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Evaluation of Coulombic Lattice Sums for Vibrational Calculations in Crystals: an Extension of Bertaut's Method

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Abstract

The well known general method due to Bertaut for calculating the Coulombic lattice sums in crystals has been extended to evaluating the Coulombic contribution to the dynamical matrices in harmonic lattice-dynamical calculations. The procedure is particularly simple and close to usual crystallographic routines, in line with Bertaut's treatment of the general problem. It involves the evaluation of first derivatives of structure factors for two satellite reflexions of indices $\mathbf{h}^0+\mathbf{q}$ and $\mathbf{h}^0-\mathbf{q}$ for each reflexion of indices $\mathbf{h}^0$, with respect to the primitive lattice, where $\mathbf{q}$ is the wave vector; the 'self' contribution can be directly evaluated from the second derivatives of $F(\mathbf{h}^0)$'s. A particularly interesting feature is that the contribution of the macroscopic field is already included, and it derives from the two satellites of $F(000)$.

Introduction

The problem of calculating various properties in crystals depending upon the vibrational spectrum has been exciting considerable interest even outside the strict field of solid-state physics. For instance, the calculation of anisotropic displacement parameters (a.d.p.'s) might become a matter of routine even for complex molecular crystals, owing to recent substantial improvements in computers and in suitable procedures [see, for instance, Gramaccioli (1987, 1989); Gramaccioli & Filippini (1983, 1985)]; also the derivation of thermodynamic properties, including entropy, specific heat and free energy, starting from force-field models seems to be one of the major goals in physical chemistry, in materials science and in geology, since it can afford a connection between a crystal structure and its stability field. In these applications, one of the basic difficulties consists in the slow convergence of the Coulombic lattice sums. This problem was first solved by Ewald (1921) by considering summation on the reciprocal lattice; a more general treatment of the same problem has been given by Bertaut (1952) and has been extended by the same author to a number of different applications (Bertaut, 1978*a*, *b*, 1983, 1985, 1986). In our opinion, Bertaut's method has the definite advantages of being very understandable and of being close to crystallographic routines. For this reason, we adopted this method for evaluating the Coulomb energy in molecular crystals (Gramaccioli & Filippini, 1979). In lattice dynamics, the coupling coefficients in the equation of motion are related to the 'static' lattice sums. Born & Thompson (1934) and Thompson (1935) considered this problem for the first time, starting from Ewald's criterion, and the use of a correct formulation for the case of sodium chloride was first due to Kellermann (1940) in his classical work. Although Kellermann's paper is clear and simple to experts in the field, its application to the general case involves considerable complexity, both in understanding the principle and in applying it in practice. In view of the simplicity of Bertaut's method, we have considered its extension to lattice dynamics as particularly interesting and useful.

Principle of the method

The elements of the dynamical matrix $\mathbf{D}$ in the harmonic approximation of crystal motion are of the kind:

$$D_{ij}^{kk'} = (m_k m_{k'})^{-1/2} \sum_l \Phi_{ij}^{kk'}(0, l) \exp(2\pi i \mathbf{q} \,.\, \Delta\mathbf{r}^l) \qquad (1)$$

where

$$\Phi_{ij}^{kk'}(0, l) = \partial^2 E / \partial x_{ik}^0 \partial x_{jk'}^l \qquad (1a)$$

(see, for instance, Willis & Pryor (1975), equation 3.10*b*), where E is the potential energy, x_{ik}^0 is a coordinate of the kth atom in the unit cell, $x_{jk'}^l$ is a coordinate of the k'th atom in the crystal, related to $x_{jk'}^0$ by a lattice translation $\mathbf{r}^l$ ($l=0$ when $\mathbf{r}^l=\mathbf{0}$), $\mathbf{q}$ is the wave vector, $\Delta\mathbf{r}^l$ is the distance between the two atoms involved, m_k and $m_{k'}$ are the masses of the atoms k and k', respectively; the summation $\sum_l$ is extended (in principle) to all the translated units in the crystal.

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If $k=k'$, D_{ij}^{kk} includes the so-called 'self terms' $\Phi_{ij}^{kk}(0,0)$:

$$\Phi_{ij}^{kk}(0,0)=\partial^2 E/\partial x_{ik}^0\partial x_{jk}^0.$$

Since we are dealing here with Coulombic energy only, the energy E can be expressed by the following series, corresponding to (41) in Bertaut (1952):

$$E=\sum_l E_l = 18\pi R^2/V\sum_{\mathbf{h}}|F(\mathbf{h})|^2 \times[\sin(\alpha)-\alpha\cos(\alpha)]^2/\alpha^8-3/(5R)\sum_j z_j^2. \qquad (2)$$

Here R is a distance not exceeding one half of the shortest distance between the atoms, z_j is the charge of the jth atom, V is the unit-cell volume, $\alpha=2\pi|\mathbf{h}|R$, and the $F(\mathbf{h})$'s are the Fourier transforms of the charge density, which for the point-charge crystal are obtained just as crystallographic structure factors, where the atomic scattering factors are replaced with atomic charges.

Insertion of the second derivatives of (2) into (1) must be done cautiously. In fact, contrary to the usual assumption in crystallography, the space-group relationships between the positions of symmetry-equivalent atoms are not necessarily respected at any instant during motion. In other words, the formula $\mathbf{x}'=\mathbf{M}\mathbf{x}+\mathbf{w}$, where $\mathbf{x}$ and $\mathbf{x}'$ are position vectors of symmetrically related atoms, $\mathbf{M}$ is a rotation matrix and $\mathbf{w}$ a translation vector holds for the average positions only, whereas it does not hold (as such) for the general case of instantaneous displacements. For this reason, the calculation of derivatives of structure factors in (2) should not be simplified on the grounds of the usual space-group-symmetry relationships.

For $\mathbf{q}=\mathbf{0}$, all the atoms related by unit-cell translations vibrate in phase, and the translational symmetry between the different unit cells is maintained. In this case, the application of Bertaut's criterion becomes very simple, by combining (1), 1(*a*) and (2):

$$D_{ij}^{kk'}=\frac{18\pi R^2}{V(m_k m_{k'})^{1/2}}\sum_{\mathbf{h}} f(\alpha_{\mathbf{h}})\frac{\partial^2|F_{\mathbf{h}}|^2}{\partial x_{ik}^0\partial x_{jk'}^0} \qquad (3)$$

where $f(\alpha_{\mathbf{h}})=[\sin(\alpha)-\alpha\cos(\alpha)]^2/\alpha^8$, a function of the indices $\mathbf{h}$ only.

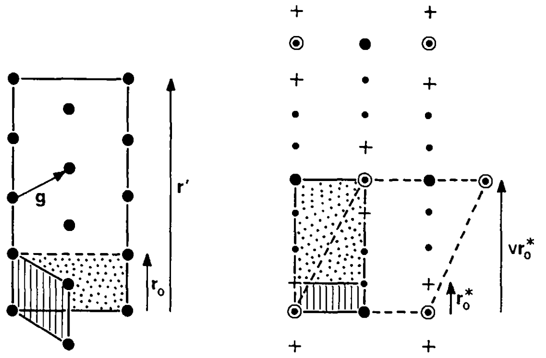
The evaluation of these second derivatives can be done in several ways. An example is given below [see (5*a*) to (6)]. The summation can be performed up to a certain limiting value of $\sin\theta/\lambda$, so that convergence is reached in practice. In spite of its relative simplicity, the case for $\mathbf{q}=\mathbf{0}$ is very useful in practical applications, since all the Raman and infrared active modes can be calculated with this assumption.

For the general case in the Brillouin zone, the application of (1) and (2) is not so straightforward. In this case, for $\mathbf{q}\neq\mathbf{0}$, as we have seen, the translational symmetry does not hold in general between different unit cells; however, it can still be assumed to hold provided a suitable multiple unit cell is chosen. For instance, a new cell could be considered where two unit-cell vectors are perpendicular to the wave vector $\mathbf{q}$ and the third is one of the original unit-cell vectors $\mathbf{r}^0$, not perpendicular to $\mathbf{q}$. Such a new unit cell (here referred to as *intermediate*) might not necessarily be primitive, and its multiplicity will be $n_d\geq 1$ (see Fig. 1*a*).

The reciprocal lattice of this intermediate cell has a certain number of additional points with respect to the starting unit cell, corresponding to extinct reflections. Starting from the intermediate cell, a still larger unit cell can be considered, where $\mathbf{r}^0$ is replaced by $\mathbf{r}'=n_f\mathbf{r}^0$; here n_f is an integer chosen in order to assign the smallest possible integral value to $n_f\mathbf{q}\,.\,\mathbf{r}^0$. This is always possible, provided $\mathbf{q}$ has rational components, an assumption which can easily be made for all practical applications. The multiplicity of this final unit cell will be $n_f n_d$ with respect to the original unit cell of the crystal.

Since the phase difference between any such final unit cells is an integral multiple of 2π, with respect to these larger cells the equivalent atoms vibrate in phase, and the translational symmetry is respected, as for $\mathbf{q}=\mathbf{0}$.

The reciprocal lattice of this final unit cell is related to the reciprocal lattice of the intermediate unit cell with multiplicity n_d, with additional points at $\mathbf{h}=\mathbf{H}^0+t\mathbf{q}$, where t is an integer ranging from 1 to n_f-1 and $\mathbf{H}^0$ is a reciprocal-lattice vector of the intermedi-



(*a*) (*b*)

Fig. 1. (*a*) An example of relationships in the direct lattice between the original unit cell (hatched), the intermediate unit cell (dotted) and the final unit cell, chosen in order to have $\mathbf{q}\,.\,\mathbf{r}=$ integer. In this particular case $\mathbf{r}^0$ is the unit-cell axis $\mathbf{c}$, and $\mathbf{q}=\mathbf{c}^*/4$. The final unit cell behaves as if $\mathbf{q}=\mathbf{0}$ with respect to the other equivalent cells in the structure, *i.e.* there is no phase variation, or better, the phase variation is dealt with at the interior of the largest cell taking the phase relationships between the smaller cells into account. In this particular case, $\hat{\mathbf{q}}$ and $\mathbf{r}^0$ are parallel (for the sake of simplicity), but they do not have to be. (*b*) A sample of the reciprocal lattice (drawn on arbitrary scale) corresponding to the situation of (*a*). Here the original (primitive) reciprocal unit cell has dashed contours; the intermediate reciprocal unit cell is dotted, and the final reciprocal unit cell is hatched. For each point of the primitive reciprocal lattice (marked by a ring) only the satellites marked by a cross should be considered.

ate unit cell. For $t = kn_f$, where k is any integer, the vector $\mathbf{h}$ will coincide with a vector $\mathbf{H}'^0$ of the reciprocal lattice of the intermediate cell, *i.e.* the indices will be integer; for $t \neq kn_f$ these indices will instead be fractional. All this is clear, if one considers that if $n_f\mathbf{q} \,.\, \mathbf{r}^0 = v$ is an integer, and calling $\mathbf{r}^{0*}$ the reciprocal-lattice vector relative to $\mathbf{r}^0$ ($\mathbf{r}^0 \,.\, \mathbf{r}^{0*} = 1$), it must hold that

$$n_f\mathbf{q} = v\mathbf{r}^{0*},$$

a vector connecting two points of the reciprocal lattice of the intermediate cell.

By reference to a picture of a reciprocal-lattice layer including the wave vector $\mathbf{q}$, the final multiple cell involves $n_f - 1$ additional points on a straight line starting from any point of the reciprocal lattice of the intermediate unit cell, until another point of this reciprocal lattice is reached (see Fig. 1*b*). If $n_d > 1$, the situation is similar to starting our consideration directly from any non-primitive unit cell. As we will see, our arguments do not necessarily imply primitive unit cells (see below).

Because the phase of motion with respect to the other cells is equal, (3) could be applied as such to the final cell, but this would lead to inconveniences in practical applications. In fact, the contributions of equivalent atoms (by unit-cell translations) in usual lattice-dynamical applications are considered together, whereas from (3) these contributions within the final unit cell are separated, leading to a very considerable increase in the order of the dynamical matrices. The problem is therefore to find a suitable strategy for reducing the order of the dynamical matrices by summing such contributions together in an appropriate way. This can be done by considering the relationships between such contributions within the largest (final) unit cell.

Keeping all this in mind, let us rewrite (3) for a general (non-zero) value of the wave vector $\mathbf{q}$:

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/V'(m_k m_{k'})^{1/2} \sum_{\mathbf{h}} f(\alpha_{\mathbf{h}}) \\ &\quad \times \sum_{l} \partial^2|F_{\mathbf{h}}|^2/\partial x_{ik}^0 \partial x_{jk'}^l \exp(2\pi i\mathbf{q} \,.\, \Delta\mathbf{r}'). \end{aligned} \tag{4}$$

The summation over l is extended to all the lattice translations within the final (largest) unit cell, since for multiples of this cell the contribution is constant. The volume $V' = n_f n_d V$ is obviously a multiple of the initial unit-cell volume V; the summation over $\mathbf{h}$ is extended to all the indices of this final multiple unit cell, most of which correspond to fractional values if referred to the original unit cell (see above).

Since $|F_{\mathbf{h}}|^2 = F_{\mathbf{h}}F_{\mathbf{h}}^*$ and $\mathbf{x}_k^l = \mathbf{x}_k^0 + \mathbf{r}^l$, it will hold that

$$\partial|F_{\mathbf{h}}|^2/\partial x_{ik}^0 = F_{\mathbf{h}}\partial F_{\mathbf{h}}^*/\partial x_{ik}^0 + F_{\mathbf{h}}^*\partial F_{\mathbf{h}}/\partial x_{ik}^0 \tag{5a}$$

$$\begin{aligned} &\partial^2|F_{\mathbf{h}}|^2/\partial x_{ik}^0 \partial x_{jk'}^l \\ &\quad = \partial F_{\mathbf{h}}/\partial x_{jk'}^l \partial F_{\mathbf{h}}^*/\partial_{ik}^0 + F_{\mathbf{h}}\partial^2 F_{\mathbf{h}}^*/\partial x_{ik}^0 \partial x_{jk'}^l \\ &\qquad + \partial F_{\mathbf{h}}^*/\partial x_{jk'}^l \partial F_{\mathbf{h}}/\partial x_{ik}^0 + F_{\mathbf{h}}^*\partial^2 F_{\mathbf{h}}/\partial x_{ik}^0 \partial x_{jk'}^l. \end{aligned} \tag{5b}$$

Since

$$\begin{aligned} \partial F_{\mathbf{h}}/\partial x_{ik}^0 &= 2\pi i h_i z_k \exp(2\pi i\mathbf{h} \,.\, \mathbf{x}_k^0) \\ \partial F_{\mathbf{h}}^*/\partial x_{ik}^0 &= -2\pi i h_i z_k \exp(-2\pi i\mathbf{h} \,.\, \mathbf{x}_k^0) \end{aligned} \tag{5c}$$

then we have

$$\begin{aligned} \partial F_{\mathbf{h}}/\partial x_{ik}^l &= \partial F_{\mathbf{h}}/\partial x_{ik}^0 \exp(2\pi i\mathbf{h} \,.\, \mathbf{r}^l) \\ \partial F_{\mathbf{h}}^*/\partial x_{ik}^l &= \partial F_{\mathbf{h}}^*/\partial x_{ik}^0 \exp(-2\pi i\mathbf{h} \,.\, \mathbf{r}^l) \end{aligned}$$

and

$$\begin{aligned} \partial^2 F_{\mathbf{h}}/\partial x_{ik}^0 \partial x_{jk'}^0 &= \delta_{kk'} 4\pi^2 h_i h_j z_k \exp(2\pi i\mathbf{h} \,.\, \mathbf{x}_k^0) \\ \partial^2 F_{\mathbf{h}}^*/\partial x_{ik}^0 \partial x_{jk'}^0 &= \delta_{kk'} 4\pi^2 h_i h_j z_k \exp(-2\pi i\mathbf{h} \,.\, \mathbf{x}_k^0) \end{aligned} \tag{5d}$$

$$\left.\begin{aligned} \partial^2 F_{\mathbf{h}}/\partial x_{ik}^0 \partial x_{jk'}^l &= 0 \\ \partial^2 F_{\mathbf{h}}^*/\partial x_{ik}^0 \partial x_{jk'}^l &= 0 \end{aligned}\right. \quad \text{if } k \neq k' \text{ and } l \neq 0. \tag{5e}$$

Here the form factor for the atom k simply corresponds to its charge $z_{k'}$ as we have seen. From (5*a*), (5*b*) and (5*e*), we have

$$\begin{aligned} \partial^2|F_{\mathbf{h}}|^2/\partial x_{ik}^0 \partial x_{jk'}^l &= \partial F_{\mathbf{h}}/\partial x_{jk'}^0 \partial F_{\mathbf{h}}^*/\partial x_{ik}^0 \exp(2\pi i\mathbf{h} \,.\, \mathbf{r}^l) \\ &\quad + \partial F_{\mathbf{h}}^*/\partial x_{jk'}^0 \partial F_{\mathbf{h}}/\partial x_{ik}^0 \exp(-2\pi i\mathbf{h} \,.\, \mathbf{r}^l) \\ &\quad + \delta_{kk'}\delta_{0l}(F_{\mathbf{h}}^*\partial^2 F_{\mathbf{h}}/\partial x_{ik}^0 \partial x_{jk}^0 \\ &\quad + F_{\mathbf{h}}\partial^2 F_{\mathbf{h}}^*/\partial x_{ik}^0 \partial x_{jk}^0). \end{aligned} \tag{6}$$

The last term in (6) is non-zero only for $k = k'$ and $l = 0$, *i.e.* it exists for the so-called 'self-terms' only. If one calls such a term $s_{ij}^{0k}(\mathbf{h})$, and considers that $\Delta\mathbf{r}^l = \Delta\mathbf{r}_{kk'} + \mathbf{r}^l$, where $\Delta\mathbf{r}_{kk'}$ is the distance between the atoms k and k' in the original unit cell and $\mathbf{r}^l = \xi\mathbf{r}^0 + \mathbf{g}$ is a lattice vector ($\mathbf{g}$ is a lattice translation within the intermediate unit cell, and ξ is an integer), it holds that:

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/V(m_k m_{k'})^{1/2} \exp(2\pi i\mathbf{q} \,.\, \Delta\mathbf{r}_{kk'}) \\ &\quad \times \sum_{\mathbf{h}} \{K^{ij}(\mathbf{h}) \sum_{\xi} \sum_{\mathbf{g}} \exp[2\pi i(\mathbf{h} + \mathbf{q}) \,.\, (\xi\mathbf{r}^0 + \mathbf{g})] \\ &\quad + K^{*ij}(\mathbf{h}) \sum_{\xi} \sum_{\mathbf{g}} \exp[2\pi i(-\mathbf{h} + \mathbf{q}) \,.\, (\xi\mathbf{r}^0 + \mathbf{g})] \\ &\quad + f(\alpha_{\mathbf{h}}) s_{ij}^{0k}(\mathbf{h})\} \end{aligned} \tag{7}$$

where

$$\begin{aligned} K^{ij}(\mathbf{h}) &= f(\alpha_{\mathbf{h}})(\partial F_{\mathbf{h}}^*/\partial x_{ik}^0 \partial F_{\mathbf{h}}/\partial x_{jk'}^0) \\ K^{*ij}(\mathbf{h}) &= f(\alpha_{\mathbf{h}})(\partial F_{\mathbf{h}}/\partial x_{ik}^0 \partial F_{\mathbf{h}}^*/\partial x_{jk'}^0). \end{aligned} \tag{8}$$

In (7) the strategy of summing together the contributions of equivalent atoms is achieved by means of the summations with respect to ξ and $\mathbf{g}$. Therefore the order of $\mathbf{D}$ is the same as for usual lattice-dynamical calculations.

Since $\mathbf{h} = \mathbf{H}^0 + t\mathbf{q}$, we have

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/V'(m_k m_{k'})^{1/2} \exp(2\pi i\mathbf{q} \,.\, \Delta\mathbf{r}_{kk'}) \sum_{\mathbf{h}} \{K^{ij}(\mathbf{h}) \\ &\quad \times \sum_{\xi} \sum_{\mathbf{g}} \exp[2\pi i(\mathbf{H}^0 + t\mathbf{q} + \mathbf{q}) \,.\, (\xi\mathbf{r}^0 + \mathbf{g})] + K^{*ij}(\mathbf{h}) \\ &\quad \times \sum_{\xi} \sum_{\mathbf{g}} \exp[2\pi i(-\mathbf{H}^0 - t\mathbf{q} + \mathbf{q}) \,.\, (\xi\mathbf{r}^0 + \mathbf{g})] \\ &\quad + f(\alpha_{\mathbf{h}}) s_{ij}^{0k}(\mathbf{h})\}. \end{aligned} \tag{9}$$

Since $\mathbf{H}^0 . \mathbf{r}^0$ is integral, and considering that $s_{ij}^{0k}(\mathbf{h}) = 0$ if $\mathbf{h} \neq \mathbf{H}^0$, we have

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/(V n_f n_d)(m_k m_{k'})^{1/2} \exp(2i\pi \mathbf{q} . \Delta\mathbf{r}_{kk'}) \\ &\quad\times \sum_{\mathbf{H}^0} \{ f(\alpha_{\mathbf{H}^0}) s_{ij}^{0k}(\mathbf{H}^0) + \sum_{\mathbf{g}} \exp(2\pi i \mathbf{H}^0 . \mathbf{g}) \\ &\quad\times \sum_t K^{ij}(\mathbf{H}^0 + t\mathbf{q}) \exp[2\pi i (t+1)\mathbf{q} . \mathbf{g}] \\ &\quad\times \sum_{\xi} \exp[2\pi i \xi (t+1)\mathbf{q} . \mathbf{r}^0] + \sum_{\mathbf{g}} \exp(-2\pi i \mathbf{H}^0 . \mathbf{g}) \\ &\quad\times \sum_t K^{*ij}(\mathbf{H}^0 + t\mathbf{q}) \exp[2\pi i (1-t)\mathbf{q} . \mathbf{g}] \\ &\quad\times \sum_{\xi} \exp[2\pi i \xi (1-t)\mathbf{q} . \mathbf{r}^0] \}. \end{aligned} \tag{10}$$

Provided $n_f m$ is an integer, it will hold that

$$\begin{aligned} \sum_{\xi=0}^{n_f-1} \exp(2\pi i m \xi) = \sum_{\xi=1}^{n_f} \exp(2\pi i m \xi) &= 0 \text{ if } m \text{ not an integer} \\ &= n_f \text{ if } m \text{ is an integer.} \end{aligned} \tag{11}$$

Here, as we have already seen, $n_f \mathbf{q} . \mathbf{r}^0$ is integral. Therefore, the summations over the index ξ in (10) are non-zero only for $t = -1$ or $t = +1$, respectively. It is easy to verify that such values of ±1 for t are the only possibilities for having non-zero summation. Let us suppose, for instance, that $(t_p + 1)\mathbf{q} . \mathbf{r}^0$ is an integer for $t_p \neq -1$. This means that $(t_p + 1) = k n_f$, with k integral, since we have chosen $n_f \mathbf{q} . \mathbf{r}^0$ as the smallest possible integer.

Therefore, $|k|$ is integral and ≥ 1.

Since, as we have seen, $n_f \mathbf{q} = v \mathbf{r}^{0*}$, we have

$$\begin{aligned} \mathbf{h} = \mathbf{H}^0 + t_p \mathbf{q} &= \mathbf{H}^0 + (k n_f - 1)\mathbf{q} = \mathbf{H}^0 + k n_f \mathbf{q} - \mathbf{q} \\ &= \mathbf{H}^0 + k v \mathbf{r}^{0*} - \mathbf{q} = \mathbf{H}'^0 - \mathbf{q}. \end{aligned} \tag{12}$$

Here $\mathbf{H}'^0$ is another reciprocal-lattice point of the intermediate cell, and the contribution for $\mathbf{h} = \mathbf{H}^0 + t_p \mathbf{q}$ coincides with the corresponding contribution for $\mathbf{h} = \mathbf{H}'^0 - \mathbf{q}$. A similar result can be obtained for $t \neq 1$ in the other summation. On such grounds, (10) can be rewritten with considerable simplification:

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/(V n_d)(m_k m_{k'})^{1/2} \exp(2\pi i \mathbf{q} . \Delta\mathbf{r}_{kk'}) \\ &\quad\times \sum_{\mathbf{H}^0} \{ s_{ij}'^{0k}(\mathbf{H}^0) + K^{ij}(\mathbf{H}^0 - \mathbf{q}) \sum_{\mathbf{g}} \exp(2\pi i \mathbf{H}^0 . \mathbf{g}) \\ &\quad+ K^{*ij}(\mathbf{H}^0 + \mathbf{q}) \sum_{\mathbf{g}} \exp(-2\pi i \mathbf{H}^0 . \mathbf{g}) \}. \end{aligned} \tag{13}$$

Here

$$s_{ij}'^{0k}(\mathbf{H}^0) = f(\alpha_{\mathbf{h}}) s_{ij}^{0k}(\mathbf{h}) / n_f.$$

Since $\sum_{\mathbf{g}} \exp(2\pi i \mathbf{H}^0 . \mathbf{g})$ and $s_{ij}'^{0k}(\mathbf{h})$ are equal to zero for extinct reflections ($F_{\mathbf{H}^0} = F_{\mathbf{H}^0}^* = 0$), or to n_d for non-extinct reflections, (13) can be further simplified, and the summation performed with respect only to non-extinct reflections, corresponding to the points $\mathbf{h}^0$ of the reciprocal lattice of the primitive unit cell of the crystal:

$$\begin{aligned} D_{ij}^{kk'} &= 18\pi R^2/ V(m_k m_{k'})^{1/2} \exp(2\pi i \mathbf{q} . \Delta\mathbf{r}_{kk'}) \\ &\quad\times \sum_{\mathbf{h}^0} \{ s_{ij}''^{0k}(\mathbf{h}^0) + K^{ij}(\mathbf{h}^0 - \mathbf{q}) + K^{*ij}(\mathbf{h}^0 + \mathbf{q}) \}. \end{aligned} \tag{14}$$

Here

$$s_{ij}''^{0k}(\mathbf{h}^0) = s_{ij}'^{0k}(\mathbf{h}^0) / n_d.$$

This means that in computing such terms using (6) $F_{\mathbf{h}}$ and $F_{\mathbf{h}}^*$ should be evaluated using only the contributions of the atoms in the *primitive* unit cell, and not those of the multiple cells. Because these terms are independent of the wave vector $\mathbf{q}$, their evaluation can be made once and for all at the beginning. This is an advantage in the case of the lengthy procedure of sampling the Brillouin zone at several points. The independence of the wave vector of such terms also means that in the diagonal blocks (3×3) of the dynamical matrix, the $s_{ij}^{0k}(\mathbf{h})$'s must correspond to the so-called 'self-terms' or 'self force constants' $\Phi_{ij}^{kk}(0,0)$. This is an alternative way for evaluating such constants, instead of the usual relationship

$$\Phi_{ij}^{kk}(0,0) = -\sum_{l} \Phi_{ij}^{kk'}(0,l). \tag{15}$$

By inspecting the preceding equations (14), (8), and (6), where the values of $s_{ij}''^{0k}$, K^{ij} and K^{*ij} are specified, we can easily see that the calculations are simple and essentially involve the usual derivatives of structure factors, as in the least-squares refinement of atomic positions in a crystal structure.

Another interesting feature of this process is that for each point $\mathbf{h}^0$ of the reciprocal lattice of the primitive cell, there are two satellite points if fractional indices $\mathbf{h}^0 + \mathbf{q}$ and $\mathbf{h}^0 - \mathbf{q}$ have to be considered. The situation recalls what is observed in incommensurate crystal structures (Bertaut, 1983, 1986) or in first-order (one-phonon) scattering in problems of thermal motion (Willis & Pryor, 1975). Needless to say, this analogy reflects close relationships in the basic physical process.

For $\mathbf{q} = \mathbf{0}$, (3) or (14) can be written as

$$\begin{aligned} D_{ij}^{kk'} &= [18\pi R^2/ V(m_k m_{k'})^{1/2}] \\ &\quad\times 2 \sum_{\mathbf{h}^0} f(\alpha_{\mathbf{h}^0}) \{ \partial A_{\mathbf{h}^0}/\partial x_{ik}^0 \partial A_{\mathbf{h}^0}/\partial x_{jk'}^0 \\ &\quad+ \partial B_{\mathbf{h}^0}/\partial x_{ik}^0 \partial B_{\mathbf{h}^0}/\partial x_{jk'}^0 + A_{\mathbf{h}^0} \partial^2 A_{\mathbf{h}^0}/\partial x_{ik}^0 \partial x_{jk'}^0 \\ &\quad+ B_{\mathbf{h}^0} \partial^2 B_{\mathbf{h}^0}/\partial x_{ik}^0 \partial x_{jk'}^0 \}. \end{aligned} \tag{16}$$

Here, as usual, $F_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}}$; the last two terms in the above equation correspond, as is obvious, to the 'self-force constants.' It is also easy to verify that in this case ($\mathbf{q} = \mathbf{0}$) the $D_{ij}^{kk'}$'s are all real, whereas for a general value of the wave vector $\mathbf{q}$ they are complex, as is required by theory.

The rate of convergence for some practical cases (NaCl and forsterite Mg_2SiO_4) appears from considering Table 1 and Fig. 2. In both cases, when

Table 1. *Analysis of convergence of frequencies of vibrational modes with respect to the maximum value of* $\sin\theta/\lambda$ (Å^{-1}) *or to the number of reflections*

Data are for NaCl with Kellermann's (1940) field for various values of the wave vector **q** (referred to non-primitive cell). The value of R is 1·995 Å. The values obtained by Kellermann are reported within parentheses below each set.

Components of **q**			$(\sin\theta/\lambda)_{\max}$	Number of reflections	Frequencies (cm^{-1})					
0·0	0·0	0·0	0·2	7	0	0	0	158	158	321
			0·3	25	0	0	0	147	147	316
			0·4	56	0	0	0	153	153	319
			0·5	84	0	0	0	152	152	319
			0·6	165	0	0	0	152	152	319
			0·75	265	0	0	0	151	151	319
					(0	0	0	152	152	320)
0·1	0·1	0·1	0·3		20i	20i	9i	145	145	313
			0·4		27	27	42	150	150	314
			0·5		27	27	45	151	151	315
			0·6		27	27	44	151	151	315
			0·75		27	27	44	151	151	315
					(27	27	45	151	151	315)
0·3	0·1	0·1	0·3		33	41	69	145	150	298
			0·4		46	50	84	150	153	300
			0·5		48	52	87	151	153	300
			0·6		47	51	84	150	153	300
			0·75		47	51	85	150	153	300
					(47	51	84	150	153	301)
0·5	0·1	0·1	0·3		51	61	113	150	152	269
			0·4		68	74	123	154	156	273
			0·5		70	77	125	155	157	273
			0·6		68	75	123	154	156	272
			0·75		68	75	124	154	156	272
					(57	83	124	150	160	273)*
0·7	0·1	0·1	0·3		71	82	142	155	156	236
			0·4		84	93	150	159	161	242
			0·5		86	95	152	161	162	243
			0·6		84	93	150	160	160	241
			0·75		84	93	150	159	160	241
					(85	93	150	159	160	243)

* These discrepancies between Kellermann's values and ours are the only ones we have noticed on an extensive exploration of the Brillouin zone. The other discrepancies (within 1 cm^{-1}) are due to rounding effects.

reflections with a maximum value of $\sin\theta/\lambda = 0{\cdot}40\ \text{Å}^{-1}$ are included, this is sufficient for most practical purposes.

In this work, the 'old' Kellermann (1940) model has been used only for testing our method and computer programs, the main advantages being its simplicity (which permits extensive and comparatively inexpensive checking) and the wealth of reported data in the original publication. Therefore, no claim is intended on grounds of a better agreement with the experimental data with respect to more recent and detailed calculations (see for instance Reid & Smith, 1970).

Kellermann's field derives from considering the charge on the Na and Cl atoms to be exactly equal to ±1 electron units; the first and second derivatives of the potential $V(r)$ around each atom are obtained from the condition of equilibrium (considering only the effects of the six nearest neighbours) and from the experimental value of the coefficient of compressibility $\kappa = 4{\cdot}16\times10^{-15}\ \text{m}^2\ \text{N}^{-1}$.

Effects of symmetry

Whereas the symmetry operations $\{\mathbf{M}|\mathbf{w}\}$ do not hold as such for instantaneous displacements, the crystal symmetry leads to equivalences between the F's or their derivatives. For instance, we have:

$$\mathbf{x}_m^0 = \mathbf{M}\mathbf{x}_k^0 + \mathbf{w} \quad \text{and} \quad \mathbf{x}_{m'}^0 = \mathbf{M}\mathbf{x}_{k'}^0 + \mathbf{w}$$

where m and m' are the atoms corresponding to k and k', respectively.

Calling $\mathbf{h}'' = (\mathbf{M}^{-1})^T\mathbf{h}$ (see 5c):

$$\partial F_{\mathbf{h}}/\partial \mathbf{x}_k^0 = 2\pi i \mathbf{h} z_k \exp(2\pi i \mathbf{h}\,.\,\mathbf{x}_k^0)$$

$$\partial F_{\mathbf{h}}^*/\partial \mathbf{x}_k^0 = -2\pi i \mathbf{h} z_k \exp(-2\pi i \mathbf{h}\,.\,\mathbf{x}_k^0)$$

$$\partial F_{\mathbf{h}''}/\partial \mathbf{x}_m^0 = 2\pi i \mathbf{h}'' z_k \exp(2\pi i \mathbf{h}''\,.\,\mathbf{x}_m^0)$$

$$= 2\pi i \mathbf{h}'' z_k \exp(2\pi i \mathbf{h}\,.\,\mathbf{x}_k^0)\exp(2\pi i \mathbf{h}''\,.\,\mathbf{w}).$$

Referring to a new axial frame transformed by **M** with respect to the first, we have

$$\mathbf{x}_k'^0 = \mathbf{M}^{-1}\mathbf{x}_k^0,$$

where $\mathbf{x}'^0_k$ is the coordinate vector of the atom k with respect to the new frame. Since $\partial F_{\mathbf{h}''}/\partial \mathbf{x}'^0_m = \mathbf{M}^T\partial F_{\mathbf{h}''}/\partial \mathbf{x}^0_m$ *etc.*, we have

$$\begin{aligned}(\partial F_{\mathbf{h}''}/\partial \mathbf{x}'^0_m)_i(\partial F^*_{\mathbf{h}''}/\partial \mathbf{x}'^0_{m'})_j &= (\mathbf{M}^T\partial F_{\mathbf{h}''}/\partial \mathbf{x}^0_m)_i(\mathbf{M}^T\partial F^*_{\mathbf{h}''}/\partial \mathbf{x}^0_{m'})_j\\ &= 4\pi^2 z_k^2 \exp(2\pi i\mathbf{h}\,.\,\mathbf{x}^0_k)\exp(2\pi i\mathbf{h}''\,.\,\mathbf{w})(\mathbf{M}^T\mathbf{h}'')_i\\ &\quad\times\exp(-2\pi i\mathbf{h}\,.\,\mathbf{x}^0_{k'})\exp(2\pi i\mathbf{h}''\,.\,\mathbf{w})(\mathbf{M}^T\mathbf{h}'')_j.\end{aligned}$$

Since $\mathbf{M}^T\mathbf{h}'' = \mathbf{h}$, we have

$$(\partial F_{\mathbf{h}''}/\partial \mathbf{x}'^0_m)_i(\partial F^*_{\mathbf{h}''}/\partial \mathbf{x}'^0_{m'})_j = (\partial F_{\mathbf{h}}/\partial \mathbf{x}^0_k)_i(\partial F^*_{\mathbf{h}}/\partial \mathbf{x}^0_{k'})_j$$

or, similarly,

$$\partial F_{\mathbf{h}''}/\partial x'^0_{im}\partial F^*_{\mathbf{h}''}/\partial \mathbf{x}'^0_{jm'} = \partial F_{\mathbf{h}}/\partial \mathbf{x}^0_{ik}\partial F^*_{\mathbf{h}}/\partial \mathbf{x}^0_{jk'}. \quad (17)$$

From (8), (14) and (17), it is easy to see that the contributions to the elements of the dynamical matrix $D^{kk'}_{ij}$ are the same for atoms related by a symmetry operation, provided: (1) the indices are also transformed; (2) the derivatives are with respect to a new axial frame, related by symmetry, so that different references for any set of non-equivalent atoms must be chosen; (3) since $\mathbf{h} = \mathbf{h}^0 \pm \mathbf{q}$, the transformation of indices also involves the *wave vector* $\mathbf{q}$. Therefore, for $\mathbf{q} \neq \mathbf{0}$, such symmetry relationships connect different dynamical matrices, where

$$\mathbf{q}'' = (\mathbf{M}^{-1})^T\mathbf{q}.$$

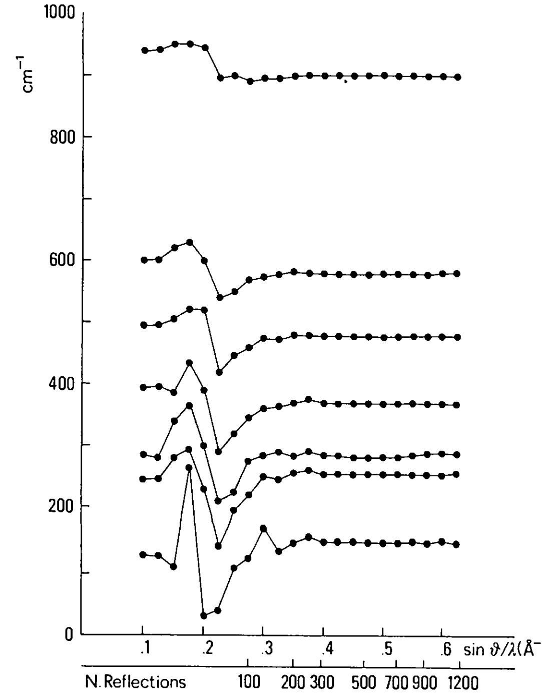


Fig. 2. Analysis of convergence of values of vibrational frequencies for forsterite Mg_2SiO_4 with different values of maximum $\sin\theta/\lambda$ or number of reflections considered. The data here reported are for $\mathbf{q} = \mathbf{0}$ and B_{3g} modes. The potential field and model are taken from Iishi (1978), with slight modifications (Pilati, Bianchi & Gramaccioli, 1990). The value of R is 0·808 Å.

All this is clearly in line with the well known symmetry relationships in the Brillouin zone (see, for instance, Filippini, Gramaccioli, Simonetta & Suffritti, 1976).

Within a single dynamical matrix, except for the special case of $\mathbf{q} = \mathbf{0}$, the symmetry relationships between the $F_{\mathbf{h}}$'s do not seem to bring any simplification. For $\mathbf{h}''^0 = -\mathbf{h}^0$, however, the contributions to the $D^{kk'}_{ij}$'s are the same, as can best be seen from (5d) and (8), considering that

$$f(\alpha_{-\mathbf{h}^0-\mathbf{q}}) = f(\alpha_{\mathbf{h}^0+\mathbf{q}}) \quad \text{and} \quad F_{\mathbf{h}} = F^*_{-\mathbf{h}}.$$

In other words, *Friedel's law holds* and this in any case dispenses the necessity of carrying on the summations on more than one-half the limiting sphere.

Influence of the wave on the electric field: TO–LO splitting

The limit for $\mathbf{q} \to \mathbf{0}$ of (14) coincides with (16). The only exception is the contribution for $\mathbf{h}^0 = \mathbf{0}$. Here, in fact, because $\mathbf{h} \to \mathbf{q}$ and (as we have seen) $\alpha = 2\pi|\mathbf{h}|R$, a singularity occurs for $f(\alpha)$:

$$\begin{aligned}\lim_{\substack{\mathbf{h}\to\mathbf{0}\\(\mathbf{q}\to\mathbf{0})}} f(\alpha) &= \lim_{\alpha\to 0}\,[\sin(\alpha) - \alpha\cos(\alpha)]^2/\alpha^8\\ &= \lim_{\alpha\to 0} 1/9\alpha^2 = \lim_{\alpha\to 0} 1/(36\pi^2R^2|\mathbf{h}|^2) = \infty. \quad (18)\end{aligned}$$

Therefore, this contribution $(D^{kk'}_{ij})_{\mathbf{h}^0=\mathbf{0}}$ will be

$$\begin{aligned}\lim_{\mathbf{q}\to\mathbf{0}} (D^{kk'}_{ij})_{\mathbf{h}^0=\mathbf{0}} = 18\pi R^2/V(m_km_{k'})^{1/2} \lim_{\mathbf{q}\to\mathbf{0}} \{&s''^{0k}_{ij}(\mathbf{0})\\ &+ (\partial F^*_{\mathbf{q}}/\partial x^0_{ik}\partial F_{\mathbf{q}}/\partial x^0_{jk'}\\ &+ \partial F_{\mathbf{q}}/\partial x^0_{ik}\partial F^*_{\mathbf{q}}/\partial x^0_{jk'})/(36\pi^2R^2|\mathbf{q}|^2)\}\end{aligned} \quad (19)$$

since

$$\lim_{\mathbf{q}\to\mathbf{0}} s''^{0k}_{ij}(\mathbf{0}) = 0$$

[because $F^*_{000} = F_{000} = \sum_k z_k$ *i.e.* the total net charge present in the cell. See also (6) and (5d) for completeness]; furthermore, considering (5c) and writing $\mathbf{q} = \hat{\mathbf{q}}|\mathbf{q}|$, where $\hat{\mathbf{q}}$ is the unit vector along the direction of $\mathbf{q}$, we have:

$$\begin{aligned}\lim_{\mathbf{q}\to\mathbf{0}} (D^{kk'}_{ij})_{\mathbf{h}^0=\mathbf{0}} &= 18\pi R^2/V(m_km_{k'})^{1/2}\\ &\quad\times \lim_{\mathbf{q}\to\mathbf{0}}\,[8\pi^2\hat{q}_i\hat{q}_j z_k z_{k'}|\mathbf{q}|^2/(36\pi^2R^2|\mathbf{q}|^2)]\\ &= 4\pi/V(m_km_{k'})^{1/2}\hat{q}_i\hat{q}_j z_k z_{k'}. \quad (20)\end{aligned}$$

Equation (20) clearly shows the limit for $\mathbf{q} \to \mathbf{0}$ not to be unique, but to depend on the direction $\hat{\mathbf{q}}$ of approach. Such a limit coincides exactly with the well known contribution of the macroscopic field set up during the vibration in the rigid-ion model, in the absence of retardation effects (see, for instance, equations A.2.19, 4.28, *etc.* in Venkataraman, Feldkamp & Sahni, 1975), which leads to the so-called TO–LO splitting of IR-active modes.

Consequently, Bertaut's method for evaluating the Coulombic lattice energy in a crystal can be usefully extended to application in lattice dynamics, and in a 'natural' way it implicitly accounts for a remarkably detailed treatment of the problem.

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Thermal Motion in Protein Crystals Estimated Using Laser-Generated Ultrasound and Young's Modulus Measurements

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Abstract

The measurement of the longitudinal speed of sound in crystals of ribonuclease-A and in human haemoglobin using laser-generated ultrasound is reported. Average values of 1784 (72) m s^{-1} and 1828 m s^{-1} were obtained. As a control the speed of sound transmitted through a compacted disc of lysozyme powder was measured as 2004 (23) m s^{-1}. The measured longitudinal acoustic velocities and the transverse velocity, estimated from a knowledge of Young's modulus, were used to estimate the acoustic contribution to the mean-square displacements of protein molecules as determined by X-ray crystallography. It was found that thermally induced acoustic vibrations make a significant contribution to the total atomic disorder, estimated to be in the range 0·04–0·11 Å^2 for the proteins studied. Such single-crystal estimates are required for calculation of the acoustic component of the diffuse scattering in protein crystal X-ray diffraction.

Introduction

X-ray diffraction from protein crystals yields patterns comprised of two components, namely, the Bragg and the diffuse scattering. The measurement of the diffuse scattering and attempts at its interpretation are a new development. The advent of area detectors, high-intensity synchrotron radiation and supercomputers means that it is now easier to try to exploit the

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