Internal-to-Cartesian Back Transformation of Molecular Geometry Steps Using High-Order Geometric Derivatives

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In geometry optimizations and molecular dynamics calculations, it is often necessary to transform a geometry step that has been determined in internal coordinates to Cartesian coordinates. A new method for performing such transformations, the high-order path-expansion (HOPE) method, is here presented. The new method treats the nonlinear relation between internal and Cartesian coordinates by means of automatic differentiation. The method is reliable, applicable to any system of internal coordinates, and computationally more efficient than the traditional method of iterative back transformations. As a bonus, the HOPE method determines not just the Cartesian step vector but also a continuous step path expressed in the form of a polynomial, which is useful for determining reaction coordinates, for integrating trajectories, and for visualization. © 2013 Wiley Periodicals, Inc.

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Introduction

The choice of the coordinate system is of paramount importance in molecular geometry optimizations. Typically, the use of internal coordinates \( q \) results in more efficient and reliable optimizations than does the use of Cartesian coordinates \( x \).[1,2] Being more “natural” or “chemical” than the rectilinear Cartesian coordinates, the curvilinear internal coordinates lead to smaller coupling constants and smaller anharmonicities than do the Cartesian coordinates. Internal coordinates are therefore the preferred coordinates in molecular geometry optimizations.

In a gradient-based molecular geometry optimization in internal coordinates, each iteration consists of the following four main steps:

1. calculation of the molecular electronic energy and its geometric derivatives at a given geometry \( x_0 \) in Cartesian coordinates;
2. definition of the internal coordinate system \( q \) and transformation of quantities such as the molecular gradient and the (approximate) molecular Hessian to this system as needed;
3. determination of the molecular geometry step \( \Delta q \) in internal coordinates;
4. determination of new Cartesian coordinates \( x_0 + \Delta x \) from \( \Delta q \).

The first of the above four optimization steps may be performed in a variety of different ways (using some standard quantum-chemistry or force-field method) and is not considered further here. The second step, the choice of internal coordinates \( q \), has been widely discussed in the literature and the following proposals have been made: natural internal coordinates,[3,4] redundant internal coordinates,[5,6] delocalized internal coordinates,[7] inverse-power distance coordinates,[8] and quasilinear curvilinear coordinates.[9] Much work has also been devoted to the third step listed above by developing improved ways of determining the geometry step \( \Delta q \)—see, for example, the reviews by Schlegel.[1,2] By contrast, the back transformation of the generated step in internal coordinates \( \Delta q \) to Cartesian coordinates \( \Delta x \) (the fourth step above) has received much less attention.

In this article, we present a new method for performing the back transformation from internal to Cartesian coordinates: the high-order path-expansion (HOPE) method. Apart from being more efficient than the previously developed methods for the back transformation, the HOPE method has the advantage of providing a smooth Cartesian path connecting the old and new geometries in geometry optimizations, classical trajectory calculations, and in calculations of intrinsic reaction coordinates.

In the following, we first describe existing methods for performing the back transformation; subsequently, we describe the HOPE method. The performance of the HOPE method is then demonstrated by applying it to a variety of medium-sized and large molecular systems.

Background

Internal-to-Cartesian back transformations

Let \( q(x) \) denote the internal coordinates associated with a given set of Cartesian coordinates \( x \). For a given internal

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coordinate step $\Delta q$, our task is to find a Cartesian displacement vector $\Delta x$ that satisfies the relation

$$ q(x_0 + \Delta x) = q_0(x_0) + \Delta q. \quad (1) $$

We begin by noting that the $M$ primitive internal coordinates $q_i$ (bond lengths, bond angles, dihedral angles, etc.) are explicit analytic functions of the $3N$ Cartesian coordinates $x$:

$$ q_i = q_i(x), \quad i = 1, 2, \ldots M. \quad (2) $$

Because the mapping from $x$ to $q$ is explicit and known, we can attempt a direct solution of eq. (1) by using Newton’s method. However, two things should be kept in mind. First, in general $M > 3N - 6$, so we have a redundant set of internal coordinates. Therefore, eq. (1) can only be solved in a least-squares sense or in a predetermined subspace of the non-redundant internal coordinates. Second, bond lengths and bond angles are periodic coordinates. Therefore, a step $\Delta q$ that takes a bond angle from 170° to 183°, for instance, should be interpreted with respect to the initial $x_0$ geometry as a step of 13°, even though the bond angle at the displaced geometry $x_0 + \Delta x$ is 177° (as bond angles $\theta$ by definition are restricted to the interval $0^\circ \leq \theta \leq 180^\circ$). Some care must therefore be taken in the characterization of solutions to eq. (1).

To set up an iterative scheme for determining $\Delta x$ from $\Delta q$, we linearize eq. (1), yielding the iterative back-transformation (IBT) step,

$$ x_{k+1} = x_k + B^+_q(x_k)q_0 + \Delta q - q_k(x_k)), \quad (3) $$

where $x_0$ is the initial geometry and $x_k = x_0 + \Delta x_k$. The rectangular matrix $B$ is the Jacobian (Wilson $B$ matrix\cite{10}) of $q$ with respect to the $3N$ Cartesian coordinates $x$:

$$ B_q(x) = \frac{\partial q_i(x)}{\partial x_j}, \quad i = 1, 2, \ldots M, \quad j = 1, 2, \ldots 3N. \quad (4) $$

The matrix $B^+_q$ is a generalized inverse of $B(x_0)$. When delocalized internal coordinates are used, then $B^+_q$ is the Moore–Penrose pseudoinverse, while subsequent $B^+_q$ are the inverses of $B_q$ computed in the range space of $B^+_q$. The iterations are terminated when the root-mean-square change in the residual in the Cartesian \cite{11} or internal\cite{12} coordinates is less than $10^{-6}$ and when the coordinates have changed by less than $10^{-12}$ from the previous iteration.\cite{12} With these thresholds, convergence is typically reached in five iterations, each requiring the computation of the (pseudo)inverse. It is possible to reduce computational effort significantly by avoiding explicit calculation of the (pseudo)inverse as proposed by Nemeth et al.\cite{13,14} by exploiting the sparsity of the $B$-matrix.

A simplified IBT (SIBT) method has also been proposed\cite{12} and implemented,\cite{11} where the same matrices $B_0$ and $B^+_q$ are used in all iterations in eq. (3), thereby avoiding the expensive repeated construction of $B^+_q$. However, the performance and reliability of the SIBT scheme have not yet been thoroughly tested.

Baker et al.\cite{12} have proposed an alternative method for performing the back transformation, which avoids the computationally expensive construction of the pseudoinverse. Their algorithm finds the Cartesian displacements by setting up a $Z$ matrix specifically for this purpose, while the step itself is taken in delocalized internal coordinates. However, when the pseudoinverse is available from another part of the optimization, the $Z$ matrix approach offers no performance advantage.

According to Baker et al.\cite{12} when delocalized internal coordinates are used, the IBT method and their iterative $Z$-matrix method both converge rapidly, even for molecules containing hundreds of atoms. However, also other sets of internal coordinates—for instance, redundant internal coordinates—may be used efficiently with these schemes.\cite{11}

One more approach to the back-transformation problem was used by Dachsel et al.\cite{15} for visualization of curvilinear molecular vibrations. This method is also based on treating nonlinear relations between internal and Cartesian coordinates as the one proposed by us in this article. It finds a discrete path in Cartesian coordinates corresponding to a set of finite displacements in curvilinear normal coordinates using the Taylor expansion of the former with respect to the latter. The derivatives are calculated with reciprocal vector bases and covariant metric tensor. To our knowledge, the method has not been implemented and tested for geometry optimization.

### High-Order Geometry Steps

Our task is to find a finite Cartesian step $\Delta x$ that corresponds to a given internal coordinate step $\Delta q$. The IBT method provides such a step, but it does not generate a continuous path from $x_0$ to $x_0 + \Delta x$ as $q$ changes from $q_0$ to $q_0 + \Delta q$. In certain situations—for example, when performing a line search during a geometry optimization—it is advantageous to have an explicit form of such a path. Here, we introduce the path variable $s$ and vary the internal coordinates linearly,

$$ q(s) = q_0 + s \Delta q, \quad (5) $$

and then solve for the corresponding Cartesian path $x(s)$. By differentiating eq. (1), we obtain a differential equation similar in form to eq. (3):

$$ B(x(s)) \dot{x}(s) = \Delta q, \quad (6) $$

with the initial condition $x(0) = x_0$. It would be possible to obtain an approximate solution to this equation by numerical integration—that is, by subdividing the $s$ range $0 \leq s \leq 1$ into smaller steps, for which an equation similar to eq. (3) is solved, following the evaluation of the pseudoinverse $B^{-1}(s)$. However, the large number of $B^{-1}$ evaluations required in this approach makes it impracticable. Instead, we shall perform the back transformation by solving directly for the Taylor expansion of a solution to eq. (6).
A pertinent question is whether this Taylor expansion converges for $s = 1$, which would give us a solution to the original problem in eq. (1). Here, we present some evidence that we will in fact be able to take large $s$ steps using high-order Taylor approximations to $x(s)$. First, in Figure 1, we have plotted several Taylor polynomial approximations to the unit circle $(\cos \theta, \sin \theta)$. The trigonometric functions are known to have everywhere convergent Taylor series—indeed, we are able to approximate the full unit circle with a 20th-order expansion. On the scale of the plot, Taylor expansions of order 4, 10, and 15 are sufficient for $45^\circ$, $180^\circ$, and $270^\circ$ arcs, respectively. Because a geometry optimization typically adjusts bond angles and rotates molecular fragments (with the atoms tracing out circular paths), we expect similar requirements for the Taylor expansions in geometry optimizations. Not surprisingly, even second- and third-order expansions are much closer to the circle than is the linear expansion for angles up to a few degrees (the typical step size in geometry optimization). We therefore expect that far fewer back transformation steps are needed when these are based on higher-order expansions.

In Figure 2, we have plotted the error

$$\delta^k(\theta) = ||x(\theta) - x^k(\theta)||$$

against $\theta$ for $K \leq 20$. If we accept an error of $10^{-6}$ Å, then a fifth-order expansion gives an acceptable accuracy for steps of

$$x^k(\theta) = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{d^k x(\theta)}{d\theta^k} |_{\theta = \theta_0} \theta^k.$$  

Figure 1. Taylor expansions to orders 1–4, 10, 15, and 20 of the unit circle $r = (\cos \theta, \sin \theta)^T$. The expansion is performed around $\theta = 0$ and plotted for $0 \leq \theta \leq 360^\circ$. The 20th-order expansion is indistinguishable from the circle on this scale.

Figure 2. Errors (in Å) of the Cartesian geometry of water with respect to the bond angle $\theta$ (in degrees) and Taylor expansion order. The expansion is performed around the equilibrium geometry of $\theta = 104.5^\circ$, with the O–H bond length fixed at 0.96 Å.

Figure 3. Optimization test set.
about 20°. As for the unit circle, an expansion of order 20 gives highly accurate results for all \( \theta \); only for extreme step lengths does the error become larger than the numerical roundoff error of about \( 10^{-18} \). We also note that nothing special happens at \( \theta = 180° \), even though the \( B \) matrix is rank deficient at this bond angle. Here, we see an advantage of the Taylor expansion relative to the IBT method, which must take care to use correct (re)definitions of bond angles when crossing this point—see the discussion in section Internal-to-Cartesian back transformations.

We therefore here propose a high-order generalization of the IBT method that aims to parameterize the whole step \( \Delta x \) in terms of a single high-order Taylor expansion. If the Taylor expansion has a too small radius of convergence, we may revert terms of a single high-order Taylor expansion. If the Taylor expansion relative to the IBT method, which must take care to use correct (re)definitions of bond angles when crossing this point—see the discussion in section Internal-to-Cartesian back transformations.

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The HOPE algorithm

In the following, we present the HOPE algorithm, which generates the Taylor expansion at \( s = 0 \) in eq. (9) of the path \( x(s) \) that satisfies eq. (10):

\[
\frac{d}{ds} q(x(s)) = \Delta q.
\]

If the series converges, we further have that \( q(x(1)) = q(x_0) + \Delta q \) up to angles “wrapping around”. As input, the algorithm requires the following parameters:

- a vector of 3N Cartesian coordinates \( x_0 \) (the starting geometry),
- an analytic definition of \( M \) internal coordinates \( q(x) \) (typically with \( M \gg N \)),
- a step \( \Delta q \) in internal coordinates,
- a convergence threshold \( \epsilon \) and a norm \( ||\cdot|| \),
- a maximum Taylor expansion order \( K \geq 1 \).

The algorithm proceeds as follows:

1. Compute the Wilson \( B \) matrix in eq. (4) at \( x_0 \); as each \( q \) depends on at most 12 Cartesian coordinates (for dihedral angles), the \( B \) matrix is sparse, and this step uses \( O(M) \) operations.
2. (Optional) Compute the pseudoinverse \( B^+ \) by a singular-value decomposition (SVD) in \( O(MN^2) \) operations. The
range space of $B^{-1}$ defines the nonredundant internal coordinates.

3. Set $k = 0$ and define $x^0 = x_0$.

a. Compute $r_{k+1}$ by computing the expansion of $\Delta x - q(x_k)$ to order $k + 1$ in $\varepsilon$ at cost $O(M^2 K^2)$, see eq. (15).

b. Determine $x_{k+1}$ by solving the linear equations in eq. (14), using the pseudoinverse from step 2 or some equivalent method such as the conjugate-gradient method. This step uses the OPE method but may possibly be done in $O(MN)$ steps by exploiting the sparsity of $B$.

c. Define $x^{k+1} = x^k + x_{k+1}$.

d. Test for convergence by testing if

$$\max(||x_k||, ||x_{k+1}||) < \varepsilon$$

(18)

and that $q(x^{k+1}(1)) - q(x_0) - \Delta q$ to a given threshold.

i. If convergence has been reached, terminate.

ii. If convergence has not been reached and if $k < K$, set $k = k + 1$ and go back to step 3a. If instead $k = K$, select an $s < 1$ such that the conditions in eq. (18) are satisfied when $s$ is replaced by $s \cdot x_0 = x^k(1)$ and $\Delta q := (1 - s)\Delta q$ and and restart by going to step 1.

Implementation details

In this subsection, we make some comments regarding the different steps of the HOPE algorithm. First, in step 1, we compute the $B$ matrix. For highly symmetric molecular configurations, this matrix may be singular with respect to some internal coordinates. A typical example is a perfectly linear triatomic molecule, for which the mapping from the bond-angle coordinate to the Cartesian coordinates is ill defined. The HOPE algorithm as stated above silently ignores singular directions but otherwise continues as usual. Such singularities must therefore be detected and dealt with outside the HOPE (or indeed IBT) scheme—for example, by slightly breaking the symmetry of the molecule.

In step 2 of the HOPE algorithm, we calculate an SVD of $B$. However, this step is not strictly necessary—all that is required is that eq. (14) can be solved in a subspace where $B$ is nonsingular. This subspace must then remain the same for all orders $k$ (and also in restarts). Essentially, what is needed is a consistent definition of the $\Delta$ relation introduced in eq. (10). Such a consistency may be achieved by using the psuedoinverse $B^{-1}$, which solves eq. (14) uniquely by providing a minimum-norm solution to the equations. However, any other method that provides a unique solution may be used—for example, the conjugate-gradient method, which may have more favorable scaling properties than the SVD method.
at each iteration stays on the continuous path between \( \mathbf{x}_0 \) and \( \mathbf{x}_0 + \Delta \mathbf{x} \), defined by eq. (17). It is possible to define a HOPE method that exactly reduces to the IBT method when \( K = 1 \), but only without a continuous path.

### Calculations

We have implemented the IBT, SIBT, and HOPE algorithms in a development version of the LSDALTON program,\(^{[19]} \) in the quasi-Newton geometry-optimization module of Bakken and Helgaker.\(^{[11]} \) In this module, the quasi-Newton step \( \Delta q \) is obtained on a basis of nonredundant eigenvectors of a molecular Hessian constructed in redundant internal coordinates. The quasi-Newton step is subsequently transformed to the basis of redundant internal coordinates \( \mathbf{q} \) and then (to perform the back transformation) to a basis of nonredundant delocalized internal coordinates, generated by performing an SVD of \( \mathbf{B} \) and removing all zero-singular-value vectors.\(^{[7]} \)

### Computational details

The performance of the IBT, SIBT, and HOPE methods is compared for the first geometry step (of length 0.5 and 1 a.u., with angles in radians) in the geometry optimization of seven medium-sized and large molecules depicted in Figure 3: cholesterol (C\(_{27} \)H\(_{44} \)O), a Si\(_{50} \) cluster,\(^{[20]} \) the cubic conformation of a protonated water cluster (H\(_2 \)O\(_{20} \))\(_2 \)H\(^+\),\(^{[21]} \) endofullerene H\(_2 \)O@C\(_{60} \) with an off-center water molecule,\(^{[22]} \) a pyridine–water cluster (C\(_{20} \)H\(_{20} \)N\(_2 \)(H\(_2 \)O)\(_2 \)H\(^+\)),\(^{[23]} \) dibenzo-18-crown-6 (C\(_{20} \)H\(_{24} \)O\(_{6} \)), and valinomycin (C\(_{54} \)H\(_{96} \)N\(_{18} \)O\(_{18} \)). All electronic-structure calculations were performed using Kohn–Sham/BLYP/6-31+G\(^*\) theory. Back-transformation convergence is controlled in both delocalized internal and Cartesian coordinates. Convergence is declared when the root-mean-square change in the coordinates is less than 10\(^{-16} \) and when this change differs by less than 10\(^{-12} \) from that of the previous iteration (or order of expansion for the HOPE method).

### Results

The main results are summarized in the Table 1, where we list the Taylor expansion order for the HOPE calculations and the number of iterations for the IBT and SIBT calculations; in the following, we shall refer to both quantities as “iterations.” The IBT method uses least iterations to achieve convergence; moreover, its performance does not depend strongly on the molecular system or on the step length. The HOPE method also converges rapidly but it is slightly more sensitive to system and step length; the maximum expansion order is never reached and hence no restart is performed. Except for the pyridine-containing cluster, expansions up to order nine are sufficient (the pyridine system required orders 13 and 19 for \( s = 0.5 \) and \( s = 1.0 \), respectively). The SIBT method exhibits the poorest convergence, requiring 36–46 iterations for (C\(_{20} \)H\(_{20} \)N\(_2 \)(H\(_2 \)O)\(_2 \)H\(^+\)) and \( s = 0.5 \). For \( s = 1.0 \), the SIBT method failed to converge and two steps of \( s = 0.5 \) were taken instead, each requiring a separate B\(^+\) evaluation. The convergence behavior of the HOPE, IBT, and SIBT methods for this system is illustrated in Figure 4.

In our implementation, the computation of B\(^+\) is at least two orders of magnitude more expensive than the computation of the geometric derivatives. Also, the cost of inverting B scales cubically with system size, whereas the calculation of derivatives scales linearly. Therefore, even though the HOPE method typically needs more iterations (more precisely, higher expansion orders) than does the IBT method, it is several times more efficient as it requires only one matrix inversion—unlike the IBT method, which requires one inversion at each iteration. We also note that the HOPE computation of internal coordinate derivatives is trivially parallelizable. Of course, computational considerations of the back transformation are typically unimportant for electronic-structure methods but for semiempirical and force-field methods they are essential. For the latter methods, internal-to-Cartesian coordinate transformations are expensive, making the optimization in Cartesian coordinates more efficient.\(^{[24]} \)

An important difference between the HOPE and IBT methods is that the latter only generates the final Cartesian coordinates \( \mathbf{x}(\mathbf{q}_0 + \Delta \mathbf{q}) \) consistent with \( \Delta \mathbf{q} \), whereas the HOPE method finds a smooth polynomial path \( \mathbf{x}(s) \) such that \( \mathbf{x}(0) = \mathbf{x}(\mathbf{q}_0) \) and \( \mathbf{x}(1) = \mathbf{x}(\mathbf{q}_0 + \Delta \mathbf{q}) \), see eq. (9). The HOPE method can therefore be used to generate smooth continuous paths from the discrete paths generated in molecular-dynamics simulations\(^{[25]} \) and in reaction-coordinate studies.\(^{[1]} \) Smooth paths can also be useful for visualizations: currently, the continuous paths needed for animations are often generated by interpolation.

### Conclusions

We have proposed and tested the HOPE method for performing back transformations of the geometry step from internal coordinates \( \mathbf{q} \) to the Cartesian \( \mathbf{x} \) frame. The HOPE method is based on the generation of a high-order Taylor expansion of \( \mathbf{q} \)
with respect to \( \mathbf{x} \), using AD techniques. It is applicable to any set of redundant or nonredundant internal coordinates, easy to implement (using AD tools), and reliable. The HOPE method is computationally more efficient and reliable than previous back-transformation methods. As a bonus, it generates a continuous path between the initial and the final geometries rather than just the final geometry, useful for backtracking and for generating smooth curves for molecular trajectories and intrinsic reaction coordinates.

**Acknowledgment**

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**APPENDIX: Numerically Stable Calculation of Internal Coordinates**

Because the HOPE method uses high-order derivatives of the internal coordinates with respect to the Cartesian molecular geometry, it is important to investigate the numerical stability of these derivatives. We use three different types of internal coordinates: bond lengths, bond angles, and dihedral angles. For a set of atoms with Cartesian coordinates \( r_i, r_2, \ldots \), we define the relative vectors \( \bar{d}_{ij} = r_i - r_j \), bond lengths \( a_{ij} \) and bond angles \( \theta_{ijk} \) as

\[
\bar{d}_{ij} = r_i - r_j, \quad a_{ij} = ||\bar{d}_{ij}||, \quad \theta_{ijk} = \arccos \left( \frac{\bar{d}_{ij} \cdot \bar{d}_{jk}}{||\bar{d}_{ij}|| ||\bar{d}_{jk}||} \right).
\]  

(A1)

These formulas generate numerically stable Taylor coefficients when used at nonzero bond lengths and bond angles not too close to 0° or 180°. Although very short bond lengths indicate an underlying problem with the molecular geometry, it is possible to have bond angles in the problematic region. These angles should be excluded from the HOPE algorithm by removing them from the set of redundant internal coordinates.

For dihedral angles, we use \( \phi_{ijk} = \arctan^2(y, x) \), where the arguments are defined as

\[
y = ||\bar{d}_{jk}|| (\bar{d}_{jk} \times \bar{d}_{ik}), \quad x = (\bar{d}_{ik} \times \bar{d}_{jk}) \cdot (\bar{d}_{ik} \times \bar{d}_{jk}).
\]  

(A2)

(A3)

The \( \arctan^2 \) function returns the angle of the point \((x, y)\) in standard polar coordinates. In the right half-plane, it is defined as \( \arctan^2(y, x) = \arctan(y/x) \) but avoids division by small numbers when the angle is close to the 90° and 270° angles, and is defined for the whole \( xy \) plane except at the origin. The AD library was extended with an implementation of \( \arctan^2 \) based on the identity

\[
\arctan^2(y, x) = 2\arctan \left( \frac{\sqrt{x^2 + y^2} - x}{y} \right).
\]  

(A4)

which is used instead of \( \arctan(y/x) \) when \( |y/x| > 1 \).

The numerical stability of the implementation was investigated by the use of the quad–double (64 decimal digits) floating-point library QD.\(^{[26]}\) Results from high-precision calculations were compared with the ones performed in double precision. Initially, the double-precision implementation suffered from large round-off errors for molecules in our test set (i.e., the pyridine system). The absolute errors of each \( \mathbf{x}_k \) vector, computed using the HOPE algorithm in double precision, are plotted in Figure A1 for \( \text{Si}_{106} \) (red) and \( \text{C}_4\text{H}_8\text{N}_2(\text{H}_2\text{O})_4\text{H}^+ \) (blue). Dots indicate the absolute magnitude of each element of \( \mathbf{x}_k \), whereas the full (dashed) lines show the absolute errors of the vectors \( \mathbf{x}_k \) with derivatives computed in double precision. The dotted (dot-dashed) lines show the errors when an unstable formula is used for the dihedral angles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Figure A1. Convergence of the HOPE method for \( \text{Si}_{106} \) (red) and \( \text{C}_4\text{H}_8\text{N}_2(\text{H}_2\text{O})_4\text{H}^+ \) (blue). Dots indicate the absolute magnitude of each element of \( \mathbf{x}_k \), whereas the full (dashed) lines show the absolute errors of the vectors \( \mathbf{x}_k \), where the unstable dihedral definition (based on \( \arctan(y/x) \)) gives useful results only to order 5 (pyridine system) or 10 (\( \text{Si}_{106} \)). At higher orders, numerical errors dominate the \( \mathbf{x}_k \) vectors, illustrating how mathematical expressions that are numerically well-behaved at low orders may become unreliable in a high-order AD context.

With the stable formulas, absolute errors are insignificant for \( k < 20 \). Nevertheless, relative errors do increase with \( k \), and the present double-precision implementation probably cannot be used much beyond order 20. Clearly, these stability observations depend strongly on the AD library used: a different software implementation would require a separate stability analysis.

**Keywords:** molecular geometry optimizations · molecular internal coordinates · coordinate transformations


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