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Citation: [The Journal of Chemical Physics](#) **17**, 659 (1949); doi: 10.1063/1.1747353

View online: <http://dx.doi.org/10.1063/1.1747353>

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A General Method of Obtaining Molecular Symmetry Coordinates*

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(Received October 13, 1948)

A general method of obtaining molecular symmetry coordinates based on the algebra of group representation theory is described. The method is direct and involves no trial and error. It presupposes a knowledge of the irreducible representations of the molecular symmetry group rather than merely of their characters. The orthogonality properties of the symmetry coordinates are derived. As an example, the method is applied to boron trifluoride (D_{3h}), with the use of both internal and Cartesian coordinates.

INTRODUCTION

TO factor the secular equation for the normal vibration frequencies of symmetrical molecules, so-called symmetry coordinates are usually employed. These are coordinates that form the basis for a completely reduced representation of the molecular symmetry group. Each symmetry coordinate belongs to one of the irreducible representations of this group, i.e., to one of the symmetry species into which the normal modes of vibration may be divided. There must be as many independent symmetry coordinates belonging to each irreducible representation as there are normal vibrations belonging to it.

Symmetry coordinates were introduced by Brester¹ who first showed how symmetry can be utilized to classify molecular vibrations. Wigner² treated this problem with the aid of group theory. Rosenthal,³ Howard and Wilson,⁴ Manneback,⁵ Redlich and Tompa,⁶ and others,⁷ have developed methods of applying various kinds of symmetry coordinates to calculate normal vibration frequencies for symmetrical molecules.

At first the symmetry coordinates were formed as linear combinations of the $3n$ Cartesian coordinates that describe small displacements of the n atomic nuclei in the molecule. If $3n$ such symmetry coordinates are used, the complete secular equation will have six zero roots. These may be eliminated, and the secular equation reduced to the order $3n-6$, by the use of the momentum or Eckart conditions.⁸ Recently, Wilson⁹ has introduced symmetry coordinates constructed from $3n-6$ or more "internal" coordinates, such as changes in bond dis-

tances or bond angles. It can be proved that these symmetry coordinates satisfy the Eckart conditions.

Although several helpful rules have been given for obtaining various types of symmetry coordinates,¹⁰ no perfectly general mathematical procedure has been given, and except for the simplest molecules, the finding of symmetry coordinates has involved a considerable amount of trial and error. It is the purpose of the present paper to describe a general group-theoretical method for obtaining molecular symmetry coordinates. For non-degenerate irreducible representations, the method is identical with that given by Eyring, Walter, and Kimball¹¹ for obtaining wave functions belonging to a given representation.

DETERMINATION OF SYMMETRY COORDINATES

The method is based on the algebra of group representation theory.¹² It will not be necessary to state the theorems used in their general form, but we shall derive them in a special and somewhat modified form that is convenient and sufficiently general for our purpose.

Let the molecular symmetry group have the order h , and let R denote any one of the symmetry operations.

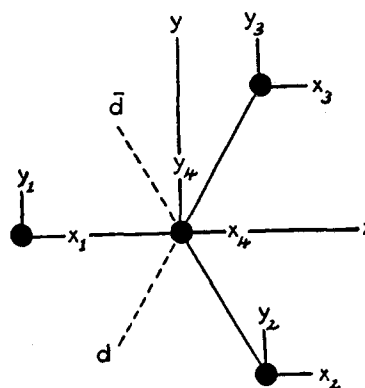


FIG. 1. Model (D_{3h}) of the boron trifluoride molecule and Cartesian coordinate system used.

* This work has been supported by Contract N7onr-398, Task Order I, with the ONR.

¹ C. J. Brester, *Kristallsymmetrie und Reststrahlen* (J. van Druten, Utrecht, 1923).

² E. Wigner, *Göttinger Nachrichten* (1930), p. 133.

³ J. E. Rosenthal, *Phys. Rev.* **45**, 538 (1934).

⁴ J. B. Howard and E. Bright Wilson, Jr., *J. Chem. Phys.* **2**, 630 (1934).

⁵ C. Manneback, *Calcul et identification des vibrations des molecules* (Editions E.D.K., Liege, 1934).

⁶ O. Redlich, *Zeits. f. Physik. Chem.* **B28**, 371 (1935); O. Redlich and H. Tompa, *J. Chem. Phys.* **5**, 529 (1937).

⁷ See in particular J. E. Rosenthal and G. M. Murphy, *Rev. Mod. Phys.* **8**, 317 (1936).

⁸ C. Eckart, *Phys. Rev.* **47**, 552 (1935).

⁹ E. Bright Wilson, Jr., *J. Chem. Phys.* **7**, 1047 (1939); **9**, 76 (1941).

¹⁰ See in particular, E. Bright Wilson, Jr., *J. Chem. Phys.* **9**, 76 (1941); T. Venkatarayudu, *Proc. Ind. Acad. Sci. A*, **17**, 50, 75 (1943); J. E. Kilpatrick, *J. Chem. Phys.* **16**, 749 (1948).

¹¹ H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, (John Wiley & Sons, Inc., New York, 1944), p. 189.

¹² See E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Friedrich Vieweg & Sohn, Braunschweig, 1931), Chapter XII.

TABLE I. Internal symmetry coordinates for BF_3 (D_{3h}).

Generating coordinate	Normalized symmetry coordinate
δ_1	$S(A_1') = 1/\sqrt{3}(\delta_1 + \delta_2 + \delta_3)$
γ	$S(A_2'') = \gamma$
δ_1	$S_{11}(E') = 1/(6)^{1/2}(2\delta_1 - \delta_2 - \delta_3)$
—	$S_{12}(E') = 1/\sqrt{2}(\delta_2 - \delta_3)$
α_{12}	$S_{21}(E') = 1/(6)^{1/2}(\alpha_{12} + \alpha_{23} - 2\alpha_{31})$
—	$S_{22}(E') = 1/\sqrt{2}(\alpha_{23} - \alpha_{12})$

Let D^i be an irreducible representation of dimension l_j . If the symmetry coordinates $S^{i_{k1}}, S^{i_{k2}}, \dots, S^{i_{kl_j}}$ transform according to the rule

$$RS^{i_{k\alpha}} = \sum_{\beta=1}^{l_j} S^{i_{k\beta}} D^i(R)_{\beta\alpha}, \quad (1)$$

they are said to belong to the irreducible representation D^i . The subscript k is used to differentiate this subset of symmetry coordinates from others belonging to the same irreducible representation. The symmetry coordinate $S^{i_{k\alpha}}$ is said to belong to the α 'th row of the irreducible representation D^i . This latter statement is meaningful only when the irreducible representation is completely given, rather than determined except for an arbitrary similarity transformation. In what follows we shall assume all of the irreducible representations of the molecular symmetry group to be completely determined. For convenience, we shall further assume that they have been chosen in such a manner that all of their matrices are real orthogonal.

The matrix elements of two irreducible representations D^i and $D^{i'}$ of the molecular symmetry group satisfy the fundamental relation

$$\sum_R D^i(R)_{\alpha\beta} D^{i'}(R)_{\alpha'\beta'} = (h/l_j) \delta_{jj'} \delta_{\alpha\alpha'} \delta_{\beta\beta'}, \quad (2)$$

where the sum is extended over all members of the group, i.e., over all symmetry operations, and where the Kronecker δ -symbol (e.g., $\delta_{jj'} = 1$ when $j = j'$, $\delta_{jj'} = 0$ when $j \neq j'$) is used on the right.

If we multiply Eq. (1) by $D^{i'}(R)_{\beta'\alpha'}$, sum over all members R of the group, and apply Eq. (2), the result is

$$\sum_R D^{i'}(R)_{\beta'\alpha'} RS^{i_{k\alpha}} = (h/l_j) \delta_{jj'} \delta_{\alpha\alpha'} S^{i_{k\beta'}}. \quad (3)$$

For $j' = j$, $\alpha' = \beta' = \alpha$, this reduces to

$$\sum_R D^i(R)_{\alpha\alpha} RS^{i_{k\alpha}} = (h/l_j) S^{i_{k\alpha}}. \quad (4)$$

On the other hand, for $j' = j$, $\alpha' = \alpha$, and $\beta' = \beta$, Eq. (3) becomes

$$\sum_R D^i(R)_{\beta\alpha} RS^{i_{k\alpha}} = (h/l_j) S^{i_{k\beta}}. \quad (5)$$

Thus, Eqs. (4) and (5) are necessary conditions that the quantities $S^{i_{k1}}, S^{i_{k2}}, \dots, S^{i_{kl_j}}$ belong to the irreducible representation D^i , or more particularly, that they transform under group operations according to Eq. (1). In Appendix I it is shown that Eq. (4) is also the sufficient condition that $S^{i_{k\alpha}}$ and its "partners" determined by Eq. (5) transform according to Eq. (1).

Thus, if a single symmetry coordinate $S^{i_{k\alpha}}$ satisfying Eq. (4) can be found, this coordinate, together with its $l_j - 1$ partners defined explicitly by Eq. (5), will form a subset of symmetry coordinates belonging to the irreducible representation D^i .

We shall now give a simple procedure for obtaining a symmetry coordinate satisfying Eq. (4). Let the (Cartesian, internal, or other) coordinates used to describe an arbitrary small distortion or displacement of the semi-rigid molecule be denoted by r_i . Any linear combination $L(r_i)$ of these coordinates can also be written as a linear function of a complete set of symmetry coordinates, i.e.,

$$L = \sum_{j'} \sum_k \sum_{\beta} C^{i'}_{k\beta} S^{i'}_{k\beta}, \quad (6)$$

where the $C^{i'}_{k\beta}$ are constants.

Now, if we operate on L with any member R of the molecular symmetry group, multiply by $D^i(R)_{\alpha\alpha}$, sum over all members of the group, and apply Eqs. (1) and (2), we obtain:

$$\begin{aligned} \sum_R D^i(R)_{\alpha\alpha} RL &= \sum_{j'} \sum_k \sum_{\beta} \sum_R C^{i'}_{k\beta} D^i(R)_{\alpha\alpha} RS^{i'}_{k\beta} \\ &= \sum_{j'} \sum_k \sum_{\beta} C^{i'}_{k\beta} (h/l_j) \delta_{jj'} \delta_{\alpha\alpha} S^{i'}_{k\beta} \\ &= (h/l_j) \sum_k C^{i'}_{k\alpha} S^{i'}_{k\alpha}. \end{aligned} \quad (7)$$

Since $\sum C^{i'}_{k\alpha} S^{i'}_{k\alpha}$ is a linear combination of symmetry coordinates that satisfy Eq. (4), it will itself satisfy Eq. (4), and so will the left member of Eq. (7).

These results provide the following method for obtaining symmetry coordinates. Choose a linear function L_k of the coordinates r_i . Then the sum

$$S^{i_{k\alpha}} = (l_j/h) \sum_R D^i(R)_{\alpha\alpha} RL_k \quad (8)$$

will be a symmetry coordinate belonging to the α 'th row of the irreducible representation D^i , and its $l_j - 1$ partners will be given by

$$S^{i_{k\beta}} = (l_j/h) \sum_R D^i(R)_{\beta\alpha} RS^{i_{k\alpha}}. \quad (9)$$

As indicated by the subscript k , there are often more than one subset of symmetry coordinates belonging to a given irreducible representation. If a_j subsets of symmetry coordinates belong to the irreducible representation D^i , it will be necessary to choose a_j linear combinations $L_k(r_i)$ such that application of Eq. (8) to each of them yields a_j symmetry coordinates $S^{i_{k\alpha}} (k=1, 2, \dots, a_j)$ that are linearly independent in terms of the r_i . The partners of each of these are then obtained by Eq. (9).

That it is possible in this manner to obtain the requisite number of independent¹³ sets of symmetry co-

¹³ The term "independent" as applied to symmetry coordinates is ambiguous. It may mean linearly independent in terms of all of the coordinates r_i , irrespective of whether or not their number exceeds the degrees of freedom of the molecular motions they are intended to describe; it may denote linear independence in terms of $3n$ coordinates required to describe any arbitrary motion of the atoms in a molecule; or it may mean linear independence in terms of a set of $3n - 6$ coordinates describing an arbitrary distortion of a (non-linear) semi-rigid molecule. Wherever not explicitly stated in the present paper, the meaning should be clear from the context.

ordinates belonging to each irreducible representation is proved in Appendix II. In fact, it is shown there that it is sufficient to put each of the linear functions $L_k(r_i)$ appearing in Eq. (8) equal to a single one of the coordinates r_i .

ORTHOGONALITY PROPERTIES OF SYMMETRY COORDINATES

Let two symmetry coordinates, expressed in terms of the coordinates r_i , be

$$S^i_{k\alpha} = \sum_i u^i_{k\alpha} r_i \quad \text{and} \quad S^{j'}_{k'\alpha'} = \sum_i u^{j'}_{k'\alpha'} r_i.$$

The scalar product of these symmetry coordinates in the space of the r_i is defined as

$$(S^i_{k\alpha} \cdot S^{j'}_{k'\alpha'}) = \sum_i u^i_{k\alpha} u^{j'}_{k'\alpha'}.$$

If this quantity vanishes, the symmetry coordinates are said to be orthogonal in the space of the original coordinates r_i . If $(S^i_{k\alpha} \cdot S^i_{k\alpha}) = 1$, $S^i_{k\alpha}$ is said to be normalized to unity.

Any two symmetry coordinates belonging to different irreducible representations or to different rows of the same irreducible representation are orthogonal in the r_i -space. To prove this, we first observe that

$$(S^i_{k\alpha} \cdot S^{j'}_{k'\alpha'}) = (RS^i_{k\alpha} \cdot RS^{j'}_{k'\alpha'}), \quad (10)$$

since the operation R is orthogonal. Applying Eq. (1) to Eq. (10), we get

$$(S^i_{k\alpha} \cdot S^{j'}_{k'\alpha'}) = (\sum_{\beta} S^i_{k\beta} D^j(R)_{\beta\alpha} \cdot \sum_{\beta'} S^{j'}_{k'\beta'} D^{j'}(R)_{\beta'\alpha'}) \\ = \sum_{\beta} \sum_{\beta'} D^j(R)_{\beta\alpha} D^{j'}(R)_{\beta'\alpha'} (S^i_{k\beta} \cdot S^{j'}_{k'\beta'}).$$

Summation of this over all members of the group and application of Eq. (2) give

$$h(S^i_{k\alpha} \cdot S^{j'}_{k'\alpha'}) = \sum_{\beta} \sum_{\beta'} (h/l_j) \delta_{jj'} \delta_{\alpha\alpha'} \delta_{\beta\beta'} (S^i_{k\beta} \cdot S^{j'}_{k'\beta'}) \\ = (h/l_j) \delta_{jj'} \delta_{\alpha\alpha'} \sum_{\beta} (S^i_{k\beta} \cdot S^{j'}_{k'\beta'}), \quad (11)$$

from which the theorem follows.

On the other hand, two symmetry coordinates belonging to the same row of a given irreducible representation, but to different subsets, will not always be orthogonal when determined by the method described in the preceding section. However, it is not difficult to make them orthogonal, and this will usually be a convenience. Let $S^i_{k\alpha}$ and $S^{i'}_{k'\alpha}$ be two such coordinates. According to Eq. (11)

$$(S^i_{k\alpha} \cdot S^{i'}_{k'\alpha}) = (1/l_j) \sum_{\beta=1}^{l_j} (S^i_{k\beta} \cdot S^{i'}_{k'\beta}).$$

The right member is independent of α ; hence

$$(S^i_{k1} \cdot S^{i'}_{k'1}) = (S^i_{k2} \cdot S^{i'}_{k'2}) = \dots = (S^i_{kl_j} \cdot S^{i'}_{k'l_j}). \quad (12)$$

Thus, if one of these scalar products vanishes, all of them will vanish.

The following procedure was therefore adopted. Whenever the symmetry coordinates belonging to the first row of a given irreducible representation, as obtained by means of Eq. (8), are not all mutually

TABLE II. Set of $3n$ orthonormal symmetry coordinates for boron trifluoride (D_{3h}).

Generating coordinate	Normalized symmetry coordinate
x_1	$S(A_1') = 12^{-1/2}(2x_1 - x_2 + \sqrt{3}y_2 - x_3 - \sqrt{3}y_3)$
y_1	$S(A_2') = 12^{-1/2}(2y_1 - \sqrt{3}x_2 - y_2 + \sqrt{3}x_3 - y_3)$
z_1	$S_1(A_2'') = 3^{-1/2}(z_1 + z_2 + z_3)$
z_4	$S_2(A_2'') = z_4$
x_1	$S_{11}(E') = 24^{-1/2}(4x_1 + x_2 - \sqrt{3}y_2 + x_3 + \sqrt{3}y_3)$
—	$S_{12}(E') = 24^{-1/2}(-\sqrt{3}x_2 + 3y_2 + \sqrt{3}x_3 + 3y_3)$
(x_2)	$S_{21}(E') = 24^{-1/2}(3x_2 + \sqrt{3}y_2 + 3x_3 - \sqrt{3}y_3)$
—	$S_{22}(E') = 24^{-1/2}(4y_1 + \sqrt{3}x_2 + y_2 - \sqrt{3}x_3 + y_3)$
x_4	$S_{31}(E') = x_4$
—	$S_{32}(E') = y_4$
z_2	$S_{11}(E'') = 2^{-1/2}(z_2 - z_3)$
—	$S_{12}(E'') = 6^{-1/2}(-2z_1 + z_2 + z_3)$

orthogonal, mutually orthogonal linear combinations of them are formed by Schmidt's orthogonalization procedure.¹⁴ These linear combinations, which are also symmetry coordinates belonging to the first row of the irreducible representation in question, are then used instead of the original symmetry coordinates, and their partners are determined by Eq. (9).

EXAMPLE: BORON TRIFLUORIDE (D_{3h})

This example has been chosen for its simplicity. A more complex example would bring out better the power of the method. We shall first use internal coordinates chosen as follows: $\delta_1, \delta_2, \delta_3$ denote infinitesimal increments in the three BF distances, $\alpha_{12}, \alpha_{23}, \alpha_{31}$ denote small changes in the three F-B-F angles, and γ denotes a small out-of-plane displacement of the boron atom. Of the $3n - 6 = 6$ normal vibrations, one belongs to each of the irreducible representations A_1' and A_2'' , and two sets of doubly degenerate vibrations belong to the two-dimensional representation E' . The characters for the one-dimensional irreducible representations of D_{3h} ¹⁵ are identical with the matrices of these representations. The matrices for the representation E' were chosen as the transformation matrices for translations T_x, T_y in the plane of the molecule.

Using as "generating coordinates" to be substituted in Eq. (8) the internal coordinates listed in the first column of Table I, we obtain from Eqs. (8) and (9) the symmetry coordinates listed in the second column. Since $S_{11}(E')$ and $S_{21}(E')$ are orthogonal, there is no need for any orthogonalization procedure. When α_{12} is used as "generating coordinate," a symmetry coordinate $\alpha_{12} + \alpha_{23} + \alpha_{31}$ belonging to A_1' is obtained. However, this vanishes, since the sum of the three F-B-F angles is 360° . Thus, the redundancy in the choice of internal coordinates has been taken into account, and Table I

¹⁴ See for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 298; or G. Birkhoff and S. MacLane, *A Survey of Modern Algebra* (The Macmillan Company, New York, 1941), p. 187.

¹⁵ Character tables may be found in reference 7 or in G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, (D. Van Nostrand Company, Inc., New York, 1945).

TABLE III. Set of $3n-6$ orthonormal symmetry coordinates for boron trifluoride (D_{3h}) orthogonal to translations and rotations

$\tilde{S}(A_1') = 12^{-1/2}(2x_1 - x_2 + \sqrt{3}y_2 - x_3 - \sqrt{3}y_3)$
$\tilde{S}(A_2'') = (3m^2 + M^2)^{-1/2}[M(z_1 + z_2 + z_3) - 3mz_4]$
$\tilde{S}_{11}(E') = (9m^2 + 3M^2)^{-1/2}[M(x_1 + x_2 + x_3) - 3mx_4]$
$\tilde{S}_{12}(E') = (9m^2 + 3M^2)^{-1/2}[M(y_1 + y_2 + y_3) - 3my_4]$
$\tilde{S}_{21}(E') = 12^{-1/2}(2x_1 - x_2 - \sqrt{3}y_2 - x_3 + \sqrt{3}y_3)$
$\tilde{S}_{22}(E') = 12^{-1/2}(-2y_1 - \sqrt{3}x_2 + y_2 + \sqrt{3}x_3 + y_3)$

includes the proper number of independent symmetry coordinates.

We shall now solve the same problem using the Cartesian coordinates defined in Fig. 1. x_i , y_i , z_i are the components of the infinitesimal displacement of the i 'th atom from its equilibrium position. Application of the general procedure yields the set of twelve symmetry coordinates listed in Table II. The "generating coordinates" used are given in the first column. In the case of $S_{21}(E')$, the generating coordinate is put in parenthesis; for when this coordinate is used, an expression is obtained for $S_{21}(E')$ which is not orthogonal to $S_{11}(E')$. Orthogonalization by Schmidt's method gives the expression for $S_{21}(E')$ listed in the table.

The Eckart conditions lead to the following relations between the symmetry coordinates

$$\begin{aligned} S(A_2') &= 0, \\ \sqrt{3}mS_1(A_2'') + MS_2(A_2'') &= 0, \\ (3/2)^{1/2}m[S_{11}(E') + S_{21}(E')] + MS_{31}(E') &= 0, \\ (3/2)^{1/2}m[S_{12}(E') + S_{22}(E')] + MS_{32}(E') &= 0, \\ S_{11}(E'') &= 0, \\ S_{12}(E'') &= 0, \end{aligned} \quad (13)$$

Here M is the mass of the boron atom and m , the mass of a fluorine atom. By means of these equations it is easy to eliminate six symmetry coordinates from the potential and kinetic energy functions.

If it is desired to choose T_x , T_y , \dots , R_z as members of a new set of orthogonal symmetry coordinates, this can be done as follows. The rotations are already present among the symmetry coordinates listed in Table II. In fact, $R_z = S_{11}(E'')$, $R_y = -S_{12}(E'')$, and $R_x = S(A_2')$. The translation T_z belongs to A_2'' . If $S_1(A_2'')$ and $S_2(A_2'')$ are subjected to a transformation defined by the matrix

$$\begin{pmatrix} \sqrt{3}\mu m & \mu M \\ \mu M & -\sqrt{3}\mu m \end{pmatrix}, \quad \text{where } \mu = (3m^2 + M^2)^{-1/2},$$

one of the new symmetry coordinates will be T_z . Since this matrix is orthogonal, the other symmetry coordinate will be orthogonal to T_z and will be normalized.

The translations T_x and T_y belong to E' . If $S_{11}(E')$, $S_{21}(E')$, and $S_{31}(E')$, and also $S_{12}(E')$, $S_{22}(E')$, and

$S_{32}(E')$, are transformed by the matrix

$$\begin{pmatrix} (3/2)^{1/2}\mu m & (3/2)^{1/2}\mu m & \mu M \\ -(1/2)^{1/2}\mu M & -(1/2)^{1/2}\mu M & \sqrt{3}\mu m \\ (1/2)^{1/2} & -(1/2)^{1/2} & 0 \end{pmatrix}$$

T_x and T_y will appear as the first coordinate of each set. This is assured by the choice of the first row of the matrix. The other rows are chosen so as to make the matrix orthogonal, thereby assuring that the other four symmetry coordinates form two orthonormal subsets orthogonal to T_x and T_y .

The six symmetry coordinates obtained in this manner are listed in Table III. Together with the translations and rotations they form a complete orthonormal set. They are equivalent to the symmetry coordinates obtained by Silver and Schaffer from mass-reduced Cartesian coordinates.¹⁶

APPENDIX I

By means of well-known theorems of group theory¹⁷ we find

$$\begin{aligned} \sum_P D^i(P)_{\alpha\gamma} P S^i_{k\gamma} &= \sum_P D^i(R^{-1}P)_{\alpha\gamma} R^{-1} P S^i_{k\gamma} \\ &= \sum_P \sum_\beta D^i(R^{-1})_{\alpha\beta} D^i(P)_{\beta\gamma} R^{-1} P S^i_{k\gamma} \\ &= R^{-1} \sum_\beta D^i(R)_{\beta\alpha} \sum_P D^i(P)_{\beta\gamma} P S^i_{k\gamma}, \end{aligned}$$

whence

$$R \sum_P D^i(P)_{\alpha\gamma} P S^i_{k\gamma} = \sum_\beta D^i(R)_{\beta\alpha} \sum_P D^i(P)_{\beta\gamma} P S^i_{k\gamma}.$$

Application of Eqs. (4) and (5) to this equation gives

$$R S^i_{k\alpha} = \sum_\beta S^i_{k\beta} D^i(R)_{\beta\alpha},$$

which is Eq. (1). Thus a function $S^i_{k\alpha}$ satisfying Eq. (4), together with its partners determined by Eq. (5), will transform according to Eq. (1).

APPENDIX II

A complete set of independent symmetry coordinates is known to exist. If a_i subsets of symmetry coordinates belong to the irreducible representation D^i , we have a_i equations of the form

$$S^i_{k\alpha} = (l_i/h) \sum_R D^i(R)_{\alpha\alpha} R S^i_{k\alpha}. \quad (14)$$

The symmetry coordinates can be expressed in terms of the internal coordinates r_i as follows

$$S^i_{k\alpha} = \sum_i b^i_{ki} r_i,$$

where the b^i_{ki} are constants. If this is substituted into Eq. (14) the following set of a_i equations are obtained.

$$\begin{aligned} \sum_i b^i_{1i} \{ (l_i/h) \sum_R D^i(R)_{\alpha\alpha} R r_i \} &= S^i_{1\alpha} \\ \sum_i b^i_{2i} \{ (l_i/h) \sum_R D^i(R)_{\alpha\alpha} R r_i \} &= S^i_{2\alpha} \\ \sum_i b^i_{a_i i} \{ (l_i/h) \sum_R D^i(R)_{\alpha\alpha} R r_i \} &= S^i_{a_i \alpha}. \end{aligned}$$

At least a_i of the quantities in the brackets must be linearly independent, for otherwise there could not be a_i independent symmetry coordinates, as there must be. But all of the expressions in the brackets are of the form of Eq. (8) with L_k put equal to an internal coordinate r_i . Thus, it is possible to find a_i independent symmetry coordinates by means of Eq. (8). Moreover, it is always sufficient to put L_k in Eq. (8) equal to an internal coordinate r_i .

¹⁶ S. Silver and W. H. Schaffer, J. Chem. Phys. **9**, 599 (1941).

¹⁷ See reference 12, Chapters VII and IX.