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Calculation of Cartesian Coordinates and Their Derivatives from Internal Molecular Coordinates*

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An algorithm is described for rapid calculation of cartesian coordinates of atoms from internal molecular coordinates. Two procedures are given for efficient calculation of first derivatives of the Cartesian coordinates with respect to internal coordinates, and the manner in which higher derivatives may be obtained is indicated.

In a wide variety of experimental and theoretical studies involving molecular geometry, a description in terms of internal molecular coordinates (bond lengths, bond and dihedral angles) must be converted to a description in a Cartesian system. Often derivatives of these Cartesian coordinates with respect to certain of the internal coordinates are also desired. While a variety of schemes for conversion from internal to Cartesian descriptions have been described for particular applications,¹ none appear to combine all the following features: (1) description in terms of an attractive

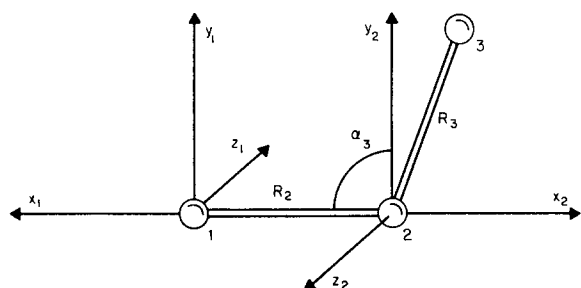


FIG. 1. Coordinate systems centered on Atoms 1 and 2.

internal coordinate system; (2) applicability to a wide variety of molecular types; (3) analytical calculation of derivatives; (4) efficient organization tailored for machine computation. A method meeting these requirements is described here. During its development over a three-year period, this method, or part thereof, has been applied successfully in such diverse areas as energy minimization in a complex model molecular force field including nonbonded repulsions,² the fitting of model structures to electron-diffraction data,³ and calculation of principal moments of inertia.

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¹ For example, (a) P. L. McCullough and P. E. McMahon, *Trans. Faraday Soc.* **60**, 2093 (1964); (b) T. Shimanouchi and S. Mizushima, *J. Chem. Phys.* **23**, 707 (1955). The matrix in Eq. (1) hereof is equivalent to Eqs. (7)–(9) in (a) and Eqs. (1) and (2) in (b).

² E. Jean Jacob, H. Bradford Thompson, and L. S. Bartell, "Influence of Nonbonded Interactions on Molecular Geometry and Energy: Calculations for Hydrocarbons Based on Urey-Bradley Field," *J. Chem. Phys.* (to be published).

³ L. S. Bartell and T. L. Boates (private communication).

CALCULATION OF COORDINATES

The calculation of coordinates as described in this section is derived from the classic procedure developed by Eyring.⁴ The specific definition of internal coordinates used here is given in the following paragraph. The next two paragraphs describe a formulation of this procedure that is readily adapted to subsequent calculation of derivatives.

A base coordinate system is defined by the positions of three atoms, numbered 1, 2, and 3. The origin is taken at Atom 1, the negative x axis passes through

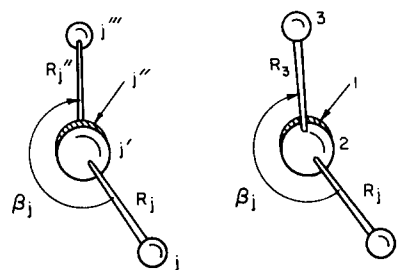


FIG. 2. Definition of the angle β . The atom j'' is directly behind j' , and 2 is directly behind 1. The left-hand figure applies to all cases except $j'=2$.

Atom 2, and Atom 3 lies in the first or second quadrant of the xy plane (see Fig. 1). Coordinates and position vectors without subscripts will refer to this coordinate system. Atom 2 is considered to be bonded to Atom 1, and the bond length must be specified. A coordinate system is defined with origin at Atom 2 and Atom 1 lying on the negative x_2 axis; Atom 3 again lies in the first or second quadrant of the x_2y_2 plane. From this point, additional atoms are added to this framework by specifying four quantities: the atom already present, to which the new atom is attached, the length of the bond thus formed, a bond angle, and a dihedral angle. In order to define the angles, the following conventions are adopted: for a general atom j , the atom to which it was attached is called j' , the atom to which j' was attached is called j'' , and the atom to which j'' was attached is called j''' . Two special cases where these definitions do not suffice are atoms attached to Atom 1 and to Atom 2. Where j is attached to Atom 2, Atom 1 is taken as j'' and Atom 3 as j''' . Where j is attached to Atom 1, Atom 2 is taken as j'' and Atom 3 as j''' .

⁴ H. Eyring, *Phys. Rev.* **39**, 746 (1932).

In this notation the bond angle α_j is the angle $jj'j''$, taken so as not to exceed 180° . The dihedral angle β_j is defined as shown in Fig. 2: looking down the bond from j' to j'' , β_j is the angle through which the image of the jj' bond must be rotated clockwise to bring it into the direction of j''' .

On each atom, a Cartesian system $x_j y_j z_j$ is now defined such that Atom j' lies on the negative x_j axis and atom j'' lies in the third or fourth quadrant of the $x_j y_j$ plane. The coordinates of a point in this system are related to the coordinates of this same point in the j' system by a rotational transformation and a translation:

$$\begin{bmatrix} x_{j'} \\ y_{j'} \\ z_{j'} \end{bmatrix} = \begin{bmatrix} -\cos\alpha_j & -\sin\alpha_j & 0 \\ \sin\alpha_j \cos\beta_j & -\cos\alpha_j \cos\beta_j & -\sin\beta_j \\ \sin\alpha_j \sin\beta_j & -\cos\alpha_j \sin\beta_j & \cos\beta_j \end{bmatrix} \begin{bmatrix} x_j \\ y_j \\ z_j \end{bmatrix} + \begin{bmatrix} -R_j \cos\alpha_j \\ R_j \sin\alpha_j \cos\beta_j \\ R_j \sin\alpha_j \sin\beta_j \end{bmatrix}. \quad (1)$$

An equivalent notation somewhat more convenient for the present discussion is

$$\begin{bmatrix} x_{j'} \\ y_{j'} \\ z_{j'} \\ 1 \end{bmatrix} = \begin{bmatrix} -\cos\alpha_j & -\sin\alpha_j & 0 & -R_j \cos\alpha_j \\ \sin\alpha_j \cos\beta_j & -\cos\alpha_j \cos\beta_j & -\sin\beta_j & R_j \sin\alpha_j \cos\beta_j \\ \sin\alpha_j \sin\beta_j & -\cos\alpha_j \sin\beta_j & \cos\beta_j & R_j \sin\alpha_j \sin\beta_j \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_j \\ y_j \\ z_j \\ 1 \end{bmatrix}. \quad (2)$$

Or using \mathbf{q}_j for the expanded coordinate vector and \mathbf{B}_j for the transformation matrix:

$$\mathbf{q}_{j'} = \mathbf{B}_j \cdot \mathbf{q}_j. \quad (3)$$

Transformation back to the base system on Atom 1 is then accomplished through a series of matrices \mathbf{B} . For example, for an atom attached to a chain that is eventually attached to Atom 3,

$$\mathbf{q}_1 = \mathbf{B}_2 \cdot \mathbf{B}_3 \cdot \dots \cdot \mathbf{B}_{j'} \cdot \mathbf{B}_j \cdot \mathbf{q}_j. \quad (4)$$

The advantage of the 4×4 matrix notation is that Eq. (4) is a simple matrix product rather than a combination of products and sums. In order to make this process applicable to Atoms 2 and 3 and the definitions of the \mathbf{B} matrices consistent, β_2 is taken as π and α_2 and β_3 as zero by definition. With these provisions, the matrices \mathbf{B} suffice to transform the position vectors of all atoms to the base system.

For convenience and efficiency it is desirable to calculate and store the 4×4 matrix \mathbf{A}_j which transforms a position vector in the j system directly to the base coordinate system:

$$\mathbf{q} = \mathbf{A}_j \cdot \mathbf{q}_j, \quad (5)$$

$$\mathbf{A}_j = \mathbf{B}_k \cdot \dots \cdot \mathbf{B}_{j'} \cdot \mathbf{B}_j, \quad (6)$$

where k is the atom number (perhaps 2) through which the atom chain from j reaches Atom 1. Clearly only a single matrix multiplication is now required as each new atom is added:

$$\mathbf{A}_j = \mathbf{A}_{j'} \cdot \mathbf{B}_j. \quad (7)$$

The matrices \mathbf{A}_j resemble the set \mathbf{B}_j in that the fourth row contains three zeros and a one in that order. Further, the first three elements of the first column of

\mathbf{A}_j are the components in the base coordinate system of a unit vector along the x_j axis. Unit vectors along the y_j and z_j axes are similarly contained in the second and third columns. The first three elements of the fourth column are the coordinates of the Atom j in the base system. These identifications may be useful in computational schemes involving particular molecular properties and will be important to one recipe for calculation of coordinate derivatives.

If only the atomic coordinates are desired, clearly the first three columns of a matrix \mathbf{A}_j need not be calculated if j is a "terminal atom," that is, if no atom is to be described as attached to it. However, all the \mathbf{A}_j 's are needed for the second (and shorter) of the two methods to be described for obtaining coordinate derivatives.

SPECIAL CASES AND METHODS

180° Bond Angles

The prescription for definition of the dihedral angle is ambiguous in the case where the bond angle is 180° . This turns out to be immaterial for a terminal atom, but when an atom j is attached to an atom j' for which $\alpha_{j'}$ is 180° , β_j and $\beta_{j'}$ must be defined in some mutually consistent manner. Two (equivalent) definitions can be used: (a) β_j and $\beta_{j'}$ can be based on a visualized related structure in which α_j is taken as just less than 180° so that the procedure of Fig. 2 can be applied; (b) looking down the bond from j' to j'' , an angle β_j can be defined as the angle through which the image of the jj' bond must be rotated clockwise to bring it into the direction of the first atom of the chain back to Atom 1 that does not lie on the $j'-j''$ bond axis. The

angle β_i is then β_j plus the sum of all the (perhaps arbitrarily defined) β values for atoms along that axis having α 's of 180° . In the case of a single $\alpha_{j'} = 180^\circ$, $\beta_i = \beta_j + \beta_{j'}$.

Dummy Atoms

Clearly, the terms "atom" and "bond" in the above discussion actually refer to points and lines within the molecular framework. It is often convenient to define "dummy atoms" so as to preserve the symmetry of a molecular description. For example, a dummy atom 1 in the description of dichloromethane in Table I simplifies a description in which the C_{2v} symmetry is enforced and the symmetry axis and planes are coordinate axes and planes in the base coordinate system.

Motion of Groups of Atoms

A second use of dummy atoms facilitates the description of the motion of a group of atoms (say a methyl group) as a single entity, as in the case of internal rotation. This is neatly accomplished by defining a dummy atom to lie at the same position as the atom at the point of attachment of the group, and then attaching the atoms of the group to the dummy. This is demonstrated for a propanelike structure in Table II: the methyl groups can be rotated as units by changing the β values for Atoms 7 and 8. The 180° α values are typical in this use of dummy atoms. However, a tip of a methyl so that its symmetry axis does not coincide with the bond axis can be accomplished by altering α_7 and α_8 .

CALCULATION OF DERIVATIVES

Matrix Formulation

Two procedures for calculating derivatives of atom coordinates with respect to changes in the internal parameters have been developed within our scheme. The first derives directly from Eq. (4):

$$(dq/d\phi_k) = \mathbf{B}_2 \cdot \mathbf{B}_3 \cdot \dots \cdot (d\mathbf{B}_k/d\phi_k) \cdot \dots \cdot \mathbf{B}_{j'} \cdot \mathbf{B}_j \cdot \mathbf{B}_j \cdot \mathbf{q}_j, \quad (8)$$

where ϕ_k represents one of the three parameters α_k , β_k , or R_k . If the \mathbf{A} matrices are available, this can be

TABLE I. Description of dichloromethane.

	Atom no.	Attached to	α	β	R
Dummy	1
C	2	1	a
H	3	2	α_1	...	RCCl
H	4	2	α_1	180°	RCCl
Cl	5	2	α_2	90°	RCH
Cl	6	2	α_2	-90°	RCH

$\alpha_1 = 180^\circ - 1/2(\text{Cl-C-Cl angle})$
 $\alpha_2 = 1/2(\text{H-C-H angle})$

* R_2 value immaterial—can be zero.

TABLE II. Description of propane.

	Atom no.	Attached to	α	β	R
Dummy	1
C Methylene	2	1	a
H Methylene	3	2	α_1	...	R_1
H Methylene	4	2	α_1	180°	R_1
C Methyl	5	2	α_2	90°	R_2
C Methyl	6	2	α_2	-90°	R_2
Dummy	7	5	180°	β_1	0
Dummy	8	6	180°	β_1	0
H Methyl	9	7	α_3	180°	R_3
H Methyl	10	7	α_3	60°	R_3
H Methyl	11	7	α_3	-60°	R_3
H Methyl	12	8	α_3	180°	R_3
H Methyl	13	8	α_3	60°	R_3
H Methyl	14	8	α_3	-60°	R_3

$\alpha_2 = 1/2(\text{C-C-C angle})$
 $\alpha_1 = 180^\circ - 1/2(\text{H-C-H angle})$
 $\alpha_3 = \text{C-C-H angle}$

* R value arbitrary.

simplified to

$$(dq/d\phi_k) = \mathbf{A}_{k'} \cdot (d\mathbf{B}_k/d\phi_k) \cdot \dots \cdot \mathbf{B}_{j'} \cdot \mathbf{B}_j \cdot \mathbf{q}_j. \quad (9)$$

If the independent parameter being varied is R_j a still further simplification applies:

$$(dq/dR_k) = \mathbf{A}_{k'} \cdot (d\mathbf{B}_k/dR_k) \cdot \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \quad (10)$$

This can be seen by noting that only the fourth column of \mathbf{B}_k contains R_k , and that the fourth element of any vector \mathbf{q}_1 is one.

The extension of this scheme to second and higher derivatives is straightforward. Of course, a derivative is zero unless the independent variables being varied all correspond to k values (atoms) in the chain connecting Atom j to Atom 1.

Vector Product Formulation

A procedure involving less computation to obtain first derivatives involves the following vector formulation: suppose an atom j lies in a portion of a molecule which is rotated through an angle ϕ about an axis A . Then the desired derivative is the vector product between a unit vector \mathbf{a} along the rotation axis and a vector to j from any position on that axis:

$$dq(j)/d\phi = \mathbf{a} \times [\mathbf{q}(j) - \mathbf{q}(i)],$$

where $\mathbf{q}(j)$ is the position vector of Atom j in the base coordinate system and $\mathbf{q}(i)$ is the position vector of any atom lying on the axis A . Upon identifying the appropriate axis of rotation we obtain

$$dq(j)/d\alpha_k = -\mathbf{a}_{z,k} \times [\mathbf{q}(j) - \mathbf{q}(k')],$$

where $\mathbf{a}_{z,k}$ is a unit vector along the z axis of the coordinate system k . We note that the components of

$a_{z,k}$ are the first three elements of the third column of the matrix A_k . Similarly

$$\begin{aligned} dq(j)/d\beta_k &= a_{z,k'} \times [q(j) - q(k')] \\ &= a_{z,k'} \times [q(j) - q(k'')]. \end{aligned}$$

It remains only to note that

$$dq(j)/dR_k = a_{z,k}.$$

EXPERIENCE

A series of FORTRAN II programs based on this scheme have been in use for over two years, on IBM 7074 and

7090 computers.⁵ The convenience and versatility of this scheme have been demonstrated in the diverse applications cited above; the basic simplicity of the internal coordinates used make it possible to describe moderately complex molecules with a minimum of pain.

⁵ The most recent version, a FORTRAN II subroutine "LINUS 2," has the following approximate running times on an IBM 7090 computer: Calculation of all cartesian coordinates, approx. 6 msec/atom, calculation of all derivatives with respect to a given internal coordinate, 0.15–0.7 msec/atom. The time for a derivative calculation depends on the type of independent variable (R , α , or β) and its location, and the coordinate calculation time depends to some degree on the sine-cosine subroutine used.

Rotational Relaxation in Polar Gases

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Rotational collision numbers for pure polar gases have been calculated by classical mechanics. For the purposes of the calculation, a polar molecule was taken to be a point dipole imbedded in a hard core and the interaction between molecules was confined to a plane. A perturbation calculation correct through third order gave the result

$$\frac{Z_{\text{rot}}(1, T)}{Z_{\text{rot}}(2, T_0)} = \frac{\gamma_1}{\gamma_2} \left(\frac{\mu_2}{\mu_1} \right)^4 \left(\frac{M_1}{M_2} \right) \left(\frac{T}{T_0} \right)^3 \left[\frac{\eta_2(T_0)}{\eta_1(T)} \right]^2 \frac{\Theta_{11}(2, T_0)}{\Theta_{11}(1, T)},$$

where the numbers 1 and 2 label chemical species, γ is the number of rotational degrees of freedom, M the molecular mass, μ the dipole moment, T the absolute temperature, T_0 a reference temperature, and η the viscosity. The function Θ_{11} has as its argument $(16\pi/5)(I/M)\eta(\pi MkT)^{-1/2}$, where I is an average moment of inertia. The theoretical results show that the rotational collision number increases for increasing temperature and decreasing dipole moments and moments of inertia. The dipole moment and moment of inertia dependence is in qualitative agreement with experiment. Since the experimental temperature dependence is somewhat in doubt, no conclusion can be made concerning the correctness of the theoretical temperature dependence.

INTRODUCTION

In comparison with vibrational relaxation, relatively little experimental data on rotational relaxation exists in the literature. This is particularly true of rotational relaxation in polar gases, and, until quite recently, experimental values have been almost nonexistent. However, recent experimental studies have yielded rotational relaxation times, or equivalently, rotational collision numbers for a number of the more common polar gases.^{1–10} Most of the available data are summarized

¹ C. E. Baker and R. S. Brokaw, *J. Chem. Phys.* **40**, 1523 (1964).

² C. E. Baker and R. S. Brokaw, *J. Chem. Phys.* **43**, 3519 (1965).

³ C. E. Baker, *J. Chem. Phys.* **46**, 2846 (1967).

⁴ C. B. Baker and N. DeHaas, *Phys. Fluids* **7**, 1400 (1964).

⁵ B. N. Srivastava and A. Das Gupta, *Phys. Fluids* **9**, 722 (1966).

⁶ K. Geide, *Acustica* **13**, 31 (1963).

⁷ H. Roesler and K.-F. Sahm, *J. Acoust. Soc. Am.* **37**, 386 (1965).

⁸ M. A. Breazeale and H. O. Kneser, *J. Acoust. Soc. Am.* **32**, 885 (1960).

⁹ H. J. Bauer and K.-F. Sahm, *J. Chem. Phys.* **42**, 3400 (1965).

¹⁰ L. M. Crapo and G. W. Flynn, *J. Chem. Phys.* **43**, 1443 (1965).

in Table I. The data⁹ for the molecule NO have not been included because it is considerably less polar than the molecules of Table I, and hence the dipole-dipole potential is probably not the dominant interaction. In addition, a Z_{rot} for ammonia, determined by Petralia,¹¹ has not been included since it is approximately four times larger than the corresponding value in Table I. In a private communication, R. S. Brokaw of this laboratory expressed the opinion that the Z_{rot} for H₂S that is given in Table I appears unrealistically large when compared with similar molecules. However, I have included it in the tabulation because it is the only data available for this molecule. Except for the fluoromethanes, the experimental collision numbers have been obtained from an analysis of either acoustic absorption or thermal conductivity measurements. The fluoromethane data was derived from nuclear magnetic resonance spectra.¹⁰ It is by no means certain that the three experimental techniques give comparable values for the rotational collision number Z_{rot} . The two molecules HCl and H₂O can be used to compare the results

¹¹ S. Petralia, *Nuovo Cimento* **10**, 817 (1953).