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# Self-Terms of Intermolecular Force Constants

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The self-terms of the intermolecular force constants are derived by employing the condition of translation invariance. The self-terms thus obtained ensure that the dynamical matrices of the crystal are always Hermitian. The role of the condition of rotation invariance is discussed. The expressions for the self-terms differ in part from those published by Dolling, Pawley & Powell [*Proc. Roy. Soc.* (1973). A**333**, 363–384]. The conditions under which the self-terms of these authors are identical with the present ones are discussed.

## 1. Introduction

In a recent paper Dolling, Pawley & Powell (1973) – hereafter referred to as DPP – published expressions for the so-called 'self-terms' of intermolecular force constants. For a molecular crystal the self-term force-constant matrix is a 6×6 matrix which can be written in the form

$$\boldsymbol{\varphi}_{66}=\begin{pmatrix}\boldsymbol{\varphi}_t & \boldsymbol{\varphi}^1_{\text{corr}}\\ \boldsymbol{\varphi}^2_{\text{corr}} & \boldsymbol{\varphi}_{\text{rot}}\end{pmatrix}, \qquad (1)$$

where $\boldsymbol{\varphi}_t$, $\boldsymbol{\varphi}_{\text{rot}}$, $\boldsymbol{\varphi}^1_{\text{corr}}$, $\boldsymbol{\varphi}^2_{\text{corr}}$ are of order 3×3 and refer to translation, rotation and correlation (of translation and rotation). DPP state that they derive the self-term matrices $\boldsymbol{\varphi}_t$ and $\boldsymbol{\varphi}^2_{\text{corr}}$ from the condition of translation invariance, and $\boldsymbol{\varphi}^1_{\text{corr}}$ and $\boldsymbol{\varphi}_{\text{rot}}$ from the condition of rotation invariance; the derivation itself is not given. DPP further remark that the blocks $\boldsymbol{\varphi}^1_{\text{corr}}$ and $\boldsymbol{\varphi}_{\text{rot}}$ of $\boldsymbol{\varphi}_{66}$ may become asymmetric, particularly when the crystal symmetry is low, so that the dynamical matrices of the crystal will no longer be Hermitian. In this situation DPP propose additional constraints on the force constants in order to guarantee that the dynamical matrices are Hermitian.

In this paper we shall rederive the self-terms of the intermolecular force constants. We shall show that

(1) simpler expressions for $\boldsymbol{\varphi}^1_{\text{corr}}$ and $\boldsymbol{\varphi}_{\text{rot}}$ can be obtained when only the condition of translation invariance is used, and that these expressions ensure that the dynamical matrices of the crystal are always Hermitian;

(2) the self-term matrices $\boldsymbol{\varphi}^1_{\text{corr}}$ and $\boldsymbol{\varphi}_{\text{rot}}$, obtained with the aid of the condition of translation invariance, are equal to DPP's expressions only when the condition of rotation invariance is imposed on the interatomic force constants used.

## 2. Derivation of the self-terms

The concept which we shall use in the following consists of treating the molecular crystal as an atomic crystal. We express the intermolecular forces through the interatomic forces which occur among the atoms of different molecules, and we exclude the interatomic forces which occur among the atoms of one and the same molecule. This procedure is advantageous in that we can introduce the conditions which are well known to hold for the interatomic force constants into our consideration and thus derive corresponding conditions for the intermolecular force constants.

First, we recall the conditions which hold for the interatomic force constants which are important for our consideration. In a preceding paper (Scheringer, 1974) we showed that the sums

$$\tfrac{1}{2}[\boldsymbol{\Phi}(lkr,l'k'r')+\boldsymbol{\Phi}^T(l'k'r',lkr)]\equiv\boldsymbol{\varphi}(lkr,l'k'r') \qquad (2a)$$

enter into the dynamical matrices of the crystal, but not into the single interatomic force-constant matrices $\boldsymbol{\Phi}(lkr,l'k'r')$. $l,l'$ denote the cells in the crystal; $k,k'$ the molecules in the cell; and $r,r'$ the atoms in the molecule. The superscript $T$ denotes the transposed matrix. With the definition (2*a*) the relation

$$\boldsymbol{\varphi}(lkr,l'k'r')=\boldsymbol{\varphi}^T(l'k'r',lkr) \qquad (2b)$$

is valid for any force-constant matrix $\boldsymbol{\Phi}(lkr,l'k'r')$. (2*b*) ensures that the dynamical matrices are Hermitian. For the cases $l'k'\neq lk$ the force constants are calculated as the second derivatives of the potential energy of the crystal, and hence the corresponding relation holds for the force constants, namely

$$\boldsymbol{\Phi}(lkr,l'k'r')=\boldsymbol{\Phi}^T(l'k'r',lkr)\,,\quad l'k'r'\neq lkr\,, \qquad (3)$$

whereby the sum (2*a*) reduces. The self-term matrix $\boldsymbol{\Phi}(lkr,lkr)$, however, is not calculated as the second derivative of the crystal potential, and thus the symmetry relation (3) cannot be applied. The self-terms are obtained from the condition of translation invariance as

$$\tfrac{1}{2}[\boldsymbol{\Phi}(lkr,lkr)+\boldsymbol{\Phi}^T(lkr,lkr)]=\boldsymbol{\varphi}(lkr,lkr)$$
$$=-\sum_{l'k'r'}{}'\boldsymbol{\Phi}\,(lkr,l'k'r')\,, \qquad (4)$$

*cf.* Martin [1971, equation (8)]. In $\sum'$ the term $l'k'r'=lkr$ is excluded. The condition of translation invariance, on the one hand, operates as the definition of the self-terms $\boldsymbol{\varphi}(lkr,lkr)$ and, on the other hand, imposes a symmetry condition on the interatomic force constants which are used on the right-hand side of (4) (the left-hand side is always symmetric). We express this symmetry condition separately by writing

$$\sum_{l'k'r'}{}' \boldsymbol{\Phi}(lkr,l'k'r') = \sum_{l'k'r'}{}' \boldsymbol{\Phi}^T(lkr,l'k'r') . \tag{5}$$

Equation (5) is always fulfilled for axially symmetric forces which depend only on the magnitude of the separation of the atoms $lkr$ and $l'k'r'$, *cf.* Maradudin, Montroll & Weiss [1963, equation (2.1.20)].

Now we take into account the fact that we treat a molecular crystal. Only interactions among atoms of different molecules are important for the intermolecular force constants. Thus we have to exclude intramolecular interactions. We can do this by writing

$$\boldsymbol{\Phi}(lkr,lkr') = \mathbf{0}, \boldsymbol{\varphi}(lkr,lkr') = \mathbf{0}, r' \neq r . \tag{6}$$

For the molecular crystal we write the intermolecular force constants by analogy with (1), in the form of a $6\times 6$ matrix

$$\boldsymbol{\Phi}_{66}(lk,l'k') = \begin{pmatrix} \boldsymbol{\Phi}_t(lk,l'k') & \boldsymbol{\Phi}^1_{\rm corr}(lk,l'k') \\ \boldsymbol{\Phi}^2_{\rm corr}(lk,l'k') & \boldsymbol{\Phi}_{\rm rot}(lk,l'k') \end{pmatrix} . \tag{7}$$

As for the atomic crystal, in the dynamical matrices of the molecular crystal only the sums

$$\tfrac{1}{2}[\boldsymbol{\Phi}_{66}(lk,l'k') + \boldsymbol{\Phi}^T_{66}(l'k',lk)] \equiv \boldsymbol{\varphi}_{66}(lk,l'k') \tag{8a}$$

occur, and not the single force-constant matrices $\boldsymbol{\Phi}_{66}(lk,l'k')$. The proof of this statement is fully analogous to that for atomic crystals, *cf.* Scheringer (1974). $\boldsymbol{\varphi}_{66}$ decomposes into the four $3\times 3$ submatrices $\boldsymbol{\varphi}_t, \boldsymbol{\varphi}^1_{\rm corr}, \boldsymbol{\varphi}^2_{\rm corr}, \boldsymbol{\varphi}_{\rm rot}$. With equation (7) and the definition (8*a*) we have for $\boldsymbol{\varphi}^1_{\rm corr}$ and $\boldsymbol{\varphi}^2_{\rm corr}$

$$\boldsymbol{\varphi}^1_{\rm corr}(lk,l'k') = \tfrac{1}{2}[\boldsymbol{\Phi}^1_{\rm corr}(lk,l'k') + \boldsymbol{\Phi}^{2T}_{\rm corr}(l'k',lk)] , \tag{8b}$$

$$\boldsymbol{\varphi}^2_{\rm corr}(lk,l'k') = \tfrac{1}{2}[\boldsymbol{\Phi}^2_{\rm corr}(lk,l'k') + \boldsymbol{\Phi}^{1T}_{\rm corr}(l'k',lk)] . \tag{8c}$$

With the definition (8*a*) the relation

$$\boldsymbol{\varphi}_{66}(lk,l'k') = \boldsymbol{\varphi}^T_{66}(l'k',lk) \tag{9}$$

holds for any force-constant matrix $\boldsymbol{\Phi}_{66}(lk,l'k')$. Equation (9) ensures that the dynamical matrices of a molecular crystal are always Hermitian. For the self-terms, $l'k'=lk$, (9) reduces to the symmetry relation $\boldsymbol{\varphi}_{66} = \boldsymbol{\varphi}^T_{66}$. Thus, as for the atomic crystal, the result for the molecular crystal holds that we need not (and are not able to) determine the self-term force-constant matrices $\boldsymbol{\Phi}_{66}(lk,lk)$, but only the symmetric matrices $\boldsymbol{\varphi}_{66}(lk,lk)$.

The intermolecular force-constants, expressed in terms of the interatomic force constants, were given by Hahn & Biem (1963), Venkataraman & Sahni (1970), DPP, and Scheringer (1973). Here, we use the matrix representation of our earlier paper. The $3\times 3$ matrices in $\boldsymbol{\Phi}_{66}$ of equation (7) have the form

$$\boldsymbol{\Phi}_t(lk,l'k') = \sum_{rr'} \boldsymbol{\Phi}(lkr,l'k'r') , \tag{10a}$$

$$\boldsymbol{\Phi}^1_{\rm corr}(lk,l'k') = \sum_{rr'} \boldsymbol{\Phi}(lkr,l'k'r')\, \mathbf{V}^T_{r'}(l'k') , \tag{10b}$$

$$\boldsymbol{\Phi}^2_{\rm corr}(lk,l'k') = \sum_{rr'} \mathbf{V}_r(lk)\boldsymbol{\Phi}(lkr,l'k'r') , \tag{10c}$$

$$\boldsymbol{\Phi}_{\rm rot}(lk,l'k') = \sum_{rr'} \mathbf{V}_r(lk)\boldsymbol{\Phi}(lkr,l'k'r')\mathbf{V}^T_{r'}(l'k') . \tag{10d}$$

The matrix $\mathbf{V}_r(lk)$ contains the Cartesian coordinates of the atom $r$ in the molecule $lk$, referred to an arbitrary molecular origin, in the form of the antisymmetric tensor

$$\mathbf{V}_r(lk) = \begin{pmatrix} 0 & -Z & Y \\ Z & 0 & -X \\ -Y & X & 0 \end{pmatrix}_{r(lk)} . \tag{11}$$

Equations (10) hold only for the cases $l'k' \neq lk$. If we insert the symmetry relation (3) for the interatomic force constants into the equation (10) for the intermolecular force constants, we obtain the analogous result, namely

$$\boldsymbol{\Phi}_{66}(lk,l'k') = \boldsymbol{\Phi}^T_{66}(l'k',lk),\ l'k' \neq lk , \tag{12a}$$

and, in particular

$$\boldsymbol{\Phi}^1_{\rm corr}(lk,l'k') = \boldsymbol{\Phi}^{2T}_{\rm corr}(l'k',lk) , \tag{12b}$$

$$\boldsymbol{\Phi}^2_{\rm corr}(lk,l'k') = \boldsymbol{\Phi}^{1T}_{\rm corr}(l'k',lk) . \tag{12c}$$

Equations (12) can also be obtained from the definition of the intermolecular force constants as the second derivatives of the potential energy of a molecular crystal with respect to the translation and libration amplitudes, *cf.* Pawley [1967, equation (3)]. With (12) $\boldsymbol{\varphi}_{66}(lk,l'k')$ reduces to $\boldsymbol{\Phi}_{66}(lk,l'k')$ so that the formulation (8) is not relevant for the cases $l'k' \neq lk$. For the self-terms $l'k'=lk$, however, (8) is important since we cannot determine the single matrices $\boldsymbol{\Phi}_{66}(lk,lk)$.

In order to derive the self-terms of the intermolecular force constants we substitute the force-constant matrices $\boldsymbol{\varphi}$ for the corresponding matrices $\boldsymbol{\Phi}$ in (10). Obviously equations (10) for the intermolecular force-constants remain unaltered in type with this procedure. We now apply the new equations (10) in order to calculate the self-terms $l'k'=lk$. By virtue of (6) [exclusion of intramolecular interactions] the double summation over $rr'$ reduces to a single summation over $r$. Then we apply the condition (4) of translation invariance whereby the double summation over $rr'$ is introduced again. This enables us to express the results in terms of the intermolecular force constants (10). With $\boldsymbol{\varphi}^1_{\rm corr}$ we then have to apply the symmetry condition (5) of translation invariance and (12*c*). Thus we obtain

$$\boldsymbol{\varphi}_t(lk,lk) = \sum_r \boldsymbol{\varphi}(lkr,lkr) = -\sum_{rr'} \sum_{l'k'}{}' \boldsymbol{\Phi}(lkr,l'k'r')$$

$$= -\sum_{l'k'}{}' \boldsymbol{\Phi}_t(lk,l'k') , \tag{13a}$$

$$\boldsymbol{\varphi}^1_{\rm corr}(lk,lk) = \sum_r \boldsymbol{\varphi}(lkr,lkr)\mathbf{V}^T_r(lk)$$

$$= -\sum_{rr'} \sum_{l'k'}{}' \boldsymbol{\Phi}(lkr,l'k'r')\mathbf{V}^T_r(lk) \tag{13b}$$

$$= -\sum_{l'k'}{}' \boldsymbol{\Phi}^1_{\rm corr}(l'k',lk) = -\sum_{l'k'}{}' \boldsymbol{\Phi}^{2T}_{\rm corr}(lk,l'k') ,$$

$$\boldsymbol{\varphi}^2_{\rm corr}(lk,lk)=\sum_r \mathbf{V}_r(lk)\boldsymbol{\varphi}'(lkr,lkr)$$

$$=-\sum_{l'k'}{}' \boldsymbol{\Phi}^2_{\rm corr}(lk,l'k')\,, \qquad (13c)$$

$$\boldsymbol{\varphi}_{\rm rot}(lk,lk)=\sum_r \mathbf{V}_r(lk)\boldsymbol{\varphi}'(lkr,lkr)\mathbf{V}^T_r(lk)$$

$$=-\sum_{l'k'}{}' \sum_{rr'} \mathbf{V}_r(lk)\boldsymbol{\Phi}(lkr,l'k'r')\mathbf{V}^T_r(lk)$$

$$\neq -\sum_{l'k'}{}' \boldsymbol{\Phi}_{\rm rot}(lk,l'k')\,. \qquad (13d)$$

Obviously the self-terms (13) satisfy the symmetry relation (9) since the matrices $\boldsymbol{\varphi}'(lkr,lkr)$ are symmetric, thus giving rise to dynamical matrices which are Hermitian. For the self-terms $\boldsymbol{\varphi}_t$ and $\boldsymbol{\varphi}^2_{\rm corr}$ we obtain a result which is formally analogous to the result for the self-terms of atomic crystals, *cf.* (13*a*) and (13*c*) with (4). The rotational self-term $\boldsymbol{\varphi}_{\rm rot}$ differs in structure from the other self-terms. We have stressed this by writing the inequality (13*d*). The result (13*d*) ensures that, for a crystal with one molecule in the unit cell, three rotational frequencies are obtained for the wave vector $\mathbf{q}=\mathbf{0}$ which are greater than zero.

## 3. The role of rotation invariance

Now we shall investigate the role rotation invariance plays with respect to the self-terms. We begin with the condition of rotation invariance for atomic crystals. We assume that the atoms are located in their equilibrium positions. Then some terms vanish in the equation for the condition of rotation invariance; these are often given in the literature. (We have already made this assumption throughout this paper since the interatomic force constants are defined as second derivatives of the crystal potential only when we make this assumption.)

There are several formulations for the condition of rotation invariance which differ in how the origin for the rotation of the crystal is chosen. Let us generally denote this origin by $\mathbf{V}_0$ and let the position of the molecule $lk$ in the crystal be $\mathbf{V}(lk)$, then the condition of rotation invariance reads

$$\sum_{l'k'r'} \boldsymbol{\varphi}(lkr,l'k'r')[\mathbf{V}^T(l'k')+\mathbf{V}^T_{r'}(l'k')-\mathbf{V}^T_0]=\mathbf{0}\,. \qquad (14)$$

[$\mathbf{V}(l'k')+\mathbf{V}_{r'}(l'k')$ is then the position of the atom $l'k'r'$ in the crystal.] For the choice of the rotation origin $\mathbf{V}_0$ of the crystal three cases are interesting:

$$\mathbf{V}_0=\mathbf{0}\,, \qquad (15a)$$

$$\mathbf{V}_0=\mathbf{V}(lk)\,, \qquad (15b)$$

$$\mathbf{V}_0=\mathbf{V}(lk)+\mathbf{V}_r(lk)\,. \qquad (15c)$$

The three formulations (15*a*), (15*b*) and (15*c*) of equation (14) are equivalent and can be transformed into each other by applying the condition of translation invariance. For $\mathbf{V}_0$ does not depend on $l'k'r'$, and we can place the $\mathbf{V}_0$ term in equation (14) in front of the sum. For this part of equation (14) we obtain

$$\mathbf{V}_0 \sum_{l'k'r'} \boldsymbol{\varphi}(lkr,l'k'r')=\mathbf{0} \qquad (16)$$

using condition (4) of translation invariance, and equations (2*a*) and (3). Hence the $\mathbf{V}_0$ term in (14) only means that in the sum over $l'k'r'$ a zero term is added.

The condition of rotation invariance in the literature [Born & Huang, 1954, equation (23.23); Leibfried, 1955, equation (36.3); Maradudin, Montroll & Weiss, 1963, equations (2.1.6) and (2.1.19)] is not correctly given in terms of the force constant matrices $\boldsymbol{\Phi}$. Rather we should write $\boldsymbol{\varphi}$ instead of $\boldsymbol{\Phi}$. The proper differentiation of $\partial\boldsymbol{\Phi}/\partial u_\alpha(lk)$ in equation (23.19) of Born & Huang (1954), and in equation (2.1.13) of Maradudin, Montroll & Weiss (1963) will yield the desired result, *cf.* Scheringer (1974).

Equation (15*a*) gives the shortest presentation of (14). With (15*b*) and (15*c*) a presentation is obtained which is independent of the chosen coordinate origin. (15*c*) is particularly advantageous in that the condition of rotation invariance is only described by the coordinates of the atoms $lkr$ and $l'k'r'$ to which the interatomic force constants are referred. With the use of (15*c*) and (14), however, it is impossible to derive self-terms for the intermolecular force constants unless one also applies the condition of translation invariance. With (15*a*) or (15*b*) self-terms can be directly derived from equation (14) which we shall do in the following.

We apply equation (14) to molecular crystals. We use the form (15*b*), $\mathbf{V}_0=\mathbf{V}(lk)$, sum over all atoms $r$ in (14), and obtain

$$\sum_{l'k'} \sum_{rr'} \boldsymbol{\varphi}(lkr,l'k'r')[\mathbf{V}^T(l'k')-\mathbf{V}^T(lk)]$$

$$+\sum_{l'k'} \sum_{rr'} \boldsymbol{\varphi}(lkr,l'k'r')\mathbf{V}^T_{r'}(l'k')=\mathbf{0}\,. \qquad (17)$$

In equation (17) we now replace the sum over $rr'$ by the intermolecular force constants (10). Since the difference $\mathbf{V}(l'k')-\mathbf{V}(lk)$ is zero for $l'k'=lk$, we can write $\sum'$ instead of $\sum$ in the first term of (17), and we can use $\boldsymbol{\Phi}$ instead of $\boldsymbol{\varphi}$. In the second term of (17) we eliminate the self-term $l'k'=lk$ and replace $\boldsymbol{\varphi}$ by $\boldsymbol{\Phi}$ in the remaining sum $\sum'$. Then we obtain from (17)

$$\boldsymbol{\varphi}^1_{\rm corr}(lk,lk)=-\sum_{l'k'}{}' \boldsymbol{\Phi}_t(lk,l'k')[\mathbf{V}^T(l'k')-\mathbf{V}^T(lk)]$$

$$-\sum_{l'k'}{}' \boldsymbol{\Phi}^1_{\rm corr}(lk,l'k')\,. \qquad (18)$$

A result analogous to (18) is obtained when we first multiply equation (14) by $\mathbf{V}_r(lk)$ from the left side and then sum over all atoms $r$. Instead of (18) we then obtain

$$\boldsymbol{\varphi}_{\rm rot}(lk,lk)=-\sum_{l'k'}{}' \boldsymbol{\Phi}^2_{\rm corr}(lk,l'k')[\mathbf{V}^T(l'k')-\mathbf{V}^T(lk)]$$

$$-\sum_{l'k'}{}' \boldsymbol{\Phi}_{\rm rot}(lk,l'k')\,. \qquad (19)$$

Now, we develop the condition of rotation invariance for molecular crystals by choosing the rotation origin (15*c*), $\mathbf{V}_0=\mathbf{V}(lk)+\mathbf{V}_r(lk)$. In equation (14) we sum over all atoms $r$, as above. In the resulting sum all terms $l'k'=lk$ vanish. For $l'k'r'=lkr$ the difference $\mathbf{V}(l'k')+\mathbf{V}_{r'}(l'k')-\mathbf{V}(lk)-\mathbf{V}_r(lk)$ is zero, and the terms $l'k'=lk$ with $r'\neq r$ are zero by virtue of equation (6). Thus no self-terms occur. Hence we can write $\sum'$ instead of $\sum$ and $\mathbf{\Phi}$ instead of $\varphi$. Then we obtain from equation (14)

$$\begin{aligned}\sum_{l'k'}{}' \sum_{rr'} \mathbf{\Phi}(lkr,l'k'r')[\mathbf{V}^T(l'k')-\mathbf{V}^T(lk)] & \\ +\sum_{l'k'}{}' \sum_{rr'} \mathbf{\Phi}(lkr,l'k'r')\mathbf{V}_{r'}^T(l'k') & \\ -\sum_{l'k'}{}' \sum_{rr'} \mathbf{\Phi}(lkr,l'k'r')\mathbf{V}_r^T(lk)=\mathbf{0}\,. & \qquad (20)\end{aligned}$$

Equation (20) represents the condition of rotation invariance for molecular crystals expressed by the interatomic force constants and coordinates of the atoms in different molecules. Equation (20) corresponds to DPP (2.11). DPP (2.11) is not fully correct; the summation in the last two terms of DPP (2.11) should also be $\sum'_{l'k'}$.

The expressions (18) and (19) for the self-terms $\varphi^1_{\text{corr}}$ and $\varphi_{\text{rot}}$ are identical with the expressions (13*b*) and (13*d*) respectively if and only if the force-constant model used satisfies the condition of rotation invariance. This can be shown by comparing the terms in equation (20) with the results (18) and (19) for the self-terms. A comparison of (18) and (20) leads to

$$\varphi^1_{\text{corr}}(lk,lk)|_{\text{eq.}(18)}=-\sum_{l'k'}{}'\sum_{rr'}\mathbf{\Phi}(lkr,l'k'r')\mathbf{V}_r^T(lk)\,. \qquad (21)$$

If one multiplies equation (20) by $\mathbf{V}_r(lk)$ from the left-hand side and then compares with (19) one obtains

$$\varphi_{\text{rot}}(lk,lk)|_{\text{eq.}(19)}= -\sum_{l'k'}{}'\sum_{rr'}\mathbf{V}_r(lk)\mathbf{\Phi}(lkr,l'k'r')\mathbf{V}_r^T(lk)\,. \qquad (22)$$

The right-hand sides of equations (21) and (22) are respectively identical with the expressions (13*b*) and (13*d*) which we have already derived from the condition of translation invariance. Since (21) and (22) can only be obtained when (20) holds our statement is proved.

Venkataraman & Sahni (1970) give sum rules for calculating the self-terms of molecular crystals, whereby they choose the rotation origin (15*a*), $\mathbf{V}_0=\mathbf{0}$. Equation (II.A.18) of these authors corresponds to our equations (17) and (18); (II.A.19) to our result (19). We note that in Venkataraman & Sahni's (1970) equations the force constants $\mathbf{\Phi}$ should be replaced by the sums $\varphi$ since self-terms occur.

The results (13*a*), (18), (13*c*), and (19) are in agreement with DPP's expressions (2.10). [Note that DPP give the self-terms expressed as elements of the dynamical matrix of zero wave vector; this gives rise to a slight change in the summation indices $l'k'$.] Comparison of the results shows that (13*b*) and (13*d*) have a simpler structure than the expressions DPP (2.10) since there is only one summation over $l'k'$, and since the lattice vectors $\mathbf{V}(l'k')-\mathbf{V}(lk)$ do not occur.

## 4. Conclusion

Since our expressions (13) for the self-terms differ from DPP's expressions (2.10) we are going to assess the usefulness of both the results for actual force-constant model calculations. Here we are guided by the fact that the dynamical matrices must be Hermitian. This requirement is a formal one, and is generally fulfilled when the (physical) conditions of translation and rotation invariance are satisfied. In actual calculations the symmetry condition (5) of translation invariance can easily be imposed on the interatomic force constants, whereas the condition (20) of rotation invariance is cumbersome to use, and in most cases (with atomic crystals) it is not explicitly applied. Probably, the condition of rotation invariance is not very stringent and its effect on a set of interatomic force-constants small.

As our derivation in §2 has shown, our self-terms (13) ensure that the dynamical matrices are Hermitian if the interatomic force constants used satisfy the symmetry condition (5) of translation invariance. However, it is not necessary to apply the condition (20) of rotation invariance with the self-terms (13) in order to obtain Hermiticity.

DPP's expressions (2·10) [our expressions (13*a*), (18), (13*c*), and (19)] generally do not fulfil the requirement of Hermiticity. In order to guarantee Hermiticity DPP propose the condition of rotation invariance as a constraint on the interatomic force constants, our equation (20), their equation (2.11). In contrast to DPP's opinion, this condition, by itself, is not sufficient to satisfy the requirement of Hermiticity, but rather, as our discussion in § 3 has shown, fulfilling the condition of rotation invariance means only that DPP's expressions (2.10) are identical with our expressions (13). Thus, in order to fulfil the requirement of Hermiticity the symmetry condition (5) of translation invariance must also be satisfied. Hence, with DPP's self-terms (2.10), the condition (20) of rotation invariance *and* the symmetry condition (5) of translation invariance must be imposed on the interatomic force constants used. [It can be shown that DPP's self-terms generally do not give rise to Hermitian dynamical matrices when only the symmetry condition (5) of translation invariance is imposed.]

Hence, we conclude that the use of (13) instead of DPP (2.10) offers three advantages. First, the essential requirement of Hermiticity is fulfilled with less effort. Secondly, the condition of rotation invariance can be used at option. Finally, the self-terms (13*b*) and (13*d*) can be calculated in a simpler manner than the corresponding expressions in DPP (2.10) since the lattice vectors $\mathbf{V}(l'k')-\mathbf{V}(lk)$ do not occur.

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# The Residual and its Use for Partial Structure Evaluation. A Critical Note on the Discriminator Function

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The value of the residual $\langle (I_{\rm obs}-I_{\rm calc})^2\rangle/\langle I^2_{\rm obs}\rangle$ will change when one or more atoms are added to an incomplete model of the structure looked for. It is possible to calculate statistically the expected values of the residual both for correct and (randomly) incorrect placing of a new fragment. The results then show that the correctness of the new atomic position(s) cannot be proved, but only estimated by means of the residual as a reliability criterion; the same conclusion applies to the discriminator function. Both the residual and the discriminator function, however, can be suitable in the elimination of incorrect atomic positions. In some cases even false pseudosymmetry, if any, can be eliminated from a tentative electron density map.

## 1. Introduction

It is necessary to have some criteria to be able to investigate the reliability of the steps to be taken in a completely automated structure evaluation.

A deconvolution of the Patterson function has been discussed previously (Lenstra & Schoone, 1973), in which, among other things, the residual $\langle (I_{\rm obs}-I_{\rm calc})^2\rangle/\langle I^2_{\rm obs}\rangle$ has been applied as a reliability criterion.

The residual as a means to interpret a tentative electron density map has already been stated (Lenstra, 1969). Other investigators have made use of, for instance, the discriminator function (Hackert & Jacobson, 1970; Jacobson, 1970) or a least-squares refinement (Koyama, Okada & Itoh, 1970) to locate additional atoms.

These three criteria are founded mainly on the plain fact that models obtained in this way are in agreement with the correct solutions of the structures. A theoretical explanation of the behaviour of the residual is given in the next section.

Another important point is the purport of 'correct and incorrect placing of an atom'. This will be discussed in detail in § 3; is provides some correction and completion of Wilson's (1969) treatment of the residual. It is shown that an incorrect addition of an atom under certain conditions may decrease the value of the residual. One special kind of incorrect positioning of the new atom which practically always results in a decreasing value of the residual is dealt with in § 4.

§ 5 relates the evaluation of these results for a practical automated structure determination.

In § 6 some remarks are made on the discriminator function.

## 2. Derivation of the values of the residual. Experimental results

For practical mathematical reasons the residual is defined as:

$$R_2\equiv\frac{\sum\limits_H (I_{\rm obs}-I_{\rm calc})^2}{\sum\limits_H I^2_{\rm obs}}$$

in which $I_{\rm obs}$ are the observed intensities and $I_{\rm calc}$ are the intensities calculated by means of the known structure model only. This implies that the observed