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An Efficient Matrix Algorithm for the Calculation of the Gradient of the Conformational Energy of Polymer Chains

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Rapidly converging algorithms for the minimization of the conformational energy function of polymer chains use the gradient of the conformational energy. We have developed an efficient algorithm for this gradient which is especially useful in the case of many geometrical variables because the calculation time is only weakly dependent on the number of variables.

1. INTRODUCTION

Large molecules, e.g., polymer chains, often have a large degree of flexibility and many different conformations [1]. These conformations may be analyzed by minimizing the conformational energy with respect to an appropriate set of geometrical variables [2]. As is well known, the parts of the conformational energy depending on the atomic distances may be calculated by a matrix algorithm due to Eyring [3]. Now a minimization algorithm for a function with many variables which will converge rapidly needs not only the function but also its gradient or even its second derivatives.

We have therefore developed an efficient matrix algorithm for the calculation of the gradient of the conformational energy. It is especially useful in the case of a large number of variables because the calculation time is weakly dependent on the number of variables. We are about to extend this algorithm to the second derivatives and to the case of several interacting chains (condensed polymers). This will be published later.

2. GEOMETRICAL DESCRIPTION OF A POLYMER CHAIN

In conformational analysis, the energy usually consists of several parts. They are listed in Table I.

As nonbonded and coulomb interactions depend on the distance, these energies are more easily calculated in Cartesian coordinates than in *chemical* or inner coordinates (bond lengths, valence angles, dihedral angles). On the other hand, hindered internal rotation, etc. are easily calculated in chemical coordinates.

We decided to use chemical coordinates as basic variables, because the sometimes-needed restrictions (fixed bond lengths or bond angles) are thus very easily realized.

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TABLE I

Parts of the Conformational Energy and Their Representation in Different Types of Coordinates

Type of energy	Type of coordinates	
	Cartesian	Chemical
Nonbonded interaction (Lennard–Jones or Buckingham type) Coulomb interaction	Easy	Complicated
Hindered interal rotation Bond length deformation Valence angle deformation	Complicated	Easy

We therefore developed an effective algorithm which handles the energies of the nonbonded type.

According to Eyring [3], rectangular coordinates are fixed to each atom of the backbone as in shown in Fig. 1. There are $S(i)$ side group atoms belonging to the backbone atom i. They are denoted with the position vectors $\mathbf{v}^{i,j}$ in the local system i ($\mathbf{v}^{i,0} = \mathbf{0}$; $j = 1,..., S(i)$).

The local systems are connected by orthogonal transformations. The transformation $i \to i+1$ is done by the matrix

$$\tilde{\mathbf{T}}^i = \begin{pmatrix} \cos\alpha^i & \sin\alpha^i & 0 \\ \sin\alpha^i \cos\varphi^i & -\cos\alpha^i \cos\varphi^i & \sin\varphi^i \\ \sin\alpha^i \sin\varphi^i & -\cos\alpha^i \sin\varphi^i & -\cos\varphi^i \end{pmatrix}. \tag{1}$$

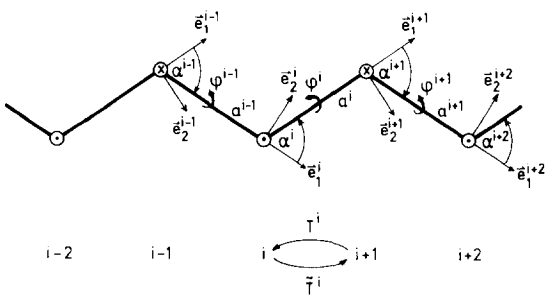

FIG. 1. Backbone with local rectangular coordinates: i, number of the local system; $\mathbf{e}_k^i$, orthonormal vectors in the local system i ($k = 1, 2, 3$); α^i, valence angle; φ^i, dihedral angle (planar backbone: all $\varphi^i = 0$); $\mathbf{a}^i$, vector of bond length $i \to i+1$, $\mathbf{a}^i = a^i \cdot \mathbf{e}_1^{i+1}$.

The inverse transformation $i+1 \to i$ is done by $\mathbf{T}^i = (\tilde{\mathbf{T}}^i)^{-1}$. By means of these matrices, all vectors are transformed to a *reference system* $i = m$ (see Eqs. (11)–(19)). Thus it is possible to calculate the distances.

In the following sections, the backbone variables (see Fig. 1) are denoted by

$$\xi^i = (\alpha^i, \varphi^i, a^i).$$

The side group variables are either the Cartesian components of the vectors $\mathbf{v}^{i,j}$ or the corresponding spherical polar coordinates. We call the side group variables $\lambda^{i,j,p}$ $(p = 1, 2, 3)$.

A matrix $\boldsymbol{\eta}$ of all variables may be defined as

$$\boldsymbol{\eta}^{i,j} = (\xi^i, \boldsymbol{\lambda}^{i,j}).$$

3. Calculation of the Conformational Energy and its Gradient

3.1 *Basic Equations*

In the following sections, only those parts of the conformational energy are considered which are dependent on the distance r of nonbonded atoms. The interaction between the atoms s and t may then by written as

$$U^{st} = U^{st}(r^{st}) = U^{st}[|\mathbf{x}^s(\boldsymbol{\eta}) - \mathbf{x}^t(\boldsymbol{\eta})|], \tag{2}$$

where $\mathbf{x}^l$ is the position vector in the reference system $i = m$ of the atom l $(l = s, t)$.

The total nonbonded interaction of N atoms is given by the double sum

$$U(\boldsymbol{\eta}) = \tfrac{1}{2} \sum_{s}^{N} \sum_{t}^{N} U^{st}. \tag{3}$$

In order to calculate this energy, all difference vectors $\mathbf{x}^s - \mathbf{x}^t$ have to be calculated by means of the transformation formulas (11)–(19). Then the distances r^{st} are calculated and the summation of the U^{st} can be performed.

The derivative of the energy with respect to an arbitrary variable η_k $(\eta_k \in \boldsymbol{\eta})$ is

$$\frac{\partial U}{\partial \eta_k} = \sum_{l=1}^{N} \frac{\partial U}{\partial \mathbf{x}^l} \cdot \frac{\partial \mathbf{x}^l}{\partial \eta_k} = \frac{1}{2} \sum_{s,t,l=1}^{N} \frac{\partial U^{st}}{\partial \mathbf{x}^1} \cdot \frac{\partial \mathbf{x}^1}{\partial \eta_k}, \qquad s \neq t. \tag{4}$$

The sum (4) reduces to

$$\frac{\partial U}{\partial \eta_k} = \frac{1}{2} \sum_{s,t=1}^{N} \left(\frac{\partial U^{st}}{\partial \mathbf{x}^s} \cdot \frac{\partial \mathbf{x}^s}{\partial \eta_k} + \frac{\partial U^{st}}{\partial \mathbf{x}^t} \cdot \frac{\partial \mathbf{x}^t}{\partial \eta_k} \right).$$

Now we use $U^{st} = U^{ts}$ and $r^{st} = r^{ts}$ to get

$$\frac{\partial U}{\partial \eta_k} = \sum_{s,t=1}^{N} \frac{\partial U^{st}}{\partial \mathbf{x}^s} \cdot \frac{\partial \mathbf{x}^s}{\partial \eta_k} = \sum_{s=1}^{N} \left(\sum_{t=1}^{N} \frac{\partial U^{st}}{\partial \mathbf{x}^s} \right) \cdot \frac{\partial \mathbf{x}^s}{\partial \eta_k}. \tag{5}$$

The first term of Eq. (5) in brackets is easily given by

$$\sum_{t=1}^{N} \frac{\partial U^{st}}{\partial \mathbf{x}^s} = \sum_{t=1}^{N} \frac{\partial U^{st}}{\partial r^{st}} \frac{\partial r^{st}}{\partial \mathbf{x}^s} = \sum_{t=1}^{N} \frac{\partial U^{st}}{\partial r^{st}} \frac{\mathbf{x}^s - \mathbf{x}^t}{r^{st}}, \quad s \neq t. \tag{6}$$

The derivative $\partial U^{st}/\partial r^{st}$ is obtained from $U^{st}(r^{st})$, the difference vectors and distances are calculated as explained above.

The special properties of the second term $\partial \mathbf{x}^s/\partial \eta_k$ (Eq. (5)) are derived in the following sections.

3.2 *Properties of the Derivatives of the Position Vectors*

The position vectors $\mathbf{x}^i$ are now characterized in more detail (in the same way as $\mathbf{v}$): The position of atom j belonging to system i is described by $\mathbf{x}^{i,j}$ (origin in coordinate system m; $j = 0$ backbone atom; $j = 1,\ldots, S(i)$ side group atoms). Equation (5) now becomes

$$\frac{\partial U}{\partial \eta_k} = \sum_{i=1}^{G} \sum_{j=0}^{S(i)} \frac{\partial U}{\partial \mathbf{x}^{i,j}} \cdot \frac{\partial \mathbf{x}^{i,j}}{\partial \eta_k}. \tag{7}$$

Index i runs over all backbone systems (G is the number of backbone atoms), and j runs over all atoms in system i. The number S of side group atoms depends on i.

It is easy to see that the second term $\partial \mathbf{x}^{i,j}/\partial \eta_k$ vanishes in many cases. Taking η_k^q to be a variable k in system q it can be seen, with Fig. 2, that

$$\begin{aligned} \frac{\partial \mathbf{x}^{i,j}}{\partial \eta_k^q} &= 0, \quad \text{for} \quad m \leqslant i < q, \\ &\neq 0, \quad \text{for} \quad m \leqslant q < i, \end{aligned} \Bigg\} \textit{ upper backbone}$$

$$\begin{aligned} &\neq 0, \quad \text{for} \quad i < q < m, \\ &= 0, \quad \text{for} \quad q < i < m, \end{aligned} \Bigg\} \textit{ lower backbone.} \tag{8}$$

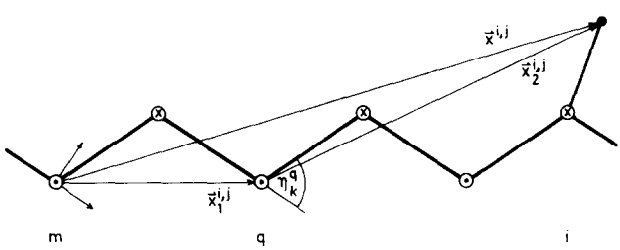

FIG. 2. Subdivision of a position vector with respect to system q. The variable η_k^q is shown as a valence angle.

Using Eq. (8), we divide Eq. (7) into three parts:

$$\frac{\partial U}{\partial \eta_k} = \sum_{i=G_o}^{m+1} \sum_{j=0}^{S(i)} \frac{\partial U}{\partial \mathbf{x}^{i,j}} \cdot \frac{\partial \mathbf{x}^{i,j}}{\partial \eta_k} + \sum_{j=0}^{S(m)} \frac{\partial U}{\partial \mathbf{x}^{m,j}} \cdot \frac{\partial \mathbf{x}^{m,j}}{\partial \eta_k} + \sum_{i=G_u}^{m-1} \sum_{j=0}^{S(i)} \frac{\partial U}{\partial \mathbf{x}^{i,j}} \cdot \frac{\partial \mathbf{x}^{i,j}}{\partial \eta_k} \tag{9}$$

$$= \frac{\partial U}{\partial \eta_k}\bigg|_{i>m} + \frac{\partial U}{\partial \eta_k}\bigg|_{i=m} + \frac{\partial U}{\partial \eta_k}\bigg|_{i<m}. \tag{10}$$

The systems of the backbone have the numbers G_u, $G_u + 1$,..., $G_o - 1$, G_o. With respect to the recursion formula developed below, it is necessary to start the summations over the systems from the ends of the backbone, i.e., $i = G_o$, $G_o - 1$,..., and $i = G_u$, $G_u + 1$,....

In order to calculate $\partial U/\partial \eta_k^q$, only one of the three terms of Eq. (9) must be considered; two always vanish. Moreover, the summation over i must be carried out only until $i = q$ (see Eq. (8)). Both effects reduce computing time.

3.3 *Transformation of the Position Vectors*

In order to deduce the recursion formula, it is useful to distinguish between the vectors characterizing backbone atoms and the vectors characterizing side group atoms (cf. Fig. 3). We write

$$\mathbf{g}^i = \mathbf{x}^{i,0}, \qquad \text{(backbone)},$$

and

$$\mathbf{s}^{i,j} = \mathbf{x}^{i,j}, \qquad j \neq 0, \qquad \text{(side group)}.$$

The transformation of the vectors $\mathbf{v}^{i,j}$ (given in the local systems) to the vectors $\mathbf{x}^{i,j}$ (given in the reference system m) is done recursively by means of the matrices $\mathbf{T}^i$. The recursion starts from the chosen reference coordinate system m and extends to both chain ends (Eqs. (12) and (16)).

For $i > m$ we have

$$\mathbf{x}^{i,j} = \mathbf{g}^i + \mathbf{M}^{i-1} \cdot \mathbf{v}^{i,j}, \tag{11}$$

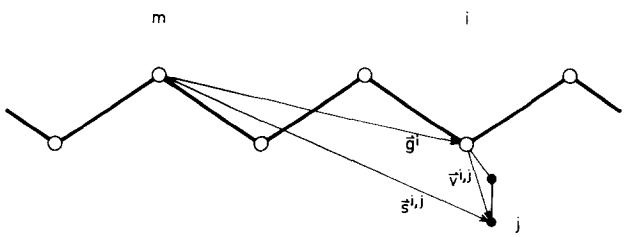

FIG. 3. Description of backbone and side group atoms.

where

$$\mathbf{M}^{i-1} = \prod_{l=m}^{i-1} \mathbf{T}^l = \mathbf{M}^{i-2} \cdot \mathbf{T}^{i-1}, \tag{12}$$

with $\mathbf{M}^{m-1} = \mathbf{E}$ (unity matrix).

For $\mathbf{v}^{i,0} \equiv \mathbf{0}$, we have

$$\mathbf{x}^{i,0} = \mathbf{g}^i, \qquad \mathbf{g}^i = \mathbf{g}^{i-1} + \mathbf{M}^{i-1} \cdot \mathbf{a}^{i-1}, \qquad \mathbf{g}^m = \mathbf{0}. \tag{13}$$

It is important to note that

$$\mathbf{g}^i = \mathbf{g}^i(\xi^m, \xi^{m+1}, \ldots, \xi^{i-1}).$$

For side group atoms ($j \neq 0$), we have

$$\mathbf{s}^{i,j} = \mathbf{g}^i + \mathbf{M}^{i-1} \cdot \mathbf{v}^{i,j}, \tag{14}$$

with

$$\mathbf{s}^{i,j} = \mathbf{s}^{i,j}(\xi^m, \xi^{m+1}, \ldots, \xi^{i-1}, \boldsymbol{\lambda}^{i,j}).$$

For $i = m$ we have

$$\mathbf{x}^{m,j} = \mathbf{s}^{m,j} = \mathbf{v}^{m,j}. \tag{15}$$

For $i < m$ the formulas are analogous.

$$\mathbf{x}^{i,j} = \mathbf{g}^i + \tilde{\mathbf{M}}^i \cdot \mathbf{v}^{i,j},$$

where

$$\tilde{\mathbf{M}}^i = \prod_{l=m-1}^{i} \tilde{\mathbf{T}}^l = \tilde{\mathbf{M}}^{i+1} \cdot \tilde{\mathbf{T}}^i, \tag{16}$$

$$\tilde{\mathbf{M}}^m = \mathbf{E} \qquad \text{(unity matrix)}. \tag{17}$$

For $\mathbf{v}^{i,0} \equiv \mathbf{0}$ we have

$$\mathbf{x}^{i,0} = \mathbf{g}^i, \qquad \mathbf{g}^i = \mathbf{g}^{i+1} - \tilde{\mathbf{M}}^{i+1} \cdot \mathbf{a}^i, \qquad \mathbf{g}^m = \mathbf{0}, \tag{18}$$

with

$$\mathbf{g}^i = \mathbf{g}^i(\xi^{m-1}, \xi^{m-2}, \ldots, \xi^i).$$

And finally,

$$\mathbf{s}^{i,j} = \mathbf{g}^i + \tilde{\mathbf{M}}^i \cdot \mathbf{v}^{i,j}, \tag{19}$$

with

$$\mathbf{s}^{i,j} = \mathbf{s}^{i,j}(\xi^{m-1}, \xi^{m-2}, \ldots, \xi^i, \boldsymbol{\lambda}^{i,j}).$$

3.4 *Derivation of Recursion Formulas for the Gradient*

We now continue to investigate the three terms of Eq. (9).

Case $i = m$

Inserting Eq. (15) into the second term of Eq. (10) gives

$$\left.\frac{\partial U}{\partial \eta_k}\right|_{i=m} = \sum_{j=1}^{S(m)} \frac{\partial U}{\partial \mathbf{s}^{m,j}} \cdot \frac{\partial \mathbf{v}^{m,j}}{\partial \eta_k}. \tag{20}$$

In the side group, we have $\partial \mathbf{v}^{m,j}/\partial \eta_k = \partial \mathbf{v}^{m,j}/\partial \lambda_k$ ($\mathbf{v}$ depends only on the local side group variables).

Taking $\lambda^{m,r,p}$ as a variable referring to the atom r in the system m ($p = 1, 2, 3$) we get

$$\left.\frac{\partial U}{\partial \lambda^{m,r,p}}\right|_{i=m} = \frac{\partial U}{\partial \mathbf{s}^{m,r}} \cdot \frac{\partial \mathbf{v}^{m,r}}{\partial \lambda^{m,r,p}}. \tag{21}$$

Case $i > m$

Inserting Eq. (11) into the first term of Eq. (9) and considering a variable in system q, we get

$$\left.\frac{\partial U}{\partial \eta_k^q}\right|_{i>m} = \sum_{i=G_o}^{m+1} \sum_{j=0}^{S(i)} \left\{ \frac{\partial U}{\partial \mathbf{x}^{i,j}} \cdot \frac{\partial \mathbf{g}^i}{\partial \eta_k^q} + \frac{\partial U}{\partial \mathbf{s}^{i,j}} \cdot \frac{\partial}{\partial \eta_k^q} (\mathbf{M}^{i-1} \cdot \mathbf{v}^{i,j}) \right\}. \tag{22}$$

The matrices $\mathbf{M}$ are defined in Eq. (12).[1]

We now look at $\partial U/\partial \xi^{q,p}|_{i>m}$ and $\partial U/\partial \lambda^{q,r,p}|_{i>m}$ which refer to the backbone part or the side group part of $\partial U/\partial \eta_k^q|_{i>m}$ and get

$$\left.\frac{\partial U}{\partial \lambda^{q,r,p}}\right|_{i>m} = \frac{\partial U}{\partial \mathbf{s}^{q,r}} \cdot \mathbf{M}^{q-1} \cdot \frac{\partial \mathbf{v}^{q,r}}{\partial \lambda^{q,r,p}} \tag{23}$$

and

$$\frac{\partial U}{\partial \xi^{q,p}} = \sum_{i=G_o}^{m+1} \sum_{j=0}^{S(i)} \left\{ \frac{\partial U}{\partial \mathbf{x}^{i,j}} \cdot \frac{\partial \mathbf{g}^i}{\partial \xi^{q,p}} + \frac{\partial U}{\partial \mathbf{s}^{i,j}} \cdot \frac{\partial \mathbf{M}^{i-1}}{\partial \xi^{q,p}} \cdot \mathbf{v}^{i,j} \right\}. \tag{24}$$

[1] For the calculations of the matrices $\mathbf{M}^{i-1}$, we can use the fact that after the recursive calculation of the conformational energy (Eqs. (1)–(3), (11)–(19)), the product matrices $\mathbf{M}^{G_o-1}$, $\mathbf{M}^{G_u}$ (Case $i < m$) at both chain ends are available. Therefore, it is convenient to invert the recursion formula Eq. (12). We then get

$$\mathbf{M}^{i-2} = \mathbf{M}^{i-1} \cdot \tilde{\mathbf{T}}^{i-1}. \tag{12a}$$

From this and from Eq. (8), the method for developing a recursion formula for the derivatives which start at the chain ends is obvious.

While Eq. (23), valid for the sidegroups, has its final form, a recursion formula is derived from Eq. (24). By means of the equation for the derivatives of the transformation matrices

$$\frac{\partial \mathbf{M}^i}{\partial \xi^{q,p}} = \frac{\partial}{\partial \xi^{q,p}} \prod_{l=m}^{i} \mathbf{T}^l \tag{25}$$

(remember that $\partial T^l/\partial \xi^{q,p} = 0$ for $q \neq l$, and therefore $\partial \mathbf{M}^i/\partial \xi^{q,p} = 0$ for $q < i$) and (cf. Eq. (8))

$$\frac{\partial \mathbf{g}^i}{\partial \xi^{q,p}} = \sum_{l=m}^{i-1} \frac{\partial \mathbf{M}^l}{\partial \xi^{q,p}} \cdot \mathbf{a}^l + \mathbf{M}^l \cdot \frac{\partial \mathbf{a}^l}{\partial \xi^{q,p}} \tag{26}$$

(remember that $\partial \mathbf{a}^l/\partial \xi^{q,p} = 0$ for $q \neq l$), Eq. (24) may be written as

$$\begin{aligned} \frac{\partial U}{\partial \xi^{q,p}}\bigg|_{i>m} = \sum_{i=G_o}^{m+1} \sum_{j=0}^{S(i)} \Bigg\{ \frac{\partial U}{\partial \mathbf{x}^{i,j}} \Bigg[\sum_{l=m}^{i-1} \left(\frac{\partial}{\partial \xi^{q,p}} \prod_{k=m}^{l} \mathbf{T}^k \right) \cdot \mathbf{a}^l + \mathbf{M}^q \cdot \frac{\partial \mathbf{a}^q}{\partial \xi^{q,p}} \Bigg] \\ + \frac{\partial U}{\partial \mathbf{s}^{i,j}} \cdot \left(\frac{\partial}{\partial \xi^{q,p}} \prod_{k=m}^{i-1} \mathbf{T}^k \right) \cdot \mathbf{v}^{i,j} \Bigg\}. \end{aligned} \tag{27}$$

If we develop Eq. (27) for consecutive backbone systems q, we get

$q = G_{lo} = n.$

$$\frac{\partial U}{\partial \xi^{n,p}}\bigg|_{i>m} = 0. \tag{28}$$

$q = n - 1.$

$$\begin{aligned} \frac{\partial U}{\partial \xi^{n-1,p}}\bigg|_{i>m} = \sum_{j=0}^{S(n)} \Bigg\{ \frac{\partial U}{\partial \mathbf{x}^{n,j}} \cdot \mathbf{M}^{n-2} \cdot \frac{\partial \mathbf{T}^{n-1}}{\partial \xi^{n-1,p}} \cdot \mathbf{a}^{n-1} + \frac{\partial U}{\partial \mathbf{x}^{n,j}} \cdot \mathbf{M}^{n-1} \cdot \frac{\partial \mathbf{a}^{n-1}}{\partial \xi^{n-1,p}} \\ + \frac{\partial U}{\partial \mathbf{s}^{n,j}} \cdot \mathbf{M}^{n-2} \cdot \frac{\mathbf{T}^{n-1}}{\partial \xi^{n-1,p}} \cdot \mathbf{v}^{n,j} \Bigg\}. \end{aligned} \tag{29}$$

$q = n - 2.$

$$\begin{aligned} \frac{\partial U}{\partial \xi^{n-2,p}}\bigg|_{i>m} = \sum_{j=0}^{S} \Bigg\{ \frac{\partial U}{\partial \mathbf{x}^{n-1,j}} \cdot \mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot \mathbf{a}^{n-2} + \frac{\partial U}{\partial \mathbf{x}^{n-1,j}} \cdot \mathbf{M}^{n-2} \cdot \frac{\partial \mathbf{a}^{n-2}}{\partial \xi^{n-2,p}} \\ + \frac{\partial U}{\partial \mathbf{s}^{n-1,j}} \cdot \mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot \mathbf{v}^{n-1,j} \\ + \frac{\partial U}{\partial \mathbf{x}^{n,j}} \cdot \left[\mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot \mathbf{a}^{n-2} + \mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot \mathbf{T}^{n-1} \cdot \mathbf{a}^{n-1} \right] \\ + \frac{\partial U}{\partial \mathbf{x}^{n,j}} \cdot \mathbf{M}^{n-2} \cdot \frac{\partial \mathbf{a}^{n-2}}{\partial \xi^{n-2,p}} + \frac{\partial U}{\partial \mathbf{s}^{n,j}} \cdot \mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot \mathbf{T}^{n-1} \cdot \mathbf{v}^{n,j} \Bigg\}. \end{aligned} \tag{30}$$

The upper limit $j = S$ depends on the actual value of the system index in each term (i.e., n or $n-1$; in general, $n, n-1,\ldots, q+1$).

Now we rearrange the terms in Eqs. (29) and (30).

$q = n - 1$.

$$\frac{\partial U}{\partial \xi^{n-1,p}}\bigg|_{i>m} = \sum_{j=0}^{S(n)} \left\{ \mathbf{M}^{n-2} \cdot \frac{\partial \mathbf{T}^{n-1}}{\partial \xi^{n-1,p}} \cdot\cdot \left[\frac{\partial U}{\partial \mathbf{x}^{n,j}} \circ \mathbf{a}^{n-1} + \frac{\partial U}{\partial \mathbf{s}^{n,j}} \circ \mathbf{v}^{n,j} \right] + \mathbf{M}^{n-1} \cdot\cdot \left[\frac{\partial U}{\partial \mathbf{x}^{n,j}} \circ \frac{\partial \mathbf{a}^{n-1}}{\partial \xi^{n-1,p}} \right] \right\} \tag{31}$$

Here $\circ$ denotes the dyadic product, and $\cdot\cdot$ the scalar product of matrices. We introduce the following abbreviations:

$$\mathbf{A}^i = \sum_{j=0}^{S(i)} \frac{\partial U}{\partial \mathbf{x}^{i,j}}, \tag{32}$$

$$\mathbf{B}^i = \sum_{j=1}^{S(i)} \frac{\partial U}{\partial \mathbf{s}^{i,j}} \circ \mathbf{v}^{i,j}, \tag{33}$$

and start the recursions with

$$\mathbf{C}^{n-1} = \mathbf{A}^n \circ \mathbf{a}^{n-1}, \tag{34a}$$

$$\mathbf{D}^{n-1} = \mathbf{B}^n, \tag{34b}$$

$$\mathbf{F}^{n-1} = \mathbf{A}^n. \tag{34c}$$

Hence

$$\frac{\partial U}{\partial \xi^{n-1,p}}\bigg|_{i>m} = \mathbf{M}^{n-2} \cdot \frac{\partial \mathbf{T}^{n-1}}{\partial \xi^{n-1,p}} \cdot\cdot (\mathbf{C}^{n-1} + \mathbf{D}^{n-1}) + \mathbf{M}^{n-1} \cdot\cdot \left(F^{n-1} \circ \frac{\partial \mathbf{a}^{n-1}}{\partial \xi^{n-1,p}} \right). \tag{31'}$$

$q = n - 2$. Eq. (30) may then be written as

$$\frac{\partial U}{\partial \xi^{n-2,p}}\bigg|_{i>m} = \mathbf{M}^{n-3} \cdot \frac{\partial \mathbf{T}^{n-2}}{\partial \xi^{n-2,p}} \cdot\cdot \left[\mathbf{T}^{n-1} \cdot \mathbf{C}^{n-1} + (\mathbf{A}^n + \mathbf{A}^{n-1}) \circ \mathbf{a}^{n-2} + \mathbf{T}^{n-1} \cdot \mathbf{D}^{n-1} + \mathbf{B}^{n-1} \right] + \mathbf{M}^{n-2} \cdot\cdot \left[(\mathbf{F}^{n-1} + \mathbf{A}^{n-1}) \circ \frac{\partial \mathbf{a}^{n-2}}{\partial \xi^{n-2,p}} \right]. \tag{35}$$

With the recursions

$$\mathbf{C}^{n-2} = \mathbf{T}^{n-1} \cdot \mathbf{C}^{n-1} + (\mathbf{A}^n + \mathbf{A}^{n-1}) \circ \mathbf{a}^{n-2}, \tag{36a}$$

$$\mathbf{D}^{n-2} = \mathbf{T}^{n-1} \cdot \mathbf{D}^{n-1} + \mathbf{B}^{n-1}, \tag{36b}$$

$$\mathbf{F}^{n-2} = \mathbf{F}^{n-1} + \mathbf{A}^{n-1}, \tag{36c}$$

we get

$$\left.\frac{\partial U}{\partial \xi^{n-2,p}}\right|_{i>m} = \mathbf{M}^{n-3} \cdot \frac{\partial T^{n-2}}{\partial \xi^{n-2,p}} \cdot\cdot (\mathbf{C}^{n-2} + \mathbf{D}^{n-2}) + \mathbf{M}^{n-2} \cdot\cdot \left(\mathbf{F}^{n-2} \circ \frac{\partial \mathbf{a}^{n-2}}{\partial \xi^{n-2,p}}\right). \quad (35')$$

This equation is of the same type as Eq. (31′) and can be easily generalized to

$$\left.\frac{\partial U}{\partial \xi^{q,p}}\right|_{i>m} = \mathbf{M}^{q-1} \cdot \frac{\partial \mathbf{T}^{q}}{\partial \xi^{q,p}} \cdot\cdot (\mathbf{C}^{q} + \mathbf{D}^{q}) + \mathbf{M}^{q} \cdot\cdot \left(\mathbf{F}^{q} \circ \frac{\partial \mathbf{a}^{q}}{\partial \xi^{q,p}}\right), \quad (37)$$

with

$$\mathbf{C}^{q} = \mathbf{T}^{q+1} \cdot \mathbf{C}^{q+1} + \sum_{\overline{i=G_o}}^{q+1} \mathbf{A}^{i} \circ \mathbf{a}^{q},\ \mathbf{C}^{G_o} = 0 \quad (38a)$$

$$\mathbf{D}^{q} = \mathbf{T}^{q+1} \cdot \mathbf{D}^{q+1} + \mathbf{B}^{q+1},\ \mathbf{D}^{G_o} = 0 \quad (38b)$$

$$\mathbf{F}^{q} = \mathbf{F}^{q+1} + \mathbf{A}^{q+1},\ \mathbf{F}^{G_o} = 0. \quad (38c)$$

Case $i < m$

The formulas for the case $i < m$ are derived in an analogous way. For the side group variables we get

$$\left.\frac{\partial U}{\partial \lambda^{q,r,p}}\right|_{i<m} = \frac{\partial U}{\partial \mathbf{s}^{q,r}} \cdot \tilde{\mathbf{M}}^{q} \cdot \frac{\partial \mathbf{v}^{q,r}}{\partial \lambda^{q,r,p}}. \quad (39)$$

For the backbone variables we get

$$\left.\frac{\partial U}{\partial \xi^{q,p}}\right|_{i<m} = \tilde{\mathbf{M}}^{q+1} \cdot \frac{\partial \tilde{\mathbf{T}}^{q}}{\partial \xi^{q,p}} \cdot\cdot (\tilde{\mathbf{C}}^{q} + \tilde{\mathbf{D}}^{q}) + \tilde{\mathbf{M}}^{q+1} \cdot\cdot \left(\tilde{\mathbf{F}} \circ \frac{\partial \mathbf{a}^{q}}{\partial \xi^{q,p}}\right) \quad (40)$$

with

$$\tilde{\mathbf{C}}^{q} = \tilde{\mathbf{T}}^{q-1} \cdot \tilde{\mathbf{C}}^{q-1} - \sum_{\overline{i=G_u}}^{q-1} \mathbf{A}^{i} \circ \mathbf{a}^{q-1},\ \tilde{\mathbf{C}}^{G_u} = 0 \quad (41a)$$

$$\tilde{\mathbf{D}}^{q} = \tilde{\mathbf{T}}^{q-1} \cdot \tilde{\mathbf{D}}^{q-1} + \mathbf{B}^{q},\ \tilde{\mathbf{D}}^{G_u - 1} = 0 \quad (41b)$$

$$\tilde{\mathbf{F}}^{q} = \tilde{\mathbf{F}}^{q-1} - \mathbf{A}^{q},\ \tilde{\mathbf{F}}^{G_u - 1} = 0. \quad (41c)$$

4. Computing Steps

We now summarize the sequence of steps to calculate the gradient in a computer program.

(i) The backbone of the chain is given by the set of variables $\boldsymbol{\xi}$ (Fig. 1) together with the transformation matrices (Eq. (1)) and their derivatives.

(ii) The side groups are defined by the local vectors $\mathbf{v}^{i,j}$ (Fig. 3) together with the set of variables $\boldsymbol{\lambda}$, from which the derivatives $\partial \mathbf{v}^{i,j}/\partial \boldsymbol{\lambda}$ are immediately obtained in the local coordinate systems.

(iii) Now the position vectors $\mathbf{x}^{i,j}$ are calculated by recursive transformations of the locally defined vectors $\mathbf{v}^{i,j}$ to the reference system m (Eqs. (11)–(19)).

(iv) Using the $\mathbf{x}^{i,j}$, the difference vectors and distances are obtained. Now the conformational energy $U^{st}(r^{st})$ and Eq. (6) can be calculated.

(v) Now we are ready to calculate the $\partial U/\partial \boldsymbol{\lambda}$ (Eqs. (21), (23), and (39)) and the $\partial U/\partial \boldsymbol{\xi}$ (Eqs. (37) and (40)) by means of the recursion formulas of Eqs. (38) and (41).

One of the main features of this algorithm is the splitting of the double sum in Eq. (5). Thus, Eq. (6) is calculated independently of the variables $\boldsymbol{\eta}$. Therefore, the time of calculation is weakly dependent on the number of variables.

5. Quantitative Estimates of the Efficiency

A simple measure of the efficiency of an algorithm which calculates the gradient vector is the relative time

$$\tau = \frac{\text{CPU time for a gradient call}}{\text{CPU time for a function call}}.$$

It decreases with increasing efficiency and will approximately show no dependence on the details of the program and the machine.

A simple algorithm (the precursor of our algorithm) calculates each element of the gradient vector independently. In this case we have, roughly, $\tau \sim n$ (the number of variables).

The numerical calculation of the gradient (finite difference approximation) needs at least $n + 1$ function calls. In order to get machine accuracy, between $2n + 1$ and $4n + 1$ additional function calls are needed (see, e.g., routine E 04HBA of the NAG-library [4]). So we have $\tau \approx n + 1, \ldots, 5n + 2$.

Measurements of τ for our algorithm are given in Table II.

TABLE II

Measurement of the Relative Time

Number of variables n	Relative time τ
48	1.7,..., 1.8
108	1.6
120	1.5
132	1.4,..., 1.5

Note. Relative time τ = (CPU-time for gradient call)/(CPU-time for a function call) for a polyethylene chain with conformational defects. The energy function has n variables.

We chose problems of conformational defects in a polyethylene chain. The energy function depends on $n = 48,..., 132$ variables. The table clearly shows that the calculation of the complete gradient vector takes less than twice the time of a function call. The relative time τ is not proportional to n. There is even a slight decrease in τ with an increasing number of variables.

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