{VR} shows that the Cartesian form of the KEO with coordinate-dependent nuclear masses retain the invariance of the problem with respect to the Euler rotations.

Summary

The aim of the current study was to construct the effective non-adiabatic kinetic energy operator for nuclear motion in a triatomic molecule. For this purpose we have generalized the original approach of Herman and Asgharian [1] (developed for a diatomic molecule) on the case of triatomic systems. The main difficulties in the rigorous extension of this approach to a triatomic molecule are related to a dramatic complication in the description of the vibrational and, especially, rotational degrees of freedom of the triatomic in contrast to the diatomic molecule. We have shown that by employing analytic variations techniques we were able to transform the Cartesian form of the nuclear KEO with coordinate-dependent reduced masses given in BF frame into the generalized (Jacobi in the present study) coordinates in arbitrarily oriented SF frame. This allows to construct the effective non-adiabatic triatomic nuclear KEO in question.

References

- [1] R. M. Herman and A. Asgharian, *J. Mol. Spectr.* **19**, 305 (1966)
- [2] M. Khoma and R. Jaquet, *J. Chem. Phys.* **147**, 114106 (2017)
- [3] R. Jaquet and M. Khoma, *J. Phys. Chem. A* **121**, 7016 (2017)
- [4] R. Jaquet and M. Khoma, *Mol. Phys.* **116**, 3507 (2018)
- [5] M. Khoma and R. Jaquet, *J. Math. Chem.* (2019) (*in print*)

- [6] P. R. Bunker and R. E. Moss, *Mol. Phys.* **33**, 417 (1977)
- [7] R. E. Moss, *Mol. Phys.* **89**, 195 (1996)
- [8] R. Jaquet, *Chem. Phys. Lett.* **302**, 27 (1999)
- [9] O. L. Polyansky, J. Tennyson, *J. Chem. Phys.* **110**, 5056 (1999)
- [10] R. A. Bachorz, W. Cencek, R. Jaquet and J. Komasa, *J. Chem. Phys.* **131**, 024105 (2009)
- [11] R. Jaquet, *Theor. Chim. Acta* **127**, 157 (2010)
- [12] R. Jaquet and M. V. Khoma, *Mol. Phys.* **110**, 669 (2012)
- [13] J. Tennyson, *J. Chem. Phys.* **145**, 120901 (2016)
- [14] W. Kutzelnigg, *Mol. Phys.* **105**, 2627 (2007)
- [15] R. Jaquet and W. Kutzelnigg, *Chem. Phys.* **346**, 69 (2008)
- [16] K. Pachucki and J. Komasa, *J. Chem. Phys.* **129**, 034102 (2008)
- [17] K. Pachucki and J. Komasa, *J. Chem. Phys.* **130**, 164113 (2009)
- [18] L. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky and J. Tennyson, *Phys. Rev. A* **88**, 032506 (2013)
- [19] L. C. Biedenharn and J. D. Louck, *Angular Momentum in Quantum Physics* (Addison-Wesley, Reading, 1981)
- [20] P. R. Bunker and P. Jensen, *Fundamentals of Molecular Symmetry* (IOP Publishing, Bristol, 2005)
- [21] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiy, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988)