

Molecular Vibrations in Nonsymmorphic Crystals

I. Symmetry Coordinates for $Pmn2_1$ (C_{2v}^7)

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The use of little-group theory and multiplier representations in deriving irreducible crystal amplitude subspaces is briefly discussed. $Pmn2_1$ symmetry coordinates are reported for all wave vectors the groups of which have the set of translations as a proper subgroup. External symmetry coordinates for all free molecules of C_{2v} symmetry are included as a special case.

In the last few years spectroscopists¹⁻² and crystallographers³ alike have expressed an increasing interest in the dynamics of molecular crystals. Despite the rapid growth of the amount of research devoted to this field, several problems merit further investigation. For instance, the usual classification of nuclear motions in terms of supposedly noninteracting external and internal modes constitutes a source of error of essentially unknown magnitude. The conditions for a separate treatment of internal and external modes to be adequate are undoubtedly met in many cases. Nevertheless, clear evidence to the contrary exists for some, inorganic⁴ as well as organic,⁵ systems. In particular, the recent "atomic crystal" type treatment given to naphthalene by Pawley and Cyvin⁵ clearly demonstrates the hazards of considering lattice phonons to be made up by rigid-body motion alone. It seems safe to assert that similar model calculations are called for in a number of other cases exhibiting low-lying "internal" bands. Whenever feasible symmetry reduction of secular equations is the obvious first step in an assessment study of the extent to which rigid-body phonons acquire a clothing of [renormalized] internal modes, and *vice versa*. This step requires some preparation which, fortunately, can be arranged to apply equally well to all crystals shearing a common space group designation. This paper serves to initiate a series devoted to the reporting of complete sets of symmetry coordinates for a collection of nonsymmorphic space groups. The collection contains selected cases covering numerous molecular crystals for which, to our knowledge, symmetry coordinates are not available in the literature. The outline of the present paper is as follows. First, we describe the adopted naming conventions

in sufficient detail to save repeated specifications in future works, listing also some pertinent group-theoretical concepts brought in to reinforce those already underlying the symmetry analysis of a gaseous molecule. Second, we present the results obtained for $Pmn2_1$, and finally we indicate how to adapt these and forthcoming results to alternative ways of specifying basis vectors of irreducible amplitude subspaces.

SALIENT CONCEPTS AND NAMING CONVENTIONS

Consider a crystal lattice with fundamental periods $\{\mathbf{a}_r; r=1,3\}$, and let T denote the infinite and discrete translational subgroup of the space group in question, G . A finite group of translations, T^N , pertaining to a cyclic lattice containing N^3 unit cells, can be obtained as the image of T under a homomorphic mapping with kernel $\{\sum_{r=1}^3 m_r N \mathbf{a}_r; (m_1, m_2, m_3) \in I \times I \times I\}$ where I designates the set of integers. G^N stands for the corresponding finite space group. Henceforth, when writing G and T , G^N and T^N are understood. Furthermore, with n referring to the number of atoms in a unit cell the $N (= 3nN^3)$ -dimensional amplitude space of the cyclic structure, H , can be endowed with a basis set $\{\mathbf{c}(l\kappa\alpha); l=1, N^3; \kappa=1, n; \alpha=1, 3\}$ where $\mathbf{c}(l\kappa\alpha)$ signifies a unit massweighted displacement of the atom at $\mathbf{x}(l\kappa)$ in the cartesian α -direction; and where, for instance, $\mathbf{c}(111)$ in component form reads

$$\mathbf{c}(111) = (1, 0, 0, \dots, 0) \quad (1)$$

Regarding $\{\mathbf{c}(l\kappa\alpha)\}$ as a fiducial frame, a unitary and linear space group operator on H , $[\mathbf{S}|\mathbf{v}(S) + \mathbf{x}(m)]$, is defined by

$$\begin{aligned} \langle \mathbf{c}(l'\kappa'\beta), [\mathbf{S}|\mathbf{v}(S) + \mathbf{x}(m)]\mathbf{c}(l\kappa\alpha) \rangle &= \delta_{l'L} \delta_{\kappa'K} S_{\beta\alpha} \\ \mathbf{x}(\mathbf{LK}) &= \mathbf{S}\mathbf{x}(l\kappa) + \mathbf{v}(S) + \mathbf{x}(m) \end{aligned} \quad (2)$$

where \mathbf{S} is a proper or improper rotation belonging to the point group of G , $\mathbf{v}(S)$ is either a nonprimitive translation or the null vector, and where $\mathbf{x}(m) \in T$. As is easy to verify, eqn. (2) makes $\{[\mathbf{S}|\mathbf{v}(S) + \mathbf{x}(m)]\}$ form a homomorphic mapping of G . Consequently $\{\mathbf{c}(l\kappa\alpha)\}$ carries a (reducible) representation of G . With an appropriate ordering of the $\mathbf{c}(l\kappa\alpha)$'s each $N \times N$ representation matrix is a monomial supermatrix form the nonvanishing elements of which are all equal and coincident with the 3×3 matrix realization of some \mathbf{S} in (the point group isomorphic to) G/T . In simplifying the dynamics it is highly useful to give explicit recognition to translational invariance by introducing the alternative basis set

$$\begin{aligned} &\mathbf{U}\{\mathbf{E}(\mathbf{k}\kappa\alpha); \kappa=1, n; \alpha=1, 3\} \text{ where} \\ &\mathbf{k} \in \{\mathbf{k}_s\} \\ \mathbf{E}(\mathbf{k}\kappa\alpha) &= N^{-3/2} \sum_l \exp[i\mathbf{k} \cdot \mathbf{x}(l)]\mathbf{c}(l\kappa\alpha) \end{aligned} \quad (3)$$

and where $\{\mathbf{k}_s\}$ constitutes a grid in reciprocal space, *viz.*

$$\mathbf{k}_s = N^{-1} \sum_{q=1}^3 s_q \mathbf{b}_q \quad (4)$$

In eqn. (4) s_q is an integer with the property that $0 \leq s_q < N$. For convenience the reciprocity relation is given by

$$\langle \mathbf{a}_p, \mathbf{b}_q \rangle = \delta_{pq} 2\pi; p, q = 1, 2, 3 \tag{5}$$

As is well known eqn. (3) describes a unitary transformation. Moreover it readily follows from eqn. (3) that, in terms of the $\mathbf{E}(\mathbf{k}\kappa\alpha)$'s, the action of a space group operator $[\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(\mathbf{m})]$ is that of mapping the subspace spanned by $\{\mathbf{E}(\mathbf{k}\kappa\alpha)$; fixed $\mathbf{k}\}$ on to the one spanned by $\{\mathbf{E}(\mathbf{S}\mathbf{k}\kappa\alpha)\}$. The mapping is effected by the $3n \times 3n$ unitary matrix

$$\Gamma(\mathbf{k}; [\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(\mathbf{m})])_{\alpha\beta\kappa\kappa'} = \delta_{\kappa'F^{-1}(\kappa; \mathbf{S})} S_{\alpha\beta} \exp[i\mathbf{k} \cdot \{[\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(\mathbf{m})]^{-1}\mathbf{x}(\kappa) - \mathbf{x}(\kappa')\}] \tag{6}$$

where, in conformity with the notation of Maradudin and Vosko,⁶ $F^{-1}(\kappa; \mathbf{S})$ denotes the type of atom deposited at a κ -site. Note that $\Gamma(\mathbf{k})$ is periodic in \mathbf{k} -space with periods \mathbf{b}_i . Under pure translations eqn. 6 implies that $\{\mathbf{E}(\mathbf{k}\kappa\alpha)$; fixed $\mathbf{k}\}$ transforms as a multiple of the irreducible representation $[\mathbf{1}|\mathbf{x}(\mathbf{m})] \rightarrow \exp[-i\mathbf{k} \cdot \mathbf{x}(\mathbf{m})]$ of the abelian T. With the notation $\{\gamma_{\mathbf{k}}(\mathbf{m})\} = \{\exp[-i\mathbf{k} \cdot \mathbf{x}(\mathbf{m})]\}$ we can, bearing in mind the normality of T as a subgroup of G, define a little group $G_{\mathbf{k}}$ as that set of elements in G which leaves $\{\gamma_{\mathbf{k}}(\mathbf{m})\}$ invariant under conjugation. For $[\mathbf{S}|\mathbf{v}(\mathbf{S}) + \mathbf{x}(\mathbf{m})]$ to be in $G_{\mathbf{k}}$ one must have

$$\mathbf{S}\mathbf{k} - \mathbf{k} = \mathbf{K} \tag{7}$$

where \mathbf{K} is a general lattice vector in reciprocal space. Accordingly, $\mathbf{T} \in G_{\mathbf{k}}$. The orbit of $\{\gamma_{\mathbf{k}}(\mathbf{m})\}$ is generated by all elements in G whose rotational operator parts do not comply with eqn. (7). The assembly of all unique wave vectors generated by {S} from \mathbf{k} , the star of \mathbf{k} , specifies the orbit. In separating the cyclic lattice amplitude space into irreducible subspaces, one subspace per orbit, it is convenient to regard each irreducible representation of G as induced by an allowable representation of $G_{\mathbf{k}}$. On the practical level this is tantamount to first grouping $\{\mathbf{k}_s\}$ into stars, then selecting one \mathbf{k} per star, and, finally, decomposing each of the manifolds spanned by a selected $\{\mathbf{E}(\mathbf{k}\kappa\alpha)\}$ set into carrier spaces for irreducible representations of the associated $G_{\mathbf{k}}$. In the following we focus attention on special \mathbf{k} values, *i.e.* wave vectors the $G_{\mathbf{k}}$'s of which are not exhausted by T. In the past, the task of actually finding the appropriate subspaces in a $\{\mathbf{E}(\mathbf{k}\kappa\alpha)\}$ space has been considered a difficult problem if the crystal be nonsymmorphic. Even the quite recent and highly prominent book by Jansen and Boon⁷ recommends Herring's method,⁸ which is based on $G_{\mathbf{k}}/T_{\mathbf{k}}$ and engendering procedures, in cases where $G_{\mathbf{k}} \neq P_{\mathbf{k}} \otimes T$. In the foregoing sentence $T_{\mathbf{k}}$ stands for the subgroup of translations for which $\exp[-i\mathbf{k} \cdot \mathbf{x}(\mathbf{m})] = 1$ while, in adherence to common practice, $P_{\mathbf{k}}$ is the point group (isomorphic to) $G_{\mathbf{k}}/T$. However, taking refuge in multiplier representations one can always proceed *via* $P_{\mathbf{k}}$, thereby maintaining the simplicity of previously reserved cases wherein $G_{\mathbf{k}} = P_{\mathbf{k}} \otimes T$. The theory of multiplier (weighted) representations has been summarized briefly, yet with great clarity, by Liubarskii.⁹ The application of this tool in crystal dynamics has been expounded in detail by Maradudin and Vosko⁶ for an infinite lattice,

and by two of the present authors¹⁰ for a finite (cyclic) lattice. Suffice it here merely to note that if each coset in the expansion

$$G_{\mathbf{k}} = \{[\mathbf{S}_f | \mathbf{v}(\mathbf{S}_f)]\mathbf{T}\}; \mathbf{S}_f \mathbf{k} - \mathbf{k} = \mathbf{K} \quad (8)$$

be mapped on *one* matrix $\hat{I}(\mathbf{S}_f)$ according to

$$\hat{I}(\mathbf{S}_f) = I(\mathbf{k}; [\mathbf{S}_f | \mathbf{v}(\mathbf{S}_f)]) \exp [i\mathbf{k} \cdot \mathbf{v}(\mathbf{S}_f)] \quad (9)$$

then, as follows by direct computation, these matrices multiply according to

$$\begin{aligned} \hat{I}(\mathbf{S}_f) \hat{I}(\mathbf{S}_r) &= \hat{I}(\mathbf{S}_f \mathbf{S}_r) \exp [-i\mathbf{K}_f \cdot \mathbf{v}(\mathbf{S}_r)] \\ \mathbf{K}_f &= \mathbf{S}_f^{-1} \mathbf{k} - \mathbf{k} \end{aligned} \quad (10)$$

and so $\{\hat{I}(\mathbf{S}_f)\}$ furnishes a multiplier representation of $P_{\mathbf{k}}$ with $\exp [-i\mathbf{K}_f \cdot \mathbf{v}(\mathbf{S}_r)]$ as the required function on $P_{\mathbf{k}} \times P_{\mathbf{k}}$ to the complex numbers. Orthogonality properties, and thereby projection operator techniques, carry over from ordinary representation theory to multiplier representation formalism without essential modifications.⁹⁻¹⁰ Therefore, the construction of a similarity transformation which decomposes $\{\hat{I}(\mathbf{S}_f)\}$ into irreducible multiplier representations of $P_{\mathbf{k}}$ does not pose a difficult problem. It follows from eqns. (6) and (9) that the very same similarity transformation turns the linear manifold spanned by $\{I(\mathbf{k}; [\mathbf{S}_f | \mathbf{v}(\mathbf{S}_f) + \mathbf{x}(\mathbf{m})]); [\mathbf{S}_f | \mathbf{v}(\mathbf{S}_f) + \mathbf{x}(\mathbf{m})] \in G_{\mathbf{k}}\}$ into a direct sum of carrier spaces for irreducible representations (in the usual sense) of $G_{\mathbf{k}}$. Thus, the nonsymmorphic cases can be handled in a way that comes close to the treatment normally given to symmorphic crystals while using $G_{\mathbf{k}} = P_{\mathbf{k}} \otimes T$. This, in bare outline, is the crux of the multiplier approach underlying the results to be presented in the ensuing section as well as in future papers. It would appear from a recent review article and references contained therein¹¹ that awareness of the method is not, as yet, sufficiently widespread.

In closing this section we add to the already listed naming conventions by writing $\hat{I}(\mathbf{S}_f)$ as

$$\begin{aligned} \hat{I}(\mathbf{S}_f)_{\alpha\beta\kappa\kappa'} &= \delta_{\kappa'F^{-1}(\kappa; \mathbf{S}_f)} S_{f\alpha\beta} d_{\kappa}(\mathbf{S}_f) \\ d_{\kappa}(\mathbf{S}_f) &= \exp [i\mathbf{k} \cdot \{\mathbf{x}(\kappa) - \mathbf{S}_f \mathbf{x}(\kappa')\}] \end{aligned} \quad (11)$$

When preparing a table of symmetry coordinates intended to cover all crystals belonging to a given space group, it proves expedient to deviate slightly from the conventional κ -labeling of the unit cell contents. It is always possible to group the κ 's so that $F(\kappa; \mathbf{S})$ is in the same set as κ , whatever the value of κ . With each space group is associated a finite number of position types as is well known. For obvious reason it suffices to carry out the symmetry analysis *once* for each site set of a specific type separately. Accordingly, we introduce $d_j^{(r)}(\mathbf{S}_f)$, $\mathbf{R}_j^{(r)}$, $I^{(r)}$, and $\{\mathbf{E}_j^{(r)}(\mathbf{k}\alpha)\}$. Here $d_j^{(r)}(\mathbf{S}_f) = d_{\kappa}(\mathbf{S}_f)$ and $\mathbf{R}_j^{(r)} = \mathbf{x}(\kappa)$ for κ referring to the j^{th} member of some r -type position set. $I^{(r)}$ is, for fixed \mathbf{k} , the subspace spanned by $\{\mathbf{E}_j^{(r)}(\mathbf{k}\alpha)\}$. The latter symbol is short for a subset selected from $\{\mathbf{E}(\mathbf{k}\alpha)\}$ by letting α traverse all sites in an r -type set. A symmetry adapted orthonormal basis in a $I^{(r)}$ will be denoted $\{\mathbf{E}_p^{(r)}(\mathbf{k})\}$, while $\{\mathbf{E}_p(\mathbf{k})\}$ refers to $\mathbf{U}_r \{\mathbf{E}_p^{(r)}(\mathbf{k})\}$. Furthermore, we will adhere to Kovalev's numbering convention for wave vectors and group operators, while using also his tabulated matrix representation.¹²

SPACE GROUP $Pmn2_1 (C_{2v}')$

This space group belongs to the orthorhombic system. It is of class $mm2 (C_{2v})$ and has a vector group which is of the simple Bravais type. The fundamental periods in configuration space are

$$\mathbf{a}_1 = (2^1t_x, 0, 0); \mathbf{a}_2 = (0, 2^2t_y, 0); \mathbf{a}_3 = (0, 0, 2^3t_z)$$

with triplets referring to a rectangular coordinate system. Similarly, the basic vectors in reciprocal space can be taken as

$$\mathbf{b}_1 = \pi(1t_x^{-1}, 0, 0); \mathbf{b}_2 = \pi(0, 2t_y^{-1}, 0); \mathbf{b}_3 = \pi(0, 0, 3t_z^{-1})$$

G/T contains elements $\{S_1, S_4, S_{26}, S_{27}\}$, S_1 denoting the identity operation and

$$S_4 = 2[001], S_{26} = \bar{2}[100], S_{27} = \bar{2}[010],$$

that is

$$S_4 = \begin{Bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{Bmatrix}, S_{26} = \begin{Bmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{Bmatrix}, S_{27} = \begin{Bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{Bmatrix}$$

The corresponding nonprimitive translations are

$$\mathbf{v}(S_4) = (1t_x, 0, 3t_z); \mathbf{v}(S_{26}) = (0, 0, 0); \mathbf{v}(S_{27}) = \mathbf{v}(S_4)$$

There are two sets of symmetry equivalent positions, a general set comprising four sites

$$\begin{aligned} \mathbf{R}_1^{(1)} &= (x, y, z) & \mathbf{R}_2^{(1)} &= (\bar{x} + 1t_x, \bar{y}, z + 3t_z) \\ \mathbf{R}_3^{(1)} &= (x + 1t_x, \bar{y}, z + 3t_z); & \mathbf{R}_4^{(1)} &= (\bar{x}, y, z) \end{aligned}$$

and a special set consisting of two members

$$\mathbf{R}_1^{(2)} = (0, y, z) \qquad \mathbf{R}_2^{(2)} = (1t_x, \bar{y}, z + 3t_z)$$

Application of group operations generate mappings

$$\begin{aligned} [S_4 | \mathbf{v}(S_4)] \rightarrow & \begin{matrix} \mathbf{R}_1^{(1)} & \mathbf{R}_2^{(1)} & \mathbf{R}_3^{(1)} & \mathbf{R}_4^{(1)} & \mathbf{R}_1^{(2)} & \mathbf{R}_2^{(2)} \\ \mathbf{R}_2^{(1)} & \mathbf{R}_1^{(1)} & \mathbf{R}_4^{(1)} & \mathbf{R}_3^{(1)} & \mathbf{R}_2^{(2)} & \mathbf{R}_1^{(2)} \end{matrix} ; \\ [S_{26} | \mathbf{v}(S_{26})] \rightarrow & \begin{matrix} \mathbf{R}_1^{(1)} & \mathbf{R}_2^{(1)} & \mathbf{R}_3^{(1)} & \mathbf{R}_4^{(1)} & \mathbf{R}_1^{(2)} & \mathbf{R}_2^{(2)} \\ \mathbf{R}_4^{(1)} & \mathbf{R}_3^{(1)} & \mathbf{R}_2^{(1)} & \mathbf{R}_1^{(1)} & \mathbf{R}_1^{(2)} & \mathbf{R}_2^{(2)} \end{matrix} ; \\ [S_{27} | \mathbf{v}(S_{27})] \rightarrow & \begin{matrix} \mathbf{R}_1^{(1)} & \mathbf{R}_2^{(1)} & \mathbf{R}_3^{(1)} & \mathbf{R}_4^{(1)} & \mathbf{R}_1^{(2)} & \mathbf{R}_2^{(2)} \\ \mathbf{R}_3^{(1)} & \mathbf{R}_4^{(1)} & \mathbf{R}_1^{(1)} & \mathbf{R}_2^{(1)} & \mathbf{R}_2^{(2)} & \mathbf{R}_1^{(2)} \end{matrix} ; \end{aligned}$$

Having recorded some general information to be tacitly used in the following we now turn to amplitude subspaces labeled by \mathbf{k} -vectors the little-groups of which are not merely T .

Symmetry at $\mathbf{k}_1 = \mu_2 \mathbf{b}_2 + \mu_3 \mathbf{b}_3 = \pi(0, \mu_2^2 t_y^{-1}, \mu_3^3 t_z^{-1})$

$$P_{\mathbf{k}_1} = G_{\mathbf{k}_1} / \Gamma = \{S_1, S_{26}\}$$

$$I^{(1)} = 6\hat{\tau}_1 + 6\hat{\tau}_2; I^{(2)} = 4\hat{\tau}_1 + 2\hat{\tau}_2$$

$d_j^{(r)}(S_{26}) = 1$ for all r, j in question.

The obtained symmetry adapted wave combinations are for a set of special positions

${}^1\hat{\tau}_1$	${}^2\hat{\tau}_1$	${}^3\hat{\tau}_1$	${}^4\hat{\tau}_1$	${}^1\hat{\tau}_2$	${}^2\hat{\tau}_2$	$(j\alpha)$	
0	0	0	0	1	0	11	= $\{ES_p^{(2)}(\mathbf{k}_1)\}$
1	0	0	0	0	0	12	
0	1	0	0	0	0	13	
0	0	0	0	0	1	21	
0	0	1	0	0	0	22	
0	0	0	1	0	0	23	

As for the general set we have found

${}^1\hat{\tau}_1$	${}^2\hat{\tau}_1$	${}^3\hat{\tau}_1$	${}^4\hat{\tau}_1$	${}^5\hat{\tau}_1$	${}^6\hat{\tau}_1$	${}^1\hat{\tau}_2$	${}^2\hat{\tau}_2$	${}^3\hat{\tau}_2$	${}^4\hat{\tau}_2$	${}^5\hat{\tau}_2$	${}^6\hat{\tau}_2$	$(j\alpha)$	
0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	11	= $\{ES_p^{(1)}(\mathbf{k}_1)\}$
$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	12	
0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	13	
0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	21	
0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	22	
0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	23	
0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	31	
0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	32	
0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	33	
0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	41	
$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	42	
0	$\frac{\sqrt{2}}{2}$	0	0	0	0	0	$\frac{\sqrt{2}}{2}$	0	0	0	0	43	

The basis vectors have been written columnwise on component form with respect to $\{E_j^{(\alpha)}(\mathbf{k}_1, \alpha)\}$. The columns headed by $(j\alpha)$ indicate the sequence of the components with respect to site number and cartesian incremental coordinates. The same ordering being understood, such columns will be omitted when listing symmetry coordinates for other wave vectors.

Symmetry at $\mathbf{k}_2 = \frac{1}{2}\mathbf{b}_1 + \mu_2\mathbf{b}_2 + \mu_3\mathbf{b}_3 = (\frac{1}{2}{}^1t_x^{-1}, \mu_2{}^2t_y^{-1}, \mu_3{}^3t_z^{-1})$.

$$\begin{aligned} P_{\mathbf{k}_2} &= \{S_1, S_{26}\} \\ \Gamma^{(1)} &= 6\hat{\tau}_1 + 6\hat{\tau}_2; \quad \Gamma^{(2)} = 3\hat{\tau}_1 + 3\hat{\tau}_2 \\ d_1^{(1)} &= d_4^{(1)} = d_1^{(2)} = 1; \quad d_2^{(1)} = d_3^{(1)} = d_2^{(2)} = -1 \end{aligned}$$

Although $P_{\mathbf{k}_2}$ coincides with $P_{\mathbf{k}_1}$, note that the reducible representations differ. $\{ES_p^{(1)}(\mathbf{k}_2)\}$ can be obtained from $\{ES_p^{(1)}(\mathbf{k}_1)\}$ provided the heading is replaced by:

$${}^1\hat{\tau}_1 \quad {}^2\hat{\tau}_1 \quad {}^3\hat{\tau}_1 \quad {}^4\hat{\tau}_2 \quad {}^5\hat{\tau}_2 \quad {}^6\hat{\tau}_2 \quad {}^1\hat{\tau}_2 \quad {}^2\hat{\tau}_2 \quad {}^3\hat{\tau}_2 \quad {}^4\hat{\tau}_1 \quad {}^5\hat{\tau}_1 \quad {}^6\hat{\tau}_1$$

In the case of $\{ES_p^{(2)}(\mathbf{k}_2)\}$ we use likewise $\{ES_p^{(2)}(\mathbf{k}_1)\}$ with a renewed heading, viz.

$${}^1\hat{\tau}_1 \quad {}^2\hat{\tau}_1 \quad {}^2\hat{\tau}_2 \quad {}^3\hat{\tau}_2 \quad {}^1\hat{\tau}_2 \quad {}^3\hat{\tau}_1$$

Symmetry at $\mathbf{k}_3 = \mu_1\mathbf{b}_1 + \mu_3\mathbf{b}_3 = \pi(\mu_1{}^1t_x^{-1}, 0, \mu_3{}^3t_z^{-1})$.

$$\begin{aligned} P_{\mathbf{k}_3} &= \{S_1, S_{27}\} \\ \Gamma^{(1)} &= 6\hat{\tau}_1 + 6\hat{\tau}_2; \quad \Gamma^{(2)} = 3\hat{\tau}_1 + 3\hat{\tau}_2 \\ d_1^{(1)} &= d_4^{(1)} = d_1^{(2)} = \eta^*; \quad d_2^{(1)} = d_3^{(1)} = d_2^{(2)} = \eta = e^{i\pi(\mu_1 + \mu_3)} \end{aligned}$$

Defining $\sigma_{\pm} = \{2(1 \pm \cos(\pi[\mu_1 + \mu_3]))\}^{\frac{1}{2}-1}$ we can write for the complex valued symmetry coordinates (see p. 2584) and

$$\begin{array}{cccccc} {}^1\hat{\tau}_1 & {}^2\hat{\tau}_1 & {}^3\hat{\tau}_1 & {}^1\hat{\tau}_2 & {}^2\hat{\tau}_2 & {}^3\hat{\tau}_2 \\ \left[\begin{array}{cccccc} \sigma_+(1+\eta^*) & 0 & 0 & \sigma_-(1-\eta^*) & 0 & 0 \\ 0 & \sigma_-(1-\eta^*) & 0 & 0 & \sigma_+(1+\eta^*) & 0 \\ 0 & 0 & \sigma_+(1+\eta^*) & 0 & 0 & \sigma_-(1-\eta^*) \\ \sigma_+(1+\eta) & 0 & 0 & \sigma_-(1-\eta) & 0 & 0 \\ 0 & \sigma_-(1-\eta) & 0 & 0 & \sigma_+(1+\eta) & 0 \\ 0 & 0 & \sigma_+(1+\eta) & 0 & 0 & \sigma_-(1-\eta) \end{array} \right] = \{ES_p^{(2)}(\mathbf{k}_3)\} \end{array}$$

Symmetry at $\mathbf{k}_4 = \mu_1\mathbf{b}_1 + \frac{1}{2}\mathbf{b}_2 + \mu_3\mathbf{b}_3 = \pi(\mu_1{}^1t_x^{-1}, \frac{1}{2}{}^2t_y^{-1}, \mu_3{}^3t_z^{-1})$.
This case does not in any way differ from the preceding one.

Symmetry at $\mathbf{k}_9 = \mu_3\mathbf{b}_3 = \pi(0, 0, \mu_3{}^3t_z^{-1})$

$$\begin{aligned} P_{\mathbf{k}_9} &= \{S_1, S_4, S_{26}, S_{27}\} \\ \Gamma^{(1)} &= 3\hat{\tau}_1 + 3\hat{\tau}_2 + 3\hat{\tau}_3 + 3\hat{\tau}_4 \\ \Gamma^{(2)} &= 2\hat{\tau}_1 + \hat{\tau}_2 + 2\hat{\tau}_3 + \hat{\tau}_4 \end{aligned}$$

$1\tau_1$	$2\tau_1$	$3\tau_1$	$4\tau_1$	$5\tau_1$	$6\tau_1$	$1\tau_2$	$2\tau_2$	$3\tau_2$	$4\tau_2$	$5\tau_2$	$6\tau_2$
$\sigma_+(1+\eta^*)$	0	0	0	0	0	$\sigma_-(1-\eta^*)$	0	0	0	0	0
0	$\sigma_-(1-\eta^*)$	0	0	0	0	0	$\sigma_+(1+\eta^*)$	0	0	0	0
0	0	$\sigma_+(1+\eta^*)$	0	0	0	0	0	$\sigma_-(1-\eta^*)$	0	0	0
0	0	0	$\sigma_+(1+\eta)$	0	0	0	0	0	$\sigma_-(1-\eta)$	0	0
0	0	0	0	$\sigma_-(1-\eta)$	0	0	0	0	0	$\sigma_+(1+\eta)$	0
0	0	0	0	0	$\sigma_+(1+\eta)$	0	0	0	0	0	$\sigma_-(1-\eta)$
$\sigma_+(1+\eta)$	0	0	0	0	0	$\sigma_-(1-\eta)$	0	0	0	0	0
0	$\sigma_-(1-\eta)$	0	0	0	0	0	$\sigma_+(1+\eta)$	0	0	0	0
0	0	$\sigma_+(1+\eta)$	0	0	0	0	0	$\sigma_-(1-\eta)$	0	0	0
0	0	0	$\sigma_+(1+\eta^*)$	0	0	0	0	0	$\sigma_-(1-\eta^*)$	0	0
0	0	0	0	$\sigma_-(1-\eta^*)$	0	0	0	0	0	$\sigma_+(1+\eta^*)$	0
0	0	0	0	0	$\sigma_+(1+\eta^*)$	0	0	0	0	0	$\sigma_-(1-\eta^*)$

$= \{ES_p^{(1)}(k_{\sigma})\}$

$$\begin{aligned} d_1^{(1)}(S_4) &= d_4^{(1)}(S_4) = d_1^{(1)}(S_{27}) = d_4^{(1)}(S_{27}) = d_1^{(2)}(S_4) = d_1^{(2)}(S_{27}) \\ &= \eta^*; d_2^{(1)}(S_4) = d_3^{(1)}(S_4) = d_2^{(1)}(S_{27}) = d_3^{(1)}(S_{27}) = d_2^{(2)}(S_4) \\ &= d_2^{(2)}(S_{27}) = \eta = e^{i\pi\mu_3}; d_1^{(1)}(S_{26}) = d_2^{(1)}(S_{26}) = d_3^{(1)}(S_{26}) \\ &= d_4^{(1)}(S_{26}) = d_1^{(2)}(S_{26}) = d_2^{(2)}(S_{26}) = 1 \end{aligned}$$

With the adjusted definition $\sigma_{\pm} = \{2(2 \pm 2 \cos(\pi\mu_3))\}^{\frac{1}{2}}^{-1}$ we obtain this time for the general set (see p. 2586) and with $\sigma_{\pm} = \{2(1 \pm \cos(\pi\mu_3))\}^{\frac{1}{2}}^{-1}$ for the special set

${}^1\hat{\tau}_1$	${}^2\hat{\tau}_1$	${}^1\hat{\tau}_2$	${}^1\hat{\tau}_3$	${}^2\hat{\tau}_3$	${}^1\hat{\tau}_4$	
$\left[\begin{array}{cccccc} 0 & 0 & \sigma_-(1-\eta^*) & 0 & 0 & \sigma_+(1+\eta^*) \\ \sigma_-(1-\eta^*) & 0 & 0 & \sigma_+(1+\eta^*) & 0 & 0 \\ 0 & \sigma_+(1+\eta^*) & 0 & 0 & \sigma_-(1-\eta^*) & 0 \\ 0 & 0 & \sigma_-(1-\eta) & 0 & 0 & \sigma_+(1+\eta) \\ \sigma_-(1-\eta) & 0 & 0 & \sigma_+(1+\eta) & 0 & 0 \\ 0 & \sigma_+(1+\eta) & 0 & 0 & \sigma_-(1-\eta) & 0 \end{array} \right] = \{ES_p^{(2)}(\mathbf{k}_9)\}$						

Symmetry at $\mathbf{k}_{18} = \frac{1}{2}\mathbf{b}_2 + \mu_3\mathbf{b}_3 = \pi(0, \frac{1}{2}{}^2t_y^{-1}, 3{}^3t_z^{-1})$.
 Here the \mathbf{k}_9 -results carry over without modification.
 Symmetry at $\mathbf{k}_{16} = \frac{1}{2}\mathbf{b}_1 + \mu_3\mathbf{b}_3 = \pi(\frac{1}{2}{}^1t_x^{-1}, 0, \mu_3{}^3t_z^{-1})$.

$$P_{\mathbf{k}_{16}} = \{S_1, S_4, S_{16}, S_{27}\}$$

$$\Gamma^{(1)} = 6\hat{\tau}; \Gamma^{(2)} = 3\hat{\tau}, \text{ where } \hat{\tau} \text{ is two-dimensional}$$

$$\begin{aligned} d_1^{(1)}(S_4) &= d_4^{(1)}(S_4) = d_1^{(2)}(S_4) = \eta = ie^{-i\pi\mu_3} \\ d_2^{(1)}(S_4) &= d_3^{(1)}(S_4) = d_2^{(2)}(S_4) = -\eta^* \\ d_1^{(1)}(S_{26}) &= d_4^{(1)}(S_{26}) = d_1^{(2)}(S_{26}) = 1 \\ d_2^{(1)}(S_{26}) &= d_3^{(1)}(S_{26}) = d_2^{(2)}(S_{26}) = -1 \\ d_1^{(1)}(S_{27}) &= d_4^{(1)}(S_{27}) = d_1^{(2)}(S_{27}) = -\eta \\ d_2^{(1)}(S_{27}) &= d_3^{(1)}(S_{27}) = d_2^{(2)}(S_{27}) = -\eta^* \end{aligned}$$

Leaving unaltered the meaning of σ_{\pm} the symmetry coordinates can be taken as shown on p. 2587 and

${}^1\hat{\tau}(1)$	${}^2\hat{\tau}(1)$	${}^3\hat{\tau}(1)$	${}^1\hat{\tau}(2)$	${}^2\hat{\tau}(2)$	${}^3\hat{\tau}(2)$	
$\left[\begin{array}{cccccc} \sigma_+(1-i\eta) & 0 & 0 & \sigma_+(\bar{1}+i\eta) & 0 & 0 \\ 0 & \sigma_+(1-i\eta) & 0 & 0 & \sigma_+(1-i\eta) & 0 \\ 0 & 0 & \sigma_-(1+i\eta) & 0 & 0 & \sigma_-(1+i\eta) \\ \sigma_+(1+i\eta^*) & 0 & 0 & \sigma_+(1+i\eta^*) & 0 & 0 \\ 0 & \sigma_+(1+i\eta^*) & 0 & 0 & \sigma_+(\bar{1}-i\eta^*) & 0 \\ 0 & 0 & \sigma_-(1-i\eta^*) & 0 & 0 & \sigma_-(\bar{1}+i\eta^*) \end{array} \right] = \{ES_p^{(2)}(\mathbf{k}_{16})\}$						

${}^1\hat{r}_1$	${}^2\hat{r}_1$	${}^3\hat{r}_1$	${}^1\hat{r}_2$	${}^2\hat{r}_2$	${}^3\hat{r}_2$	${}^1\hat{r}_3$	${}^2\hat{r}_3$	${}^3\hat{r}_3$	${}^1\hat{r}_4$	${}^2\hat{r}_4$	${}^3\hat{r}_4$
$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$
$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1+\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1-\eta) \\ 0 \end{matrix}$
$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta) \\ 0 \end{matrix}$
$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1-\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1-\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1-\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} \sigma_-(1+\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} \sigma_+(1+\eta^*) \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_-(1+\eta^*) \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ \sigma_+(1-\eta^*) \\ 0 \end{matrix}$

= {ES_p⁽¹⁾(k_g)}

${}^1\mathcal{F}_{(1)}$	${}^2\mathcal{F}_{(1)}$	${}^3\mathcal{F}_{(1)}$	${}^4\mathcal{F}_{(1)}$	${}^5\mathcal{F}_{(1)}$	${}^6\mathcal{F}_{(1)}$	${}^1\mathcal{F}_{(2)}$	${}^2\mathcal{F}_{(2)}$	${}^3\mathcal{F}_{(2)}$	${}^4\mathcal{F}_{(2)}$	${}^5\mathcal{F}_{(2)}$	${}^6\mathcal{F}_{(2)}$
$\sigma_+(1-i\eta)$	0	0	0	0	0	0	0	0	$\sigma_+(\bar{1}+i\eta)$	0	0
0	$\sigma_+(1-i\eta)$	0	0	0	0	0	0	0	0	$\sigma_+(1-i\eta)$	0
0	0	$\sigma_-(1+i\eta)$	0	0	0	0	0	0	0	0	$\sigma_-(1+i\eta)$
$\sigma_+(1+i\eta^*)$	0	0	0	0	0	0	0	0	$\sigma_+(1+i\eta^*)$	0	0
0	$\sigma_+(1+i\eta^*)$	0	0	0	0	0	0	0	0	$\sigma_+(\bar{1}+i\eta^*)$	0
0	0	$\sigma_-(1-i\eta^*)$	0	0	0	0	0	0	0	0	$\sigma_-(\bar{1}+i\eta^*)$
0	0	0	$\sigma_+(1+i\eta^*)$	0	0	$\sigma_+(1+i\eta^*)$	0	0	0	0	0
0	0	0	0	$\sigma_+(1+i\eta^*)$	0	0	$\sigma_+(\bar{1}-i\eta^*)$	0	0	0	0
0	0	0	0	0	$\sigma_-(1-i\eta^*)$	0	0	$\sigma_-(\bar{1}+i\eta^*)$	0	0	0
0	0	0	$\sigma_+(1-i\eta)$	0	0	$\sigma_+(\bar{1}+i\eta)$	0	0	0	0	0
0	0	0	0	$\sigma_+(1-i\eta)$	0	0	$\sigma_+(1-i\eta)$	0	0	0	0
0	0	0	0	0	$\sigma_-(1+i\eta)$	0	0	$\sigma_-(1+i\eta)$	0	0	0

= $\{\mathbf{E}_p^{(1)}\mathbf{k}_a\}$. Integers in brackets '(1), (2)' label the basis vectors of the carrier space.

Symmetry at $\mathbf{k}_{17} = \frac{1}{2}\mathbf{b}_1 + \frac{1}{2}\mathbf{b}_2 + \mu_3\mathbf{b}_3 = \pi(\frac{1}{2}^1t_x^{-1}, \frac{1}{2}^2t_y^{-1}, \mu_3^3t_z^{-1})$.
 In this case the \mathbf{k}_{16} Γ decompositions and wave combinations apply.

Connection with free molecule symmetry coordinates. In closing this section it seems worth mentioning that the $\{\mathbf{ES}_p^{(v)}(\mathbf{k}_1)\}$ tables also serve as suitable (external) symmetry coordinates for all free molecules with symmetry $mm2$ (C_{2v}).

CHOICE OF MOLECULAR LATTICE BASIS

From a group theoretical viewpoint there is no essential distinction between "atomic" and "molecular" crystals. The atomic mode of description admits symmetry information to be condensed in finite tables, and is in our opinion the better choice for tabulation purposes. On the other hand, given a crystal and evidence to the effect that chemically characteristic clusters of atoms display a considerable measure of independence, then a molecule oriented depiction of crystal space events would seem warranted. For the sake of future convenience in relating the solid state behaviour of molecules to their gaseous performances we list the following formulae and notation rules. Let n_m be the number of molecules in a unit cell and n_a^q the number of atoms in the q^{th} molecule, *i.e.* $n = \sum_{q=1}^{n_m} n_a^q$. Let furthermore \mathbf{x}_q be the $3n_a^q$ -tuple specifying massweighted cartesian displacements of the atoms of the q^{th} molecule in the crystal fixed frame, \mathbf{s}_q^i be a $(3n_a^q - 6)$ -tuple forming a suitable set of internal coordinates, and \mathbf{s}_q^e be a 6-tuple making up the mass-weighted Eckart coordinates of the q^{th} molecule. Then, whatever frame be used in specifying \mathbf{s}_q^i and \mathbf{s}_q^e , we are at liberty to write

$$\mathbf{x}_q = \mathbf{A}^q \mathbf{s}_q, \mathbf{s}_q = \begin{bmatrix} \mathbf{s}_q^i \\ \mathbf{s}_q^e \end{bmatrix} \quad (12)$$

where the rightmost six columns of the $3n_a^q \times 3n_a^q$ matrix \mathbf{A}^q relate to the Eckart coordinates. We now change lattice basis from $\{\mathbf{E}(\mathbf{k}\alpha)\}$ to $\{\mathbf{E}_m(\mathbf{k}q\mathbf{s})\}$, the latter being defined by

$$\mathbf{E}_m(\mathbf{k}q\mathbf{s}) = \sum_{i=1}^{3n_a^q} A_{is}^q \mathbf{E}(\mathbf{k}i) \quad (13)$$

where i refers to $\alpha\alpha$ pairs of molecule q . If \mathbf{E}^k be a $3n$ -coordinate-tuple relating to $\{\mathbf{E}(\mathbf{k}\alpha\alpha); \text{fixed } \mathbf{k}\}$ and \mathbf{E}_m^k the one pertaining to $\{\mathbf{E}_m(\mathbf{k}q\mathbf{s}); \text{fixed } \mathbf{k}\}$ then

$$\mathbf{E}^k = \mathbf{A} \mathbf{E}_m^k \quad (14)$$

with the $3n \times 3n$ \mathbf{A} being determined in terms of $\{\mathbf{A}^q\}$ to within the latitude associated with alternative ordering of basis vectors in the two sets involved. Deceeing that the matrix $\mathbf{ES}(\mathbf{k})$ be defined according to

$$\mathbf{ES}_p(\mathbf{k}) = \sum_{i=1}^{3n} \mathbf{ES}(\mathbf{k})_{ip} \mathbf{E}(\mathbf{k}i) \quad (15)$$

then the $3n$ -coordinate-tuple \mathbf{ES}^k relative to $\{\mathbf{ES}_p(\mathbf{k}); \text{fixed } \mathbf{k}\}$ is obtainable from

$$\mathbf{E}^k = \mathbf{ES}(\mathbf{k})\mathbf{ES}^k \quad (16)$$

while \mathbf{ES}^k and \mathbf{E}_m^k are connected through

$$\mathbf{ES}^k = \mathbf{ES}(\mathbf{k})^{-1} \mathbf{A} \mathbf{E}_m^k \quad (17)$$

If $G_k = T$, then obviously $\mathbf{ES}(\mathbf{k})$ can be identified with $\mathbf{1}$. It is clear that rigid-body translations, or infinitesimal rotations, of molecules comprising a lattice constitute an amplitude subspace which is stable under G . Accordingly, the basis vectors of the two manifolds involved can be enumerated so as to yield an $\mathbf{ES}(\mathbf{k})^{-1} \mathbf{A}$ composed of three blocks along the diagonal, one associated with symmetrized lattice waves of internal molecular deformation, the others with wave propagation of rigid-body displacements. In other words, internal motion, rigid-body translations, and rigid-body and practically commuting rotations can be symmetry analyzed separately.¹³ Apart from this, no special structure can generally be attributed to $\mathbf{ES}(\mathbf{k})^{-1} \mathbf{A}$. If we denote by $\mathbf{D}_m(\mathbf{k})$ the $3n \times 3n$ Fourier transformed dynamical matrix relative to $\{\mathbf{E}_m(\mathbf{k}\alpha\beta); \text{fixed } \mathbf{k}\}$ and by $\mathbf{D}(\mathbf{k})$ its $\{\mathbf{E}(\mathbf{k}\alpha\alpha); \text{fixed } \mathbf{k}\}$ -basis counterpart, we have

$$\mathbf{D}_m(\mathbf{k}) = \mathbf{A}^{-1} \mathbf{D}(\mathbf{k}) \mathbf{A} \quad (18)$$

The symmetry transform, *i.e.* the dynamical matrix relative to $\{\mathbf{ES}_p(\mathbf{k}); \text{fixed } \mathbf{k}\}$, reads

$$\mathbf{DS}(\mathbf{k}) = \mathbf{ES}(\mathbf{k})^{-1} \mathbf{D}(\mathbf{k}) \mathbf{ES}(\mathbf{k}) \quad (19)$$

or

$$\mathbf{DS}(\mathbf{k}) = \mathbf{ES}(\mathbf{k})^{-1} \mathbf{A} \mathbf{D}_m(\mathbf{k}) \mathbf{A}^{-1} \mathbf{ES}(\mathbf{k}) \quad (20)$$

A final comment on $\mathbf{ES}(\mathbf{k})$, \mathbf{A}^q , and \mathbf{A} is in order. For practical reasons we consider a nondiagonal metric tensor to be a nuisance in a Brillouin zone treatment if n be large. Accordingly, we shall henceforth assume $\mathbf{ES}(\mathbf{k})$, \mathbf{A}^q , and \mathbf{A} to be unitary unless stated otherwise. This convention violates somewhat the normal practice of molecular spectroscopy. To take into account the characteristic features of molecular structure it is customary in dealing with gaseous molecules to adopt coordinates frequently involving a nondiagonal metric tensor the inverse of which is invariably known as Wilson's \mathbf{G} matrix. We would be in remiss not to mention that similar choices of coordinates have been advocated also for molecular crystals.¹⁴⁻¹⁶ However, although occasionally imposing reference states for internal deformations which are difficult to visualize, our restriction on \mathbf{A}^q and \mathbf{A} in no way precludes efficient use of data on free molecules in constructing crystal force fields.

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