The Journal of Chemical Physics

RESEARCH ARTICLE | DECEMBER 18 2023

A general expression for vibrational Hamiltonians expressed in oblique coordinates

Mark A. Boyer ; Edwin L. Sibert, III

J. Chem. Phys. 159, 234108 (2023)
https://doi.org/10.1063/5.0181135

AIP Publishing

The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

A general expression for vibrational Hamiltonians expressed in oblique coordinates

Cite as: J. Chem. Phys. 159, 234108 (2023); doi: 10.1063/5.0181135
Submitted: 14 October 2023 • Accepted: 29 November 2023 •
Published Online: 18 December 2023

Mark A. Boyer[a] and Edwin L. Sibert III[b]

AFFILIATIONS

Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

[a]maboyer2@wisc.edu
[b]Author to whom correspondence should be addressed: elsibert@wisc.edu

ABSTRACT

We examine the properties of oblique coordinates. The coordinates, introduced by Zúñiga *et al.* [J. Phys. B: At., Mol. Opt. Phys. **52**, 055101, (2019)], reduce vibrational mode-mixing and enhance the quality of vibrational assignments in quantum mechanical investigations of two-dimensional model Hamiltonians. Oblique coordinates are obtained by making non-orthogonal rotations of the original coordinates that convert the matrix representation of the quadratic Hamiltonian operator into a block-diagonal matrix where the blocks are distinguished by the total quanta of vibrational excitation. Using techniques for the polar decomposition of matrices, we present a scheme for finding these coordinates for systems of arbitrary dimensions. Several molecular examples are presented that highlight the advantages of these coordinates.

I. INTRODUCTION

The choice of coordinates is central to optimal theoretical treatments of molecular vibrations.[1–8] Early works focused on improving self-consistent field treatments of molecular vibrations by rotating the normal coordinates.[1,2] McCoy and Sibert[3] compared the convergence of perturbative results for curvilinear and rectilinear normal coordinates of linear molecules, demonstrating the advantages of the curvilinear representation in instances of strong couplings. Mayrhofer and Sibert[9] extended those ideas by varying the curvature of the coordinates. Bastida *et al.*[10] generalized a class of orthogonal coordinates known as hyperspherical coordinates to improve the vibrational assignments of the eigenstates of triatomic molecules. Joubert-Doriol *et al.*,[4] focusing on multiconfiguration time-dependent Hartree methods, considered a range of molecular systems to illustrate the implications of these choices and the advantages they incur. Cheng and Steele[11] describe algorithms for defining local modes and convincingly demonstrate the advantages of treating anharmonicities in these modes vs normal modes. In related work, Molina *et al.*[12] and Zimmerman and Smereka[5] selected two criteria for the optimal rotation of local coordinates that, in an unbiased way, highlight the interplay between minimizing quadratic couplings via the normal modes and minimizing anharmonic couplings via local modes.

The goal of all these studies is to find coordinates that lead to enhanced separability of the molecular wavefunctions in order to ease the interpretation of spectra and dynamics, as well as to provide a Hamiltonian matrix that is easy to express and whose lowest energy eigenfunctions are obtained with a minimal number of basis functions. With this goal in mind, Zúñiga *et al.*[7,8] examined a set of coordinates, which they call the oblique coordinates. In contrast to many of the above-mentioned studies, which focused on orthogonal rotations of coordinates, these latter studies explicitly focused on how one might scale or skew the coordinates in order to minimize couplings. A distinguishing feature of the oblique coordinates is that the Hamiltonian matrix is block-diagonal at the harmonic level; each block contains states with the same total number of vibrational quanta of excitation. This feature reduces the mixing due to the quadratic terms. In addition, the avoidance of coordinate rotation from the initial internal coordinates leaves the large anharmonic couplings, which are mostly diagonal in internal coordinates, as diagonal couplings in the oblique coordinates. These authors clearly demonstrate the advantages of this coordinate set for two-dimensional systems but have not yet extended the idea to multiple dimensions. In this paper, we do just that.

This paper is organized as follows. In Sec. II, we define oblique coordinates in terms of linear transformations from internal coordinates. In Sec. III, we present the equations for these coordinates

using techniques for the polar decomposition of matrices. We use the formaldehyde and ammonia molecules to illustrate the properties of these coordinates in Sec. IV and summarize our findings in Sec. V.

II. BACKGROUND

We take as our starting point the classical form for a harmonic, internal coordinate Hamiltonian expressed in internal coordinates **r** and conjugate momenta **p** using the notation of Wilson *et al.*,[13]

$$H = \frac{1}{2}\left[\mathbf{p}^{\mathrm{T}}\mathbf{g}\mathbf{p} + \mathbf{r}^{\mathrm{T}}\mathbf{f}\mathbf{r}\right]. \tag{1}$$

If we scale the coordinates $R_i = [f_{ii}/g_{ii}]^{1/4} r_i$, this leads to a Hamiltonian with the same form

$$H = \frac{1}{2}\left[\mathbf{P}^{\mathrm{T}}\mathbf{G}\mathbf{P} + \mathbf{R}^{\mathrm{T}}\mathbf{F}\mathbf{R}\right], \tag{2}$$

but with

$$\omega_i = F_{ii} = G_{ii} = \sqrt{f_{ii}g_{ii}}. \tag{3}$$

Writing the above Hamiltonian in terms of raising and lowering operators

$$R_i = \left[\frac{\hbar}{2}\right]^{1/2}(a_i^\dagger + a_i), \tag{4}$$

one obtains

$$\hat{H}/\hbar = \sum_{i=1}^{N}\omega_i\left(a_i^\dagger a_i + \frac{1}{2}\right) + \sum_{i\neq j}(F_{ij}+G_{ij})(a_i^\dagger a_j + a_i a_j^\dagger)/2 + \sum_{i\neq j}(F_{ij}-G_{ij})(a_i^\dagger a_j^\dagger + a_i a_j)/2. \tag{5}$$

The first term describes the diagonal harmonic contribution; the second term describes the coupling between states with the same total number of quanta; and the last term describes the coupling between states differing in the total number of quanta by two. If **F** = **G**, then the last term is zero, and the Hamiltonian matrix is block-diagonal. As an example, states corresponding to the fundamentals are decoupled from all other states. In a local mode treatment, this scenario is desirable since the coupling is restricted.[7,8]

To find a representation with the above-mentioned property, we note that a linear transformation

$$\mathbf{R}' = \mathbf{A}\mathbf{R}; \qquad \mathbf{P}' = [\mathbf{A}^{-1}]^{\mathrm{T}}\mathbf{P}, \tag{6}$$

leads to a Hamiltonian with a form identical to that of Eq. (2) but with

$$\mathbf{G}' = \mathbf{A}\mathbf{G}\mathbf{A}^{T}; \qquad \mathbf{F}' = [\mathbf{A}^{-1}]^{T}\mathbf{F}A^{-1}. \tag{7}$$

As such, the goal of this work is to find transformations **A** that lead to **F**′ = **G**′.

III. DERIVATION OF OBLIQUE COORDINATES

We note that if a Hamiltonian has **F** = **G**, then any orthogonal transformation of the coordinates leads to a Hamiltonian that also has this form. Zúñiga *et al.*[7] also recognized this flexibility in their study of two-dimensional Hamiltonians. The best-known members of this class of Hamiltonians are the scaled normal coordinates. If **R**′ are the normal coordinates, then both the **F**′ and **G**′ matrices are diagonal. The normal coordinates can then be scaled so that $F'_{ii} = G'_{ii}$. With this approach, we can write

$$\mathbf{A}_Q \equiv \mathbf{\Omega}^{1/2}\mathbf{L}^{-1}, \tag{8}$$

where **Ω** is a diagonal scaling matrix whose elements are the normal mode frequencies, and **L** is obtained following the methods of Wilson *et al.*[13] A subscript *Q* has been added to the above **A** matrix to indicate that this is a specific choice of all the possible **A** matrices. This notation allows us to conveniently express all other possible choices for **A** as

$$\mathbf{A} = \mathbf{V}\mathbf{A}_Q, \tag{9}$$

where **V** is an arbitrary orthogonal transformation.

A useful choice for **V** is to choose it so that it yields an **A** that minimizes the differences between the **R** and **R**′ coordinates. To find such a transformation, we turn to the concept of the polar decomposition of matrices.[14] Polar decomposition is a well-studied technique for decomposing a matrix into a product form that has been described as being analogous to writing a complex number in the $re^{i\theta}$ form. The central idea here is that any square matrix **A** can be written in the form **A** = **U**$\mathcal{P}$, where **U** is an orthogonal transformation and

$$\mathcal{P} = [\mathbf{A}^{T}\mathbf{A}]^{1/2}, \tag{10}$$

is a positive semi-definite symmetric matrix. This matrix is readily evaluated with standard techniques for finding square roots of matrices. The most direct route for finding $\mathcal{P}$ follows from the singular value decomposition of **A**. Since **A** is positive semi-definite, the matrix $\mathcal{P}$ is unique.

If **A** = **A**$_Q$, then both **U** and $\mathcal{P}$ have important properties. Of all possible orthogonal transformations **V**, the matrix **U** is the "best" approximation for the transformation from the internal coordinates **R** to the dimensionless normal coordinates. More specifically, the orthogonal transformation **V** that minimizes the Frobenius norm

$$\|\mathbf{A}-\mathbf{V}\|_F = \left[\sum_i\sum_j (A_{ij}-V_{ij})^2\right]^{1/2}, \tag{11}$$

can be shown to be **V** = **U**.

With the above in mind, we now consider a second choice for **A** in addition to that of Eq. (8). We define

$$\mathbf{A}_O \equiv \mathcal{P} = \left[[\mathbf{L}^{-1}]^{T}\mathbf{\Omega}\mathbf{L}^{-1}\right]^{1/2}. \tag{12}$$

We refer to the coordinates obtained via this transformation as the oblique coordinates. If **A** = **A**$_O$ in Eq. (11), then the orthogonal

matrix **V** that best describes $\mathbf{A}_O$ is the identity matrix. Of all possible orthogonal transformations **V**, the identity matrix is the "best" approximation for the transformation from the internal coordinates **R** to the oblique coordinates.

The main ideas can now be summarized. Equation (9) defines the linear transformations that lead to $\mathbf{F}' = \mathbf{G}'$. The transformation to scaled normal modes $\mathbf{A}_Q$ is one of the possible choices for **A**, and all other choices can be obtained by multiplying $\mathbf{A}_Q$ by an orthogonal matrix. The oblique coordinates are defined by the polar decomposition of $\mathbf{A}_Q$. This decomposition allows us to write the normal mode transformation of Eq. (8) as a product of an orthogonal transformation **U** and a symmetric, positive, semi-definite matrix $\mathbf{A}_O$. In order to minimize the difference between the oblique coordinates and the scaled internal coordinates, we choose the transformation matrix for the oblique coordinates to be $\mathbf{A}_O$.

The oblique coordinates are not unique. The oblique coordinates, as we define them, are defined relative to the initial internal coordinates **R**. Since there is more than one way to choose the internal coordinates of a molecule, there is also more than one way to choose the oblique coordinates. All of the inherent advantages and difficulties of choosing an initial set of internal coordinates extend to the choice of oblique coordinates. The oblique coordinates simply provide a way to improve upon the initial choice of internal coordinates.

IV. MOLECULAR EXAMPLES AND DISCUSSION

In this section and in the supplementary material, we show several examples that illustrate that the oblique coordinates are often similar to the internal coordinates yet offer the advantage of reduced couplings. Two additional properties of this transformation are that the transformation does not change the underlying symmetry present in the initial internal coordinates, and if one chooses to transform from the oblique coordinates to the normal coordinates, then the mixing that occurs between the oblique coordinates is the result of an orthogonal transformation.

In the examples that follow, the **F** matrices have been evaluated at the MP2/aug-cc-pvDZ level of theory/basis using the Gaussian 16 software package,[15] and the **G** matrices have been evaluated via numerical differentiation of the internal coordinates.

A. H_2CO example

To start, we consider the subspace of internal coordinates of formaldehyde containing the OC stretch, the CH stretches, and the OCH bends. The hydrogen out-of-plane motion has been excluded from the analysis as it has different symmetry and, therefore, does not mix with the other coordinates in this treatment. The initial **F** and **G** matrices in dimensionless internal modes are

$$\mathbf{F} = \begin{pmatrix} 1744.2 & 142.1 & 142.1 & 196.7 & 196.7 \\ & 3031.0 & 35.6 & -52.0 & -138.4 \\ & & 3031.0 & -138.4 & -52.0 \\ & & & 1478.8 & 513.0 \\ & & & & 1478.8 \end{pmatrix}, \quad (13)$$

$$\mathbf{G} = \begin{pmatrix} 1744.2 & -253.8 & -253.8 & -264.2 & -264.2 \\ & 3031.0 & -105.6 & -116.5 & 251.0 \\ & & 3031.0 & 251.0 & -116.5 \\ & & & 1478.8 & -188.2 \\ & & & & 1478.8 \end{pmatrix}. \quad (14)$$

In these matrices, the first row is the OC stretch, the next two are the CH stretches, and the remaining two are the OCH bends. By definition, the diagonal elements of these two matrices are identical; only the upper triangle is provided, as the matrices are necessarily symmetric.

After applying a polar decomposition to the normal mode transformation obtained by a Wilson FG analysis, we obtain the oblique transformation

$$\mathbf{A}_O = \begin{pmatrix} 1.014 & 0.042 & 0.042 & 0.075 & 0.075 \\ & 1.003 & 0.012 & 0.007 & -0.038 \\ & & 1.003 & -0.038 & 0.007 \\ & & & 1.002 & 0.125 \\ & & & & 1.002 \end{pmatrix}, \quad (15)$$

that transforms **F** and **G** into

$$\mathbf{F}' = \mathbf{G}' = \begin{pmatrix} 1694.7 & -49.8 & -49.8 & -53.2 & -53.2 \\ & 3013.8 & -40.7 & -74.6 & 39.8 \\ & & 3013.8 & 39.8 & -74.6 \\ & & & 1411.7 & 152.2 \\ & & & & 1411.7 \end{pmatrix}. \quad (16)$$

The above symmetric matrix $\mathbf{A}_O$ is nearly the identity matrix—that is, it introduces only a small skew to the internal coordinates.

As noted earlier, $\mathbf{F}' = \mathbf{G}'$ may be diagonalized to obtain an orthogonal transformation to the normal mode coordinates. In addition, the oblique coordinates retain the symmetries of the internal coordinates, i.e., the CH stretches remain degenerate, as do the OCH bends, and the coupling between one CH stretch and its corresponding OCH bend is identical to the coupling between the other CH stretch and its corresponding bend. More concretely, if we define symmetry coordinates $\mathbf{S} = \mathbf{UR}$ where **U** is a unitary transformation that leads to a block-diagonal matrix $\mathbf{UFU}^\dagger$, then $\mathbf{UF}'\mathbf{U}^\dagger$ will also be block-diagonal.

In many systems, the optimal choice of internal coordinates depends on the problem one is trying to solve. We illustrate how these choices affect the oblique coordinates for NH_3 directly below and for the water dimer in the supplementary material. We also provide in the supplementary material a Python script that can be used for carrying out the transformations described in this paper.

B. Ammonia

Ammonia has a natural set of symmetry preserving internal coordinates, with three NH stretches and three HNH scissor modes (bends),

$$\mathbf{F} = \begin{pmatrix} 3608.5 & -27.7 & -27.7 & 255.0 & 255.0 & 43.3 \\ & 3608.5 & -27.7 & 255.0 & 43.3 & 255.0 \\ & & 3608.5 & 43.3 & 255.0 & 255.0 \\ & & & 1480.0 & -132.9 & -132.9 \\ & & & & 1480.0 & -132.9 \\ & & & & & 1480.0 \end{pmatrix}, \quad (17)$$

$$\mathbf{G} = \begin{pmatrix} 3608.5 & -69.9 & -69.9 & -104.0 & -104.0 & 84.4 \\ & 3608.5 & -69.9 & -104.0 & 84.4 & -104.0 \\ & & 3608.5 & 84.4 & -104.0 & -104.0 \\ & & & 1480.0 & -262.7 & -262.7 \\ & & & & 1480.0 & -262.7 \\ & & & & & 1480.0 \end{pmatrix}. \quad (18)$$

Applying an oblique transformation to these **F** and **G** matrices, one obtains

$$\mathbf{F}' = \begin{pmatrix} 3595.3 & -54.4 & -54.4 & 72.0 & 72.0 & 56.5 \\ & 3595.3 & -54.4 & 72.0 & 56.5 & 72.0 \\ & & 3595.3 & 56.5 & 72.0 & 72.0 \\ & & & 1464.0 & -205.0 & -205.0 \\ & & & & 1464.0 & -205.0 \\ & & & & & 1464.0 \end{pmatrix}. \quad (19)$$

One can see that for this set of coordinates, one retains the inherent symmetries on the NH stretches and HNH bends.

As an aside, we note that Hamiltonian matrices of the above-mentioned form also appear in local mode treatments of CH stretches and HCH bends.[6,16,17] This form is desired due to its simplicity for interpreting couplings while nearly retaining the equivalency to normal mode results upon diagonalization of the local mode Hamiltonian matrices. The slight difference from the normal mode results is due to neglecting those terms analogous to those in the last line of Eq. (5). This approximation is a good one for CH stretches and HCH bends since the bilinear couplings are typically smaller in magnitude (~30 cm^{-1}) and the coupled states are distant in energy. For the above-mentioned case of the ammonia HNH bend vibrations, the analogous couplings are substantially larger and cannot be ignored. In order to express the local mode HNH vibrations with small Hamiltonian matrices, it is necessary to use oblique coordinates.

The transformation matrix

$$\mathbf{A}_O = \begin{pmatrix} 1.000 & 0.002 & 0.002 & 0.037 & 0.037 & 0.000 \\ & 1.000 & 0.002 & 0.037 & 0.000 & 0.037 \\ & & 1.000 & 0.000 & 0.037 & 0.037 \\ & & & 1.004 & 0.023 & 0.023 \\ & & & & 1.004 & 0.023 \\ & & & & & 1.004 \end{pmatrix} \quad (20)$$

is similar to the identity matrix as it was for formaldehyde.

This choice of coordinates, however, cannot be written as a single set of angle-bend-dihedral coordinates as encoded by a single Z-matrix. Using a naïve set of Z-matrix coordinates with three NH stretches, two HNH bends, and one dihedral angle, the symmetry is not preserved, as is evident in the following **F** and **G** matrices:

$$\mathbf{F} = \begin{pmatrix} 3608.5 & -27.7 & -27.7 & 225.1 & 225.1 & 43.1 \\ & 3608.5 & -27.7 & 143.8 & -57.0 & 253.9 \\ & & 3608.5 & -57.0 & 143.8 & 253.9 \\ & & & 1646.2 & 196.2 & -692.0 \\ & & & & 1646.2 & -692.0 \\ & & & & & 1467.0 \end{pmatrix}, \quad (21)$$

$$\mathbf{G} = \begin{pmatrix} 3608.5 & -69.9 & -69.9 & -109.7 & -109.7 & 0.0 \\ & 3608.5 & -69.9 & -109.7 & 89.0 & -112.5 \\ & & 3608.5 & 89.0 & -109.7 & -112.5 \\ & & & 1646.2 & -292.3 & 244.6 \\ & & & & 1646.2 & 244.6 \\ & & & & & 1467.0 \end{pmatrix}. \quad (22)$$

This choice of coordinates leads to

$$\mathbf{F}' = \begin{pmatrix} 3596.6 & -53.0 & -53.0 & 55.6 & 55.6 & 65.1 \\ & 3596.7 & -53.1 & 45.9 & 32.3 & 84.4 \\ & & 3596.7 & 32.3 & 45.9 & 84.4 \\ & & & 1545.9 & -123.1 & -214.4 \\ & & & & 1545.9 & -214.4 \\ & & & & & 1296.2 \end{pmatrix}, \quad (23)$$

for which there is a break in the degeneracy of the NH stretches. While initially concerning, this symmetry breaking demonstrates that the oblique transformation preserves the total symmetry of the chosen coordinates, allowing breaks in symmetry to be detected before the normal modes are constructed by mixing the coordinates. As in the above-mentioned cases,

$$\mathbf{A}_O = \begin{pmatrix} 1.000 & 0.003 & 0.003 & 0.035 & 0.035 & 0.007 \\ & 1.000 & 0.002 & 0.025 & -0.011 & 0.039 \\ & & 1.000 & -0.011 & 0.025 & 0.039 \\ & & & 0.995 & 0.065 & -0.169 \\ & & & & 0.995 & -0.169 \\ & & & & & 0.972 \end{pmatrix} \quad (24)$$

is similar to the identity matrix, despite the presence of much larger off-diagonal couplings between the bends and dihedral angles.

Since the transformation from internal coordinates to oblique coordinates is linear, the corresponding quantum mechanical Hamiltonians have forms that are similar to the analogous forms used for internal coordinates, whether they be defined as linear combinations of Cartesian displacements, in which case one uses a

Watson Hamiltonian,[18] or true bond/angle extension coordinates, in which case one can follow the strategies of Meyer and Günthard.[19]

V. SUMMARY

In this paper, we extend the work of Zúñiga *et al.*,[7,8] who demonstrated the utility of a class of coordinates, which they call oblique coordinates. They highlight many of the interesting properties of these coordinates and convincingly show that these coordinates lead to reduced couplings in two-dimensional Hamiltonians. These coordinates resemble internal coordinates but have the distinguishing feature that the off-diagonal quadratic couplings lead to Hamiltonian matrices that are block-diagonal, where each block is distinguished by the total number of vibrational quanta. In this paper, we generalize their work to multi-dimensional Hamiltonians using ideas taken from the polar decomposition of matrices in order to derive the linear transformation matrix between oblique and internal coordinates. We have highlighted the properties of the transformation and provided several examples to illustrate the central ideas.

We have not illustrated the advantages of these coordinates generally for treating anharmonicities, as we are building on the previous studies of Zúñiga *et al.* on specific systems in which state assignments are improved with these coordinates.[7,8] We expect the coordinates to be most useful when one wishes to examine dynamics in local representations where anharmonic effects are not dominant and where quadratic couplings are relatively large. The scissor vibrations of ammonia were discussed as an example of such a scenario.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional examples of oblique coordinates as well as a Python script for finding these coordinates.

ACKNOWLEDGMENTS

MAB and ELS gratefully acknowledge support from NSF via Grant No. CHE-1900095.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Mark A. Boyer: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal). **Edwin L. Sibert III**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Writing – original draft (equal).

DATA AVAILABILITY

All data that support the findings of this study are available in the article or in the supplementary material.

REFERENCES

[1]T. C. Thompson and D. G. Truhlar, "Optimization of vibrational coordinates, with an application to the water molecule," J. Chem. Phys. **77**(6), 3031–3035 (1982).
[2]Z. Bacic, R. B. Gerber, and M. A. Ratner, "Vibrational levels and tunneling dynamics by the optimal coordinates, self-consistent field method: A study of hydrocyanic acid ⇄ hydroisocyanic acid," J. Phys. Chem. **90**(16), 3606–3612 (1986).
[3]A. B. McCoy and E. L. Sibert, "Perturbative calculations of vibrational (J = 0) energy levels of linear molecules in normal coordinate representations," J. Chem. Phys. **95**(5), 3476–3487 (1991).
[4]L. Joubert-Doriol, B. Lasorne, F. Gatti, M. Schröder, O. Vendrell, and H. D. Meyer, "Suitable coordinates for quantum dynamics: Applications using the multiconfiguration time-dependent Hartree (MCTDH) algorithm," Comput. Theor. Chem. **990**, 75–89 (2012).
[5]P. M. Zimmerman and P. Smereka, "Optimizing vibrational coordinates to modulate intermode coupling," J. Chem. Theory Comput. **12**(4), 1883–1891 (2016).
[6]E. L. Sibert, "Modeling vibrational anharmonicity in infrared spectra of high frequency vibrations of polyatomic molecules," J. Chem. Phys. **150**(9), 090901 (2019).
[7]J. Zúñiga, A. Bastida, and A. Requena, "Quantum solutions of identical linearly coupled harmonic oscillators using oblique coordinates," J. Phys. B: At., Mol. Opt. Phys. **52**(5), 055101 (2019).
[8]J. Zúñiga, A. Bastida, and A. Requena, "Quantum description of linearly coupled harmonic oscillator systems using oblique coordinates," J. Phys. B: At., Mol. Opt. Phys. **53**(2), 025101 (2020).
[9]R. C. Mayrhofer and E. L. Sibert, "Investigating optimal coordinates for describing vibrational motion," Theor. Chim. Acta **92**(2), 107–122 (1995).
[10]A. Bastida, A. Requena, and J. Zuñiga, "Generalized hyperspherical coordinates for molecular vibrations," J. Phys. Chem. **97**(22), 5831–5835 (1993).
[11]X. Cheng and R. P. Steele, "Efficient anharmonic vibrational spectroscopy for large molecules using local-mode coordinates," J. Chem. Phys. **141**(10), 104105 (2014).
[12]A. Molina, P. Smereka, and P. M. Zimmerman, "Exploring the relationship between vibrational mode locality and coupling using constrained optimization," J. Chem. Phys. **144**(12), 124111 (2016).
[13]E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
[14]N. J. Higham, C. Mehl, and F. Tisseur, "The canonical generalized polar decomposition," SIAM J. Matrix Anal. Appl. **31**(4), 2163–2180 (2010).
[15]M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji *et al.*, *GAUSSIAN 16 Revision C.01*, Gaussian Inc., Wallingford, CT, 2016.
[16]D. P. Tabor, D. M. Hewett, S. Bocklitz, J. A. Korn, A. J. Tomaine, A. K. Ghosh, T. S. Zwier, and E. L. Sibert III, "Anharmonic modeling of the conformation-specific IR spectra of ethyl, *n*-propyl, and *n*-butylbenzene," J. Chem. Phys. **144**(22), 224310 (2016).
[17]P. F. Bernath and E. L. Sibert III, "Cyclohexane vibrations: High-resolution spectra and anharmonic local mode calculations," J. Phys. Chem. A **124**(48), 9991–10000 (2020).
[18]J. K. G. Watson, "Simplification of the molecular vibration-rotation Hamiltonian," Mol. Phys. **100**(1), 47–54 (2002).
[19]R. Meyer and H. S. H. Günthard, "General internal motion of molecules, classical and quantum-mechanical Hamiltonian," J. Chem. Phys. **49**(4), 1510–1520 (1968).