Computation of Internal Coordinates, Derivatives, and Gradient Expressions: Torsion and Improper Torsion

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ABSTRACT: Laplacians and gradient dot products are required for the recently developed internal coordinate quantum Monte Carlo method. New formulas are presented for these quantities for torsion and improper torsion angles. The Laplacians can also be used to economize calculation of sets of second derivatives used in molecular mechanics and other methods. Formulas for torsion angle gradient dot products and Laplacians, and completely new formulas for improper torsion, are presented. In addition, calculations of $\cos\tau$ and $\sin\tau$, some suitable for energy subroutines and others for force subroutines, are shown. Finally, in a related development, several sets of conditions for three atom linearity or four atom planarity involving internal coordinate derivatives are reported. J Comput Chem 21: 553–561, 2000

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Introduction

Potential energy surfaces for polymer, biological, and other systems are usually written as sums of bond stretch, bend, torsion, and other interactions. Commonly used molecular simulation techniques such as molecular dynamics[1] and molecular mechanics[2] require the corresponding internal coordinates as well as their first and sometimes second derivatives. For any potential energy term $V(\phi)$, where ϕ is an internal coordinate, the first and second derivatives are

$$\frac{\partial V}{\partial q_i} = \frac{\partial V}{\partial \phi}\frac{\partial \phi}{\partial q_i} \tag{1a}$$

$$\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\partial V}{\partial \phi}\frac{\partial^2 \phi}{\partial q_i \partial q_j} + \frac{\partial^2 V}{\partial q_i \partial q_j}\frac{\partial \phi}{\partial q_i}\frac{\partial \phi}{\partial q_j} \tag{1b}$$

where the most computational effort is spent on internal coordinates and their derivatives. Over the years, considerable effort has been expended

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in optimizing these calculations by judicious use of the chain rule, sometimes with the help of rotational transformations or other mathematical devices.[3–9] Our group has evolved an approach (named GSF—geometric statement function method) in which three- and four-atom internal coordinates and derivatives by using are computed using those for two- and three-body interactions contained therein as intermediates.[7, 8, 10, 11] Our recently developed general bond network method automates the bookkeeping required for this part of the calculation while making optimal use of our formulas.[12]

Because of the large computational effort, mathematical singularities, and the well-known $1/\sin\tau$ problem, the torsion angle (τ, $\cos\tau$, $\sin\tau$) has attracted much attention. It is not uncommon for the torsional potential energy to be asymmetric with respect to the direction of rotation around a chemical bond (clockwise vs. counterclockwise). This can occur in some polymer systems such as Teflon, but more notably in biological simulations where nonbonded and other interactions are lumped into a torsional term. Typically, such terms are parameterized in part by τ or $\sin\tau$, which are antisymmetric with respect to the direction of rotation. Swope and Ferguson[3] give a particularly complete discussion of mathematical issues for torsion interactions (and also for three-atom bend angles); Bekker et al.[5] and Wilson, Decius, and Cross[12] also discuss these issues. Different computational schemes have been implemented by, among others, Miller et al.,[4] Bekker et al.,[5] Jung,[6] Blondel and Karplus,[9] and Tuzun et al.[8]

The recently developed internal coordinate quantum Monte Carlo (ICQMC) method[13] requires, in addition to first derivatives, Laplacians and gradient products of internal coordinates. Because the Laplacians often have particularly simple formulas, they can also be used to economize calculation of second derivatives required in classical simulation methods. New formulas for $\nabla_i\phi\cdot\nabla_i\phi$ and $\nabla_i^2\phi$, where ϕ are torsion or improper torsion coordinates, as well as a few updated formulas for individual derivatives, are presented here.

Finally, some new computational schemes for calculating $\cos\tau$ and $\sin\tau$ are presented. Because force calculations require intermediates not used in energy calculations, optimal calculation sequences for $\cos\tau$ and $\sin\tau$ differ between force and energy subroutines. A related development leads to an interesting set of conditions required for the planarity of four atoms. Similar conditions are derived for improper torsion interactions.

Stretch, r, and Bend Angle, $\cos\theta$ and θ

Because internal coordinates are typically defined in terms of vector dot products, vector identities prove useful for deriving formulas involving them. The following are used extensively in this article:

$$\boldsymbol{a}\times\boldsymbol{a}=\boldsymbol{0} \tag{2a}$$

$$\boldsymbol{a}\times\boldsymbol{b}=-\boldsymbol{b}\times\boldsymbol{a} \tag{2b}$$

$$\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}=\boldsymbol{b}\cdot\boldsymbol{c}\times\boldsymbol{a}=\boldsymbol{c}\cdot\boldsymbol{a}\times\boldsymbol{b} \tag{2c}$$

$$\boldsymbol{a}\times(\boldsymbol{b}\times\boldsymbol{c})=(\boldsymbol{a}\cdot\boldsymbol{c})\boldsymbol{b}-(\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{c} \tag{2d}$$

$$(\boldsymbol{a}\times\boldsymbol{b})\cdot(\boldsymbol{c}\times\boldsymbol{d})=(\boldsymbol{a}\cdot\boldsymbol{c})(\boldsymbol{b}\cdot\boldsymbol{d})-(\boldsymbol{a}\cdot\boldsymbol{d})(\boldsymbol{b}\cdot\boldsymbol{c}) \tag{2e}$$

We now illustrate the gradient approach for a bond distance coordinate. Using the convention

$$\boldsymbol{r}_{ij}=\boldsymbol{r}_j-\boldsymbol{r}_i$$

we note that a unit vector can be written in terms of bond distance partial derivatives

$$\hat{\boldsymbol{r}}_{21}=-\hat{\boldsymbol{r}}_{12}=\frac{\partial r_{12}}{\partial x_1}\boldsymbol{i}+\frac{\partial r_{12}}{\partial y_1}\boldsymbol{j}+\frac{\partial r_{12}}{\partial z_1}\boldsymbol{k}$$

Diagonal second derivatives of a bond distance can be written

$$\frac{\partial^2 r}{\partial q_i^2}=\frac{1}{r}\left[1-\left(\frac{\partial r}{\partial q_i}\right)^2\right]=\frac{1}{r}\left(1+\frac{\partial r}{\partial q_i}\right)\left(1-\frac{\partial r}{\partial q_i}\right) \tag{3}$$

where q is x, y, or z. Here, as elsewhere in this article, the expression $1-x^2$ is computed as $(1+x)(1-x)$ for numerical accuracy. From eq. (3), the Laplacians are

$$\nabla_1^2 r=\nabla_2^2=\frac{n-\hat{\boldsymbol{r}}_{21}\cdot\hat{\boldsymbol{r}}_{21}}{r}=\frac{n-1}{r} \tag{4}$$

where n is the number of spatial dimensions (in this article and in most other molecular simulations, 3). This can be used to economize the calculation of a single diagonal second derivative

$$\frac{\partial^2 r}{\partial x_1^2}=\frac{1}{r}+\frac{1}{r}-\frac{\partial^2 r}{\partial y_1^2}-\frac{\partial^2 r}{\partial z_1^2} \tag{5}$$

which eliminates two multiplications (no divisions are performed here because $1/r$ is calculated earlier, while computing first derivatives). Savings for other interaction types are even greater.

A bend angle 123 is normally defined by

$$\cos\theta_{123}=\hat{r}_{21}\cdot\hat{r}_{23}$$

Formulas for first derivatives will be used later:

$$\nabla_1 \cos\theta_{123} = -\frac{\cos\theta_{123}\,\hat{r}_{21} + \hat{r}_{32}}{r_{12}} = \frac{\hat{r}_{32} \times (\hat{r}_{21} \times \hat{r}_{32})}{r_{12}} \quad (6a)$$

$$\nabla_3 \cos\theta_{123} = \frac{\cos\theta_{123}\,\hat{r}_{32} + \hat{r}_{21}}{r_{23}} = \frac{\hat{r}_{21} \times (\hat{r}_{32} \times \hat{r}_{21})}{r_{23}} \quad (6b)$$

$$\nabla_i \theta_{123} = -\frac{1}{\sin\theta_{123}} \nabla_i \cos\theta_{123} \quad (6c)$$

From eq. (6a), it is easily seen that the atom 1 gradient vector is perpendicular to the 12-bond axis and lies in the 123 plane. A similar statement holds for atom 3. We will return to this point in the discussion of four atom planarity conditions.

Torsion angle, $\cos\tau$ and $\sin\tau$

Force calculations require derivative intermediates that are not required in energy calculations for most efficient computation. For this reason, strategies for the most efficient computation of torsion angles, $\cos\tau$ and $\sin\tau$, are different in force and energy calculations. We begin with $\cos\tau$. The torsion angle for a four-atom sequence labeled 1234 can be written

$$\cos\tau = \frac{\cos\theta_{123}\cos\theta_{234} - \hat{r}_{21} \cdot \hat{r}_{43}}{\sin\theta_{123}\sin\theta_{234}} \quad (7)$$

This result can be used to obtain

$$\nabla_3\theta_{123} \cdot \nabla_2\theta_{234} = \frac{\cos\tau}{r_{23}^2}$$

from which a formula more efficient than eq. (7) immediately follows:

$$\cos\tau = r_{23}^2\left(\frac{\partial\theta_{123}}{\partial x_3}\frac{\partial\theta_{234}}{\partial x_2} + \frac{\partial\theta_{123}}{\partial y_3}\frac{\partial\theta_{234}}{\partial y_2} + \frac{\partial\theta_{123}}{\partial z_3}\frac{\partial\theta_{234}}{\partial z_2}\right) \quad (8)$$

Equation (7) is best used in energy subroutines. Within the current GSF approach, bend angle derivatives are used in force, not energy calculations. Although eq. (8), by itself, has fewer operations than eq. (7), the additional expense of adding bend angle derivatives to energy subroutines would more than negate this advantage. Equation (8) should, therefore, be used only in force subroutines.

If either internal bend angle sequence 123 or 234 is linear, then the torsion angle 1234 is undefined, and the derivatives singular[3, 14] because $\sin\theta_{123}$ and/or $\sin\theta_{234}$ vanish. However, it is assumed throughout this article that no such condition occurs.

If a potential energy surface does not distinguish the direction of rotation (clockwise or counterclockwise) about any bond axis, then torsion interactions are best parameterized by $\cos\tau$, which has this symmetry. When it is necessary to account for the direction of rotation, torsion interactions are typically written in the form

$$\cos(n\tau + \alpha) = f(\cos\tau) + \sin\tau\, g(\cos\tau)$$

where n is an integer, α an offset angle, and f and g polynomials in $\cos\tau$ that can be obtained by trigonometric identities. Here, $\sin\tau$ is the antisymmetric part.

Often, $\sin\tau$ is calculated from $\cos\tau$ by the usual square root, in addition to a sign. To calculate the sign, we refer to Figure 1, which shows a four-atom torsion sequence looking down the 23 bond axis. If we define the 23 vector to lie along the negative z-axis and the 21 vector to lie in the yz plane, and with a positive y component, then $\boldsymbol{r}_{21}\boldsymbol{x}\boldsymbol{r}_{32}$ lies on the x-axis. Whether the torsion angle is positive or negative depends on whether $\boldsymbol{r}_{43}$ has a positive or negative projection on the x-axis, i.e., on the sign of $\boldsymbol{r}_{43}\cdot\boldsymbol{r}_{21}\boldsymbol{x}\boldsymbol{r}_{32}$.

An efficient calculation $\sin\tau$ inside of energy subroutines is now shown. From the chain rule,

$$\nabla_i \cos\tau = -\sin\tau\, \nabla_i\tau$$

Recently, Bekker et al. presented formulas for first derivatives of τ that we rewrite, for convenience, in

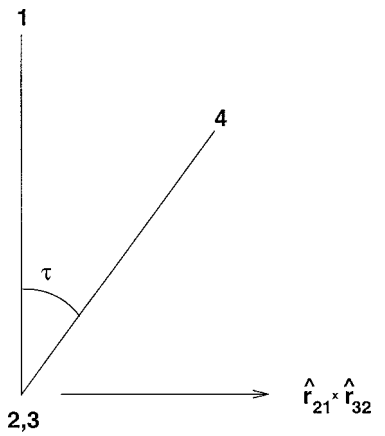

FIGURE 1. A positive torsion angle τ. The 23 vector lies in the negative z direction, and the 21 vector within the yz plane and with a positive y component. The 43 axis has a negative component along $\boldsymbol{r}_{21}\boldsymbol{x}\boldsymbol{r}_{32}$, which lies in the positive x direction. Combined with the negative sign in eq. (24), this yields a positive torsion angle.

the following form

$$\nabla_1\tau = -\frac{1}{r_{12}\sin^2\theta_{123}}\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32} \tag{9a}$$

$$\nabla_4\tau = -\frac{1}{r_{34}\sin^2\theta_{234}}\hat{\boldsymbol{r}}_{43}\times\hat{\boldsymbol{r}}_{32} \tag{9b}$$

$$\nabla_2\tau = c_{123}\nabla_1\tau - b_{432}\nabla_4\tau \tag{9c}$$

where

$$c_{123} = \frac{r_{12}\cos\theta_{123}}{r_{23}} - 1 \qquad b_{432} = \frac{r_{34}\cos\theta_{234}}{r_{23}} \tag{9d}$$

In the Appendix, it is shown that

$$\nabla_1\cos\tau = -\frac{\hat{\boldsymbol{r}}_{43}\cdot\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}}{r_{12}\sin^3\theta_{123}\sin\theta_{234}}\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32} \tag{10a}$$

$$\nabla_4\cos\tau = -\frac{\hat{\boldsymbol{r}}_{43}\cdot\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}}{r_{34}\sin^3\theta_{234}\sin\theta_{123}}\hat{\boldsymbol{r}}_{43}\times\hat{\boldsymbol{r}}_{32} \tag{10b}$$

From eqs. (9a) and (10a), or from eqs. (9b) and (10b), it immediately follows that

$$\sin\tau = -\frac{\hat{\boldsymbol{r}}_{43}\cdot\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}}{\sin\theta_{123}\sin\theta_{234}} \tag{11}$$

This formula is equivalent to an expression by Blondel and Karplus but rewritten in a form more convenient for our purposes. Equation (11) is most suitable for use in energy subroutines. Derivatives of r are previously used to calculate $\cos\theta$; $1/\sin\theta$ is previously used for $\cos\tau$. Thus, to evaluate eq. (11) requires only multiplications and additions. The calculation sequence of Karplus requires calculating magnitudes of three vectors, which requires square roots.

A more efficient method for calculating $\sin\tau$ within force subroutines is to pick a q_i and to use

$$\sin\tau = \frac{\partial\cos\tau/\partial q_i}{\partial\tau/\partial q_i} \tag{12}$$

since derivatives of $\cos\tau$ are required as part of the force calculation, and because derivatives of τ have particularly simple formulas.

Of course, the first and second derivatives of $\sin\tau$ are still required. From the chain rule, these are

$$\frac{\partial\sin\tau}{\partial q_i} = \cos\tau\frac{\partial\tau}{\partial q_i} \tag{13a}$$

$$\frac{\partial^2\sin\tau}{\partial q_i\partial q_j'} = \cos\tau\frac{\partial^2\tau}{\partial q_i\partial q_j'} + \frac{\partial\cos\tau}{\partial q_j'}\frac{\partial\tau}{\partial q_i} \tag{13b}$$

a form in which the right-hand sides are easily calculated.

GRADIENT PRODUCTS AND LAPLACIANS, $\cos\tau$ AND $\sin\tau$

To calculate gradient products and Laplacians, we have recently found it to be most efficient to work with derivatives of τ. Applying the chain rule yields

$$\frac{\partial^2\cos\tau}{\partial q_i^2} = -\sin\tau\frac{\partial^2\tau}{\partial q_i^2} - \cos\tau\frac{\partial\tau}{\partial q_i}\frac{\partial\tau}{\partial q_i} \tag{14}$$

In the Appendix, it is proven that

$$\nabla_1^2\tau = \nabla_2^2\tau = \nabla_3^2\tau = \nabla_4^2\tau = 0 \tag{15}$$

From these results it follows that

$$\nabla_i^2\cos\tau = -\cos\tau\,\nabla_i\tau\cdot\nabla_i\tau \tag{16a}$$

$$\nabla_i^2\sin\tau = -\sin\tau\,\nabla_i\tau\cdot\nabla_i\tau \tag{16b}$$

$$\begin{aligned}\nabla_i\cos\tau\cdot\nabla_i\cos\tau &= (1+\cos\tau)(1-\cos\tau)\nabla_i\tau\cdot\nabla_i\tau\\ &= -\sin\tau\,\nabla_i^2\sin\tau\end{aligned} \tag{16c}$$

$$\begin{aligned}\nabla_i\sin\tau\cdot\nabla_i\sin\tau &= \cos^2\tau\,\nabla_i\tau\cdot\nabla_i\tau\\ &= -\cos\tau\,\nabla_i^2\cos\tau\end{aligned} \tag{16d}$$

From eq. (9) and some vector identities we find

$$\nabla_1\tau\cdot\nabla_1\tau = d_{123}^2 \tag{17a}$$

$$\nabla_4\tau\cdot\nabla_4\tau = d_{432}^2 \tag{17b}$$

$$\nabla_1\tau\cdot\nabla_4\tau = -\cos\tau\,d_{123}d_{432} \tag{17c}$$

where

$$d_{123} = \frac{1}{r_{12}\sin\theta_{123}} \qquad d_{432} = \frac{1}{r_{34}\sin\theta_{234}} \tag{17d}$$

It is proven in the Appendix that

$$\nabla_1\tau\cdot\nabla_3\tau = c_{123}\nabla_1\tau\cdot\nabla_1\tau - b_{432}\nabla_1\tau\cdot\nabla_4\tau \tag{18a}$$

$$\nabla_2\tau\cdot\nabla_4\tau = c_{123}\nabla_1\tau\cdot\nabla_4\tau - b_{432}\nabla_4\tau\cdot\nabla_4\tau \tag{18b}$$

$$\nabla_2\tau\cdot\nabla_2\tau = c_{123}\nabla_1\tau\cdot\nabla_2\tau - b_{432}\nabla_2\tau\cdot\nabla_4\tau \tag{18c}$$

$$\begin{aligned}\nabla_3\tau\cdot\nabla_3\tau = {}& c_{432}^2\nabla_1\tau\cdot\nabla_1\tau + b_{123}^2\nabla_4\tau\cdot\nabla_4\tau\\ &- 2c_{432}b_{123}\nabla_1\tau\cdot\nabla_4\tau\end{aligned} \tag{18d}$$

Substituting these results into eqs. (16a)–(16d) yields the required gradient expressions. Equation (18d), which follows directly from translational invariance, holds in a similar manner for $\cos\tau$ and $\sin\tau$.

FOUR-ATOM PLANARITY CONDITIONS

The fact that four atoms 1234 in a torsion sequence are planar can be expressed as a single condition, namely $\cos\tau = \pm1$ or $\sin\tau = 0$. However, an interesting set of three required conditions for planarity can be obtained by requiring the 34-bond axis to lie entirely in the 123 plane. From the

definition of a bend angle, it can be seen that

$$\hat{v}_1 = \hat{r}_{32} \qquad \hat{v}_2 = \frac{\hat{r}_{21} + \cos\theta_{123}\,\hat{r}_{32}}{\sin\theta_{123}} = -\nabla_3\theta_{123}$$

form an orthonormal set that spans the 123 plane. If 1234 are planar, then the out-of-plane components of r_{34} vanish:

$$v = \hat{r}_{34} - (\hat{r}_{34}\cdot\hat{v}_1)\hat{v}_1 - (\hat{r}_{34}\cdot\hat{v}_2)\hat{v}_2 = \mathbf{0}$$

With the help of

$$\hat{r}_{34}\cdot\hat{v}_2 = -\sin\theta_{234}\cos\tau$$

it follows that

$$v = r_{23}\sin\theta_{234}(\nabla_2\theta_{234} \mp \nabla_3\theta_{123}) \quad \text{if} \quad \cos\tau = \pm 1$$

and from there

$$\frac{\partial\theta_{234}}{\partial q_2} = \pm\frac{\partial\theta_{123}}{\partial q_3} \quad \text{if} \quad \cos\tau = \pm 1 \tag{19}$$

The reverse of this result, i.e., that $\cos\tau = \pm 1$ if the partial derivatives are equal or have the same magnitude but opposite sign, follows directly from eq. (8) and from

$$\nabla_3\theta_{123}\cdot\nabla_3\theta_{123} = \frac{1}{r_{23}^2}$$

These results can be interpreted geometrically as follows. The atom three-gradient vector for the 123 bend interaction is perpendicular to the 23-bond axis, and lies in the 123 plane. The atom two-gradient vector for the 234 bond interaction is perpendicular to the 23-bond axis, and lies in the 234 plane. If the four atoms are planar, then the two gradient vectors point in the same or exactly opposite directions, depending on whether $\cos\tau$ is 1 or -1 (Fig. 2a and b).

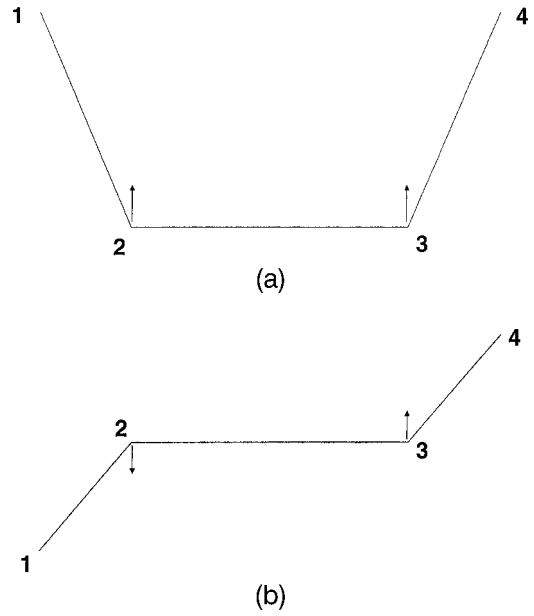

FIGURE 2. Internal bend angle gradient vectors within a torsion interaction in which the atoms are planar: atom 2 gradient vector for bend angle 234 and atom 3 gradient vector for bend angle 123. (a) $\cos\tau = 1$, and (b) $\cos\tau = -1$.

Improper Torsion, $\sin\omega$

GRADIENT PRODUCTS AND LAPLACIANS

An improper torsion angle is used to parameterize the deviation from planarity of a set of four atoms. This is commonly used, for example, for aromatic systems in which the bond network is favored to be planar. We define atom 4 to be the center atom, and the improper torsion angle the deviation of atom 1 from the 243 plane. This can be calculated as follows:

$$\sin\omega = \frac{\hat{r_{41}}\cdot\hat{r_{42}}\times\hat{r_{43}}}{\sin\theta_{243}} \tag{20}$$

After defining

$$c_{243} = \frac{1}{r_{42}\sin\theta_{243}} \qquad c_{342} = \frac{1}{r_{43}\sin\theta_{243}} \tag{21a}$$

$$f_{23} = \frac{c_{243}}{r_{41}\sin\theta_{243}}(\cos\theta_{143}\cos\theta_{243} - \cos\theta_{142}) \tag{21b}$$

$$f_{32} = \frac{c_{342}}{r_{41}\sin\theta_{243}}(\cos\theta_{142}\cos\theta_{243} - \cos\theta_{143}) \tag{21c}$$

$$g = (1+\sin\omega)(1-\sin\omega) \tag{21d}$$

$$h = \sin\omega\cos\theta_{243} \tag{21e}$$

for the sake of convenience, from previously derived formulas for first derivatives, we obtain

$$\nabla_1\sin\omega\cdot\nabla_1\sin\omega = \frac{g}{r_{41}^2} \tag{22a}$$

$$\nabla_2\sin\omega\cdot\nabla_2\sin\omega = c_{243}^2\big[(1+\cos\theta_{143}) \times (1-\cos\theta_{143}) - h^2\big] \tag{22b}$$

$$\nabla_3\sin\omega\cdot\nabla_3\sin\omega = c_{342}^2\big[(1+\cos\theta_{142}) \times (1-\cos\theta_{142}) - h^2\big] \tag{22c}$$

$$\nabla_1\sin\omega\cdot\nabla_2\sin\omega = gf_{23} \tag{22d}$$

$$\nabla_1\sin\omega\cdot\nabla_3\sin\omega = gf_{32} \tag{22e}$$

$$\nabla_2\sin\omega\cdot\nabla_3\sin\omega = c_{243}c_{342}(\cos\theta_{142}\cos\theta_{143} - g\cos\theta_{243}) \tag{22f}$$

From translational invariance, we obtain

$$\begin{aligned}\nabla_4 \sin\omega \cdot \nabla_4 \sin\omega &= \nabla_1 \sin\omega \cdot \nabla_1 \sin\omega + \nabla_2 \sin\omega \cdot \nabla_2 \sin\omega \\ &+ \nabla_3 \sin\omega \cdot \nabla_3 \sin\omega + 2(\nabla_1 \sin\omega \cdot \nabla_2 \sin\omega \\ &+ \nabla_1 \sin\omega \cdot \nabla_3 \sin\omega + \nabla_2 \sin\omega \cdot \nabla_3 \sin\omega)\end{aligned} \tag{22g}$$

The Laplacians are

$$\nabla_1^2 \sin\omega = -\frac{2\sin\omega}{r_{41}^2} \tag{23a}$$

$$\nabla_2^2 \sin\omega = -c_{243}^2 \sin\omega \tag{23b}$$

$$\nabla_3^2 \sin\omega = -c_{342}^2 \sin\omega \tag{23c}$$

$$\nabla_1 \cdot \nabla_2 \sin\omega = -\sin\omega f_{23} \tag{23d}$$

$$\nabla_1 \cdot \nabla_3 \sin\omega = -\sin\omega f_{32} \tag{23e}$$

$$\nabla_2 \cdot \nabla_3 \sin\omega = c_{243}c_{342}h \tag{23f}$$

and, from translational invariance,

$$\begin{aligned}\nabla_4^2 \sin\omega = \nabla_1^2 \sin\omega + \nabla_2^2 \sin\omega + \nabla_3^2 \sin\omega \\ + 2(\nabla_1 \cdot \nabla_2 \sin\omega + \nabla_1 \cdot \nabla_3 \sin\omega \\ + \nabla_2 \cdot \nabla_3 \sin\omega)\end{aligned} \tag{23g}$$

FOUR-ATOM PLANARITY CONDITIONS

For an improper torsion angle, the analysis proceeds in a similar manner as for torsion. Remembering that atom 4, the central atom, is connected to atoms 1, 2, and 3, if the four atoms are planar, then the three unit vectors

$$\frac{\hat{\boldsymbol{r}}_{41} \times \hat{\boldsymbol{r}}_{42}}{\sin\theta_{142}} \qquad \frac{\hat{\boldsymbol{r}}_{42} \times \hat{\boldsymbol{r}}_{43}}{\sin\theta_{243}} \qquad \frac{\hat{\boldsymbol{r}}_{43} \times \hat{\boldsymbol{r}}_{41}}{\sin\theta_{143}}$$

point in the same or opposite directions. (In real molecular simulations, where equilibrium bond angles are at or near 120 degrees, they would almost certainly point in the same direction). Thus,

$$\begin{aligned}&\frac{\hat{\boldsymbol{r}}_{41} \times \hat{\boldsymbol{r}}_{42}}{\sin\theta_{142}} \cdot \frac{\hat{\boldsymbol{r}}_{42} \times \hat{\boldsymbol{r}}_{43}}{\sin\theta_{243}} \\ &\quad = \frac{\cos\theta_{142}\cos\theta_{243} - \cos\theta_{143}}{\sin\theta_{142}\sin\theta_{243}} = s_1\end{aligned} \tag{24a}$$

$$\begin{aligned}&\frac{\hat{\boldsymbol{r}}_{42} \times \hat{\boldsymbol{r}}_{43}}{\sin\theta_{243}} \cdot \frac{\hat{\boldsymbol{r}}_{43} \times \hat{\boldsymbol{r}}_{41}}{\sin\theta_{143}} \\ &\quad = \frac{\cos\theta_{243}\cos\theta_{143} - \cos\theta_{142}}{\sin\theta_{243}\sin\theta_{143}} = s_2\end{aligned} \tag{24b}$$

$$\begin{aligned}&\frac{\hat{\boldsymbol{r}}_{43} \times \hat{\boldsymbol{r}}_{41}}{\sin\theta_{143}} \cdot \frac{\hat{\boldsymbol{r}}_{41} \times \hat{\boldsymbol{r}}_{42}}{\sin\theta_{142}} \\ &\quad = \frac{\cos\theta_{143}\cos\theta_{142} - \cos\theta_{243}}{\sin\theta_{143}\sin\theta_{142}} = s_1 s_2\end{aligned} \tag{24c}$$

where $s_1 = \pm 1$ and $s_2 = \pm 1$ in the case of four-atom planarity. The unit vectors

$$\boldsymbol{v}_1 = \hat{\boldsymbol{r}}_{42} \qquad \boldsymbol{v}_2 = \frac{\hat{\boldsymbol{r}}_{43} - \cos\theta_{243}\,\hat{\boldsymbol{r}}_{42}}{\sin\theta_{243}} = -r_{42}\nabla_2\theta_{243}$$

form an orthonormal set that spans the 243 plane. The out of plane projection of $\boldsymbol{r}_{41}$ must vanish:

$$\boldsymbol{v} = \hat{\boldsymbol{r}}_{41} - (\hat{\boldsymbol{r}}_{41} \cdot \boldsymbol{v}_1)\boldsymbol{v}_1 - (\hat{\boldsymbol{r}}_{41} \cdot \boldsymbol{v}_2)\boldsymbol{v}_2 = \boldsymbol{0}$$

The first two terms after the first equals sign add to $-r_{42}\nabla_2 \cos\theta_{142}$. Dividing both sides by $r_{42}\sin\theta_{142}$ and applying eq. (24a) yields

$$\frac{\partial\theta_{142}}{\partial q_2} = -s_1\frac{\partial\theta_{243}}{\partial q_2} \tag{25a}$$

A similar analysis applied to the unit vectors

$$\boldsymbol{v}_1 = \hat{\boldsymbol{r}}_{43} \qquad \boldsymbol{v}_2 = \frac{\hat{\boldsymbol{r}}_{42} - \cos\theta_{243}\,\hat{\boldsymbol{r}}_{43}}{\sin\theta_{243}} = r_{43}\nabla_3\theta_{243}$$

yields

$$\frac{\partial\theta_{143}}{\partial q_3} = -s_2\frac{\partial\theta_{243}}{\partial q_3} \tag{25b}$$

Similar analyses for atom 2 projecting out of the 143 plane or atom 3 projecting out of the 142 plane yields these same conditions, and, in addition,

$$\frac{\partial\theta_{142}}{\partial q_1} = -s_1 s_2\frac{\partial\theta_{143}}{\partial q_1} \tag{25c}$$

These results can be interpreted geometrically as follows. The atom 3 gradient vector for the 143-bend interaction is perpendicular to the 43-bond axis and lies in the 143 plane. The atom 3 gradient vector for the 243-bond interaction is perpendicular to the 43-bond axis and lies in the 243 plane. If the four atoms are planar, then the two gradient vectors point in the same or exactly opposite directions, depending on whether s_2 is 1 or -1 (Fig. 3). Similar statements

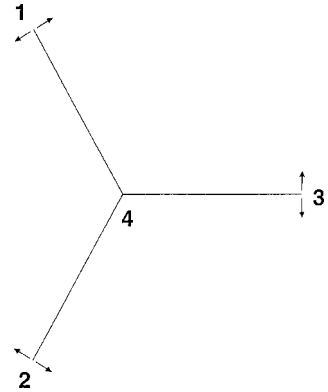

FIGURE 3. Satellite atom gradient vectors for bend interactions within a single improper torsion angle in which the atoms are planar.

hold for the other conditions derived here. From this discussion, the reverse of eqs. (25a)–(25c) holds: beginning with any of these conditions, it follows that $\sin\omega = 0$.

As a side note, similar arguments can be used to show that a bend sequence 123 is linear, i.e.,

$$\cos\theta_{123} = \pm 1$$

if and only if

$$\frac{\partial r_{12}}{\partial q_1} = \mp\frac{\partial r_{23}}{\partial q_2}$$

Results and Discussion

All of the formulas presented here were tested on 50 sets of 2000 points (100,000 points total). A 200-point bond network was randomly generated; each point was made to connect to three or four others. The number of connections was three for tests of improper torsion angle formulas and four otherwise. Within a given bond network, every possible stretch, bend, torsion, and improper torsion sequence was investigated. This made for as stringent as possible a test for the formulas: a wider range of angles and bond distances was covered than in typical molecular simulations.

Tables of internal coordinates and their first and second derivatives were calculated in IEEE double precision, our normal working precision, by our GSF/general bond network approach, with some updated formulas shown here. Laplacians and other quantities involving gradients were calculated from the individual derivatives and compared to our formulas. The two schemes for calculating $\cos\tau$ and $\sin\tau$ were also compared. In every case, the results agreed to within 10^{-12} or to within 12 significant figures. Similar accuracy is achieved in the computation of individual derivatives.

Calculation of a single second partial derivative by way of the Laplacian typically saves between one-third and one-half of the computational effort for diagonal second derivatives over use of the full formula. The overall calculation time for full tables of second derivatives up to torsion or improper torsion (in normal coordinate analysis, for example) is reduced by on the order of 4% from the current GSF/general bond network method. The consequences in classical molecular simulations will vary according to the specifics of the problem.

In ICQMC calculations, the savings will be much greater. A single iteration consists of changing the coordinates of the particles followed by several computations in which the Laplacians and other gradient related quantities are required. In the second stage, no individual first or second partial derivatives are required. Using the gradient formulas eliminates almost half of the overall simulation time.

To test the speed of the calculations we modified the previous version of our code (without gradients) to calculate the Hessian matrix for a linear bond network with 200 atoms with potential energy terms $V(r) = r^3$, $V(\cos\theta) = \cos^3\theta$, $V(\cos\tau) = \cos^3\tau$ (no table lookups for potential energy parameters). The code was written to allow repeated builds of the Hessian matrix so as to obtain a nonnegligible CPU time. Computations were performed on an SGI O2 in double precision. In one set of 10 timing runs, the Hessian matrix was built 12,000 times; in another set of 10, 24,000 times. Subtracting the two average CPU times yielded 0.00576 CPU seconds per Hessian matrix build. A similar calculation was performed on code modified from Ponder's Tinker package version 3.7; this package was chosen in large part because it is well developed and freely available on the Web.[15] The final result was 0.0453 CPU seconds per build, about nine times larger than our result. The most recent version of our code (with the gradients included) was 3% faster than the previous version.

In this particular example, one bond can be part of three bends and four torsions. In Ponder's code, because the derivatives are calculated one atom (three rows) at a time, there are duplicate calculations (a high-end estimate, leading to a smaller estimated time per derivative calculation, is a duplication factor of 4). For more connected bond networks, the difference in times would be expected to be larger still. Dividing the Tinker result by 4 gives a rough comparison with the code reported here of the degree of algebraic optimization; this yields a factor of just over 2 less algebraically optimized than our code). However, it should be noted that storage of the interaction tables makes our code require more memory. The previous discussion did not include improper torsion; however, we would expect similar results as above.

Finally, the four-atom planarity conditions were tested. Sets of 2000 coplanar points were generated as follows. Two vectors were randomly chosen; the coordinates of each point were random linear combinations of these two vectors. The equality of the various partial derivatives, and the vector dot products in eqs. (25a)–(25c), were tested. These results also agreed to within 10^{-12} or 12 significant figures.

The improper torsion formulas shown here are for one atom deviating from planarity. The MM4

potential energy surface is parametrized by three interlocking improper torsion angles. We have previously observed that the triple vector product in eq. (20) is an intermediate (which we denote E) that appears in all three angles. We found further that by using derivatives of E, the treatment of interlocking angles could be optimized further for both first and second derivatives. However, this advantage does not extend to Laplacians or gradient dot products; the formulas for these are made more complicated by writing them in terms of Laplacians and gradient dot products of E.

Conclusions

Faster formulas for the gradient dot products and Laplacians of $\cos\tau$, and completely new formulas for $\sin\tau$ and τ and improper torsion angles, are reported. Such expressions are required in the recently developed internal coordinate quantum Monte Carlo method; the use of these expressions makes ICQMC calculations practical. In addition, the Laplacians can be used to economize the calculation of tables of second derivatives, which are required in several classical simulation methods. This strategy can reduce overall simulation times by a few percent, which can prove significant in long simulations, and does not detract from the accuracy of the calculations.

We also report new calculation sequences $\cos\tau$ and $\sin\tau$. Intermediates required for force calculations are different from those for energy calculations. Because of this, optimal calculation sequences, some of them newly derived, for $\cos\tau$ and $\sin\tau$ are different for force and energy subroutines. These formulas are accurate to better than 12 significant figures in IEEE double precision. In either case, no additional square roots are required.

Finally, a set of required conditions for the planarity of four atoms in a torsion sequence, and several sets for an improper torsion sequence, are presented. These results can be interpreted geometrically in terms of internal bend angle gradient vectors, which lie within the bend angle plane.

Appendix

To derive eq. (10a), we begin with

$$\nabla_1 \cos\tau = \frac{r_{23}}{r_{12}\sin\theta_{123}}\left(\cos\tau\frac{\partial\theta_{123}}{\partial q_3} - \frac{\partial\theta_{234}}{\partial q_2}\right) \quad \text{(A1)}$$

It is simple to prove that

$$\hat{\boldsymbol{r}}_{21}\cdot\nabla_1\theta_{123} = \hat{\boldsymbol{r}}_{32}\cdot\nabla_3\theta_{123} = 0 \quad \text{(A2)}$$

$$\hat{\boldsymbol{r}}_{21}\cdot\nabla_3\theta_{123} = -\frac{\sin\theta_{123}}{r_{23}} \quad \text{(A3)}$$

and, with the help of eq. (7),

$$\hat{\boldsymbol{r}}_{21}\cdot\nabla_2\theta_{234} = -\frac{\sin\theta_{123}\cos\tau}{r_{23}} \quad \text{(A4)}$$

From these results, it follows that

$$\hat{\boldsymbol{r}}_{21}\cdot\nabla_1\cos\tau = \hat{\boldsymbol{r}}_{32}\cdot\nabla_1\cos\tau = 0 \quad \text{(A5)}$$

Similarly,

$$\hat{\boldsymbol{r}}_{43}\cdot\nabla_4\cos\tau = \hat{\boldsymbol{r}}_{32}\cdot\nabla_4\cos\tau = 0 \quad \text{(A6)}$$

Because the gradient vector is perpendicular to $\boldsymbol{r}_{21}$ and $\boldsymbol{r}_{32}$, it must be parallel to their crossproduct, which is also perpendicular to these two vectors. If two vectors $\boldsymbol{f}$ and $\boldsymbol{g}$ are parallel

$$\boldsymbol{f} = c\boldsymbol{g} \quad \text{(A7)}$$

then the proportionality constant c can be calculated from

$$c = \frac{\boldsymbol{f}\cdot\boldsymbol{g}}{\boldsymbol{g}\cdot\boldsymbol{g}} \quad \text{(A8)}$$

With the help of eq. (4), it follows that

$$\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}\cdot\nabla_3\cos\theta_{123} = 0 \quad \text{(A9)}$$

$$\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}\cdot\nabla_2\cos\theta_{234} = \frac{\hat{\boldsymbol{r}}_{43}\cdot\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}}{r_{23}\sin\theta_{234}} \quad \text{(A10)}$$

and from there

$$\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}\cdot\nabla_1\cos\tau = -\frac{\hat{\boldsymbol{r}}_{43}\cdot\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}}{r_{12}\sin\theta_{123}\sin\theta_{234}} \quad \text{(A11)}$$

Finally, by using Lagrange's vector identity, eq. (2e), it can be shown that

$$\left(\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}\right)\cdot\left(\hat{\boldsymbol{r}}_{21}\times\hat{\boldsymbol{r}}_{32}\right) = \sin^2\theta_{123} \quad \text{(A12)}$$

Substituting these results into eq. (A8) yields eq. (10a). Equation (10b) can be derived in a similar manner.

To prove eq. (15), we begin with

$$\frac{\partial^2\tau}{\partial q_1^2} = -\frac{2r_{23}}{r_{12}\sin^2\theta_{123}}\frac{\partial\cos\theta_{123}}{\partial q_3}\frac{\partial\tau}{\partial q_1} \quad \text{(A13)}$$

From eqs. (2a), (14), and (21), we find

$$\nabla_3\cos\theta_{123}\cdot\nabla_1\tau = 0 \quad \text{(A14)}$$

which, when combined with (A13), yields

$$\nabla_1^2\tau = 0 \quad \text{(A15)}$$

The Laplacian for atom 4 can be derived in a similar manner. From

$$\frac{\partial^2\tau}{\partial q_2 \partial q_4} = -b_{432}\frac{\partial^2\tau}{\partial q_4^2} - \frac{1}{r_{23}}\frac{\partial r_{23}}{\partial q_2}\frac{\partial \tau}{\partial q_4} \tag{A16}$$

and from (A6), we obtain

$$\nabla_2 \cdot \nabla_4 \tau = 0 \tag{A17}$$

From

$$\frac{\partial^2\tau}{\partial q_1 \partial q_2} = c_{123}\frac{\partial^2\tau}{\partial q_1^2} - \frac{1}{r_{23}}\frac{\partial r_{23}}{\partial q_2}\frac{\partial \tau}{\partial q_1} \tag{A18}$$

and from (A5) and (A15) we obtain

$$\nabla_1 \cdot \nabla_2 \tau = 0 \tag{A19}$$

From

$$\frac{\partial^2\tau}{\partial q_1 \partial q_4} = 0 \tag{A20}$$

it immediately follows that

$$\nabla_1 \cdot \nabla_4 \tau = 0 \tag{A21}$$

From there, eqs. (18a)–(18c) follow from eq. (17). From

$$\begin{aligned}\frac{\partial^2\tau}{\partial q_2^2} = c_{123}\frac{\partial^2\tau}{\partial q_1 \partial q_2} - b_{423}\frac{\partial^2\tau}{\partial q_2 \partial q_4} \\ - \frac{1}{r_{23}}\left\{\frac{\partial r_{23}}{\partial q_2}\frac{\partial \tau}{\partial q_2} + r_{12}\frac{\partial \cos\theta_{123}}{\partial q_3}\frac{\partial \tau}{\partial q_1}\right. \\ \left. + r_{34}\frac{\partial \cos\theta_{234}}{\partial q_2}\frac{\partial \tau}{\partial q_4}\right\}\end{aligned} \tag{A22}$$

combined with (A17), (A19), eq. (17), and similar results, we obtain

$$\nabla_2^2 \tau = 0 \tag{A23}$$

Laplacian expressions involving atom 3 can be derived from translational invariance. For example,

$$\nabla_2 \cdot \nabla_3 \tau = -\left(\nabla_1 \cdot \nabla_2 \tau + \nabla_2^2 \tau + \nabla_2 \cdot \nabla_4 \tau\right) = 0 \tag{A24}$$

The Laplacian for atom 3 can be proven to vanish from several more applications of translational invariance. This completes the derivation of eq. (15).

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