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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2001 issue.

NOTES

Gradients of vibrational coordinates from the variation of coordinates along the path of a particle

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The elements of the reciprocal metric tensor $[\mathbf{g}]$, which appear in the exact internal kinetic energy operator,^{1,2}

$$\hat{F}^{(\text{int})} = \sum_{ij} \left[-\frac{\hbar^2}{2} \left(\frac{\partial}{\partial q_i} + \frac{1}{J} \frac{\partial J}{\partial q_i} \right) g^{(q_i q_j)} \frac{\partial}{\partial q_j} - \frac{1}{2} g^{(L_i L_j)} \hat{l}_i \hat{l}_j - \frac{\hbar}{2} g^{(L_i q_j)} \hat{l}_i \frac{\partial}{\partial q_j} - \frac{\hbar}{2} \left(\frac{\partial}{\partial q_i} + \frac{1}{J} \frac{\partial J}{\partial q_i} \right) g^{(q_i L_j)} \hat{l}_j \right] \quad (1)$$

of a polyatomic molecule can, in principle, be written as the mass-weighted sum of the inner products of the measuring vectors $\mathbf{e}_\alpha^{(q_i)}$ associated with the coordinates q_i (or, in the case of rotational degrees of freedom, to the body-frame components $\hat{l}_i = \mathbf{u}' \cdot \hat{\mathbf{I}}$ of the angular momentum operator $\hat{\mathbf{I}}$), and to the nuclei of the molecule as

$$g^{(q_i q_j)} = \sum_{\alpha} \frac{1}{m_{\alpha}} \mathbf{e}_{\alpha}^{(q_i)} \cdot \mathbf{e}_{\alpha}^{(q_j)}, \quad (2)$$

where N is the number of the particles, and m_{α} is the mass of the particle α . The J in Eq. (1) is the (absolute value of the) Jacobian, the indices i and j run from 1 to $3N-6$ for the shape coordinates, and from 1 to 3 for the angular momentum components, and to be precise, it is supposed that the integrations are performed using the volume-element $d\tau = J dq_1 dq_2 \dots$. The values of the measuring vectors $\mathbf{e}_{\alpha}^{(q_i)}$ at the reference configuration are the familiar Wilson's s -vectors.³ In the case of vibrational degrees of freedom, the measuring vectors are the gradients of the vibrational coordinates,

$$\mathbf{e}_{\alpha}^{(q_i)} = \nabla_{\alpha} q_i. \quad (3)$$

It has been shown in Ref. 1 that the gradients can be directly and easily obtained for any geometrically defined shape coordinates by the vectorial differentiation. However, there is

in some cases a more practical way to obtain these gradients from the variation of the coordinate q_i along the path $\mathbf{x}_{\alpha}(t)$ of the particle α as (p. 108 of Ref. 4)

$$\dot{q}_i = \sum_{\alpha} \dot{\mathbf{x}}_{\alpha}(t) \cdot \nabla_{\alpha} q_i, \quad (4)$$

where I use the short-hand notation $\dot{F} = dF/dt$, and t is some scalar parameter. It should be mentioned, that all the rules of the scalar differentiation apply, with an exception of the commutativity. For example, the product rule reads as

$$\frac{d}{dt}(FG) = \dot{F}G + F\dot{G}, \quad (5)$$

because generally $\dot{F}G \neq G\dot{F}$ unless one of them is a scalar (or a trivector). In order to give the reader a chance to compare the present method to other methods, I rederive the known gradients for the bond stretching.^{1,3}

Example 1: The most basic of all possible internal coordinates is the bond length $r_{\alpha\beta} = |\mathbf{r}_{\alpha\beta}| = (\mathbf{r}_{\alpha\beta} \cdot \mathbf{r}_{\alpha\beta})^{1/2}$, where $\mathbf{r}_{\alpha\beta} = \mathbf{x}_{\beta} - \mathbf{x}_{\alpha}$. When both sides of the equation,

$$r_{\alpha\beta}^2 = \mathbf{r}_{\alpha\beta} \cdot \mathbf{r}_{\alpha\beta} \quad (6)$$

are differentiated with respect to some scalar parameter t , the result

$$2r_{\alpha\beta} \dot{r}_{\alpha\beta} = 2\mathbf{r}_{\alpha\beta} \cdot \dot{\mathbf{r}}_{\alpha\beta} \quad (7)$$

follows. When the terms are rearranged, one obtains

$$\dot{r}_{\alpha\beta} = \frac{\mathbf{r}_{\alpha\beta} \cdot \dot{\mathbf{r}}_{\alpha\beta}}{r_{\alpha\beta}} = \frac{\mathbf{r}_{\alpha\beta} \cdot (\dot{\mathbf{x}}_{\beta} - \dot{\mathbf{x}}_{\alpha})}{r_{\alpha\beta}}, \quad (8)$$

where the coordinate gradients are easily picked with the help of Eq. (4) as

$$\nabla_{\beta} r_{\alpha\beta} = \frac{\mathbf{r}_{\alpha\beta}}{r_{\alpha\beta}} = -\nabla_{\alpha} r_{\alpha\beta}. \quad (9)$$

The present approach can often be used effectively to find the gradients of the shape coordinates, which are given as *implicit* functions of the nuclear positions, and would be

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very difficult (or impossible) to obtain by other methods. As an example of this kind, I derive the gradients of the eigenvalues λ_1 , λ_2 , and λ_3 of the moment tensor

$$\mathfrak{M}(\boldsymbol{\omega}) = \sum_{\alpha} m_{\alpha} \mathbf{y}_{\alpha} \mathbf{y}_{\alpha} \cdot \boldsymbol{\omega}, \quad (10)$$

where \mathbf{y}_{α} is the internal (center-of-the-mass) position

$$\mathbf{y}_{\alpha} = \mathbf{x}_{\alpha} - \mathbf{X} \quad (11)$$

and

$$\mathbf{X} = \sum_{\alpha} \frac{m_{\alpha} \mathbf{x}_{\alpha}}{M} \quad (12)$$

is the center-of-mass of the molecule ($M = \sum_{\alpha} m_{\alpha}$ is the mass of the molecule). Incidentally, the eigenvectors \mathbf{u}'_1 , \mathbf{u}'_2 , and \mathbf{u}'_3 of the moment tensor are the principal axes of the molecule, because the moment tensor is related to the inertia tensor $\mathfrak{I}(\boldsymbol{\omega})$ as

$$\mathfrak{I}(\boldsymbol{\omega}) = \sum_{\alpha} m_{\alpha} \mathbf{y}_{\alpha}^2 \boldsymbol{\omega} - \mathfrak{M}(\boldsymbol{\omega}). \quad (13)$$

The eigenvalues of moment tensor (or related coordinates, such as principal moments of inertia) have been used successfully to describe many of the most interesting features of reactive scattering involving three and four particle systems (such as atom and diatom reaction); see, e.g., Refs. 5–8. To my knowledge, the gradients of the eigenvalues of moment tensor have not been presented before in the literature.

Example 2: To find out the gradients of the eigenvalues of the moment tensor, we differentiate both sides of the eigenequation,

$$\mathfrak{M}(\mathbf{u}'_i) = \lambda_i \mathbf{u}'_i. \quad (14)$$

By substituting $\dot{\mathbf{u}}'_i = \boldsymbol{\omega} \times \mathbf{u}'_i$ (p. 100, Ref. 4) to the result, which in turn is dotted with \mathbf{u}'_i , an equation

$$\sum_{\alpha} m_{\alpha} \mathbf{u}'_i \cdot (\dot{\mathbf{y}}_{\alpha} \mathbf{y}_{\alpha} \cdot \mathbf{u}'_i + \mathbf{y}_{\alpha} \dot{\mathbf{y}}_{\alpha} \cdot \mathbf{u}'_i + \mathbf{y}_{\alpha} \mathbf{y}_{\alpha} \cdot \boldsymbol{\omega} \times \mathbf{u}'_i) = \dot{\lambda}_i \quad (15)$$

follows. Because

$$\begin{aligned} \mathbf{u}'_i \cdot \mathfrak{M}(\boldsymbol{\omega} \times \mathbf{u}'_i) &= \mathbf{u}'_i \cdot \mathfrak{M}\left(\sum_j^3 \omega_j \mathbf{u}'_j \times \mathbf{u}'_i\right) \\ &= \mathbf{u}'_i \cdot \mathfrak{M}(-\omega_j \mathbf{u}'_k + \omega_k \mathbf{u}'_j) = 0 \end{aligned} \quad (16)$$

(where $\omega_k = \boldsymbol{\omega} \cdot \mathbf{u}'_k$, and the indices i, j, k are in cyclic order in the second last term in the right-hand side) as seen by the direct substitution of Eq. (14), one concludes that

$$\begin{aligned} \dot{\lambda}_i &= \sum_{\alpha} 2m_{\alpha} \mathbf{y}_{\alpha} \cdot \mathbf{u}'_i \mathbf{u}'_i \cdot \dot{\mathbf{y}}_{\alpha} \\ &= \sum_{\alpha} 2m_{\alpha} \mathbf{y}_{\alpha} \cdot \mathbf{u}'_i \mathbf{u}'_i \cdot \left(\dot{\mathbf{x}}_{\alpha} - \sum_{\beta} \frac{m_{\beta} \dot{\mathbf{x}}_{\beta}}{M}\right) \end{aligned} \quad (17)$$

and the coordinate gradients are extracted as

$$\begin{aligned} \nabla_{\alpha} \lambda_i &= 2m_{\alpha} \left(1 - \frac{m_{\alpha}}{M}\right) \mathbf{y}_{\alpha} \cdot \mathbf{u}'_i \mathbf{u}'_i - \sum_{\beta \neq \alpha}^N 2m_{\beta} \frac{m_{\alpha}}{M} \mathbf{y}_{\beta} \cdot \mathbf{u}'_i \mathbf{u}'_i \\ &= \sum_{\beta}^N 2m_{\beta} \left(\delta_{\alpha\beta} - \frac{m_{\alpha}}{M}\right) \mathbf{y}_{\beta} \cdot \mathbf{u}'_i \mathbf{u}'_i, \end{aligned} \quad (18)$$

where $\delta_{\alpha\beta}$ is the Kronecker's delta ($\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, and zero otherwise). However, because $\sum_{\beta} m_{\beta} \mathbf{y}_{\beta} = 0$, the sum over the index β may be omitted, and the result can be simplified to

$$\nabla_{\alpha} \lambda_i = 2m_{\alpha} \mathbf{y}_{\alpha} \cdot \mathbf{u}'_i \mathbf{u}'_i. \quad (19)$$

It should be emphasized that Eq. (19) applies to a general N -body system without any restriction to number of particles. Because the eigenvectors \mathbf{u}'_i can be calculated relatively straightforwardly as functions of \mathbf{y}_{α} (see Ref. 4), it should be simple to obtain the explicit expressions for the kinetic energy operator of an arbitrary N -body system (at least if it is simple to express $\mathbf{y}_{\alpha} \cdot \mathbf{y}_{\beta}$ in terms of the coordinates used). On the other hand, if the reciprocal metric tensor $g^{(q_i q_j)}$ is obtained as the inverse of covariant metric tensor $g_{q_i q_j}$ (as in Ref. 8), the expressions depend crucially on the number of nuclei, and in practice one needs to invert $g_{q_i q_j}$ separately for the systems of different size.

The method presented here also has the advantage that the gradients of the implicitly defined coordinates can often be obtained without the need to represent the coordinate in question explicitly in terms of the nuclear positions. Furthermore, the scalar differentiation used in this method is commutative operation, unlike the differentiation with respect to the position vector \mathbf{x}_{α} , i.e., $(d/dt)(C\hat{F}) = C\dot{F}$, where C is any multivector independent of t . Thus, the reader who is not familiar with geometric algebra may find the current method more readily adopted than the method presented in Ref. 1.

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