Symmetry Matrices in Normal Coordinate Analysis

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from a thermal theory. The correlation between V_b and R obtained here is quite as satisfactory as that between V_b and p_H pointed out by Tanford and Pease.[1] Moreover, the correlation is also satisfactory for the other combinations of E and H' (rather better for E equal to 50,000 and T_e about 1000°K and for both values of T_e when E is 100,000; rather less good for both values of T_e (i.e., H') when E is 30,000). The interpretation is therefore hardly at all dependent on the exact values assumed for E and H'.

There is one point that may be added here. The line in Fig. 1 can reasonably be extrapolated to pass through $V_b=0$, $R=1$, which is to be expected theoretically on the thermal theory since no flame could propagate if T_f were less than T_e, according to this theory.

Our general conclusion, therefore, is that the results of Jahn do not enable us to decide whether thermal conduction or radical diffusion is more important in the propagation of carbon monoxide-oxygen flames. We are, at the moment, carrying out determinations of burning velocities which we hope will help in deciding the relative importance of these two factors in the propagation of certain flames.

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Symmetry Matrices in Normal Coordinate Analysis

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A general symmetry matrix, U_n, has been derived which may be used to combine n equivalent coordinates in a molecule having the symmetry of any cyclic or dihedral point group of multiplicity n. The direct products $U_2 \times U_n$ and $U_2 \times U_2 \times U_n$ may be used in the cases of $2n$ and $4n$ equivalent coordinates. The symmetry type of each row of the symmetry matrices used has been determined.

THE secular equation necessary for a normal coordinate treatment of the vibrations of a molecule with N degrees of freedom may be represented by a polynomial equation of degree N, a determinantal equation of degree N or a matrix of order N. The superficial form of the secular equation varies with the choice of coordinates but the roots (which are simply related to the vibrational frequencies of the molecule) are independent of this choice. Wilson[1] has given a very convenient method by which the secular equation can be set up in terms of any given set of coordinates.

A set of valence-bond and valence-angle increases is usually not the best choice of coordinates that can be made. The use instead of certain linear combinations of these elementary coordinates may lead to a considerably factored form of the secular equation. Just which combinations, if any, are suitable is dependent on the symmetry of the molecule. This factorization decreases considerably the number of terms that need be calculated and replaces one equation of high degree with several of lower degree.

The choice of these linear combinations of elementary valence coordinates (symmetry coordinates) has frequently been left to the experience and intuition of the worker. Wilson[1] has given some rules which must be satisfied by a set of symmetry coordinates. Venkatarayudu[2] has given a method for determining symmetry coordinates that is related to the method given in this paper. Eyring, Walter and Kimball[3] have given a method which was derived for use with wave functions but may be applied to the problem of symmetry coordinates. In this method it is necessary to investigate the action of each of the symmetry operations of the point group appro-

[1] E. Bright Wilson, Jr., J. Chem. Phys. 9, 97 (1941).

[2] T. Venkatarayudu, Proc. Ind. Acad. Sci. **17a**, 50 (1943).

[3] H. Eyring, J. Walter and G. Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York), Eq. (10.47), p. 189.

TABLE I. General character table for C_{nv} and D_n.

C_{nv}* / D_n	C_n^m / C_n^m	(*Fused into one class for n odd.*) $(n/2)\sigma_v$ / $(n/2)C_2$	$(n/2)\sigma_v'$ / $(n/2)C_2'$
A_1	1	1	1
A_2	1	−1	−1
E_1	$2\cos m\omega$	0	0
E_2	$2\cos 2m\omega$	0	0
...	...	...	...
E_p	$2\cos pm\omega$	0	0
B_1**	$(-1)^m$	1	−1
B_2**	$(-1)^m$	−1	1

* The first column of characters represents the characters for n elements. $m=1, 2, \ldots n$. $p=(n-2)/2$ for n even, $(n-1)/2$ for n odd. $\omega=2\pi/n$ radiians. The two A representations may be regarded as a degenerate E_0; the two B representations as $E_{\frac{1}{2}n}$ (when $\frac{1}{2}n$ is integral).
** Drop out for n odd.

priate to the system under consideration upon the elementary valence coordinates. Glockler[4] has used a similar method for determining nondegenerate symmetry coordinates.

It is the purpose of this paper to discuss a method which, in very many cases, leads immediately to a suitable set of symmetry coordinates. An $n\times n$ matrix (U_n) is given as a function of n. U_n may be used to combine n equivalent coordinates in any of the common cyclic or dihedral groups of order n. The first row of U_n always gives an A symmetry coordinate, the next two an E_1 doubly degenerate pair, the next two an E_2 pair, etc., and the last row (present only when n is even) a B coordinate. Similarly, the direct products $U_2\times U_n$ and $U_2\times U_2\times U_n$ may be used to combine $2n$ and $4n$, respectively, equivalent coordinates in a group of multiplicity n (C_{nv}, D_n, D_{nh}, etc.). In the three cases just mentioned (n, $2n$, and $4n$ equivalent coordinates), the rows of the symmetry matrix occur in one, two and four sets of n rows. The auxiliary superscripts ($'$ and $''$) are always the same for every symmetry coordinate in any one set of n.

Although the proofs of these properties are somewhat lengthy, the symmetry matrices here defined may be used immediately in any appropriate problem.

EQUIVALENT COORDINATES

A molecule is said to have the symmetry G if the permutations of the sets of equivalent atoms in the molecule form a representation of the point group G. Certain bonds and certain angles will also be permuted among themselves by the action of a given permutation P of G. A set of bonds or a set of angles which are completely permuted among themselves by the elements P of G are called a set of equivalent bonds or angles, respectively. Internal coordinates, however, are increases in bond lengths and valence angles. It is possible to associate a set of equivalent points, not necessarily coinciding with any set of equivalent atoms, with each set of equivalent bonds or angles. These sets are useful in calculating, for example, how many C−H stretching vibrations there are in a given symmetry type in a given molecule. However, for our present purpose, we need a set of vectors to associate with each set of equivalent coordinates (changes in sets of equivalent bonds or angles). For a given set of equivalent bond length changes, a unit vector may be associated with each bond, with some uniform convention as to direction. For a set of equivalent angles changes, the vectors may be oriented perpendicular to the planes of the angles, also with a uniform convention as to direction. A similar convention may be devised for other types of deformation, such as torsion.

It does not follow that a given permutation P (of G) will merely permute the vectors associated with a set of equivalent coordinates among themselves. There may be, in addition, changes of sign. That is, if a given P moves the atoms which define vector $\mathbf{R}_i$ to the position formerly occupied by the atoms which define $\mathbf{R}_j$, we say $PR_i=R_j$. On the other hand, if $\mathbf{R}_i$ moves to the former position of $\mathbf{R}_j$ but is oriented in the opposite direction, we have $PR_i=-R_j$.

We can readily express the whole family of such equations in matrix notation. Let R be the column matrix with elements R_i and R^* be the column matrix with the elements PR_i. We then have

$$R^*=PR. \tag{1}$$

There will be a square matrix P for each element of G and together they form a reducible representation of G. In the case of the cyclic and dihedral groups, the elements of the matrices P consist of zero or plus or minus unity. There will be not more than one unity in any one row or column.

[4] G. Glockler, Rev. Mod. Phys. **15**, 111 (1943).

It is informative to set up such matrices in a few actual cases but we shall show that it is not usually necessary to do so in order to choose suitable symmetry coordinates.

The matrices P will always be blocked out along the main diagonal at least to the extent necessary to separate the sets of equivalent coordinates. Corresponding diagonal minors from each P also are reducible representations of G and frequently it is convenient to treat them separately. A representation of G consisting of one or more diagonal minors of the complete P's will be designated P_q, where the subscript will indicate the coordinates involved, except when no confusion is likely to arise by the omission of the subscript.

Let U be some square matrix that when multiplied on R, generates a new set of coordinates $\mathfrak{R}$:

$$\mathfrak{R} = UR. \tag{2}$$

If we require that U be ortho-normal, in place of Eq. (1) we have

$$\mathfrak{R}^* = (UPU')\mathfrak{R} \tag{3}$$

Eq. (3) obviously can also be written in terms of $\mathfrak{R}_q$ and P_q.

Now if a matrix U can be found that will transform the reducible representations P to the irreducible representations of G, that matrix U consists of just the symmetry coefficients we need. How this can be done in many cases will be shown in the following sections.

POINT GROUPS C_{nv} AND D_n

These two families may be treated together since, for any particular value of n, C_{nv} is isomorphic with D_n. Both have $2n$ elements: n are proper rotations about the main symmetry axis (C_n); the remaining n are dihedral elements.

The first n elements may be represented by C_n^m, where m takes the values 1, 2, 3, $\cdots n$. C_n^m is the mth power of C_n and represents a rotation of $m(2\pi/n)$ radians. The way in which these elements separate into classes is not important for our present purposes.

The n dihedral elements consist of reflections through n vertical planes (σ_v) in the case of C_{nv} and of rotations about n dihedral twofold axes (C_2) in the case of D_n. In both cases these n elements fall into a single class when n is odd but divide into two classes ($n/2$ elements to each) when n is even.

The characters of the irreducible representations of both of these groups are given in a condensed notation in Table I.

It is now time to introduce a matrix which will be the basis for all of our symmetry combinations. Let $\omega = 2\pi/n$, where n is some integer. Write the following array of terms:

cos0	cos0	cos0	cos0	
sin0	sin0	sin0	sin0	
cos0	cosω	cos2ω	cos3ω	$\cdots$
sin0	sinω	sin2ω	sin3ω	
cos0	cos2ω	cos4ω	cos6ω	
sin0	sin2ω	sin4ω	sin6ω	
$\cdots$	$\cdots$	$\cdots$	$\cdots$	

After n columns the terms will repeat; consequently retain only the first n columns. Cross out all rows consisting wholly of zeros and retain only the first n rows which remain. This square array we will call the matrix V_n. The first row will always have $+1$ for every element and will be followed, according to whether n is even or odd, by $(n-2)/2$ or $(n-1)/2$ pairs of cosine-sine rows. If n is even, there will be a final row consisting alternatingly of $+1$ and -1. We will refer to the first row and the last row (when n is even) as odd rows.

V_n is normalized by the factor $(1/n)^{\frac{1}{2}}$ for the odd rows and by $(2/n)^{\frac{1}{2}}$ for each of the other rows. A matrix N_n that will normalize V_n by premultiplication is diagonal and has for elements $(1/n)^{\frac{1}{2}}$, followed by $(2/n)^{\frac{1}{2}}$ for each row of the cosine-sine row pairs. If n is even, there will be a final element $(1/n)^{\frac{1}{2}}$. The normalized form of V_n we will call U_n:

$$U_n = N_n V_n. \tag{4}$$

The preceding discussion is illustrated by the two examples, $n=3$ and $n=6$:*

* A number of special cases of U_n have been used before. U_2, U_3, U_4* and U_6 are well known (although not always written in the order given here). U_5 has been used in a treatment of cyclopentane (Kilpatrick, Pitzer and Spitzer, J. Am. Chem. Soc. 69, 2483 (1947)).

$$V_3=\begin{bmatrix}1 & 1 & 1\\ 1 & \cos 2\pi/3 & \cos 4\pi/3\\ 0 & \sin 2\pi/3 & \sin 4\pi/3\end{bmatrix}=\begin{bmatrix}1 & 1 & 1\\ 1 & -1/2 & -1/2\\ 0 & (3/4)^{\frac{1}{2}} & -(3/4)^{\frac{1}{2}}\end{bmatrix}, \tag{5}$$

$$U_3=\begin{bmatrix}(1/3)^{\frac{1}{2}} & 0 & 0\\ 0 & (2/3)^{\frac{1}{2}} & 0\\ 0 & 0 & (2/3)^{\frac{1}{2}}\end{bmatrix}\begin{bmatrix}1 & 1 & 1\\ 1 & -1/2 & -1/2\\ 0 & (3/4)^{\frac{1}{2}} & -(3/4)^{\frac{1}{2}}\end{bmatrix}=\begin{bmatrix}(1/3)^{\frac{1}{2}} & (1/3)^{\frac{1}{2}} & (1/3)^{\frac{1}{2}}\\ (2/3)^{\frac{1}{2}} & -(1/6)^{\frac{1}{2}} & -(1/6)^{\frac{1}{2}}\\ 0 & (1/2)^{\frac{1}{2}} & -(1/2)^{\frac{1}{2}}\end{bmatrix}, \tag{6}$$

$$V_6=\begin{bmatrix}1 & 1 & 1 & 1 & 1 & 1\\ 1 & \cos 2\pi/6 & \cos 4\pi/6 & \cos 6\pi/6 & \cos 8\pi/6 & \cos 10\pi/6\\ 0 & \sin 2\pi/6 & \sin 4\pi/6 & \sin 6\pi/6 & \sin 8\pi/6 & \sin 10\pi/6\\ 1 & \cos 4\pi/6 & \cos 8\pi/6 & \cos 12\pi/6 & \cos 16\pi/6 & \cos 20\pi/6\\ 0 & \sin 4\pi/6 & \sin 8\pi/6 & \sin 12\pi/6 & \sin 16\pi/6 & \sin 20\pi/6\\ 1 & -1 & 1 & -1 & 1 & -1\end{bmatrix}, \tag{7}$$

$$U_6=\begin{bmatrix}(1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}}\\ (1/3)^{\frac{1}{2}} & 1/2(1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}} & -(1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}} & 1/2(1/3)^{\frac{1}{2}}\\ 0 & 1/2 & 1/2 & 0 & -1/2 & -1/2\\ (1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}} & (1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}} & -1/2(1/3)^{\frac{1}{2}}\\ 0 & 1/2 & -1/2 & 0 & 1/2 & -1/2\\ (1/6)^{\frac{1}{2}} & -(1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & -(1/6)^{\frac{1}{2}} & (1/6)^{\frac{1}{2}} & -(1/6)^{\frac{1}{2}}\end{bmatrix}. \tag{8}$$

U_n is readily seen to be orthonormal from the trigonometric identities of Appendix I. We shall now show how it may be used as a symmetry matrix.

Case 1. n equivalent coordinates

The coordinates should be numbered and oriented so that the rotation C_n^m merely permutes the several R_i cyclically: $C_n^m R_i = R_{i+m}$. For example, if $n=5$, $m=2$:

$$\begin{bmatrix}0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0\end{bmatrix}\begin{bmatrix}R_1\\ R_2\\ R_3\\ R_4\\ R_5\end{bmatrix}=\begin{bmatrix}R_4\\ R_5\\ R_1\\ R_2\\ R_3\end{bmatrix}. \tag{9}$$

The elements of P for C_n^m are given by

$$P_{ij}=\delta_{i,\,j+m}. \tag{10}$$

We are using the convention that subscripts i, $i\pm n$, $i\pm 2n$, etc., are equivalent.

Let A be defined by

$$A=U_nPU_n'=N_nV_nPV_n'N_n' =N_n^2V_nPV_n'. \tag{11}$$

We shall prove that

$$A=\Gamma=(\Gamma_1+\Gamma_2+\Gamma_3+\cdots) \tag{12}$$

where the right hand member is the direct sum of the irreducible representations of the group G, i.e., a matrix composed of square blocks along its main diagonal and with each block an irreducible representation of G.

On expanding Eq. (6) we have

$$\begin{aligned}(N^{-2}A)_{ij}&=\sum_r\sum_s V_{ir}P_{rs}V_{sj}\\ &=\sum_r\sum_s V_{ir}V_{js}\delta_{r,\,s+m}\\ &=\sum_{r=1}^{n}V_{i,\,r}V_{j,\,r-m}.\end{aligned} \tag{13}$$

The elements A_{11} and (if n is even) A_{nn} are readily evaluated. They are

$$A_{11}=1,\quad A_{nn}=(-1)^m \text{ (if } n \text{ is even)}. \tag{14}$$

The general form of the cosine-sine elements of V may be written as

$$V_{i,\,r}=\begin{Bmatrix}\cos(i/2)(r-1)\omega\\ \sin((i-1)/2)(r-1)\omega\end{Bmatrix}, \tag{15}$$

$$\text{according to } i\begin{Bmatrix}\text{even}\\ \text{odd}\end{Bmatrix}.$$

Therefore for the as yet undetermined elements of A,

$$A_{ij}=-\frac{2}{n}\sum_{r=1}^{n}\begin{Bmatrix}\cos(i/2)(r-1)\omega\\ \sin((i-1)/2)(r-1)\omega\end{Bmatrix}\times\begin{Bmatrix}\cos(i/2)(r-m-1)\omega\\ \sin((j-1)/2)(r-m-1)\omega\end{Bmatrix}$$
$$=-\frac{2}{n}\sum_{r=1}^{n}\begin{Bmatrix}\cos(i/2)r\omega\\ \sin((i-1)/2)r\omega\end{Bmatrix}\times\begin{Bmatrix}\cos(j/2)(r-m)\omega\\ \sin((j-1)/2)(r-m)\omega\end{Bmatrix} \tag{16}$$

where again the upper or lower term is to be used according to whether i or j, as the case may be, is even or odd.

When Eq. (11) is reduced by means of the identities of Appendix I, we are able to write:

$$A=\begin{bmatrix}1 & 0 & 0 & 0 & 0 & \\ 0 & \cos m\omega & -\sin m\omega & 0 & 0 & \\ 0 & \sin m\omega & \cos m\omega & 0 & 0 & \cdots\\ 0 & 0 & 0 & \cos 2m\omega & -\sin 2m\omega & \\ 0 & 0 & 0 & \sin 2m\omega & \cos 2m\omega & \\ 0 & 0 & 0 & 0 & 0 & \\ & & & \cdots & & \end{bmatrix}. \tag{17}$$

If n is even, the final diagonal term is $(-1)^m$.

This matrix is composed of the irreducible representations of C_{nv} or D_n for the elements C_n^m. The traces of each of the diagonal blocks correspond, in order, to the characters for C_n^m of Table I.

In a very similar fashion it can be shown that, for any of the dihedral elements, A is blocked off at least as much as in Eq. (17) and that the traces are as follows: for the first and last (if n is even) elements, corresponding to the odd rows of U, $+1$ or -1; for each of the cosine-sine row pairs of U, zero.

We have now established the following result: U_n is a suitable symmetry matrix for combining n equivalent coordinates in molecules of symmetry C_{nv} or D_n. The first row pair is identified with E_1, the second with E_2, and so on to E_p. The first row of U_n is A_1 or A_2 and the final odd row, if it occurs, B_1 or B_2. This final identification of the odd rows is probably most easily made by inspection.

Case 2. $2n$ equivalent coordinates

It will always be found that a set of $2n$ equivalent coordinates can be resolved into two sets of n each and into n sets of 2 each. They can be numbered according to two conventions, (1), number the first set of n cyclically from 1 to n and the second set from $n+1$ to $2n$, with the ith coordinate of the first set paired with its mate, the $n+i$th of the second set, (2), assign odd index numbers to the first set and even numbers to the second, using a similar cyclic convention.

With index numbers assigned by the first convention, a suitable symmetry matrix is the direct product[5] of U_2 and U_n:

$$U_2\times U_n=\begin{bmatrix}(1/2)^{\frac{1}{2}}U_n, & (1/2)^{\frac{1}{2}}U_n\\ (1/2)^{\frac{1}{2}}U_n, & -(1/2)^{\frac{1}{2}}U_n\end{bmatrix}. \tag{18}$$

There will now be two rows corresponding to each row of U_n. Following the argument of case 1, we see that rows 1 and $n+1$ will correspond to A-modes (one will be A_1 and the other A_2) and that rows n and $2n$ (if there is a final odd row in U_n) will correspond to B_1 or B_2. Similarly, the two pairs of rows formed from the ith cosine-sine pair of U_n will both correspond to E_i.

This procedure corresponds to taking n-fold combinations of the two sets of n coordinates and then taking symmetric and antisymmetric combinations of these combinations. The second numbering convention would require the opposite direct product, U_n and U_2, and corresponds to first taking symmetric-antisymmetric combinations, followed by n-fold combinations of each type. The two differ only in the order of the

[5] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys., 8, 317 (1936).

TABLE II. Condensed character tables for D_{nh}.

D_{nh}, n odd ($p=(n-1)/2$)	C_n^m	nC_2	S_n^m	$n\sigma_v$
A_1'	1	1	1	1
A_2'	1	−1	1	−1
E_1'	$2\cos m\omega$	0	$2\cos m\omega$	0
...	...	...	...	...
E_p'	$2\cos pm\omega$	0	$2\cos pm\omega$	0
A_1''	1	1	−1	−1
A_2''	1	−1	−1	−1
E_1''	$2\cos m\omega$	0	$-2\cos m\omega$	0
...	...	...	...	...
E_p''	$2\cos pm\omega$	0	$-2\cos pm\omega$	0

D_{nh}, n even ($p=(n-2)/2$)	C_n^m	$\frac{1}{2}nC_2$	$\frac{1}{2}nC_2'$	S_n^m	$\frac{1}{2}n\sigma_v$	$\frac{1}{2}n\sigma_{v'}$
A_1'	1	1	1	1	1	1
A_2'	1	−1	−1	1	−1	−1
E_1'	$2\cos m\omega$	0	0	$2\cos m\omega$	0	0
...	...	...	...	...	...	...
E_p'	$2\cos pm\omega$	0	0	$2\cos pm\omega$	0	0
B_1'	$(-1)^m$	1	−1	$(-1)^m$	1	−1
B_2'	$(-1)^m$	−1	1	$(-1)^m$	−1	1
A_1''	1	1	1	−1	−1	−1
A_2''	1	−1	−1	−1	1	1
E_1''	$2\cos m\omega$	0	0	$-2\cos m\omega$	0	0
...	...	...	...	...	...	...
E_p''	$2\cos pm\omega$	0	0	$-2\cos pm\omega$	0	0
B_1''	$(-1)^m$	+1	−1	$-(-1)^m$	−1	1
B_2''	$(-1)^m$	−1	1	$-(-1)^m$	1	−1

terms in the rows and columns of the symmetry matrix. The second convention has the disadvantage of separating the cosine-sine pairs.

POINT GROUP D_{nh}

There are $4n$ elements in D_{nh}; the $2n$ elements of D_n and $2n$ others, formed by multiplying the elements of D_n by a horizontal reflection, σ_h. There are also twice as many symmetry types as in D_n, since each type in D_n splits into two types in D_{nh}, symmetric and antisymmetric, respectively, to the additional symmetry elements. The condensed character tables for D_{nh}, n even or odd, are given in Table II. In this case it is too complicated to write the characters for n both even and odd together in one table.

The conventional way of writing the character table for D_{nh}, n even, differs from that for D_{nh}, n odd. Since D_{nh} is formed from D_n by adding a horizontal plane of symmetry, we write the character table as the direct product of C_h and D_n, for n either even or odd. This convention makes the use of our symmetry matrix somewhat simpler. However, when n is even, D_{nh} contains an element of inversion ($S_n^{\frac{1}{2}n}\equiv I$). A classification of symmetry types with respect to inversion rather than with respect to reflection in a horizontal plane is generally more useful. This classification can be made as follows. Symmetry types symmetric to inversion (g) have a positive character for $S_n^{\frac{1}{2}n}(\equiv I)$. Thus, $A_1'=A_{1g}$, $A_2'=A_{2g}$, $A_1''=A_{1u}$ and $A_2''=A_{2u}$ for all values of n. When $\frac{1}{2}n$ is even, $B_1'=B_{1g}$, $B_2'=B_{2g}$, $B_1''=B_{1u}$, $B_2''=B_{2u}$. For $\frac{1}{2}n$ odd, the subscripts g and u are interchanged. The E' types with even subscripts are g and those with odd subscripts are u. The reverse is true for E''.

In D_{nh}, sets of n, $2n$ or $4n$ equivalent coordinates are possible.

Case 1. n equivalent coordinates

The analysis for n coordinates in D_n applies here for the first $2n$ elements of D_{nh}. We need, then, merely to investigate the properties of the second $2n$ elements. The P matrix for σ_h for n equivalent coordinates can consist only of either plus or minus the identity matrix, that is, the operation σ_h will either leave the R_i unchanged or merely reverse their signs without permuting them. It follows that the matrix A for each of the second $2n$ elements is either plus or minus the A matrix for the corresponding element from the first group of $2n$ elements. By reference to Table II, we see that this means that the n symmetry coordinates all correspond to either the upper half or the lower half of the character table. It is therefore actually necessary to investigate the symmetry properties of only the symmetry coordinate formed from the first row (the simple sum of the n coordinates) of U_n with respect to only one of the second $2n$ elements. The most convenient choice is $\sigma_h(\equiv S_n^n)$.

We now have the results: matrix U_n is suitable for combining n equivalent coordinates in a molecule of symmetry D_{nh}. The first row of U_n has the symmetry A and the last odd row, if present, symmetry B, with subscripts 1 or 2 according to their behavior with respect to the dihedral two-fold axes (C_2) of symmetry. The row pairs are E_1, E_2, etc., in the order in which they are written in the matrix. So far these results are identical with those of C_{nv} and D_n. The whole set of n symmetry coordinates is symmetric or antisymmetric to σ_h (′ or ″) ac-

cording to the behavior of the first symmetry coordinate (the first row of U_n) with respect to σ_h. When n is even, the primes of the symmetry type symbols may be replaced with g and u, according to the rules already given.

Case 2. $2n$ equivalent coordinates

A convenient numbering and orientation convention is the first one mentioned for $2n$ coordinates in C_{nv}. The operation C_n^m then raises the index number of a coordinate in the first set of n coordinates by m, within a cycle of n. Similarly, C_n^m also increases the index number of a coordinate in the second set of n coordinates by m, within its cycle of n. For example, if $n=5$, $C_5^2R_1=R_3$, $C_5^2R_4=R_1$, $C_5^2R_6=R_8$ and $C_5^2R_9=R_6$. The result of $S_n^m(\equiv\sigma_h C_n^m)$ is a little more complicated. The index number of R_i is increased by m, within the cycle of its own set of n; it is then increased by n, within a cycle of $2n$, which changes it to a coordinate of the other set. For example, for $n=5$, $S_5^2R_1=R_8$ and $S_5^2R_9=R_1$.

If we let P_n be the matrix of degree n defined by Eq. (5), the permutation matrix for C_n^m is

$$\begin{bmatrix} P_n & 0 \\ 0 & P_n \end{bmatrix}$$

and for S_n^m,

$$\begin{bmatrix} 0 & P_n \\ P_n & 0 \end{bmatrix}$$

It immediately follows that $U_2\times U_n$ is a suitable symmetry matrix:

$$\begin{bmatrix} (1/2)^{\frac{1}{2}}U_n & (1/2)^{\frac{1}{2}}U_n \\ (1/2)^{\frac{1}{2}}U_n & -(1/2)^{\frac{1}{2}}U_n \end{bmatrix}\begin{bmatrix} P_n & 0 \\ 0 & P_n \end{bmatrix} \times\begin{bmatrix} (1/2)^{\frac{1}{2}}U_n' & (1/2)^{\frac{1}{2}}U_n' \\ (1/2)^{\frac{1}{2}}U_n' & -(1/2)^{\frac{1}{2}}U_n' \end{bmatrix} =\begin{bmatrix} U_nP_nU_n' & 0 \\ 0 & U_nP_nU_n' \end{bmatrix}$$

$$\begin{bmatrix} (1/2)^{\frac{1}{2}}U_n & (1/2)^{\frac{1}{2}}U_n \\ (1/2)^{\frac{1}{2}}U_n & -(1/2)^{\frac{1}{2}}U_n \end{bmatrix}\begin{bmatrix} 0 & P_n \\ P_n & 0 \end{bmatrix} \times\begin{bmatrix} (1/2)^{\frac{1}{2}}U_n' & (1/2)^{\frac{1}{2}}U_n' \\ (1/2)^{\frac{1}{2}}U_n' & -(1/2)^{\frac{1}{2}}U_n' \end{bmatrix} =\begin{bmatrix} U_nP_nU_n' & 0 \\ 0 & -U_nP_nU_n' \end{bmatrix}. \quad (20)$$

We have already evaluated $U_nP_nU_n'$ (Eqs. (6), (12)). By comparison with the character table for D_{nh}, we see that the first row of $U_2\times U_n$ is A_1' or A_2' and the $n+1$th row, A_1'' or A_2''. The first set of cosine-sine pairs are E_1', E_2', $\cdots$, in order and the second set of row pairs, E_1'', E_2'', etc. When n is even, the nth row is B_1' or B_2' and the $2n$th row, B_1'' or B_2''. As before, the subscripts 1 and 2 on A and B coordinates are determined by the symmetry properties of these coordinates with respect to the dihedral elements of symmetry. This is always easy to determine in the case of nondegenerate coordinates.

Case 3. $4n$ equivalent coordinates

In this case it is difficult to make a general statement concerning numbering the coordinates. There will be four sets of n each and n sets of four each. It is probably best to number each set of n cyclically as usual. The ambiguity comes in the choice of which set of n to be the first set, which to be the second set, etc.

It might be expected that $U_4\times U_n$ would be a suitable symmetry matrix. This is not exactly the case. A slight modification of U_4 may, however, be used.

The reader may have observed that an alternative form of U_n could be written with imaginary exponentials. It is not quite so obvious that an arbitrary phase angle may be added to each element of any cosine-sine row pair. The standard form of U_4 is:

$$U_4=\begin{bmatrix} 1/2 & 1/2 & 1/2 & 1/2 \\ (1/2)^{\frac{1}{2}} & 0 & -(1/2)^{\frac{1}{2}} & 0 \\ 0 & (1/2)^{\frac{1}{2}} & 0 & -(1/2)^{\frac{1}{2}} \\ 1/2 & -1/2 & 1/2 & -1/2 \end{bmatrix}. \quad (21)$$

The addition of a phase angle of 45° to the middle row pair changes U_4 to a somewhat more symmetric form:

$$U_4^*=\begin{bmatrix} 1/2 & 1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & -1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 & -1/2 \\ 1/2 & -1/2 & 1/2 & -1/2 \end{bmatrix}. \quad (22)$$

This matrix, U_4^*, happens to be the direct product of U_2 on U_2 with the last two columns interchanged. It is for this reason that $U_4^*\times U_n$ is suitable in this case. The four sets of equivalent coordinates are equivalent to each other in pairs, in different ways, according to the symmetry

element considered. Symmetric-antisymmetric combinations of symmetric-antisymmetric combinations are called for.

$U_4^* \times U_n$ is divided into four sets of n rows. The methods of the preceding sections show that within any one set of n rows, the identification is A, E_1, E_2, $\cdots$, B, as before. Each set of n rows is $'$ or $''$, according to their symmetry with respect to σ_h. This question can be answered in the following way. Let R_i be a typical coordinate from the first set of n coordinates and R_j, R_k and R_l be the corresponding coordinates from the other three sets of n, i.e., R_i, R_j, R_k and R_l form a typical set of four. These four coordinates (or more generally, the four sets of n to which they belong) can be identified with the four columns of U_4^* (Eq. (22)). The four rows of U_4^* correspond to the four sets of n rows of the whole symmetry matrix. The behavior of R_i, R_j, R_k and R_l with respect to σ_h tells us the symmetry of each row of U_4^* to this same operation and in turn, the symmetry of each of the four sets of n rows of the whole symmetry matrix. For example, let R_i, R_j, R_k and R_l be, respectively, from the first, second, third and fourth sets of n coordinates. They therefore correspond to the first, second, third, and fourth columns of U_4^*, in order. Now assume that σ_h interchanges R_i and R_j and also R_k and R_l. It is obvious that rows one and three of U_4^* are symmetric to this operation and rows two and four, antisymmetric. Therefore, the first and third sets of n rows of $U_4^* \times U_n$ are symmetric to $\sigma_h(')$ and the second and fourth sets, antisymmetric ($''$). The subscripts of the non-degenerate rows are determined as before by reference to the dihedral elements. Of course, $U_2 \times U_2$ may be used instead of U_4^*.

OTHER POINT GROUPS

It does not seem worth while to treat the point groups C_n, C_{nh}, S_n, S_{nv} or D_{nd} in a general fashion, since so few examples of each occur in nature. The matrices appropriate to the first four families are quite similar to those already discussed. The only important example of D_{nd} is D_{3d}. In this case, $U_2 \times U_3$ is suitable for 6 equivalent coordinates.

The matrix U_n was designed particularly for the cyclic and dihedral groups. It is useful, however, in some other cases. For example, in the case of methane (T_d), a set of four equivalent C−H stretchings and a set of six H−C−H bendings occur. U_4 and U_6 are suitable modes of combination respectively, for either of the two sets alone. The former gives one A combination and the three components of a T_2 combination. The latter gives one redundant (identically zero) combination, an E and a T_2. However, the two T_2 modes are not oriented similarly in space. This defect can be remedied by taking three-fold combinations of the last three rows of U_4,

$$\begin{bmatrix} 1 & 0 \\ 0 & U_3 \end{bmatrix} [U_4] \begin{bmatrix} 1 & 0 \\ 0 & U_3' \end{bmatrix}.$$

This new four-fold set of symmetry coordinates gives a T_2 family that is aligned with the T_2 from the six angular coordinates by means of U_6.

In conclusion, a few suggestions are appropriate as to symmetry combinations that may be used in certain cases other than the basic ones previously treated.

Frequently, it is desirable to combine certain symmetry coordinates, formed from different sets of equivalent coordinates, by means of U_2, U_3 or U_4 in order to force a redundant combination of elementary coordinates to appear. A case of this sort occurs in CH_3X. There are four elementary bond stretchings and two sets of three angle bendings, a total of ten. There are only nine internal degrees of freedom. If the three-fold combinations of HCH bendings are combined with the three-fold combinations of HCX bendings in symmetric-antisymmetric pairs, the symmetric combination of the A_1 coordinates from each source will be a null or redundant combination and can be dropped. If in place of this procedure, one or the other of these two A_1 coordinates were dropped, a fallacious interaction potential term would be necessary in the potential expression for the molecule.

Sometimes several groups of atoms, each group with the same symmetry G' which may be different from the symmetry of whole molecule, G, are found in one molecule. It is then desirable to take combinations of the coordinates equivalent under G', whether or not these are equivalent under G, and then to combine these combinations under G. As an example, in the case of isobutane,

the three CH stretchings and the six angular bendings of each methyl group (C_{3v}) may be combined as in the preceding paragraph. These combinations may then be combined, respectively, under the symmetry of whole molecule (C_{3v} again in this case).

A case of misalignment of degenerate coordinates, analogous to the case mentioned in methane, may appear in ring molecules. If the components of two or more degenerate symmetry coordinates of the same symmetry type are not oriented similarly in the plane perpendicular to the main symmetry axis, the secular equation will not factor properly. This situation may be cured by introducing a phase angle into one or the other of the symmetry matrices. The angle required can often be found by inspection.

APPENDIX I

Let

$$z = e^{i\omega} = \cos\omega + i\sin\omega,$$

$$z^{rm} = \cos rm\omega + i\sin rm\omega,$$

$$\sum_{r=1}^{n} z^{rm} = z^m + z^{2m} + z^{3m} + \cdots + z^{nm},$$

$$= 1 + z^m + z^{2m} + \cdots + z^{(n-1)m},$$

$$(1 - z^m)\sum z^{rm} = 1 - z^{nm} = 0,$$

since

$$z^{nm} = e^{inm\omega} = e^{2\pi mi} = 1.$$

If $m \neq 0, \pm n, \pm 2n, \cdots$, we have $\sum z^{rm} = 0$. Since both the real and imaginary parts of this complex number are zero,

$$\sum_{r=1}^{n} \cos rm\omega = \sum_{r=1}^{n} \sin rm\omega = 0.$$

In the same manner, from

$$\sum z^{2rm} = \sum z^{rm} z^{rm}$$
$$= \sum \cos^2 rm\omega - \sum \sin^2 rm\omega + 2i \sum \cos rm\omega \cdot \sin rm\omega$$

we find

$$\sum \cos^2 rm\omega - \sum \sin^2 rm\omega = 0,$$
$$\sum \cos rm\omega \cdot \sin rm\omega = 0.$$

From

$$\sum z^{rm} z^{-rm} = n,$$

we have

$$\sum \cos^2 rm\omega + \sum \sin^2 rm\omega = n.$$

Therefore,

$$\sum_{r=1}^{n} \cos^2 rm\omega = \sum \sin^2 rm\omega = \tfrac{1}{2}n$$

with the restriction $m \neq 0, \pm\frac{1}{2}n, \pm n, \pm\frac{3}{2}n, \cdots$.

The following identities may be proved in a similar manner:

$$\sum_{r=1}^{n} \cos rs\omega \cdot \cos rt\omega = 0,$$

$$\sum_{r=1}^{n} \sin rs\omega \cdot \sin rt\omega = 0,$$

$$\sum_{r=1}^{n} \cos rs\omega \cdot \sin rt\omega = 0,$$

with the restriction $s \pm t \neq 0, \pm n, \pm 2n, \cdots$.