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Rovibrational Molecular Hamiltonian in Mixed Bond-Angle and Umbrella-Like Coordinates

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A new exact quantum mechanical rovibrational Hamiltonian operator for molecules exhibiting large amplitude inversion and torsion motions is derived. The derivation is based on a division of a molecule into two parts: a frame and a top. The nuclei of the frame only are used to construct a molecular system of axes. The inversion motion of the frame is described in the umbrella-like coordinates, whereas the torsion motion of the top is described by the nonstandard torsion angle defined in terms of the nuclear vectors and one of the molecular axes. The internal coordinates chosen take into account the properties of the inversion and torsion motions. Vibrational **s** and rotational $\mathbf{\Omega}$ vectors obtained for the introduced internal coordinates determine the rovibrational tensor **G** defined by simple scalar products of these vectors. The Jacobian of the transformation from the Cartesian to the internal coordinates considered and the **G** tensor specify the rovibrational Hamiltonian. As a result, the Hamiltonian for penta-atomic molecules like NH_2OH with one inverter is presented and a complete set of the formulas necessary to write down the Hamiltonian of more complex molecules, like NH_2NH_2 with two inverters, is reported. The approach considered is essentially general and sufficiently simple, as demonstrated by derivation of a polyatomic molecule Hamiltonian in polyspherical coordinates, obtained by other methods with much greater efforts.

I. Introduction

A rigorous quantum mechanical treatment of internal molecular motions, reaction dynamics, and molecular spectra requires derivation of the molecular Hamiltonian operator composed of the kinetic energy operator $\hat{T}$ and the potential energy term V. The Hamiltonian operator can be straightforwardly written in the Cartesian coordinates; however, its eigenfunctions cannot be really calculated due to a high dimensionality of the dynamical problem. A translation invariance of the Hamiltonian allows a separation of only three Cartesian coordinates of the center of mass, but further exact reduction of the coordinate space is impossible.

Nevertheless, an approximate reduction can be achieved by choosing properly new generalized coordinates. The molecular rotational degrees of freedom, represented by the Euler angles specifying the orientation of a molecular system of axes (MSA) attached to a moving nuclear frame, can be approximately separated from the molecular internal motions.[1,2]

A further separation among the internal nuclear motions can be achieved by introducing generalized nuclear coordinates q adapted to the properties of the potential energy surface $V(q)$ of a molecule. A choice of the coordinates q is a nontrivial problem, because they should satisfy a few important optimum criteria. Optimal internal coordinates can be found only for special models of the potential $V(q)$. The familiar rectilinear normal coordinates,[3] widely used for semirigid molecules, are adapted to a simple model potential function $V(q)$, which is a quadratic polynomial in the coordinates q. However, such a potential function is inappropriate when large amplitude motions, like internal rotation, inversion, etc., have to be considered. Moreover, the coordinates q generate an unfactorizable pseudopotential term in the Watson Hamiltonian.[4]

Another familiar set of the internal coordinates, which we further refer to as the bond-angle coordinates, is more convenient in the treatment of large amplitude motions. The bond-angle coordinates of N-atomic molecule are based on a set of $N - 1$ internuclear vectors parametrized by their lengths and spherical angles. This set can be constructed from any internuclear vectors, for example, bond vectors, various kinds of Jacobi and Radau orthogonal vectors, etc.

Two kinds of the angles are commonly used. If all the spherical angles are defined with respect to a single global system of axes formed by the first two internuclear vectors, then they are called “polyspherical”.[5−8] They are convenient in the treatment of loosely bound molecular complexes.

The spherical coordinates can also be defined locally between pairs of vectors (bond angles) or triples of vectors (dihedral angles). Such angles are used to define the familiar valence coordinates and other bond-angle coordinates. These coordinates have to obey some validity conditions, which limit their use in specific cases. A detailed discussion of the above conditions is given in the work of Frederick and Woywod.[9]

Besides the mathematical restrictions imposed on the bond-angle coordinates, some other restrictions of a physical nature follow from the properties of the potential energy which governs the nuclear large amplitude motions. The inversion motion of the NH_3 molecule is a good illustration of this problem. Recently, it has been shown that the valence angles with the torsion angle between two NH_2 planes as the inversion coordinate cannot be used to define the Hamiltonian of the flexible model for the inversion.[10] These coordinates behave in a pathological way, because the minimum energy path on the potential energy surface along the inversion coordinate may bifurcate. This phenomenon prevents a definition of a correct flexible model of the inversion motion in ammonia and similar molecules, e.g., amines containing the NH_2 group.

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A pathological behavior of the flexible Hamiltonian, expressed in the bond-angle coordinates, has been found also in hydroxylamine, NH_2OH, in which the inversion motion of the NH_2 group is strongly coupled to the torsion of the OH bond about the ON bond.[11] The bond-angle coordinates, e.g., the NH_2 twisting angle, treated as the flexible parameters change rapidly along the inversion and torsion coordinates.

The problems mentioned above have been solved by introducing a new type of the angular coordinates, namely, the umbrella-like (UL) coordinates adapted to the inversion motion. They contain the “umbrella” angle α that can be easily defined for a one-dimensional inversion motion in ammonia, namely, α is the angle between the C_{3v} symmetry axis of the NH_3 molecule and one of the N−H bonds. When all vibrations including asymmetric distortions of the molecule must be considered, then the definition of the inversion angle is not obvious. Papoušek, and Špirko[12] defined the inversion angle ρ for ammonia by introducing a moving pyramidal reference frame of the C_{3v} symmetry. The remaining molecular distortions have been described by the variables built from the valence coordinates. The exact Hamiltonian could not be derived for such coordinates. Instead, it was expanded in a Taylor series of the distortion coordinates.

Later, it has been shown that the umbrella angle can be defined for one-dimensional inversion models also for molecules of low symmetry.[13] A complete set of the UL coordinates has been first introduced for hydrazine, NH_2NH_2, with two NH_2 inverters coupled to the internal rotation about the N−N bond.[14] A three-dimensional potential surface depending on the two NH_2 umbrella angles and the torsion angle was calculated by optimizing all the remaining internal coordinates. No pathological behavior of these coordinates was found, so the flexible Hamiltonian could be determined using a fully numerical method.

The first exact vibrational Hamiltonian for the ammonia molecule in the UL coordinates has been reported in an analytical form by Handy et al.[15] and the complete rovibrational Hamiltonian in these coordinates for ammonia has been derived by us.[16] The UL coordinates significantly extend the possibility of an adequate description of the large amplitude motions in molecules. Naturally, they can be employed together with the bond-angle coordinates.

The goal of this paper is to derive an exact rovibrational quantum mechanical kinetic energy operator $\hat{T}$ expressed by a set of internal coordinates containing both the UL and the bond-angle coordinates. Significant effort has been devoted in the past to derive the operator $\hat{T}$ for the internal bond-angle coordinates and various rotational coordinates defined by the MSA. In most of recent works the operator $\hat{T}$ has been obtained from the Laplacian operator written in the Cartesian coordinates of the nuclear vectors measured with respect to the laboratory system of axes (LSA). This Laplacian has been transformed directly to the internal and rotational coordinates.[17−22] This transformation was executed using complex intermediate expressions for the angular momentum operators. To avoid this difficulty, Schwenke proposed an alternative simpler method by factorizing out the Euler angles.[23]

The complexity of a direct transformation method appeared due to a rotational noninvariance of the Euler angles. This method has been simplified by introducing infinitesimal rotational coordinates, instead of the Euler angles, yielding $\hat{T}$ directly in terms of the angular momentum operators.[24,25] Recently, the same hint has been used by Watson, who derived $\hat{T}$ in general bond-angle coordinates for various types of molecules.[26]

Here, we use the direct transformation method developed by Louck et al.[27,28] Their method has not been popular despite its attractive features. It exploits the rotational invariance and allows a representation of $\hat{T}$ in terms of the vibrational **s** vectors and rotational **Ω** vectors. The technique of the **s** vectors has been first developed in the framework of the classical mechanics and has been used to express the kinetic energy T in terms of the rovibrational tensor **G**.[3,29−31]

In this paper we derive the vibrational **s** vectors and rotational **Ω** vectors for complex molecules exhibiting the large amplitude inversion and torsion motions. In section 2, the Laplacian for a general N-atomic molecule is transformed directly to the rovibrational operator $\hat{T}$ defined in an arbitrary set of the curvilinear internal coordinates and in an arbitrary rotating molecular frame specified by MSA. This operator is expressed by the rovibrational tensor **G** represented by dot products of the **s** and **Ω** vectors. These general results are applied in section 3 to the polyspherical coordinates for which the **s** and **Ω** vectors, together with the **G** tensor are obtained in extremely simple analytical formulas. Section 4 is devoted to the UL coordinates where the analytical **s** and **Ω** vectors are derived for molecules including various inverting groups. Section 5 is a concluding summary. A complete rovibrational tensor **G** for a typical pentaatomic molecule with one inverter is presented in the Supporting Information.

II. General Form of the Rovibrational Hamiltonian

The relative motions of N nuclei in a molecule can be defined by separating of the motion of the molecular center of mass. This separation is easily achieved by the transformation of the N original nuclear position vectors $\mathbf{R}_k$, defined in LSA, to new $N-1$ internuclear vectors $\mathbf{r}_i$ and the center of mass vector $\mathbf{r}_{\rm cm} = \sum_k m_k\mathbf{R}_k/\sum_k m_k$, where m_k is the mass of the $k^{\rm th}$ nucleus. The transformation $(\mathbf{R}_k) \rightarrow (\mathbf{r}_i,\mathbf{r}_{\rm cm})$ is linear

$$\mathbf{r}_i = \sum_{k=1}^{N} A_{ik}\mathbf{R}_k \tag{1}$$

and converts the kinetic energy operator $\hat{T}_{\rm m}$ of the molecule nuclei

$$\hat{T}_{\rm m} = -\frac{1}{2}\hbar^2\sum_{k=1}^{N}\frac{1}{m_k}\frac{\partial^2}{\partial \mathbf{R}_k^{\,2}} \tag{2}$$

to a sum of the kinetic energy operators of the center of mass and of the relative motions of the nuclei

$$\hat{T} = -\frac{1}{2}\hbar^2\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\frac{1}{m_{i,j}}\frac{\partial^2}{\partial \mathbf{r}_i\partial \mathbf{r}_j} \tag{3}$$

with the effective masses given by

$$\frac{1}{m_{i,j}} = \sum_{k=1}^{N}\frac{A_{ik}A_{jk}}{m_k} \tag{4}$$

This transformation also separates the angular momentum of the center of mass from the angular momentum associated with the $N-1$ internuclear vectors

$$\hat{\mathbf{J}} = -i\hbar\sum_{i=1}^{N-1}\mathbf{r}_i \times \frac{\partial}{\partial \mathbf{r}_i} \tag{5}$$

Clearly, the contribution of the center of mass to the kinetic energy and angular momentum can be ignored.

The 3(N - 1) LSA components $r_{i\alpha} = \mathbf{i}_\alpha\cdot\mathbf{r}_i$ of the vectors $\mathbf{r}_i$ on the three orthonormal LSA basis vectors $\mathbf{i}_\alpha$ ($\alpha = x, y, z$) can be used to define the three rotational variables $\boldsymbol{\varepsilon}$ and $3N - 6$ internal variables $\mathbf{q} = (q_1, q_2, ..., q_{3N-6})$. The transformation $(\mathbf{r}_i) \rightarrow (\boldsymbol{\varepsilon}, \mathbf{q})$ induces the corresponding transformation of the momentum operators. As derived in Appendix 1 of the Supporting Information, the operators $\hat{\mathbf{p}}_i = -i\hbar\partial/\partial\mathbf{r}_i$ transform according to

$$\hat{\mathbf{p}}_i = \mathbf{s}_i^\nu \hat{p}_\nu - \mathbf{\Omega}_i^\rho \hat{J}'_\rho \tag{6}$$

where we apply Einstein's summation convention to the Greek indices. The gradients of the q_ν variables

$$\mathbf{s}_i^\nu = \frac{\partial q_\nu}{\partial \mathbf{r}_i} \tag{7}$$

are the well-known $\mathbf{s}_i^\nu$ vectors associated to the vibrational momenta $\hat{p}_\nu = -i\hbar\partial/\partial q_\nu$ (the indices of these vectors will be dropped when they are unnecessary). The vectors $\mathbf{\Omega}_i^\rho = \Omega_{i\alpha}^\rho \mathbf{i}_\alpha$ are defined by

$$\Omega_{i\alpha}^\rho = \mathbf{e}_\gamma\cdot\frac{\partial \mathbf{e}_\beta}{\partial r_{i\alpha}} \tag{8}$$

where the indices ρ, γ, β are in cyclic order. The basis vectors $\mathbf{e}_\alpha$ specify the MSA orientation relative to LSA. The $\mathbf{\Omega}_i^\rho$ vectors correspond to the ρ^{th} MSA component of the angular momentum operator $\hat{J}'_\rho$.

Equation 8 was derived earlier by Cowell and Handy[25] using the "semi-intuitive" method of infinitesimal rotations of Lukka.[24] As shown in Appendix 1, this result can be derived in a rigorous way from a general formalism, and it is a consequence of the mathematical theory of rotations. It follows from general properties of the rotating molecular basis relative to LSA basis.

Equation 8 has been known for a long time, but somehow it has been rarely used. It has been applied to the Watson Hamiltonian in normal coordinates with Eckart axes already in 1976 by Louck and Galbraith.[27] For the principal axis system, the rotational $\mathbf{\Omega}$-vectors have been derived by several authors.[27,31,32] Recently, these results have been rederived by Watson.[26]

The transformation (6) of the momenta is general for rotationally invariant coordinates and convenient in applications, because all complications inherent in using explicitly the Euler angles disappear. The main problem consists in determining the components of the vibrational $\mathbf{s}$ and rotational $\mathbf{\Omega}$ vectors. The calculation of $\mathbf{\Omega}$ needs only the MSA basis orts as known functions of the internuclear vectors.

Under the transformation of the linear momenta, the kinetic energy operator $\hat{T}$ takes a transparent form

$$\hat{T} = \frac{1}{2}(\hat{p}_\mu^+ g^{\mu\nu}\hat{p}_\nu + \hat{p}_\mu^+ C_\alpha^\mu \hat{J}_\alpha + \hat{J}_\alpha \tilde{C}_\alpha^\mu \hat{p}_\mu + \mu_{\alpha\beta} J_\alpha \hat{J}_\beta) \tag{9}$$

where hereafter the "prim" on the components of the angular momentum operator is omitted for convenience. In eq 9 we use the operators

$$\hat{p}_\mu^+ = \hat{p}_\mu - i\hbar\frac{\partial \ln J_q}{\partial q_\mu}$$

conjugate to $\hat{p}_\mu$. The form of $\hat{p}_\mu^+$ is determined by the normalization condition for a wavefunction ψ

$$\int |\psi|^2 J_q \, d\mathbf{q} \, d\boldsymbol{\varepsilon} = 1 \tag{10}$$

where J_q is a part of the Jacobian of the transformation that refers to the internal coordinates $\mathbf{q}$, and $d\boldsymbol{\varepsilon}$ is the volume element for the rotational coordinates.

The elements $g^{\mu\nu}$, C_α^μ, and $\mu_{\alpha\beta}$, which are the components of the rovibrational tensor $\mathbf{G}$ are defined by simple sums of the $\mathbf{s}_i^\nu$ and $\mathbf{\Omega}_i^\alpha$ dot products. The vibrational tensor

$$g^{\mu\nu} = \sum_{i,j}\frac{1}{m_{i,j}}\mathbf{s}_i^\mu\cdot\mathbf{s}_j^\nu \tag{11}$$

the Coriolis tensor

$$C_\alpha^\mu = -\sum_{i,j}\frac{1}{m_{i,j}}\mathbf{s}_i^\mu\cdot\mathbf{\Omega}_j^\alpha \tag{12}$$

and the rotational tensor $\mu_{\alpha\beta}$ that plays the role of an effective reciprocal tensor of inertia

$$\mu_{\alpha\beta} = \sum_{i,j}\frac{1}{m_{i,j}}\mathbf{\Omega}_i^\alpha\cdot\mathbf{\Omega}_j^\beta \tag{13}$$

together with the Jacobian J_q define the operator $\hat{T}$. Its explicit analytical form has been determined for polyspherical[6-8] and valence coordinates[9,33] using various derivation methods. At present, the popular methodology consists in a direct transformation of the operator $\hat{T}$ from the LSA Cartesian coordinates to the internal and rotational coordinates. The complicated procedure of the transformation to selected internal coordinates and a chosen MSA should be carried out from beginning to the end. A recent example is the work of Schwenke.[23]

In this paper, we use also the direct transformation method, however, the results expressed in the eqs 9−13 are general, independent of a specific choice of the MSA and of the coordinates q_ν. Thus, the representation of the tensor $\mathbf{G}$ with the help of auxiliary vectors $\mathbf{s}_i^\nu$ and $\mathbf{\Omega}_i^\alpha$ seems to be the most convenient way of the derivation of $\hat{T}$. Such a representation allows us to simplify and formalize a complex algebra. What one needs to do is

i. define the internuclear vectors $\mathbf{r}_i$ adapted to the structure of a molecule,

ii. construct the MSA basis orts $\mathbf{e}_\alpha$ from the internuclear vectors,

iii. specify the rotationally invariant internal coordinates q_ν.

In the following it is necessary to perform the differentiation operations to define the $\mathbf{s}_i^\nu$ and $\mathbf{\Omega}_i^\alpha$ vectors. Moreover, now we can report these vectors for most typical MSA and internal coordinates to apply them to the molecules of user interest. Then a whole analytical work necessary to derive the tensor $\mathbf{G}$ is reduced to easy calculations of dot products of the above vectors.

To derive the $\mathbf{\Omega}_i^\alpha$ vectors for some special cases, Pesonen[34] has proposed the geometric algebra approach, grounded on the rotational measuring vectors. However, his approach needs a special formalism.

To complete the derivation procedure, it remains to determine a Jacobian for the chosen coordinates q_ν. The most desired ones are those for which the Jacobian becomes factorizable. The bond-angle coordinates based on various vector types: the bonds, Jacobi or Radau vectors, etc., fulfill this condition. For the UL coordinates it is also possible to obtain the Jacobian in the factorizable form. These coordinates can be considered essentially as quasispherical ones. Other types of coordinates lead to necessity of calculation of multidimensional integrals[24,26,35] due to unfactorizable **G** and J_q. In such a case it is very hard to carry out the computational work with the Hamiltonian.

III. s and Ω Vectors for the Polyspherical Coordinates

Practical usefulness and the efficiency of the **s** and **Ω** vector formalism will be illustrated here on the example of the polyspherical coordinates. The $\hat{T}$ operator for these coordinates has been derived earlier by Gatti et al.[6−8] The internuclear vectors $\mathbf{r}_i$ are parametrized by their lengths r_i and the spherical (θ_i,φ_i) angles measured with respect to the MSA based on two last vectors $\mathbf{r}_n$ and $\mathbf{r}_{n-1}$ forming the angle θ_{n-1}. The MSA basis ort $\mathbf{e}_3$ is simply the unit vector ρ_n along the vector $\mathbf{r}_n$:

$$\mathbf{e}_3 = \boldsymbol{\rho}_n = \frac{\mathbf{r}_n}{r_n}$$

$\mathbf{e}_1$ is perpendicular to $\mathbf{e}_3$ and lies in the $(\mathbf{r}_n,\mathbf{r}_{n-1})$ plane, so it is given by

$$\mathbf{e}_1 = \frac{1}{\sin\theta_{n-1}}(\boldsymbol{\rho}_{n-1} - \boldsymbol{\rho}_n \cos\theta_{n-1})$$

and

$$\mathbf{e}_2 = \mathbf{e}_3 \times \mathbf{e}_1 = \frac{\boldsymbol{\rho}_n \times \boldsymbol{\rho}_{n-1}}{\sin\theta_{n-1}}$$

The substitution of the above expressions to eq 8 gives immediately

$$\boldsymbol{\Omega}_i^1 = \frac{\delta_{i,n}}{r_n}\mathbf{e}_2 \qquad \boldsymbol{\Omega}_i^2 = -\frac{\delta_{i,n}}{r_n}\mathbf{e}_1$$
$$\boldsymbol{\Omega}_i^3 = -\frac{\delta_{i,n-1}}{r_{n-1}\sin\theta_{n-1}}\mathbf{e}_2 + \cot\theta_{n-1}\boldsymbol{\Omega}_i^1 \qquad (14)$$

The **s** vectors for the polyspherical coordinates can be derived equally easily and their analytical forms are the following

$$\mathbf{s}_i^{r_j} = \delta_{i,j}\boldsymbol{\rho}_j \qquad i,j \le n$$
$$\mathbf{s}_i^{\theta_j} = -\frac{1}{\sin\theta_j}\left[\frac{\delta_{i,j}}{r_j}(\mathbf{e}_3 - \boldsymbol{\rho}_j\cos\theta_j) + \frac{\delta_{i,n}}{r_n}(\boldsymbol{\rho}_j - \mathbf{e}_3\cos\theta_j)\right] \qquad i \le n, j \le n-1 \quad (15)$$
$$\mathbf{s}_i^{\varphi_j} = \frac{\delta_{i,j}}{r_j\sin^2\theta_j}\mathbf{e}_3\times\boldsymbol{\rho}_j - \frac{\delta_{i,n-1}}{r_{n-1}\sin\theta_{n-1}}\mathbf{e}_2 + \frac{\delta_{i,n}}{r_n}\left(\cot\theta_{n-1}\mathbf{e}_2 - \frac{\cot\theta_j}{\sin\theta_j}\mathbf{e}_3\times\boldsymbol{\rho}_j\right) \qquad i \le n, j \le n-2$$

A complete set of the **s** and **Ω** vectors presented is enough for the construction of the **G** tensor by forming the dot products in eqs 11−13. They are very simple and yield immediately the formulas for **G** reported in ref 8. The Jacobian for the polyspherical coordinates, as a product of the standard Jacobians for the usual one-particle spherical coordinates, determines together with **G** the operator $\hat{T}$.

IV. s and Ω Vectors for the Inversion and Torsion Coordinates of a Single Inverter and Two Linked Inverters

IV.1. s and Ω Vectors of the Umbrella-Like Coordinates. The power of the method presented allows us to apply it to probably the most complex, but the most interesting, case considered, where one part of a molecule is described by the UL coordinates and the other part by the bond-angle coordinates. Such a choice is unavoidable for an adequate description of the inversion and torsion dynamics of the typical amino ($-NH_2$) groups contained in amine molecules. Here we will distinguish two general classes of the amines, where the amino group is linked to a remaining part of the molecule through a fragment that cannot invert (class 1) or can invert (class 2). The molecules of the type NH_2-O-R, NH_2-CH_2-R, etc., with an arbitrary group R of atoms belong to the first class. The molecules such as NH_2-NH-R, $NH_2-NR_1R_2$, etc., where two neighbor groups can invert, belong to the second class.

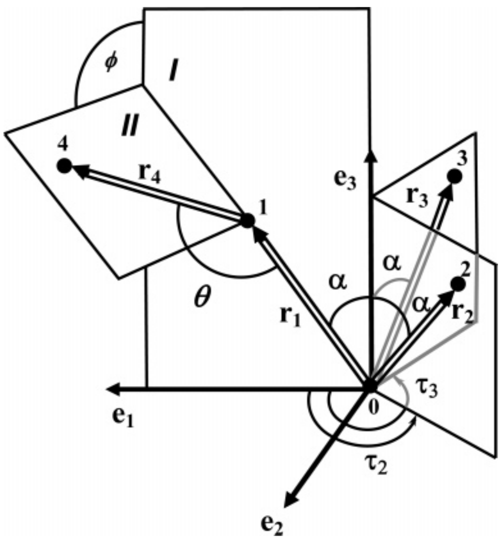

Figure 1. MSA basis vectors $\mathbf{e}_\alpha$ and the internal coordinates of the frame.

In this section we will consider the first class of the molecules and derive the **s** and **Ω** vectors necessary for the construction of a complete tensor **G**. The internuclear vectors $\mathbf{r}_i$ chosen for the most essential part (a core) of the molecule considered are shown in Figure 1. Additional nuclei can be attached to the core, but they are not shown. The vectors $\mathbf{r}_i = \mathbf{R}_k - \mathbf{R}_l$ connect the neighbor nuclei k^{th} and l^{th}, and they reflect the bonding pattern in a simple amine, like NH_2OH. Naturally, another set of the vectors $\mathbf{r}_i$ can be chosen, for example, the Jacobi or Radau vectors. However, for a different choice of $\mathbf{r}_i$ only the mass coefficients $m_{i,j}$ in eq 3 change.

In further considerations, following ref 36, a part of the molecule whose bond vectors are (not) involved in the construction of MSA will be called a “frame” (“top”). Here, the frame corresponding to the NH_2O group of the example NH_2OH molecule includes the nuclei with the indices 0, 1, 2, and 3. For the description of the inversion motion of the frame we introduce the UL coordinates. They include the bond lengths $\mathbf{r}_i$ for $i = 1, 2, 3$, and the angles α, τ_2, and τ_3. The angle α as the inversion coordinate is defined in conjunction with the MSA basis vectors $\mathbf{e}_\alpha$ with the origin in the 0^{th} nucleus. The vector $\mathbf{e}_3$ makes the same angle α with all the frame bond vectors $\mathbf{r}_i$. The vector $\mathbf{e}_1$ lies in the plane *I* formed by the vectors $\mathbf{r}_1$ and $\mathbf{e}_3$. The vector $\mathbf{e}_2$ is perpendicular to the $(\mathbf{e}_1, \mathbf{e}_3)$ plane. The vectors $\mathbf{e}_i$ form a right-handed MSA system.

The vector $\mathbf{e}_3$ is a trisector for the pyramid formed by the frame bond vectors. The angle $\tau_2(\tau_3)$ is an azimuthal angle of the vector $\mathbf{r}_2$ ($\mathbf{r}_3$), defined as a dihedral angle between the $(\mathbf{e}_1,\mathbf{e}_3)$ plane and the plane containing $\mathbf{e}_3$ and $\mathbf{r}_2$ ($\mathbf{r}_3$). The frame coordinates are the same as those defined for ammonia in ref 16.

The bond vector $\mathbf{r}_4$ is the top part of the molecule. It is described by the angles similar to the familiar valence coordinates. The angle θ between $-\mathbf{r}_1$ and $\mathbf{r}_4$ is the bending angle, and ϕ is a dihedral angle formed by the plane $I = (\mathbf{r}_1, \mathbf{e}_3)$ and the plane $II = (\mathbf{r}_1, \mathbf{r}_4)$. Other bond vectors of the top attached to the first nucleus, not shown in Figure 1, can be parametrized by the same type of the bond-angle coordinates. It is enough to consider only one vector of the top because the results for a general case of many vectors in the top will be analogous.

The properties of the coordinates introduced have been tested first on the NH_3 molecule for which the minimum energy path (MEP) along the inversion coordinate α has been calculated. To determine MEP, the internal coordinates $\mathbf{q}^f = (r_1, r_2, r_3, \tau_2, \tau_3)$ treated as flexible parameters have been optimized at a tight level using the ab initio second-order Møller−Plesset method with the Dunning's aug-cc-pVTZ basis set.[37] The calculations have been carried out by employing GAUSSIAN03 program.[38]

The results obtained show that the optimized parameters $\mathbf{q}^f$ vary smoothly with the decreasing of α down to its critical value, $\alpha_c \cong 24.4°$, which describes a strongly deformed molecular configuration. At this angle, the NH_3 molecule looses the C_{3v} symmetry because one of the three NH bonds rapidly gets longer. As a result, the MEP is split into three equivalent branches corresponding to the molecular structures $\mathbf{q}^f(\alpha_c)$ of the C_{2v} symmetry. Clearly, the effective inversion potential cannot be defined for $\alpha < \alpha_c$. However, the energy at $\alpha = \alpha_c$ is extremely high, $E(\alpha_c) \cong 6 \times 10^4$ cm^{-1}. Thus the MEP branching does not play any role in the bound states of ammonia.

A more complex behavior has been revealed in NH_2OH in which a two-dimensional flexible potential surface $E(\alpha,\phi)$ has been investigated. Such a surface is necessary for the calculation of the inversion−torsion levels of NH_2OH. The most important are the sections of this surface at $\phi = 0$ and 180°, because the saddle point corresponding to the torsion potential barrier and the energy minimum are placed at $(\alpha, \phi) = (90°, 0°)$ and $(65.8°, 180°)$, correspondingly. The section $E(\alpha,180°)$ defines the constrained MEP passing through the energy minimum. The molecular geometry preserves its C_s symmetry along this MEP down to the critical angle, $\alpha_c \cong 24.4°$. At this angle, one of the NH bonds rapidly gets longer and the proton jumps into the region near the O nucleus. As a result, the new symmetry broken configuration is formed and the MEP bifurcates into two equivalent branches. The energy at the bifurcation is too high to influence the bond inversion-torsion states. A similar bifurcation has been found for $\phi = 0$ in the MEP passing through the torsion barrier at the angle $\alpha_c \cong 26.3°$.

Here we give formulas for the MSA Cartesian coordinates, the $\mathbf{s}$ and $\mathbf{\Omega}$ vectors and the Jacobian for the internal coordinates introduced. The UL and valence variables define the Cartesian coordinates $r'_{i\beta}$ of the four nuclear vectors $\mathbf{r}_i$ in the selected MSA. These components are given by

$$\begin{array}{lll} r'_{1x} = r_1 \sin\alpha & r'_{2x} = r_2 \sin\alpha \cos\tau_2 & r'_{3x} = r_3 \sin\alpha \cos\tau_3 \\ r'_{1y} = 0 & r'_{2y} = r_2 \sin\alpha \sin\tau_2 & r'_{3y} = r_3 \sin\alpha \sin\tau_3 \\ r'_{1z} = r_1 \cos\alpha & r'_{2z} = r_2 \cos\alpha & r'_{3z} = r_3 \cos\alpha \end{array} \tag{16}$$

for the frame and

$$r'_{4x} = r_4 \sin\gamma \cos\tau_4 \quad r'_{4y} = r_4 \sin\gamma \sin\tau_4 \quad r'_{4z} = r_4 \cos\gamma \tag{17}$$

for the top, where γ and τ_4 are the spherical coordinates of the bond $\mathbf{r_4}$ shifted to the MSA. The formulas of the spherical trigonometry for connections between the angles introduced

$$\begin{gathered} \cos\gamma = -\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos\phi \\ \sin\phi\sin\theta = \sin\gamma\sin\tau_4 \\ -\cos\theta = -\cos\alpha\cos\gamma + \sin\alpha\sin\gamma\cos\tau_4 \end{gathered}$$

allow one to express $r'_{4\alpha}$ by the valence angles

$$\begin{gathered} r'_{4x} = r_4(-\sin\alpha\cos\theta - \cos\alpha\sin\theta\cos\phi) \\ r'_{4y} = r_4 \sin\theta\sin\phi \\ r'_{4z} = r_4(-\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos\phi) \end{gathered} \tag{18}$$

The Jacobian J_q of the transformation in eq 10 equals $J_q = J_{UL}J_V$, where J_{UL} is the Jacobian of the transformation to the UL coordinates of the frame and J_V is the Jacobian of the transformation to the valence coordinates of the top. The Jacobian J_{UL} has been already derived earlier[15,16]

$$J_{UL} = 4(r_1r_2r_3)^2 \sin^3\alpha \sin\frac{\tau_1}{2} \sin\frac{\tau_2}{2} \sin\frac{\tau_3}{2} \tag{19}$$

where $\tau_1 = \tau_3 - \tau_2$ and the rigorous constraints for the angular coordinates are $0 \le \tau_2 \le \tau_3 \le 2\pi$, $0 \le \alpha \le \pi$. The Jacobian J_V has a standard form for the spherical coordinates and it can be written for the variables γ and τ_4 as

$$J'_V = r_4 \sin\gamma$$

Taking into account that $\partial(\gamma,\tau_4)/\partial(\theta,\phi) = \sin\theta/\sin\gamma$ and $J_V = [\partial(\gamma,\tau_4)/\partial(\theta,\phi)]J'_V$, we obtain for our valence coordinates the desired result $J_V = r_4 \sin\theta$. Thus, the Jacobian J_q of the resulting transformation takes the final form

$$J_q = 4\sin^3\alpha \sin\frac{\tau_1}{2} \sin\frac{\tau_2}{2} \sin\frac{\tau_3}{2} \sin\theta \prod_{i=1}^{4} r_i^2 \tag{20}$$

To determine the vectors $\mathbf{\Omega}_i^\rho$ one needs to define the MSA basis vectors $\mathbf{e}_\beta$. Here, we will express them by the bond vectors $\mathbf{r}_i$ of the frame only, because they determine directly the geometry of the inverter. For such a choice the basis vectors $\mathbf{e}_\beta$ are the same as those determined for the ammonia molecule, namely

$$\mathbf{e}_\beta = \frac{1}{\sin\alpha}\sum_{i=1}^{3} S_{\beta,i}\boldsymbol{\rho}_i \qquad \text{for} \qquad \beta = 1,2 \text{ and } \mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2 \tag{21}$$

As a consequence, the $\mathbf{\Omega}_i^\rho$ vectors derived in ref 16 can be applied to the molecules considered here. These vectors

$$\mathbf{\Omega}_i^1 = -\frac{S_{2,i}}{r_i \sin\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_i \cos\alpha) \tag{22}$$

$$\mathbf{\Omega}_i^2 = \frac{S_{1,i}}{r_i \sin\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_i \cos\alpha) \tag{23}$$

$$\mathbf{\Omega}_i^3 = -\frac{\delta_{i,1}}{r_i \sin\alpha}\mathbf{e}_2 + \cot\alpha\,\mathbf{\Omega}_i^1 \tag{24}$$

are expressed conveniently by the unit vectors $\boldsymbol{\rho}_i$ and basis orts $\mathbf{e}_\beta$ depending on the internal coordinates contained in the structural elements $S_{\beta,i}$:

$$S_{1,1} = -\frac{1}{2}\left(\cot\frac{\tau_2}{2}\cot\frac{\tau_3}{2} - 1\right) \qquad S_{1,2} = \frac{1}{2}\left(\cot\frac{\tau_2}{2}\cot\frac{\tau_1}{2} - 1\right)$$
$$S_{1,3} = -\frac{1}{2}\left(\cot\frac{\tau_3}{2}\cot\frac{\tau_1}{2} + 1\right) \tag{25}$$
$$S_{2,1} = -\frac{1}{2}\left(\cot\frac{\tau_2}{2} + \cot\frac{\tau_3}{2}\right) \qquad S_{2,2} = \frac{1}{2}\left(\cot\frac{\tau_2}{2} + \cot\frac{\tau_1}{2}\right)$$
$$S_{2,3} = \frac{1}{2}\left(\cot\frac{\tau_3}{2} - \cot\frac{\tau_1}{2}\right)$$

The vibrational **s** vectors can be written in the two alternative ways as $\mathbf{s}_i^{\nu} = s_{i\alpha}^{\nu}\mathbf{i}_{\alpha} = s'^{\nu}_{i\alpha}\mathbf{e}_{\alpha}$. The components $s'^{\nu}_{i\beta} = \partial q_{\nu}/\partial r'_{i\beta}$ can be obtained from the transformation of the linear momentum operators $\hat{p}_{i,\beta} = -i\hbar\partial/\partial r'_{i\beta}$ from the MSA Cartesian to the internal coordinates. Such a transformation has been executed in two steps.[16] In the first step $C \rightarrow V$, Cartesian MSA coordinates have been transformed to the valence coordinates. After the second step $V \rightarrow UL$, the operators $\hat{p}_{i,\beta}$ have been transformed to $\hat{p}_{\nu}$ defined in the *UL* coordinates, using the connection between the valence and the *UL* coordinates. The eq 64 of ref (16) connecting $\hat{p}_{i,\beta}$ and $\hat{p}_{\nu} = -i\hbar\partial/\partial q_{\nu}$ for $\nu = r_1,r_2,r_3,\alpha,\tau_2,\tau_3$ gives directly the coefficients $s'^{\nu}_{i\alpha}$, from which the $\mathbf{s}_i^{\nu}$ vectors are easily obtained as the functions of the UL coordinates

$$\mathbf{s}_i^{\mathrm{r}_j} = \delta_{i,j}\boldsymbol{\rho}_j$$
$$\mathbf{s}_i^{\alpha} = \frac{(S_{1,i} - \delta_{1,i})(\mathbf{e}_3 - \boldsymbol{\rho}_i\cos\alpha)}{r_i\sin\alpha}$$
$$\mathbf{s}_i^{\tau_2} = \frac{(\mathbf{e}_3 - \boldsymbol{\rho}_i\cos\alpha)T_{2,i} - \delta_{i,2}\sin\tau_i\mathbf{e}_1 - (\delta_{i,1} - \delta_{i,2}\cos\tau_i)\mathbf{e}_2}{r_i\sin\alpha} \tag{26}$$
$$\mathbf{s}_i^{\tau_3} = \frac{(\mathbf{e}_3 - \boldsymbol{\rho}_i\cos\alpha)T_{3,i} - \delta_{i,3}\sin\tau_i\mathbf{e}_1 - (\delta_{i,1} - \delta_{i,3}\cos\tau_i)\mathbf{e}_2}{r_i\sin\alpha}$$

where the unit vectors ρ_i along the corresponding bonds have, according to eq 16, the following MSA components

$$\boldsymbol{\rho}_1 = [\sin\alpha, 0, \cos\alpha]$$
$$\boldsymbol{\rho}_2 = [\sin\alpha\cos\tau_2, \sin\alpha\sin\tau_2, \cos\alpha] \tag{27}$$
$$\boldsymbol{\rho}_3 = [\sin\alpha\cos\tau_3, \sin\alpha\sin\tau_3, \cos\alpha]$$

The new structural coefficients $T_{\beta,j}$ ($\beta = 2, 3$) in eq 26 are defined as follows

$$T_{2,1} = \cot\alpha\cot\frac{\tau_3}{2} \qquad T_{2,2} = -\cot\alpha\cot\frac{\tau_1}{2}$$
$$T_{2,3} = -T_{2,1} - T_{2,2} \tag{28}$$
$$T_{3,1} = \cot\alpha\cot\frac{\tau_2}{2} \qquad T_{3,2} = -\cot\alpha\left(\cot\frac{\tau_2}{2} + \cot\frac{\tau_1}{2}\right)$$
$$T_{3,3} = -T_{3,1} - T_{3,2}$$

IV.2. s Vectors of the Molecular Top. Derivation of the **s** vectors for the valence coordinates r_4, θ of the molecular top is simple, although there are some peculiarities concerning the angle ϕ because this angle is defined not only by the bond vectors $\mathbf{r}_i$ but also by the z' molecular axis parallel to $\mathbf{e}_3$. The $s_{i\alpha}^{r_4}$ and $s_{i\alpha}^{\theta}$ can be obtained immediately from their definitions

$$s_{i\alpha}^{r_4} = \frac{\partial r_4}{\partial r_{i\alpha}} = \delta_{i,4}\rho_{4\alpha} \tag{29}$$

$$s_{i\alpha}^{\theta} = \frac{\partial\theta}{\partial r_{i\alpha}} = -\frac{1}{\sin\theta}\frac{\partial\cos\theta}{\partial r_{i\alpha}} = \frac{1}{\sin\theta}\frac{\partial}{\partial r_{i\alpha}}(\boldsymbol{\rho}_1\cdot\boldsymbol{\rho}_4) \tag{30}$$

where $\boldsymbol{\rho}_4$ has the following components in MSA:

$$\boldsymbol{\rho}_4 = [-\sin\alpha\cos\theta - \cos\alpha\sin\theta\cos\phi, \sin\phi\sin\theta, -\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos\phi]$$

The nonzero vectors $\mathbf{s}_i^{r_4}$ and $\mathbf{s}_i^{\theta}$ are

$$\mathbf{s}_4^{r_4} = \boldsymbol{\rho}_4$$
$$\mathbf{s}_1^{\theta} = \frac{1}{r_1\sin\theta}(\boldsymbol{\rho}_4 + \boldsymbol{\rho}_1\cos\theta) \tag{31}$$
$$\mathbf{s}_4^{\theta} = \frac{1}{r_4\sin\theta}(\boldsymbol{\rho}_1 + \boldsymbol{\rho}_4\cos\theta)$$

To find the components $s_{i\alpha}^{\phi}$, we use the standard relation that connects the **s** vectors and the classical velocity vectors. For the torsion angle ϕ this relation reads

$$\dot{\phi} = \sum_{i=1}^{4}\frac{\partial\phi}{\partial\mathbf{r}_i}\cdot\dot{\mathbf{r}}_i = \sum_{i=1}^{4}\mathbf{s}_i^{\phi}\cdot\dot{\mathbf{r}}_i \tag{32}$$

In our case, the rotation axis for the torsion angle ϕ coincides with the bond vector $\mathbf{r}_1$. This angle is defined as the dihedral angle between the planes *I* and *II* (the "book" angle); see Figure 1. The velocity of a change in the dihedral angle under displacement velocities of the nuclei defining these planes equals the sum[39]

$$\dot{\phi} = -\frac{\mathbf{n}_1}{\sin\alpha}\cdot(\dot{\mathbf{R}}_{\mathbf{e}_3} - \dot{\mathbf{R}}_0) + \frac{\cot\alpha}{r_1}\mathbf{n}_1\cdot(\dot{\mathbf{R}}_1 - \dot{\mathbf{R}}_0) - \frac{\mathbf{n}_2}{r_4\sin\theta}\cdot(\dot{\mathbf{R}}_4 - \dot{\mathbf{R}}_1) + \frac{\cot\theta}{r_1}\mathbf{n}_2\cdot(\dot{\mathbf{R}}_0 - \dot{\mathbf{R}}_1) \tag{33}$$

where $\mathbf{R}_{\mathbf{e}_3}$ is the radius-vector of the end of the ort $\mathbf{e}_3$ and $\mathbf{R}_0$, $\mathbf{R}_1$, and $\mathbf{R}_4$ are the nuclear position vectors of the corresponding nuclei with the origin in LSA. We choose $\dot{\phi} > 0$ when ϕ increases. Replacing $\mathbf{R}_i$ by the bond vectors $\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_0$, $\mathbf{r}_4 = \mathbf{R}_4 - \mathbf{R}_1$, and $\mathbf{e}_3 = \mathbf{R}_{\mathbf{e}_3} - \mathbf{R}_0$ we have

$$\dot{\phi} = -\frac{\mathbf{n}_1\cdot\dot{\mathbf{e}}_3}{\sin\alpha} + \left(\frac{\cot\alpha}{r_1}\mathbf{n}_1 - \frac{\cot\theta}{r_1}\mathbf{n}_2\right)\cdot\dot{\mathbf{r}}_1 - \frac{\mathbf{n}_2\cdot\dot{\mathbf{r}}_4}{r_4\sin\theta} \tag{34}$$

where $\mathbf{n}_1 = (\mathbf{e}_3 \times \boldsymbol{\rho}_1)/\sin\alpha$ and $\mathbf{n}_2 = (\boldsymbol{\rho}_1 \times \boldsymbol{\rho}_4)/\sin\theta$ are the unit vectors normal to the planes *I* and *II*, respectively. Now, let us define the time derivative

$$\dot{\mathbf{e}}_3 = \sum_{i=1}^{3}\frac{\partial\mathbf{e}_3}{\partial r_{i\alpha}}\dot{r}_{i\alpha} = \sum_{i=1}^{3}\mathbf{e}_3 \times \boldsymbol{\Omega}_{i\alpha}\dot{r}_{i\alpha} \tag{35}$$

where we have used the equation $\partial\mathbf{e}_{\beta}/\partial r_{i\alpha} = \mathbf{e}_{\beta} \times \boldsymbol{\Omega}_{i\alpha}$. As $\mathbf{n}_1 = \mathbf{e}_2$, the first term in the right side of eq 34 can be written as follows

$$\frac{\mathbf{n}_1\cdot\dot{\mathbf{e}}_3}{\sin\alpha} = \frac{\mathbf{e}_2}{\sin\alpha}\cdot\sum_{i=1}^{3}(\mathbf{e}_3\times\boldsymbol{\Omega}_{i\alpha})(\mathbf{i}_\alpha\cdot\dot{\mathbf{r}}_i) = \sum_{i=1}^{3}\mathbf{b}_i\cdot\dot{\mathbf{r}}_i$$

where, for shortness, we introduce the vectors

$$\mathbf{b}_i = \frac{1}{\sin\alpha}[\boldsymbol{\Omega}_{i\alpha}\cdot(\mathbf{e}_2\times\mathbf{e}_3)]\mathbf{i}_\alpha = \frac{1}{\sin\alpha}\boldsymbol{\Omega}^1_{i\alpha}\mathbf{i}_\alpha \tag{36}$$

Substituting eq 22 for $\Omega^1_{i\alpha}$ into eq 36, we have

$$\mathbf{b}_i = -\frac{S_{2,i}}{r_i\sin^2\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_i\cos\alpha) \tag{37}$$

Thus, eq 34 can be represented as

$$\dot{\phi} = -\sum_{i=1}^{3}\mathbf{b}_i\cdot\dot{\mathbf{r}}_i + \left(\frac{\cot\alpha}{r_1}\mathbf{n}_1 - \frac{\cot\theta}{r_1}\mathbf{n}_2\right)\cdot\dot{\mathbf{r}}_1 - \frac{\mathbf{n}_2\cdot\dot{\mathbf{r}}_4}{r_4\sin\theta} \tag{38}$$

Now, comparing this equation with eq 32 we finally obtain

$$\begin{aligned}
\mathbf{s}^{\phi}_1 &= \frac{S_{2,1}}{r_1\sin^2\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_1\cos\alpha) + \left(\frac{\cot\alpha}{r_1}\mathbf{n}_1 - \frac{\cot\theta}{r_1}\mathbf{n}_2\right)\\
\mathbf{s}^{\phi}_2 &= \frac{S_{2,2}}{r_2\sin^2\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_2\cos\alpha)\\
\mathbf{s}^{\phi}_3 &= \frac{S_{2,3}}{r_3\sin^2\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_3\cos\alpha)\\
\mathbf{s}^{\phi}_4 &= -\frac{\mathbf{n}_2}{r_4\sin\theta}
\end{aligned} \tag{39}$$

These expressions can be written in a compact form

$$\begin{aligned}
\mathbf{s}^{\phi}_i &= \frac{S_{2,i}}{r_i\sin^2\alpha}(\mathbf{e}_3 - \boldsymbol{\rho}_1\cos\alpha) + \frac{\delta_{i,1}}{r_1}\left(\cot\alpha\mathbf{e}_2 - \frac{\cos\theta}{\sin^2\theta}\boldsymbol{\rho}_1\times\boldsymbol{\rho}_4\right) \quad \text{for} \quad i = 1-3\\
\mathbf{s}^{\phi}_4 &= -\frac{\boldsymbol{\rho}_1\times\boldsymbol{\rho}_4}{r_4\sin^2\theta}
\end{aligned} \tag{40}$$

where the term containing the cross product can be represented by the basis vectors

$$\frac{\boldsymbol{\rho}_1\times\mathbf{r}_4}{\sin\theta} = -\cos\alpha\sin\phi\mathbf{e}_1 - \cos\phi\mathbf{e}_2 + \sin\alpha\sin\phi\mathbf{e}_3$$

The set of **s** and **Ω** vectors derived for a core molecule containing a single inverter is sufficient to construct a complete rovibrational tensor **G**. It is reported in the Appendix 2 (Supporting Information) for a penta-atomic molecule of the NH_2OH type. As mentioned earlier, these vectors can be used to construct the tensor **G** for more complex molecules, containing a few inverters if they are not linked directly, for example, $NH_2-CH_2-NH_2$.

A desired property of the **G** tensor is that it has a factorizable form, being a sum of products of the functions depending on a single coordinate. The **G** tensor obtained is factorizable, except for the coordinates τ_2 and τ_3 that enter in the functions $\cot^n(\tau_1/2)$, where $\tau_1 = \tau_3 - \tau_2$ and $n = 1$ and 2. The variational calculations of the rovibrational states require the Hamiltonian

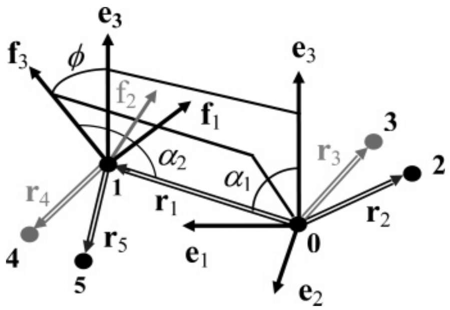

Figure 2. Frame $\mathbf{e}_\alpha$ and top $\mathbf{f}_\alpha$ basis vectors of a molecule with two linked inverters.

matrix elements $\int\Phi_i(\mathbf{q})\,\hat{H}\Phi_j(\mathbf{q})\,J_q\,\mathrm{d}\mathbf{q}$ with some basis functions $\{\Phi_i(\mathbf{q})\}$, which usually are chosen as products of one-coordinate orthogonal functions $\Phi_i(\mathbf{q}) = \prod_{k=1}^{6}\varphi_{n_k}(q_k)$. Thus, $\hat{H}$ expressed by the UL coordinates generates matrix elements that can be reduced to one- and two-dimensional integrals. The last integrals over τ_2 and τ_3 must be calculated by a two-dimensional numerical integration. It is not difficult to calculate numerically such integrals using Gaussian quadratures. Alternatively, as indicated in ref 16, the two-dimensional integration can be avoided using the basis functions weighted by the factor $\sin(\tau_1/2)\,\sin(\tau_2/2)\,\sin(\tau_3/2)$, which transforms $\cot^n(\tau_1/2)$ to the factorizable functions. However, the new weight factor destroys the orthogonality of the initial two-dimensional basis $\{\varphi_{n_2}(\tau_2)\,\varphi_{n_3}(\tau_3)\}$. This problem can be solved by performing numerically the orthogonalization of this basis set modified by the new weight factor.

Another desired feature of **G** is its small Coriolis part, which depends, however, on the MSA choice. An optimum MSA cannot be provided in a general case, because the Coriolis coupling depends strongly on the nuclear masses. For example, the MSA with the one of its axes directed along the $\mathbf{r}_1$ vector would be a good choice for a molecule with the heavy nuclei $i = 0$, 1 and light nuclei $i = 2$, 3, 4. However, for all the heavy nuclei, except for $i = 4$, the better choice would be that shown in Figure 1. The MSA defined in this paper can be adapted to a molecule under consideration by rotating this MSA to minimize the Coriolis coupling. A convenient method of reducing this coupling presented in ref 36 can be applied to an arbitrary molecule. The MSA rotation changes the Coriolis and rotation part of the Hamiltonian according to eqs 19 and 20 of ref 36, whereas the vibrational part of $\hat{H}$ is invariant. Although the Coriolis coupling cannot be cancelled completely, it can be always significantly reduced allowing efficient calculations of the rovibrational energy levels.

IV.3. s Vectors for the Inversion and Torsion Coordinates of Two Linked Inverters. Molecules with two linked inverters, like hydrazine, that can execute the inversion and relative torsion motions can also be described in terms of the frame and top. A core of such a molecule is shown in Figure 2. The frame is defined by the bond vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$, whereas the top involves the vectors $\mathbf{r}_4$ and $\mathbf{r}_5$.

The orientations of the frame and of the top can be conveniently described using two sets of unit vectors attached to these groups: $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ and $(\mathbf{f}_1, \mathbf{f}_2, \mathbf{f}_3)$. The vectors $\mathbf{e}_\alpha$ are defined identically as in the previous case, whereas $\mathbf{f}_\alpha$ are defined as shown in Figure 2. The vector $\mathbf{f}_3$ is a trisector of the pyramidal angle of the top, $\mathbf{f}_1$ lies in the plane $(\mathbf{f}_3, \mathbf{r}_1)$ and is directed toward the 0th central nucleus, and $\mathbf{f}_2 = \mathbf{f}_3\times\mathbf{f}_1$. The internal angular coordinates $(\alpha_2, \tau_4, \tau_5)$ of the top are defined in the analogous way as the coordinates $(\alpha_1, \tau_2, \tau_3)$ of the frame. For example, τ_4 is the dihedral angle between the planes $(\mathbf{f}_3, \mathbf{f}_1)$

and ($\mathbf{r}_4$, $\mathbf{f}_3$). The last angular internal coordinate, namely the torsion angle ϕ, should be introduced to describe the relative orientation of the frame and the top. This angle is defined as a dihedral angle between the planes ($\mathbf{e}_3$, $\mathbf{r}_1$) and ($\mathbf{f}_3$, $-\mathbf{r}_1$).

The internal coordinates (r_1, r_2, r_3, r_4, r_5, α_1, α_2, τ_2, τ_3, τ_4, τ_5, ϕ) introduced for the core molecule behave in a regular way. The search for the bifurcations in hydrazine supported earlier results.[14] No pathology in the three-dimensional flexible model including (α_1, α_2, ϕ) as dynamical variables has been found in the energy region of the bound states.

The coordinates $r^{\mathrm{t}}_{i\alpha}$ of the top nuclei have the simplest form in the local axis system attached to the ($\mathbf{f}_1$, $\mathbf{f}_2$, $\mathbf{f}_3$) frame, namely, for $i = 4, 5$

$$r^{\mathrm{t}}_{ix} = r_i \sin \alpha_2 \cos \tau_i$$

$$r^{\mathrm{t}}_{iy} = r_i \sin \alpha_2 \cos \tau_i$$

$$r^{\mathrm{t}}_{iz} = r_i \cos \alpha_2$$

and for $i = 0$

$$r^{\mathrm{t}}_{0x} = -r_{1x} = r_1 \sin \alpha_2$$

$$r^{\mathrm{t}}_{0y} = -r_{1y} = 0$$

$$r^{\mathrm{t}}_{0z} = -r_{1z} = r_1 \cos \alpha_2$$

These coordinates, expressed in the MSA basis that is common for all the molecule vectors, take the form

$$\begin{bmatrix} r^{t}_{ix'} \\ r^{t}_{iy'} \\ r^{t}_{iz'} \end{bmatrix} = \begin{bmatrix} \mathbf{e}_1\cdot\mathbf{f}_1 & \mathbf{e}_1\cdot\mathbf{f}_2 & \mathbf{e}_1\cdot\mathbf{f}_3 \\ \mathbf{e}_2\cdot\mathbf{f}_1 & \mathbf{e}_2\cdot\mathbf{f}_2 & \mathbf{e}_2\cdot\mathbf{f}_3 \\ \mathbf{e}_3\cdot\mathbf{f}_1 & \mathbf{e}_3\cdot\mathbf{f}_2 & \mathbf{e}_3\cdot\mathbf{f}_3 \end{bmatrix} \begin{bmatrix} r^{\mathrm{t}}_{ix} \\ r^{\mathrm{t}}_{iy} \\ r^{\mathrm{t}}_{iz} \end{bmatrix} \tag{41}$$

where

$$\begin{aligned} \mathbf{e}_1\cdot\mathbf{f}_1 &= \cos\phi \cos\alpha_1 \cos\alpha_2 - \sin\alpha_1 \sin\alpha_2 \\ \mathbf{e}_1\cdot\mathbf{f}_2 &= -\sin\phi \cos\alpha_1 \\ \mathbf{e}_1\cdot\mathbf{f}_3 &= -\cos\phi\cos\alpha_1 \sin\alpha_2 - \sin\alpha_1 \cos\alpha_2 \\ \mathbf{e}_2\cdot\mathbf{f}_1 &= -\sin\phi \cos\alpha_2 \\ \mathbf{e}_2\cdot\mathbf{f}_2 &= -\cos\phi \\ \mathbf{e}_2\cdot\mathbf{f}_3 &= \sin\phi \sin\alpha_2 \\ \mathbf{e}_3\cdot\mathbf{f}_1 &= -\cos\phi \sin\alpha_1 \cos\alpha_2 - \cos\alpha_1 \sin\alpha_2 \\ \mathbf{e}_3\cdot\mathbf{f}_2 &= \sin\phi \sin\alpha_1 \\ \mathbf{e}_3\cdot\mathbf{f}_3 &= \cos\phi \sin\alpha_1 \sin\alpha_2 - \cos\alpha_1 \cos\alpha_2 \end{aligned} \tag{42}$$

Now, let us calculate the velocity of the torsion angle $\dot{\phi}$. It is a sum of two components

$$\dot{\phi} = \dot{\phi}_1 + \dot{\phi}_2$$

where

$$\dot{\phi}_1 = -\frac{\mathbf{e}_2}{\sin\alpha_1}\cdot\left(\dot{\mathbf{e}}_3 - \cos\alpha_1 \frac{\dot{\mathbf{r}}_1}{r_1}\right) = -\sum_{i=1,2,3} \mathbf{b}^{(\mathrm{I})}_i\cdot\dot{\mathbf{r}}_i + \frac{\cot\alpha_1}{r_1}\mathbf{e}_2\cdot\dot{\mathbf{r}}_1$$

The vectors $\mathbf{b}^{(\mathrm{I})}_i$ for the first (I) group are determined according to eq 37. The velocity $\dot{\phi}_2$ can be calculated in a similar way

$$\dot{\phi}_2 = -\frac{\mathbf{f}_2}{\sin\alpha_2}\cdot\left(\dot{\mathbf{f}}_3 - \cos\alpha_2 \frac{\dot{\mathbf{r}}_0}{r_1}\right) = -\sum_{i=0,4,5} \mathbf{b}^{(\mathrm{II})}_i\cdot\dot{\mathbf{r}}_i + \frac{\cot\alpha_2}{r_1}\mathbf{f}_2\cdot\dot{\mathbf{r}}_0$$

where the vectors $\mathbf{b}^{(\mathrm{II})}_i$ for the second (II) group are determined analogously to eq 37 with changing $\mathbf{e}_3$ to $\mathbf{f}_3$, $\boldsymbol{\rho}_0$ to $-\boldsymbol{\rho}_1$, and $\boldsymbol{\rho}_i$ to $\boldsymbol{\rho}_{i+2}$ for $i = 2, 3$. Thus, for $\mathbf{s}^{\phi}_i$-vectors we have

$$\begin{aligned} \mathbf{s}^{\phi}_1 &= \frac{S_{2,1}}{r_1 \sin^2\alpha_1}(\mathbf{e}_3 - \boldsymbol{\rho}_1 \cos\alpha_1) + \frac{\cot\alpha_1}{r_1}\mathbf{e}_2 - \\ &\qquad \frac{S_{2,0}}{r_1 \sin^2\alpha_2}(\mathbf{f}_3 + \boldsymbol{\rho}_1 \cos\alpha_2) - \frac{\cot\alpha_2}{r_1}\mathbf{f}_2 \\ \mathbf{s}^{\phi}_i &= \frac{S_{2,i}}{r_i \sin^2\alpha_1}(\mathbf{e}_3 - \boldsymbol{\rho}_i \cos\alpha_1) \qquad \text{for} \qquad i = 2, 3 \\ \mathbf{s}^{\phi}_i &= -\frac{S_{2,i}}{r_{\mathrm{i}} \sin^2\alpha_2}(\mathbf{f}_3 - \boldsymbol{\rho}_i \cos\alpha_2) \qquad \text{for} \qquad i = 4, 5 \end{aligned} \tag{43}$$

where the structural variables for $i = 0{,}4{,}5$ are determined as

$$\begin{aligned} S_{2,0} &= -\frac{1}{2}\left(\cot\frac{\tau_4}{2} + \cot\frac{\tau_5}{2}\right) \\ S_{2,4} &= \frac{1}{2}\left(\cot\frac{\tau_4}{2} + \cot\frac{\tau_5 - \tau_4}{2}\right) \\ S_{2,5} &= \frac{1}{2}\left(\cot\frac{\tau_5}{2} - \cot\frac{\tau_5 - \tau_4}{2}\right) \end{aligned} \tag{44}$$

Let us write the $\mathbf{s}$ vectors for the top variables. For the local basis $\mathbf{f}_\alpha$ we have

$$(\mathbf{s}^{t})^{\nu}_i = (s^{t})^{\nu}_{i\alpha}\mathbf{i}_\alpha = (s^{t'})^{\nu}_{i\alpha}\mathbf{f}_\alpha$$

where $(s^{t})^{\nu}_{i\alpha}$ and $(s^{t'})^{\nu}_{i\alpha}$ are the components of the $(\mathbf{s}^{t})^{\nu}_i$-vectors relative LSA and the local system of axes *II*, respectively, and a connection between them is

$$(s^{t})^{\nu}_{i\alpha} = (\mathbf{i}_\alpha\cdot\mathbf{f}_\beta)(s^{t'})^{\nu}_{i\beta} = R^{t}_{\alpha\beta}(s^{t'})^{\nu}_{i\beta}$$

Here $R^{t}_{\alpha\beta}$ is a matrix of direction cosines of the top basis with respect to LSA, and $(q_\nu) = (r_1, r_4, r_5, \alpha_2, \tau_4, \tau_5)$. Taking into account the equality $\boldsymbol{\rho}_0 = -\boldsymbol{\rho}_1$ we have also

$$(s^{t})^{\nu}_{0\alpha} = -(s^{t})^{\nu}_{1\alpha}$$

To find $(s^{t'})^{\nu}_{i\alpha} = \partial q_\nu/\partial r^{t}_{i\alpha}$, we transform the momentum operators to the internal variables using the method analogous to that applied to the frame momentum operators. As a result, the top **s** vectors, with the superscript *t* dropped, can be written as

$$\mathbf{s}_i^{r_j} = \delta_{i,j}\boldsymbol{\rho}_j \qquad \text{for} \qquad i, j = 4, 5$$

$$\mathbf{s}_1^{\alpha_2} = -\mathbf{s}_0^{\alpha_2} = -\frac{(S_{1,0} - 1)(\mathbf{f}_3 + \boldsymbol{\rho}_1 \cos \alpha_2)}{r_1 \sin \alpha_2} \tag{45}$$

$$\mathbf{s}_i^{\alpha_2} = \frac{S_{1,i}(\mathbf{f}_3 - \boldsymbol{\rho}_i \cos \alpha_2)}{r_i \sin \alpha_2} \qquad \text{for} \qquad i = 4, 5$$

$$\mathbf{s}_1^{\tau_4} = -\mathbf{s}_0^{\tau_4} = -\frac{T_{4,0}(\mathbf{f}_3 + \boldsymbol{\rho}_1 \cos \alpha_2) - \mathbf{f}_2}{r_1 \sin \alpha_2}$$

$$\mathbf{s}_i^{\tau_4} = \frac{T_{4,i}(\mathbf{f}_3 - \boldsymbol{\rho}_i \cos \alpha_2) + \delta_{i,4}(\cos \tau_i \mathbf{f}_2 - \sin \tau_i \mathbf{f}_1)}{r_i \sin \alpha_2} \qquad \text{for} \qquad i = 4, 5$$

$$\mathbf{s}_1^{\tau_5} = -\mathbf{s}_0^{\tau_5} = -\frac{T_{5,0}(\mathbf{f}_3 + \boldsymbol{\rho}_1 \cos \alpha_2) - \mathbf{f}_2}{r_1 \sin \alpha_2}$$

$$\mathbf{s}_i^{\tau_5} = \frac{T_{5,i}(\mathbf{f}_3 - \boldsymbol{\rho}_i \cos \alpha_2) + \delta_{i,5}(\cos \tau_i \mathbf{f}_2 - \sin \tau_i \mathbf{f}_1)}{r_i \sin \alpha_2} \qquad \text{for} \qquad i = 4, 5$$

The new structural coefficients introduced for the top are

$$S_{1,0} = -\frac{1}{2}\left(\cot\frac{\tau_4}{2}\cot\frac{\tau_5}{2} - 1\right)$$

$$S_{1,4} = \frac{1}{2}\left(\cot\frac{\tau_4}{2}\cot\frac{\tau_5 - \tau_4}{2} - 1\right) \tag{46}$$

$$S_{1,5} = -\frac{1}{2}\left(\cot\frac{\tau_5}{2}\cot\frac{\tau_5 - \tau_4}{2} + 1\right)$$

$$T_{4,0} = \cot \alpha_2 \cot \frac{\tau_5}{2} \qquad T_{4,4} = -\cot \alpha_2 \cot \frac{\tau_5 - \tau_4}{2}$$

$$T_{4,5} = -T_{4,0} - T_{4,4}$$

$$T_{5,0} = \cot \alpha_2 \cot \frac{\tau_4}{2}$$

$$T_{5,4} = -\cot \alpha_2\left(\cot\frac{\tau_4}{2} + \cot\frac{\tau_5 - \tau_4}{2}\right)$$

$$T_{5,5} = -T_{5,0} - T_{5,4}$$

To derive the matrix **G**, it is necessary to find the dot products of the basis vectors with each other and with the unit bond vectors, i.e., $\mathbf{e}_\alpha \cdot \mathbf{f}_\beta$, $\mathbf{e}_\alpha \cdot \boldsymbol{\rho}_i$, and $\mathbf{f}_\alpha \cdot \boldsymbol{\rho}_i$ for $i = 1-5$. The scalar products $\mathbf{e}_\alpha \cdot \mathbf{f}_\beta$ are given above, and the remaining ones are

for $i = 1$

$$\begin{aligned} \mathbf{e}_1 \cdot \boldsymbol{\rho}_1 &= \sin \alpha_1 & \mathbf{f}_1 \cdot \boldsymbol{\rho}_1 &= -\sin \alpha_2 \\ \mathbf{e}_2 \cdot \boldsymbol{\rho}_1 &= 0 & \mathbf{f}_2 \cdot \boldsymbol{\rho}_1 &= 0 \\ \mathbf{e}_3 \cdot \boldsymbol{\rho}_1 &= \cos \alpha_1 & \mathbf{f}_3 \cdot \boldsymbol{\rho}_1 &= -\cos \alpha_2 \end{aligned} \tag{47}$$

for $i = 2, 3$

$$\mathbf{e}_1 \cdot \boldsymbol{\rho}_i = \sin \alpha_1 \cos \tau_i$$

$$\mathbf{e}_2 \cdot \boldsymbol{\rho}_i = \sin \alpha_1 \sin \tau_i$$

$$\mathbf{e}_3 \cdot \boldsymbol{\rho}_i = \cos \alpha_1$$

$$\begin{aligned} \mathbf{f}_1 \cdot \boldsymbol{\rho}_i = {} & -\sin \alpha_2(\cos^2 \alpha_1 + \sin^2 \alpha_1 \cos \tau_i) - \\ & \sin \alpha_1 \cos \alpha_2[\cos \alpha_1 \cos \phi(1 - \cos \tau_i) + \sin \phi \sin \tau_i] \end{aligned}$$

$$\mathbf{f}_2 \cdot \boldsymbol{\rho}_i = \sin \alpha_1[\cos \alpha_1 \sin \phi(1 - \cos \tau_i) - \cos \phi \sin \tau_i]$$

$$\begin{aligned} \mathbf{f}_3 \cdot \boldsymbol{\rho}_i = {} & -\cos \alpha_2(\cos^2 \alpha_1 + \sin^2 \alpha_1 \cos \tau_i) + \\ & \sin \alpha_1 \sin \alpha_2[\cos \alpha_1 \cos \phi(1 - \cos \tau_i) + \sin \phi \sin \tau_i] \end{aligned}$$

for $i = 4, 5$

$$\mathbf{f}_1 \cdot \boldsymbol{\rho}_i = \sin \alpha_2 \cos \tau_i$$

$$\mathbf{f}_2 \cdot \boldsymbol{\rho}_i = \sin \alpha_2 \sin \tau_i$$

$$\mathbf{f}_3 \cdot \boldsymbol{\rho}_i = \cos \alpha_2$$

$$\begin{aligned} \mathbf{e}_1 \cdot \boldsymbol{\rho}_i = {} & -\sin \alpha_1(\cos^2 \alpha_2 + \sin^2 \alpha_2 \cos \tau_i) - \\ & \cos \alpha_1 \sin \alpha_2[\cos \alpha_2 \cos \phi(1 - \cos \tau_i) + \sin \phi \sin \tau_i] \end{aligned}$$

$$\mathbf{e}_2 \cdot \boldsymbol{\rho}_i = \sin \alpha_2[\cos \alpha_2 \sin \phi(1 - \cos \tau_i) - \cos \phi \sin \tau_i]$$

$$\begin{aligned} \mathbf{e}_3 \cdot \boldsymbol{\rho}_i = {} & -\cos \alpha_1(\cos^2 \alpha_2 + \sin^2 \alpha_2 \cos \tau_i) + \\ & \sin \alpha_1 \sin \alpha_2[\cos \alpha_2 \cos \phi(1 - \cos \tau_i) + \sin \phi \sin \tau_i] \end{aligned}$$

For the internal coordinates of the frame $q_I = (r_1, r_2, r_3, \alpha_1, \tau_2, \tau_3)$ we have already derived the Jacobian in the form of eq 19 with α replaced by α_1. To determine the contribution of the internal coordinates of the top $q_{II} = (r_4, r_5, \alpha_2, \tau_4, \tau_5, \phi)$ to the Jacobian, let us notice that the transformation from the Cartesian coordinates of the top $r_{i\alpha}^t$ to its valence coordinates $q_{II}^{\mathrm{V}} = (r_4, r_5, \cos \theta_{14}, \cos \theta_{15}, \tau_{45}, \phi)$ has the Jacobian

$$J_{\mathrm{V}}^{II} = r_4^{\,2} r_5^{\,2} \sin \theta_{14} \sin \theta_{15}$$

The dihedral angles τ_{45}, ϕ are the azimuthal angles so their contribution to the Jacobian equals 1. Now, let us make the transition from the valence angles to the umbrella-like angles $\theta_{14}, \theta_{15}, \tau_{45} \longmapsto \alpha_2, \tau_4, \tau_5$. As a result, we get the Jacobian that takes a similar form as for the frame

$$J_{\mathrm{UL}}^{II} = 4 r_4^{\,2} r_5^{\,2} \sin^3 \alpha_2 \sin \frac{\tau_4}{2} \sin \frac{\tau_5}{2} \sin \frac{\tau_5 - \tau_4}{2} \tag{48}$$

The full Jacobian J_q including the contribution from the top and frame is the product $J_{\mathrm{UL}}^{I} J_{\mathrm{UL}}^{II}$. The determined Jacobian and the **s** and Ω vectors for the considered "core" molecule are sufficient to write down its rovibrational tensor **G** and the corresponding operator $\hat{T}$.

V. Conclusions

In this paper a new exact quantum mechanical rovibrational Hamiltonian operator for molecules exhibiting large amplitude inversion and torsion motions is derived. To derive it, we use the method exploiting the idea of the rotational invariance, allowing us to express the angular momentum operators directly by the elements of the rotation matrix. It is practical in applications because all complications resulting from implementing explicitly the Euler angles disappear. This method allows us to represent the Hamiltonian in some canonical form, which delivers the users from the necessity to carry out the laborious work to derive the Hamiltonian for a chosen internal coordinates and MSA. The whole analytical work is focused on derivation of the **s** and **Ω** vectors that is a simple enough task. The canonical form of the Hamiltonian is determined in terms of the scalar products of these vectors, that is, an elementary operation, although cumbersome. We have shown on the example of the polyspherical coordinates, the simplicity and efficiency of the proposed derivation procedure.

The **s** and **Ω** vectors are reported for the core molecules with one and two linked inverters. These vectors, together with the vectors for polyspherical coordinates reported here and the known vectors for the standard valence coordinates, are sufficient for the construction of the rovibrational **G** tensor for a variety of polyatomic molecules with many inverters.

Supporting Information Available: Appendix 1 describing the coordinate and momenta transformations. Appendix 2 defining the analytical **G** tensor for a penta-atomic molecule, like NH_2OH with one inverter. This material is available free of charge via the Internet at http://pubs.acs.org.

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