



A perturbative approach for the construction of the non-adiabatic nuclear kinetic energy operator for diatomic and triatomic systems

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Abstract

In this work, we derive an effective *non-adiabatic* kinetic energy operator for nuclear motion in triatomic molecules on the basis of perturbation theory. For this purpose, we extended the approach of Herman and Asgharian (J Mol Spectr 19:305, 1966) originally developed for diatomic systems. General perturbative-type expressions for effective distance-dependent reduced nuclear masses have been obtained for a triatomic system. It is shown that in the diatomic limit our method reproduces correctly the previous known result of Herman and Asgharian.

Keywords Non-adiabaticity · Perturbation expansion · Nuclear kinetic energy operator · Distance-dependent masses

Mathematics Subject Classification 81Q05 · 81Q15

1 Introduction

One of the most elegant approaches to account for the total contribution of non-adiabatic effects to a given electronic state has been proposed by Herman and Asgharian [1] and consists of the construction of an effective Hamiltonian, or to be more precise an effective kinetic energy operator (KEO) based on second-order per-

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turbative analysis of the exact KEO. This leads to non-adiabatic investigations using a single potential energy surface with distance-dependent effective nuclear masses within the different kinetic energy operator terms. The essence of [1] consists in the treatment of the nuclear gradient operators as perturbation in the Born–Oppenheimer (or adiabatic) approach. Because of the general properties of the adiabatic wavefunctions the leading non-zero corrections to the bound energy of the system arises in the second-order of the standard Rayleigh–Schrödinger perturbation theory. In case of the ro-vibrational spectrum of a system one can interpret the obtained second-order corrections as a first-order correction to an effective nuclear KEO in question [1]. First implementations and applications by the present authors have been published recently [2–4].

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 [1,5–9] that this assumption is reasonable as a first order correction. In the case of H_3^+ , earlier calculations [10–13] 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 [1,12,14–17] 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.

Let us note briefly other approaches to account for the non-adiabatic effects. A method employing the Bunker and Moss formalism [5] with simultaneous consideration of many electronic states has been developed for one-electron systems in [19,20], and for multi-electronic systems in [21,22]. An empirical approach employing energy-dependent corrections was suggested in [23,24] and extended in [25]. The most recent reviews on the accuracy of calculated rotation-vibration spectra can be found in [26–28].

It should be noticed, that the approach of Herman and Asgharian is useful only for weak non-adiabatic interactions, whereas strong non-adiabatic interactions need direct coupled surface calculations based on explicit derivative couplings (first and second derivatives of the electronic wavefunction with respect to nuclear motion) or diabatic potential approaches.

The practical realization of the Herman–Asgharian algorithm consists of the construction of an perturbation expansion for the intermediate nuclear kinetic energy operator 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. In principle, it is not necessary, that BF and SF are arbitrarily oriented with respect to each other. One can superimpose the SF and BF frames. However, in this case the technical difficulties arise with the exponentiation [29] of the infinitesimally small Euler angles to obtain the angular part of the kinetic energy operator in the explicit form. Applications of infinitesimal Euler rotations in the derivation of the molecular KEO are given in [30].

The differential operators which enter into the intermediate Cartesian nuclear KEO are multiplied by prefactors, which are referred as distance-dependent (or coordinate-dependent) contributions to reduced nuclear masses. These prefactors are not only different for each single operator but also defined in a uniquely chosen BF frame. Consequently, the resulting total nuclear KEO can no longer be represented as a simple sum of Laplace operators of nuclear coordinates (that would be possible in case of conventional nuclear masses). Instead, one has to deal with the transformation of each individual differential operator from the BF frame into the SF frame with subsequent 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.

In our previous work [2] (hereafter referred to as I) we have constructed the general expression for the nuclear kinetic energy operator in molecular (Jacobi) coordinates with distance-dependent masses (DDM) for each nuclei. In paper I we did not specify any explicit representation for the ad-hoc introduced nuclear DDM and considered only the main contributions which come from the diagonal differential operators in the Cartesian form of the nuclear KEO. In the present work, we extended the technique of analytic variations of nuclear coordinates, described in I, on the operators of the mixed derivatives. This allows us to construct a complete non-adiabatic nuclear KEO for triatomic systems starting from the perturbative type (or Herman–Asgharian type) Cartesian expressions of the KEO in the BF frame. The distance-dependent contributions to the reduced nuclear masses are explicitly represented through derivative matrix elements between the electronic wave functions of different electronic states.

The structure of the paper is the following. In Sect. 2 we construct the general perturbation scheme for the derivation of the non-adiabatic corrections to the ro-vibrational energies for a triatomic molecule. In Sect. 3 the obtained corrections are used to deduce the effective Hamiltonian in molecular (Jacobi) coordinates. In Sect. 4 we demonstrate that our approach, applied to a diatomic system, reproduces correctly the results of [1] (without additional assumptions used by the authors of [1]). Concluding remarks are given in Sect. 5. Technical details concerning the transformation of the differential operators from Cartesian BF to molecular SF coordinates are given in “Appendix A”. In “Appendix B” we describe a recurrent scheme for the calculation of some matrix elements between associated Legendre functions needed in the applications.

2 Perturbation expansion for the non-adiabatic contributions

The application of the method of distance-dependent corrections to nuclear masses [1] 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 (13) and further], which

depends on the relative position of the nuclei and on the chosen directions of the coordinate axis. Therefore, to keep the meaning (i.e. the numerical values) 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 three Euler angles $\Omega = \{\delta, \gamma, \varphi\}$. We employ the passive picture (see [31,32]) 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 (I.1)); we shall use the index I whenever referring to the formulae of paper I).

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 $\mathbf{Q} = \{r, R, \theta\}$. 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 \mathbf{r} and \mathbf{R} . We shall denote the Cartesian coordinates of the vectors \mathbf{r} , \mathbf{R} in the BF frame as follows

$$\mathbf{R}(X, Y, Z), \quad \mathbf{r}(x, y, z). \quad (1)$$

The geometry of the molecular system and notations of the coordinate frames are shown in Fig. 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.

We shall follow, to a large extent, the ideas formulated in [1], albeit generalized to the case of three nuclei. For Jacobi coordinates (1) the nuclear reduced masses are given by

$$\mu_r^{-1} = m_1^{-1} + m_2^{-1}, \quad \mu_R^{-1} = (m_1 + m_2)^{-1} + m_3^{-1}, \quad (2)$$

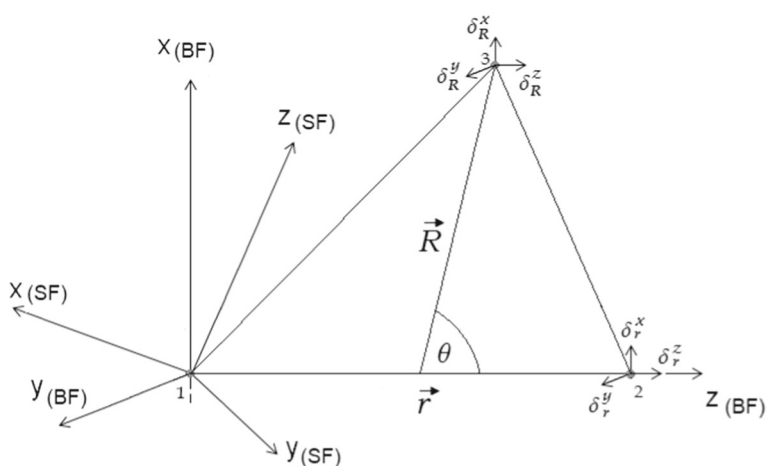


Fig. 1 Coordinate frames for a triatomic molecular system; $\delta_{R,r}^{x,y,z}$ schematically represents the variations of the Cartesian components of the Jacobi vectors \mathbf{R} and \mathbf{r} in the BF frame

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

$$\left(T + V(\mathbf{Q}, \mathbf{q}) - E\right)\psi(\mathbf{Q}, \mathbf{q}) = 0, \quad (3)$$

where T is the complete translation-free kinetic energy operator of the whole system, \mathbf{q} denotes the complete set of electronic coordinates, $V(\mathbf{Q}, \mathbf{q})$ 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 $\varphi_\lambda(\mathbf{q}|\mathbf{Q})$ and nuclear $v_\lambda^k(\mathbf{Q})$ wave functions

$$\psi(\mathbf{Q}, \mathbf{q}) = \sum_{\lambda k} C_{\lambda k} \varphi_\lambda(\mathbf{q}|\mathbf{Q}) v_\lambda^k(\mathbf{Q}) \equiv \sum_{\lambda k} C_{\lambda k} |\lambda k\rangle, \quad (4)$$

where the symbols λ denote the electronic and k the nuclear state, respectively. Substituting the expansion for ψ into the Schrödinger equation (3) we come to the standard adiabatic approximation for the nuclear motion

$$\left[-\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_r} \nabla_r^2 + E_\lambda^{AD} - E\right] \varphi_\lambda v_\lambda^k + W \varphi_\lambda v_\lambda^k = 0, \quad (5)$$

$E_\lambda^{AD} \equiv E_\lambda^{AD}(\mathbf{Q})$ is the adiabatic potential energy surface (PES) and W denotes the operator of non-adiabaticity

$$W = -\frac{\hbar^2}{\mu_R} \nabla_R^{(n)} \cdot \nabla_R^{(e)} - \frac{\hbar^2}{\mu_r} \nabla_r^{(n)} \cdot \nabla_r^{(e)}. \quad (6)$$

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

$$\left(-\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_r} \nabla_r^2 + E_\lambda^{AD}(\mathbf{Q}) - E_{\lambda k}\right) v_\lambda^k(\mathbf{Q}) = 0. \quad (7)$$

Considering the functions v_λ^k in (7) as a zero approximation, one may treat (5) 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

$$E_{\lambda k}^{(2)} = - \sum_{a=r,R} \sum_{\lambda' k' \neq \lambda k} \left(\frac{\hbar^4}{\mu_a^2} \right) \frac{\langle \lambda k | \nabla_a^{(e)} \lambda' \cdot \nabla_a^{(n)} k' \rangle \langle \lambda' k' | \nabla_a^{(e)} \lambda \cdot \nabla_a^{(n)} k \rangle}{E_{\lambda' k'} - E_{\lambda k}}. \quad (8)$$

Representing the vectors \mathbf{r} and \mathbf{R} in (8) in Cartesian coordinates, we introduce the common symbols χ, η, ζ , which depend parametrically on a as follows

$$\chi, \eta, \zeta = \begin{cases} x, y, z, & a = r, \\ X, Y, Z, & a = R. \end{cases} \quad (9)$$

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

$$\partial_\alpha (\mathbf{n}_i \psi) = \mathbf{n}_i \partial_\alpha \psi, \quad \alpha = \chi, \eta, \zeta, \quad (10)$$

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 (9)]

$$\langle \lambda k | \nabla_a^{(e)} \lambda' \cdot \nabla_a^{(n)} k' \rangle = \sum_{\alpha=\chi, \eta, \zeta} \langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle \langle k | \partial_\alpha^{(n)} k' \rangle, \quad a = r, R. \quad (11)$$

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 (8). Therefore, the difference $E_{\lambda' k'} - E_{\lambda k}$ can be approximated by $E_{\lambda'} - E_\lambda$, and (8) leads to

$$E_{\lambda k}^{(2)} = - \sum_{a=r, R} \frac{\hbar^4}{\mu_a^2} \times \left\langle k \left| \sum_{\lambda' \neq \lambda} \sum_{\alpha=\chi, \eta, \zeta} \frac{\langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle}{E_{\lambda'} - E_\lambda} \partial_\alpha^{(n)} \sum_{\beta=\chi, \eta, \zeta} \langle \lambda' | \partial_\beta^{(e)} \lambda \rangle \partial_\beta^{(n)} \right| k \right\rangle. \quad (12)$$

Let us to introduce the following abbreviations for the matrix element

$$\omega_\alpha^{\lambda \lambda'} = \langle \lambda | \partial_\alpha^{(e)} \lambda' \rangle, \quad \alpha = \chi, \eta, \zeta. \quad (13)$$

Computing the sums in (12), 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 $E_{\lambda k}^{(2)}$ [reminding the definitions in (9)]:

$$E_{\lambda k}^{(2)} = \sum_{a=r, R} \frac{\hbar^2}{2\mu_a} \left\langle k \left| \frac{2\hbar^2}{\mu_a} \sum_{\lambda' \neq \lambda} \frac{1}{E_{\lambda'} - E_\lambda} \left[\omega_\chi^2 \frac{\partial^2}{\partial \chi^2} + \omega_\eta^2 \frac{\partial^2}{\partial \eta^2} + \omega_\zeta^2 \frac{\partial^2}{\partial \zeta^2} \right. \right. \right. \\ + \omega_\chi \omega_\eta (\partial_\chi \partial_\eta + \partial_\eta \partial_\chi) + \omega_\chi \omega_\zeta (\partial_\chi \partial_\zeta + \partial_\zeta \partial_\chi) + \omega_\eta \omega_\zeta (\partial_\eta \partial_\zeta + \partial_\zeta \partial_\eta) \\ + (\omega_\chi \partial_\chi \omega_\chi + \omega_\eta \partial_\eta \omega_\chi + \omega_\zeta \partial_\zeta \omega_\chi) \partial_\chi + (\omega_\chi \partial_\chi \omega_\eta + \omega_\eta \partial_\eta \omega_\eta + \omega_\zeta \partial_\zeta \omega_\eta) \partial_\eta \\ \left. \left. \left. + (\omega_\chi \partial_\chi \omega_\zeta + \omega_\eta \partial_\eta \omega_\zeta + \omega_\zeta \partial_\zeta \omega_\zeta) \partial_\zeta \right] \right| k \right\rangle. \quad (14)$$

For the sake of compactness in (14), and in the following, we omit the superscripts in the notation for $\omega_\alpha^{\lambda\lambda'}$. Notice, in contrast to I, in the present work we take into account also the terms with mixed contributions $\omega_\alpha\omega_\beta$ for $\alpha \neq \beta$. Hence, expression (14) represents the complete non-adiabatic contribution in the second order of perturbation theory.

3 The non-adiabatic KEO for a triatomic system

3.1 The general derivation

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 (14) as

$$E_{\lambda k}^{(2)} = \langle k | T_{\text{na}} | k \rangle. \quad (15)$$

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 Fig. 1. In the present work we use the molecular embedding with the diatom vector \mathbf{r} aligned along the z -axis and the vector \mathbf{R} in the xz -plane (we denote this embedding as $[\mathbf{r} || z]$). The operator T_{na}

$$T_{\text{na}} \equiv T_{\text{na}}^{(1)} + T_{\text{na}}^{(2)}, \quad (16)$$

can be written immediately by comparing (14) and (15):

$$\begin{aligned} T_{\text{na}}^{(1)} = & -\frac{\hbar^2}{2\mu_r} \left[G_{xx}^{(r)} \frac{\partial^2}{\partial x^2} + G_{yy}^{(r)} \frac{\partial^2}{\partial y^2} + G_{zz}^{(r)} \frac{\partial^2}{\partial z^2} \right] \\ & -\frac{\hbar^2}{2\mu_R} \left[G_{XX}^{(R)} \frac{\partial^2}{\partial X^2} + G_{YY}^{(R)} \frac{\partial^2}{\partial Y^2} + G_{ZZ}^{(R)} \frac{\partial^2}{\partial Z^2} \right], \end{aligned} \quad (17)$$

and

$$\begin{aligned} T_{\text{na}}^{(2)} = & -\frac{\hbar^2}{2\mu_r} \left[G_{xy}^{(r)} \mathcal{O}_{xy} + G_{xz}^{(r)} \mathcal{O}_{xz} + G_{yz}^{(r)} \mathcal{O}_{yz} + g_x^{(r)} \partial_x + g_y^{(r)} \partial_y + g_z^{(r)} \partial_z \right] \\ & -\frac{\hbar^2}{2\mu_R} \left[G_{XY}^{(R)} \mathcal{O}_{XY} + G_{XZ}^{(R)} \mathcal{O}_{XZ} + G_{YZ}^{(R)} \mathcal{O}_{YZ} + g_X^{(R)} \partial_X + g_Y^{(R)} \partial_Y + g_Z^{(R)} \partial_Z \right], \end{aligned} \quad (18)$$

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

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

$$g_{\alpha}^{(a)} = -\frac{2\hbar^2}{\mu_{\alpha}} \sum_{\lambda' \neq \lambda} \frac{\omega_{\lambda'} \partial_{\lambda'} \omega_{\alpha} + \omega_{\eta} \partial_{\eta} \omega_{\alpha} + \omega_{\zeta} \partial_{\zeta} \omega_{\alpha}}{E_{\lambda'} - E_{\lambda}}, \quad \alpha, \beta = \chi, \eta, \zeta. \quad (19)$$

Let the symbol T_0 indicates the conventional (constant nuclear masses) trinuclear KEO. The operator $T_0 + T_{\text{na}}$ represents the most complete non-adiabatic KEO in the sense formulated in the previous section. To separate the pure vibrational $T_V^{(n)}$ and vibration-rotational $T_{VR}^{(n)}$ terms in the KEO we use the following notations

$$T_{\text{na}}^{(n)} = T_V^{(n)} + T_{VR}^{(n)}, \quad n = 1, 2. \quad (20)$$

Therefore, an effective Schrödinger equation for nuclear motion can be written as

$$\left(T_0 + T_{\text{na}} + E_{\lambda}^{AD}(\mathbf{Q}) - E_{\lambda k} \right) v_{\lambda}^k(\mathbf{Q}) = 0. \quad (21)$$

In case of embedding $[\mathbf{r} || z]$, the conventional kinetic energy operator $T_0 = T_V^{(0)} + T_{VR}^{(0)}$ reads

$$T_V^{(0)} = -\frac{\hbar^2}{2\mu_r} \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\hbar^2}{2\mu_R} \frac{1}{R} \frac{\partial^2}{\partial R^2} R - \frac{\hbar^2}{2} \left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right), \quad (22)$$

$$T_{VR}^{(0)} = \frac{1}{2\mu_r r^2} \left[\Pi_x^2 + \Pi_y^2 + \Pi_z^2 \cot^2 \theta + (\Pi_x \Pi_z + \Pi_z \Pi_x) \cot \theta \right] - \frac{i\hbar}{\mu_r r^2} \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) \Pi_y + \frac{1}{2\mu_R R^2} \frac{\Pi_z^2}{\sin^2 \theta}. \quad (23)$$

Π_x , Π_y and Π_z are the total orbital momentum operators (see [32], par. 5.5.2; or I, (I.A1); to be precise, we use the complex conjugated expressions of the orbital momentum operators adopted in [32]).

The representation of the BF differential operators in (17), as seen in the SF frame for embedding $[\mathbf{r} || z]$ (see Fig. 1) has been given in I. Hence, to represent the operator $T_{\text{na}}^{(1)}$ in the SF Jacobi coordinates we use expressions (I.48) and (I.49).

Notice, in I we have included the constant reduced nuclear masses μ_R , μ_r into the definition of the DDMs $\mu_{2,3}^{(x,y,z)}$ (in the notations adopted in I) whereas in the present work we have separated out the conventional part T_0 of the total KEO. One should bear in mind, that the $\mu_{2,3}^{(x,y,z)}$ and functions $G_{\alpha\beta}^{(a)}$ and $g_{\alpha}^{(a)}$, defined by (19), are formally related as follows

$$\frac{1}{\mu_2^{(\alpha)}} = \frac{1 + G_{\alpha\alpha}^{(r)}}{\mu_r}, \quad \frac{1}{\mu_3^{(\beta)}} = \frac{1 + G_{\beta\beta}^{(R)}}{\mu_R}, \quad (24)$$

where $\alpha = x, y, z$ and $\beta = X, Y, Z$. To obtain the SF representation for the operators ∂_{α} and $\mathcal{O}_{\alpha\beta}$ ($\alpha \neq \beta$), needed for construction of the operator $T_{\text{na}}^{(2)}$, we employ the same

technique as described in I. The details of the derivation are given in the “Appendix A”. Finally, this leads to the following expression for the operator $T_V^{(1)} + T_V^{(2)}$ (vibrational part of T_{na})

$$\begin{aligned}
 T_V^{(1)} + T_V^{(2)} = & -\frac{\hbar^2}{2\mu_r} G_{zz}^{(r)} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R} G_1^{(R)} \frac{\partial^2}{\partial R^2} \\
 & - \frac{\hbar^2}{2\mu_r} \left(G_{xx}^{(r)} + G_{yy}^{(r)} \right) \frac{1}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2\mu_r} g_z^{(r)} \frac{\partial}{\partial r} - \frac{\hbar^2 g_{(+)} \partial}{2\mu_R \partial R} \\
 & - \frac{\hbar^2}{2\mu_R} \left(G_3^{(R)} + 2G_1^{(R)} \right) \frac{1}{R} \frac{\partial}{\partial R} \\
 & - \frac{\hbar^2}{2\mu_r} G_{xx}^{(r)} \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} - \frac{\hbar^2}{2\mu_R} G_4^{(R)} \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} \\
 & - \frac{\hbar^2 g_{(-)} \partial}{2\mu_R R \partial \theta} - \frac{\hbar^2}{2\mu_r} G_{xz}^{(r)} \frac{2}{r^2} \frac{\partial}{\partial \theta} - \frac{\hbar^2}{2} \left(\frac{G_{yy}^{(r)}}{r^2 \mu_r} + \frac{G_{YY}^{(R)}}{R^2 \mu_R} \right) \cot \theta \frac{\partial}{\partial \theta} \\
 & + \frac{\hbar^2}{2\mu_r} g_x^{(r)} \frac{1}{r} \frac{\partial}{\partial \theta} - \frac{\hbar^2}{2\mu_R} G_5^{(R)} \frac{1}{R^2} \frac{\partial}{\partial \theta} + \frac{\hbar^2}{2\mu_R} G_5^{(R)} \frac{1}{R} \frac{\partial^2}{\partial R \partial \theta} \\
 & + \frac{\hbar^2}{2\mu_r} G_{xz}^{(r)} \frac{2}{r} \frac{\partial^2}{\partial r \partial \theta}. \tag{25}
 \end{aligned}$$

The operator $T_{VR}^{(1)} + T_{VR}^{(2)}$ for the vibration-rotational part of T_{na} is given as

$$\begin{aligned}
 T_{VR}^{(1)} + T_{VR}^{(2)} = & \frac{1}{2} \left(\frac{\sin^{-2} \theta}{\mu_R R^2} G_{YY}^{(R)} + \frac{\cot^2 \theta}{\mu_r r^2} G_{yy}^{(r)} \right) \Pi_z^2 - i\hbar \left(\frac{G_{xy}^{(r)}}{\mu_r r^2} + \frac{G_{XY}^{(R)}}{\mu_R R^2} \right) \frac{\Pi_z}{\sin^2 \theta} \\
 & + \frac{1}{2r^2 \mu_r} \left(\Pi_x^2 G_{yy}^{(r)} + G_{xx}^{(r)} \Pi_y^2 + G_{yy}^{(r)} \cot \theta \mathcal{P}_{xz} \right) + \frac{i\hbar}{2\mu_R R} \frac{g_Y^{(R)}}{\sin \theta} \Pi_z \\
 & - \frac{i\hbar}{2r^2 \mu_r} \left(2G_{xx}^{(r)} \frac{\partial}{\partial \theta} + G_{yy}^{(r)} \cot \theta - r g_x^{(r)} \right) \Pi_y \\
 & + \frac{i\hbar}{r^2 \mu_r} G_{xy}^{(r)} (\Pi_x + \cot \theta \Pi_z) \frac{\partial}{\partial \theta} \\
 & + \frac{i\hbar}{\mu_r} G_{xz}^{(r)} \left(\frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \right) \Pi_y - \frac{1}{r^2 \mu_r} G_{xy}^{(r)} \mathcal{P}_{xyz} \\
 & + \frac{i\hbar}{R^2 \mu_R} G_{XY}^{(R)} \cot \theta \frac{\partial}{\partial \theta} \Pi_z \\
 & - \frac{i\hbar}{\mu_r} \left(G_{yz}^{(r)} \left(\frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \right) + \frac{g_y^{(r)}}{2r} \right) (\Pi_x + \cot \theta \Pi_z) \\
 & + \frac{i\hbar}{\mu_R} G_{XY}^{(R)} \frac{1}{R} \frac{\partial}{\partial R} \Pi_z + \frac{i\hbar}{\mu_R} G_{YZ}^{(R)} \left(\frac{\cot \theta}{R} \frac{\partial}{\partial R} - \frac{1}{R^2} \frac{\partial}{\partial \theta} \right) \Pi_z. \tag{26}
 \end{aligned}$$

For the sake of brevity we use the following short notations

$$\mathcal{P}_{xz} = \Pi_x \Pi_z + \Pi_z \Pi_x, \quad \mathcal{P}_{xyz} = \Pi_y \Pi_x + \cot \theta \Pi_y \Pi_z, \quad (27)$$

$$\begin{aligned} G_1^{(R)} &= G_{XX}^{(R)} \sin^2 \theta + G_{ZZ}^{(R)} \cos^2 \theta + G_{XZ}^{(R)} \sin 2\theta, \\ G_2^{(r)} &= G_{xx}^{(r)} + G_{yy}^{(r)} - 2G_{zz}^{(r)}, \quad G_2^{(R)} = G_{XX}^{(R)} - 2G_{YY}^{(R)} + G_{ZZ}^{(R)}, \\ G_3^{(R)} &= G_{XX}^{(R)} [1 - 3 \sin^2 \theta] + G_{ZZ}^{(R)} [1 - 3 \cos^2 \theta] + G_{YY}^{(R)} - 3G_{XZ}^{(R)} \sin 2\theta, \\ G_4^{(R)} &= G_{XX}^{(R)} \cos^2 \theta + G_{ZZ}^{(R)} \sin^2 \theta - G_{XZ}^{(R)} \sin 2\theta, \\ G_5^{(R)} &= [G_{ZZ}^{(R)} - G_{XX}^{(R)}] \sin 2\theta - 2G_{XZ}^{(R)} \cos 2\theta, \end{aligned} \quad (28)$$

$$g_{(+)} = g_X^{(R)} \sin \theta + g_Z^{(R)} \cos \theta, \quad g_{(-)} = g_X^{(R)} \cos \theta - g_Z^{(R)} \sin \theta. \quad (29)$$

The substitution $\Psi \rightarrow \frac{1}{rR} \Psi$ eliminates the first radial derivatives in the KEO $T_V^{(0)}$ which is transformed as a result into the expression denoted by $\bar{T}_V^{(0)}$ (see (I.54) but with constant masses), whereas $\bar{T}_{VR}^{(0)} = T_{VR}^{(0)}$. Similarly, the transformed KEO $\bar{T}_{na} \equiv \bar{T}_V + \bar{T}_{VR}$ can be represented by the following expressions:

$$\bar{T}_V = T_V^{(1)} + T_V^{(2)} + \Delta T_V, \quad \bar{T}_{VR} = T_{VR}^{(1)} + T_{VR}^{(2)} + \Delta T_{VR}, \quad (30)$$

with

$$\begin{aligned} \Delta T_V &= \frac{\hbar^2}{\mu_r r} G_{zz}^{(r)} \frac{\partial}{\partial r} + \frac{\hbar^2}{\mu_R R} G_1^{(R)} \frac{\partial}{\partial R} - \hbar^2 \left(\frac{G_{xz}^{(r)}}{\mu_r r^2} + \frac{G_5^{(R)}}{2\mu_R R^2} \right) \frac{\partial}{\partial \theta} \\ &+ \frac{\hbar^2}{2\mu_r} \left(\frac{G_2^{(r)}}{r^2} + \frac{g_z^{(r)}}{r} \right) \\ &+ \frac{\hbar^2}{4\mu_R R^2} (3G_4^{(R)} - 3G_1^{(R)} - G_2^{(R)}) + \frac{\hbar^2}{2\mu_R R^2} g_{(+)}. \end{aligned} \quad (31)$$

ΔT_{VR} is given by

$$\begin{aligned} \Delta T_{VR} &= -\frac{i\hbar}{\mu_r r^2} G_{xz}^{(r)} \Pi_y + \frac{i\hbar}{\mu_r r^2} G_{yz}^{(r)} (\Pi_x + \Pi_z \cot \theta) \\ &- \frac{i\hbar}{\mu_R R^2} G_{XY}^{(R)} \Pi_z - \frac{i\hbar}{\mu_R R^2} G_{YZ}^{(R)} \Pi_z \cot \theta. \end{aligned} \quad (32)$$

3.2 The effective kinetic energy operator

The effective KEO is obtained by integrating the expressions \bar{T}_0 , \bar{T}_V and \bar{T}_{VR} over Wigner D -functions $|J M k\rangle$ and normalized associated Legendre polynomials $|lk\rangle$ [see (I.63), (I.C1)]. We denote the corresponding effective \bar{T} operator as $\langle \bar{T} \rangle_\Omega$ and $\langle \bar{T} \rangle_{\Omega, \theta}$. The subscripts denote the angular variables on which the integration is carried out [for more details see [33] or (I.64)]. For the sake of brevity we introduce the

following short notations

$$G_+^{(r)} = G_{xx}^{(r)} + G_{yy}^{(r)}, \quad G_-^{(r)} = G_{xx}^{(r)} - G_{yy}^{(r)}. \quad (33)$$

The effective $\bar{T}_V^{(0)}$, $\bar{T}_V^{(1)}$ and $\bar{T}_V^{(2)}$ expressions read

$$\begin{aligned} \langle \bar{T}_V^{(0)} \rangle_{\Omega, \theta} &= -\frac{\hbar^2}{2} \left[\frac{1}{\mu_r} \frac{\partial^2}{\partial r^2} + \frac{1}{\mu_R} \frac{\partial^2}{\partial R^2} - \ell(\ell+1) \left(\frac{1}{\mu_r r^2} + \frac{1}{\mu_R R^2} \right) \right] \delta_{k'k} \delta_{\ell'\ell} \\ &\quad - \frac{\hbar^2 k^2}{2} \left(\frac{1}{\mu_r r^2} + \frac{1}{\mu_R R^2} \right) \langle \ell'k | \sin^{-2} \theta | \ell k \rangle \delta_{k'k}, \end{aligned} \quad (34)$$

$$\begin{aligned} \langle \bar{T}_V^{(1)} \rangle_{\Omega, \theta} &= -\frac{\hbar^2}{2} \left[\frac{G_{zz}^{(r)}}{\mu_r} \frac{\partial^2}{\partial r^2} + \frac{G_1^{(R)}}{\mu_R} \frac{\partial^2}{\partial R^2} \right] \delta_{k'k} \delta_{\ell'\ell} - \frac{\hbar^2}{2} \left[\frac{G_{yy}^{(r)}}{\mu_r r^2} + \frac{G_{YY}^{(R)}}{\mu_R R^2} \right] \\ &\quad \times \langle \ell'k | \cot \theta \frac{\partial}{\partial \theta} | \ell k \rangle \delta_{k'k} - \frac{\hbar^2}{2} \left[\frac{G_{xx}^{(r)}}{\mu_r r^2} + \frac{G_4^{(R)}}{\mu_R R^2} \right] \langle \ell'k | \frac{\partial^2}{\partial \theta^2} | \ell k \rangle \delta_{k'k}. \end{aligned} \quad (35)$$

and

$$\begin{aligned} \langle \bar{T}_V^{(2)} \rangle_{\Omega, \theta} &= -\frac{\hbar^2}{2\mu_r} \left[g_z^{(r)} + \frac{G_2^{(r)}}{r} \right] \left[\frac{\partial}{\partial r} - \frac{1}{r} \right] \delta_{k'k} \delta_{\ell'\ell} - \frac{\hbar^2}{2\mu_R} \left[g_{(+)} + \frac{G_3^{(R)}}{R} \right] \\ &\quad \times \left[\frac{\partial}{\partial R} - \frac{1}{R} \right] \delta_{k'k} \delta_{\ell'\ell} + \frac{\hbar^2}{2} \left(\frac{g_x^{(r)}}{\mu_r r} - \frac{g_{(-)}}{\mu_R R} - \frac{2G_5}{\mu_R R^2} - \frac{4G_{xz}^{(r)}}{\mu_r r^2} \right. \\ &\quad \left. + \frac{G_5^{(R)}}{\mu_R R} \frac{\partial}{\partial R} + \frac{2G_{xz}^{(r)}}{\mu_r r} \frac{\partial}{\partial r} \right) \langle \ell'k | \frac{\partial}{\partial \theta} | \ell k \rangle \delta_{k'k}. \end{aligned} \quad (36)$$

We performed similar derivations for the effective $\bar{T}_{VR}^{(0)}$, $\bar{T}_{VR}^{(1)}$ and $\bar{T}_{VR}^{(2)}$. The result is

$$\begin{aligned} \langle \bar{T}_{VR}^{(0)} \rangle_{\Omega} &= \left[\frac{\hbar^2 [J(J+1) - 2k^2]}{2\mu_r r^2} + \frac{\hbar^2 k^2}{\sin^2 \theta} \left(\frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \right] \delta_{k'k} \\ &\quad + \frac{\hbar^2 C_{Jk}^+ \hat{\Theta}_-^{(0)}}{2\mu_r r^2} \delta_{k'k+1} + \frac{\hbar^2 C_{Jk}^- \hat{\Theta}_+^{(0)}}{2\mu_r r^2} \delta_{k'k-1}, \end{aligned} \quad (37)$$

$$\begin{aligned} \langle \bar{T}_{VR}^{(1)} \rangle_{\Omega} &= \left[\frac{\hbar^2 (J(J+1) - 2k^2)}{2r^2} \frac{G_{yy}^{(r)}}{\mu_r} + \frac{\hbar^2 k^2}{\sin^2 \theta} \left(\frac{1}{2r^2} \frac{G_{yy}^{(r)}}{\mu_r} + \frac{1}{2R^2} \frac{G_{YY}^{(R)}}{\mu_R} \right) \right. \\ &\quad \left. + \frac{\hbar^2 G_-^{(r)}}{8\mu_r r^2} \left(C_{Jk}^- C_{Jk-1}^+ + C_{Jk}^+ C_{Jk+1}^- \right) \right] \delta_{k'k} \\ &\quad + \frac{\hbar^2 C_{Jk}^+ \hat{\Theta}_-^{(1)}}{2\mu_r r^2} \delta_{k'k+1} + \frac{\hbar^2 C_{Jk}^- \hat{\Theta}_+^{(1)}}{2\mu_r r^2} \delta_{k'k-1} \\ &\quad - \frac{\hbar^2 G_-^{(r)}}{8\mu_r r^2} \left(C_{Jk}^- C_{Jk-1}^- \delta_{k'k-2} + C_{Jk}^+ C_{Jk+1}^+ \delta_{k'k+2} \right) \end{aligned} \quad (38)$$

$$\left\langle \bar{T}_{VR}^{(2)} \right\rangle_{\Omega} = \frac{\hbar^2}{2\mu_r r} \left[\frac{g_x^{(r)}}{2} + G_{xz}^{(r)} \left(\frac{\partial}{\partial r} - \frac{2}{r} \right) \right] \left(C_{Jk}^+ \delta_{k',k+1} - C_{Jk}^- \delta_{k',k-1} \right), \quad (39)$$

with

$$\hat{\Theta}_{\pm}^{(0)} = k \cot \theta \pm \frac{\partial}{\partial \theta}, \quad \hat{\Theta}_{\pm}^{(1)} = k G_{yy}^{(r)} \cot \theta \pm G_{xx}^{(r)} \frac{\partial}{\partial \theta}. \quad (40)$$

Finally, after integration over the associated Legendre polynomials $|\ell k\rangle$ we obtain

$$\left\langle \bar{T}_{VR}^{(0)} \right\rangle_{\Omega, \theta} = \frac{\hbar^2 [J(J+1) - 2k^2]}{2\mu_r r^2} \delta_{k'k} \delta_{\ell'\ell} + \frac{\hbar^2 k^2}{2} \left[\frac{1}{\mu_r r^2} + \frac{1}{\mu_R R^2} \right] \\ \times \left\langle \ell' k | \sin^{-2} \theta | \ell k \right\rangle \delta_{k'k} - \delta_{\ell'\ell} \frac{\hbar^2}{2\mu_r r^2} (\delta_{k'k+1} C_{Jk}^+ C_{\ell k}^+ + \delta_{k'k-1} C_{Jk}^- C_{\ell k}^-), \quad (41)$$

$$\left\langle \bar{T}_{VR}^{(1)} \right\rangle_{\Omega, \theta} = \frac{\hbar^2}{2} \left[\frac{(J(J+1) - 2k^2)}{r^2} \frac{G_{yy}^{(r)}}{\mu_r} \delta_{\ell'\ell} + k^2 \left[\frac{G_{yy}^{(r)}}{\mu_r r^2} + \frac{G_{YY}^{(R)}}{\mu_R R^2} \right] \right] \\ \times \left\langle \ell' k | \sin^{-2} \theta | \ell k \right\rangle \delta_{k'k} - \frac{\hbar^2 G_{+}^{(r)}}{4\mu_r r^2} \left[C_{Jk}^+ C_{\ell k}^+ \delta_{k'k+1} + C_{Jk}^- C_{\ell k}^- \delta_{k'k-1} \right] \delta_{\ell'\ell} \\ + \frac{\hbar^2 G_{-}^{(r)}}{8\mu_r r^2} \left[C_{Jk}^- C_{Jk-1}^+ + C_{Jk}^+ C_{Jk+1}^- \right] \delta_{k'k} \delta_{\ell'\ell} \\ + \frac{\hbar^2 G_{-}^{(r)}}{4\mu_r r^2} \left(\delta_{k'k+1} \langle \ell' k^+ | \ell k^- \rangle C_{Jk}^+ C_{\ell k}^- + \delta_{k'k-1} \langle \ell' k^- | \ell k^+ \rangle C_{Jk}^- C_{\ell k}^+ \right) \\ - \frac{\hbar^2 G_{-}^{(r)}}{8\mu_r r^2} \left(\delta_{k'k+1} \langle \ell' k^+ | \ell k \rangle C_{Jk}^+ C_{Jk+1}^+ + \delta_{k'k-1} \langle \ell' k^- | \ell k \rangle C_{Jk}^- C_{Jk-1}^- \right), \quad (42)$$

and

$$\left\langle \bar{T}_{VR}^{(2)} \right\rangle_{\Omega, \theta} = \frac{\hbar^2}{2\mu_r r} \left[\frac{g_x^{(r)}}{2} + G_{xz}^{(r)} \left(\frac{\partial}{\partial r} - \frac{2}{r} \right) \right] \\ \times \left(C_{Jk}^+ \langle \ell' k^+ | \ell k \rangle \delta_{k'k^+} - C_{Jk}^- \langle \ell' k^- | \ell k \rangle \delta_{k'k^-} \right), \quad (43)$$

where $k^{\pm} = k \pm 1$ and $k_{\pm} = k \pm 2$. Note, the largest portion of the operator $T_{VR}^{(2)}$ is non-Hermitian, hence expression (43) is obtained after the transformation $\bar{T}_{VR} = \frac{1}{2}(\bar{T}_{VR} + \bar{T}_{VR}^{\dagger})$. The complete effective nuclear KEO can be given as a sum

$$\bar{T} = \sum_{n=0}^2 \left\langle \bar{T}_V^{(n)} \right\rangle_{\Omega, \theta} + \left\langle \bar{T}_{VR}^{(n)} \right\rangle_{\Omega, \theta}. \quad (44)$$

4 The non-adiabatic KEO for a diatomic system

Let us derive the effective non-adiabatic KEO for a diatomic molecule in the electronic state Σ to compare with the results obtained in [1]. We shall place the internuclear vector \mathbf{r} along the BF axis \mathbf{z} . Taking into account the symmetry of the diatomic

molecule ($\omega_x = \omega_y$) we can introduce the following coefficients

$$A_{\lambda\lambda'} = \langle \lambda | \partial_x \lambda' \rangle \langle \lambda' | \partial_x \lambda \rangle = \langle \lambda | \partial_y \lambda' \rangle \langle \lambda' | \partial_y \lambda \rangle, \quad (45)$$

$$C_{\lambda\lambda'} = \langle \lambda | \partial_z \lambda' \rangle \langle \lambda' | \partial_z \lambda \rangle. \quad (46)$$

Assuming cylindrical symmetry for the state of interest (i.e. Σ), the expressions of the type

$$\partial_\alpha \langle \lambda' | \partial_\beta \lambda \rangle, \quad \alpha \neq \beta \quad (47)$$

are zero (see also [1]) and derivation of the effective KEO can be greatly simplified. The differential BF operators ∂_α ($\alpha = x, y, z$) can be given in the SF spherical coordinates $\{r, \theta, \varphi\}$ by exploiting the same techniques as used in the previous section; see also “Appendix A”. The result is

$$\partial_x = \frac{1}{r} \frac{\partial}{\partial \theta}, \quad \partial_y = \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi}, \quad \partial_z = \frac{\partial}{\partial r}. \quad (48)$$

It is important that expressions (48), as well as (49) and (50) further, are obtained under the geometrical constraint represented by the embedding of the molecular axis, [$\mathbf{r} \parallel \mathbf{z}$] in our case. As a consequence, the BF operator $\frac{\partial}{\partial z}$, for instance, is given in the SF frame by a simple partial derivative $\frac{\partial}{\partial r}$ (see also the discussion after equation (24) of [1]).

With the help of (48) we can analyse the contribution $\langle k | \hat{O} | k \rangle$ from all terms (with $a = r$) in (14). Because of angular symmetry of the diatomic nuclear wave function $|k\rangle$ (in the absence of external fields), which are the properly symmetrized spherical harmonics $Y_{jm}(\theta, \varphi)$, the matrix elements $\langle k | \partial_x | k \rangle$ and $\langle k | \partial_y | k \rangle$ are zero (this can be easily verified by direct calculation), and can be dropped from (14). By the same reason we can drop the matrix elements $\langle k | \hat{O} | k \rangle$, where the operators \hat{O} is represented by the following mixed derivatives

$$\begin{aligned} \partial_x \partial_y + \partial_y \partial_x &= 2 \left(\frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \theta \partial \varphi} - \frac{\cot \theta}{r^2 \sin \theta} \frac{\partial}{\partial \varphi} \right), \\ \partial_x \partial_z + \partial_z \partial_x &= 2 \left(\frac{1}{r} \frac{\partial^2}{\partial r \partial \theta} - \frac{1}{r^2} \frac{\partial}{\partial \theta} \right), \\ \partial_y \partial_z + \partial_z \partial_y &= 2 \left(\frac{1}{r \sin \theta} \frac{\partial^2}{\partial r \partial \varphi} - \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \varphi} \right). \end{aligned} \quad (49)$$

Therefore, the only non-zero contribution to $E_{\lambda k}^{(2)}$ results from the operator ∂_z and the second-order derivative operators $\frac{\partial^2}{\partial x^2}$, $\frac{\partial^2}{\partial y^2}$, $\frac{\partial^2}{\partial z^2}$, which are given by

$$\begin{aligned} \frac{\partial^2}{\partial x^2} &= \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2}, \\ \frac{\partial^2}{\partial y^2} &= \frac{1}{r} \frac{\partial}{\partial r} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}, \end{aligned}$$

$$\frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2}. \quad (50)$$

Hence, we come to the following representation for $E_{\lambda k}^{(2)}$:

$$E_{\lambda k}^{(2)} = -\frac{\hbar^2}{2\mu_r} \left\langle k \left| \frac{2\hbar^2}{\mu_r} \sum_{\lambda' \neq \lambda} (E_{\lambda'} - E_\lambda)^{-1} \left[A_{\lambda\lambda'} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + C_{\lambda\lambda'} \frac{\partial^2}{\partial z^2} \right. \right. \right. \\ \left. \left. \left. - (\omega_x \partial_x \omega_z + \omega_y \partial_y \omega_z + \omega_z \partial_z \omega_z) \partial_z \right] \right| k \right\rangle. \quad (51)$$

Using (48) and (50) we reach

$$E_{\lambda k}^{(2)} = -\frac{\hbar^2}{2\mu_r} \left\langle k \left| \frac{2\hbar^2}{\mu_r} \sum_{\lambda' \neq \lambda} (E_{\lambda'} - E_\lambda)^{-1} \left[A_{\lambda\lambda'} \nabla_r^2 + (C_{\lambda\lambda'} - A_{\lambda\lambda'}) \frac{\partial^2}{\partial r^2} \right. \right. \right. \\ \left. \left. \left. - (\omega_x \partial_x \omega_z + \omega_y \partial_y \omega_z + \omega_z \partial_z \omega_z) \frac{\partial}{\partial r} \right] \right| k \right\rangle. \quad (52)$$

∇_r^2 denotes the full Laplacian operator: $\nabla_r^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2r^2} \hat{\ell}^2$. Introducing the functions

$$G_1(r) = \frac{2\hbar^2}{\mu_r} \sum_{\lambda' \neq \lambda} \frac{A_{\lambda\lambda'}}{(E_{\lambda'} - E_\lambda)}, \quad G_2(r) = \frac{2\hbar^2}{\mu_r} \sum_{\lambda' \neq \lambda} \frac{C_{\lambda\lambda'}}{(E_{\lambda'} - E_\lambda)}, \quad (53)$$

$$G_3(r) = -\frac{\hbar^2 r}{\mu_r} \sum_{\lambda' \neq \lambda} \frac{\omega_x \partial_x \omega_z + \omega_y \partial_y \omega_z + \omega_z \partial_z \omega_z}{(E_{\lambda'} - E_\lambda)}, \quad (54)$$

we can rewrite $E_{\lambda k}^{(2)}$ in the following way

$$E_{\lambda k}^{(2)} = -\frac{\hbar^2}{2\mu_r} \left\langle k \left| G_1(r) \nabla_r^2 + [G_2(r) - G_1(r)] \frac{\partial^2}{\partial r^2} + G_3(r) \frac{2}{r} \frac{\partial}{\partial r} \right| k \right\rangle. \quad (55)$$

According to the [1], (55) can be interpreted as if the nuclear motion were governed by an effective perturbation of the form

$$H_{\text{eff}} = -\frac{\hbar^2}{2\mu_r} \left(G_1(r) \nabla_r^2 + [G_2(r) - G_1(r)] \frac{\partial^2}{\partial r^2} + G_3(r) \frac{2}{r} \frac{\partial}{\partial r} \right). \quad (56)$$

Hence, by expression (56), we have demonstrated that in the diatomic limit we reproduce correctly the non-adiabatic nuclear Hamiltonian obtained in [1]. Note, that in [1] the matrix elements $\partial_x \langle \lambda' | \partial_x \lambda \rangle$ and $\partial_y \langle \lambda' | \partial_y \lambda \rangle$ were neglected because of its negligibly small numeric contribution. Therefore, if one omit the terms $\omega_x \partial_x \omega_z$ and $\omega_y \partial_y \omega_z$ as

suggested in [1] the expression for $G_3(r)$ can be further simplified to $G_3^{HA}(r)$

$$G_3^{HA}(r) = \frac{\hbar^2 r}{\mu_r} \sum_{\lambda' \neq \lambda} \frac{\langle \lambda | \partial_z \lambda' \rangle \partial_z \langle \lambda' | \partial_z \lambda \rangle}{(E_{\lambda'} - E_{\lambda})}. \quad (57)$$

Expression (57) [instead of (54)] has been used in [1] to construct the final representation for the effective non-adiabatic Hamiltonian for diatomic molecules.

5 Summary

The aim of the current study was to construct the effective *non-adiabatic* kinetic energy operator for nuclear motion in a triatomic molecule. The purpose of such operator is to simulate, within a certain order of accuracy, a full N -body level of theory but staying in the paradigm of the adiabatic theory (i.e. utilizing the concept of adiabatic potential energy surfaces). The derivation has been carried out in the spirit of the work of Herman and Asgharian [1], resulting in distance-dependent contributions to effective reduced nuclear masses. The main difficulties in the rigorous extension of this approach to a triatomic molecule (originally developed for a diatomic molecule) is the transformation of each individual differential operator with mass-prefactors defined in the BF frame into an arbitrarily oriented SF frame. These difficulties in the derivation 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. By employing analytic variations techniques (described in I) we were able to perform this transformation and construct the effective triatomic nuclear KEO in question. We also reproduce the KEO of [1] for homonuclear diatomics and obtain the terms neglected in [1] needed for the non-adiabatic investigation of heteronuclear diatomic systems.

In the derivation of the KEO the distance-dependent contributions to reduced nuclear masses arise from the application of perturbation theory. The non-adiabaticity is represented by the small terms $G_{\alpha,\beta}^{(a)}$ and $g_{\alpha}^{(a)}$: they are of the order of $O(\mu_r^{-1})$ and $O(\mu_R^{-1})$ and neglected in the adiabatic approximation. The major limitation of the present study is the requirement for “smallness” of the non-adiabaticity. This condition is not fulfilled near avoided crossings or conical intersections where the matrix elements ω_{α} , see (13), become very large or singular.

Preliminary applications for the rovibrational spectrum of H_3^+ have been already performed [3,4]. For the use of the new presented kinetic energy operator we have to calculate first all new distance-dependent mass prefactors $G_{\alpha,\beta}^{(a)}$ (with $\alpha \neq \beta$) and $g_{\alpha}^{(a)}$ [see (25) and (26)] which had not been used before. Then we can analyze, how strong the additional influence of these additional mass-prefactors will be on the rovibrational spectrum.

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Appendices

A Derivation of the operators ∂_α and $\partial_\alpha\partial_\beta$ in the SF frame

In the notations of the variations we shall use the conventions adopted in I. The set of variations of the molecular (Jacobi) SF coordinates $r, R, \theta, \delta, \gamma,$ and φ are denoted by the symbol $\{\delta u\}_{\alpha\beta}$ and ordered in the same way as described by (I.B7). The subscripts α and β denotes the Cartesian BF coordinates of the *same* Jacobi vector \mathbf{r} or \mathbf{R} , i.e. $\alpha, \beta = x, y, z$ or $\alpha, \beta = X, Y, Z$ ($\alpha \neq \beta$); f is the dummy function. In the present work the Cartesian BF coordinates (in contrast to I) are not primed.

We shall demonstrate the transformation of the mixed derivatives $\partial_\alpha\partial_\beta$ from Cartesian BF coordinates into the SF molecular coordinates. Essentially, the procedure has been described in I [see (I.9)–(I.14), (I.77)]. Here, instead of (I.10) we use the finite difference representation for the mixed derivatives $\partial_\alpha\partial_\beta$

$$\partial_\alpha\partial_\beta f = \frac{1}{\delta\alpha\delta\beta} \left[\delta_2 f - \delta_1^{(\alpha)} f - \delta_1^{(\beta)} f \right], \quad (58)$$

with $\delta_1^{(\alpha)} f = f(\alpha + \delta\alpha) - f(\alpha)$, $\delta_1^{(\beta)} f = f(\beta + \delta\beta) - f(\beta)$ and $\delta_2 f = f(\alpha + \delta\alpha, \beta + \delta\beta) - f(\alpha, \beta)$. We treat $\delta_1 f$ and $\delta_2 f$ in exactly the same manner as described by (I.12) and (I.14), albeit for $\delta_2 f$ the variations of the molecular coordinates $\{\delta u\}$ are represented by simultaneous variations of two independent BF Cartesian coordinates $\delta\alpha$ and $\delta\beta$. We start from the two Cartesian BF variations $\delta\alpha$ and $\delta\beta$, next we find the corresponding variations of the Cartesian SF variables with the help of the transformation (I.9). The obtained SF variations are then substituted into (I.13) that gives the following expressions for $\{\delta u\}_{\alpha\beta}$

$$\begin{aligned} \{\delta u\}_{xy} = & \left\{ \frac{\delta x^2}{2r} + \frac{\delta y^2}{2r}, 0, \frac{\delta y^2 \cot \theta}{2r^2} - \frac{\delta x}{r}, \right. \\ & \frac{\cot \gamma \sin 2\varphi}{2r^2 \sin \gamma} (\delta y^2 - \delta x^2) - \frac{\delta x \delta y \cot \gamma \cos 2\varphi}{r^2 \sin \gamma} + \frac{\delta x \sin \varphi}{r \sin \gamma} + \frac{\delta y \cos \varphi}{r \sin \gamma}, \\ & \frac{\cot \gamma}{2r^2} \left(\delta x^2 \sin^2 \varphi + \delta x \delta y \sin 2\varphi + \delta y^2 \cos^2 \varphi \right) + \frac{1}{r} \left(\delta x \cos \varphi - \delta y \sin \varphi \right), \\ & \frac{\sin 2\varphi}{8r^2 \sin^2 \gamma} \left(3\delta x^2 + \cos 2\gamma (\delta x^2 - \delta y^2) - 3\delta y^2 \right) + \frac{\delta x \delta y (3 + \cos 2\gamma) \cos 2\varphi}{4r^2 \sin^2 \gamma} \\ & \left. + \frac{\delta x \delta y}{2r^2} - \frac{\delta x \delta y}{r^2 \sin^2 \theta} - \frac{\cot \gamma}{r} (\delta x \sin \varphi + \delta y \cos \varphi) - \frac{\delta y \cot \theta}{r} \right\}, \quad (59) \end{aligned}$$

$$\begin{aligned} \{\delta u\}_{xz} = & \left\{ \frac{\delta x^2}{2r} + \delta z, 0, \frac{\delta x \delta z}{r^2} - \frac{\delta x}{r}, \frac{\delta x \sin \varphi}{r \sin \gamma} - \frac{\delta x^2 \cot \gamma \sin 2\varphi}{2r^2 \sin \gamma} \right. \\ & - \frac{\delta x \delta z \sin \varphi}{r^2 \sin \gamma}, \frac{\delta x^2 \cot \gamma \sin^2 \varphi}{2r^2} + \frac{(r \delta x - \delta x \delta z) \cos \varphi}{r^2}, \\ & \left. \frac{\delta x^2 [3 + \cos 2\gamma] \sin 2\varphi}{8r^2 \sin^2 \gamma} + \frac{(\delta x \delta z - r \delta x) \cot \gamma \sin \varphi}{r^2} \right\}, \quad (60) \end{aligned}$$

$$\{\delta u\}_{yz} = \left\{ \frac{\delta y^2}{2r} + \delta z, 0, \frac{\delta y^2 \cot \theta}{2r^2}, \frac{\cos \varphi (\delta y^2 \cot \gamma \sin \varphi + r \delta y - \delta y \delta z)}{r^2 \sin \gamma}, \right. \\ \left. \frac{\delta y^2 \cot \gamma \cos^2 \varphi}{2r^2} + \frac{\delta y \delta z \sin \varphi}{r^2} - \frac{\delta y \sin \varphi}{r}, -\frac{\delta y^2 (3 + \cos 2\gamma) \sin 2\varphi}{8r^2 \sin^2 \gamma} \right. \\ \left. + \frac{\delta y \delta z \cot \gamma \cos \varphi}{r^2} + \frac{\delta y \delta z \cot \theta}{r^2} - \frac{\delta y \cot \gamma \cos \varphi}{r} - \frac{\delta y \cot \theta}{r} \right\}, \quad (61)$$

and

$$\{\delta u\}_{XY} = \left\{ 0, \frac{\delta X^2 \cos^2 \theta}{2R} + \delta X \sin \theta + \frac{\delta Y^2}{2R}, \right. \\ \left. -\frac{\delta X^2 \sin 2\theta}{2R^2} + \frac{\delta X \cos \theta}{R} + \frac{\delta Y^2 \cot \theta}{2R^2}, 0, 0, \frac{\delta Y}{R \sin \theta} - \frac{\delta X \delta Y}{R^2 \sin^2 \theta} \right\}, \quad (62)$$

$$\{\delta u\}_{XZ} = \left\{ 0, \frac{\delta X^2 \cos^2 \theta}{2R} - \frac{\delta X \delta Z \sin 2\theta}{2R} + \frac{\delta Z^2 \sin^2 \theta}{2R} \right. \\ \left. + \delta X \sin \theta + \delta Z \cos \theta, \frac{(\delta Z^2 - \delta X^2) \sin 2\theta}{2R^2} \right. \\ \left. - \frac{\delta X \delta Z \cos 2\theta}{R^2} + \frac{\delta X \cos \theta}{R} - \frac{\delta Z \sin \theta}{R}, 0, 0, 0 \right\}, \quad (63)$$

$$\{\delta u\}_{YZ} = \left\{ 0, \frac{\delta Y^2 + \delta Z^2 \sin^2 \theta}{2R} + \delta Z \cos \theta, \frac{1}{2R^2} (\delta Y^2 \cot \theta + \delta Z^2 \sin 2\theta) \right. \\ \left. - \frac{\delta Z \sin \theta}{R}, 0, 0, \frac{\delta Y}{R \sin \theta} \right\}. \quad (64)$$

With the help of (I.14) we compute $\delta_1 f$ [using the variations (I.B8), (I.B9)] and $\delta_2 f$ [using the variations (59)–(64)] and substitute the obtained results into (58). Taking the limit $\delta\alpha \rightarrow 0$, $\delta\beta \rightarrow 0$ in (58) we get the expression for the operator $\partial_\alpha \partial_\beta$ in the SF frame. Calculating the limit one should bear in mind that $\delta\alpha$ and $\delta\beta$ are of the same order of magnitude. As an example, consider the case of the $\partial_x \partial_y$ operator (obviously, $\partial_x \partial_y = \partial_y \partial_x$). Substituting all variations into (58) we reach the final result

$$\partial_x \partial_y = \frac{\sin 2\varphi}{2r^2} \left(\cot \gamma \frac{\partial}{\partial \gamma} - \frac{\partial^2}{\partial \gamma^2} \right) + \frac{\cos 2\varphi}{r^2 \sin \gamma} \frac{\partial^2}{\partial \delta \partial \gamma} + \frac{\sin 2\varphi}{2r^2 \sin^2 \gamma} \frac{\partial^2}{\partial \delta^2} \\ + \left(\frac{\cos^2 \varphi - \cos^2 \gamma \sin^2 \varphi}{r^2 \sin^2 \gamma} - \frac{1}{r^2 \sin^2 \theta} \right) \frac{\partial}{\partial \varphi} - \frac{\cot \gamma \cos 2\varphi}{r^2 \sin \gamma} \frac{\partial}{\partial \delta} \\ - \left[\frac{\cot \theta \sin \varphi}{r^2 \sin \gamma} + \frac{\cot \gamma \sin 2\varphi}{r^2 \sin \gamma} \right] \frac{\partial^2}{\partial \delta \partial \varphi} - \frac{\cos \varphi}{r^2 \sin \gamma} \frac{\partial^2}{\partial \theta \partial \delta} \\ + \frac{\cot \gamma \cos \varphi + \cot \theta}{r^2} \frac{\partial^2}{\partial \theta \partial \varphi} - \left[\frac{\cot \gamma \cos 2\varphi}{r^2} + \frac{\cot \theta \cos \varphi}{r^2} \right] \frac{\partial^2}{\partial \gamma \partial \varphi}$$

$$+ \frac{\sin \varphi}{r^2} \frac{\partial^2}{\partial \theta \partial \gamma} + \left(\frac{\cot \gamma \cot \theta \sin \varphi}{r^2} + \frac{\cot^2 \gamma \sin 2\varphi}{2r^2} \right) \frac{\partial^2}{\partial \varphi^2}. \quad (65)$$

Using the representations of the total angular momentum operators Π_x , Π_y and Π_z [see (I.A1)] the expression for $\partial_x \partial_y$ can be expressed in a more compact form:

$$\partial_x \partial_y = \frac{1}{\hbar^2 r^2} \left[\Pi_y \Pi_x + \cot \theta \Pi_y \Pi_z \right] + \frac{i}{\hbar r^2} \csc^2 \theta \Pi_z - \frac{i}{\hbar r^2} \left[\Pi_x + \cot \theta \Pi_z \right] \frac{\partial}{\partial \theta}. \quad (66)$$

In the same manner we can compute all operators and finally arrive at the following representations for operators $\mathcal{O}_{\alpha\beta}$

$$\mathcal{O}_{xy} = \frac{2}{\hbar^2 r^2} \left[\Pi_y \Pi_x + \cot \theta \Pi_y \Pi_z + \frac{i\hbar \Pi_z}{\sin^2 \theta} - i\hbar (\Pi_x + \cot \theta \Pi_z) \frac{\partial}{\partial \theta} \right], \quad (67)$$

$$\mathcal{O}_{xz} = \left(\frac{2}{r^2} - \frac{2}{r} \frac{\partial}{\partial r} \right) \left(\frac{i}{\hbar} \Pi_y + \frac{\partial}{\partial \theta} \right), \quad (68)$$

$$\mathcal{O}_{yz} = \frac{2i}{\hbar} \left(\frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} \right) (\Pi_x + \cot \theta \Pi_z), \quad (69)$$

$$\mathcal{O}_{xY} = -\frac{2i}{\hbar} \left(\frac{1}{R} \frac{\partial}{\partial R} + \frac{\cot \theta}{R^2} \frac{\partial}{\partial \theta} - \frac{\csc^2 \theta}{R^2} \right) \Pi_z, \quad (70)$$

$$\mathcal{O}_{xZ} = \left(\frac{2}{R} \frac{\partial}{\partial R} - \frac{2}{R^2} \right) \cos 2\theta \frac{\partial}{\partial \theta} + \sin 2\theta \left(\frac{\partial^2}{\partial R^2} - \frac{1}{R} \frac{\partial}{\partial R} - \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} \right), \quad (71)$$

$$\mathcal{O}_{YZ} = -\frac{2i}{\hbar} \left(\frac{\cot \theta}{R} \frac{\partial}{\partial R} - \frac{1}{R^2} \frac{\partial}{\partial \theta} \right) \Pi_z. \quad (72)$$

The transformation of the 1st-order derivative operators ∂_α is considerably simpler and can be done within the same technique by employing variations (I.B8), (I.B9) and the standard definition for the 1st-order derivative operator [which we use now in place of (I.10)]

$$\partial_\alpha f = \lim_{\delta\alpha \rightarrow 0} \frac{\delta_1^{(\alpha)} f}{\delta\alpha}, \quad (73)$$

Obviously, for the purpose of the ∂_α transformation, one needs the linear parts (with respect to the $\delta\alpha$) of the expressions (I.13), (I.14), (I.B8) and (I.B9) only. One finally obtains the following representations for the ∂_α operators in the SF frame:

$$\partial_x = -\frac{1}{r} \frac{\partial}{\partial \theta} - \frac{i\Pi_y}{\hbar r}, \quad \partial_y = \frac{i}{\hbar r} (\Pi_x + \cot \theta \Pi_z), \quad \partial_z = \frac{\partial}{\partial r},$$

$$\partial_X = \frac{\cos \theta}{R} \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial}{\partial R}, \quad \partial_Y = -\frac{i}{\hbar} \frac{\Pi_z}{R \sin \theta}, \quad (74)$$

$$\partial_Z = \cos \theta \frac{\partial}{\partial R} - \frac{\sin \theta}{R} \frac{\partial}{\partial \theta}. \quad (75)$$

The representations for the differential operators (65)–(72), (74) and (75) [as well as (48)–(50) for the diatomic molecule] are obtained under the geometrical constraints presented by the embedding $[\mathbf{r} \parallel \mathbf{z}]$ of the Jacobi vectors \mathbf{R} and \mathbf{r} in the BF frame.

Finally we give the variations needed to transform the BF Cartesian derivative operators ∂_α and $\partial_{\alpha\beta}$ ($\alpha, \beta = x, y, z$) into spherical SF coordinates $\{r, \theta, \varphi\}$ used in Sect. 4 for the diatomic system:

$$\{\delta u\}_x = \left\{ \frac{\delta x^2}{2r}, \frac{\delta x}{r}, 0 \right\}, \quad \{\delta u\}_y = \left\{ \frac{\delta y^2}{2r}, \frac{\delta y^2 \cot \theta}{2r^2}, \frac{\delta y}{r \sin \theta} \right\},$$

$$\{\delta u\}_z = \{\delta z, 0, 0\}. \quad (76)$$

$$\{\delta u\}_{xy} = \left\{ \frac{\delta x^2 + \delta y^2}{2r}, \frac{2r\delta x + \cot \theta \delta y^2}{2r^2}, \frac{\delta y}{r \sin \theta} - \frac{\delta x \delta y \cos \theta}{r^2 \sin^2 \theta} \right\},$$

$$\{\delta u\}_{xz} = \left\{ \delta z + \frac{\delta x^2}{2r}, -\frac{\delta x \delta z}{r^2} + \frac{\delta x}{r}, 0 \right\},$$

$$\{\delta u\}_{yz} = \left\{ \delta z + \frac{\delta y^2}{2r}, \frac{\delta y^2 \cot \theta}{2r^2}, -\frac{\delta y \delta z}{r^2 \sin \theta} + \frac{\delta y}{r \sin \theta} \right\}. \quad (77)$$

B The recurrent relations between the matrix elements involving the associated Legendre polynomials

The general expression for the matrix elements $\langle n' m' | nm \rangle$, (I.C9), rather impractical for the large values of n', n, m' and m , because of the presence of numerous factorials and summations. Here we give the simple recurrent schemes for calculation of these matrix elements for some combinations of the quantum numbers. Namely, we consider the case $m' - m = 2$. The mentioned restriction on the quantum numbers related to the practical needs in the calculation of the effective Hamiltonian [see (42) as an example].

We shall use the ideas used in the [34]. The associated Legendre polynomials $P_n^m(x)$ can be defined by the following two equivalent representations

$$P_n^m(x) = (-1)^m \frac{(1-x^2)^{m/2}}{2^n n!} \partial_x^{n+m} (x^2-1)^n$$

$$= \frac{(n+m)!}{2^n n! (n-m)!} (1-x^2)^{-m/2} \partial_x^{n-m} (x^2-1)^n, \quad (78)$$

where (similarly as in the previous sections) the symbol ∂_x^k denotes the k -th derivative on the variable x .

We shall use the following relation [see [35], (8.733-4)]

$$P_{n-1}^m(x) - P_{n+1}^m(x) = (2n+1)\sqrt{1-x^2} P_n^{m-1}(x). \quad (79)$$

In the calculations of the integrals it is convenient to use the un-normalized expressions (78) for associated Legendre polynomials. The standard normalization coefficient B_{nm}

reads

$$\int_{-1}^{+1} [B_{nm} P_n^m(x)]^2 dx = 1, \quad B_{nm} = \sqrt{\frac{(2n+1)(n-m)!}{2(n+m)!}}. \quad (80)$$

Let us introduce the following notation for the matrix elements with the polynomials $P_n^m(x)$

$$\int_{-1}^{+1} P_n^{m'}(x) P_n^m(x) dx = \langle P_n^{m'} | P_n^m \rangle. \quad (81)$$

We are going to derive: (i) the recurrent relations between the matrix elements $\langle P_n^m | P_n^{m-2} \rangle$ and $\langle P_n^{m-1} | P_n^{m+1} \rangle$ (type I); (ii) the matrix elements $\langle P_n^2 | P_{n-k}^0 \rangle$, $k = 2, 4, \dots, n$, where n is an even number (type II). Without loss of generality we assume that the quantum numbers m and m' in (81) are positive, i.e. for the matrix elements of the type I, $m \geq 2$.

B.1 Matrix elements of the type I

Let us to introduce a short notation $I_{nm} = \langle P_n^m | P_n^{m-2} \rangle$. We shall derive the relation between the matrix elements I_{nm} and I_{nm+1} , where $I_{nm+1} = \langle P_n^{m-1} | P_n^{m+1} \rangle = \langle P_n^{m+1} | P_n^{m-1} \rangle$. By using the representation (78) we have

$$I_{nm} = C_{nm} \int_{-1}^{+1} (1-x^2) \partial_x^k q_n(x) \partial_x^{p+2} q_n(x) dx, \quad q_n(x) = (x^2-1)^n, \quad (82)$$

where $k = n + m$, $p = n - m$, and

$$C_{nm} = \frac{(-1)^m (n+m-2)!}{[2^n n!]^2 (n-m+2)!}. \quad (83)$$

Integrating by parts in (82) [$I_{nm} \equiv \int u dv$, where $u = (1-x^2) \partial_x^k q_n(x)$] the I_{nm} can be represented as follows:

$$\begin{aligned} I_{nm} = & -C_{nm} \int_{-1}^{+1} (1-x^2) \partial_x^{k+1} q_n(x) \partial_x^{p+1} q_n(x) dx \\ & + 2C_{nm} \int_{-1}^{+1} x \partial_x^k q_n(x) \partial_x^{p+1} q_n(x) dx = -C_{nm} I_{nm}^{(0)} + 2C_{nm} I_{nm}^{(1)}. \end{aligned} \quad (84)$$

Consider (84) at $m = n$ (i.e. $k = 2n$ and $p = 0$), which give us the matrix element $I_{nn} \equiv \langle P_n^n | P_n^{n-2} \rangle$. Because of $\partial_x^{k+1} q_n(x) \equiv 0$, the first integral $I_{nm}^{(0)}$ in (84) is zero and I_{nn} is represented solely by the second integral $I_{nm}^{(1)}$. Integrating the $I_{nm}^{(1)}$ by parts (with $u = x$) and using the relation

$$\int_{-1}^{+1} \partial_x^k q_n(x) \partial_x^p q_n(x) dx = K_{nm}, \quad K_{nm} = \frac{2(-1)^m (2^n n!)^2}{2n+1}, \quad (85)$$

we reach the final result for the matrix element I_{nn}

$$I_{nn} = -2C_{nn} \int_{-1}^{+1} \partial_x^k q_n(x) \partial_x^p q_n(x) dx = \frac{-2(2n - 2)!}{2n + 1}. \tag{86}$$

Consider now the general case, $n > m$. The integral $I_{nm}^{(0)}$ in the (84) represents (up to a constant) the matrix element I_{nm+1} [one can see this immediately, by comparing the expression for $I_{nm}^{(0)}$ with the (82)], therefore we can write

$$I_{nm} = -\frac{C_{nm}}{C_{nm+1}} I_{nm+1} + 2C_{nm} I_{nm}^{(1)}. \tag{87}$$

Integrating $I_{nm}^{(1)}$ by parts (with the $u = x \partial_x^k q_n(x)$) we obtain

$$I_{nm}^{(1)} = -K_{nm} - I_{nm}^{(2)}, \tag{88}$$

where $I_{nm}^{(2)}$ can be treated in the same way and result is

$$I_{nm}^{(2)} = \int_{-1}^{+1} x \partial_x^{k+1} q_n(x) \partial_x^p q_n(x) dx = -K_{nm+1} - I_{nm}^{(3)}. \tag{89}$$

We can write a general expression for $I_{nm}^{(r)}$ as follows

$$I_{nm}^{(r)} = -K_{nm+r-1} - I_{nm}^{(r+1)}, \tag{90}$$

where

$$I_{nm}^{(r)} = \int_{-1}^{+1} x \partial_x^{k+r-1} q_n(x) \partial_x^{p-r+2} q_n(x) dx. \tag{91}$$

The last non-zero integral $I_{nm}^{(N)}$ ($r = N$) can be determined from the condition $k + N - 1 = 2n$ (i.e. $N = n - m + 1$) and the result is $I_{nm}^{(N)} = K_{nm}$. Therefore, by using the recurrence relation (90) we can obtain the $I_{nm}^{(1)}$, namely

$$I_{nm}^{(1)} = -(n - m + 1)K_{nm}. \tag{92}$$

Substituting this expression for $I_{nm}^{(1)}$ into the (87) we finally reach the resulting recurrence relation

$$I_{nm} = \frac{I_{nm+1}}{(n + m - 1)(n - m + 1)} - \frac{4(n + 1 - m)(n + m - 2)!}{(2n + 1)(n - m + 2)!}. \tag{93}$$

The recurrent relation (93) together with initial value for I_{nn} , (86), allows to calculate the all necessary matrix elements of the type $\langle P_n^m | P_n^{m-2} \rangle$.

B.2 Matrix elements of the type II

First we shall demonstrate that for $k > 0$ the auxiliary integral J_k equal to zero

$$J_k \equiv \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n \left[\partial_x^{n-k-2} (x^2-1)^{n-k-1} \right] dx = 0. \quad (94)$$

By means of the representations (78) we have

$$(1-x^2) \partial_x^{n+2} (x^2-1)^n \propto P_n^2(x), \quad (95)$$

$$\partial_x^{n-k-2} (x^2-1)^{n-k-1} \propto \sqrt{1-x^2} P_{n-k-1}^1(x). \quad (96)$$

Using now relation (79) the right-hand side of the (96) can be given as the linear combination of $P_{n-k-2}^2(x)$ and $P_{n-k}^2(x)$, therefore the integral J_k can be represented as follows

$$J_k \propto \int_{-1}^{+1} P_n^2(x) (a P_{n-k-2}^2(x) + b P_{n-k}^2(x)) dx, \quad (97)$$

The explicit expressions of the coefficients a and b can be obtained directly from (79). From the representation (97) it is obvious, that $J_k = 0$ (for $k > 0$) due to orthogonality properties of the associated Legendre polynomials.

Let us prove now the following relation

$$\langle P_n^2 | P_{n-k}^0 \rangle = \langle P_n^2 | P_{n-k-2}^0 \rangle = \dots = \langle P_n^2 | P_0^0 \rangle. \quad (98)$$

We shall use the induction method. Obviously, it is enough to show that relation

$$\langle P_n^2 | P_{n-k}^0 \rangle = \langle P_n^2 | P_{n-k-2}^0 \rangle \quad (99)$$

holds for arbitrary $k > 0$. Let us introduce the following notations: $\langle P_n^2 | P_{n-k}^0 \rangle \equiv J_A$ and $\langle P_n^2 | P_{n-k-2}^0 \rangle \equiv J_B$. Using the representation (78) we have

$$J_A = C_k \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n \left[\partial_x^{n-k} (x^2-1)^{n-k} \right] dx, \quad (100)$$

$$J_B = C_{k+2} \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n \left[\partial_x^{n-k-2} (x^2-1)^{n-k-2} \right] dx, \quad (101)$$

where

$$C_k = \left[2^{2n-k} n!(n-k)! \right]^{-1}. \quad (102)$$

Consider (100). We have,

$$\partial_x^{n-k} (x^2-1)^{n-k} = a_1 \partial_x^{n-k-2} (x^2-1)^{n-k-1} + a_2 \partial_x^{n-k-2} (x^2-1)^{n-k-2},$$

where $a_1 = 2(n-k)(2n-2k-1)$, $a_2 = 4(n-k)(n-k-1)$. Hence,

$$\begin{aligned}
 J_A &= C_k a_1 \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n \left[\partial_x^{n-k-2} (x^2-1)^{n-k-1} \right] dx \\
 &\quad + C_k a_2 \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n \left[\partial_x^{n-k-2} (x^2-1)^{n-k-2} \right] dx.
 \end{aligned}
 \tag{103}$$

The first integral in (103) is zero, see (94). Taking into account that $C_k a_2 = C_{k+2}$, one can find immediately, that the second integral in (103) coincides with J_B . Hence, we obtain $J_A = J_B$, which completes the proof of the relation (99); by induction this also proves the relation (98).

Finally, we need the explicit expression for any of the matrix elements in (98). For this purpose we shall obtain the expression for the simplest one $J_0 = \langle P_n^2 | P_0^0 \rangle$. The integral J_0 is quite trivial and can be obtained by sequential use of the relation (8.735) in [35]. However, to keep the representation self consistent we give below a short derivation. Integrating J_0 by parts twice we obtain

$$\begin{aligned}
 J_0 &= C_n \int_{-1}^{+1} (1-x^2) \partial_x^{n+2} (x^2-1)^n dx \\
 &= -4C_n \int_{-1}^{+1} \partial_x^n (x^2-1)^n dx + 2C_n uv \Big|_{-1}^{+1},
 \end{aligned}
 \tag{104}$$

where $u = x$ and $v = \partial_x^n (x^2-1)^n$. The integrand in the second line of (104) is the Legendre polynomial $P_n^0(x)$, therefore the corresponding integral is zero due to orthogonality properties. Hence $J_0 = 2C_n uv \Big|_{-1}^{+1}$ and can be calculated as follows

$$\begin{aligned}
 J_0 &= 2C_n \left[x \partial_x^n (x^2-1)^n \right]_{-1}^{+1} \\
 &= 4C_n \sum_{k=n/2}^n (-1)^{n-k} \frac{n!}{k!(n-k)!} \frac{(2k)!}{(2k-n)!} \\
 &= C_n 2^{n+2} n! = 4.
 \end{aligned}
 \tag{105}$$

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