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Self Terms in External-Mode Formalism

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Abstract

Self force constants $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$, that are needed in lattice dynamical calculations making use of external-mode formalism, are obtained. There is a need to include quadratic components in angular displacements (of clusters) while computing atomic displacements. In particular, the rotation–rotation self force constant $\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ derives an extra term because of the quadratic terms. Implications of this term in lattice dynamical calculations are discussed.

I. Introduction

Lattice dynamics of complex crystals is often simplified by using the external-mode formalism (Venkataraman & Sahni, 1970), wherein normal modes of the system are derived by assuming that (tightly bound) groups of atoms undergo only external displacements. (By external displacements we mean that groups undergo only translation or rotation *as a whole* and thus no internal distortion of the group enters the discussion in any way.) Venkataraman & Sahni (1970), whose notation we follow here, have discussed how, for this formulation, the force constants connecting different clusters, $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}\left[\begin{pmatrix} l \\ \kappa \end{pmatrix} \neq \begin{pmatrix} l' \\ \kappa' \end{pmatrix}\right]$, can be related to the *interatomic* force constants between atoms on the two clusters $\varphi_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \\ k & k' \end{pmatrix}$ (Venkataraman & Sahni, 1970, equations II.A.58*a–d*). Of course, it is understood that if we write $\varphi_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \\ k & k' \end{pmatrix}$ as a double derivative of the potential energy V, namely

$$\varphi_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \\ k & k' \end{pmatrix} = \left.\frac{\partial^2 V}{\partial u_\alpha\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}\partial u_\beta\begin{pmatrix} l' \\ \kappa' \\ k' \end{pmatrix}}\right|_0, \qquad (1)$$

then V contains only *intercluster interactions*. Since, in explicit calculations of normal modes, one needs to know the self force constants $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ as well, one may use the translational and rotational sum rules (Venkataraman & Sahni, 1970, equations II.A.16–19) to deduce their expressions.

An alternative scheme for obtaining the self force constants was presented by Scheringer (1974).† He employed certain conditions valid for interatomic force constants $\varphi_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \\ k & k' \end{pmatrix}$ and obtained expressions for self force constants $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ (Scheringer, 1974, equations 13*a–d*). There is, however, a subtle point which was obscured in his treatment and it will be our aim here not only to indicate that point, but also to demonstrate that for a proper derivation of the rotational self force constant $\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ atomic movements up to second order in rotational displacements have to be retained.

II. Derivation of self terms

Expressions for $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}$, $\left[\begin{pmatrix} l \\ \kappa \end{pmatrix} \neq \begin{pmatrix} l' \\ \kappa' \end{pmatrix}\right]$ in terms of

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† Scheringer (1974) had observed that lattice dynamical equations of motion involved the symmetrized form of force-constant matrices. Consequently, he employed $\Phi + \Phi^T$ (where the superscript T denotes the transposed matrix) for discussing the dynamics. We shall return to this point later.

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interatomic force constants have already been obtained by Venkataraman & Sahni (1970). Let us obtain expressions for $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$. For this, we assume that the potential energy V is a function of atomic coordinates, *viz*

$$V\left(\ldots \mathbf{r}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}, \mathbf{r}\begin{pmatrix} l' \\ \kappa' \\ k' \end{pmatrix}, \ldots\right). \tag{2}$$

Now, since in external-normal-mode calculations, no intracluster distortions are admitted, we may write the instantaneous atomic positions in terms of external displacements, that is

$$\mathbf{r}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix} = \mathbf{X}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix} + \mathbf{u}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix} = \mathbf{X}\begin{pmatrix} l \\ \kappa \end{pmatrix} + \mathbf{X}(k) + \mathbf{u}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}, \tag{3}$$

with

$$u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix} = u^t_\delta\begin{pmatrix} l \\ \kappa \end{pmatrix} + \sum_{\mu\nu} u^r_\mu\begin{pmatrix} l \\ \kappa \end{pmatrix} X_\nu(k)\,\varepsilon_{\mu\nu\delta} + \mathrm{HO}_\delta\left\{\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}\right\}, \tag{4}$$

where $\mathbf{u}^t\begin{pmatrix} l \\ \kappa \end{pmatrix}$ and $\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}$ denote the translation and rotation respectively of $\begin{pmatrix} l \\ \kappa \end{pmatrix}$ and $\mathrm{HO}_\delta\left\{\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}\right\}$ contains all the terms beyond first order in $\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}$. When (3) and (4) are substituted in (2) and a series expansion of V in terms of the displacements $\left\{\mathbf{u}^{t/r}\begin{pmatrix} l \\ \kappa \end{pmatrix}\right\}$ is set up, we can readily arrive at expressions for external force constants. The important point to note is that in the case $\left\{\begin{pmatrix} l \\ \kappa \end{pmatrix} \neq \begin{pmatrix} l' \\ \kappa' \end{pmatrix}\right\}$ the coefficient of the $u^i_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix} u^j_\beta\begin{pmatrix} l' \\ \kappa' \end{pmatrix}$ term in the expansion of potential energy, which determines $\varphi^{ij}_{\alpha\beta}\begin{pmatrix} l & l' \\ \kappa & \kappa' \end{pmatrix}$, derives its contribution only from the linear dependence of $\mathbf{u}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ on $\mathbf{u}^t\begin{pmatrix} l \\ \kappa \end{pmatrix}$ and $\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}$, and of $\mathbf{u}\begin{pmatrix} l' \\ \kappa' \\ k' \end{pmatrix}$ on $\mathbf{u}^t\begin{pmatrix} l' \\ \kappa' \end{pmatrix}$ and $\mathbf{u}^r\begin{pmatrix} l' \\ \kappa' \end{pmatrix}$. Similarly, for $\varphi^{tt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$, $\varphi^{tr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ and $\varphi^{rt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$, explicit series expansions yield

$$\varphi^{tt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa}\sum_{k'\in\kappa} \varphi_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k' \end{pmatrix}, \tag{5}$$

$$\varphi^{tr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa}\sum_{k'\in\kappa}\sum_{\delta\nu} \varphi_{\alpha\delta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k' \end{pmatrix} X_\nu(k')\,\varepsilon_{\beta\nu\delta}, \tag{6}$$

$$\varphi^{rt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa}\sum_{k'\in\kappa}\sum_{\delta\nu} \varphi_{\delta\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k' \end{pmatrix} X_\nu(k')\,\varepsilon_{\alpha\nu\delta}. \tag{7}$$

Here again the *linear* dependence of $\mathbf{u}\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ on $\mathbf{u}^t\begin{pmatrix} l \\ \kappa \end{pmatrix}$ and $\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}$ alone contributes. We may emphasize what we have already stated, that, because V is supposed to contain only *inter*cluster interactions, we may, *purely formally*, accomplish this by setting $\varphi_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k' \end{pmatrix}$ equal to zero for $k \neq k'$. However, one should not assume that by doing this we are implying that *intra*cluster frequencies are zero; we are simply using an artifact to show that in discussing the external normal modes no internal distortions of the clusters are admitted. With this understanding, (5) to (7) may be rewritten as

$$\varphi^{tt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa} \varphi^{tt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k \end{pmatrix}, \tag{5a}$$

$$\varphi^{tr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa}\sum_{\delta\nu} \varphi_{\alpha\delta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k \end{pmatrix} X_\nu(k)\,\varepsilon_{\beta\nu\delta}, \tag{6a}$$

$$\varphi^{rt}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{k\in\kappa}\sum_{\delta\nu} \varphi_{\delta\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k \end{pmatrix} X_\nu(k)\,\varepsilon_{\alpha\nu\delta}. \tag{7a}$$

These expressions agree with those obtained by Scheringer (1974) (*cf.* equations 13*a*–*c*). Turning to $\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$, we must now note the important fact implied in (4), namely that $u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ contains quadratic dependence in the components $\left\{u^r_\mu\begin{pmatrix} l \\ \kappa \end{pmatrix}\right\}$ because of higher-order terms. More specifically,

$$\frac{\partial^2 u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}}{\partial u^r_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix} \partial u^r_\beta\begin{pmatrix} l \\ \kappa \end{pmatrix}} = \frac{\partial^2 \mathrm{HO}_\delta\left\{\mathbf{u}^r\begin{pmatrix} l \\ \kappa \end{pmatrix}\right\}}{\partial u^r_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix} \partial u^r_\beta\begin{pmatrix} l \\ \kappa \end{pmatrix}} = A^\delta_{\alpha\beta} \neq 0, \tag{8}$$

in general, and in fact one finds an additional term in the expression for $\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}$ owing to this feature; that is

$$\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} = \sum_{\substack{k\in\kappa \\ \nu\delta\nu'\delta'}} \varphi_{\delta\delta'}\begin{pmatrix} l & l \\ \kappa & \kappa \\ k & k \end{pmatrix} X_\nu(k)\, X_{\nu'}(k)\, \varepsilon_{\alpha\nu\delta}\, \varepsilon_{\beta\nu'\delta'} + \sum_{k\in\kappa}\sum_{\delta} \frac{\partial V}{\partial u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}}\Bigg|_0 \frac{\partial^2 u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}}{\partial u^r_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix} \partial u^r_\beta\begin{pmatrix} l \\ \kappa \end{pmatrix}}. \quad (9)$$

The second term on the right side does not occur in Scheringer's (1974) expression (*cf.* his equation 13*d*), and to this extent his expression is incomplete.

III. Implications of the additional term in rotation–rotation self force constant

For exploring the implications of the additional term, we may separately consider Scheringer's formulation of lattice dynamics and the usual one (Venkataraman & Sahni, 1970). We observe that Scheringer's approach uses symmetrized form of force constants for setting up the dynamical matrix, whereas the usual one does not. Clearly, therefore, we will require only the symmetrized part of the additional term for the former formulation, whereas for the latter formulation the form of the additional term given in (9) would be utilized.

Now, like any second-rank tensor, the additional term can also be expressed as a sum of a symmetric part and an antisymmetric (AS) part. Of these two parts, only the former part will enter Scheringer's formulation, whereas both parts will enter the usual formulation. Consequently, the difference between the two formulations can arise only on account of the AS part,

$$\left\{\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} - \varphi^{rr}_{\beta\alpha}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}\right\}.$$

From the results given in the Appendix (see equation *A*.8), one can see that

$$\left\{\varphi^{rr}_{\alpha\beta}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix} - \varphi^{rr}_{\beta\alpha}\begin{pmatrix} l & l \\ \kappa & \kappa \end{pmatrix}\right\} = \sum_{\nu} \varphi^r_\nu\begin{pmatrix} l \\ \kappa \end{pmatrix} \varepsilon_{\alpha\beta\nu}. \quad (10)$$

Hence, the AS part is related to the torques on the clusters. In any realistic calculation, one must ensure that the dynamics pertain to an equilibrium configuration, for which the forces and torques on the clusters necessarily vanish (Chaplot, Sahni & Rao, 1979). It follows that the AS part is identically zero, and so the additional term affects both the lattice dynamical formulations in the same fashion. We may emphasize that since in the external-mode formalism only the 'external potential' is retained in the discussion, the quantities $\varphi_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ occurring in our equations refer only to what may be termed 'external forces' on the atoms. Generally speaking, these external forces on individual atoms by themselves do not vanish* and thus inclusion of the second term in (9) is obligatory.

In writing his equation (14), Scheringer (1974) omitted the first-order derivative terms of the type $\varphi_\alpha\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ (*cf.* Born & Huang, 1954, equations 23.22 and 23.23). However, as pointed out above, these terms should have been retained in the external-mode approach. If one included the first-order-derivative terms and used the amended version of Scheringer's (1974) equation (19), one can at once retrieve the missing term, which has been derived by us using the higher-order terms in (4).

APPENDIX

The second term in (9) may be written as

$$\sum_{k\in\kappa}\sum_{\delta} \varphi_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix} \frac{\partial^2 u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}}{\partial u^r_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix} \partial u^r_\beta\begin{pmatrix} l \\ \kappa \end{pmatrix}}\Bigg|_0 = ST_{\alpha\beta}, \quad (A1)$$

say. Here, while computing the partial derivatives, we will follow the standard convention of giving sequential increments to the relevant independent variables and thus, for $\alpha \neq \beta$, it will be understood that $u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$ is obtained by first performing the rotation $u^r_\beta\begin{pmatrix} l \\ \kappa \end{pmatrix}$ and then $u^r_\alpha\begin{pmatrix} l \\ \kappa \end{pmatrix}$. We shall denote this by $\left\{u_\delta\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}\right\}_{\alpha+\beta}$

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* Only if we computed the *total* force on the $\begin{pmatrix} l \\ \kappa \\ k \end{pmatrix}$th atom (*i.e.* external plus internal force) could we appeal to the equilibrium condition of standard Born–Huang formulation of lattice dynamics and claim that the total force is zero. Separately, the internal and external forces are, in general, not zero.

Accordingly, ST_{yx} will be obtained from

$$\left\{u_\delta\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}\right\}_{Y+X} = (\mathbf{R}_{Y+X} - \mathbb{1})\,\mathbf{X}(k), \qquad (A2)$$

where the rotation matrix $\mathbf{R}_{Y+X}$ is given by

$$\mathbf{R}_{Y+X} = \begin{bmatrix} 1-\frac{1}{2}\left\{u_Y^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\right\}^2 & 0 & u_Y^r\begin{pmatrix}l\\ \kappa\end{pmatrix} \\ 0 & 1 & 0 \\ -u_Y^r\begin{pmatrix}l\\ \kappa\end{pmatrix} & 0 & 1-\frac{1}{2}\left\{u_Y^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\right\}^2 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1-\frac{1}{2}\left\{u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\right\}^2 & -u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix} \\ 0 & u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix} & 1-\frac{1}{2}\left\{u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\right\}^2 \end{bmatrix}. \qquad (A3)$$

From equations ($A1$) to ($A3$),

$$ST_{YX} = \sum_{k\in\kappa}\sum_{\delta}\varphi_\delta\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}\left.\frac{\partial^2\left\{u_\delta\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}\right\}_{Y+X}}{\partial u_Y^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\partial u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix}}\right|_0$$

$$= \sum_{k\in\kappa}{}'\varphi_X\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_Y(k). \qquad (A4)$$

Similarly, one can verify that

$$ST_{XY} = \sum_{k\in\kappa}\varphi_Y\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_X(k). \qquad (A5)$$

It is easy to verify that

$$ST_{XX} = \sum_{k\in\kappa}\sum_{\delta}\varphi_\delta\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}\left.\frac{\partial^2\left\{u_\delta\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}\right\}_{X+X}}{\partial u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix}\partial u_X^r\begin{pmatrix}l\\ \kappa\end{pmatrix}}\right|_0$$

$$= -\sum_{k\in\kappa}\left\{\varphi_Z\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_Y(k) + \varphi_Z\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_Z(k)\right\}. \qquad (A6)$$

From ($A4$) and ($A5$), we find that

$$ST_{XY} - ST_{YX} = \sum_{k\in\kappa}\left\{\varphi_Y\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_X(k) - \varphi_X\begin{pmatrix}l\\ \kappa\\ k\end{pmatrix}X_Y(k)\right\}. \qquad (A7)$$

We can at once recognize the right side of ($A7$) to be the Z component of the torque $\varphi_Z^r\begin{pmatrix}l\\ \kappa\end{pmatrix}$ on the $\begin{pmatrix}l\\ \kappa\end{pmatrix}$th cluster. Thus ($A7$) may be generalized to the form

$$ST_{\alpha\beta} - ST_{\beta\alpha} = \sum_{\nu}\varepsilon_{\alpha\beta\nu}\varphi_\nu^r\begin{pmatrix}l\\ \kappa\end{pmatrix}. \qquad (A8)$$

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