General derivative relations for anharmonic force fields

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The brace notation, introduced by Allen and Császár (1993, *J. chem. Phys.*, **98**, 2983), provides a simple and compact way to deal with derivatives of arbitrary non-tensorial quantities. One of its main advantages is that it builds the permutational symmetry of the derivatives directly into the formalism. The brace notation is applied to formulate the general nth-order Cartesian derivatives of internal coordinates, and to provide closed forms for general, nth-order transformation equations of anharmonic force fields, expressed as Taylor series, from internal to Cartesian or normal coordinate spaces.

1. Introduction

One of the first steps in analyses of the internal motion of molecular species is the selection of an appropriate set of structural and dynamical coordinates. Considerable effort has been devoted toward understanding the properties of different orthogonal or non-orthogonal, rectilinear or curvilinear coordinate systems, and the transformation of scalar and vector quantities from one coordinate system to another [1–16]. Thus, the theory is well established and many important aspects are covered in standard textbooks [2, 9]. Still, as shown here, improvements can be made in treatments of coordinate systems employed in theoretical chemistry.

Equations expressing the transformation of derivatives from internal coordinates into the Cartesian space, and vice versa, are cumbersome due to the nonlinear nature of common internal coordinate systems. About ten years ago Neto, in a series of papers [10–14], introduced elements of tensor theory as an aid to derivation, simplification and computation of these bulky expressions. This approach seemed logical, as tensor theory is concerned with how particular mathematical quantities (a given set of functions) behave under general coordinate transformations. However, most quan-

tities which appear in anharmonic force field studies are non-tensorial†. Nevertheless, the basic idea of Neto was to introduce derivatives of the metric tensor to express second- and higher-order coefficients of the transformation equations, as usual in such mathematical theories. More explicitly, Neto employed Christoffel symbols of the second kind, which are third-order covariant affine tensors formed as appropriate sums of partial derivatives of the metric tensor. To calculate the Christoffel symbols, the metric tensor must be given in advance, as noted by Neto, which, with the aid of computer algebra systems (CAS), can indeed be achieved easily [17]. Neto observed [11] that the quadratic and cubic geometric derivative relations‡ can be cast into a form involving Christoffel symbols of the second kind and their first derivatives. It is shown here that a conceptually simpler and more compact representation of these expressions can be achieved without any explicit reference to the usual elements of tensor algebra and derivatives of tensors.

2. The brace notation

In the theory of molecular vibrations, complications arise from the transformation of coordinates from one set to another when the transformation equations are nonlinear. If two distinct sets of n independent coordinates are denoted by covariant vector components r_i and q_r, such a transformation would take the general form

$$r_i = X_i^r q_r + \tfrac{1}{2} X_i^{rs} q_r q_s + \tfrac{1}{6} X_i^{rst} q_r q_s q_t + \tfrac{1}{24} X_i^{rstu} q_r q_s q_t q_u + \dots . \tag{1}$$

In this equation the summation convention has been adopted, where independent summations are assumed over each index that is repeated as both a superscript and a subscript. The transformation coefficients $X_i^{rs\dots}$ are defined by the equations

$$X_i^r = \partial r_i / \partial q_r, \tag{2}$$

$$X_i^{rs} = \partial^2 r_i / \partial q_r \partial q_s, \tag{3}$$

$$X_i^{rst} = \partial^3 r_i / \partial q_r \partial q_s \partial q_t, \tag{4}$$

and

$$X_i^{rstu} = \partial^4 r_i / \partial q_r \partial q_s \partial q_t \partial q_u, \tag{5}$$

etc. The presence of non-zero higher derivatives implies that the transformation is nonlinear.

When we wish to use the X elements to transform the potential energy V, for example, from the r representation to the q representation, we obtain somewhat complex transformation equations involving sums over many permutations of the indices. For example, if the expansion of V in the two sets of coordinates is written

$$V = V^e + V^i r_i + \tfrac{1}{2} V^{ij} r_i r_j + \tfrac{1}{6} V^{ijk} r_i r_j r_k + \dots$$

$$= V^e + V^r q_r + \tfrac{1}{2} V^{rs} q_r q_s + \tfrac{1}{6} V^{rst} q_r q_s q_t + \dots , \tag{6}$$

then it may be shown that the expansion coefficients are related by the equations

$$V^r = V^i X_i^r = V^i X_i\{r\}, \tag{7}$$

$$V^{rs} = V^{ij} X_i^r X_j^s + V^i X_i^{rs} = V^{ij} X_{ij}\{r, s\} + V^i X_i\{rs\}, \tag{8}$$

and

$$V^{rst} = V^{ijk} X_i^r X_j^s X_k^t + V^{ij}(X_i^{rs} X_j^t + X_i^{rt} X_j^s + X_i^{st} X_j^r) + V^i X_i^{rst}$$

$$= V^{ijk} X_{ijk}\{r, s, t\} + V^{ij} X_{ij}\{rs, t\} + V^i X_i\{rst\}. \tag{9}$$

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† Neto showed, e.g., in equations (27) and (28) of [10], that the second-order transformation equation can be expressed in a form which represents a formal tensor transformation.

‡ Note that equations $(26a)$–$(26c)$ of [11] are equivalent to equations (8), (16) and (17) of [16], respectively.

Table 1. Total number of terms, $\mathscr{L}(K, n)$, represented by the brace notation in second through fifth order in relation to permutation groups S_n.

Group	Class	Order	$X_{\alpha_1 \alpha_2 \cdots \alpha_n}$	$\mathscr{L}(K, n)$
S_2	1^2	1	$\{\beta_1, \beta_2\}$	1
S_3	1^3	1	$\{\beta_1, \beta_2, \beta_3\}$	1
	12	3	$\{\beta_1 \beta_2, \beta_3\}$	3
	3	2	$\{\beta_1 \beta_2 \beta_3\}$	1
S_4	1^4	1	$\{\beta_1, \beta_2, \beta_3, \beta_4\}$	1
	$1^2 2$	6	$\{\beta_1 \beta_2, \beta_3, \beta_4\}$	6
	13	8	$\{\beta_1 \beta_2 \beta_3, \beta_4\}$	4
	2^2	3	$\{\beta_1 \beta_2, \beta_3 \beta_4\}$	3
	4	6	$\{\beta_1 \beta_2 \beta_3 \beta_4\}$	1
S_5	1^5	1	$\{\beta_1, \beta_2, \beta_3, \beta_4, \beta_5\}$	1
	$1^3 2$	10	$\{\beta_1 \beta_2, \beta_3, \beta_4, \beta_5\}$	10
	$1^2 3$	20	$\{\beta_1 \beta_2 \beta_3, \beta_4, \beta_5\}$	10
	$1 2^2$	15	$\{\beta_1 \beta_2, \beta_3 \beta_4, \beta_5\}$	15
	14	30	$\{\beta_1 \beta_2 \beta_3 \beta_4, \beta_5\}$	5
	23	20	$\{\beta_1 \beta_2 \beta_3, \beta_4 \beta_5\}$	10
	5	24	$\{\beta_1 \beta_2 \beta_3 \beta_4 \beta_5\}$	1

[a] It is clear, see also the text, that for a given partition of segment length K in the group S_n, $\mathscr{L}(K, n) = n! / [\prod_{k=1}^{\lambda} (l_k!)^{m_k} (m_k!)]$, where λ is the number of distinct lengths in the partition, l_k is the length of the kth segment and m_k is the number of occurrences of the same segment length.

In equations (7)–(9) the brace notation [16] is introduced, which is defined as follows:

$$X_{\alpha_1 \alpha_2 \cdots \alpha_n}\{\beta_1 \gamma_1 \cdots, \beta_2 \gamma_2 \cdots, \cdots, \beta_n \gamma_n \cdots\}$$
$$\equiv \sum_{\mathscr{L}} X_{\alpha_1 \alpha_2 \cdots \alpha_n}[\mathscr{C}_{\mathscr{L}}(\beta_1 \gamma_1 \cdots, \beta_2 \gamma_2 \cdots, \cdots, \beta_n \gamma_n \cdots)], \quad (10)$$

where X is an arbitrary quantity, and $\mathscr{L}$ enumerates all unique combinations $\mathscr{C}_{\mathscr{L}}$ of a given composite list of indices, while

$$X_{\alpha_1 \alpha_2 \cdots \alpha_n}[\beta_1 \gamma_1 \cdots, \beta_2 \gamma_2 \cdots, \cdots, \beta_n \gamma_n \cdots] \equiv X_{\alpha_1}^{\beta_1 \gamma_1 \cdots} X_{\alpha_2}^{\beta_2 \gamma_2 \cdots} \cdots X_{\alpha_n}^{\beta_n \gamma_n \cdots}, \quad (11)$$

and typically

$$X_{\alpha_1}^{\beta_1 \gamma_1 \cdots} \equiv \left(\frac{\partial^n r_{\alpha_1}}{\partial q_{\beta_1} \partial q_{\gamma_1} \cdots} \right), \quad (12)$$

with q and r denoting arbitrary coordinate systems. The following example,

$$X_{\alpha_1 \alpha_2}\{\beta\gamma, \delta\} \equiv X_{\alpha_1 \alpha_2}[\beta\gamma, \delta] + X_{\alpha_1 \alpha_2}[\beta\delta, \gamma] + X_{\alpha_1 \alpha_2}[\gamma\delta, \beta]$$
$$\equiv X_{\alpha_1}^{\beta\gamma} X_{\alpha_2}^{\delta} + X_{\alpha_1}^{\beta\delta} X_{\alpha_2}^{\gamma} + X_{\alpha_1}^{\gamma\delta} X_{\alpha_2}^{\beta}, \quad (13)$$

elucidates the notation.

As is clear from the examples above, a central feature of the notation is that it introduces in the braces the permutation of indices of coordinates with respect to which the derivatives are to be formed. This has important ramifications if the brace notation is to be used for quantities which are derivatives of scalars. To emphasize the

close connection between permutational symmetry and the brace notation, the number of terms represented by the brace notation is given, for a few representative cases, in table 1. Note that the total number of terms indicated in the last column of table 1 would not necessarily arise in every case, the structure of X might have to be considered in order to ascertain the permutational properties of the braces [16]. Nevertheless, in the cases to follow, all terms referred to in table 1 are present.

3.   Applications of the notation

Examples are presented to highlight the merits of the brace notation when working with curvilinear internal coordinates as used in molecular spectroscopy, which are scalars even in their most general definition, measuring arbitrary distances and angles within a molecule.

3.1. **B** *tensors*

The brace notation proves powerful in the formulation of **B** tensor elements of arbitrary order, i.e., the general nth-order derivatives of internal coordinates with respect to the Cartesian position vectors of the constituent atoms. In demonstrating the brace formulation here for three basic internal coordinates—bond distances (R), valence bond angles (ϕ) and torsion angles (τ)—the following notation is adopted: a, b, c and d (generically a_i or b_i) represent constituent atoms; α, β, γ, δ and σ (generically α_i) denote Cartesian variables x, y or z; $\mathscr{P}_{\mathscr{N}_K}^{(K, \, m_n)}$ is an operator for the partition $\mathscr{N}_K$ which divides a list of m_n indices $\mu_{m_n} = a_1 \alpha_1 a_1 \alpha_2 \ldots a_1 \alpha_{m_1} a_2 \alpha_{m_1+1} a_2 \alpha_{m_1+2} \ldots a_2 \alpha_{m_2} a_3 \alpha_{m_2+1} a_3 \alpha_{m_2+2} \ldots a_3 \alpha_{m_3} \ldots a_n \alpha_{m_{n-1}+1} a_n \alpha_{m_{n-1}+2} \ldots a_n \alpha_{m_n}$ into K segments $\{l_i; i = 1, 2, \ldots, K\}$, and $\mathscr{L}(K, m_n)$ is the number of such unique partitions $\mathscr{N}_K$. The $\mathscr{P}_{\mathscr{N}_K}^{(K, \, m_n)}$ operator is prevalent in the algebra of the symmetric group S_{m_n} and is similar to the entity $\mathscr{P}_{a, \mathscr{N}}^{(K; \, n)}$ defined by Allen and Császár [16]; it maintains the initial lexical ordering within μ, but the segment lengths are now ordered arbitrarily as $l_1 \leqslant l_2 \ldots \leqslant l_K$.

Direct differentiation shows that for atom a the first- and second-order **B** tensor elements of the bond-stretching coordinate R_{ab} are simply

$$B_R^{a\alpha} \equiv \frac{\partial R_{ab}}{\partial \alpha_a} = R_{ab}^{-1}(\alpha_a - \alpha_b) = -\frac{\partial R_{ab}}{\partial \alpha_b} = -B_R^{b\alpha} \qquad (14)$$

and

$$B_R^{a\alpha a\beta} \equiv \frac{\partial^2 R_{ab}}{\partial \alpha_a \partial \beta_a} = -R_{ab}^{-1}(B_R^{a\alpha} B_R^{a\beta} - \delta_{\alpha\beta}). \qquad (15)$$

The quantity $B_R^{a\alpha}$ is a component of the ubiquitous El'yashevich–Wilson **B** matrix [2], and it can be rendered collectively as $\mathbf{b}_R^a \equiv (B_R^{ax}, B_R^{ay}, B_R^{az}) = \mathbf{e}_{ab}$, where $\mathbf{e}_{ab}$ is the unit vector directed from a to b. In equation (15), $\delta_{\alpha\beta}$ is the Kronecker delta symbol. A common factor of R_{ab}^{-1} and products of lower-order tensor elements appear in all bond-stretch derivative expressions. For all orders greater than two, the general formula becomes

$$B_R^{a\alpha_1 \, a\alpha_2 \ldots a\alpha_n} = -R_{ab}^{-1} \sum_{\mathscr{N}}^{\mathscr{L}(2; \, n)} B_{R^{(2)}} \{\mathscr{P}_{\mathscr{N}}^{(2; \, n)}(a\alpha_1 \, a\alpha_2 \ldots a\alpha_n)\}, \qquad (16)$$

which involves partitions of the indices into two segments, these being applied to a product of two lower-order **B** tensor elements for R_{ab}, as signified by the $R^{(2)}$ subscript in the brace notation. To illustrate the notation, consider the fourth-order expression.

The unique partitions of 4 into 2 segments are (13) and (2^2). As shown in table 1, the braces for (13) and (2^2) embody 4 and 3 terms, respectively; hence,

$$B_R^{a\alpha\beta a\gamma a\delta} \equiv \frac{\partial^4 R_{ab}}{\partial\alpha_a\partial\beta_a\partial\gamma_a\partial\delta_a} = -R_{ab}^{-1}(B_R^{a\alpha}B_R^{a\beta a\gamma a\delta} + B_R^{a\beta}B_R^{a\alpha a\gamma a\delta} + B_R^{a\gamma}B_R^{a\alpha a\beta a\delta} + B_R^{a\delta}B_R^{a\alpha a\beta a\gamma})$$

$$- R_{ab}^{-1}(B_R^{a\alpha a\beta}B_R^{a\gamma a\delta} + B_R^{a\alpha a\gamma}B_R^{a\beta a\delta} + B_R^{a\alpha a\delta}B_R^{a\beta a\gamma}). \tag{17}$$

The structure of equation (16) facilitates the recursive construction of high-order **B** tensors from collections of lower-order counterparts with minimal arithmetic requirements, a highly desirable property for practical applications which motivates similar formulations for other coordinates.

For the valence bond angle ϕ_{abc}, the key to the general formulation is the identification

$$B_\phi^{a\alpha} = R_{ab}^{-1}\csc\phi[(\mathbf{e}_{bc}\cdot\mathbf{e}_{ba})\mathbf{e}_{ba} - \mathbf{e}_{bc}]_\alpha = -\csc\phi\sum_{\sigma\in\{x,y,z\}}B_{R_{ab}}^{a\sigma a\alpha}B_{R_{bc}}^{c\sigma}, \tag{18}$$

where $\mathbf{e}_{ab}$ and $\mathbf{e}_{bc}$ are again unit vectors directed from atoms a to b and b to c, respectively. Note that the convenient contraction of terms into a dot product over $\{x,y,z\}$ of first- and second-order *stretching* tensors allows equation (16) to be utilized. Differentiation of equation (18) with respect to the terminal atoms a and c, followed by back substitution from the same equation to eliminate the original summation over σ, yields

$$B_\phi^{a\alpha a\beta} = -\cot\phi B_\phi^{a\alpha}B_\phi^{a\beta} - \csc\phi\sum_{\sigma\in\{x,y,z\}}B_{R_{ab}}^{a\sigma a\alpha a\beta}B_{R_{bc}}^{c\sigma} \tag{19}$$

and

$$B_\phi^{a\alpha c\beta} = -\cot\phi B_\phi^{a\alpha}B_\phi^{c\beta} - \csc\phi\sum_{\sigma\in\{x,y,z\}}B_{R_{ab}}^{a\sigma a\alpha}B_{R_{bc}}^{c\sigma c\beta}. \tag{20}$$

This scheme can be implemented repeatedly to reveal the following generic form:

$$B_\phi^{a\alpha_1 a\alpha_2\ldots a\alpha_m c\alpha_{m+1} c\alpha_{m+2}\ldots c\alpha_n} = \sum_{K=2}^n f_K(\phi)\sum_{\mathcal{N}_K}^{\mathscr{B}(K,n)} B_{\phi^{(K)}}\{\mathscr{P}_{\mathcal{N}_K}^{(K,n)}(a\alpha_1 a\alpha_2\ldots a\alpha_m c\alpha_{m+1} c\alpha_{m+2}\ldots c\alpha_n)\}$$

$$- \csc\phi\sum_{\sigma\in\{x,y,z\}}B_{R_{ab},R_{bc}}[a\sigma a\alpha_1 a\alpha_2\ldots a\alpha_m, c\sigma c\alpha_{m+1} c\alpha_{m+2}\ldots c\alpha_n], \tag{21}$$

in which

$$f_K(\phi) = \begin{cases} 1 & \text{if } K \text{ odd,} \\ (-1)^{K/2}\cot\phi & \text{if } K \text{ even.} \end{cases} \tag{22}$$

The double summation constituting the first term of equation (21) now includes all partitions of n with number of segments K greater than 1, and the indices divided by the operator $\mathscr{P}_{\mathcal{N}_K}^{(K,n)}$ are applied via the brace symbol to products of K lower-order **B** tensors of ϕ. In the fourth-order case, the partition list is (13), (2^2), ($1^2 2$) and (1^4), the respective brace symbols representing 4, 3, 6 and 1 terms. Thus,

$$B_\phi^{a\alpha a\beta a\gamma a\delta} = -\cot\phi(B_\phi^{a\alpha}B_\phi^{a\beta a\gamma a\delta} + B_\phi^{a\beta}B_\phi^{a\alpha a\gamma a\delta} + B_\phi^{a\gamma}B_\phi^{a\alpha a\beta a\delta} + B_\phi^{a\delta}B_\phi^{a\alpha a\beta a\gamma})$$

$$- \cot\phi(B_\phi^{a\alpha a\beta}B_\phi^{a\gamma a\delta} + B_\phi^{a\alpha a\gamma}B_\phi^{a\beta a\delta} + B_\phi^{a\alpha a\delta}B_\phi^{a\beta a\gamma})$$

$$+ (B_\phi^{a\alpha}B_\phi^{a\beta}B_\phi^{a\gamma a\delta} + B_\phi^{a\alpha}B_\phi^{a\gamma}B_\phi^{a\beta a\delta} + B_\phi^{a\alpha}B_\phi^{a\delta}B_\phi^{a\beta a\gamma}$$

$$+ B_\phi^{a\beta}B_\phi^{a\gamma}B_\phi^{a\alpha a\delta} + B_\phi^{a\beta}B_\phi^{a\delta}B_\phi^{a\alpha a\gamma} + B_\phi^{a\gamma}B_\phi^{a\delta}B_\phi^{a\alpha a\beta})$$

$$+ \cot\phi B_\phi^{a\alpha}B_\phi^{a\beta}B_\phi^{a\gamma}B_\phi^{a\delta} - \csc\phi\sum_{\sigma\in\{x,y,z\}}B_{R_{ab}}^{a\sigma a\alpha a\beta a\gamma a\delta}B_{R_{bc}}^{c\sigma} \tag{23}$$

for the $a\alpha a\beta a\gamma a\delta$ derivative, with all a/c cross-derivatives being of identical form.

The terminal-atom derivatives of the dihedral angle τ_{abcd} are perhaps best obtained from the customary first-order vector expression

$$\mathbf{b}_\tau^a = \frac{\mathbf{e}_{ba} \times \mathbf{e}_{bc}}{R_{ab}\sin^2\phi_{abc}},$$ (24)

because this form is devoid of $\sin\tau$ or $\cos\tau$ factors in the denominator which give rise to point singularities at planar or perpendicular conformations. The substitutions $\mathbf{e}_{bc} = \mathbf{b}_{R_{bc}}^c$ and $\mathbf{e}_{ba} = [R_{ab}\sin\phi_{abc}\mathbf{b}_{\phi_{abc}}^a + \mathbf{e}_{bc}]\sec\phi_{abc}$ in the numerator of equation (24) provide the compact form

$$\sin(2\phi_{abc})B_\tau^{a\alpha_1} = 2(\mathbf{b}_{\phi_{abc}}^2 \times \mathbf{b}_{R_{bc}}^c)_{\alpha_1}.$$ (25)

To differentiate the left side of equation (25), a generalized product rule for partial derivatives is useful, as formulated conveniently in brace notation:

$$B_{f \times g}^{\mu_n} = fB_g^{\mu_n} + gB_f^{\mu_n} + \sum_{\mathcal{N}}^{\mathcal{L}(2;\,n)}(B_{f,g}\{\mathscr{P}_{\mathcal{N}}^{(2;\,n)}(\mu_n)\} + B_{g,f}\{\mathscr{P}_{\mathcal{N}}^{(2;\,n)}(\mu_n)\}).$$ (26)

Accordingly, the recursive formula

$$\sin(2\phi_{abc})B_\tau^{a\alpha_1 a\alpha_2 \ldots a\alpha_m} = 2(\mathbf{b}_{\phi_{abc}}^{a\alpha_1 a\alpha_2 \ldots a\alpha_m} \times \mathbf{b}_{R_{bc}}^c)_{\alpha_1} - B_\tau^{a\alpha_1}B_{\sin(2\phi_{abc})}^{a\alpha_2 \ldots a\alpha_m}$$

$$- \sum_{\mathcal{N}}^{\mathcal{L}(2;\,n)}(B_{\tau,\sin(2\phi_{abc})}\{a\alpha_1 \mathscr{P}_{\mathcal{N}}^{(2;\,n)}(a\alpha_2 \ldots a\alpha_m)\} + B_{\sin(2\phi_{abc}),\tau}\{\mathscr{P}_{\mathcal{N}}^{(2;\,n)}(a\alpha_2 \ldots a\alpha_m)a\alpha_1\})$$ (27)

is obtained for a-atom derivatives of τ. All a/d terminal-atom cross-derivatives vanish, as revealed by equation (24). The utility of equation (27) hinges not only on equation (21) for the evaluation of $\mathbf{b}_{\phi_{abc}}^{a\alpha_1 a\alpha_2 \ldots a\alpha_m}$ but also on a means of computing $\mathbf{B}$ tensor elements of the composite function $\sin(2\phi_{abc})$. Fortunately, the latter can be built up from ϕ_{abc} counterparts using another inductively-derived formula involving sums over partitions:

$$B^{a\alpha_1 a\alpha_2 \ldots a\alpha_m b\alpha_{m+1} b\alpha_{m+2} \ldots b\alpha_n c\alpha_{n+1} \alpha_{n+2} \ldots c\alpha_p} =$$

$$\sum_{K=1}^{P} h_K(\phi)\sum_{\mathcal{N}_K}^{\mathcal{L}(K,P)}\eta_{\mathcal{N}_K}B_{\phi^{(K)}}[\mathscr{P}_{\mathcal{N}_K}^{(K,\,P)}(a\alpha_1 a\alpha_2 \ldots a\alpha_m b\alpha_{m+1} b\alpha_{m+2} \ldots b\alpha_n c\alpha_{n+1} c\alpha_{n+2} \ldots c\alpha_p)].$$ (28)

The summand therein involves a $\mathbf{B}$-tensor bracket rather than a brace, whereas

$$h_K(\phi) = \begin{cases} (-1)^{(K-1)/2}\cos\phi & \text{if } K \text{ odd}, \\ (-1)^{K/2}\sin\phi & \text{if } K \text{ even}, \end{cases}$$ (29)

and $\eta_{\mathcal{N}}$ is a combinatoric factor. If there are $\lambda_{\mathcal{N}}$ distinct lengths in the partition of p into K segments, and length l_j appears n_j times, then $\sum_{j=1}^{\lambda_{\mathcal{N}}}n_j l_j = p$, $\sum_{j=1}^{\lambda_{\mathcal{N}}}n_j = K$, and it happens that

$$\eta_{\mathcal{N}} = \frac{p!}{\prod_{j=1}^{\lambda_{\mathcal{N}}}(l_j!)^{n_j}(n_j!)}.$$ (30)

Translational invariance conditions reduce the number of explicit formulas of arbitrary order which are required to generate complete sets of $\mathbf{B}$ tensors for force field transformations. For any two-point coordinate (Q_2) such as the bond distance R_{ab}, all b-atom derivatives can be replaced with a-atom counterparts according to

$$B_{Q_2}^{a\alpha_1 a\alpha_2 \ldots a\alpha_m b\alpha_{m+1} b\alpha_{m+2} \ldots b\alpha_n} = (-1)^{n-m}B_{Q_2}^{a\alpha_1 a\alpha_2 \ldots a\alpha_m a\alpha_{m+1} a\alpha_{m+2} \ldots a\alpha_n}.$$ (31)

For a general n-point coordinate (Q_n), translational invariance can be invoked successively to eliminate all indices involving an arbitrarily chosen atom a_2:

$$B_{Q_n}^{a_1\alpha_1 a_1\alpha_2\cdots a_1\alpha_{m_1} a_2\alpha_{m_1+1} a_2\alpha_{m_1+2}\cdots a_2\alpha_{m_2} a_3\alpha_{m_2+1} a_3\alpha_{m_2+2}\cdots a_3\alpha_{m_3}\cdots a_n\alpha_{m_{n-1}+1} a_n\alpha_{m_{n-1}+2}\cdots a_n\alpha_{m_n}}$$

$$= -\sum_{b_1} B_{Q_n}^{a_1\alpha_1 a_1\alpha_2\cdots a_1\alpha_{m_1} b_1\alpha_{m_1+1} a_2\alpha_{m_1+2}\cdots a_2\alpha_{m_2} a_3\alpha_{m_2+1} a_3\alpha_{m_2+2}\cdots a_3\alpha_{m_3}\cdots a_n\alpha_{m_{n-1}+1} a_n\alpha_{m_{n-1}+2}\cdots a_n\alpha_{m_n}}$$

$$= (-1)^{m_2-m_1}$$

$$\sum_{b_1 b_2\cdots b_{m_2-m_1}} B_{Q_n}^{a_1\alpha_1 a_1\alpha_2\cdots a_1\alpha_{m_1} b_1\alpha_{m_1+1} b_2\alpha_{m_1+2}\cdots b_{m_2-m_1}\alpha_{m_2} a_3\alpha_{m_2+1} a_3\alpha_{m_2+2}\cdots a_3\alpha_{m_3}\cdots a_n\alpha_{m_{n-1}+1} a_n\alpha_{m_{n-1}+2}\cdots a_n\alpha_{m_n}},$$

$$(32)$$

where atoms $b_i \in \{a_k; k = 1, 3, 4, \ldots, n\}$. In essence, the first equivalence in equation (32) constitutes an efficacious, recursive algorithm for building up **B** tensors involving atom a_2. For the valence bond angle ϕ_{abc}, equations (21) and (32) are thus sufficient to compute a complete set of nth-order derivatives. For the dihedral angle τ_{abcd}, explicit derivative formulae involving a central atom cannot be avoided, however, because only indices of atom b or c can be fully replaced via equation (32). The use of rotational invariance relations does not solve this problem, because their structure requires at least some **B** tensor components of three distinct atoms as an initial input. Ostensibly, explicit torsional derivative formulae for all combinations of $a/b/d$ type are thus necessary. However, any **B** tensor element involving *both* terminal atoms vanishes, so that only diagonal a, b and d as well as off-diagonal a/b and b/d derivative types are requisite. Equation (27) nicely accounts for the diagonal a and d elements, but the explicit formulae for the other three types are not compact.

Note, finally, that all formulae but the translational invariance conditions presented in this section were checked with the powerful CAS program *Mathematica* [18].

3.2. *Force field transformation* 1

This application of the brace notation considers nonlinear force constant transformations between internal and Cartesian spaces. Because the molecular potential energy surface does not depend on the external variables (translation and rotation) of the system, the components of the Cartesian gradient can be determined via a linear, tensorial transformation of the internal forces alone

$$V^r = V^i B_i^r, \tag{33}$$

where V^r and V^i are used to denote Cartesian- and internal-coordinate potential energy derivatives, respectively, and the summation should, of course, go through M, the number of internal coordinates. In third order, a transformation expression for the cubic force constant matrix in Cartesian coordinates arises by direct differentiation of equation (33), resulting in

$$V^{rst} = V^i B^i\{rst\} + V^{ij} B^{ij}\{rs, t\} + V^{ijk} B^{ijk}\{r, s, t\}. \tag{34}$$

With the aid of the brace notation, the general transformation equation can be written in the following abstract form:

$$V^{i_1 i_2\cdots i_n} = \sum_{K=1}^{n} \left[\sum_{P_1 P_2\cdots P_K}^{M} V^{P_1 P_2\cdots P_K} \sum_{n=1}^{\mathscr{L}(K, n)} B^{P_1 P_2\cdots P_K}\{\mathscr{P}_{\mathscr{N}}^{(K, n)}(i_1 i_2\cdots i_n)\} \right] \tag{35}$$

In equation (35) no use of the Einstein summation convention was made to show

details of the summation limits. The similar structure of equations (16), (21), (28) and (35) is expected as derivatives of internal coordinates, and derivatives of the molecular potential energy, another scalar, are formulated therein. Note, finally, that a general equation governing the inverse transformation of Cartesian force fields into internal coordinate ones is given, using the brace notation, in [16].

3.3. *Force field transformation* 2

A simplified method of setting up the required nonlinear coordinate transformations from curvilinear internal coordinates to simple normal coordinates has been described, some time ago, by Hoy, Mills and Strey [7b]. The transformation coefficients were called the **L** tensor elements and the transformation equation in second and third orders were provided as

$$\Phi^{rr} = \lambda_r = f^{ij} L_i^r L_j^r, \text{ no sum over } r, \tag{36}$$

and

$$\Phi^{rst} = f^{ijk} L_i^r L_j^s L_k^t + f^{ij}(L_i^{rs} L_j^t + L_i^{rt} L_j^s + L_i^{st} L_j^r), \tag{37}$$

where the coefficients $\lambda_r = 4\pi^2 c^2 \omega_r^2$ are the harmonic force constants; the first derivative elements of the **L** tensor are identical to the familiar **L** matrix [2], the f^{ij} and f^{ijk} are second- and third-order force constants in internal coordinates, respectively, while Φ^{rr} and Φ^{rst} are second- and third-order force constants in normal cordinates, respectively.

In the brace notation the third- and fourth-order transformation equations, presented in equation (11) of [7b], are simply rewritten as

$$\Phi^{rst} = f^{ijk} L_{ijk}\{r, s, t\} + f^{ij} L_{ij}\{rs, t\} \tag{38}$$

and

$$\Phi^{rstu} = f^{ijkl} L_{ijkl}\{r, s, t, u\} + f^{ijk} L_{ijk}\{rs, t, u\} + f^{ij}(L_{ij}\{rs, tu\} + L_{ij}\{rst, u\}). \tag{39}$$

It is clear from the structure of the above equations that the transformation terms can be cast into a general form, valid through nth order, as follows:

$$\Phi^{i_1 i_2 \cdots i_n} = \sum_{K=2}^{n} \left[\sum_{P_1 P_2 \cdots P_K}^{M} f^{P_1 P_2 \cdots P_K} \sum_{\mathcal{N}=1}^{\mathscr{L}(K, n)} L_{P_1 P_2 \cdots P_K} \{\mathscr{P}_{\mathscr{N}}^{(K, n)}(i_1 i_2 \cdots i_n)\} \right]. \tag{40}$$

The great similarity of equations (35) and (40) is obvious. The main difference between the two equations is that while B_i^r can be given analytically, L_j^r, for obvious reasons, cannot. A further difference is that the first summation in equation (40) goes only from $K = 2$, as in this case no first-order derivatives (forces) are of interest.

4. Summary

In the theory of molecular vibrations complications arise in nonlinear transformation among coordinate sets, but it is shown here that the brace notation introduced in equations (10)–(12) provides a simple and compact way to deal with the derivatives arising in the equations. The main advantage of the notation is that it builds the permutational symmetry of the derivatives directly into the formalism, thus simplifying the appearance of the related expressions significantly and allowing a straightforward way for their generalization. In this communication the brace notation is applied to formulate the general nth-order Cartesian derivatives of internal

coordinates. Due to the required translational invariance condition pertaining to the derivatives, all Cartesian derivatives of the stretching and the bending coordinate can be determined from the expression given for one centre. Closed forms for general, *n*th-order transformation equations of anharmonic force fields, expressed as Taylor series, from internal to Cartesian or normal coordinate spaces are also given. A related expression, governing the inverse transformation of Cartesian force fields into the internal space is given, using the same brace notation, in [16].

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