

# Translational and Rotational Symmetries of Molecular Geometrical Derivatives

Trygve Helgaker

Department of Chemistry, Aarhus University, DK-8000 Århus C, Denmark

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The translational and rotational symmetries of molecular geometrical derivatives are discussed. Simple formulas are presented for calculating the full set of Cartesian derivatives from a set of independent derivatives. The formulas are general and can be applied to any property to any order.

**Dedicated to Professor Otto Bastiansen on his 70th birthday**

Quantum chemical *ab initio* methods have in recent years emerged as a reliable technique for investigating gas-phase molecular structures. The calculation of geometrical derivatives plays an important role in such studies. These derivatives are needed not only to determine equilibrium geometries, but also to calculate various properties such as vibrational frequencies and intensities.

For technical reasons geometrical derivatives are calculated with respect to Cartesian displacements of the nuclei. Because of translational and rotational symmetries, such derivatives are not independent. For example, in an isolated molecule only  $3N-m$  Cartesian forces are independent [ $N$  is the number of atoms and  $m$  is the number of translational and rotational degrees of freedom (5 or 6)]. The remaining forces can be determined from the translational and rotational invariance of the energy. This has two useful applications. First, the number of derivatives that must be calculated *ab initio* may be reduced. This is especially useful for small molecules. Alternatively, one may calculate all derivatives *ab initio* and simply use translational and rotational symmetries as an easy check on the calculation.

The problem of calculating derivatives from symmetry considerations may appear rather trivial, especially in comparison with the complexity of *ab initio* calculations. Nevertheless, most discussions so far have been restricted to special

low-order cases.<sup>1-4</sup> As higher derivatives of various properties are being addressed, it becomes desirable to solve this problem in a general way. The simple recursive scheme presented below can be applied to derivatives of any property and to any order. The only restriction is that in order to determine the full set of derivatives to a given order, one must first calculate all derivatives of lower orders. In practice this is not a problem since these are available anyway from the *ab initio* calculation.

## The relationship between dependent and independent derivatives

Let  $F^{(n)}$  denote the  $(3N)^n$   $n$ 'th-order geometrical derivatives of some molecular property, for example the energy or a component of the dipole moment. Let us assume that we know  $(3N-m)^{n+1}$  appropriately chosen components of  $F^{(n+1)}$  and all components of  $F^{(n)}$ . We wish to derive an expression which allows us to calculate the remaining  $(3N)^{n+1} - (3N-m)^{n+1}$  components of  $F^{(n+1)}$  from the translational and rotational symmetries of  $F^{(n)}$ . For the sake of simplicity we will assume that the molecule is non-linear, so that  $m$  is equal to 6.

We denote the translational and rotational coordinates by  $\{Q_x, Q_y, Q_z, R_x, R_y, R_z\}$  or collectively by  $\{r_i | i=1,6\}$ . The  $3N$  Cartesian coordinates are denoted by  $\{x_i, y_i, z_i | i=1, N\}$  or

$\{\zeta_i | i=1, 3N\}$ . Using the chain rule for differentiation we obtain

$$\begin{aligned} (\partial F^{(n)}_{i_1 i_2 \dots i_n} / \partial r_j) = \\ \sum_{k=1}^{3N} (\partial F^{(n)}_{i_1 i_2 \dots i_n} / \partial \zeta_k) (\partial \zeta_k / \partial r_j). \end{aligned} \quad (1)$$

We may write this equation in matrix form

$$\mathbf{T}(6 \times 3N) \mathbf{A}(3N) = \mathbf{B}(6) \quad (2)$$

where the dimensions are indicated in parentheses and

$$T_{jk} = \partial \zeta_k / \partial r_j \quad (3)$$

$$A_k = \partial F^{(n)}_{i_1 i_2 \dots i_n} / \partial \zeta_k = F^{(n+1)}_{i_1 i_2 \dots i_n k} \quad (4)$$

$$B_j = \partial F^{(n)}_{i_1 i_2 \dots i_n} / \partial r_j. \quad (5)$$

Eqn. (2) relates  $F^{(n+1)}$  to the translational and rotational derivatives of  $F^{(n)}$ . There is one set of equations for each component of  $F^{(n)}$ .

Selecting 6 independent Cartesian coordinates, we may reorder the columns of  $\mathbf{T}$  so that the first 6 are linearly independent. We may then write  $\mathbf{T}$  as

$$\mathbf{T}(6 \times 3N) = [\mathbf{T}_D(6 \times 6) \mathbf{T}_1\{6 \times (3N-6)\}] \quad (6)$$

where  $\mathbf{T}_D$  is non-singular. Reordering the rows of  $\mathbf{A}$  in the same way

$$\mathbf{A}(3N) = \begin{bmatrix} \mathbf{A}_D(6) \\ \mathbf{A}_1(3N-6) \end{bmatrix} \quad (7)$$

we find that eqn. (2) may be written as

$$\mathbf{T}_D \mathbf{A}_D + \mathbf{T}_1 \mathbf{A}_1 = \mathbf{B} \quad (8)$$

or equivalently

$$\mathbf{A}_D = \mathbf{T}_D^{-1}(\mathbf{B} - \mathbf{T}_1 \mathbf{A}_1). \quad (9)$$

This equation relates 6 dependent derivatives  $\mathbf{A}_D$  to  $3N-6$  independent derivatives  $\mathbf{A}_1$  in a linear way. The transformation matrix  $\mathbf{T}_D^{-1} \mathbf{T}_1$  is independent of the property and can be calculated once and for all. It only remains to describe the calculation of  $\mathbf{T}$  and  $\mathbf{B}$ .

### Calculation of the $\mathbf{T}$ matrix

The  $\mathbf{T}$  matrix contains the partial derivatives of the Cartesian coordinates with respect to the translational and rotational coordinates. Its elements may be determined from the expressions

$$\partial / \partial Q_x = \sum_k \partial / \partial x_k, \quad (10)$$

$$\partial / \partial Q_y = \sum_k \partial / \partial y_k, \quad (11)$$

$$\partial / \partial Q_z = \sum_k \partial / \partial z_k, \quad (12)$$

$$\partial / \partial R_x = \sum_k [y_k (\partial / \partial z_k) - z_k (\partial / \partial y_k)], \quad (13)$$

$$\partial / \partial R_y = \sum_k [z_k (\partial / \partial x_k) - x_k (\partial / \partial z_k)], \quad (14)$$

$$\partial / \partial R_z = \sum_k [x_k (\partial / \partial y_k) - y_k (\partial / \partial x_k)], \quad (15)$$

where the summations are over all atoms. The following columns of  $\mathbf{T}$  correspond to the coordinates of atom  $k$ :

$$\mathbf{T}_k = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & -z_k & y_k \\ z_k & 0 & -x_k \\ -y_k & x_k & 0 \end{bmatrix}. \quad (16)$$

Note that  $\mathbf{T}$  depends on the geometry only.

### Calculation of the $\mathbf{B}$ matrix

To obtain expressions for the elements of  $\mathbf{B}$  we first consider the commutators between the partial derivatives with respect to  $r_j$  and  $\zeta_i$ . From eqns. (10)–(15) we find that the only non-vanishing commutators are

$$[\partial / \partial R_x, \partial / \partial y_i] = -\partial / \partial z_i, \quad (17)$$

$$[\partial/\partial R_x, \partial/\partial z_i] = \partial/\partial y_i, \quad (18) \quad \mathbf{f}_D = \mathbf{T}_D^{-1} \mathbf{T}_i \mathbf{f}_i. \quad (26)$$

$$[\partial/\partial R_y, \partial/\partial x_i] = \partial/\partial z_i, \quad (19) \quad \mathbf{B} \text{ vanishes since the energy is independent of the}$$

$$[\partial/\partial R_y, \partial/\partial z_i] = -\partial/\partial x_i, \quad (20) \quad \text{orientation of the molecule. When } \mathbf{A} \text{ corresponds}$$

$$[\partial/\partial R_z, \partial/\partial x_i] = -\partial/\partial y_i, \quad (21) \quad \text{to the part of the Hessian which is obtained by}$$

$$[\partial/\partial R_z, \partial/\partial y_i] = \partial/\partial x_i. \quad (22) \quad \text{differentiating the Cartesian forces } f_x, f_y, \text{ and } f_z$$

We use the notation

$$[\partial/\partial r_j, \partial/\partial \zeta_i] = a_{ji} \partial/\partial \zeta_{[j,i]} \quad (23) \quad \text{on a single nucleus (i.e., a matrix } \mathbf{g} \text{ consisting of}$$

for a general commutator, where  $a_{ji}$  is 0, -1, or +1. Repeated use of this equation gives

$$\partial F^{(n)}_{i_1 i_2 \dots i_n} / \partial r_j = \sum_{k=1}^n (a_{j i_k} F^{(n)}_{i_1 i_2 \dots i_{k-1} [j, i_k] i_{k+1} \dots i_n}) \quad (27)$$

$$+ (\partial F / \partial r_j)^{(n)}_{i_1 i_2 \dots i_n} \quad (24)$$

in an obvious notation.

From expression (24) we see that the derivatives of  $F^{(n)}$  in general contain  $n+1$  terms. For translations, the first  $n$  vanish since the commutators are zero. For rotations, they are obtained by rotating one index at a time according to the commutator relationships (17)–(22) between the rotational and Cartesian coordinates. The last term is determined from the translational and rotational properties of  $F$ . For the energy this term vanishes. For other properties such as the dipole moment it is non-vanishing and must be obtained from the translational and rotational symmetries of that property.

As an illustration, we consider the derivative of  $E_{xyz}$  with respect to rotation about the  $z$  axis. Assuming all coordinates belong to the same atom we obtain

$$\begin{aligned} \partial E_{xyz} / \partial R_z &= E_{[z,x]yz} + E_{x[z,y]z} + E_{xy[z,z]} + (\partial E / \partial R_z)_{xyz} \\ &= -E_{yyz} + E_{xxz} \end{aligned} \quad (25)$$

where the last two terms vanish.

## Examples

When  $\mathbf{A}$  represents the energy gradient  $\mathbf{f}$  (the forces on the nuclei), eqn. (9) reduces to

where  $\mathbf{B}$  is the matrix [use Eqn. (24)]:

$$\mathbf{B} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & -f_z & f_y \\ f_z & 0 & -f_x \\ -f_y & f_x & 0 \end{bmatrix}. \quad (28)$$

$\mathbf{B}$  vanishes at equilibrium since the gradient  $\mathbf{f}$  is zero at this geometry. Expressions (27) and (28) correspond to those derived by Page *et al.*<sup>1</sup> and later simplified by Lee *et al.*<sup>4</sup> There is one set of eqns. (27) for each atom in the molecule.

The dependent elements of the dipole gradient may be calculated from a similar set of eqns. (27).<sup>3</sup> The three-column matrix  $\mathbf{g}$  now contains the gradients of the dipole components  $\mu_x$ ,  $\mu_y$ , and  $\mu_z$ , and  $\mathbf{B}$  becomes [use eqn. (24)]:

$$\mathbf{B} = \begin{bmatrix} q & 0 & 0 \\ 0 & q & 0 \\ 0 & 0 & q \\ 0 & -\mu_z & \mu_y \\ \mu_z & 0 & -\mu_x \\ -\mu_y & \mu_x & 0 \end{bmatrix}, \quad (29)$$

where  $q$  is the total molecular charge. Eqn. (29) corresponds to the translational and rotational sum rules given for example by Fowler and Buckingham.<sup>5</sup>

The above examples illustrate the simplicity and usefulness of the technique. Whenever a new property is considered one only has to set up a new  $\mathbf{B}$  matrix based on eqn. (24) and the translational and rotational symmetries of the property in question.

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