General formulation of rovibrational kinetic energy operators and matrix elements in internal bond-angle coordinates using factorized Jacobians

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We show how inverse metric tensors and rovibrational kinetic energy operators in terms of internal bond-angle coordinates can be obtained analytically following a factorization of the Jacobian worked out by Frederick and Woywod. The structure of these Jacobians is exploited in two ways: On the one hand, the elements of the metric tensor as well as its determinant all have the form $\sum r^m \sin(\alpha_n) \cos(\beta_o)$. This form can be preserved by working with the adjugate metric tensor that can be obtained without divisions. On the other hand, the adjugate can be obtained with less effort by exploiting the lower triangular structure of the Jacobians. Together with a suitable choice of the wavefunction, we avoid singularities and show how to obtain analytical expressions for the rovibrational kinetic energy matrix elements.

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I. INTRODUCTION

Thermochemical and kinetic properties are often affected strongly by coupled large-amplitude motions (LAMs), e.g. for loosely bonded complexes as molecular clusters[1] and transition states[2]. An exact treatment of the coupled anharmonic degrees of freedom (DOFs) is tedious and has so far been limited to systems of six atoms at most[3]. Potential energy functions for internal DOFs are formulated in internal coordinates that lead in turn to very complicated expressions for the kinetic energy. In many studies, the form of the kinetic energy operator (KEO) is worked out for the case under consideration, yielding expressions that are several pages long[4–6] or the operators are generated by a computer procedure and evaluated numerically[7].

Various researchers have proposed approximations to the coupled LAM problem: Miyoshi incorporated the various torsional minima with their respective harmonic frequencies in a rotational-conformer distribution partition function[8]. Truhlar et al. developed the Internal-Coordinate Multi-Structural Approximation[9]. They showed that coupled anharmonic motion affects thermochemical and kinetic calculations in terms of partition functions and rate constants by one to two orders of magnitude[9,10]. Fernández-Ramos presented an approach to couple two hindered rotations while neglecting coupling to external rotation as well as coupling to further internal modes[11].

The foundations of exact approaches to the coupled LAM problem reach back to the early decades of the last century. Boris Podolsky showed in 1928 how to transform the Schrödinger Equation from Cartesian coordinates to different (e.g. internal) coordinates[12]. The equations are formulated for a single moving particle of reduced mass μ, but the results are valid in general for conservative many-particle systems. For an integration volume element $\mathrm{d}u$, the Schrödinger Equation with eigenenergies E and potential energy V in internal coordinates u_i, u_j with the metric tensor G reads:

$$\sum_{i,j} \frac{1}{\sqrt[4]{\det(\mathsf{G})}} \frac{\partial}{\partial u_i} \left(\sqrt{\det(\mathsf{G})} \left(\mathsf{G}^{-1}\right)_{ij} \frac{\partial}{\partial u_j} \frac{1}{\sqrt[4]{\det(\mathsf{G})}} \psi \right) + \frac{8\pi^2\mu}{h^2}(E-V)\psi = 0 \tag{1}$$

For an integration volume element $\sqrt{\det(\mathsf{G})}\mathrm{d}u$ in turn, the Schrödinger Equation looks different:

$$\sum_{i,j} \frac{1}{\sqrt{\det(\mathsf{G})}} \frac{\partial}{\partial u_i} \left(\sqrt{\det(\mathsf{G})} \left(\mathsf{G}^{-1}\right)_{ij} \frac{\partial}{\partial u_j} \psi \right) + \frac{8\pi^2\mu}{h^2}(E-V)\psi = 0 \tag{2}$$

In this work, we use a factorization worked out by Frederick and Woywod[5] to derive the KEO in eq. 2 and the corresponding matrix elements for the general rovibrational case in internal coordinates. Frederick and Woywod choose the integration volume to be du, thus working with eq. 1; they discuss other forms as well. Their specific choice yields extrapotential terms that are tabulated in their work together with the metric elements for the non-rotating case. The consequences of the choice of the volume element are discussed by Nauts and Chapuisat[13] in 1985. Later, the same authors and Belafhal discussed various forms of extrapotential terms[14]. In this work, we will choose the volume element $\sqrt{\det(\mathsf{G})}\mathrm{d}u$ that does not lead to extrapotential terms. This means that we will work with the form of the Schrödinger equation given in eq. 2.

Frederick and Woywod[5] used factorization to deduce the determinant of the metric respectively the Jacobian as the simple expression:

$$\sqrt{\det(\mathsf{G})} = \pm\det(\mathsf{J}) = \pm\sin\beta\prod_{k=2}^{N} r_k^2 \prod_{l=3}^{N}\sin\phi_l \prod_{i=1}^{N} m_i^3 \tag{3}$$

Here enter besides the radii r only the bond angles ϕ, not the torsional angles, and only one of the Eulerian angles of overall rotation, β. Frederick and Woywod use a mass-weighted metric that involves the product $\prod_{i=1}^{N} m_i^3$ in the Jacobian determinant while Podolsky includes the reduced mass of his one-particle problem in the coefficient of the eigenenergies, thus rendering the metric a purely geometrical entity. Though Frederick and Woywod obtained the determinant very elegantly using their factorization, they formulate KEOs using an older method from Wilson et al.[15], restricting the approach to the non-rotating case. The result for the determinant was reported at the same time by Makarewicz and Skalozub[16] restricted to internal motion; later[17] rovibrational coupling was taken into account.

As stated by Frederick and Woywod[5], "one can take advantage of the general properties of the Jacobian determinant to produce simpler expressions that generalize to any molecular system." In this study, we will further explore general properties of the Jacobian matrices, that is their triangular form (when written in 3 × 3 and 6 × 6 blocks, respectively) and the algebraic structure of the terms of the Jacobian matrix elements. The triangular form eases inversion. We further use fraction-free adjugates instead of inverse matrices in order to preserve the algebraic structure ($\sum r^m \sin(\alpha_n)\cos(\beta_o)$, cf. eq. 18) of the entries of the matrices.

II. FACTORIZATION OF THE JACOBIAN: IDEA AND APPLICABILITY

To show the applicability of the factorization approach worked out by Frederick and Woywod[5] for the determination of not only the determinant but also of the inverse of the metric and of KEOs, we briefly summarize the idea of factorizing the Jacobian: The metric tensor needed in the KEO (cf. eqs. 1, 2) can be written for internal bond-angle coordinates embedded in euclidean Cartesian space as:

$$\mathsf{G} = \mathsf{J}^{\mathrm{T}} \cdot \mathsf{J} \tag{4}$$

We start from the Cartesian space-fixed coordinates $\boldsymbol{x}$ to construct Jacobi vectors $\boldsymbol{\delta}$ representing the difference between the positions of two subsequent atoms:

$$\boldsymbol{\delta}_i = \boldsymbol{x}_i - \boldsymbol{x}_{i-1} \tag{5}$$

A primed molecule-fixed system can be constructed from the unprimed space-fixed system with a shift by the center-of-mass position $\boldsymbol{r}_{\mathrm{com}}$ and external rotation by the Euler rotation matrix S_{r}:

$$\boldsymbol{x}_i = \boldsymbol{r}_{\mathrm{com}} + \mathsf{S}_{\mathrm{r}} \cdot \boldsymbol{x}_i^{'} \tag{6}$$

The primed molecule-fixed system is rotated in such a way that its $x^{'}$-axis passes through the first two atoms and the $y^{'}$-axis is chosen to lie in the plane in which the first three atoms lie. The center-of-mass position $\boldsymbol{r}_{\mathrm{com}}$ is subtracted from all atom positions which removes coupling to translational motion that can usually be described very well with a quasi-classical expression. If we construct primed molecule-fixed Jacobi vectors

$$\boldsymbol{\delta}_i^{'} = \boldsymbol{x}_i^{'} - \boldsymbol{x}_{i-1}^{'} \tag{7}$$

they are not affected by the shift of the origin except the first one that reads $\boldsymbol{\delta}_1^{'} = \boldsymbol{x}_1^{'} - \boldsymbol{x}_0^{'} = 0 - (-\boldsymbol{r}_{\mathrm{com}}) = \boldsymbol{r}_{\mathrm{com}}$. The Euler rotation matrix S_{r} reads:

$$\mathsf{S}_{\mathrm{r}}(\alpha, \beta, \gamma) = \begin{pmatrix} \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & -\cos\alpha\sin\gamma - \sin\alpha\cos\beta\cos\gamma & \sin\alpha\sin\beta \\ \sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma & -\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma & -\cos\alpha\sin\beta \\ \sin\beta\sin\gamma & \sin\beta\cos\gamma & \cos\beta \end{pmatrix} \tag{8}$$

This yields the following relationship for the Jacobi vectors:

$$\boldsymbol{\delta}_i = \mathsf{S}_{\mathrm{r}}(\boldsymbol{\theta}_{\mathrm{e}}) \cdot \boldsymbol{\delta}_i^{'} \tag{9}$$

Here, the three Euler angles of external rotation are collected in $\boldsymbol{\theta}_\mathrm{e} = (\alpha, \beta, \gamma)$.

The first coordinate transformation from $\{\boldsymbol{x}_i\}$ to $\{\boldsymbol{r}_\mathrm{com}|\boldsymbol{\delta}_i\}$ according to eq. 5 is collected in the Jacobian matrix J_1 (that we never need; instead we report the inverse J_1^{-1} directly), while the second transformation from $\{\boldsymbol{r}_\mathrm{com}|\boldsymbol{\delta}_i\}$ to internal coordinates $\{\boldsymbol{r}_\mathrm{com}|\boldsymbol{\theta}_\mathrm{e}|\boldsymbol{u}_i\}$ collected in J_2 contains the rotation mentioned above (from $\boldsymbol{\delta}_i$ to $\boldsymbol{\delta}_i^{'}$, eq. 9) as well as the transformation of the Jacobi-vectors $\boldsymbol{\delta}_i^{'}$ to internal coordinates $\boldsymbol{u}_j$.

The coordinates are collected in vectors of three elements, starting with the Euler angles $\boldsymbol{\theta}_\mathbf{e} = (\alpha, \beta, \gamma)$ and the first three internal coordinates $\boldsymbol{u}_{2,3} = (r_2, r_3, \phi_3)$. All further internal coordinate vectors $\boldsymbol{u}_i$, $i \geq 4$, are composed of a distance r_i, a bending angle ϕ_i and a dihedral angle τ_i. The distance r_i is measured between the atom i and the atom to which it is related ($i-1$ for sequential connectivity); similarly, ϕ_i would be the bending angle between atoms i, $i-1$ and $i-2$ for sequential connectivity and τ_i the torsional, i.e. dihedral angle between atoms i, $i-1$, $i-2$ and $i-3$ if all atoms are sequentially connected. If the structure is branched, the atoms that i is related to have indices lower than just $i-1, 2, 3$ as outlined in section II A. The "derivatives" of the Jacobi-vectors with respect to (wrt.) Eulerian or internal coordinate vectors are an abbreviation for the 3×3 matrix where row m and column n contain the derivative of Jacobi-vector element m wrt. coordinate n:

$$\frac{\partial \boldsymbol{\delta}}{\partial \boldsymbol{u}} := \frac{\partial \delta_m}{\partial u_n} = \begin{pmatrix} \frac{\partial \delta_{i,x}}{\partial u_{j,r}} & \frac{\partial \delta_{i,x}}{\partial u_{j,\phi}} & \frac{\partial \delta_{i,x}}{\partial u_{j,\tau}} \\ \frac{\partial \delta_{i,y}}{\partial u_{j,r}} & \frac{\partial \delta_{i,y}}{\partial u_{j,\phi}} & \frac{\partial \delta_{i,y}}{\partial u_{j,\tau}} \\ \frac{\partial \delta_{i,z}}{\partial u_{j,r}} & \frac{\partial \delta_{i,z}}{\partial u_{j,\phi}} & \frac{\partial \delta_{i,z}}{\partial u_{j,\tau}} \end{pmatrix} \tag{10}$$

with the displayed 3×3 matrix being a showcase for an internal coordinate $\boldsymbol{u}_{i \geq 4}$. The second Jacobian therefore reads in terms of 3×3 blocks:

$$\mathsf{J}_2 = \frac{\partial \boldsymbol{\delta}_i}{\partial \boldsymbol{u}_j} = \begin{pmatrix} \mathsf{I} & 0 & 0 & 0 & 0 & \dots \\ 0 & \frac{\partial \boldsymbol{\delta}_2}{\partial \boldsymbol{\theta}_\mathrm{e}} & \frac{\partial \boldsymbol{\delta}_2}{\partial \boldsymbol{u}_{2,3}} & 0 & 0 & \dots \\ 0 & \frac{\partial \boldsymbol{\delta}_3}{\partial \boldsymbol{\theta}_\mathrm{e}} & \frac{\partial \boldsymbol{\delta}_3}{\partial \boldsymbol{u}_{2,3}} & 0 & 0 & \dots \\ 0 & \frac{\partial \boldsymbol{\delta}_4}{\partial \boldsymbol{\theta}_\mathrm{e}} & \frac{\partial \boldsymbol{\delta}_4}{\partial \boldsymbol{u}_{2,3}} & \frac{\partial \boldsymbol{\delta}_4}{\partial \boldsymbol{u}_4} & 0 & \dots \\ 0 & \frac{\partial \boldsymbol{\delta}_5}{\partial \boldsymbol{\theta}_\mathrm{e}} & \frac{\partial \boldsymbol{\delta}_5}{\partial \boldsymbol{u}_{2,3}} & \frac{\partial \boldsymbol{\delta}_5}{\partial \boldsymbol{u}_4} & \frac{\partial \boldsymbol{\delta}_5}{\partial \boldsymbol{u}_5} & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \tag{11}$$

J_2 is a lower triangular matrix when the second and third column are collected into one. We therefore group the matrix in 3×3-blocks except in the second and third column where we group the elements in 3×6 and 6×6 blocks. The overall Jacobian to be used to formulate the metric tensor therefore reads

$$\mathsf{J} = \sqrt{M_{ij}} \frac{\partial x_i}{\partial u_j} = \sqrt{M_{ij}} \sum_k \frac{\partial x_i}{\partial \delta_k} \cdot \frac{\partial \delta_k}{\partial u_j} = \mathsf{M}^{\frac{1}{2}} \cdot \mathsf{J}_1 \cdot \mathsf{J}_2 \tag{12}$$

where M is a diagonal matrix containing the respective atomic masses.

A. Chains and branches

The first Jacobian J_1 strongly depends on the "connectivity" of the molecule, i.e. the way in which the atom positions are defined wrt. previous atoms. J_1 is composed of 3×3 blocks of plus and minus unit matrices I and zeros. For special cases as e.g. sequential connectivity one can give general expressions for the inverse of J_1. For sequential connectivity, i.e. each atom is related to the one before it (a "chain"), we arrive at:

$$\mathsf{J}_1^{-1} = \frac{\partial \delta_i}{\partial x_j} = \begin{pmatrix} \frac{m_1}{m_{\mathrm{tot}}} & 0 & 0 & \frac{m_2}{M} & \ldots & \ldots & \ldots & \frac{m_N}{m_{\mathrm{tot}}} & 0 & 0 \\ 0 & \frac{m_1}{m_{\mathrm{tot}}} & 0 & 0 & \ldots & \ldots & \ldots & 0 & \frac{m_N}{m_{\mathrm{tot}}} & 0 \\ 0 & 0 & \frac{m_1}{m_{\mathrm{tot}}} & 0 & \ldots & \ldots & \ldots & 0 & 0 & \frac{m_N}{m_{\mathrm{tot}}} \\ -1 & 0 & 0 & 1 & \ldots & \ldots & \ldots & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & \ldots & \ldots & \ldots & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & \ldots & \ldots & \ldots & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & \ldots & \ldots & \ldots & 0 & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & 1 & 0 & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & 0 & 1 & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & 0 & 0 & 1 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & -1 & 0 & 0 & 1 \end{pmatrix} \tag{13}$$

Here, the symbol $m_{\mathrm{tot}} = \sum_{i=1}^{N} m_i$ is the total mass of the system of N atoms. The first three rows result from the derivative of the origin (in the center of nuclear mass) $\boldsymbol{r}_{\mathrm{com}}$ wrt. the Cartesian coordinates atom $1, 2, \cdots, N$. The second three rows represent the change of $\boldsymbol{\delta}_2$ with x_1, y_1, z_1 and with x_2, y_2, z_2 and so on. If all atoms are sequentially connected, there will be a band structure below the first three rows. The product $\mathsf{J}_1^{-1} \cdot \mathrm{adj}(\mathsf{M}) \cdot \mathsf{J}_1^{-1,\mathrm{T}}$ that we need later (eq. 14) is then made up of four blocks (cf. eq. 25 for the adjugate of M): On the upper left, there is a 3×3 diagonal matrix containing $\det(\mathsf{M}) = \prod m_i^3$. The lower left $(3N-3)\times 3$ and upper right $3\times(3N-3)$ blocks are zero because in a field-free environment intramolecular motion is decoupled from translational motion. The lower right $(3N-3)\times(3N-3)$ matrix is a Toeplitz band matrix containing $\frac{\det(\mathsf{M})}{m_i}+\frac{\det(\mathsf{M})}{m_{i-1}}$ on the major diagonal and $-\frac{\det(\mathsf{M})}{m_{i-1}}$ on the minor diagonals.

For branched structures, more than one atoms are linked to a precedent atom i. This means that a later atom k is not defined wrt. $j=k-1$ but wrt. e.g. the previous atom i. In the case of a methyl group one would probably relate the three hydrogens j,k,l to the carbon i. Then, the left neighbors to the diagonal 3×3 blocks j,k,l that are on the minor diagonal in the same rows j,k,l, respectively, will not contain the $-\mathsf{I}$ block, but these rows will show this $-\mathsf{I}$ block all in the same column i because all atoms j,k,l have defined their Jacobi vectors by subtracting the position of atom i. The only effect on the second Jacobian are the vanishing off-diagonal entries $\frac{\partial\boldsymbol{\delta}_{k,l}}{\partial\boldsymbol{u}_{j,k}}$. These zero matrices on the lower left come from atoms k,l not being affected by rotations of all previously defined atoms, e.g. j,k, but only by those of its branch, in our example atom i. Kinetically, there is no kind of coupling between branches. Wilson, Decius and Cross state that if coordinates happen to be orthogonal to each other, their common G-matrix element will be zero and that this will clearly be the case if the two coordinates do not share a common atom[15]. The atoms of different branches could even occupy the same position; hardness of the atoms arises only from potential energy terms.

III. INVERSION OF THE METRIC TENSOR

The inverse metric tensor needed in eqs. 1, 2 can be factorized according to eq. 12 as

$$\mathsf{G}^{-1}=\mathsf{J}^{-1}\mathsf{J}^{-1,\mathrm{T}}=\mathsf{J}_2^{-1}\mathsf{J}_1^{-1}\mathsf{M}^{-1}\mathsf{J}_1^{-1,\mathrm{T}}\mathsf{J}_2^{-1,\mathrm{T}} \tag{14}$$

The inverse of J_1 has been already sketched in section II A. J_1^{-1} can be directly written down similar to eq. 13.

The inverse can generally be written using the adjugate matrix, not to be confused with the adjoint matrix:

$$\mathrm{adj}\,(\mathsf{G})=\det\,(\mathsf{G})\cdot\mathsf{G}^{-1} \tag{15}$$

The determinant is already known generally from Frederick and Woywod[5] (cf. eq. 3) for arbitrary sequentially-connected and branched molecules. For J_1, the determinant always amounts to ±1, so the adjugate is directly known as well. One benefit of working with the adjugate instead of the inverse matrix is that the adjugate can be computed generally from division-free algorithms[18,19]. This preserves the structure of the elements of the metric tensor. All elements of the metric tensor are of the following form (as will be shown in section III B):

$$
\begin{aligned}
G_{ij} &= \sum_k c_k \prod_{l=2}^{N} r_l^{m_{l,k}} \prod_{p=3}^{2N-1} \sin(n_{p,k}\tau_p)\cos(o_{p,k}\tau_p) && (16)\\
&= \sum_k c_k \exp\left(\sum_{l=2}^{N} m_{l,k}\ln(r_l) + \sum_{p=3}^{2N-1} \mathrm{i}\widetilde{o}_{p,k}\tau_p\right) && (17)\\
&= \sum_k c_k \exp\left(\boldsymbol{o}_k \cdot \boldsymbol{q}\right) && (18)
\end{aligned}
$$

The trigonometric functions are expressed as complex exponentials using the imaginary unit i. The radial coordinates r and angular coordinates τ are collected in the coordinate vector $\boldsymbol{q} = (\ln(r_l)|\mathrm{i}\cdot\tau_p)^{\mathrm{T}}$ and the corresponding powers $m_{l,k}$ and orders $\widetilde{o}_{p,k}$ are collected in the order vector $\boldsymbol{o}_k = (m_{l,k}|\widetilde{o}_{p,k})$. For each order combination k there exists a coefficient c_k to form the term k in the sum. The form of the elements G_{ij} is preserved during addition and multiplication (and even when taking the derivative or integrating). Because the adjugate can be obtained solely using multiplications and additions, the elements of the adjugate metric tensor must have the same structure as the elements of the metric tensor itself — the form presented in eq. 18. This point will be shown in detail in subsection III B. Addition and multiplication of the terms in eq. 18 is a task of simple bookkeeping: If terms share the same order, the coefficients c_k are added; if not, they contribute separate terms to the sum. Multiplication leads to addition of the order vectors and multiplication of the coefficients c_k. To obtain the adjugate of the metric tensor one can thus use a simple bookkeeping script instead of having to use a sophisticated computer algebra software. The inverse is then simply obtained according to eq. 15 by dividing each element of the adjugate by the generally known determinant from eq. 3.

The computation of the adjugate Jacobian matrix using the factorization of Frederick and Woywod[5] is particularly simple due to the lower triangular structure of the Jacobians when written in 3 × 3 and 6 × 6 blocks, respectively. Before we show the inversion of J_2 using its specific structure, we further motivate the use of the adjugate matrix from the formulation of the matrix elements.

A. Formulation of the kinetic energy matrix elements

The matrix elements for the kinetic energy follow from the KEO:

$$T_{ab} = \langle\psi_a|\hat{T}|\psi_b\rangle = \int \mathrm{d}\tau \psi_a^* \hat{T} \psi_b \tag{19}$$

We choose the volume element to be

$$\mathrm{d}\tau = \det(\mathsf{J})\mathrm{d}u \tag{20}$$

Then according to Podolsky[12] the KEO reads

$$\hat{T} = \frac{-\hbar^2}{2\mu \cdot \det(\mathsf{J})} \sum_{i,j} \frac{\partial}{\partial u_i} \det(\mathsf{J}) \left(\mathsf{G}^{-1}\right)_{ij} \frac{\partial}{\partial u_j} \tag{21}$$

In this equation for a single moving particle, the reduced mass is factored out, so the inverse metric is a purely geometrical expression. Frederick and Woywod[5] use a mass weighted metric which is reflected in eq. 12. Therefore, in our equations no reduced mass factor μ appears. Furthermore, the determinant of J from the volume element cancels with the coefficient of the KEO, so the matrix element reads:

$$\begin{aligned} T_{ab} &= \frac{-\hbar^2}{2} \int \mathrm{d}u\, \psi_a^* \sum_{i,j} \frac{\partial}{\partial u_i} \det(\mathsf{J}) \left(\mathsf{G}^{-1}\right)_{ij} \frac{\partial}{\partial u_j} \psi_b \\ &= \frac{-\hbar^2}{2} \int \mathrm{d}u\, \psi_a^* \sum_{i,j} \frac{\partial}{\partial u_i} \det(\mathsf{J})^{-1} \mathrm{adj}\left(\mathsf{G}\right)_{ij} \frac{\partial}{\partial u_j} \psi_b \end{aligned} \tag{22}$$

We can split up the adjugate computation of the metric tensor using the straightforward factorization proposed by Frederick and Woywod[5] implied by eq. 4 and eq. 12:

$$\mathrm{adj}\left(\mathsf{G}\right) = \det(\mathsf{G}) \cdot \mathsf{G}^{-1} = \det(\mathsf{G}) \cdot \mathsf{J}^{-1}(\mathsf{J}^{-1})^{\mathrm{T}}$$

$$\mathrm{adj}\left(\mathsf{G}\right) = \det(\mathsf{G}) \cdot \mathsf{J}_2^{-1}\mathsf{J}_1^{-1}\mathsf{M}^{-1}(\mathsf{J}_1^{-1})^{\mathrm{T}}(\mathsf{J}_2^{-1})^{\mathrm{T}} \tag{23}$$

$$\mathrm{adj}\left(\mathsf{G}\right) = \mathrm{adj}(\mathsf{J}_2)\mathrm{adj}(\mathsf{J}_1)\mathrm{adj}(\mathsf{M})\mathrm{adj}(\mathsf{J}_1)^{\mathrm{T}}\mathrm{adj}(\mathsf{J}_2)^{\mathrm{T}} \tag{24}$$

The adjugates of J_1 and M are easily computed: As stated above, since the determinant of J_1 amounts to ± 1, we can insert eq. 13 for its adjugate. The adjugate of M results from

$$\mathrm{adj}(\mathsf{M}) = \det(\mathsf{M}) \cdot \mathsf{M}^{-1} \tag{25}$$

M^{-1} is a diagonal matrix obtained in a straightforward way from M. It simply carries the reciprocal of the respective atomic masses. The adjugate of J_2 can be computed making use of its lower triangular form when written in 3×3 blocks.

B. Structure of the Jacobian of the second coordinate transformation

The computation of the adjugate metric tensor, especially of the remaining part J_2 of the Jacobian, is facilitated by two structural properties: On the one hand, all elements are of the form of eq. 18. On the other hand, J_2 is a lower triangular matrix.

The first point is evident from the following: The space-fixed Jacobi vectors $\boldsymbol{\delta}_i$ are obtained from the Cartesian coordinates $\boldsymbol{x}_i$ just by subtraction via the first coordinate transformation in J_1 that clearly preserves the form of eq. 18 (since subtraction is multiplication by -1 and addition). Rotated and translated molecule-fixed Jacobi vectors $\boldsymbol{\delta}_i^{'}$ are obtained by multiplication by the Euler rotation matrix S_r according to eq. 9. From eq. 8 one can easily see that S_r is made up solely of eq. 18-elements and their form is preserved under multiplication by matrices and vectors that as well consist of eq. 18-elements since matrix multiplication is made up of additions and multiplications. According to Frederick and Woywod[5], the Jacobi vectors $\boldsymbol{\delta}_i^{'}(\boldsymbol{u})$ can be expressed in terms of internal coordinates, using rotation matrices around $\boldsymbol{x}^{'}$ and $\boldsymbol{z}^{'}$, in the following way:

$$\boldsymbol{\delta}_2^{'} = r_2\boldsymbol{e}_{x'} \tag{26}$$

$$\boldsymbol{\delta}'_3 = -r_3\mathsf{R}_{z'}(\phi_3)\cdot\boldsymbol{e}_{x'} \tag{27}$$

$$\boldsymbol{\delta}'_4 = r_4\mathsf{R}_{z'}(\phi_3)\mathsf{R}_{x'}(\tau_4)\mathsf{R}_{z'}(\phi_4)\cdot\boldsymbol{e}_{x'} \tag{28}$$

The rotation matrices $\mathsf{R}_{z'}(\phi_i)$ and $\mathsf{R}_{x'}(\tau_i)$ rotate the coordinate system so that the $x^{'}$-axis points in direction of the bond that carries atom i. The orientation, though, can change; e.g. in a sequentially connected molecule, the orientation of the $x^{'}$-axis is alternant. The R-matrices are given by Frederick and Woywod[5] as

$$\mathsf{R}_{z'}(\phi_i) = \begin{pmatrix} \cos(\phi_i) & \sin(\phi_i) & 0 \\ -\sin(\phi_i) & \cos(\phi_i) & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{29}$$

$$\mathsf{R}_{x'}(\tau_i) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\tau_i) & \sin(\tau_i) \\ 0 & -\sin(\tau_i) & \cos(\tau_i) \end{pmatrix} \tag{30}$$

These matrices are composed of eq. 18-elements as well. The product of the rotation matrices can be collected in an overall rotation matrix S_v

$$\mathsf{S}_\mathrm{v}(\phi_3...\phi_k, \tau_4...\tau_k) := \mathsf{R}_{z'}(\phi_3) \cdot \prod_{i=4}^{k} \mathsf{R}_{z'}(\phi_i) \cdot \mathsf{R}_{x'}(\tau_i) \tag{31}$$

Then one can express the ith Jacobi vector as

$$\boldsymbol{\delta}_i^{'} = \boldsymbol{x}_i^{'} - \boldsymbol{x}_{i-1}^{'} = (-1)^m r_i^n \mathsf{S}_\mathrm{v}(\phi_3...\phi_i, \tau_4...\tau_i) \cdot \boldsymbol{e}_{x'} \tag{32}$$

while the index m here corresponds to the different orientations of the $\boldsymbol{x}^{'}$-axis. Multiplication and addition preserves the structure of the terms in eq. 18; so $\boldsymbol{\delta}_i^{'}$ and $\boldsymbol{\delta}_i$ from eqns. 32 and 9 must have the structure of eq. 18 as well.

Now one can expand the "derivatives" in eq. 11 according to the product rule to be $\frac{\partial}{\partial \boldsymbol{\theta}_\mathrm{e}} \mathsf{S}_\mathrm{r} \cdot \boldsymbol{\delta}_i^{'}$ for columns 4 to 6 and to be $\mathsf{S}_\mathrm{r} \cdot \frac{\partial}{\partial u_j} \boldsymbol{\delta}_i^{'}$ for further columns, the "derivatives" wrt. vectors again signifying abbreviations for 3×3 matrices explained in the context of eq. 11. With this, we can write the second Jacobian matrix starting from eq. 11 as:

$$\mathsf{J}_2 = \begin{pmatrix} \mathsf{I} & 0 & 0 & 0 & ... \\ 0 & \frac{\partial \boldsymbol{\delta}_2}{\partial \boldsymbol{\theta}_\mathrm{e}} & \mathsf{S}_\mathrm{r} \cdot \frac{\partial}{\partial \boldsymbol{u}_{2,3}} \boldsymbol{\delta}_2^{'} & 0 & ... \\ 0 & \frac{\partial \boldsymbol{\delta}_3}{\partial \boldsymbol{\theta}_\mathrm{e}} & \mathsf{S}_\mathrm{r} \cdot \frac{\partial}{\partial \boldsymbol{u}_{2,3}} \boldsymbol{\delta}_3^{'} & 0 & ... \\ 0 & \frac{\partial \boldsymbol{\delta}_4}{\partial \boldsymbol{\theta}_\mathrm{e}} & \mathsf{S}_\mathrm{r} \cdot \frac{\partial}{\partial \boldsymbol{u}_{2,3}} \boldsymbol{\delta}_4^{'} & \mathsf{S}_\mathrm{r} \cdot \frac{\partial}{\partial \boldsymbol{u}_4} \boldsymbol{\delta}_4^{'} & ... \\ ... & ... & ... & ... & ... \end{pmatrix} \tag{33}$$

Since the derivative preserves the structure of the terms in eq. 18 as well, all elements of J_2 must have the structure of eq. 18 as well, *q.e.d.*.

C. Triangular (block) matrix adjugate

Since the determinant factors for a triangular (block) matrix, we can write for the adjugate of the block matrix:

$$\mathrm{adj}\left(\begin{bmatrix} \mathsf{A} & 0 \\ \mathsf{C} & \mathsf{D} \end{bmatrix}\right) = \det\left(\begin{bmatrix} \mathsf{A} & 0 \\ \mathsf{C} & \mathsf{D} \end{bmatrix}\right) \cdot \begin{bmatrix} \mathsf{A}^{-1} & 0 \\ -\mathsf{D}^{-1} \cdot \mathsf{C} \cdot \mathsf{A}^{-1} & \mathsf{D}^{-1} \end{bmatrix} \tag{34}$$

$$= \det(\mathsf{A}) \cdot \det(\mathsf{D}) \cdot \begin{bmatrix} \mathsf{A}^{-1} & 0 \\ -\mathsf{D}^{-1} \cdot \mathsf{C} \cdot \mathsf{A}^{-1} & \mathsf{D}^{-1} \end{bmatrix} \tag{35}$$

$$= \begin{bmatrix} \det(\mathsf{D}) \cdot \mathrm{adj}(\mathsf{A}) & 0 \\ -\mathrm{adj}(\mathsf{D}) \cdot \mathsf{C} \cdot \mathrm{adj}(\mathsf{A}) & \det(\mathsf{A}) \cdot \mathrm{adj}(\mathsf{D}) \end{bmatrix} \tag{36}$$

The blocks A and D need to be square matrices, C and $\mathsf{0}$ can be rectangular. Applied to J_2 for a larger part of the molecule (at atom i), the matrix would read:

$$\mathsf{J}_{2,i} = \begin{bmatrix} \mathsf{J}_{2,i-1} & \mathsf{0} \\ \mathsf{C}_i & \sigma_i \end{bmatrix} \tag{37}$$

and its adjugate:

$$\mathrm{adj}(\mathsf{J}_{2,i}) = \begin{bmatrix} \det(\sigma_i) \cdot \mathrm{adj}(\mathsf{J}_{2,i-1}) & \mathsf{0} \\ -\mathrm{adj}(\sigma_i) \cdot \mathsf{C}_i \cdot \mathrm{adj}(\mathsf{J}_{2,i-1}) & \det(\mathsf{J}_{2,i-1}) \cdot \mathrm{adj}(\sigma_i) \end{bmatrix} \tag{38}$$

The rectangular matrix C_i can be read by choosing the appropriate row from the matrix J_2 in eq. 33. Frederick and Woywod[5] report the matrix σ_i to be:

$$\sigma_i = (-1)^m \mathsf{S}_\mathrm{r} \cdot \mathsf{S}_\mathrm{v} \cdot \begin{pmatrix} \cos(\phi_i) & -r_i \sin(\phi_i) & 0 \\ -\cos(\tau_i)\sin(\phi_i) & -r_i \cos(\tau_i)\cos(\phi_i) & r_i \sin(\tau_i)\sin(\phi_i) \\ \sin(\tau_i)\sin(\phi_i) & r_i \sin(\tau_i)\cos(\phi_i) & r_i \cos(\tau_i)\sin(\phi_i) \end{pmatrix} \tag{39}$$

We compute the adjugate of σ_i as:

$$\begin{aligned} \mathrm{adj}(\sigma_i) &= r_i^2 \sin(\phi_i) \cdot {\sigma_\mathrm{i}}^{-1} \\ &= \begin{pmatrix} r_i^2 \sin(\phi_i)\cos(\phi_i) & -r_i^2 \sin^2(\phi_i)\cos(\tau_i) & r_i^2 \sin^2(\phi_i)\sin(\tau i) \\ -r_i \sin^2(\phi_i) & -r_i \sin(\phi_i)\cos(\phi_i)\cos(\tau_i) & r_i \sin(\phi_i)\cos(\phi_i)\sin(\tau_i) \\ 0 & r_i \sin(\tau_i) & r_i \cos(\tau_i) \end{pmatrix} \cdot \\ &\cdot \mathsf{S}_\mathrm{v}^\mathrm{T} \cdot \mathsf{S}_\mathrm{r}^\mathrm{T} \cdot (-1)^m \end{aligned}$$

The rotation matrices S contribute a factor of 1 to the determinant and their inverse is simply their transpose. The determinant of σ_i is known from the work of Frederick and Woywod[5] as

$$\det(\sigma_i) = \pm r_i^2 \sin(\phi_i) \tag{40}$$

It is worth noting that the structure of the elements of σ and of $\mathrm{adj}(\sigma)$ is of the form of eq. 18. The adjugate of the submatrix $\mathsf{J}_{2,i-1}$ can be obtained in the same way as the adjugate of $\mathsf{J}_{2,i}$ itself. The determinant of the submatrix $\mathsf{J}_{2,i-1}$ is already known from the result of Frederick and Woywod[5] as:

$$\det(\mathsf{J}_{2,i-1}) = \pm \sin(\beta) \prod_{n=2}^{i-1} r_n^2 \prod_{l=3}^{i-1} \sin(\phi_l) \tag{41}$$

We already have computed the adjugate for the 3-atomic system (cf. appendix A). All elements of that matrix are of the form of eq. 18. Eq. 38 therefore allows us to derive the adjugate for a N-atomic molecule subsequently starting with the 3-atomic subsystem. Because matrix multiplication preserves the form of eq. 18-elements, all elements of adj J_2 must be of the form of eq. 18.

The KEO reads, when the adjugate metric from eq. 24 is inserted into eq. 21:

$$\hat{T} = \frac{-\hbar^2}{2} \det(\mathsf{J})^{-1} \sum_{i,j} \frac{\partial}{\partial u_i} \det(\mathsf{J})^{-1} \mathrm{adj}(\mathsf{J}_2)\mathrm{adj}(\mathsf{J}_1)\mathrm{adj}(\mathsf{M})\mathrm{adj}(\mathsf{J}_1)^{\mathrm{T}}\mathrm{adj}(\mathsf{J}_2)^{\mathrm{T}} \frac{\partial}{\partial u_j} \tag{42}$$

$$= \frac{-\hbar^2}{2} \det(\mathsf{J})^{-1} \sum_{i,j} \frac{\partial}{\partial u_i} \det(\mathsf{J})^{-1} \sum_{k} c_k \exp\left(\boldsymbol{o}_k \cdot \boldsymbol{q}\right) \frac{\partial}{\partial u_j} \tag{43}$$

The form of the adjugate metric tensor from eq. 18 will be preserved under differentiation, integration, multiplication and addition as long as no division is required. However, equation 22 shows that one division by the determinant is needed in the computation of matrix elements. In the following section, we will show that such fractions are not allowed in the integrals of the matrix elements so that valid wavefunctions need to be designed in a way that the division by the determinant is cancelled.

IV. VALID WAVEFUNCTIONS

Matrix elements using the KEO from eq. 43 in eqs. 19 and 20 read:

$$T_{ab} = \frac{-\hbar^2}{2} \int \mathrm{d}u \, \psi_a^* \sum_{i,j,k} \frac{\partial}{\partial u_i} \det(\mathsf{J})^{-1} c_k \exp\left(\boldsymbol{o}_k \cdot \boldsymbol{q}\right) \frac{\partial}{\partial u_j} \psi_b \tag{44}$$

It is desirable to formulate the wavefunction as well in the form of eq. 18

$$\psi_{\text{ansatz}} := \sum_{\kappa} c_\kappa \exp\left(\boldsymbol{o}_\kappa \cdot \boldsymbol{q}\right) \tag{45}$$

because the form remains unchanged upon differentiation and integration. Nevertheless, there are physical restrictions to such wavefunctions: Physically acceptable wavefunctions ψ_{phys} need to be designed in a way that the integrals within the matrix elements do not diverge. Convergence of the integrals for the radii r^m going to ∞ can be achieved by exponential damping terms in the wavefunction. Divergence for the radii approaching 0 or for the angles at 0 or π arises from integration over 1/r or 1/sin. The wavefunction is thus to be chosen such that no terms 1/r or 1/sin arise in the integrals. This can be achieved e.g. by discarding all orders of 0 and 1 from the radial wavefunction or equivalently by introducing a radial correction factor:

$$f_{\mathrm{r}} := \prod_{l=2}^{N} r_l^2 = \exp\left(\sum_{l=2}^{N} 2\ln\left(r_l\right)\right) \tag{46}$$

The angular part of the wavefunction has to ensure that $1/\sin(\phi)$ always vanishes, a factor that results as well from the division by the determinant of the Jacobian. This can be achieved by multiplying the wavefunction by $\sin^2\phi$. Then as well in the terms where the wavefunction is differentiated once wrt. ϕ one $\sin\phi$ is still left to cancel with the determinant of the Jacobian. This ensures the wavefunction will be single-valued and differentiable (without break and cusp) at the poles $\phi = 0, \pi$. Thereby, the wavefunction is artificially forced to take a value of zero at the poles. This behavior is a shortcoming of polyspherical coordinates in general; because the determinant of the Jacobian for polyspherical internal coordinates always will take the form of eq. 3, the wavefunction never can have a nonzero value at the poles. According to Bramley et al. the multi-valuedness of the wavefunction would not affect the results, because the integration volume near the poles goes to zero anyway[4]. Nevertheless, taking the limit of a product for one factor approaching 0 and one approaching ∞ may lead to any value, not necessarily to 0. In our formulation in eq. 22 one can see that the $\det(\mathsf{J})$-weighting of the integration volume cancels with a part of the KEO – so the integrand may approach different limits for different dihedral angles as the bending angle approaches 0 or π. This unphysical behavior is prevented by the proposed multiplication by $\sin^2\phi$. One can introduce an angular correction factor according to:

$$f_{\phi} := \prod_{p=3}^{N} \sin^2\left(\phi_p\right) = \prod_{p=3}^{N}\left(\frac{1}{2} - \frac{1}{4}\exp\left(2\mathrm{i}\phi_p\right) - \frac{1}{4}\exp\left(-2\mathrm{i}\phi_p\right)\right) \tag{47}$$

This product can be multiplied out and then be written in the form of eq. 18.

Fourier functions are commonly used to fit torsional potentials, e.g. in the python package TAMkin[20] for the treatment of one-dimensional internal rotations. It is therefore natural to use the form of eq. 18 for the angular potential energy functions. The radial dependence of the potential energy can be locally expanded in a power series in r. Then, one has to assure the correct behavior near 0 and ∞. Since the potential energy function will be multiplied two times by basis functions containing r to powers of at least two, as mentioned above and additionally by a factor of r^2 arising from the volume element (cf. eq. 20), one can use radial potential energy functions with exponents from 0 down to -6 without producing divergent integrals.

Multiplication of the wave functions by exponential damping terms $\exp\left(-ar^{y}\right)$ will both allow r^{-m} terms in the potential energy function to rise to ∞ when $r \to 0$, making the nuclei repel each other, and dampen all terms when $r \to \infty$. Different dissociation limits for different $r_l \to \infty$ are possible in V while potential energy matrix elements V_{ab} remain convergent. One would therefore multibly by a damping factor f_{damp} defined as:

$$f_{\text{damp}} := \prod_{l=2}^{N} \exp\left(-ar_l^{y}\right) \tag{48}$$

The physically acceptable wavefunction ψ_{phys} can then be written as:

$$\psi_{\text{phys}} := f_{\text{r}} f_{\phi} f_{\text{damp}} \psi_{\text{ansatz}} = \sum_{\kappa} \prod_{l=2}^{N} r_l^2 \exp\left(-ar_l^{y}\right) \prod_{p=3}^{N} \sin^2\left(\phi_p\right) c_\kappa \exp\left(\boldsymbol{o}_\kappa \cdot \boldsymbol{q}\right) \tag{49}$$

Resulting matrix elements will be of the form (where the coefficients c_k and the oreder vector $\boldsymbol{o}_k$ is altered for the multiplication by f_ϕ and f_{damp}):

$$\begin{aligned} X_{a,b} = &\int_{r_2=0}^{r_2=\infty} \cdots \int_{r_N=0}^{r_N=\infty} \int_{\phi_3=0}^{\phi_3=\pi} \cdots \int_{\phi_N=0}^{\phi_N=\pi} \int_{\tau_4=0}^{\tau_4=2\pi} \cdots \int_{\tau_N=0}^{\tau_N=2\pi} \mathrm{d}u_1 \cdots \mathrm{d}u_{3N-6} \\ &\sum_k c_k \exp\left(-a\left(\sum_{l=2}^{N} r_l^{y}\right) \boldsymbol{o}_k \cdot \boldsymbol{q}\right) \end{aligned} \tag{50}$$

These integrals can be evaluated analytically and, according to Fubini's theorem[21], one by one. The argument of the exponential function contains one term per coordinate when the radial terms are sorted into terms like $r_l^{m_l} \exp(-ar_l^{y})$. Integration can thus be performed for one coordinate after the other, treating all other coordinates as factors independent of the current coordinate and factoring them out. Integration thus yields:

$$\begin{aligned} X_{a,b} = \sum_k c_k &\int_{r_2=0}^{r_2=\infty} \mathrm{d}r_2\, r_2^{m_{2,k}} \exp\left(-ar_2^{y}\right) \times \cdots \times \int_{r_N=0}^{r_N=\infty} \mathrm{d}r_N\, r_N^{m_{N,k}} \exp\left(-ar_N^{y}\right) \times \\ &\int_{\phi_3=0}^{\phi_3=\pi} \mathrm{d}\phi_3\, \exp\left(\mathrm{i}\tilde{o}_{3,\text{angle}}\phi_3\right) \times \cdots \times \int_{\phi_N=0}^{\phi_N=\pi} \mathrm{d}\phi_N\, \exp\left(\mathrm{i}\tilde{o}_{N,\text{angle}}\phi_N\right) \times \\ &\int_{\tau_4=0}^{\tau_4=2\pi} \mathrm{d}\tau_4\, \exp\left(\mathrm{i}\tilde{o}_{4,\text{dihed}}\tau_4\right) \times \cdots \times \int_{\tau_N=0}^{\tau_N=2\pi} \mathrm{d}\tau_N\, \exp\left(\mathrm{i}\tilde{o}_{N,\text{dihed}}\tau_N\right) \end{aligned} \tag{51}$$

The integrals over radial coordinates yield:

$$\int_0^\infty \mathrm{d}r\, r^m \cdot \exp\left(-ar^{y}\right) = \frac{1}{y} a^{-\frac{m+1}{y}} \Gamma\left(\frac{m+1}{y}\right) \tag{52}$$

For the special case of $y = 1$ the Gamma function yields $\Gamma(m+1) = m!$.

For the special case of $y = 2$ the Gamma function yields:

$$\Gamma\left(\frac{m+1}{2}\right) = \sqrt{\frac{\pi}{4^m}}\frac{(m)!}{(m/2)!} \qquad \text{for } m \text{ even} \tag{53}$$

$$\Gamma\left(\frac{m+1}{2}\right) = \left(\frac{m-1}{2}\right)! \qquad \text{for } m \text{ odd} \tag{54}$$

The integrals over angular coordinates yield in the case of $\tilde{o} = 0$:

$$\int_0^\pi \mathrm{d}\phi \underbrace{\exp(0)}_{1} = [\phi]_0^\pi = \pi \tag{55}$$

for integration over angles. Integration over dihedral angles ranges from 0 to 2π and results therefore in 2π. In the case of $\tilde{o} \neq 0$ all integrals vanish except for $\tilde{o} = 1$ for angles ϕ:

$$\int_0^\pi \mathrm{d}\phi \exp(\mathrm{i}\phi) = \int_0^\pi \mathrm{d}\phi \cos(\phi) + \mathrm{i}\int_0^\pi \mathrm{d}\phi \sin(\phi) = 0 + 2\mathrm{i} \tag{56}$$

For dihedral angles τ integration from 0 to 2π yields 0 again.

Both cases ($\tilde{o} = 0$ and $\tilde{o} = 1$) will appear frequently because one needs to use both negative and positive orders in the Fourier expansion with complex exponentials. Then in products of such functions the orders will frequently sum up to zero or one. All other terms can be discarded.

In subsequent work we will test the behavior of these wavefunctions, orthonormal sets of them and potential energy functions for some molecules.

V. CONCLUSIONS

We have shown how the inverse metric tensor and the kinetic energy operator can be obtained analytically following a factorization proposed by Frederick and Woywod[5]. The elements of the adjugate metric tensor as well as its determinant all have the form $\sum r^m \sin(\alpha_n)\cos(\beta_o)$. This holds both for sequentially connected and branched molecules. A suitable choice of the wavefunction and the potential energy function avoids singularities and yields analytical expressions for the rovibrational kinetic energy matrix elements.

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Appendix A: Jacobian for the three-atomic case

The main problem for the three-atomic case is the determination of the inverse of the second Jacobian matrix from Equation 11. This Jacobian matrix $\mathsf{J}_2 = \mathsf{A}$ reads:

$$
\begin{aligned}
A_{1,1} &= -r_2(\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma) \\
A_{1,2} &= r_2 \sin\alpha\sin\beta\sin\gamma \\
A_{1,3} &= -r_2(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma) \\
A_{1,4} &= \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma \\
A_{1,5} &= 0 \\
A_{1,6} &= 0 \\
A_{2,1} &= r_2(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma) \\
A_{2,2} &= -r_2 \cos\alpha\sin\beta\sin\gamma \\
A_{2,3} &= -r_2(\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma) \\
A_{2,4} &= \sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma \\
A_{2,5} &= 0 \\
A_{2,6} &= 0 \\
A_{3,1} &= 0 \\
A_{3,2} &= r_2 \cos\beta\sin\gamma \\
A_{3,3} &= r_2 \sin\beta\cos\gamma \\
A_{3,4} &= \sin\beta\sin\gamma \\
A_{3,5} &= 0 \\
A_{3,6} &= 0 \\
A_{4,1} &= r_3 \cos\alpha\cos\beta(\sin\gamma\cos\phi_3 - \cos\gamma\sin\phi_3) + \sin\alpha(\cos\gamma\cos\phi_3 + \sin\gamma\sin\phi_3) \\
A_{4,2} &= r_3 \sin\alpha\sin\beta(\cos\gamma\sin\phi_3 - \sin\gamma\cos\phi_3) \\
A_{4,3} &= r_3(\sin\alpha\cos\beta(\sin\gamma\sin\phi_3 + \cos\gamma\cos\phi_3) + \cos\alpha(\sin\gamma\cos\phi_3 - \cos\gamma\sin\phi_3) \\
A_{4,4} &= 0 \\
A_{4,5} &= -(\cos\phi_3(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma) + \sin\phi_3(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma)) \\
A_{4,6} &= r_3(\sin\phi_3(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma) - \cos\phi_3(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma)) \\
A_{5,1} &= -r_3(\cos\phi_3(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma) + \sin\phi_3(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma)) \\
A_{5,2} &= r_3 \cos\alpha\sin\beta (\sin\gamma\cos\phi_3 - \cos\gamma\sin\phi_3) \\
A_{5,3} &= -r_3(\sin\phi_3(\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma - \cos\phi_3(\sin\alpha\sin\gamma - \cos\alpha\cos\beta\cos\gamma)) \\
A_{5,4} &= 0 \\
A_{5,5} &= -(\cos\phi_3(\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma) + \sin\phi_3(\sin\alpha\sin\gamma - \cos\alpha\cos\beta\cos\gamma)) \\
A_{5,6} &= r_3(\sin\phi_3(\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma) - \cos\phi_3(\sin\alpha\sin\gamma - \cos\alpha\cos\beta\cos\gamma)) \\
A_{6,1} &= 0 \\
A_{6,2} &= r_3 \cos\beta(\cos\gamma\sin\phi_3 - \sin\gamma\cos\phi_3) \\
A_{6,3} &= -r_3 \sin\beta(\cos\gamma\cos\phi_3 + \sin\gamma\sin\phi_3) \\
A_{6,4} &= 0 \\
A_{6,5} &= \sin\beta(\cos\gamma\sin\phi_3 - \sin\gamma\cos\phi_3) \\
A_{6,6} &= r_3 \sin\beta(\cos\gamma\cos\phi_3 + \sin\gamma\sin\phi_3)
\end{aligned}
$$

The inverse of A times its determinant of $r_2^2 r_3^2 \sin(\beta)\sin(\phi_3)$ will be called $\mathrm{adj}(\mathsf{A}) =$

$\mathsf{B} = r_2^2 r_3^2 \sin(\beta) \sin(\phi_3) \cdot \mathsf{A}^{-1}$ and reads (when we multiply by the determinant, eventually a preceding unity matrix block would be multiplied by this as well):

$$
\begin{aligned}
B_{1,1} &= r_2 r_3^2 \sin(\alpha)\sin(\beta)(\cos(\phi_3)\sin(\gamma) - \sin(\phi_3)\cos(\gamma))\\
B_{1,2} &= -r_2 r_3^2 \cos(\alpha)\sin(\beta)(\cos(\phi_3)\sin(\gamma) - \sin(\phi_3)\cos(\gamma))\\
B_{1,3} &= r_2 r_3^2 \cos(\beta)(\cos(\phi_3)\sin(\gamma) - \sin(\phi_3)\cos(\gamma))\\
B_{1,4} &= r_2^2 r_3 \sin(\alpha)\sin(\beta)\sin(\gamma)\\
B_{1,5} &= -r_2^2 r_3 \cos(\alpha)\sin(\beta)\sin(\gamma)\\
B_{1,6} &= r_2^2 r_3 \cos(\beta)\sin(\gamma)\\
B_{2,1} &= r_2 r_3^2 \sin(\alpha)\sin(\beta)^2(\cos(\phi_3)\cos(\gamma) + \sin(\phi_3)\sin(\gamma))\\
B_{2,2} &= -r_2 r_3^2 \cos(\alpha)\sin(\beta)^2(\cos(\phi_3)\cos(\gamma) + \sin(\phi_3)\sin(\gamma))\\
B_{2,3} &= r_2 r_3^2 \cos(\beta)\sin(\beta)(\cos(\phi_3)\cos(\gamma) + \sin(\phi_3)\sin(\gamma))\\
B_{2,4} &= r_2^2 r_3 \sin(\alpha)\sin^2(\beta)\cos(\gamma)\\
B_{2,5} &= -r_2^2 r_3 \cos(\alpha)\sin^2(\beta)\cos(\gamma)\\
B_{2,6} &= r_2^2 r_3 \cos(\beta)\sin(\beta)\cos(\gamma)\\
B_{3,1} &= -r_2 r_3^2 \sin(\gamma)\sin(\beta)(\cos(\phi_3)\sin(\alpha)\cos(\beta) + \sin(\phi_3)\cos(\alpha))\\
B_{3,2} &= r_2 r_3^2 \sin(\gamma)\sin(\beta)(\cos(\phi_3)\cos(\alpha)\cos(\beta) - \sin(\phi_3)\sin(\alpha))\\
B_{3,3} &= -r_2 r_3^2 (\cos(\phi_3)\sin(\gamma)\cos(\beta)^2 - \sin(\phi_3)\cos(\gamma))\\
B_{3,4} &= -r_2^2 r_3 \sin(\alpha)\sin(\beta)\cos(\beta)\sin(\gamma)\\
B_{3,5} &= r_2^2 r_3 \cos(\alpha)\sin(\beta)\cos(\beta)\sin(\gamma)\\
B_{3,6} &= -r_2^2 r_3 \cos^2(\beta)\sin(\gamma)\\
B_{4,1} &= r_2^2 r_3^2 \sin(\phi_3)\sin(\beta)(\cos(\alpha)\cos(\gamma) - \sin(\alpha)\cos(\beta)\sin(\gamma))\\
B_{4,2} &= r_2^2 r_3^2 \sin(\phi_3)\sin(\beta)(\sin(\alpha)\cos(\gamma) + \cos(\alpha)\cos(\beta)\sin(\gamma))\\
B_{4,3} &= r_2^2 r_3^2 \sin(\phi_3)\sin^2(\beta)\sin(\gamma)\\
B_{4,4} &= 0\\
B_{4,5} &= 0\\
B_{4,6} &= 0\\
B_{5,1} &= 0\\
B_{5,2} &= 0\\
B_{5,3} &= 0\\
B_{5,4} &= r_2^2 r_3^2 \sin(\beta)(\cos^2(\phi_3)(\sin(\alpha)\cos(\beta)\cos(\gamma) + \cos(\alpha)\sin(\gamma)) + \cos(\phi_3)\sin(\phi_3) \times\\
&\times (\sin(\gamma)\sin(\alpha)\cos(\beta) - \cos(\alpha)\cos(\gamma)) - \sin(\alpha)\cos(\beta)\cos(\gamma) - \cos(\alpha)\sin(\gamma))\\
B_{5,5} &= r_2^2 r_3^2 \sin(\beta)(-\cos^2(\phi_3)(\cos(\alpha)\cos(\beta)\cos(\gamma) - \sin(\alpha)\sin(\gamma)) - \cos(\phi_3)\sin(\phi_3) \times\\
&\times (\sin(\gamma)\cos(\alpha)\cos(\beta) + \sin(\alpha)\cos(\gamma)) + \cos(\alpha)\cos(\beta)\cos(\gamma) - \sin(\alpha)\sin(\gamma))\\
B_{5,6} &= r_2^2 r_3^2 \sin^2(\beta)(\cos(\gamma)\sin^2(\phi_3) - \sin(\gamma)\sin(\phi_3)\cos(\phi_3))\\
B_{6,1} &= -r_2 r_3^2 \sin(\phi_3)\sin(\beta)(\cos(\alpha)\sin(\gamma) + \sin(\alpha)\cos(\beta)\cos(\gamma))\\
B_{6,2} &= -r_2 r_3^2 \sin(\phi_3)\sin(\beta)(\sin(\alpha)\sin(\gamma) - \cos(\alpha)\cos(\beta)\cos(\gamma))\\
B_{6,3} &= r_1 r_3^2 \sin(\phi_3)\sin^2(\beta)\cos(\gamma)\\
B_{6,4} &= -r_2^2 r_3 \sin(\phi_3)\sin(\beta)(\sin(\alpha)\cos(\beta)(\cos(\gamma)\cos(\phi_3) +\\
&+ \sin(\gamma)\sin(\phi_3)) + \cos(\alpha)(\cos(\phi_3)\sin(\gamma) - \sin(\phi_3)\cos(\gamma)))\\
B_{6,5} &= r_2^2 r_3 \sin(\phi_3)\sin(\beta)(\cos(\alpha)\cos(\beta)(\cos(\gamma)\cos(\phi_3) +\\
&+ \sin(\gamma)\sin(\phi_3)) + \sin(\alpha)(\sin(\phi_3)\cos(\gamma) - \cos(\phi_3)\sin(\gamma)))\\
B_{6,6} &= r_2^2 r_3 \sin(\phi_3)\sin^2(\beta)(\cos(\gamma)\cos(\phi_3) + \sin(\gamma)\sin(\phi_3))
\end{aligned}
$$

REFERENCES

[1] M. Umer, W. A. Kopp, and K. Leonhard, J. Chem. Phys. **143**, 214306 (2015).

[2] W. A. Kopp, R. T. Langer, M. Döntgen, and K. Leonhard, J. Phys. Chem. A **117**, 6757 (2013).

[3] G. Avila and T. Carrington, Jr., J. Chem. Phys. **135**, 064101 (2011).

[4] M. J. Bramley, W. H. G. Jr., and N. C. Handy, Mol. Phys. **73**, 1183 (1991), http://dx.doi.org/10.1080/00268979100101871.

[5] J. H. Frederick and C. Woywood, J. Chem. Phys. **111**, 7255 (1999).

[6] F. Gatti, C. Munoz, and C. Iung, J. Chem. Phys. **114**, 8275 (2001).

[7] D. Lauvergnat and A. Nauts, J. Chem. Phys. **116**, 8560 (2002).

[8] A. Miyoshi, Int. J. Chem. Kinet. **42**, 273 (2010).

[9] J. Zheng, T. Yu, E. Papajak, I. M. Alecu, S. L. Mielke, and D. G. Truhlar, Phys. Chem. Chem. Phys. **13**, 10885 (2011).

[10] P. Seal, E. Papajak, and D. G. Truhlar, J. Phys. Chem. Lett. **3**, 264 (2012).

[11] A. Fernández-Ramos, J. Chem. Phys. **138**, 134112 (2013).

[12] B. Podolsky, Phys. Rev. **32**, 812 (1928).

[13] A. Nauts and X. Chapuisat, Mol. Phys. **55**, 1287 (1985).

[14] X. Chapuisat, A. Belafhal, and A. Nauts, J Molec Spec **149**, 274 (1991).

[15] E. Wilson, J. Decius, and P. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., 1955).

[16] J. Makarewicz and A. Skalozub, Chem. Phys. Lett. **306**, 352 (1999).

[17] J. Makarewicz and A. Skalozub, J. Phys. Chem. A **111**, 7860 (2007), pMID: 17637044, http://dx.doi.org/10.1021/jp071862q.

[18] T. R. Seifullin, Cybern. Syst. Anal. **38**, 650 (2002).

[19] G. Villard, J. Symb. Comput. **46**, 773 (2011).

[20] A. Ghysels, T. Verstraelen, K. Hemelsoet, M. Waroquier, and V. Van Speybroeck, J. Chem. Inf. Model. **50**, 1736 (2010).

[21] G. Fubini, Rom. Acc. L. Rend. **16**, 608 (1907).