A Tabulation of General Formulas for Inverse Kinetic Energy Matrix Elements in Acyclic Molecules

J. C. Decius

Citation: The Journal of Chemical Physics **16**, 1025 (1948); doi: 10.1063/1.1746719
View online: http://dx.doi.org/10.1063/1.1746719
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/16/11?ver=pdfcov
Published by the AIP Publishing

A Tabulation of General Formulas for Inverse Kinetic Energy Matrix Elements in Acyclic Molecules

J. C. DECIUS*
Metcalf Research Laboratory, Brown University, Providence, Rhode Island

(Received April 12, 1948)

In terms of internal coordinates of the bond stretching and bending type, together with a torsional type of coordinate, general formulas for inverse kinetic energy matrix elements have been computed for all 33 possible acyclic configurations involving the given types of coordinates. Tabulations are given both for the general case and for three special cases in which all valence angles of the configuration are assumed to be 90°, 109°28′, and 120°, respectively.

I. INTRODUCTION

GENERAL methods for setting up the secular determinant for molecular vibrations have been given by Wilson[1,2] and by Eliashevich[3] in a form which makes use of internal coordinates adapted to the valence structure of the molecule. Since the transformation from this basis to a basis adapted to the irreducible representations of the group of symmetry operations is now well known, and since methods for performing the numerical solutions of the separate factors of the secular determinant are being facilitated through the use of machines,[4–7] the calculation of the elements of the inverse kinetic energy matrix seems likely to emerge as one of the more laborious steps in the process of computing the vibration frequencies of a molecule. In this connection, it might be mentioned that a recent paper by Wilson[8] provides a scheme whereby the potential energy coefficients can perhaps most conveniently be determined as unknowns to fit a given set of observed frequencies; this method similarly makes use of the inverse kinetic energy matrix.

In view of these facts, a tabulation of general and special algebraic formulas for the inverse kinetic energy matrix elements has been prepared in the hope of reducing the time consumed in calculating normal vibration frequencies. These formulas, which express the result of the transformation from Cartesian to valence-type internal coordinates of small displacements of the atoms from their equilibrium positions, may all be derived from the fundamental formula as given by Wilson,[2]

$$g_{qq'}=\sum_{k=1}^{N}\mathbf{S}_{qk}\cdot\mathbf{S}_{q'k}\mu_k, \tag{1}$$

in which $g_{qq'}$ is a matrix element associated with the coordinates q and q'; $\mathbf{S}_{qk}$ is a vector representing the contribution of the kth atom to the coordinate q, μ_k is the reciprocal mass of the kth atom, and the summation is extended (formally) over all N atoms of the molecule.

Two types of internal coordinates have been principally used to date: the change in distance between two bonded atoms and the change in angle between two bonds having an atom in common. A third type of coordinate is suggested by the resistance to torsion about, e.g., the carbon-carbon bond in ethane. As a general definition of a coordinate of a third type, we adopt the change in dihedral angle between planes of atoms (123) and (234), where neither (123) nor (234) are colinear and where bonds exist between 1 and 2, 2 and 3, 3 and 4. Such a coordinate appears naturally in the C_2 model of H_2O_2, for example.

II. NOTATION AND CLASSIFICATION OF THE INVERSE KINETIC ENERGY MATRIX ELEMENTS

The three types of coordinates described above will be identified by the symbols r, ϕ, and τ

* This work was supported by the Office of Naval Research under Contract N6ori-88, Task Order No. 1.

[1] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939).
[2] E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).
[3] M. Eliashevich, Comptes rendus U.R.S.S. **28**, 605 (1940).
[4] G. K. Carter and G. Kron, J. Chem. Phys. **14**, 32 (1946).
[5] A. A. Frost and M. Tamres, J. Chem. Phys. **15**, 383 (1947).
[6] R. H. Hughes and E. B. Wilson, Jr., Rev. Sci. Inst. **18**, 103 (1947).
[7] W. A. Adcock, Rev. Sci. Inst. **19**, 181 (1948).
[8] E. B. Wilson, Jr., J. Chem. Phys. **15**, 736 (1947).

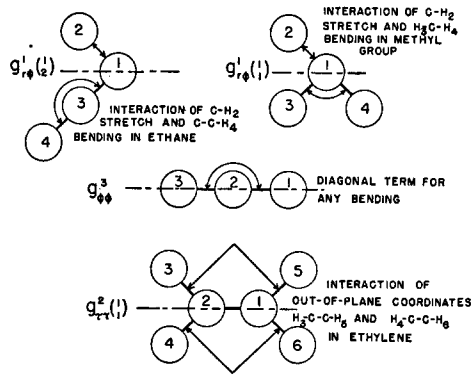


FIG. 1. Examples of notation.

referring to stretching, bending, and twisting, respectively; thus $g_{r\tau}$ will represent a matrix element involving the interaction of a stretching and a torsional coordinate. Similarly, $\mathbf{S}_{\phi k}$ will represent the contribution of the kth atom to a bending coordinate. The equilibrium configuration of the molecule will define the following set of symbols numerically:

$Q_{ij}=Q_{ji}=$*reciprocal* of equilibrium distance between ith and jth atoms,

$\phi_{ijk}=\phi_{kji}(=\phi_j)=$equilibrium angle between bonds $i-j$ and $k-j$,

$\tau_{ijkl}=\tau_{lkji}(=\tau_{il}=\tau_{li}=$equilibrium dihedral angle between planes of atoms (ijk) and (jkl).

TABLE I. Notations and numbers of distinct configurations for inverse kinetic energy matrix elements in acyclic structure.

q	q'	p	$np_{qq'}$	$\binom{C_{q1}}{C_{q'1}}$
r	r	2	1	$\binom{0}{0}$
		1	1	$\binom{1}{1}$
r	ϕ	2	1	$\binom{0}{1}$
		1	2	$\binom{1}{2}$, $\binom{1}{1}$
r	τ	2	2	$\binom{0}{2}$, $\binom{0}{1}$
		1	2	$\binom{1}{3}$, $\binom{1}{2}$
ϕ	ϕ	3	1	$\binom{0}{0}$
		2	2	$\binom{1}{1}$, $\binom{1}{0}$
		1	3	$\binom{2}{2}$, $\binom{2}{1}$, $\binom{1}{1}$
ϕ	τ	3	1	$\binom{0}{1}$
		2	3	$\binom{1}{2}$, $\binom{1}{1}$, $\binom{1}{0}$
		1	4	$\binom{2}{3}$, $\binom{2}{2}$, $\binom{1}{3}$, $\binom{1}{2}$
τ	τ	4	1	$\binom{0}{0}$
		3	2	$\binom{1}{1}$, $\binom{1}{0}$
		2	4	$\binom{2}{2}$, $\binom{2}{1}$, $\binom{2}{0}$, $\binom{1}{1}$
		1	3	$\binom{3}{3}$, $\binom{3}{2}$, $\binom{2}{2}$

As will be seen below, the simplified notation in parentheses will be used, or the subscripts may be omitted entirely, wherever no ambiguity arises. The angles ϕ and τ will have the following ranges: $0<\phi\leq\pi$; $-\pi<\tau\leq+\pi$. The sign of τ is determined through the following convention: viewing the configuration $(ijkl)$ along the line $j-k$, with j nearer the observer than k, let τ be positive if it is traced from the projections of $i-j$ to $l-k$ in the clockwise sense.

Wilson[2] has given expressions for $\mathbf{S}_{rk}$ and $\mathbf{S}_{\phi k}$ (the contribution of the kth atom to the stretching and bending coordinates, respectively) in terms of the above quantities and of unit vectors, $\mathbf{e}_{kl}$, directed from the kth to the lth atom: to these formulas, we now append appropriate expressions for the torsional type of coordinate ($\mathbf{S}_{\tau k}$). It is assumed that the atoms are bonded together in numerical order.

$$\mathbf{S}_{r1}=\mathbf{e}_{21}, \tag{2}$$

$$\mathbf{S}_{r2}=\{12\}\mathbf{S}_{r1}, \tag{3}$$

$$\mathbf{S}_{\phi1}=\frac{Q_{21}}{\sin\phi_2}(\cos\phi_2\mathbf{e}_{21}-\mathbf{e}_{23})=Q_{21}\mathbf{e}_{12}\times\frac{(\mathbf{e}_{12}\times\mathbf{e}_{23})}{\sin\phi_2}, \tag{4}$$

$$\mathbf{S}_{\phi2}=-(\mathbf{S}_{\phi1}+\mathbf{S}_{\phi3}), \tag{5}$$

$$\mathbf{S}_{\phi3}=\{13\}\mathbf{S}_{\phi1}, \tag{6}$$

$$\mathbf{S}_{\tau1}=-\frac{Q_{12}}{\sin\phi_2}\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2}, \tag{7}$$

$$\mathbf{S}_{\tau2}=\left[\frac{Q_{12}}{\sin\phi_2}-(\cos\tau_{14}\cot\phi_3+\cot\phi_2)Q_{23}\right]\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2}, \\ -\cot\phi_3\sin\tau_{14}Q_{23}\mathbf{e}_{23}\times\left(\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2}\right), \tag{8}$$

$$\mathbf{S}_{\tau3}=\{(14)(23)\}\mathbf{S}_{\tau2}, \tag{9}$$

and

$$\mathbf{S}_{\tau4}=\{(14)(23)\}\mathbf{S}_{\tau1}. \tag{10}$$

In Eqs. (3), (6), (9), and (10) the expression in brackets signifies a permutation of atomic subscripts to be performed upon the previous expression as indicated.

The classification of the matrix elements depends, in the first place, upon the fact that they can be non-vanishing only if the two coor-

TABLE II. General formulas for inverse kinetic energy matrix elements in acyclic structures.

Type	Formula
g^2_{rr}	$\mu_1+\mu_2$
g^1_{rr}	$\cos\phi\mu_1$
$g^2_{r\phi}$	$-\sin\phi Q_{23}\mu_2$
$g^1_{r\phi}\binom{1}{2}$	$\sin\phi_1\cos\tau Q_{13}\mu_1$
$\binom{1}{1}$	$-(\psi^1_{234}Q_{13}+\psi^1_{243}Q_{14})\dfrac{\mu_1}{\sin\phi_{314}}$
$g^2_{rr}\binom{0}{2}$	$-\sin\phi_2\cot\phi_3\sin\tau Q_{23}\mu_2$
$\binom{0}{1}$	0
$g^1_{rr}\binom{1}{3}$	$-\dfrac{\sin\phi_1}{\sin\phi_3}\sin\tau_{24}Q_{13}\mu_1$
$\binom{1}{2}$	$-\sin\phi_{123}\left[\dfrac{\sin\delta^4{}_{52}}{\sin\phi_{315}}Q_{15}+(\cot\phi_3\sin\tau_{24}-\cot\phi_{315}\sin\delta^4{}_{52})Q_{13}\right]\mu_1$
$g^3_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3+(Q^2{}_{12}+Q^2{}_{23}-2\cos\phi Q_{12}Q_{23})\mu_2$
$g^2_{\phi\phi}\binom{1}{1}$	$\dfrac{\psi^2{}_{314}}{\sin\phi_{123}\sin\phi_{124}}\Big\{Q^2{}_{12}\mu_1+\Big[(Q_{12}-\cos\phi_{123}Q_{23}-\cos\phi_{124}Q_{24})Q_{12}+\dfrac{\cos\phi_{324}\cos\phi_{123}\cos\phi_{124}-\cos^2\phi_{123}-\cos^2\phi_{124}+1}{\psi^2{}_{314}}Q_{23}Q_{24}\Big]\mu_2\Big\}$
$\binom{1}{0}$	$-\cos\tau Q_{12}[(Q_{12}-\cos\phi_1Q_{14})\mu_1+(Q_{12}-\cos\phi_2Q_{23})\mu_2]$
$g^1_{\phi\phi}\binom{2}{2}$	$-(\sin\tau_{25}\sin\tau_{34}+\cos\tau_{25}\cos\tau_{34}\cos\phi_1)Q_{12}Q_{14}\mu_1$
$\binom{2}{1}$	$[(\sin\phi_{214}\cos\phi_{415}\cos\tau_{34}-\sin\phi_{215}\cos\tau_{35})Q_{14}+(\sin\phi_{215}\cos\phi_{415}\cos\tau_{35}-\sin\phi_{214}\cos\tau_{34})Q_{15}]\dfrac{Q_{12}\mu_1}{\sin\phi_{415}}$
$\binom{1}{1}$	$[(\psi^1_{435}-\cos\phi_{214}\psi^1_{235})Q_{12}Q_{13}+(\psi^1_{453}-\cos\phi_{214}\psi^1_{253})Q_{12}Q_{15}+(\psi^1_{235}-\cos\phi_{214}\psi^1_{435})Q_{14}Q_{13}+(\psi'_{253}-\cos\phi_{214}\psi'_{453})Q_{14}Q_{15}]\dfrac{\mu_1}{\sin\phi_{214}\sin\phi_{315}}$
$g^3_{\phi\tau}$	$\dfrac{\sin\tau}{\sin\phi_3}Q_{23}[\cos\phi_3(Q_{23}-\cos\phi_2Q_{12})\mu_2-(Q_{34}-\cos\phi_3Q_{23})\mu_3]$
$g^2_{\phi\tau}\binom{1}{2}$	$\dfrac{\sin\phi_{324}\sin\delta^5{}_{13}}{\sin\phi_{123}\sin\phi_{124}}Q^2{}_{12}\mu_1+\Big[\sin\delta^5{}_{13}(Q_{12}-\cos\phi_{123}Q_{23})S^{24}{}_{15}+\dfrac{\cot\phi_4\sin\tau_{15}}{\sin\phi_{123}}[\sin\phi_{324}\cos\delta^5{}_{13}(Q_{12}-\cos\phi_{123}Q_{23})+\sin\phi_{124}(Q_{23}-\cos\phi_{123}Q_{12})]Q_{24}\Big]\mu_2$
$\binom{1}{1}$	$\Big[(\cot\phi_{124}\sin\delta^5{}_{34}+\cot\phi_1\sin\tau_{35})Q_{12}-\dfrac{\sin\tau_{35}}{\sin\phi_1}Q_{15}\Big]Q_{12}\mu_1+\Big[(\cot\phi_{124}\sin\delta^5{}_{34}+\cot\phi_1\sin\tau_{35})Q_{12}-\dfrac{\sin\delta^5{}_{34}}{\sin\phi_{124}}Q_{24}\Big](Q_{12}-\cos\phi_{123}Q_{23})\mu_2$
$\binom{1}{0}$	$Q_{12}\Big[(\sin\tau_{34}S^{14}{}_{25}+\cos\phi_1\cot\phi_4\sin\tau_{25}\cos\tau_{34}Q_{14})\mu_1+\dfrac{\sin\tau_{34}}{\sin\phi_1}(Q_{12}-\cos\phi_2Q_{23})\mu_2\Big]$
$g^1_{\phi\tau}\binom{2}{2}$	$(\sin\tau_{25}\cos\tau_{34}\cos\phi_1-\cos\tau_{25}\sin\tau_{34})\dfrac{Q_{12}Q_{14}}{\sin\phi_4}\mu_1$
$\binom{2}{2}$	$[(\sin\phi_{214}\cos\phi_{216}\sin\tau_{34}-\cos\phi_{214}\sin\phi_{216}\sin\tau_{36})S^{14}{}_{65}+\cot\phi_4[(\sin\phi_{214}\cos\phi_{216}\cos\tau_{34}-\cos\phi_{214}\sin\phi_{216}\cos\tau_{36})\cos\phi_{214}-\sin^2\phi_{214}\sin\phi_{416}\sin\tau_{34}\sin\delta^5{}_{62}]\sin\tau_{56}Q_{14}]\dfrac{Q_{12}}{\sin\phi_{416}}\mu_1$
$\binom{1}{3}$	$[(\sin\phi_{316}\sin\tau_{46}-\sin\phi_{213}\sin\tau_{24}\cos\phi_{216})Q_{12}+(\sin\phi_{213}\sin\tau_{24}-\sin\phi_{316}\sin\tau_{46}\cos\phi_{216})Q_{16}]\dfrac{Q_{13}}{\sin\phi_3\sin\phi_{216}}\mu_1$
$\binom{1}{2}$	$[[\sin\phi_{213}\sin\delta^4{}_{62}(Q_{15}-\cos\phi_{215}Q_{12})+\sin\phi_{513}\sin\delta^4{}_{65}(Q_{12}-\cos\phi_{215}Q_{15})]S^{13}{}_{64}+\cot\phi_3\sin\tau_{46}[\sin\phi_{213}\cos\delta^4{}_{62}(Q_{15}-\cos\phi_{215}Q_{12})+\sin\phi_{513}\cos\delta^4{}_{65}(Q_{12}-\cos\phi_{215}Q_{15})]Q_{13}]\dfrac{\mu_1}{\sin\phi_{215}}$

TABLE II.—*Continued.*

Type	Formula
$g^4{}_{\tau\tau}$	$\left(\frac{Q_{12}}{\sin\phi_2}\right)^2\mu_1+\left(\frac{Q_{34}}{\sin\phi_3}\right)^2\mu_4+[(S^{23}{}_{14})^2+\cot^2\phi_3\sin^2\tau Q^2{}_{23}]\mu_2+[(S^{32}{}_{41})^2+\cot^2\phi_2\sin^2\tau Q^2{}_{23}]\mu_3$
$g^3{}_{\tau\tau}(^1_1)$	$\left(\frac{Q_{12}}{\sin\phi_2}\right)^2\mu_1+(S^{23}{}_{14}S^{23}{}_{15}+\cot\phi_{234}\cot\phi_{235}\sin\tau_{14}\sin\tau_{15}Q^2{}_{23})\mu_2+[\cos\delta^1{}_{54}(S^{32}{}_{41}S^{32}{}_{51}+\cot^2\phi_2\sin\tau_{14}\sin\tau_{15}Q^2{}_{23})$ $+\cot\phi_2\sin\delta^1{}_{54}(\sin\tau_{14}S^{32}{}_{51}-\sin\tau_{15}S^{32}{}_{41})Q_{23}]\mu_3$
$(^1_0)$	$\left[(\cot\phi_2+\cot\phi_1\cos\tau_{35})Q_{12}-\frac{\cos\tau_{35}}{\sin\phi_1}Q_{15}\right]\frac{Q_{12}}{\sin\phi_2}\mu_1+\left[(\cot\phi_2+\cot\phi_3\cos\tau_{14})Q_{32}-\frac{\cos\tau_{14}}{\sin\phi_3}Q_{34}\right]\frac{Q_{32}}{\sin\phi_2}\mu_3$ $-[S^{23}{}_{14}S^{21}{}_{35}+\cot\phi_1\cot\phi_3\cos\phi_2\sin\tau_{14}\sin\tau_{35}Q_{12}Q_{32}]\mu_2$
$g^2{}_{\tau\tau}(^2_2)$	$\frac{\psi^2{}_{315}}{\sin\phi_{123}\sin\phi_{125}}\left\{\frac{Q^2{}_{12}}{\sin\phi_{123}\sin\phi_{125}}\mu_1+\left[S^{23}{}_{14}S^{25}{}_{16}+\sin\phi_{325}[\cot\phi_{123}\cot\phi_3\sin\tau_{14}\sin\delta^6{}_{13}S^{25}{}_{16}Q_{23}\right.\right.$ $+\cot\phi_{125}\cot\phi_5\sin\tau_{16}\sin\delta^4{}_{15}S^{23}{}_{14}Q_{25}]+\cot\phi_3\cot\phi_5\sin\tau_{14}\sin\tau_{16}$ $\left.\left.\times\frac{1-\cos^2\phi_{123}-\cos^2\phi_{125}+\cos\phi_{325}\cos\phi_{123}\cos\phi_{125}}{\psi^2{}_{315}}Q_{23}Q_{25}\right]\mu_2\right\}$
$(^2_1)$	$\left[(\cot\phi_1\cos\tau_{36}+\cot\phi_{125}\cos\delta^6{}_{53})Q_{12}-\frac{\cos\tau_{36}}{\sin\phi_1}Q_{16}\right]\frac{Q_{12}}{\sin\phi_{123}}\mu_1-(\cos\delta^6{}_{53}S^{23}{}_{14}S^{21}{}_{56}+\cot\phi_3\cos\phi_{123}\sin\tau_{14}\sin\delta^6{}_{53}S^{21}{}_{56}Q_{23}$ $-\cot\phi_1\sin\tau_{56}\sin\delta^6{}_{53}S^{23}{}_{14}Q_{12}+\cot\phi_1\cot\phi_3\cos\phi_{123}\sin\tau_{14}\sin\tau_{56}\cos\delta^6{}_{53}Q_{12}Q_{23})\mu_2$
$(^2_0)$	$Q_{12}\left[(\cos\tau_{35}S^{15}{}_{26}-\cot\phi_5\cos\phi_1\sin\tau_{35}\sin\tau_{26}Q_{15})\frac{\mu_1}{\sin\phi_2}+(\cos\tau_{35}S^{23}{}_{14}-\cot\phi_3\cos\phi_2\sin\tau_{35}\sin\tau_{14}Q_{23})\frac{\mu_2}{\sin\phi_1}\right]$
$(^1_1)$	$[\cos\delta^3{}_{65}(S^{12}{}_{53}S^{12}{}_{64}+\cot\phi_{123}\cot\phi_{124}\sin\tau_{35}\sin\tau_{46}Q^2{}_{12})+\sin\delta^3{}_{65}(\cot\phi_{123}\sin\tau_{35}S^{12}{}_{64}-\cot\phi_{124}\sin\tau_{46}S^{12}{}_{53})Q_{12}]\mu_1$ $+[\cos\delta^5{}_{43}(S^{21}{}_{35}S^{21}{}_{46}+\cot\phi_{215}\cot\phi_{216}\sin\tau_{35}\sin\tau_{46}Q^2{}_{12})+\sin\delta^5{}_{43}(\cot\phi_{215}\sin\tau_{35}S^{21}{}_{46}-\cot\phi_{216}\sin\tau_{46}S^{21}{}_{35})Q_{12}]\mu_2$
$g^1{}_{\tau\tau}(^3_3)$	$(\sin\tau_{35}\sin\tau_{26}\cos\phi_1-\cos\tau_{35}\cos\tau_{26})\frac{Q_{12}}{\sin\phi_2}\frac{Q_{15}}{\sin\phi_5}\mu_1$
$(^3_2)$	$\left[(\cos\tau_{35}\cos\delta^6{}_{72}-\sin\tau_{35}\sin\delta^6{}_{72}\cos\phi_{215})\frac{Q_{17}}{\sin\phi_{517}}-[\cot\phi_{517}(\cos\tau_{35}\cos\delta^6{}_{72}-\sin\tau_{35}\sin\delta^6{}_{72}\cos\phi_{215})\right.$ $\left.+\cot\phi_5(\cos\tau_{35}\cos\tau_{26}+\sin\tau_{35}\sin\tau_{26}\cos\phi_{215})]Q_{15}\right]\frac{Q_{12}}{\sin\phi_2}\mu_1$
$(^2_2)$	$\left\{\frac{\cos\phi_{214}\cos\phi_{617}-\cos\phi_{217}\cos\phi_{416}}{\sin\phi_{216}\sin\phi_{417}}S^{12}{}_{63}S^{14}{}_{75}-\frac{\cot\phi_2\sin\tau_{36}}{\sin\phi_{216}}(\sin\phi_{416}\sin\delta^5{}_{67}-\cos\phi_{216}\sin\phi_{214}\sin\delta^5{}_{27})S^{14}{}_{75}Q_{12}\right.$ $-\frac{\cot\phi_4\sin\tau_{57}}{\sin\phi_{417}}(\sin\phi_{217}\sin\delta^3{}_{76}-\cos\phi_{417}\sin\phi_{214}\sin\delta^3{}_{46})S^{12}{}_{63}Q_{14}$ $\left.+\cot\phi_2\cot\phi_4\sin\tau_{36}\sin\tau_{57}\left[\frac{\cos\phi_{214}(\cos\phi_{214}\cos\phi_{617}-\cos\phi_{416}\cos\phi_{217})}{\sin\phi_{216}\sin\phi_{417}}-\sin^2\phi_{214}\sin\delta^5{}_{27}\sin\delta^3{}_{46}\right]Q_{12}Q_{14}\right\}\mu_1$

dinates involved possess one or more atoms in common. In the subsequent tabulations this number of common atoms is indicated by the superscript p; writing the subscripts always in such an order that $\alpha\leq\alpha'$, where α = number of atoms in first coordinate, α' = number of atoms in second coordinate, it is clear that $1\leq p\leq\alpha$. In the present paper, only acyclic configurations of atoms defining the superposition of coordinates q and q' will be considered, i.e., the collection of atoms and bonds will be "trees" in the topological sense as defined by Cayley.[9] This being the case, it is possible to specify the distinct types of configurations uniquely through the following system of notation: imagine the set of common atoms to be drawn in a horizontal line, with the residual atoms of coordinate q drawn in lines with slopes of $\pm 45°$ upwards away from each end of the common set, and with the residual atoms of coordinate q' similarly drawn downwards (see Fig. 1). Then a two by two matrix, C, whose elements are the numbers of residual atoms in the corresponding corners of the pattern just described, would define the configuration precisely. However, only the first column of this

[9] A. Cayley, Phil. Mag. **13**, 172 (1857).

matrix need be given, since $C_{q1}+C_{q2}=\alpha-p$ and $C_{q'1}+C_{q'2}=\alpha'-p$. Furthermore, in computing the number of distinct configurations, the equivalence of the atoms in each coordinate by pairs beginning at the ends and progressing towards the center must be considered (corresponding to the permutation symbols in Eqs. (2) to (10)). For example, if q is a stretching coordinate (type r) and q' is a bending coordinate (type ϕ), and an interaction term with two common atoms is under consideration ($g^2{}_{r\phi}$), one could represent such an interaction by the matrices $\binom{00}{10}$ or $\binom{00}{01}$ which correspond, respectively, to cases in which the non-common atom of the ϕ coordinate is the first or third atom in the set defining ϕ, reading from left to right in the standard configuration diagram described above. Because of the equivalence of the S vectors for the two atoms of coordinate r and for the first and third atoms of coordinate ϕ, the two matrices represent equivalent interaction terms; in the tables, the first column of C is given where C is chosen in such a way that $C_{q1}\geq C_{q2}$, and if $C_{q1}=C_{q2}$, such that $C_{q'1}\geq C_{q'2}$. Explicit solutions of the combinatorial problem, giving the number, $n^p{}_{qq'}$ of distinct $g^p{}_{qq'}$, in terms of α, α', and p may be readily obtained, but the results are merely summarized in Table I. The columns headed by q, q', p, and $n^p{}_{qq'}$ need no further definition; the final column gives the first column of the matrix C for each distinct $g^p{}_{qq'}$ (i.e., the number of residual atoms of coordinate q above a similar number for coordinate q' at the left-hand end of the pattern).

Finally, it is necessary to establish a convention for numbering the atoms in each of the 33 possible configurations described above. The system followed throughout the tabulation of formulas given below in Section III is as follows: the numbering starts with the atoms common to both coordinates, reading from right to left along the horizontal line described above; the residual atoms are then numbered outwards from the set of common atoms, taking the upper left, lower left, upper right, and lower right corners of the diagram in that order. It is furthermore to be understood that C_{q1} and $C_{q'1}$ refer to the total number of residual atoms of each coordinate at the left-hand end of the diagram. This is illustrated in Fig. 1 for several configurations; examples of coordinates from well-known molecules are cited with each configuration diagram in the figure.

III. TABULATION OF FORMULAS

In the succeeding tables, it will be found that the algebraic expressions become rather cumbersome toward the end in the general case. While one purpose of the collection of formulas is to be as explicit as possible, some abbreviations are

TABLE III. Special formulas: all $\phi=90°$.

$g^2{}_{rr}$	$\mu_1+\mu_2$
$g^1{}_{rr}$	0
$g^2{}_{r\phi}$	$-Q_{23}\mu_2$
$g^1{}_{r\phi}\binom{1}{2}$	$\cos\tau Q_{13}\mu_1$
$\binom{1}{1}$	0
$g^2{}_{rr}\binom{0}{2}$	0
$\binom{0}{1}$	0
$g^1{}_{rr}\binom{1}{3}$	$-\sin\tau_{24}Q_{13}\mu_1$
$\binom{1}{2}$	$\pm Q_{15}\mu_1$ $\quad[\pm\delta^4{}_{25}]$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3+(Q^2{}_{12}+Q^2{}_{23})\mu_2$
$g^2{}_{\phi\phi}\binom{1}{1}$	$Q_{23}Q_{24}\mu_2$
$\binom{1}{0}$	$-\cos\tau Q^2{}_{12}(\mu_1+\mu_2)$
$g^1{}_{\phi\phi}\binom{2}{2}$	$-\sin\tau_{25}\sin\tau_{34}Q_{12}Q_{14}\mu_1$
$\binom{2}{1}$	$-(\cos\tau_{35}Q_{14}+\cos\tau_{34}Q_{15})Q_{12}\mu_1$
$\binom{1}{1}$	——
$g^3{}_{\phi\tau}$	$-\sin\tau Q_{23}Q_{34}\mu_3$
$g^2{}_{\phi\tau}\binom{1}{2}$	$\pm Q^2{}_{12}(\mu_1+\mu_2)$ $\quad[\pm\delta^5{}_{13}]$
$\binom{1}{1}$	$-Q_{12}(\sin\tau_{35}Q_{15}\mu_1\pm Q_{24}\mu_2)$ $\quad[\pm\delta^5{}_{34}]$
$\binom{1}{0}$	$\sin\tau_{34}Q^2{}_{12}(\mu_1+\mu_2)$
$g^1{}_{\phi\tau}\binom{2}{3}$	$-\cos\tau_{25}\sin\tau_{34}Q_{12}Q_{14}\mu_1$
$\binom{2}{2}$	0
$\binom{1}{3}$	$(\sin\tau_{64}Q_{12}+\sin\tau_{24}Q_{16})Q_{13}\mu_1$
$\binom{1}{2}$	——
$g^4{}_{\tau\tau}$	$Q^2{}_{12}(\mu_1+\mu_2)+Q^2{}_{34}(\mu_3+\mu_4)$
$g^3{}_{\tau\tau}\binom{1}{1}$	$Q^2{}_{12}(\mu_1+\mu_2)$
$\binom{1}{0}$	$-(\cos\tau_{35}Q_{15}Q_{12}\mu_1+\cos\tau_{14}Q_{34}Q_{32}\mu_3+Q_{12}Q_{32}\mu_2)$
$g^2{}_{\tau\tau}\binom{2}{2}$	0
$\binom{2}{1}$	$-\cos\tau_{36}Q_{12}Q_{16}\mu_1$
$\binom{2}{0}$	$\cos\tau_{35}Q^2{}_{12}(\mu_1+\mu_2)$
$\binom{1}{1}$	0
$g^1{}_{\tau\tau}\binom{3}{3}$	$-\cos\tau_{35}\cos\tau_{26}Q_{12}Q_{15}\mu_1$
$\binom{3}{2}$	0
$\binom{2}{2}$	——

TABLE IV. Special formulas: all $\phi = 109°28'$.

$g^2{}_{rr}$	$\mu_1+\mu_2$
$g^1{}_{rr}$	$-\mu_1/3$
$g^2{}_{r\phi}$	$-(2)^{\frac{1}{2}}Q_{23}\mu_2/3$
$g^1{}_{r\phi}(^1_2)$	$(2)^{\frac{1}{2}}\cos\tau Q_{13}\mu_1/3$
$(^1_1)$	$(2)^{\frac{1}{2}}(Q_{13}+Q_{14})\mu_1/3$
$g^2{}_{rr}(^0_2)$	$\sin\tau Q_{23}\mu_2/3$
$(^0_1)$	0
$g^1{}_{rr}(^1_3)$	$-\sin\tau_{24}Q_{13}\mu_1$
$(^1_2)$	$[\pm 3^{\frac{1}{2}}Q_{15}+(2\sin\tau_{24}\pm 3^{\frac{1}{2}})Q_{13}]\mu_1/6$ $[\pm\delta^4{}_{25}]$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3+(3Q^2{}_{12}+3Q^2{}_{23}+2Q_{12}Q_{23})\mu_2/3$
$g^2{}_{\phi\phi}(^1_1)$	$-(1/6)[3Q^2{}_{21}\mu_1+[3Q^2{}_{21}+(Q_{23}+Q_{24})Q_{21}-5Q_{23}Q_{24}]\mu_2]$
$(^1_0)$	$-(1/3)\cos\tau Q_{12}[(3Q_{12}+Q_{14})\mu_1+(3Q_{12}+Q_{23})\mu_2]$
$g^1{}_{\phi\phi}(^2_2)$	$-(1/3)(3\sin\tau_{25}\sin\tau_{34}-\cos\tau_{25}\cos\tau_{34})Q_{12}Q_{14}\mu_1$
$(^2_1)$	$-(1/3)[(3\cos\tau_{35}+\cos\tau_{34})Q_{14}+(3\cos\tau_{34}+\cos\tau_{35})Q_{15}]Q_{12}\mu_1$
$(^1_1)$	$-(2/3)(Q_{12}+Q_{14})(Q_{13}+Q_{15})\mu_1$
$g^1{}_{\phi\tau}(^1_3)$	$(2)^{-\frac{1}{2}}[(3\sin\tau_{64}+\sin\tau_{24})Q_{12}+(3\sin\tau_{24}+\sin\tau_{64})Q_{16}]Q_{13}\mu_1$
$(^1_2)$	$(2^{\frac{1}{2}}/24)[\pm 2\cdot 3^{\frac{1}{2}}(Q_{15}-Q_{12})Q_{16}+[(\pm 3^{\frac{1}{2}}-2\sin\tau_{24})(3Q_{15}+Q_{12})+(\mp 3^{\frac{1}{2}}-2\sin\tau_{54})(3Q_{12}+Q_{15})]Q_{13}]\mu_1$ $[\pm\delta^4{}_{25}]$
$g^4{}_{\tau\tau}$	$(1/8)[9Q^2{}_{12}\mu_1+9Q^2{}_{34}\mu_4+[9Q^2{}_{12}+2(1+\cos\tau)Q^2{}_{23}+6(1+\cos\tau)Q_{12}Q_{23}]\mu_2$ $+[9Q^2{}_{34}+2(1+\cos\tau)Q^2{}_{23}+6(1+\cos\tau)Q_{34}Q_{23}]\mu_3]$
$g^3{}_{\tau\tau}(^1_1)$	$(1/16)\{18Q^2{}_{12}\mu_1+[18Q^2{}_{12}+6(2+\cos\tau_{14}+\cos\tau_{15})Q_{12}Q_{23}+(1+2\cos\tau_{14}+2\cos\tau_{15})Q^2{}_{23}]\mu_2$ $+[(1+2\cos\tau_{14}+2\cos\tau_{15})Q^2{}_{23}+3Q_{23}[(2\cos\tau_{14}-1)Q_{34}+(2\cos\tau_{15}-1)Q_{35}]-9Q_{34}Q_{35}]\mu_3\}$
$(^1_0)$	$-(1/24)\{9Q_{12}[(1+\cos\tau_{35})Q_{12}+3\cos\tau_{35}Q_{15}]\mu_1+9Q_{23}[(1+\cos\tau_{14})Q_{23}+3\cos\tau_{14}Q_{34}]\mu_3$ $+[3[3Q_{12}+(1+\cos\tau_{14})Q_{23}][3Q_{23}+(1+\cos\tau_{36})Q_{12}]-\sin\tau_{14}\sin\tau_{35}Q_{12}Q_{23}]\mu_2\}$
$g^2{}_{\tau\tau}(^2_2)$	$-(1/96)\{54Q^2{}_{12}\mu_1+[54Q^2{}_{12}+3Q_{12}[(6(1+\cos\tau_{14})\mp 3^{\frac{1}{2}}\sin\tau_{14})Q_{23}+(6(1+\cos\tau_{16})\pm 3^{\frac{1}{2}}\sin\tau_{16})Q_{25}]$ $+[6(1+\cos\tau_{14})(1+\cos\tau_{16})-10\sin\tau_{14}\sin\tau_{16}\pm 3^{\frac{1}{2}}(\sin(\tau_{16}-\tau_{14})+\sin\tau_{16}-\sin\tau_{14})]Q_{23}Q_{25}]\mu_2\}$ $[\pm\delta^4{}_{15}]$
$(^2_1)$	$-(1/48)\{[9(2\cos\tau_{63}-1)Q_{12}+54\cos\tau_{63}Q_{16}]Q_{12}\mu_1-[3[3Q_{12}+(1+\cos\tau_{14})Q_{23}][3Q_{25}+(1+\cos\tau_{56})Q_{12}]$ $\mp 3^{\frac{1}{2}}\sin\tau_{14}[3Q_{25}+(1+\cos\tau_{56})Q_{12}]Q_{23}\mp 3^{\frac{1}{2}}\sin\tau_{56}[3Q_{12}+(1+\cos\tau_{14})Q_{23}]Q_{12}-\sin\tau_{14}\sin\tau_{56}Q_{12}Q_{23}]\mu_2\}$ $[\pm\delta^6{}_{53}]$
$(^2_0)$	$(1/8)Q_{12}\{[9\cos\tau_{35}Q_{12}+[3\cos\tau_{35}(1+\cos\tau_{26})-\sin\tau_{35}\sin\tau_{26}]Q_{15}]\mu_1$ $+[9\cos\tau_{35}Q_{12}+[3\cos\tau_{35}(1+\cos\tau_{14})-\sin\tau_{35}\sin\tau_{14}]Q_{23}]\mu_2\}$
$(^1_1)$	$-(1/16)\{[[3Q_{15}+(1+\cos\tau_{53})Q_{12}][3Q_{16}+(1+\cos\tau_{64})Q_{12}]+\sin\tau_{53}\sin\tau_{64}Q^2{}_{12}$ $\pm 3^{\frac{1}{2}}\sin\tau_{64}Q_{12}[3Q_{15}+(1+\cos\tau_{53})Q_{12}]\mp 3^{\frac{1}{2}}\sin\tau_{53}Q_{12}[3Q_{16}+(1+\cos\tau_{64})Q_{12}]]\mu_1$ $[\pm\delta^3{}_{56}]$
	$+[[3Q_{23}+(1+\cos\tau_{35})Q_{21}][3Q_{24}+(1+\cos\tau_{46})Q_{21}]+\sin\tau_{35}\sin\tau_{46}Q^2{}_{21}$ $\mp 3^{\frac{1}{2}}\sin\tau_{46}Q_{21}[3Q_{23}+(1+\cos\tau_{35})Q_{21}]\pm 3^{\frac{1}{2}}\sin\tau_{35}Q_{21}[3Q_{24}+(1+\cos\tau_{46})Q_{21}]]\mu_2$ $[\pm\delta^5{}_{34}]$
$g^1{}_{\tau\tau}(^3_3)$	$-(3/8)(3\cos\tau_{35}\cos\tau_{26}+\sin\tau_{35}\sin\tau_{26})Q_{12}Q_{15}\mu_1$
$(^3_2)$	$(1/16)[3^{\frac{1}{2}}(\pm\sin\tau_{35}-3^{\frac{1}{2}}\cos\tau_{35})Q_{17}+[3\cos\tau_{35}(2\cos\tau_{26}-1)+\sin\tau_{35}(\pm 3^{\frac{1}{2}}-2\sin\tau_{26})]Q_{15}]Q_{12}\mu_1$ $[\pm\delta^6{}_{72}]$
$(^2_2)$	$(1/24)\{\pm 3^{\frac{1}{2}}[\sin\tau_{63}[3Q_{17}+(1+\cos\tau_{75})Q_{14}]Q_{12}+\sin\tau_{75}[3Q_{16}+(1+\cos\tau_{63})Q_{12}]Q_{14}]$ $-2\sin\tau_{63}\sin\tau_{75}Q_{12}Q_{14}\}\mu_1$ $[\pm\delta^5{}_{67}]$

imperative. The following have been adopted:

$$\psi^i{}_{jkl}=\psi^i{}_{lkj}=\cos\phi_{jil}-\cos\phi_{jik}\cos\phi_{kil},$$

$$S^{ik}{}_{il}=(Q_{ij}/\sin\phi_{ijk})-(\cos\tau_{il}\cot\phi_{jkl}+\cot\phi_{ijk})Q_{jk},$$

and

$$\delta^k{}_{ij}=\tau_{ik}-\tau_{jk}.$$

The transformation properties of the several types of $g^p{}_{qq'}$ should be noted carefully. Under a reflection (generally an improper rotation), coordinates of the first two types are unchanged, whereas the third type, the twisting, suffers a change of sign.

Thus, the blocks of the G Matrix corresponding to elements of the types $g^p{}_{rr}$ and $g^p{}_{\phi\tau}$ for enantiomorphous configurations will be found to change sign. The eigenvalues are unaffected, of course,

since similar blocks in the F (potential energy) matrix also change sign.

Table II contains the general expressions (the symbol $\begin{pmatrix} C_{q1} \\ C_{q'1} \end{pmatrix}$ is omitted wherever $n^p{}_{qq'}=1$); in cases of extreme symmetry, it may occasionally be found preferable to develop the formulas by simplifying Eqs. (2) to (10) first and substituting in Eq. (1), using the table as a check. In cases practically devoid of symmetry, the general formulas serve both for direct calculation, and as a means of assessing ahead of time the magnitude of the numerical labor.

In addition to the general case, the appropriate expressions for the $g^p{}_{qq'}$ are given in Tables III, IV, and V for the cases in which all ϕ assume the special values of 90°, 109°28′ (tetrahedral angle), and 120°. In Tables III and IV, some of the formulas will be found to contain a choice of sign. The proper sign is readily determined by taking the upper sign throughout if a $\delta^k{}_{ij}$ enclosed in brackets after the formula in question is positive or the lower sign if $\delta^k{}_{ij}$ is negative (the sign of $\delta^k{}_{ij}$ follows the same convention as that for τ_{ij}). There is just one case, namely, $g^2{}_{\tau\tau}\binom{1}{1}$ in Table IV, in which there occur two simultaneous choices of sign. As indicated in the table, upper signs are to be chosen for the coefficient of μ_1, if $\delta^3{}_{56}$ is positive, lower if $\delta^3{}_{56}$ is negative, whereas $\delta^5{}_{34}$ provides a similar criterion for the choice of signs in the coefficients of μ_2.

Finally, it should be noted that the formulas for $g^1{}_{\phi\phi}\binom{1}{1}$, $g^1{}_{\phi\tau}\binom{1}{2}$, and $g^1{}_{\tau\tau}\binom{2}{2}$ are left blank in Tables III and V. This is because the associated configurations involve a tetravalent atom at which it is geometrically impossible to satisfy the condition that *all* bond angles be 90° or 120°.

TABLE V. Special formulas: all $\phi=120°$.

$g^2{}_{rr}$	$\mu_1+\mu_2$	$g^2{}_{\phi\phi}\binom{1}{1}$	$-(1/2)[2Q^2{}_{12}\mu_1+[Q_{12}(2Q_{12}+Q_{23}+Q_{24})-Q_{23}Q_{24}]\mu_2]$
$g^1{}_{rr}$	$-\mu_1/2$	$\binom{1}{0}$	$-(1/2)\cos\tau Q_{12}[(2Q_{12}+Q_{14})\mu_1+(2Q_{12}+Q_{23})\mu_2]$
$g^2{}_{r\phi}$	$-(3^{\frac{1}{2}}/2)Q_{23}\mu_2$	$g^1{}_{\phi\phi}\binom{2}{2}$	$(1/2)(\cos\tau_{25}\cos\tau_{34}-2\sin\tau_{25}\sin\tau_{34})Q_{12}Q_{14}\mu_1$
$g^1{}_{r\phi}\binom{1}{2}$	$(3^{\frac{1}{2}}/2)\cos\tau Q_{13}\mu_1$	$\binom{2}{1}$	$(1/2)\cos\tau_{34}(Q_{15}-Q_{14})Q_{12}\mu_1$
$\binom{1}{1}$	$(3^{\frac{1}{2}}/2)(Q_{13}+Q_{14})\mu_1$	$\binom{1}{1}$	——
$g^2{}_{\tau\tau}\binom{0}{2}$	$(1/2)\sin\tau Q_{23}\mu_2$	$g^3{}_{\phi\tau}$	$-(3^{\frac{1}{2}}/6)\sin\tau Q_{23}[(2Q_{23}+Q_{12})\mu_2+2(2Q_{34}+Q_{23})\mu_3]$
$\binom{0}{1}$	0	$g^2{}_{\phi\tau}\binom{1}{2}$	$(3^{\frac{1}{2}}/6)\sin\tau_{15}(Q_{12}-Q_{23})Q_{24}\mu_2$
$g^1{}_{\tau\tau}\binom{1}{3}$	$-\sin\tau_{24}Q_{13}\mu_1$	$\binom{1}{1}$	$-(3^{\frac{1}{2}}/6)\sin\tau_{35}Q_{12}[2(2Q_{15}+Q_{12})\mu_1+(2Q_{12}+Q_{23})\mu_2]$
$\binom{1}{2}$	$(1/2)\sin\tau_{24}Q_{13}\mu_1$	$\binom{1}{0}$	$(3^{\frac{1}{2}}/6)Q_{12}\{[2\sin\tau_{34}[2Q_{12}+(1+\cos\tau_{25})Q_{14}]+\sin\tau_{25}\cos\tau_{34}Q_{14}]\mu_1$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3$		$+2\sin\tau_{34}(2Q_{12}+Q_{23})\mu_2\}$
	$+(Q^2{}_{12}+Q^2{}_{23}+Q_{12}Q_{23})\mu_2$	$g^1{}_{\phi\tau}\binom{2}{3}$	$-(3^{-\frac{1}{2}})(\sin\tau_{25}\cos\tau_{34}+2\cos\tau_{25}\sin\tau_{34})Q_{12}Q_{14}\mu_1$
$g^1{}_{\phi\tau}\binom{2}{2}$	$(3^{\frac{1}{2}}/6)Q_{12}[4\sin\tau_{36}Q_{16}+[2(1+\cos\tau_{56})\sin\tau_{36}+\cos\tau_{36}\sin\tau_{56}]Q_{14}]\mu_1$		
$\binom{1}{3}$	$(3^{-\frac{1}{2}})\sin\tau_{24}(Q_{16}-Q_{12})Q_{13}\mu_1$		
$\binom{1}{2}$	——		
$g^4{}_{\tau\tau}$	$(2/3)[2Q^2{}_{12}\mu_1+2Q^2{}_{34}\mu_4+[2Q^2{}_{12}+(1+\cos\tau)Q^2{}_{23}+2(1+\cos\tau)Q_{12}Q_{23}]\mu_2$		
	$+[2Q^2{}_{34}+(1+\cos\tau)Q^2{}_{23}+2(1+\cos\tau)Q_{34}Q_{23}]\mu_3]$		
$g^3{}_{\tau\tau}\binom{1}{1}$	$(2/3)\{2Q^2{}_{12}\mu_1+2Q_{12}(Q_{12}+Q_{23})\mu_2-[2Q_{34}Q_{35}+[(1+\cos\tau_{14})Q_{35}+(1-\cos\tau_{14})Q_{34}]Q_{23}]\mu_3\}$		
$\binom{1}{0}$	$-(1/6)\{4[(1+\cos\tau_{36})Q_{12}+2\cos\tau_{35}Q_{15}]Q_{12}\mu_1+4[(1+\cos\tau_{14})Q_{32}+2\cos\tau_{14}Q_{34}]Q_{32}\mu_3$		
	$+[4[(1+\cos\tau_{35})Q^2{}_{12}+(1+\cos\tau_{14})Q^2{}_{23}]+[8+2(1+\cos\tau_{14})(1+\cos\tau_{35})-\sin\tau_{14}\sin\tau_{35}]Q_{12}Q_{32}]\mu_2\}$		
$g^2{}_{\tau\tau}\binom{2}{2}$	$-(1/6)\{8Q^2{}_{12}\mu_1+[2[2Q_{12}+(1+\cos\tau_{14})Q_{23}][2Q_{12}+(1+\cos\tau_{16})Q_{25}]-\sin\tau_{14}\sin\tau_{16}Q_{23}Q_{25}]\mu_2\}$		
$\binom{2}{1}$	$(1/6)\{4[(1-\cos\tau_{36})Q_{12}-2\cos\tau_{36}Q_{16}]Q_{12}\mu_1+[2[2Q_{12}+(1+\cos\tau_{14})Q_{23}][2Q_{25}+(1+\cos\tau_{56})Q_{12}]$		
	$-\sin\tau_{14}\sin\tau_{56}Q_{12}Q_{23}]\mu_2\}$		
$\binom{2}{0}$	$(1/3)Q_{12}\{[2\cos\tau_{35}[2Q_{12}+(1+\cos\tau_{26})Q_{15}]-\sin\tau_{35}\sin\tau_{26}Q_{15}]\mu_1$		
	$+[2\cos\tau_{35}[2Q_{12}+(1+\cos\tau_{14})Q_{23}]-\sin\tau_{35}\sin\tau_{14}Q_{23}]\mu_2\}$		
$\binom{1}{1}$	$-(2/3)[[2Q_{15}Q_{16}+(1+\cos\tau_{35})Q_{12}(Q_{12}+Q_{15}+Q_{16})]\mu_1+[2Q_{23}Q_{24}+(1+\cos\tau_{35})Q_{12}(Q_{12}+Q_{23}+Q_{24})]\mu_2]$		
$g^1{}_{\tau\tau}\binom{3}{3}$	$-(2/3)(\sin\tau_{35}\sin\tau_{26}+2\cos\tau_{35}\cos\tau_{26})Q_{12}Q_{15}\mu_1$		
$\binom{3}{2}$	$-(1/3)[4\cos\tau_{35}Q_{17}+[2\cos\tau_{35}(1-\cos\tau_{26})+\sin\tau_{35}\sin\tau_{26}]Q_{15}]Q_{12}\mu_1$		
$\binom{2}{2}$	——		

IV. EXAMPLES OF APPLICATION TO SPECIFIC MOLECULES

1. H_2O_2 (C_2 Symmetry)

Choose as internal coordinates the O−O and O−H stretches (calling the coordinates P and R_i, respectively), the O−O−H bending (α_i), the H−O−O−H twisting (β); the index i on R and α identifies the H atom involved. Let $Q_{O-O}=P_0$, $Q_{O-H}=R_0$, $\phi_{O-O-H}=\alpha_0$, $\tau_{H-O-O-H}=\beta_0$. Then the following elements of the G matrix associated with the indicated coordinates may be found from Table II.

TABLE VI.

Coordinate pair	Type	Formula
PP	g^2_{rr}	$2\mu_o$
PR_i	g^1_{rr}	$\cos\alpha_0\mu_o$
$P\alpha_i$	$g^2_{r\phi}$	$-\sin\alpha_0 R_0\mu_o$
$P\beta$	$g^2_{r\tau}(^0_1)$	0
R_iR_i	g^2_{rr}	$\mu_o+\mu_H$
R_1R_2	——	0
$R_i\alpha_i$	$g^2_{r\phi}$	$-\sin\alpha_0 P_0\mu_o$
$R_1\alpha_2$	$g^1_{r\phi}(^1_2)$	$\sin\alpha_0\cos\beta_0 P_0\mu_o$
$R_i\beta$	$g^2_{r\tau}(^0_2)$	$-\cos\alpha_0\sin\beta_0 P_0\mu_o$
$\alpha_i\alpha_i$	$g^3_{\phi\phi}$	$R^2_0\mu_H+(2P^2_0+R^2_0-2\cos\alpha_0 P_0R_0)\mu_o$
$\alpha_1\alpha_2$	$g^2_{\phi\phi}(^1_0)$	$-2\cos\beta_0(P_0-\cos\alpha_0R_0)P_0\mu_o$
$\alpha_i\beta$	$g^3_{\phi\tau}$	$\frac{\sin\beta_0}{\sin\alpha_0}[2\cos\alpha_0P_0-(1+\cos^2\alpha_0)R_0]P_0\mu_o$
$\beta\beta$	$g^4_{\tau\tau}$	$\frac{2}{\sin^2\alpha_0}[R^2_0\mu_H+[R^2_0+2\cos\alpha_0(1+\cos\beta_0)\times(\cos\alpha_0P_0-R_0)P_0]\mu_o]$

2. C_3H_8 (Propane; C_{2v} Symmetry)

Assume tetrahedral valence angles throughout; consider one H on each methyl group and the three C to be coplanar and of the form indicated in Fig. 2. Then all τ are either $\pm60°$ or 180°. With atoms numbered as indicated in Fig. 2, choose the following coordinates:

TABLE VII.

Type	Symbol	Number	Detailed description
Stretching	P_i	2	C_3-C_i
Stretching	R_{ij}	4	C_i-H_{ij}
Stretching	S_i	2	C_i-H_{i3}
Stretching	T_i	2	C_3-H_{3i}
Bending	α_{ij}	4	$H_{ij}-C_i-H_{i3}$
Bending	β_i	2	$H_{i1}-C_i-H_{i2}$
Bending	γ	1	$H_{31}-C_3-H_{32}$
Bending	δ_{ij}	4	$H_{ij}-C_i-C_3$
Bending	ϵ_i	2	$H_{i3}-C_i-C_3$
Bending	ζ_{ij}	4	$H_{3j}-C_3-C_i$
Bending	η	1	$C_1-C_2-C_3$
Twisting	τ_i	2	$H_{i3}-C_i-C_3-C_{i\pm1}$

Count of these coordinates reveals three redundancies which correspond to the vanishing sums of six bending coordinates at each carbon atom. The special notation for the elements of the G matrix is given below, only the first row from each set of symmetrically equivalent coordinates being required.

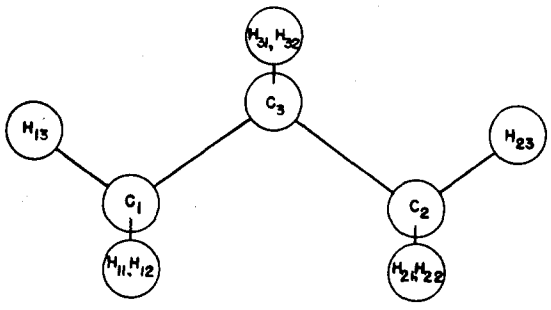
	P_1	P_2	R_{11}	R_{12}	R_{21}	R_{22}	S_1	S_2	T_1	T_2	α_{11}	α_{12}	α_{21}	α_{22}	β_1	β_2	γ
P_1	g^1_P	g^2_P	g_{PR}	g_{PR}	0	0	g_{PS}	0	g_{PT}	g_{PT}	$g_{P\alpha}$	$g_{P\alpha}$	0	0	$g_{P\beta}$	0	$g_{P\gamma}$
R_{11}			g^1_R	g^2_R	0	0	g_{RS}	0	0	0	$g^1_{R\alpha}$	$g^2_{R\alpha}$	0	0	$g_{R\beta}$	0	0
S_1							g_S	0	0	0	$g_{S\alpha}$	$g_{S\alpha}$	0	0	$g_{S\beta}$	0	0
T_1									g^1_T	g^2_T	0	0	0	0	0	0	$g_{T\gamma}$
α_{11}											g^1_α	g^2_α	0	0	$g_{\alpha\beta}$	0	0
β_1															g_β	0	0
γ																	g_γ

	δ_{11}	δ_{12}	δ_{21}	δ_{22}	ϵ_1	ϵ_2	ζ_{11}	ζ_{12}	ζ_{21}	ζ_{22}	η	τ_1	τ_2
P_1	$g^1_{P\delta}$	$g^1_{P\delta}$	$g^2_{P\delta}$	$g^2_{P\delta}$	$g^1_{P\epsilon}$	$g^2_{P\epsilon}$	$g^1_{P\zeta}$	$g^1_{P\zeta}$	$g^2_{P\zeta}$	$g^2_{P\zeta}$	$g_{P\eta}$	$g^1_{P\tau}$	$g^2_{P\tau}$
R_{11}	$g^1_{R\delta}$	$g^2_{R\delta}$	0	0	$g_{R\epsilon}$	0	$g^1_{R\zeta}$	$g^2_{R\zeta}$	0	0	$g_{R\eta}$	$g^1_{R\tau}$	$g^2_{R\tau}$
S_1	$g_{S\delta}$	$g_{S\delta}$	0	0	$g_{S\epsilon}$	0	$g_{S\zeta}$	$g_{S\zeta}$	0	0	$g_{S\eta}$	$g^1_{S\tau}$	$g^2_{S\tau}$
T_1	$g^1_{T\delta}$	$g^2_{T\delta}$	$g^1_{T\delta}$	$g^2_{T\delta}$	$g_{T\epsilon}$	$g_{T\epsilon}$	$g^1_{T\zeta}$	$g^2_{T\zeta}$	$g^1_{T\zeta}$	$g^2_{T\zeta}$	$g_{T\eta}$	$g_{T\tau}$	$-g_{T\tau}$
α_{11}	$g^1_{\alpha\delta}$	$g^2_{\alpha\delta}$	0	0	$g_{\alpha\epsilon}$	0	$g^1_{\alpha\zeta}$	$g^2_{\alpha\zeta}$	0	0	$g_{\alpha\eta}$	$g^1_{\alpha\tau}$	$g^2_{\alpha\tau}$
β_1	$g_{\beta\delta}$	$g_{\beta\delta}$	0	0	$g_{\beta\epsilon}$	0	$g_{\beta\zeta}$	$g_{\beta\zeta}$	0	0	$g_{\beta\eta}$	$g^1_{\beta\tau}$	$g^2_{\beta\tau}$
γ	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\epsilon}$	$g_{\gamma\epsilon}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\eta}$	$g_{\gamma\tau}$	$g_{\gamma\tau}$
δ_{11}	g^1_δ	g^2_δ	g^3_δ	g^4_δ	$g^1_{\delta\epsilon}$	$g^2_{\delta\epsilon}$	$g^1_{\delta\zeta}$	$g^2_{\delta\zeta}$	$g^3_{\delta\zeta}$	$g^4_{\delta\zeta}$	$g_{\delta\eta}$	$g^1_{\delta\tau}$	$g^2_{\delta\tau}$
ϵ_1					g^1_ϵ	g^2_ϵ	$g^1_{\epsilon\zeta}$	$g^1_{\epsilon\zeta}$	$g^2_{\epsilon\zeta}$	$g^2_{\epsilon\zeta}$	$g_{\epsilon\eta}$	$g^1_{\epsilon\tau}$	$g^2_{\epsilon\tau}$
ζ_{11}							g^1_ζ	g^2_ζ	g^3_ζ	g^4_ζ	$g_{\zeta\eta}$	$g^1_{\zeta\tau}$	$g^2_{\zeta\tau}$
η											g_η	$g_{\eta\tau}$	$g_{\eta\tau}$
τ_1												g^1_τ	g^2_τ

The zeros in this matrix arise simply because the pairs of coordinates in question possess no common atoms. The matrix elements $g^1{}_{P\tau}$, $g^2{}_{P\tau}$, $g^1{}_{S\tau}$, $g^2{}_{S\tau}$, $g^1{}_{\beta\tau}$, $g^2{}_{\beta\tau}$, $g_{\gamma\tau}$, $g^1{}_{\epsilon\tau}$, $g^2{}_{\epsilon\tau}$, $g_{\eta\tau}$ also vanish without detailed calculation, since they represent interactions of one of the first two types of coordinates with the third type and the configurations of atoms defining them contain a plane of symmetry ($g^1{}_{P\tau}$ would vanish even without symmetry, being of type $g^2{}_{r\tau}\binom{0}{1}$). Many of the remaining elements are equal: formulas for them are obtained by substitution of appropriate values for τ in Table IV. It is assumed that all C−H distances are equal; the reciprocal of such a distance is designated by R_0 and that of the C−C distance by P_0. Certain elements, fol-

TABLE VIII.

Type	G elements in $CH_3CH_2CH_3$	Formula
$g^2{}_{rr}$	$g^1{}_P$	$2\mu_C$
	$g^1{}_R=g^1{}_S=g^1{}_T$	$\mu_C+\mu_H$
$g^1{}_{rr}$	$g^2{}_P=g_{PR}=g_{PS}=g_{PT}=g^2{}_R=g_{RS}=g^2{}_T$	$-\mu_C/3$
$g^2{}_{r\phi}$	$g^1{}_{P\delta}=g^1{}_{P\epsilon}=g^1{}_{P\zeta}=g^1{}_{R\alpha}=g_{R\beta}=g_{S\alpha}=g_{T\gamma}$	$-(2\frac{1}{3}/3)R_0\mu_C$
	$g_{P\eta}=g^1{}_{R\delta}=g_{S\epsilon}=g^1{}_{T\zeta}$	$-(2\frac{1}{3}/3)-P_0\mu_C$
$g^1{}_{r\phi}\binom{1}{2}$	$g^2{}_{P\delta}=g^1{}_{R\zeta}=g_{R\eta}=g_{S\zeta}=g^1{}_{T\delta}=g_{T\epsilon}$	$(2\frac{1}{3}/3)P_0\mu_C$
	$g^2{}_{P\epsilon}=g^2{}_{R\zeta}=g_{S\eta}=g^2{}_{T\delta}$	$-(2\frac{1}{3}/3)P_0\mu_C$
$\binom{1}{1}$	$g_{P\alpha}=g_{P\beta}=g_{P\gamma}=g^2{}_{R\alpha}=g_{S\beta}$	$(2\frac{1}{3}/3)R_0\mu_C$
	$g^2{}_{P\zeta}=g^2{}_{R\delta}=g_{R\epsilon}=g_{S\delta}=g^2{}_{T\zeta}$	$(2\frac{1}{3}/3)(P_0+R_0)\mu_C$
	$g_{T\eta}$	$(2\frac{1}{3}/3)P_0\mu_C$
$g^1{}_{r\tau}\binom{1}{3}$	$g^2{}_{R\tau}(\pm)$	$-(3\frac{1}{3}/2)P_0\mu_C$
$\binom{1}{2}$	$g^1{}_{R\tau}(\pm)=g_{T\tau}(\pm)$	$-(3\frac{1}{3}/2)R_0\mu_C$
$g^3{}_{\phi\phi}$	$g^1{}_\alpha=g_\beta=g_\gamma$	$(2/3)R^2{}_0(3\mu_H+4\mu_C)$
	$g^1{}_\delta=g^1{}_\epsilon=g^1{}_\zeta$	$R_0{}^2\mu_H+(3R^2{}_0+6P^2{}_0+2R_0P_0)\mu_C/3$
	g_η	$(14/3)P^2{}_0\mu_C$
$g^2{}_{\phi\phi}\binom{1}{1}$	$g^2{}_\alpha=g_{\alpha\beta}$	$-(1/2)R^2{}_0\mu_H$
	$g^2{}_\delta=g^1{}_{\delta\epsilon}=g^2{}_\zeta$	$-(1/6)(6P^2{}_0-5R^2{}_0+2P_0R_0)\mu_C$
	$g^3{}_\zeta$	$-(1/6)[3R^2{}_0\mu_H+(3R_0+5P_0)(R_0-P_0)\mu_C]$
	$g^1{}_{\alpha\delta}=g_{\alpha\epsilon}=g_{\beta\delta}=g_{\gamma\eta}$	$-(1/6)[3R^2{}_0\mu_H+4R_0(R_0-P_0)\mu_C]$
	$g_{\zeta\eta}$	$-(1/6)(7P_0-4R_0)P_0\mu_C$
$\binom{1}{0}$	$g^2{}_{\delta\zeta}$	$(2/3)(3P_0+R_0)P_0\mu_C$
	$g_{\epsilon\eta}$	$(1/3)(7P_0+R_0)P_0\mu_C$
	$g^1{}_{\delta\zeta}=g^1{}_{\epsilon\zeta}$	$-(1/3)(3P_0+R_0)P_0\mu_C$
	$g_{\delta\eta}$	$-(1/6)(7P_0+R_0)P_0\mu_C$
$g^1{}_{\phi\phi}\binom{2}{2}$	$g^2{}_\epsilon$	$(1/3)P^2{}_0\mu_C$
	$g^3{}_\delta$	$(5/6)P^2{}_0\mu_C$
	$g^4{}_\delta$	$-(2/3)P^2{}_0\mu_C$
	$g^2{}_{\delta\epsilon}$	$-(1/6)P^2{}_0\mu_C$
$\binom{2}{1}$	$g^1{}_{\alpha\zeta}=g_{\beta\eta}=g_{\gamma\epsilon}$	$(4/3)P_0R_0\mu_C$
	$g^2{}_{\alpha\zeta}=g_{\alpha\eta}=g_{\beta\zeta}=g_{\gamma\delta}$	$-(2/3)P_0R_0\mu_C$
	$g^3{}_{\delta\zeta}$	$(2/3)(P_0+R_0)P_0\mu_C$
	$g^4{}_{\delta\zeta}$	$(1/6)(R_0-5P_0)P_0\mu_C$
	$g^2{}_{\epsilon\zeta}$	$(1/6)(P_0-5R_0)P_0\mu_C$
$\binom{1}{1}$	$g_{\gamma\eta}$	$-(8/3)P_0R_0\mu_C$
	$g^4{}_\zeta$	$-(2/3)(P_0+R_0)^2\mu_C$
	$g^2{}_{\alpha\delta}=g_{\beta\epsilon}$	$-(4/3)(P_0+R_0)R_0\mu_C$
$g^2{}_{\phi\tau}\binom{1}{2}$	$g^1{}_{\alpha\tau}(\pm)$	$(6\frac{1}{3}/8)R^2{}_0(3\mu_H+4\mu_C)$
	$g^2{}_{\zeta\tau}(\pm)$	$-(6\frac{1}{3}/8)(6P_0+R_0)P_0\mu_C$
$\binom{1}{1}$	$g^1{}_{\delta\tau}(\pm)$	$(6\frac{1}{3}/8)R^2{}_0\mu_C$
	$g^1{}_{\zeta\tau}(\pm)$	$(6\frac{1}{3}/8)(3P_0-2R_0)P_0\mu_C$
$\binom{1}{0}$	$g^2{}_{\delta\tau}(\pm)$	$6\frac{1}{3}(6P_0+R_0)P_0\mu_C$
$g^1{}_{\phi\tau}\binom{1}{3}$	$g^2{}_{\alpha\tau}(\pm)$	$(6\frac{1}{3}/2)P_0R_0\mu_C$
$g^4{}_{\tau\tau}$	$g^1{}_\tau$	$(9/8)[R^2{}_0\mu_H+(2P^2{}_0+R^2{}_0)\mu_C]$
$g^3{}_{\tau\tau}\binom{1}{0}$	$g^2{}_\tau$	$(9/8)(2R_0-P_0)P_0\mu_C$



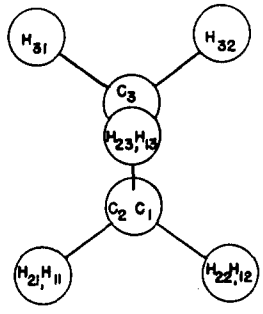


FIG. 2. Numbering of atoms in C_3H_8.

lowed by a $(\pm)$, would exhibit alternation of sign if the complete G matrix, rather than just the first row from each symmetrically equivalent set had been written out.

V. CONCLUSIONS

A few remarks on the limits of applicability of these formulas are necessary. In the first place, it remains to be seen whether the torsional type of coordinate introduced here will prove to be practical in the treatment of restricted rotation as a small vibration. This is not only a question of the magnitude of the potential barrier hindering the rotation and the quality of the harmonic approximation in the trough of the potential energy *versus* angle of torsion, but also of whether or not the vibrational potential function is reasonably diagonal in terms of this type of force constant. It should be mentioned at this point that such torsional frequencies as are known at present are usually known or inferred to be quite low by comparison with the bending and stretching frequencies, at least in the case of hydrocarbons. Taylor and Pitzer[10] have shown that an approximate treatment of such cases may advantageously be carried through in terms of the kinetic energy matrix (not its inverse).

From a purely kinematical point of view, the set of coordinates chosen here is inadequate for the treatment of such planar molecules as BF_3 or CH_2O which possess no chain of bonded atoms with a length of four atoms; when a structure similar to that of such molecules forms a part of a larger molecule, the same coordinate deficiency will remain. Another type of deficiency of the tables occurs when a part of the molecule contains a chain of 3 or more colinear atoms, since one or more dihedral angles become indeterminate. On the other hand, a large number of the G matrix elements for many cyclic molecules may be found in the tables, including, for example, all necessary in-plane interaction elements for benzene.

[10] W. J. Taylor and K. S. Pitzer, J. Research Nat. Bur. Stand. **38**, 1 (1947).