Acta Cryst. (1979). A**35**, 703–713

Description of Molecular Distortions in Terms of Symmetry Coordinates

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(*Received* 2 *February* 1979; *accepted* 12 *March* 1979)

Abstract

Symmetry coordinates are useful for describing nuclear arrangements of molecules that can be regarded as being distorted versions of more symmetrical reference structures. The symmetry coordinate description provides a basis for analysing how displacements along particular subsets of symmetry coordinates destroy certain symmetry elements of the reference structure but preserve others (kernel and co-kernel symmetries). It also helps in visualising the symmetry properties of special subspaces of the $(3N-6)$-dimensional internal coordinate space. Some problems concerning the choice of the reference point group are mentioned. It is shown that the symmetry properties of molecules possessing N cyclic degrees of freedom (*e.g.* torsion angles) are conveniently described in terms of N-dimensional space groups.

1. Introduction

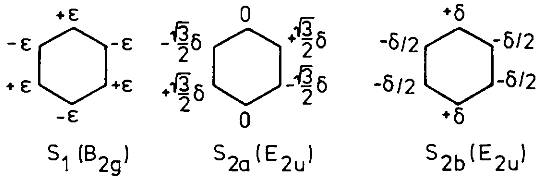
It is often useful to regard the observed structure of a molecule or molecular fragment as a distorted version of a more symmetrical reference structure. In previous papers (Murray-Rust, Bürgi & Dunitz, 1978*a*,*b*; hereinafter MBD*a*,*b*) we have discussed some advantages of using symmetry coordinates for describing static distortions of MX_4 molecules from T_d-symmetrical reference structures. In this type of treatment the total distortion is regarded as a sum of displacements along some set of symmetry coordinates of the reference molecule. By fixing some of these displacements to zero, the observed structure can be related to other structures that retain some symmetry elements of the reference point group. In the present paper we consider how the approach outlined in MBD*a* can be generalized to describe distortions from a reference structure of any given symmetry.

The essential feature of the symmetry-coordinate description is that the total distortion is broken down into various components, each preserving some of the symmetry elements of the reference structure. An arbitrary displacement along a given symmetry coordinate transforming as a particular irreducible representation (IR) preserves at least a certain symmetry known as the kernel symmetry of the IR in question. This kernel symmetry can easily be found from a character table; the symmetry elements preserved are just those whose characters equal the character of the identity element, *i.e.* those represented by unit matrices in the IR in question. Thus the kernel symmetry group is built from complete classes of the reference symmetry group. However, a displacement along a symmetry coordinate transforming as a degenerate IR may preserve a higher symmetry than the kernel symmetry, *i.e.* it may be transformed into itself by symmetry operations not belonging to the kernel of the IR. This higher symmetry is called the co-kernel (Melvin, 1956; McDowell, 1965) or epikernel (Ascher, 1977) symmetry.

A good example of the distinction between kernel and co-kernel symmetry is provided by the three symmetry coordinates that describe out-of-plane deformations of a regular hexagon (Fig. 1). In terms of the IR's of the point group D_{6h}, the $\mathbf{S}_1$ coordinate transforms as B_{2g}, while $\mathbf{S}_{2a}$ and $\mathbf{S}_{2b}$ transform as the degenerate IR E_{2u}. The characters of these representations are:

	I	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0

From this it follows that a displacement along the $\mathbf{S}_1$ coordinate preserves the symmetry elements (I, $2C_3$, $3C_2''$, i, $2S_6$, $3\sigma_v$), *i.e.* those forming the D_{3d} point group. This is the kernel symmetry of the B_{2g}



$S_1\,(B_{2g})$ $S_{2a}\,(E_{2u})$ $S_{2b}\,(E_{2u})$

Fig. 1. The three out-of-plane deformations of a regular hexagon.

0567-7394/79/050703-11$01.00

representation. The kernel symmetry of the degenerate E_{2u} representation is only C_2. From Fig. 1 it is clear that while a displacement along $\mathbf{S}_1$ indeed preserves D_{3d} symmetry, a displacement along either $\mathbf{S}_{2a}$ or $\mathbf{S}_{2b}$ preserves a higher symmetry (D_2 or C_{2v} respectively) than the kernel symmetry C_2. Furthermore, it is easily shown that these higher symmetries do not apply to an arbitrary displacement that transforms as E_{2u}. Since the $\mathbf{S}_{2a}$ and $\mathbf{S}_{2b}$ coordinates are degenerate, any normalized linear combination

$$\mathbf{S}_{2a} \cos \alpha + \mathbf{S}_{2b} \sin \alpha$$

is an equally good choice for one of a pair of symmetry coordinates transforming as E_{2u}. For an arbitrary value of α, a displacement along such a coordinate will preserve only the kernel symmetry C_2, the only non-trivial symmetry element common to $\mathbf{S}_{2a}$ and $\mathbf{S}_{2b}$. It is only for certain special values of α that the higher co-kernel symmetries apply ($\alpha = 0$, 60, 120° for D_2, $\alpha =$ 30, 90, 150° for C_{2v}), Fig. 2.

The possible co-kernel symmetries of degenerate IR's are not as simple to derive as the kernel symmetries and they can be looked at from several points of view. We prefer to think of co-kernel symmetries in terms of the symmetry properties of a vector space that can be associated with the IR in question; the eigenvectors (special positions) of this vector space can be said to correspond to possible co-kernel symmetries. We now proceed to a more formal discussion of some of the points raised in this *Introduction*.

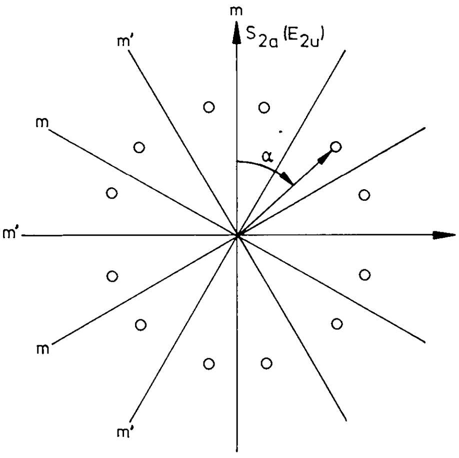


Fig. 2. Deformation space for the degenerate pair of symmetry coordinates $S_{2a}(E_{2u})$ and $S_{2b}(E_{2u})$ that describe out-of-plane deformations of a regular hexagon (Fig. 1). The symmetry of the space is $6m$. Displacement vectors pointing along the mirror lines m at $\alpha = 0$, 60, 120° correspond to deformations that preserve C_{2v} symmetry of the hexagon; vectors pointing along the mirror lines m' at $\alpha = 30$, 90, 150° correspond to deformations that preserve D_2 symmetry of the hexagon. For an arbitrary value of α the displacement vector corresponds to a deformation that preserves only C_2 symmetry, the kernel symmetry of the E_{2u} irreducible representation. There are 12 such isometric deformations.

Table 1. *Kernel, co-kernel symmetries and* **H** *groups for degenerate IR's of common point groups*

Elements of **G** preserved in **K** or **CoK** are given in brackets where necessary to specify the orientation of such elements. The symbols are those used by Wilson, Decius & Cross (1955). Special positions (SP) of the displacement vector corresponding to a particular co-kernel symmetry are listed only for cubic **H** groups and are identified by their point symmetry and, where necessary, one of the equivalent positions, as listed in *International Tables for X-ray Crystallography* (1952).

G	Γ_j	**K**	**CoK**	**H**
C_3	E	C_1	–	3
C_4	E	C_1	–	4
C_5	E_1	C_1	–	5
	E_2	C_1	–	5
C_6	E_1	C_1	–	6
	E_2	C_2	–	3
D_3	E	C_1	C_2	$3m$
D_4	E	C_1	$C_2(C_2')$ $C_2(C_2'')$	$4m$
D_5	E_1	C_1	C_2	$5m$
	E_2	C_1	C_2	$5m$
D_6	E_1	C_1	$C_2(C_2')$ $C_2(C_2'')$	$6m$
	E_2	$C_2(C_2)$	D_2	$3m$
C_{3v}	E	C_1	C_s	$3m$
C_{4v}	E	C_1	$C_s(\sigma_v)$ $C_s(\sigma_d)$	$4m$
C_{5v}	E_1	C_1	C_s	$5m$
	E_2	C_1	C_s	$5m$
C_{6v}	E_1	C_1	$C_s(\sigma_v)$ $C_s(\sigma_d)$	$6m$
	E_2	C_2	C_{2v}	$3m$
C_{3h}	E'	C_s	–	3
	E''	C_1	–	6
C_{4h}	E_g	C_i	–	4
	E_u	C_s	–	4
C_{5h}	E_1'	C_s	–	5
	E_2'	C_s	–	5
	E_1''	C_1	–	10
	E_2''	C_1	–	10
C_{6h}	E_{1g}	C_i	–	6
	E_{2g}	C_{2h}	–	3
	E_{1u}	C_s	–	6
	E_{2u}	C_2	–	6
D_{3h}	E'	$C_s(\sigma_h)$	C_{2v}	$3m$
	E''	C_1	C_2 $C_s(\sigma_v)$	$6m$
D_{4h}	E_g	C_i	$C_{2h}(C_2')$ $C_{2h}(C_2'')$	$4m$
	E_u	$C_s(\sigma_h)$	$C_{2v}(C_2')$ $C_{2v}(C_2'')$	$4m$
D_{5h}	E_1'	$C_s(\sigma_h)$	C_{2v}	$5m$
	E_2'	$C_s(\sigma_h)$	C_{2v}	$5m$
	E_1''	C_1	$C_s(\sigma_v)$ C_2	$10m$
	E_2''	C_1	$C_s(\sigma_v)$ C_2	$10m$
D_{6h}	E_{1g}	C_i	$C_{2h}(C_2')$ $C_{2h}(C_2'')$	$6m$
	E_{2g}	$C_{2h}(C_2)$	D_{2h}	$3m$
	E_{1u}	$C_s(\sigma_h)$	$C_{2v}(C_2')$ $C_{2v}(C_2'')$	$6m$
	E_{2u}	$C_2(C_2)$	$C_{2v}(\sigma_v)$ D_2	$6m$

Table 1 (*cont.*)

G	Γ_j	**K**	**CoK**	**H**
S_4	E	C_1	–	4
S_6	E_g	C_i	–	3
	E_u	C_1	–	6
S_8	E_1	C_1	–	8
	E_2	C_2	–	4
	E_3	C_1	–	8
D_{2d}	E	C_1	$C_2(C_2')$	$4m$
			$C_s(\sigma_d)$	
D_{3d}	E_g	C_i	C_{2h}	$3m$
	E_u	C_1	C_2	$6m$
			C_s	
D_{4d}	E_1	C_1	$C_2(C_2')$	$8m$
			C_s	
	E_2	$C_2(C_2)$	C_{2v}	$4m$
			D_2	
	E_3	C_1	$C_2(C_2')$	$8m$
			C_s	
D_{5d}	E_{1g}	C_i	C_{2h}	$5m$
	E_{2g}	C_i	C_{2h}	$5m$
	E_{1u}	C_1	C_2	$10m$
			C_s	
	E_{2u}	C_1	C_2	$10m$
			C_s	
D_{6d}	E_1	C_1	$C_2(C_2')$	$12m$
			C_s	
	E_2	$C_2(C_2)$	C_{2v}	$6m$
			D_2	
	E_3	C_3	C_{3v}	$4m$
			D_3	
	E_4	S_4	D_{2d}	$3m$
	E_5	C_1	$C_2(C_2')$	$12m$
			C_s	
$C_{\infty v}$	E_1	C_1	C_s	∞m
	E_2	C_1	C_s	∞m
	etc.			
$D_{\infty h}$	Π_g	C_i	$C_{2h}(C_2)$	∞m
	Δ_g	C_i	$C_{2h}(C_2)$	∞m
	etc.			
	Π_u	C_1	$C_{2v}(C_2)$	∞m
	Δ_u	C_1	$C_{2v}(C_2)$	∞m
	etc.			

Table 1 (*cont.*)

G	Γ_j	**K**	**CoK**	**H**	**SP**
T	E	D_2	–	3	
	T	C_1	C_2	23	2
			C_3		3
T_d	E	D_2	D_{2d}	$3m$	
	T_1	C_1	S_4	432	4
			C_3		3
			C_s		2
	T_2	C_1	C_{2v}	$\bar{4}3m$	mm
			C_{3v}		$3m$
			C_s		m
T_h	E_g	D_{2h}	–	3	
	E_u	D_2	–	6	
	T_g	C_i	C_{2h}	23	2
			S_6		3
	T_u	C_1	C_{2v}	$m3$	mm
			C_3		3
			C_s		m
O	E	$D_2(C_4^2)$	D_4	$3m$	
	T_1	C_1	C_4	432	4
			C_3		3
			$C_2(C_2)$		2
	T_2	C_1	$D_2(C_4^2,C_2)$	$\bar{4}3m$	mm
			D_3		$3m$
			$C_2(C_2)$		m
O_h	E_g	$D_{2h}(C_4^2,C_4^2)$	D_{4h}	$3m$	
	E_u	$D_2(C_4^2,C_4^2)$	D_4	$6m$	
			D_{2d}		
	T_{1g}	C_i	C_{4h}	432	4
			S_6		3
			$C_{2h}(C_2)$		2
	T_{2g}	C_i	$D_{2h}(C_4^2,C_4^2)$	$\bar{4}3m$	mm
			D_{3d}		$3m$
			$C_{2h}(C_2)$		m
	T_{1u}	C_1	C_{4v}	$m3m$	$4mm$
			C_{3v}		$3m$
			$C_{2v}(C_2)$		mm
			$C_s(\sigma_d)$		$m(xxz)$
			$C_s(\sigma_h)$		$m(oyz)$
	T_{2u}	C_1	$D_{2d}(C_4^2,C_2)$	$m3m$	$4mm$
			D_3		$3m$
			$C_{2v}(C_2)$		mm
			$C_2(C_2)$		$m(xxz)$
			$C_s(\sigma_h)$		$m(oyz)$

2. Kernels, homomorphic images and co-kernels

Every irreducible representation Γ_j of a point group **G** is associated with an invariant subgroup, $\mathbf{K}(\mathbf{G},\Gamma_j)$, called the kernel of the representation. Its elements are the elements of **G** represented in Γ_j by unit matrices, *i.e.* the elements of **G** whose characters in Γ_j equal the character of the identity element. In general, more than one class of elements of **G** is represented in Γ_j by the same matrix. The set of distinct matrices form another group, $\mathbf{H}(\mathbf{G},\Gamma_j)$, the homomorphic image of **G** with **K** serving as the kernel of the homomorphism. The order h of **H** equals g/k where g is the order of **G** and k the order of **K**; this follows since **H** is isomorphic with the factor or quotient group **G**/**K**.

A displacement that transforms as Γ_j is transformed into itself by all operations in **K**. It therefore shows at least the kernel symmetry, and so does the configuration obtained by applying the displacement to the reference molecule. We shall refer to such a configuration as a kernel configuration. In general, operations not belonging to **K** (we call them R) convert the displacement into other displacements that are equivalent in the sense that they correspond to the same changes in interatomic distances and angles, but distinct in the sense that they correspond, in general, to different orientations of the distortion, that is, they produce isometric nuclear configurations.

The group $\mathbf{H}(\mathbf{G},\Gamma_j)$ can be regarded as the set of operations that convert a displacement vector transforming as Γ_j into an equivalent displacement vector

(Fig. 2).* If we interpret **H** as a point group, we can talk about special positions of this group. Such positions are associated with elements of **H** that are images of operations R of **G** not contained in **K**. Different special positions correspond to different operations.

Since every position, special or general, may also be identified with a Γ_j displacement vector, it follows that there are operations R of **G** not contained in **K** that leave the orientation of particular Γ_j displacements (those corresponding to vectors in special positions) unchanged. Thus, although a displacement in Γ_j shows at least the kernel symmetry of Γ_j it may show a higher symmetry called the co-kernel symmetry (Melvin, 1956) and symbolized $\mathbf{CoK}(\mathbf{G},\Gamma_j,R)$. As McDowell (1965) has pointed out, this can arise only for displacements transforming as certain degenerate representations. Table 1 contains a list of **K**, **CoK** and **H** groups for all degenerate representations of the common point groups.

2.1. *Non-degenerate representations*

The transformation matrices that form these representations are either $[+1]$ or $[-1]$, so the only **H** groups possible are of order one for the totally symmetric representation and of order two for the other non-degenerate representations.

A displacement along a symmetry coordinate transforming as a non-degenerate IR spans a one-dimensional space in which the only possible point symmetry groups $\mathbf{H}(\mathbf{G},\Gamma_i)$ are 1 and m.*

For a totally symmetric representation, $\mathbf{H}=\mathbf{1}$, $\mathbf{K}=\mathbf{G}$; hence a displacement transforming as this IR retains the point group symmetry of the reference molecule. The displacement vectors $D_i\mathbf{S}_i$ and $-D_i\mathbf{S}_i$ correspond to different configurations, *e.g.* one may lead to a lengthening of a particular set of symmetry-equivalent bonds, the other to a contraction.

For a non-totally symmetric representation, **K** is a group of order $g/2$ and $\mathbf{H}=m$. Thus $D_i\mathbf{S}_i$ and $-D_i\mathbf{S}_i$ correspond to equivalent configurations, differing in orientation, with a kernel symmetry **K** lower than that of the reference molecule.

2.2. *Doubly degenerate representations* (E)

The transformation matrices are all of the type

$$\begin{bmatrix} \cos 2\pi j/n & \sin 2\pi j/n \\ -\sin 2\pi j/n & \cos 2\pi j/n \end{bmatrix},$$

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* We talk sometimes about displacements, sometimes about displacement vectors. In the former case we are concerned with variance or invariance under the symmetry operations of the reference point group **G**; in the latter with variance or invariance under symmetry operations of the **H** group.

* To avoid confusion we shall use Hermann–Mauguin symbols (m, 3, $3m$, 432, *etc.*) to describe point groups isomorphic with **H** groups. Schönfliess symbols (C_s, C_3, C_{3v}, T, *etc.*) are reserved for describing the point group **G** of the reference molecule, its kernel **K** and possible co-kernels **CoK**.

Scheme 1. *Derivation of* **H**, **K** *and* **CoK** *for* A_{2u} *and* E_{2g} *representations of* D_{6h}

$$\begin{array}{cccccccccccccc}
R & I & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v & \\
M & \begin{bmatrix} 1&0&0\\0&1&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} \frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&\frac{1}{2}&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} \bar{1}&0&0\\0&\bar{1}&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} 1&0&0\\0&\bar{1}&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} \bar{1}&0&0\\0&1&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} \bar{1}&0&0\\0&\bar{1}&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} \frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&\frac{1}{2}&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} 1&0&0\\0&1&0\\0&0&\bar{1} \end{bmatrix} & \begin{bmatrix} \bar{1}&0&0\\0&1&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} 1&0&0\\0&\bar{1}&0\\0&0&1 \end{bmatrix} & \begin{bmatrix} x\\y\\z \end{bmatrix} \\
M(A_{2u}) & (1) & (1) & (1) & (1) & (-1) & (-1) & (-1) & (-1) & (-1) & (-1) & (1) & (1) & (z) \\
M(E_{2g}) & \begin{bmatrix} 1&0\\0&1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix} & \begin{bmatrix} 1&0\\0&1 \end{bmatrix} & \begin{bmatrix} 1&0\\0&\bar{1} \end{bmatrix} & \begin{bmatrix} 1&0\\0&\bar{1} \end{bmatrix} & \begin{bmatrix} 1&0\\0&1 \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix} & \begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix} & \begin{bmatrix} 1&0\\0&1 \end{bmatrix} & \begin{bmatrix} 1&0\\0&\bar{1} \end{bmatrix} & \begin{bmatrix} 1&0\\0&\bar{1} \end{bmatrix} & \begin{bmatrix} x^2-y^2\\2xy \end{bmatrix}
\end{array}$$

The matrices M transform a vector (x,y,z) into a symmetry-equivalent one. The basis vectors are $\mathbf{e}_z$ parallel to C_6, $\mathbf{e}_x$ parallel to C_2', and $\mathbf{e}_y$ parallel to C_2''.
The matrices $M(A_{2u})$ are obtained by transforming z by the matrices M. The kernel is composed of the elements I, $2C_6$, $2C_3$, C_2, $3\sigma_d$, $3\sigma_v$ that yield unit matrices ($\mathbf{K}=C_{6v}$, $k=12$). Elements of **H** are (1) and (−1), $\mathbf{H}=m$, $h=2$: no co-kernel symmetry.
The matrices $M(E_{2g})$ are obtained by transforming x and y by the matrices M, substituting the transformed x and y into the expressions x^2-y^2, $2xy$, and comparing the transformed and untransformed expressions. The kernel is composed of the elements I, C_2, i, σ_h that yield unit matrices ($\mathbf{K}=C_{2h}$, $k=4$). Elements of **H** are:

$$\begin{bmatrix} 1&0\\0&1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix}\begin{bmatrix} -\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2} \end{bmatrix}\begin{bmatrix} 1&0\\0&\bar{1} \end{bmatrix}\begin{bmatrix} -\frac{1}{2}&-\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&\frac{1}{2} \end{bmatrix}\begin{bmatrix} -\frac{1}{2}&\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&\frac{1}{2} \end{bmatrix}.$$

$\mathbf{H}=3m$, $h=6$. Co-kernel symmetry $D_{2h}=\mathbf{K}(I,C_2,i,\sigma_h)+\mathbf{K}C_2'=\mathbf{K}+\mathbf{K}C_2''=\mathbf{K}+\mathbf{K}\sigma_v=\mathbf{K}+\mathbf{K}\sigma_d=\mathbf{K}+C_2'+C_2''+\sigma_v+\sigma_d$.

where n is the order of the rotation axis (proper or improper) and j is an integer.

The **H** groups formed by these matrices are isomorphic with the cyclic groups n or the dihedral groups nm $(n \geq 3)$ and are listed in Table 1 for doubly degenerate IR's of all important point groups **G**. The derivation for two such groups, $\mathbf{H}(D_{6h},A_{2u})$ and $\mathbf{H}(D_{6h},E_{2g})$ is given in Scheme 1.

Recall that there are two general positions for the one-dimensional point-group $\mathbf{H} = m$: D and $-D$; there are no special positions except $D = 0$. Similarly, for the cyclic groups $\mathbf{H} = n$ there are n general positions and no special positions except $D = 0$. However, for the dihedral groups $\mathbf{H} = nm$, there are $2n$ general positions and either one or two sets of n special positions (the mirror lines), depending on whether n is odd or even. A displacement vector that happens to lie in one of these special positions is left unaltered by the corresponding reflection operation of $\mathbf{H} = nm$ and hence the displacement itself is left unaltered by the corresponding operation R of the reference point group **G** (or operations, R', R'',..., since elements belonging to different classes of **G** may have the same image in **H**). The displacement vector is, however, altered by the other reflection operations of $\mathbf{H} = nm$, the displacement by the corresponding operations of **G**. The operations R, R', R'' ... do not belong to the kernel $\mathbf{K}(\mathbf{G},\Gamma_j)$ since their images in **H** are not unit matrices. Any R in **G** which has as its image a mirror line in **H** may be associated with **K** to form a co-set $\mathbf{K}R$, and combination of this co-set with the kernel forms a co-kernel, $\mathbf{CoK}(\mathbf{G},E_j,R)$. The co-kernel is a non-invariant subgroup of **G** since it includes the operations R, R', R'' ... but excludes other operations belonging to the same classes as these operations. For doubly degenerate IR's the only co-kernel generators R are σ_v, σ_d, C_2' and C_2''. For $\mathbf{H} = nm$ with n even, there are two classes of mirror lines, m and m', and therefore also two kinds of co-kernel which are isomorphic but composed of elements belonging to different classes of **G**. For n even, moreover, $D_i\mathbf{S}_i$ and $-D_i\mathbf{S}_i$ correspond to equivalent configurations, which is not the case for n odd.

Scheme 2. *Derivation of* **H**, **K** *and* **CoK** *for* T_{1g}, T_{2g} *and* E_g *representations of* O_h

$$
\begin{array}{cccccccccccc}
R & I & 8C_3 & 6C_2 & 6C_4 & 3C_2'=3C_4^2 & i & 6S_4 & 8S_6 & 3\sigma_h & 6\sigma_d & \\
M_R & \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&1&0\\\bar{1}&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\1&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\0&0&\bar{1}\\\bar{1}&0&0\end{bmatrix} & \begin{bmatrix}1&0&0\\0&1&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}x\\y\\z\end{bmatrix} \\
M(T_{1g}) & \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&1&0\\\bar{1}&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix} & \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\\bar{1}&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\\bar{1}&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}R(x)\\R(y)\\R(z)\end{bmatrix} \\
M(T_{2g}) & \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} & \begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\1&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix} & \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&\bar{1}&0\\1&0&0\\0&0&\bar{1}\end{bmatrix} & \begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix} & \begin{bmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{bmatrix} & \begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix} & \begin{bmatrix}yz\\zx\\xy\end{bmatrix} \\
M(E_g) & \begin{bmatrix}1&0\\0&1\end{bmatrix} & \begin{bmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{bmatrix} & \begin{bmatrix}1&0\\0&\bar{1}\end{bmatrix} & \begin{bmatrix}1&0\\0&\bar{1}\end{bmatrix} & \begin{bmatrix}1&0\\0&1\end{bmatrix} & \begin{bmatrix}1&0\\0&1\end{bmatrix} & \begin{bmatrix}1&0\\0&\bar{1}\end{bmatrix} & \begin{bmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{bmatrix} & \begin{bmatrix}1&0\\0&1\end{bmatrix} & \begin{bmatrix}1&0\\0&\bar{1}\end{bmatrix} & \begin{bmatrix}2z^2-x^2-y^2\\\sqrt{3}(x^2-y^2)\end{bmatrix}
\end{array}
$$

The matrices M transform a vector (x,y,z) into a symmetry-equivalent one. The base vectors $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ are parallel to the $C_2' = C_4^2$ axes.
The matrices $M(T_{1g})$ are obtained by transforming x, y, and z by the matrices M, substituting the transformed values into the expressions $R(x) = (0,y,0) \times (0,0,z)$ *etc.*, and comparing transformed and untransformed expressions. The kernel is composed of the elements I, i that yield unit matrices ($\mathbf{K} = C_i$, $k = 2$). Elements of the **H** group are the matrices corresponding to I, $8C_3$, $6C_2$, $6C_4$, $3C_2'$ ($\mathbf{H} = 432$, $h = 24$).
Co-kernel symmetries $S_6 = \mathbf{K}(I,i) + \mathbf{K}[C_3 + C_3^2] = \mathbf{K} + C_3 + C_3^2 + S_6 + S_6^5$,
$C_{2h} = \mathbf{K}(I,i) + \mathbf{K}C_2 = \mathbf{K} + C_2 + \sigma_h$,
$C_{4h} = \mathbf{K}(I,i) + \mathbf{K}[C_4 + C_4^2 + C_4^3] = \mathbf{K} + C_4 + S_4 + C_2' + \sigma_h + C_4^3 + S_4^3$.
The matrices $M(T_{2g})$ are obtained by following an analogous procedure for the expressions yz, zx, xy.
The kernel is composed of the elements I, i that yield unit matrices ($\mathbf{K} = C_i$, $k = 2$).
Elements of the **H** group are the matrices corresponding to I, $8C_3$, $6C_2$, $6C_4$, $3C_2'$ ($\mathbf{H} = \bar{4}3m$, $h = 24$).
Co-kernel symmetries: $D_{3d} = \mathbf{K}(I,i) + \mathbf{K}[C_3 + C_3^2 + \sigma(xy) + \sigma(yz) + \sigma(zx)] = \mathbf{K} + 2C_3 + 2S_6 + 3\sigma_d + 3C_2$,
$D_{2h} = \mathbf{K}(I,i) + \mathbf{K}[C_2' + \sigma(xy) + \sigma(x\bar{y})] = \mathbf{K} + 3C_2 + 3\sigma$,
$C_{2h} = \mathbf{K}(I,i) + \mathbf{K}\sigma(xy) = \mathbf{K} + \sigma_h + C_2$.
The matrices $M(E_g)$ are obtained by following an analogous procedure for the expressions $(2z^2 - x^2 - y^2)$, $\sqrt{3}(x^2 - y^2)$.
The kernel is composed of the elements I, $3C_2'$, i, $3\sigma_h$ that yield unit matrices ($\mathbf{K} = D_{2h}$, $k = 8$).
The **H** group is $3m$, $h = 6$ [see example 1, case of $D_{6h}(E_{2g})$].
Co-kernel symmetry $D_{4h} = \mathbf{K}(I,3C_2,i,3\sigma_h) + \mathbf{K}C_4$.

2.3. *Triply degenerate representations* (*T*)*

For triply degenerate representations the **H** groups are formed by three-dimensional matrices and are isomorphic to cubic groups (Table 1, Scheme 2). For these groups there are two kinds of special positions: lines (one degree of freedom) and planes (two degrees of freedom). The operations associated with both kinds are possible co-kernel generators (they are images of some R in **G** but not in **K**). Note that the **H** groups $\bar{4}3m$ and 432, though isomorphic, are not equivalent in this context as they are associated with different special positions. For T_{ju}, representations $D_i\mathbf{S}_i$ and $-D_i\mathbf{S}_i$ correspond to equivalent configurations since $\mathbf{H} = m3m$ or $m3$, which contain $\bar{1}$ as image of i in O_h or T_h respectively. For all other representations this is the case only if $D_i\mathbf{S}_i$ is perpendicular to a dyad axis (2) or mirror plane (m) of **H**.

2.4. *Reducible representations*

A displacement vector containing components transforming as different IR's transforms as a reducible representation of **G** whose character is equal to the sum of the characters of the IR's involved. The kernel symmetries of reducible representations are determined in the same way as for IR's, and similarly for their **H** groups. For example, for the reducible representation of the point group C_{2v} built from the IR's A_2, B_1, B_2, the three-dimensional **H** group may be shown to be 222 with special positions along the coordinate axes. Similarly, for the reducible representation of C_4 built from the IR's B and E, the three-dimensional **H** group is $\bar{4}$. Possible co-kernel symmetries of displacements transforming as reducible representations may be derived by inspection of the special positions of the appropriate **H** group. However, with increase in the dimensionality of the reducible representation, the interpretation of the **H** group as a geometrical point group becomes less helpful in visualizing its symmetry properties: it is difficult to visualize geometric symmetry operations even in four-dimensional space.

2.5. *Choice of basis vectors*

By a suitable choice of basis vectors it is possible to express the special positions of **H** in a particularly simple form. For example, with $\mathbf{H} = 3m$ or $\mathbf{H} = 6m$ it is advantageous to use a trigonal or hexagonal coordinate system, as in crystallography. Another possibility is to use polar coordinates, r, φ. The angular coordinate is conveniently chosen so that $\varphi = 2\pi j/n$ ($j = 1, 2, \ldots, n$) at the mirror lines. For the cubic groups one has the alternative of using Cartesian basis vectors or a set of four linearly dependent, non-orthogonal basis vectors directed along the threefold axes and related by $\mathbf{S}_a + \mathbf{S}_b + \mathbf{S}_c + \mathbf{S}_d = 0$.

In general it is advantageous to choose a set of symmetry displacement coordinates so that at least one such coordinate coincides with a special position of **H**. Different sets of symmetry displacement coordinates transforming as the same IR should be chosen so that one coordinate of each set coincides with the same special position of **H** and not with an equivalent one. This ensures the easy recognition of co-kernel symmetries (MBD*a*).

Co-kernel symmetry of normal vibration modes has been discussed by McDowell (1965), but our treatment differs in some respects from his. Any displacement resulting from distortion along a degenerate pair or triple of normal vibrations must possess at least the kernel symmetry of the appropriate IR, but the individual components may be chosen to show a higher symmetry, a co-kernel symmetry. In this sense, the co-kernel symmetry of a normal mode may indeed be said to 'depend on the choice of basis set', as McDowell puts it. In our treatment, co-kernel symmetry occurs if the displacement vector lies in a special position of the **H** group, and this coincidence of displacement vector and special position does *not* depend on the choice of basis set. All that can be said is that a suitable basis set expresses components of a displacement vector showing co-kernel symmetry in a specially simple form.

3. Kernel, co-kernel and averaged configurations

The overall distortion can be expressed as a displacement vector $\mathbf{D} = d_j\mathbf{p}_j = [d_j(\text{obs}) - d_j(\text{ref})]\,\mathbf{p}_j$ where d_j's are components along some set of internal displacement coordinates $\mathbf{p}_j$ (bond lengths, bond angles, *etc.*). Given the reference point group **G** we may also write $\mathbf{D} = D_i\mathbf{S}_i$ where D_i's are displacements along a set of orthonormal symmetry displacement coordinates $\mathbf{S}_i = T_{ij}\mathbf{p}_j$. Since the transformation is unitary, the matrix **T** that transforms the initial basis vectors $\mathbf{p}_j$ into the new basis vectors $\mathbf{S}_i$ also transforms the initial displacements d_j into the new symmetry displacements D_i, *i.e.* $D_i = T_{ij}d_j$.

Just as the operation of the total displacement vector on the reference structure leads to the observed structure, so a subset of symmetry displacements can be chosen to produce the structure of an idealized molecule that contains only a part of the overall distortion of the observed molecule. Such a structure can be selected to have particular kernel or co-kernel symmetries and we shall refer to it as a kernel or co-kernel configuration. A subset of symmetry displacements belonging to a particular representation produces a configuration which necessarily shows the kernel symmetry of that representation, and appropriately chosen subsets produce configurations with co-kernel

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* Icosahedral groups, which in addition to triply degenerate also have quadruply and quintuply degenerate IR's, will not be discussed here.

symmetries. The parameters that describe a particular kernel or co-kernel configuration are given by

$$d_j(\mathsf{K}) \text{ or } d_j(\mathsf{CoK}) = d_j(\text{ref}) + T_{ji}D_i,$$

summed over the relevant subset of symmetry displacements. The kernel or co-kernel configurations thus correspond to the configurations that the molecule *would have* if certain symmetry displacements were zero.

Any idealized configuration obtained by appropriate averaging over the internal parameters of a molecule is a kernel or co-kernel configuration. On the other hand, as pointed out in MBD*a* (§ 3), not every kernel or co-kernel configuration can be obtained by a simple averaging process (see also §4.2).

4. Examples

4.1. MXY_2 molecule with $\mathsf{G} = C_{2v}$

Consider the case of an observed MXY_2 molecule that is to be related to a reference molecule with C_{2v} symmetry and coordinates $\mathbf{p}_j$. There are $3 \times 4 - 6$ independent $\mathbf{p}_j$'s, of which $2 \times 4 - 3 = 5$ can be chosen in the plane of the reference molecule. As independent internal coordinates $\mathbf{p}_j$ we take $\mathbf{r}_x$, $\mathbf{r}_{y1}$, $\mathbf{r}_{y2}$, $\boldsymbol{\theta}_1$, $\boldsymbol{\theta}_2$ and $\boldsymbol{\Delta}$ (Fig. 3). The corresponding symmetry coordinates are obtained from these by the transformation:

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{r}_{y1} \\ \mathbf{r}_{y2} \\ \mathbf{r}_x \\ \boldsymbol{\theta}_1 \\ \boldsymbol{\theta}_2 \\ \boldsymbol{\Delta} \end{bmatrix} = \begin{bmatrix} \mathbf{S}_1(A_1) \\ \mathbf{S}_4(B_2) \\ \mathbf{S}_2(A_1) \\ \mathbf{S}_3(A_1) \\ \mathbf{S}_5(B_2) \\ \mathbf{S}_6(B_1) \end{bmatrix}$$

The displacements D_i along these coordinates $\mathbf{S}_i$ are obtained by substituting $d_j = d_j(\text{obs}) - d_j(\text{ref})$ for $\mathbf{p}_j$ in the above expression, but it is only for the totally symmetric coordinates that the reference values are actually required; for the other coordinates they cancel out. Three symmetry displacement coordinates transform as A_1; any other set of three, mutually orthogonal, normalized, linear combinations of these could serve as an alternative set of basis vectors, for example:

$$\mathbf{S}_1'(A_1) = \sqrt{\frac{2}{3}}\left(\mathbf{S}_1 + \frac{1}{\sqrt{2}}\mathbf{S}_2\right) = \frac{1}{\sqrt{3}}(\mathbf{r}_x + \mathbf{r}_{y1} + \mathbf{r}_{y2}),$$

$$\mathbf{S}_2'(A_1) = \sqrt{\frac{2}{3}}\left(-\frac{1}{\sqrt{2}}\mathbf{S}_1 + \mathbf{S}_2\right)$$

$$= \frac{1}{\sqrt{6}}(2\mathbf{r}_x - \mathbf{r}_{y1} - \mathbf{r}_{y2}),$$

$$\mathbf{S}_3'(A_1) = \mathbf{S}_3.$$

The unprimed coordinates are the simplest, but the primed ones might be useful if comparisons are to be made between distortions of MXY_2 and MY_3 molecules, as will be seen in the next example. The kernel symmetries are $\mathsf{K}(A_1) = C_{2v}$, $\mathsf{K}(B_1) = C_s(\sigma_v)$, $\mathsf{K}(B_2) = C_s(\sigma_v')$. There are no co-kernel symmetries.

4.2. MY_3 molecule with $\mathsf{G} = D_{3h}$

The internal coordinates are $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, $\boldsymbol{\theta}_1$, $\boldsymbol{\theta}_2$, $\boldsymbol{\theta}_3$, $\boldsymbol{\Delta}$ (analogous to Fig. 3) with one equation of constraint.* The symmetry coordinates are:

$$\mathbf{S}_1(A_1') = \frac{1}{\sqrt{3}}(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3),$$

$$\mathbf{S}_2(A_2'') = \boldsymbol{\Delta},$$

$$\mathbf{S}_{3a}(E') = \frac{1}{\sqrt{6}}(2\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{r}_3),$$

$$\mathbf{S}_{3b}(E') = \frac{1}{\sqrt{2}}(\mathbf{r}_2 - \mathbf{r}_3),$$

$$\mathbf{S}_{4a}(E') = \frac{1}{\sqrt{6}}(2\boldsymbol{\theta}_1 - \boldsymbol{\theta}_2 - \boldsymbol{\theta}_3),$$

$$\mathbf{S}_{4b}(E') = \frac{1}{\sqrt{2}}(\boldsymbol{\theta}_2 - \boldsymbol{\theta}_3).$$

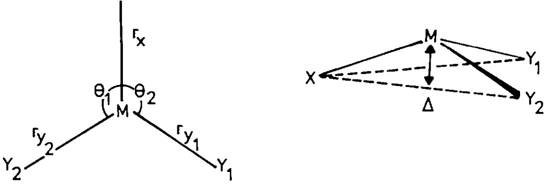

Fig. 3. Internal coordinates for MXY_2 molecule with C_{2v} reference symmetry.

$$* \varDelta^2 = \{\sin^2\theta_1/d_1^2 + \sin^2\theta_2/d_2^2 + \sin^2\theta_3/d_3^2 + 2(\cos\theta_1\cos\theta_2 - \cos\theta_3)/d_1d_2 + 2(\cos\theta_2\cos\theta_3 - \cos\theta_1)/d_2d_3 + 2(\cos\theta_1\cos\theta_3 - \cos\theta_2)/d_1d_3\}^{-1}\Omega^2,$$

where

$$\Omega^2 = 1 - \cos^2\theta_1 - \cos^2\theta_2 - \cos^2\theta_3 + 2\cos\theta_1\cos\theta_2\cos\theta_3.$$

The kernels are $\mathbf{K}(A_1') = D_{3h}$, $\mathbf{K}(A_2'') = C_{3v}$, $\mathbf{K}(E') = C_s(\sigma_h)$. The $\mathbf{S}_{3a}$ and $\mathbf{S}_{4a}$ coordinates are chosen so that both are transformed into themselves by the mirror plane passing through $\mathbf{r}_1$ and bisecting θ_1 in the reference molecule. Displacements along $\mathbf{S}_{3a}$ or $\mathbf{S}_{4a}$ or both show co-kernel symmetry, $\mathbf{CoK}(E',\sigma_v) = C_{2v}$.

For observed bond lengths d_1, d_2, d_3 and an arbitrarily chosen reference bond length d_0, the bond lengths of the E' co-kernel configuration are obtained from

$$\begin{bmatrix} d_1' \\ d_2' \\ d_3' \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \sqrt{3}d_0 \\ \frac{1}{\sqrt{6}}(2d_1 - d_2 - d_3) \\ 0 \end{bmatrix}$$

as

$$d_1' = d_0 + \tfrac{1}{3}(2d_1 - d_2 - d_3),$$
$$d_2' = d_3' = d_0 - \tfrac{1}{6}(2d_1 - d_2 - d_3).$$

The overall C_{2v} co-kernel configuration involves displacements along $\mathbf{S}_1(A_1')$ ($\mathbf{K} = D_{3h}$, a supergroup of C_{2v}) as well as $\mathbf{S}_{3a}(E')$, and its bond lengths are:

$$\begin{aligned} d_1'' &= d_0 + \tfrac{1}{3}(2d_1 - d_2 - d_3) \\ &\quad + \tfrac{1}{3}(d_1 + d_2 + d_3 - 3d_0) = d_1, \\ d_2'' = d_3'' &= d_0 - \tfrac{1}{6}(2d_1 - d_2 - d_3) \\ &\quad + \tfrac{1}{3}(d_1 + d_2 + d_3 - 3d_0) = \tfrac{1}{2}(d_2 + d_3), \end{aligned}$$

the same as obtained by averaging with respect to C_{2v} symmetry.

The redundant coordinate

$$\mathbf{S}_5(A_1') = \frac{1}{\sqrt{3}}(\boldsymbol{\theta}_1 + \boldsymbol{\theta}_2 + \boldsymbol{\theta}_3)$$

is also suitable to describe the out-of-plane displacement provided we neglect the sense of this displacement. A displacement along $\mathbf{S}_5$ can be related to the square of the out-of-plane displacement Δ by the approximation

$$S_2^2 = \Delta^2 \simeq S_1^2(2\pi\sqrt{3} - S_5)/9 \simeq d^2(2\pi/\sqrt{3} - S_5)/3,$$

where d is the mean bond length.

4.3. *Out-of-plane distortion of a regular pentagon with* $\mathbf{G} = D_{5h}$

There are nine displacement coordinates, of which seven lie in the plane of the pentagon. The two remaining symmetry displacement coordinates transform together as the E_2'' representation of D_{5h} ($\mathbf{K} = 1$, $\mathbf{H} = 10m$, Scheme 3);

$$S_a(E_2'') = \sqrt{\tfrac{2}{5}} \sum_i z_i \cos 4\pi i/5,$$

$$S_b(E_2'') = \sqrt{\tfrac{2}{5}} \sum_i z_i \sin 4\pi i/5,$$

z_i being the deviation of the ith atom ($i = 1, 2, 3, 4, 5$) from the plane of the regular pentagon, *i.e.* the mean plane of the distorted pentagon. Alternatively, the displacement vector may be expressed in terms of polar coordinates R, α;

$$R = (S_a^2 + S_b^2)^{1/2},$$
$$\cos\alpha = S_a/R, \quad \sin\alpha = S_b/R.$$

In the above description, $\mathbf{S}_a$ and $\mathbf{S}_b$ are chosen to lie in mirror lines of $\mathbf{H}$; the mirror line (m) occupied by $\mathbf{S}_a$ ($\alpha = 0$) is the image of a σ_v operation of $\mathbf{G}$, the one (m') occupied by $\mathbf{S}_b$ ($\alpha = 90°$) is the image of a C_2 operation, so that although $\mathbf{S}_a$ and $\mathbf{S}_b$ each corresponds to a co-kernel symmetry, the two symmetries are different. In fact, a distortion along $\mathbf{S}_a$ corresponds to a mirror-symmetric envelope form, a distortion along $\mathbf{S}_b$

Scheme 3. *Derivation of* **H**, **K** *and* **CoK** *for* E_2'' *representation of* D_{5h}

$$\begin{array}{cccccccccc}
R & I & 2C_5 & 2C_5^2 & 5C_2 & \sigma_h & 2S_5 & 2S_5^3 & 5\sigma_v & \\
M & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} C & S & 0 \\ -S & C & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} C' & S' & 0 \\ -S' & C' & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} C & S & 0 \\ -S & C & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} C' & -S' & 0 \\ S' & C' & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} x \\ y \\ z \end{bmatrix} \\
M(E_2'') & \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} C' & S' \\ -S' & C' \end{bmatrix} & \begin{bmatrix} C & -S \\ S & C \end{bmatrix} & \begin{bmatrix} \bar{1} & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} -C' & -S' \\ S' & -C' \end{bmatrix} & \begin{bmatrix} -C & S \\ -S & -C \end{bmatrix} & \begin{bmatrix} 1 & 0 \\ 0 & \bar{1} \end{bmatrix} & \begin{bmatrix} (x^2-y^2)z \\ 2xyz \end{bmatrix}
\end{array}$$

where $C = \cos 2\pi/5$, $S = \sin 2\pi/5$, $C' = \cos 4\pi/5$ and $S' = \sin 4\pi/5$.
The matrices $M(E_2'')$ are obtained by procedures analogous to those followed in Scheme 1.
They represent the operations (1), $2(5^2)$, $2(5^{-1})$, $5(m)$, (2), $2(10^{-1})$, $2(10^3)$, $5(m')$; $\mathbf{H} = 10m$, $h = 20$.
The kernel consists of I, $\mathbf{K} = C_1$, $k = 1$. Co-kernel symmetries are $C_s = (I + \sigma_v)$, and $C_2 = (I + C_2')$.

to the twist form with a dyad axis (Fig. 4). Rotation of the displacement vector through $4\pi n/5$ produces an equivalent distortion that differs from the original only by rotation of the pentagon through $2\pi n/5$. Rotation of the displacement vector through 180° produces an equivalent distortion related to the original by reflection in the plane of the pentagon: the dyad axis of **H** is the image of the σ_h operation of **G**.

This discussion constitutes a group-theoretical background for the description of out-of-plane distortions of cyclopentane rings by Pitzer & Donath (1959) and Altona, Geise & Romers (1968). The latter authors use torsion angles φ_j around bonds j instead of z_i's of atoms i as the out-of-plane coordinates. The φ's and z's transform in the same way, and the three conditions that reduce the five φ's or z's to only two independent out-of-plane coordinates are of the same form:

$$S(A_1') = \frac{1}{\sqrt{5}} \sum p_i = 0,$$

$$S_a(E_1'') = \sqrt{\tfrac{2}{5}} \sum p_i \cos 2\pi i/5 = 0,$$

$$S_b(E_1'') = \sqrt{\tfrac{2}{5}} \sum p_i \sin 2\pi i/5 = 0.$$

These equations are strictly valid only for infinitesimal puckering amplitudes although they hold well even for strongly puckered rings. The geometric meaning of the constraints is different for the φ's and z's. For the z's (positional coordinates) they are the conditions of no net translation or rotation; for the φ's (internal coordinates) they are the ring closure conditions for an equilateral pentagon.

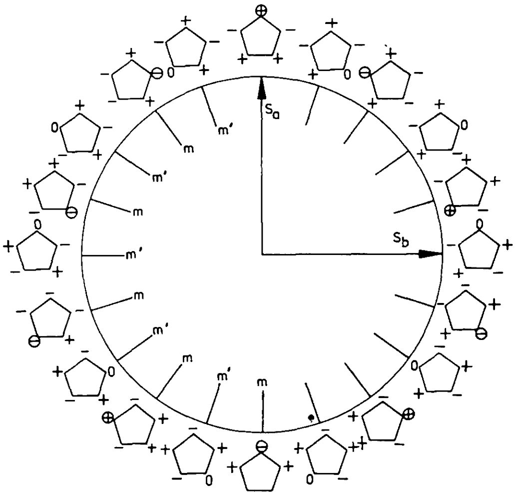

Fig. 4. Deformation space for the degenerate pair of symmetry coordinates $S_a(E_2'')$ and $S_b(E_2'')$ that describe out-of-plane deformations of a regular pentagon. The symmetry of the space is $10m$. Displacement vectors along any of the mirror lines m (or m') preserve C_s (or C_2) symmetry of the pentagon. The series of non-planar pentagons so obtained is indicated schematically (the circles identify the vertex that lies in the mirror plane of each C_s-symmetric pentagon). A displacement vector in an arbitrary direction preserves no non-trivial symmetry elements of the pentagon: the kernel symmetry of the E_2'' irreducible representation consists only of the identity operation.

4.4. *Out-of-plane distortion of regular hexagon with* $\mathbf{G} = D_{6h}$

This is the example that was briefly referred to in the *Introduction*. Of the three out-of-plane symmetry displacement coordinates, one transforms as the B_{2g} representation of D_{6h} ($\mathbf{K} = D_{3d}$, $\mathbf{H} = m$) while the other two transform as E_{2u} ($\mathbf{K} = C_2$, $\mathbf{H} = 6m$), Figs. 1 and 2.

$$S(B_{2g}) = \frac{1}{\sqrt{6}} \sum_i z_i(-1)^i,$$

$$S_a(E_{2u}) = \frac{1}{\sqrt{3}} \sum_i z_i \cos 4\pi i/6,$$

$$S_b(E_{2u}) = \frac{1}{\sqrt{3}} \sum_i z_i \sin 4\pi i/6.$$

Further discussion follows closely along the lines of the previous section.

4.5. *Jahn–Teller distortion of* MX_6 *molecule with* $\mathbf{G} = O_h$

Octahedral MX_6 molecules with M = Cu(II), Ag(II), low-spin Co(II) or high-spin Cr(II) show a $(t_{2g}^6 e_g^3)$, $(t_{2g}^6 e_g^1)$ or $(t_{2g}^3 e_g^1)$ electronic configuration corresponding to an electronically degenerate ^2E_g ground state and are thus expected to undergo Jahn–Teller distortion along displacement coordinates of E_g symmetry. These may be defined as

$$S_{2a}(E_g) = \frac{1}{\sqrt{12}} (2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6),$$

$$S_{2b}(E_g) = \tfrac{1}{2}(r_2 - r_3 + r_5 - r_6).$$

Of the six M–X distances $r_1, r_2, \ldots, r_6$, we choose r_i and r_{i+3} to be co-linear. The kernel symmetry $\mathbf{K}(E_g) = D_{2h}$, and $\mathbf{H}(O_h, E_g) = 3m$. In the above description the basis vector $\mathbf{S}_{2a}$ is chosen to lie in a mirror line of **H**. This line is the image of $2C_4$, $2C_2$, $2S_4$, and $2\sigma_d$ operations of the reference point group, so the co-kernel symmetry of a displacement along $\mathbf{S}_{2a}$ is D_{4h}. A positive displacement corresponds to tetragonal elongation of the MX_6 molecule, a negative displacement to tetragonal compression, *i.e.* $D_{2a}\mathbf{S}_{2a}$ and $-D_{2a}\mathbf{S}_{2a}$ are non-equivalent. The orthogonal basis vector $\mathbf{S}_{2b}$ does not lie on a mirror line of **H**, and a corresponding displacement shows only the kernel symmetry; $D_{2b}\mathbf{S}_{2b}$ and $-D_{2b}\mathbf{S}_{2b}$ describe equivalent distortions since they are related by a mirror line of **H**.

In terms of polar coordinates

$$R = (S_{2a}^2 + S_{2b}^2)^{1/2},$$

$$\cos\alpha = S_{2a}/R, \quad \sin\alpha = S_{2b}/R.$$

The energy surface for the E_g subspace has been studied extensively (Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979) and shows minima at $R = R_{JT} \neq 0$, $\alpha = 0$, $2\pi/3$, and $4\pi/3$ (tetragonal elongation). Saddle points occur at $R \sim R_{JT}$, $\alpha = \pi/3$, π, and $5\pi/3$ (tetragonal compression). This type of potential is commonly described as a 'warped Mexican hat' potential (Fig. 5).

5. Isometric groups

The above discussion is concerned with special aspects of the more general group-theoretical treatment of isometric groups given by Bauder, Meyer & Günthard (1974), who provide a basis for determining symmetry properties of many-dimensional energy hypersurfaces relevant to the dynamics of molecular isomerizations.

We start by defining a molecular fragment, its reference structure with point symmetry **G**, and a set of coordinates (internals, Cartesians, symmetry coordinates) that constitute a basis for a representation of **G**. Symmetry-equivalent distortions of the fragment must be energetically equivalent, *i.e.* the energy hypersurface must be invariant to all symmetry operations of **G**. However, it is generally not so easy to visualize symmetry properties in the many-dimensional space that is involved. Our discussion is meant to help visualization of the symmetry properties of particular subspaces of the $(3N-6)$-dimensional internal coordinate space, subspaces containing symmetry coordinates transforming as a given IR. In this connection it is helpful to interpret the **H** groups as point symmetry groups in one-, two- or three-dimensional space. The eigenvectors of the transformation matrices constituting a given **H** group are then readily recognized as the special positions of that **H** group. These special positions correspond to the fixed points of internal isometric groups.

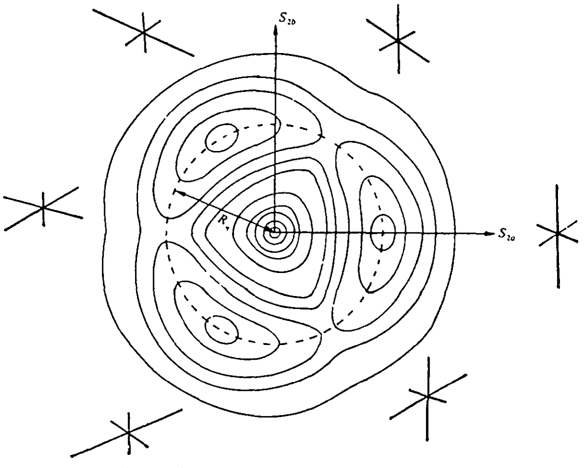

Fig. 5. Warped Mexican-hat type of potential surface for Jahn–Teller distortion of MX_6 molecule with O_h reference symmetry, based on the symmetry coordinates $S_{2a}(E_g)$ and $S_{2b}(E_g)$. The symmetry of the deformation space is $3m$, and displacement vectors along the mirror lines correspond to deformations that preserve D_{4h} symmetry (elongated or compressed octahedron).

6. Choice of reference group G

6.1. *General remarks*

So far we have implicitly taken for granted that the reference group **G** is the point group associated with a reference molecule. This is unobjectionable as long as the distortions involved are small enough or of such a nature that they do not convert the reference structure into another structure that could equally well serve as the reference. Depending on the problem, the group **G** may also be chosen as that formed by *all* operations that convert a given reference structure into isometric structures. These operations may include, for example, inversion, internal rotations, as well as the operations of the point group of the reference structure. Two examples illustrate these general remarks.

For an MX_4 molecule the reference point group **G** could be chosen as T_d or D_{4h} or any of their subgroups. With $\mathbf{G} = T_d$ there is one particular displacement coordinate, $S_a(E)$, that eventually produces a D_{4h} structure and, if followed further, leads to the T_d structure of opposite chirality to the initial one. For a complete description of this process, the appropriate reference group **G** has to contain an inversion operation (even though this is not present in T_d) leading to a group isomorphic with O_h.

A second example is provided by diphenylmethane, where conformations with the planes of both phenyl groups either parallel or perpendicular to the C–CH$_2$–C plane have C_{2v} symmetry. Rotation of either phenyl group through π produces a conformation that is isometric with the initial one. Symmetry operations of this kind are not included in point groups but they have to be allowed for in the group of all operations that leave the reference structure invariant (Longuet-Higgins, 1963; Altmann, 1967; Bauder, Meyer & Günthard, 1974).

6.2. *Periodic* **H** *groups*

In the previous example, the torsion angles about the C–CH$_2$ bonds are cyclic coordinates. The **H** group describing the symmetry properties of displacement vectors involving these coordinates may be derived in just the same way as for non-cyclic coordinates but it now corresponds to an infinite group containing elements of translational symmetry, in other words, to a *space group* rather than to a point group (Fig. 6). We can define the torsion angles as φ_1 and φ_2 modulo π, in which case the **H** group relevant to the two torsional degrees of freedom can be shown to be *cmm* with the coordinate axes along the symmetry coordinates

$$S_a(A_2) = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2),$$

$$S_b(B_1) = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2).$$

The special positions (0,0), $(\pi/2,\pi/2)$ correspond to molecular conformations with C_{2v} symmetry, the positions with $\varphi_1 = -\varphi_2$ $(S_a = 0)$ and with $\varphi_1 = 0$, $\varphi_2 = \pi/2$ or $\varphi_1 = \pi/2$, $\varphi_2 = 0$ correspond to conformations with C_s symmetry, and positions with $\varphi_1 = \varphi_2$ $(S_b = 0)$ correspond to conformations with C_2 symmetry.

Non-rigid molecules that can be regarded as consisting of a set of internal rotors superimposed on an essentially rigid frame (*e.g.* diphenylmethane), can always be described in terms of the appropriate periodic **H** group. The general positions of these groups depend essentially on the appropriate point group symmetry **F** of the frame, while the lattice translations depend on the periodicities of the rotors. For N m-fold rotors, there are m^N lattice points in the N-dimensional hypercube of edge 2π, and the number of general positions within such a hypercube becomes $m^N f$ where f is the order of **F**. Special positions of the periodic **H** group correspond to molecular conformations that are distinguished by having some non-trivial point group symmetry (kernel or co-kernel symmetry). For triphenylmethane (three twofold rotors, $\mathbf{F} = C_{3v}$), the **H** group relevant to the three torsional degrees of freedom is $R32$ (order six) with eight lattice points in the cube $(2\pi)^3$. For trimethylboron (three threefold rotors, $\mathbf{F} = D_{3h}$), the corresponding **H** group is $R\bar{3}c$ (order 12) with 27 lattice points in the cube. For tetraphenylmethane (four twofold rotors, $\mathbf{F} = T_d$), the corresponding **H** group is four-dimensional. It can be described as having 16-fold KU-centring (Wondratschek, Bülow & Neubüser, 1971) and 384 general positions (*i.e.* 24 in the primitive cell), and it is isomorphic with space group 24/04/01/002 in the classification of Brown, Bülow, Neubüser, Wondratschek & Zassenhaus (1978). For this molecule there is an additional complication. The highest point group symmetry of tetraphenylmethane is D_{2d} for special orientations of the phenyl groups. Rotation of the phenyl groups away from these special orientations lowers the molecular symmetry; however, certain finite rotations produce conformations that again have D_{2d} symmetry, but with the S_4 axis in a different direction to the initial one. The rotations in question correspond to displacement vectors that lie in the special positions of highest multiplicity (24) in the four-dimensional space group. The properties of periodic **H** groups will be discussed in more detail elsewhere (Bürgi & Dunitz, 1979; see also Dunitz, 1979).

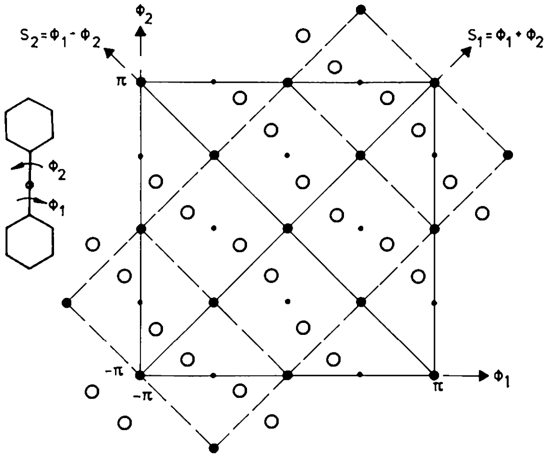

Fig. 6. The 16 general positions (open circles) in the square of area $(2\pi)^2$ correspond to 16 isometric conformations of diphenylmethane with different values of the torsion angles φ_1 and φ_2. If the pattern is extended indefinitely its primitive lattice has translations $\varphi_1 = \pi$, $\varphi_2 = \pi$, and its plane group is *cmm* (with unit translations of the centred cell along $\mathbf{S}_1 = \varphi_1 + \varphi_2$, $\mathbf{S}_2 = \varphi_1 - \varphi_2$). The special positions of this plane group correspond to conformations with non-trivial symmetry: (0,0), *etc.*, C_{2v}; $(\frac{1}{4},\frac{1}{4})$, *etc.*, C_s; $(S_1,0)$, C_2; $(0,S_2)$, *etc.*, C_s.

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