Calculation of Cartesian Coordinates and Their Derivatives from Internal Molecular Coordinates. II. Second and Higher Derivatives and Derivatives of Vectors

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A process is given to extend a previously described algorithm so as to calculate analytically second and higher partial derivatives of Cartesian with respect to internal molecular coordinates within molecules. Each derivative calculation requires at most a single vector multiplication per order and is thus much faster than calculation of the original coordinates. An algorithm is also presented to calculate derivatives of a variety of vectors within molecules with respect to internal coordinates.

Chemists must frequently convert a molecular description in terms of bond lengths and bond and dihedral angles into a description in a Cartesian framework. Beginning with the classic work of Eyring,[1] a common procedure has been to attach each atom to the already defined framework in such a way as to define a coordinate system on the new atom, and then work backward through the successive rotations and translations to the basic system on the first atom.[2] In the first paper of this series[3] (referred to hereafter as I) an algorithm in this tradition was described, tailored to machine computation. This algorithm has two advantages over prior methods: the translation and rotation to the base system is performed in a single matrix multiplication, and very rapid analytical calculation of the first derivatives of Cartesian coordinates with respect to internal coordinates are possible.

In this paper the vector product formulation of the derivative calculation will be applied to the calculation of derivatives of general vectors imbedded in portions of a molecule. This in turn permits simple and rapid calculation of second and higher partial derivatives of Cartesian coordinates with respect to internal coordinates. Second partial derivatives are of importance in certain nonlinear multiple regression calculations of the Newton–Raphson type.[4] We hope to use them to solve certain annoying problems involving ring closure under selected constraints upon internal coordinates.

COORDINATE AND DERIVATIVE CALCULATION

In I, each atom j was attached to an atom j', which had been attached to j'', which in turn had been attached to j''', in a chain leading eventually back to atom 1. Definitions for j'' and j''' were developed where j' was atom 1 or atom 2 so as to make the algorithm self-consistent. For each atom, a method was outlined to calculate the position vector $\mathbf{q}(j)$ of atom j in the base Cartesian coordinate system, and to calculate a 3×3 matrix A_j. A_j defined a rotational transformation of a right-handed coordinate system on atom j, such that the x_j axis lay along the bond from j' to j, the z_j axis was perpendicular to the plane defined by atoms j, j', and j'', and the atom j'' lay in the first or second quadrant of the xy plane. The internal coordinates were R_j, the jj' bond length; α_j, the $jj'j''$ angle (taken so as

not to exceed $180°$); and a dihedral angle β_j. β_j was defined as the dihedral angle, viewed looking down the $j'j''$ bond, required to rotate the jj' bond clockwise so as to eclipse the $j''j'''$ bond. Special cases and specifics regarding the calculations are given in I.

TABLE I. Selected second derivatives.

j[a]	$\partial^2\mathbf{q}(j)/\partial\alpha_6\partial\alpha_9$		$\partial^2\mathbf{q}(j)/\partial\beta_6\partial\alpha_9$
	x[a]	y[a]	z[a]
9	1.535	0.000	-1.535
10	0.0	0.0	0.0
11	0.0	0.0	0.0
12	2.060	-1.442	-2.060
13	1.902	0.518	-1.902
14	1.902	0.518	-1.902
15	1.698	-1.965	-1.698
16	1.698	-1.965	-1.698
17	3.160	-1.433	-3.160

	$\partial^2\mathbf{q}(j)/\partial R_6\partial\beta_6$	$\partial^2\mathbf{q}(j)/\partial\alpha_6{}^2$	
	z[a]	x[a]	y[a]
6	-0.940	-0.525	1.439
7	0.0	0.0	0.0
8	0.0	0.0	0.0
9	-0.940	-2.060	1.431
10	-0.940	-0.163	1.963
11	-0.940	-0.163	1.963
12	-0.940	-2.585	2.871
13	-0.940	-2.427	0.911
14	-0.940	-2.427	0.911
15	-0.940	-2.223	3.395
16	-0.940	-2.223	3.395
17	-0.940	-3.685	2.856

[a] Where j, or components (x, y, z) are omitted, all second partial derivative (components) were zero.

The columns of the $\mathbf{A}_k$ matrix contain the components in the base coordinate system of unit vectors along the axes of coordinate system k. For example, the first column forms a unit vector, $\mathbf{a}_x$, along the kk' bond. If atom j is any atom attached through a chain containing

k, the differential of $\mathbf{q}(j)$ with respect to R_k is then

$$\partial \mathbf{q}(j)/\partial R_k = \mathbf{a}_x k. \qquad (1)$$

Partial derivatives with respect to the angular coordinates were also given in I in terms of vector products:

$$\partial \mathbf{q}(j)/\partial \alpha_k = -\mathbf{a}_{zk} \times [\mathbf{q}(j) - \mathbf{q}(k')], \qquad (2)$$

$$\partial \mathbf{q}(j)/\partial \beta_k = \mathbf{a}_{xk} \times [\mathbf{q}(j) - \mathbf{q}(k')]$$

$$= \mathbf{a}_{xk'} \times [\mathbf{q}(j) - \mathbf{q}(k'')]. \qquad (3)$$

In the sections that follow, it will be shown that these are special cases of a general process for calculating derivatives of vectors imbedded in portions of molecules. In particular, derivatives of dipole moment contributions, and second and higher derivatives of Cartesian coordinates may be obtained.

DERIVATIVES OF VECTORS WITHIN MOLECULES

Suppose that a portion of a molecule is rotated about a given axis, and that the portion rotated contains a vector $\mathbf{u}$. If $\mathbf{a}$ is a unit vector along the direction of rotation, the derivative of this vector with respect to rotation about the given axis is

$$d\mathbf{u}/d\phi = \mathbf{a} \times \mathbf{u}, \qquad (4)$$

where ϕ is the angle of rotation, taken to increase with clockwise motion as viewed down the vector $\mathbf{a}$. This cannot be applied directly to the vector $\mathbf{q}(j)$ representing the atomic position of atom j, but Eqs. (2) and (3) can be derived by observing (a) that the vector sums bracketed in each equation do lie entirely within the portions rotated, (b) that $\partial \mathbf{q}(k')/\partial \alpha_k$, $\partial \mathbf{q}(k')/\partial \beta_{k'}$, and $\partial \mathbf{q}(k'')/\partial \beta_{k'}$ are all zero, and (c) that vector products are associative.

TABLE II. Model description of pentane.

Atom no.	Attached to	R	α	β
C	1	0	0.0	0.0	0.0
C	2	1	1.535	0.0	0.0
H	3	2	1.100	109.5	0.0
H	4	2	1.100	109.5	120.0
H	5	2	1.100	109.5	240.0
C	6	1	1.535	110.0	180.0
H	7	1	1.100	109.5	300.0
H	8	1	1.100	109.5	60.0
C	9	6	1.535	110.0	180.0
H	10	6	1.100	109.5	300.0
H	11	6	1.100	109.5	60.0
C	12	9	1.535	110.0	180.0
H	13	9	1.100	109.5	300.0
H	14	9	1.100	109.5	60.0
H	15	12	1.100	109.5	300.0
H	16	12	1.100	109.5	60.0
H	17	12	1.100	109.5	180.0

It is useful to note that any vector $\mathbf{u}$ with one end fixed at a point $\mathbf{q}(m)$ in the stationary portion of the molecule and the other at $\mathbf{q}(j)$ in the moving portion also has derivatives given by the right hand portions of Eqs. (1)–(3). This follows directly, since $\mathbf{u} = \mathbf{q}(j) - \mathbf{q}(m)$, and $\mathbf{q}(m)$ is independent of α_k, β_k, or R_k. Since many vectors of interest in a molecule are either localized or defined by a pair of points, the relations discussed here should have wide applicability.

SECOND AND HIGHER DERIVATIVES

Since the first derivatives of $\mathbf{q}(j)$ are vectors, the second and higher derivatives can be found by the same process as the first. The resultant equations for second partial derivatives are

$$\partial^2 \mathbf{q}(j)/\partial R_l \partial R_k = 0, \qquad l \lessgtr k;$$

$$\partial^2 \mathbf{q}(j)/\partial R_l \partial \alpha_k = 0, \qquad l < k;$$

$$\partial^2 \mathbf{q}(j)/\partial R_l \partial \beta_k = 0, \qquad l < k;$$

$$\partial^2 \mathbf{q}(j)/\partial \alpha_l \partial R_k = -\mathbf{a}_{zl} \times \partial \mathbf{q}(j)/\partial R_k, \qquad l \lessgtr k;$$

$$\partial^2 \mathbf{q}(j)/\partial \alpha_l \partial \alpha_k = -\mathbf{a}_{zl} \times \partial \mathbf{q}(j)/\partial \alpha_k, \qquad l \lessgtr k;$$

$$\partial^2 \mathbf{q}(j)/\partial \alpha_l \partial \beta_k = -\mathbf{a}_{zl} \times \partial \mathbf{q}(j)/\partial \beta k, \qquad l < k;$$

$$\partial^2 \mathbf{q}(j)/\partial \beta_l \partial R_k = \mathbf{a}_{xl'} \times \partial \mathbf{q}(j)/\partial R_k, \qquad l \lessgtr k;$$

$$\partial^2 \mathbf{q}(j)/\partial \beta_l \partial \alpha_k = \mathbf{a}_{xl'} \times \partial \mathbf{q}(j)/\partial \alpha_k, \qquad l \lessgtr k;$$

$$\partial^2 \mathbf{q}(j)/\partial \beta_l \partial \beta_k = \mathbf{a}_{xl'} \times \partial \mathbf{q}(j)/\partial \beta_k, \qquad l \lessgtr k. \qquad (5)$$

In using these equations, careful note must be taken of the appropriate relationship between l and k. Where the inequality given does not apply, the relationship $\partial^2 \mathbf{q}(j)/\partial u \partial v = \partial^2 \mathbf{q}(j)/\partial v \partial u$ must be used. The inequalities are required because the vector must be multiplied by a vector which lies within the molecular portion moved. Expansion of the first derivatives above will show the requirements given to be appropriate.[5] It is, of course, also essential that the atoms k and l both be in the chain linking atom j to the origin at atom 1; otherwise the derivative is zero.

Second and higher derivatives become by this algorithm a useful and practical ingredient in extensive calculations. The array of second derivatives is three dimensional and might seem awesome in terms of both storage and computation time. However, once first derivatives are available, each nonzero second derivative requires a single vector multiplication. While a very large fraction of the derivatives are zero, the nonzero values are not trivial, as shown in Table I for a model molecule on which the algorithm was tested.[5] The molecular description (as described in I) is given in Table II. In extensive machine calculations, it will probably be advantageous at times to recalculate second derivatives as needed rather than to store very large arrays.

Higher order derivatives are in principal obtainable by exactly the same algorithm; there is no limit in

theory to the order analytically calculable, should the need arise.

ACKNOWLEDGMENT

[1] H. Eyring, Phys. Rev. 39, 746 (1932).
[2] A description of a very versatile program for calculation of Cartesian from internal coordinates is given by R. L. Hilderbrandt, J. Chem. Phys. 51, 1654 (1969). Hilderbrandt uses a different basic approach, within which differentials must be approximated by finite differences.
[3] H. B. Thompson, J. Chem. Phys. 47, 3407 (1967).

[4] Specifically, in least-squares fits to observed data using a general nonlinear function of several variables, the Newton–Raphson approach requires second partial derivatives of the function with respect to the parameters. These terms distinguish the Newton–Raphson from the Gauss–Newton procedure. For discussions of scientific applications, see T. G. Strand, D. A. Kohl, and R. A. Bonham, J. Chem. Phys. 39, 1307 (1963); R. E. Barieau and B. J. Dalton, U.S. Bur. Mines Rept. Invest. 6900 (1967), and references cited therein. The second derivatives discussed here will thus be of interest where a fit in terms of internal coordinates is required but the function in question is most easily calculated in a Cartesian framework.
[5] Details of the algorithm have been checked by comparison with finite-difference computations, using the FORTRAN II program LINUS (see I, Ref. 5) to obtain vectors and first derivatives. While these checks verified the algorithm, they also demonstrated that finite difference calculations of second partial derivatives on a seven-significant-figure machine are unreliable in the third figure.

Anisotropic Chemical Shifts in Trigonal Cobalt Carbonyls Containing Metal–Metal Bonds*

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The ^{59}Co NMR was studied in a number of single crystals and solutions of cobalt carbonyl complexes $X_3MCo(CO)_4$ (M = Si, Ge, Sn, Pb; X = Cl, Br, I, C_6H_5) containing metal–metal bonds. The z component of the chemical shift as determined by single crystal measurements in $I_3GeCo(CO)_4$, $Br_3SnCo(CO)_4$, and $(C_6H_5)_3SnCo(CO)_4$ was found to be constant within the series and showed a paramagnetic contribution of at least 3.6‰. As ligand field theory predicts no paramagnetic shift in this case, the data showed that for low oxidation state complexes the chemical shift can only be explained using MO theory. Good agreement with experiment was obtained using MO coefficients for the isoelectronic $Fe(CO)_5$. The paramagnetic contributions to the x and y components of the shift vary considerably within the series (3.3‰–5.0‰). These variations were attributed to differences in the metal–metal bonds. It was found that for a given X the shifts do not vary linearly as the atomic weight of M is changed. This was attributed to differences in the importance of π-bonding effects for the metal–metal bonds. The data suggest that in this series π-bonding effects are strongest for the Co–Sn bond.

INTRODUCTION

The chemical shifts in diamagnetic cobalt complexes are particularly large.[1] Recently it was shown[2] that anisotropic shifts can be determined for ^{59}Co by single crystal measurements. The anisotropies were especially strong for compounds containing nonionic bonds like the cobaltocenium ion.[2] A series of compounds, $X_3M–Co(CO)_4$ (X = halogen, phenyl; M = Si, Ge, Sn, Pb), containing metal–metal bonds have been synthesized[3,4] recently and the pure NQR spectra of ^{59}Co have been studied.[5-7] Infrared and NQR studies have been interpreted as evidence for M–Co π bonding.[4,5,8,9] Separation of σ- and π-bonding effects, however, was found to be difficult. A study of the chemical shift of ^{59}Co in these compounds provides additional information about the electronic structure. The z component of the shift tensor should be constant for the different members of this series, which have approximately C_{3v} symmetry at the cobalt site.[10] Therefore only representative compounds of the series have to be studied as single crystals and measurements of the isotropic chemical shift

in solution is sufficient for the others. The x and y components of the shift tensor depend on the cobalt $3d$ orbitals forming the metal–metal bond and their relative values within the series are directly related to differences in the Co–M bonds.

EXPERIMENTAL

The substituted tetracarbonyl cobalt compounds were synthesized according to the literature[3,4] and their identity and purity checked through their infrared spectra and NQR frequencies. Solutions (*n*-pentane) for the determination of the isotropic chemical shifts were prepared under nitrogen. The ^{59}Co lines observed are rather weak due to the low solubility of the compounds. For this reason acetone had to be used as a solvent to observe the ^{59}Co resonance in $(C_6H_5)_3GeCo(CO)_4$.

Single Crystals

$Br_3SnCo(CO)_4$: A single crystal of the tribromotin derivative was obtained by slowly evaporating a *n*-hexane solution in a dry nitrogen atmosphere. A crys-