ROSSMANN, M. G. (1972). *The Molecular Replacement Method.* New York: Gordon & Breach.
ROSSMANN, M. G. & BLOW, D. M. (1961). *Acta Cryst.* **14**, 641–647.
ROSSMANN, M. G. & BLOW, D. M. (1962). *Acta Cryst.* **15**, 24–31.
ROSSMANN, M. G. & BLOW, D. M. (1963). *Acta Cryst.* **16**, 39–45.
ROSSMANN, M. G., BLOW, D. M., HARDING, M. M. & COLLER, E. (1964). *Acta Cryst.* **17**, 338–342.
ROSSMANN, M. G., FORD, G. C., WATSON, H. C. & BANASZAK, L. J. (1972). *J. Mol. Biol.* **64**, 237–249.
SCHWARTZ, L. (1967). *Méthodes Mathématiques pour les Sciences Physiques.* Paris: Hermann.
SHANNON, C. E. (1949). *Proc. Inst. Radio Engrs. New York*, **37**, 10–21.
SIM, G. A. (1959). *Acta Cryst.* **12**, 813–815.
SWEET, R. M., WRIGHT, H. T., JANIN, J., CHOTHIA, C. H. & BLOW, D. M. (1974). *Biochemistry*, **13**, 4212–4228.
TEN EYCK, L. F. (1973). *Acta Cryst.* **A29**, 183–191.

Acta Cryst. (1976). A**32**, 847

Applications of the Ewald Method. I. Calculation of Multipole Lattice Sums

BY P. G. CUMMINS* AND D. A. DUNMUR

Department of Chemistry, The University, Sheffield S3 7HF, England

AND R. W. MUNN AND R. J. NEWHAM

Department of Chemistry, UMIST, Manchester M60 1QD, England

(*Received* 20 *February* 1976; *accepted* 18 *March* 1976)

General principles of the Ewald method for evaluating multipole lattice sums are reviewed. The method is used to derive an expression for the Lorentz-factor dipole tensor sum in a form convenient for computation, and comparisons are made with the direct and plane-wise summation methods. Expressions are also given for computing quadrupole and octopole sums by the Ewald method. The effect of crystal symmetry on lattice sums is outlined; the number of independent sums relating different pairs of equivalent sublattices does not exceed the total number of such sublattices. Numerical results are given for the dipole lattice sums of hydrogen cyanide, benzene, durene, anthracene and pyrene. Quadrupole sums are given for cuprous chloride and pyrene, and octupole sums are given for hydrogen cyanide, benzene and anthracene. For dipole lattice sums, the Ewald method converges much faster than direct summation; for higher multipole sums, the Ewald method has no special advantage in speed, but may prove convenient, especially when sums are required for strained lattices.

Introduction

Quantitative microscopic interpretation of many physical properties of crystals requires a knowledge of some type of lattice sum. Calculations of the internal energies of crystals involve a wide range of lattice sums (charge–charge, dipole–dipole, quadrupole–quadrupole, *etc.*), depending on the form of the potential function assumed (Born & Huang, 1954; Rae, 1969; Craig, Mason, Pauling & Santry, 1965; Aung & Strauss, 1973). Similarly, the interpretation of electronic spectra of crystals requires the evaluation of dipole–dipole and higher-order lattice sums (Craig & Walmsley, 1963; Decius, 1968; Philpott & Lee, 1973; Frech, 1973). The response of crystals to electric fields as measured by their dielectric properties (Agranovich, 1974; Sinha, Gupta & Price, 1974; Bolton, Fawcett & Gurney, 1962; Tessman, Kahn & Shockley, 1953; Koikov & Rozova, 1967) or Stark spectroscopy (Hochstrasser, 1973; Dunmur & Munn, 1975; Chen, Hanson & Fox, 1975) again requires a knowledge of appropriate lattice sums for its microscopic interpretation. The effect of static or dynamic strain on all these properties is principally due to changes in the lattice sums, which in turn may be expressed in terms of higher-order lattice sums. There is therefore ample reason for the continuing interest in methods for evaluating lattice sums of various types (Hove & Krumhansl, 1953; De Wette & Schacher 1965; Bruesch & Lietz, 1970; Philpott, 1973; Aung & Strauss, 1973; Philpott & Mahan, 1973).

Two basic approaches may be followed in evaluating lattice sums: summation of the appropriate function over all points of the direct lattice, or summation after transformation from the direct to some other lattice, usually the reciprocal lattice. There are however difficulties with either approach. Values of certain direct lattice sums are only conditionally convergent, and it becomes necessary to define a summation shape outside which all lattice points are excluded (Philpott & Lee, 1973; Burrows & Kettle, 1975). This problem

---

* Present address: Department of Chemistry, University of Southern California, Los Angeles, California 90007, U.S.A.

manifests itself in the transformed sum over the reciprocal lattice as a singularity, such that the value of the sum depends on the direction from which the singularity is approached in reciprocal space (Aung & Strauss, 1973).

Recent attention has mostly been focused on the Ewald method for evaluating dipole lattice sums (Born & Huang, 1954, p. 248), using either a two-dimensional transformation (plane-wise summation: Philpott, 1973) or the complete three-dimensional transformation (Aung & Strauss, 1973; Dunmur, 1972). The Ewald method splits a lattice sum into two parts, one summed over the direct lattice and one over the reciprocal lattice. Its advantage is that it assigns the singularity in reciprocal space to the macroscopic electric field, leaving sums which are absolutely convergent and hence free of the difficulty of shape-dependent results such as arise in direct dipole lattice summations.

The formal extension of both two and three-dimensional Ewald-type transformations to the calculation of multipole lattice sums has recently been given (Aung & Strauss, 1973; Philpott & Mahan, 1973). In this and Part II of this series (Cummins, Dunmur, Munn & Newham, 1976) we consider specifically the lattice sums that arise in the calculation of lattice energies for molecular crystals and in the interpretation of the static dielectric properties of crystals. In the present paper we give expressions, in a form suitable for computation, for the sums giving the electric field due to a lattice of dipoles, quadrupoles or octupoles. Numerical results are presented for some crystals of interest. Although many of the results given here can be found in the literature, they are widely scattered, and appear in various apparently unrelated forms. Our aim here has been to collect together the most useful formulae, to explain how they are related to other similar formulae, and to explain how they may be interpreted in physical terms where appropriate. We hope to help those who need to calculate simple multipole sums to do so without having to resort to extensive algebraic derivations. In Part II we show how the Ewald method can be used to calculate the more complicated lattice sums governing the strain dependence of the permittivity and of lattice dipole–dipole energies.

Lattice multipole sums

(i) *Principles*

The electric field in a crystal may be regarded as originating from two sources: charges and multipoles outside the crystal (including surface charges), and multipoles distributed over the crystal lattice. Field sources outside the crystal give rise to the macroscopic electric field, which depends on the size and shape of the crystal. Multipoles distributed over a crystal lattice may be permanent properties of the molecules or ions in the structure, or they may be induced by an electromagnetic or lattice wave. In the former case, the permanent multipoles contribute to the internal energy of the crystal, while in the latter case the induced multipoles are interpreted as the microscopic response of the crystal to an electromagnetic field or lattice wave.

In a compound lattice consisting of Z interpenetrating sublattices, the position of a lattice point with respect to an arbitrary origin can be written as

$$\mathbf{r}(l,k)=\mathbf{r}(l)+\mathbf{r}(k)\,, \tag{1}$$

where

$$\mathbf{r}(l)=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3\,, \tag{2}$$

$\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the basic vectors of the unit cell, and l_1, l_2 and l_3 are integers denoting the unit cell in which the point lies. The vector $\mathbf{r}(k)$ denotes the position of the kth site (sublattice) within this cell, and can be written as

$$\mathbf{r}(k)=c_1(k)\mathbf{a}_1+c_2(k)\mathbf{a}_2+c_3(k)\mathbf{a}_3\,, \tag{3}$$

where $c_1(k)$, $c_2(k)$ and $c_3(k)$ lie between 0 and 1. If the crystal contains a distribution of multipoles, their value will depend on the sublattice on which they are situated. They will also in general be modulated in space with a wave of wave vector $\mathbf{y}$. Hence the multipole $\mathsf{M}^{(n)}$ at the lattice site (l,k) can be written as

$$\mathsf{M}^{(n)}(l,k;\mathbf{y})=\mathsf{M}^{(n)}(k)\exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l,k)\,. \tag{4}$$

Here the superscript n denotes the order of the multipole, taken as a 2^n-pole; then for a monopole (charge) $n=0$, for a dipole $n=1$, for a quadrupole $n=2$, and so on. With this choice, the tensor rank of the multipole is also n. Note that unless $\mathbf{y}=0$ the amplitudes $\mathsf{M}^{(n)}(k)$ required to produce a given distribution of multipoles $\mathsf{M}^{(n)}(l,k;\mathbf{y})$ depend on the choice of origin for $\mathbf{r}(l,k)$.

The electric field at a point $\mathbf{r}$ due to a multipole at the lattice point (l,k) is given by

$$\mathbf{F}(\mathbf{r})=(1/4\pi\varepsilon_0)\mathsf{T}^{(n+1)}[\mathbf{r}(l,k)-\mathbf{r}]\,.\,\mathsf{M}^{(n)}(l,k;\mathbf{y})\,, \tag{5}$$

where the single dot denotes an $n$fold inner product of the tensors. The quantity $\mathsf{T}^{(n)}(\mathbf{r})$ is the nth derivative with respect to $\mathbf{r}$ of $1/r$, which is usually called the 2^{n-1}-pole tensor and is of rank n; for example, the second-rank dipole tensor gives the field due to a dipole, which is a first-rank tensor (vector). The field at a point in a crystal due to an array of multipoles is given by summing equation (5) over l and k. Using equation (4) we can write this sum as

$$\mathbf{F}(\mathbf{r})=(1/\varepsilon_0)\sum_k\{\sum_l \boldsymbol{\nabla}^{(n+1)}|\mathbf{r}(l,k)-\mathbf{r}|^{-1} \times\exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l)/4\pi\}\,.\,\mathsf{M}^{(n)}(k)\exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(k)\,. \tag{6}$$

The quantity in curly brackets is a lattice multipole sum, which may be evaluated for a general point in the crystal for arbitrary $\mathbf{y}$. Most commonly one needs only the electric field at a particular sublattice point k' within the unit cell $l=0$, in which case the limit of equation (6) as $\mathbf{r}\to\mathbf{r}(0,k')$ is needed.

The method of Ewald for evaluating lattice sums is described in detail by Born & Huang (1954, p. 248). As explained in the *Introduction*, the method divides the sum in two parts, which are sums over the direct and reciprocal lattices respectively. The relative size of the two parts is governed by an arbitrary inverse length C. After this transformation, the field at $\mathbf{r}$ can be written as

$$\begin{aligned}\mathbf{F}(\mathbf{r}) = (1/\varepsilon_0) \sum_k \{ \sum_l (1/4\pi)\boldsymbol{\nabla}^{(n+1)}(CH[C|\mathbf{r}(l,k)-\mathbf{r}|] \\ \times \exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l) + (\pi/vC^2)G[\pi^2|\mathbf{y}(l)+\mathbf{y}|^2/C^2] \\ \times \exp 2\pi i[\mathbf{y}(l)+\mathbf{y}]\,.\,[\mathbf{r}-\mathbf{r}(k)])\}\,.\,\mathsf{M}^{(n)}(k) \\ \times \exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(k)\,. \qquad (7)\end{aligned}$$

Here the functions $H(x)$ and $G(x)$ are defined as

$$H(x) = (1-\operatorname{erf} x)/x \qquad (8)$$

$$G(x) = \exp(-x)/x\,, \qquad (9)$$

and $\mathbf{y}(l)$ is a reciprocal lattice vector. Both H and G are rapidly decreasing functions of x, so that the transformed sum converges rapidly. The transformation separates the weakly-damped oscillations which make the original series poorly convergent; in reciprocal space these oscillations are largely damped out. The rate of convergence can be optimized by varying C, but it is usually adequate to set $C = \pi^{1/2}/v^{-1/3}$, where v is the unit cell volume. It can be shown that for a dipole sum over a simple cubic lattice, this choice of C makes the term in H for each l equal and opposite to the term in G for the same l, leaving the whole sum determined by the terms for $l=0$ (Frech, 1973). We now derive the form taken by equation (7) with this value of C for lattices of point dipoles, quadrupoles and octupoles. In each case we consider the field at the point $(0,k)$ in the long-wavelength limit $\mathbf{y} \rightarrow 0$, when a sublattice carries the same multipole at each point.

(ii) *Dipole lattice sums*

The electric field in a lattice of point dipoles is given by setting $n=1$ in equation (7). In this case, the multipole tensor $\mathsf{T}^{(2)}$ varies as r^{-3}, while the number of dipoles in a sphere of radius r varies as r^3. As a result, the sum is only conditionally convergent as $\mathbf{y} \rightarrow 0$. Examination of equation (7) shows that it is the term in G for $l=0$ which is not well-behaved, being an irregular function of $\mathbf{y}$ in this limit. However, it has been shown (Born & Huang, 1954, p. 248) that this irregular part gives the macroscopic field $\mathbf{E}$. The electric field in a lattice of dipoles as $\mathbf{y} \rightarrow 0$ may thus be written as

$$\mathbf{F}(k) = \mathbf{E} + \sum_{k'} \mathsf{L}(kk')\,.\,\mathsf{M}^{(1)}(k')/\varepsilon_0 v\,. \qquad (10)$$

The dimensionless Lorentz-factor tensor introduced previously (Dunmur, 1972) is the regular part of equation (7) evaluated in the limit $\mathbf{r} \rightarrow \mathbf{r}(0,k')$. It can be expressed as

$$\begin{aligned}L_{\alpha\beta}(kk') = H^0_{\alpha\beta}(kk') + \sum_l{}' \{H_{\alpha\beta}[\mathbf{R}_{kk'}(l)] \\ - G_{\alpha\beta}[\mathbf{Q}(l)] \cos 2\mathbf{Q}(l)\,.\,\mathbf{R}_{kk'}(0)\} \qquad (11)\end{aligned}$$

where the sum over l excludes $l=0$, and

$$\mathbf{R}_{kk'}(l) = (\pi^{1/2}/v^{1/3})[\mathbf{r}(l,k') - \mathbf{r}(k)]\,, \qquad (12)$$

$$\mathbf{Q}(l) = \pi^{1/2}v^{1/3}\mathbf{y}(l)\,. \qquad (13)$$

The expressions for $H_{\alpha\beta}(\mathbf{R})$ and $G_{\alpha\beta}(\mathbf{Q})$ are given in the Appendix.

The first term on the right-hand side of equation (11) is the contribution to the direct lattice sum for $l=0$. When $k \neq k'$, $H^0_{\alpha\beta}(kk')$ becomes simply $H_{\alpha\beta}[\mathbf{R}_{kk'}(0)]$, but when $k=k'$ $\mathbf{R}_{kk'}(0)$ is zero and $H_{\alpha\beta}$ would diverge. However, this divergence can be understood as the infinite self field at a dipole due to itself, which is actually part of the macroscopic field, as explained by Robinson (1973). As equation (10) shows, the Lorentz-factor tensor describes the difference between the local field at a molecule and the macroscopic field, and this difference arises solely from dipoles other than the one considered. If therefore the field due to the dipole at $(0,k)$ is subtracted from equation (7) before taking the limit $\mathbf{r} \rightarrow \mathbf{r}(0,k)$, it is found that $H^0_{\alpha\beta}(kk)$ is the regular function

$$H^0_{\alpha\beta}(kk) = \tfrac{1}{3}\delta_{\alpha\beta}\,. \qquad (14)$$

The tensor $\mathsf{L}(kk')$ is symmetrical both in its Cartesian components and in the indices k and k'. Its trace is unity, so that under isotropic symmetry it is diagonal with elements equal to one third, which gives by equation (10) the standard result of Lorentz for the local field in a polarized continuum. The summation in equation (11) is absolutely convergent, its value being independent of the order in which the terms are taken. The Lorentz-factor tensor is therefore independent of shape, and the result corresponds to a dipole lattice sum for an infinite crystal, with no points excluded.

The quantity obtained by direct summation of the dipole tensor depends on the cavity shape defined implicitly or explicitly by the summation. For a spherical sample, the result is

$$\sum_{(\text{sphere})}{}' \mathsf{T}^{(2)}(l,kk') = (4\pi/v)[\mathsf{L}(kk') - \tfrac{1}{3}\mathsf{I}]\,, \qquad (15)$$

where the last term is equivalent to the Lorentz cavity field. Dipole lattice sums have also been evaluated by plane-wise summation (De Wette & Schacher, 1965; Philpott, 1973). The field due to an infinite plane of dipoles falls off very rapidly with perpendicular distance from the plane, all but a few percent being contributed by the plane containing the point in question (Mahan & Obermair, 1969). Dipole lattice sums calculated by plane-wise summation correspond to summation over an infinitely extended slab. For such a summation over planes with unit normal $\mathbf{n}$, the result is

$$\sum_{(\text{planes}\perp\mathbf{n})}{}' \mathsf{T}^{(2)}\,(l,kk') = (4\pi/v)[\mathsf{L}(kk') - \mathbf{nn}]\,. \tag{16}$$

The plane-wise sums quoted by Philpott (1972) are opposite in sign to this, and a factor $v/4\pi$ larger. The plane-wise sums quoted by Philpott (1973) are also opposite in sign, and more importantly have been converted to give energies of interaction of unit dipoles along the various molecular axes (see later).

(iii) *Quadrupole lattice sums*

The extension of the Ewald method for a lattice of quadrupoles is straightforward; the field at a point on sublattice k follows on setting $n=2$ in equation (7). The sum in this case is regular as $\mathbf{y}\to 0$, and in this limit the field is

$$F_\alpha(k) = \sum_{k'} L_{\alpha\beta\gamma}(kk')M^{(2)}_{\beta\gamma}(k')/\varepsilon_0 v\,, \tag{17}$$

where the third-rank tensor $L_{\alpha\beta\gamma}(kk')$ is given by

$$L_{\alpha\beta\gamma}(kk') = H^0_{\alpha\beta\gamma}(kk') + \sum_l{}' \{H_{\alpha\beta\gamma}[\mathbf{R}_{kk'}(l)] + G_{\alpha\beta\gamma}[\mathbf{Q}(l)]\sin 2\mathbf{Q}(l)\,.\,\mathbf{R}_{kk'}(0)\}\,. \tag{18}$$

Once again, the term for $l=0$ in the direct lattice sum has been separated out. When $k\neq k'$, $H^0_{\alpha\beta\gamma}(kk')$ is equal to $H_{\alpha\beta\gamma}[\mathbf{R}_{kk'}(0)]$, but when $k=k'$ we have again to subtract the infinite self field of a quadrupole at itself before taking the limit $\mathbf{r}\to\mathbf{r}(0,k)$. The result is

$$H^0_{\alpha\beta\gamma}(kk) = 0\,. \tag{19}$$

The expressions for $H_{\alpha\beta\gamma}(\mathbf{R})$ and $G_{\alpha\beta\gamma}(\mathbf{Q})$ are given in the Appendix.

The quantity $L_{\alpha\beta\gamma}(kk')$ has the dimensions of reciprocal length. It is related to the direct lattice sum of the quadrupole tensor by

$$L_{\alpha\beta\gamma}(kk') = (v/4\pi)\sum_l{}' T^{(3)}_{\alpha\beta\gamma}(l,kk')\,. \tag{20}$$

It is symmetric in the indices $\alpha\beta\gamma$ but antisymmetric in k and k', so that $L_{\alpha\beta\gamma}(kk)=0$. Quadrupole sums satisfy the condition

$$L_{\alpha\alpha\gamma}(kk') = 0\,, \tag{21}$$

which follows directly from the definition of the quadrupole tensor and can be regarded as an expression of Laplace's equation.

(iv) *Octupole lattice sums*

With $n=3$ in equation (7), the field at a point on sublattice k due to an array of octupoles is obtained as

$$F_\alpha(k) = \sum_{k'} L_{\alpha\beta\gamma\delta}(kk')M^{(3)}_{\beta\gamma\delta}(k')/\varepsilon_0 v\,. \tag{22}$$

The limit $\mathbf{y}\to 0$ again poses no problems. The octupole lattice sum $L_{\alpha\beta\gamma\delta}(kk')$ is given by

$$L_{\alpha\beta\gamma\delta}(kk') = H^0_{\alpha\beta\gamma\delta}(kk') + \sum_l{}' \{H_{\alpha\beta\gamma\delta}[\mathbf{R}_{kk'}(l)] + G_{\alpha\beta\gamma\delta}[\mathbf{Q}(l)]\cos 2\mathbf{Q}(l)\,.\,\mathbf{R}_{kk'}(0)\}\,, \tag{23}$$

where $H_{\alpha\beta\gamma\delta}(\mathbf{R})$ and $G_{\alpha\beta\gamma\delta}(\mathbf{Q})$ are defined in the Appendix, and by arguments similar to those used previously

$$H^0_{\alpha\beta\gamma\delta}(kk') = H_{\alpha\beta\gamma\delta}[R_{kk'}(0)]\ (k\neq k') \tag{24}$$

$$H^0_{\alpha\beta\gamma\delta}(kk) = -(2\pi/5v^{2/3})\,(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\,. \tag{25}$$

The dimensions of $L_{\alpha\beta\gamma\delta}(kk')$ are $(\text{length})^{-2}$. It is related to the direct lattice sum of $\mathsf{T}^{(4)}(l,kk')$ by an equation similar in form to equation (20). It is symmetric in the indices $\alpha\beta\gamma\delta$ and also in k and k'. Octupole sums satisfy the condition

$$L_{\alpha\alpha\gamma\delta}(kk') = 0\,. \tag{26}$$

(v) *Effect of crystal symmetry*

The symmetry of the crystal can have two effects on lattice multipole sums. For a given k and k' it may require certain components to be equal or zero, while for different pairs of sublattices k and k' it may require certain components to be equal or equal and opposite.

The former effect is rather subtle, because the sums are functions of the vector $\mathbf{r}(k)$–$\mathbf{r}(k')$. When $k=k'$, the vector degenerates to a point, and each lattice sum must transform into itself under the operations of the crystal point group. The independent non-zero components can then be determined by standard means (Bhagavantam, 1966). However, when $k\neq k'$ the lattice tensor sum only possesses the symmetry of the crystal point group if the vector $\mathbf{r}(k)$–$\mathbf{r}(k')$ transforms under the operations of the point group into itself or into another vector differing by a lattice vector $\mathbf{r}(l)$.

The effect of symmetry in relating different pairs of sublattices is more straightforward. If the vector $\mathbf{r}(k)$–$\mathbf{r}(k')$ is carried by an operation of the crystal space group into the vector joining another pair of sublattices (modulo a reciprocal lattice vector), then the two lattice sums are related. The relation is obtained by transforming the first lattice sum to new axes defined by the transformation matrix for the non-translational part of the space-group operation, using standard techniques for tensors (Temple, 1967). As a special case, lattice sums for $k=k'$ are the same for all k. These relationships ensure that the sum over all k and k' of a lattice sum, which is characteristic of the unit cell and hence of the whole crystal, satisfies the requirements of the point group symmetry.

The relationships also reduce the number of pairs kk' for which sums need to be calculated. Each sum is symmetric or antisymmetric in k and k' according to whether its rank is even or odd, so that for Z sublattices there are at most $\frac{1}{2}Z(Z-1)$ independent sums with $k\neq k'$. For a particular k, there are $Z-1$ different pairs kk' with $k\neq k'$. If all sublattices are equivalent, there are $Z-1$ ways of transforming k into a different sublattice k'', and $Z-2$ ways of transforming k' into a sublattice different from k and k''. The $Z-1$ pairs kk' can thus be transformed into $\frac{1}{2}(Z-1)(Z-2)$ different unordered pairs; together, these pairs exhaust the total $\frac{1}{2}Z(Z-1)$. It follows that there are only $Z-1$ independent sums for $k \neq k'$, to which all the others are related. There is one independent sum for $k=k'$, so that for Z equivalent sublattices there are altogether Z independent lattice sums. These are conveniently calculated by fixing k and allowing k' to take all values. It is important to note that although there are at most Z independent lattice sums in a crystal containing Z equivalent sublattices, the relationships between these and the remaining $\frac{1}{2}Z(Z-1)$ sublattice sums are determined by the symmetry operations that relate the vectors $\mathbf{r}(k)-\mathbf{r}(k')$. Thus the dependent sublattice sums may differ from the related independent ones by having some elements opposite in sign or transposed in position.

Numerical results and discussion

We have calculated dipole, quadrupole, and octupole sums for a number of crystals of interest. In addition to using the Ewald method, we have also performed direct summations over a spherical volume. Satisfactory agreement was obtained (*e.g.* within 0·1% for the dipole sums). The test for convergence was that a fixed number of contributions to each sum should fall below a pre-set value; some care in applying this test is necessary, particularly in highly anisotropic lattices, since a series of small contributions may be followed by a much larger one when a new shell of lattice points is begun [defined by the largest of the integers l_1, l_2 and l_3 in equation (2)]. For the dipole sums, convergence to 1 part in 10^5 was obtained by summing the Ewald formula over a few hundred points, whereas the direct sum over a spherical volume required up to 35000 points to give convergence even to 1 part in 10^4. For the other sums, the rates of convergence were more nearly comparable.

Our results for Lorentz-factor tensors (dipole lattice sums) are given in Table 1; further details are given by Cummins (1974) and Newham (1975). The tetragonal modification of *hydrogen cyanide* has been the subject of lattice-energy studies, and our results agree with those deduced from the work of Rae (1969) (see also Munn & Newham, 1976). *Anthracene* is the most studied of molecular crystals, for which lattice sums have been used in exciton calculations (Craig & Walmsley 1963; Philpott 1972, 1973) and in dielectric theory (Cummins, Dunmur & Munn, 1973). Our results may be compared with the plane sums of Philpott (1973) through equation (16). They are in exact agreement when transformed to the same axes if account is taken of the unit conversion factor $4\pi \times 10^6$ cm^{-1} Å/8·6104v. Our results for *durene* agree with those obtained by Chen *et al.* (1975) for analysing Stark spectroscopic measurements, except that in their $L_{xz}(11)$ the last two figures appear to have been transposed. In *benzene*, the molecules occupy special positions, with the result that $\mathsf{L}(kk')$ always transforms according to the full orthorhombic point group and there are only four different $\mathsf{L}(kk')$. In *pyrene*, on the other hand, the molecules occupy general positions such that the vectors between the pairs of sublattices 1 and 2 or 3 and 4 (related by inversion) have no special components. The result is that $\mathsf{L}(12)$ and $\mathsf{L}(34)$

Table 1. *Lorentz-factor tensor components $L_{\alpha\beta}(kk')$ referred to crystal axes (taken as abc' for anthracene, durene and pyrene)*

	αβ					
kk'	*xx*	*xy*	*xz*	*yy*	*yz*	*zz*
Hydrogen cyanide						
11	0·3311	0	0	0·3311	0	0·3377
Anthracene						
11	0·1530	0	0·0162	0·8208	0	0·0262
12	1·2417	0	−0·0158	0·3538	0	−0·5955
Durene						
11	−0·1300	0	−0·2170	0·8464	0	0·2836
12	0·8352	0	0·2034	0·0614	0	0·1034
Benzene						
11	0·4207	0	0	0·0473	0	0·5319
12	0·3230	0	0	0·8443	0	−0·1674
13	0·9695	0	0	−0·7587	0	0·7891
14	−0·2239	0	0	0·9359	0	0·2877
Pyrene						
11	−0·0736	0	−0·1321	0·4421	0	0·6315
12	1·2667	−1·6776	0·6609	0·5109	−0·4891	−0·7776
13	1·0789	0	0·1038	0·0026	0	−0·0815
14	0·3961	0	−0·1191	0·7885	0	−0·1846

do not transform according to the monoclinic point group and differ in the signs of their *xy* and *yz* components.

Quadrupole lattice sums are zero if they transform according to a point group containing the inversion operation. The highest-symmetry point groups not containing this operation are 23 and $\bar{4}3m$. *Cuprous chloride* belongs to the $\bar{4}3m$ point group, with the copper and chlorine sublattices occupying special positions. Hence there is only one non-zero component of the quadrupole lattice sum:

$$L_{xyz}(12)=6{\cdot}1125/a\,,$$

where a is the conventional unit-cell dimension. There are also non-zero quadrupole sums for *pyrene*, for which our results are summarized in Table 2. The vector joining sublattices 1 and 2 has no special components, and so all components $L_{\alpha\beta\gamma}$ (12) are non-zero; the components of $\mathsf{L}^{(3)}(34)$ are equal to those of $\mathsf{L}^{(3)}(12)$ in magnitude, with the sign changed for every time y occurs. The vector between sublattices 1 and 3 has special x and z components, leaving non-zero components $L_{\alpha\beta\gamma}(13)$ only if $(\alpha\beta\gamma)$ contains y once or three times. Conversely, the vector between sublattices 1 and 4 has a special y component, leaving non-zero components $L_{\alpha\beta\gamma}(14)$ only if $(\alpha\beta\gamma)$ contains y twice or not at all. All the sums satisfy the condition (21).

Table 2. *Quadrupole tensor component sums $L_{\alpha\beta\gamma}(kk')/\text{Å}^{-1}$ referred to crystal abc′ axes for pyrene*

		kk′	
$\alpha\beta\gamma$	12	13	14
xxx	0·1708	0	−0·3476
xxy	1·2204	−0·1599	0
xxz	−0·4217	0	−0·1057
yyx	−0·6990	0	0·4724
yyy	−0·8529	0·1423	0
yyz	−0·2077	0	−0·0848
zzx	0·5281	0	−0·1249
zzy	−0·3676	0·0175	0
zzz	0·6294	0	0·1905
xyz	0·5167	−0·0060	0

All crystals have non-zero octupole lattice sums, a selection of which is given in Table 3. These sums give not only the field due to a lattice of octupoles but also the energy of interaction of a lattice of quadrupoles. For *benzene* our results agree with the quadrupole–quadrupole energy calculated by Craig *et al.* (1965). All the octupole sums satisfy the condition (26).

The numerical results presented here illustrate the range of behaviour that multipole lattice sums can exhibit. In a number of cases the results give in explicit form information implicit in previous published work. The independent non-zero components of the multipole tensor sums are determined by the symmetry of the Bravais lattice about a point at a position (within a unit cell) defined by the vector between the pair of sublattices concerned. When the molecules are in general positions, as in pyrene, the pattern of components may thus differ considerably from that implied by the point symmetry of the lattice itself.

Table 3. *Octupole tensor component sums $L_{\alpha\beta\gamma\delta}(kk')/\text{Å}^{-2}$ referred to crystal axes (taken as abc′ for anthracene)*

		kk′		
$\alpha\beta\gamma\delta$	11	12	13	14
Hydrogen cyanide				
xxxx	−0·1545			
xxyy	0·0996			
xxzz	0·0550			
zzzz	−0·1101			
Anthracene				
xxxx	0·1219	−0·1618		
xxxz	−0·0087	0·0085		
xxyy	−0·1210	0·4367		
xxzz	−0·0009	−0·2750		
yyxz	−0·0003	−0·0003		
yyyy	0·2392	−0·3462		
yyzz	−0·1183	−0·0906		
zzxz	0·0090	−0·0082		
zzzz	0·1192	0·3655		
Benzene				
xxxx	0·1214	−0·1991	0·1690	−0·4141
xxyy	−0·0415	0·2440	−0·1211	−0·2338
xxzz	−0·0799	−0·0450	−0·0479	0·6479
yyyy	0·1006	−0·1510	−0·1324	0·4278
yyzz	−0·0591	−0·0930	0·2535	−0·1940
zzzz	0·1391	0·1379	−0·2056	−0·4539

The speed of the Ewald method in calculating dipole lattice sums has already been stressed. Another advantage of the Ewald method over the direct method stems from the conditions $L_{\alpha\alpha}(kk')=1$ and equations (21) and (26). These are automatically satisfied for each lattice point in a direct summation, but not in the Ewald method, where part of the tensor for any one direct lattice point has been transformed into contributions at all reciprocal lattice points. As a result, the conditions are satisfied only to the extent that the slower of the two sums has converged. For quadrupole and octupole sums, the Ewald method has little advantage in speed over direct summation. However, with the expressions given here it is convenient to use the Ewald method for quadrupoles and octupoles if it is also to be used for dipoles. Moreover, the calculation of multipole lattice sums by the Ewald method for $\mathbf{y}\neq 0$ provides a direct route to the strain dependence of lower multipole lattice sums, as described in Part II (Cummins, Dunmur, Munn & Newham, 1976).

We thank the Science Research Council (U.K.) for Research Studentships (PGC and RJN).

APPENDIX

Here we collect the expressions for the quantities $H_{\alpha\beta..}(\mathbf{R})$ and $G_{\alpha\beta..}(\mathbf{Q})$ in equations (11), (18), and (22).

$$H_{\alpha\beta}(\mathbf{R})=\frac{\pi^{1/2}}{4R^5}(3R_\alpha R_\beta-R^2\delta_{\alpha\beta})(1-\mathrm{erf}\,R)$$
$$+\tfrac{1}{2}\left[\left(\frac{3}{R^4}+\frac{2}{R^2}\right)R_\alpha R_\beta-\frac{\delta_{\alpha\beta}}{R^2}\right]\exp(-R^2)\,. \tag{A1}$$

$$G_{\alpha\beta}(\mathbf{Q})=(Q_\alpha Q_\beta/Q^2)\exp(-Q^2)\,. \tag{A2}$$

$$H_{\alpha\beta\gamma}(\mathbf{R})=\frac{\pi}{4v^{1/3}R^7}[3(\delta_{\alpha\beta}R_\gamma+\delta_{\beta\gamma}R_\alpha+\delta_{\gamma\alpha}R_\beta)R^2$$
$$-15R_\alpha R_\beta R_\gamma](1-\mathrm{erf}\,R)$$
$$+\frac{\pi^{1/2}}{2v^{1/3}}\left[\left(\frac{3}{R^4}+\frac{2}{R^2}\right)(\delta_{\alpha\beta}R_\gamma+\delta_{\beta\gamma}R_\alpha+\delta_{\gamma\alpha}R_\beta)\right.$$
$$\left.-\left(\frac{15}{R^6}+\frac{10}{R^4}+\frac{4}{R^2}\right)R_\alpha R_\beta R_\gamma\right]\exp(-R^2)\,. \tag{A3}$$

$$G_{\alpha\beta\gamma}(\mathbf{Q})=(2\pi^{1/2}/v^{1/3})Q_\gamma G_{\alpha\beta}(\mathbf{Q})\,. \tag{A4}$$

$$H_{\alpha\beta\gamma\delta}(\mathbf{R})=\frac{\pi^{3/2}}{4v^{2/3}R^9}[3R^4(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})$$
$$-15R^2(\delta_{\alpha\beta}R_\gamma R_\delta+\delta_{\beta\gamma}R_\delta R_\alpha+\delta_{\gamma\delta}R_\alpha R_\beta$$
$$+\delta_{\delta\alpha}R_\beta R_\gamma+\delta_{\alpha\gamma}R_\beta R_\delta+\delta_{\beta\delta}R_\alpha R_\gamma)$$
$$+105R_\alpha R_\beta R_\gamma R_\delta](1-\mathrm{erf}\,R)$$
$$+\frac{\pi}{2v^{2/3}}\left[\left(\frac{3}{R^4}+\frac{2}{R^2}\right)(\delta_{\alpha\gamma}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\right.$$
$$-\left(\frac{15}{R^6}+\frac{10}{R^4}+\frac{4}{R^2}\right)(\delta_{\alpha\beta}R_\gamma R_\delta+\delta_{\beta\gamma}R_\delta R_\alpha$$
$$+\delta_{\gamma\delta}R_\alpha R_\beta+\delta_{\delta\alpha}R_\beta R_\gamma+\delta_{\alpha\gamma}R_\beta R_\delta+\delta_{\beta\delta}R_\alpha R_\gamma)$$
$$\left.+\left(\frac{105}{R^8}+\frac{70}{R^6}+\frac{28}{R^4}+\frac{8}{R^2}\right)R_\alpha R_\beta R_\gamma R_\delta\right]$$
$$\times\exp(-R^2)\,. \tag{A5}$$

$$G_{\alpha\beta\gamma\delta}(\mathbf{Q})=(2\pi^{1/2}/v^{1/3})Q_\delta G_{\alpha\beta\gamma}(\mathbf{Q})\,. \tag{A6}$$

In all these expressions, $R\equiv|\mathbf{R}|$ and $Q\equiv|\mathbf{Q}|$. The results are consistent with those obtained by Leech & Pawley (1975).

References

Agranovich, V. M. (1974). *Sov. Phys. Usp.* **17**, 103–117.

Aung, S. & Strauss, H. L. (1973). *J. Chem. Phys.* **58**, 2737–2745.

Bhagavantam, S. (1966). *Crystal Symmetry and Physical Properties.* New York: Academic Press.

Bolton, H. C., Fawcett, W. & Gurney, I. D. C. (1962). *Proc. Phys. Soc.* **80**, 199–208.

Born, M. & Huang, K. (1954). *Dynamical Theory of Crystal Lattices.* Oxford Univ. Press.

Bruesch, P. & Lietz, M. (1970). *J. Phys. Chem. Solids*, **31**, 1137–1141.

Burrows, E. L. & Kettle, S. F. A. (1975). *J. Chem. Educ.* **52**, 58–59.

Chen, F. P., Hanson, D. M. & Fox, D. (1975). *J. Chem. Phys.* **63**, 3878–3885.

Craig, D. P., Mason, R., Pauling, P. & Santry, D. P. (1965). *Proc. Roy. Soc. Lond.* A**286**, 98–116.

Craig, D. P. & Walmsley, S. H. (1963). *Physics and Chemistry of the Organic Solid State*, Vol. 1, p. 586. New York: Interscience.

Cummins, P. G. (1974). Ph.D. Thesis, Univ. of Sheffield.

Cummins, P. G., Dunmur, D. A. & Munn, R. W. (1973). *Chem. Phys. Lett.* **22**, 519–522.

Cummins, P. G., Dunmur, D. A., Munn, R. W. & Newham, R. J. (1976). *Acta Cryst.* A**32**, 854–858.

Decius, J. C. (1968). *J. Chem. Phys.* **49**, 1387–1392.

DeWette, F. W. & Schacher, G. E. (1965). *Phys. Rev.* **137**, A78–A91.

Dunmur, D. A. (1972). *Mol. Phys.* **23**, 109–115.

Dunmur, D. A. & Munn, R. W. (1975). *Chem. Phys.* **11**, 297–306.

Frech, R. (1973). *J. Chem. Phys.* **58**, 2177–2180.

Hochstrasser, R. M. (1973). *Acc. Chem. Res.* **6**, 263–269.

Hove, J. & Krumhansl, J. A. (1953). *Phys. Rev.* **92**, 569–572.

Koikov, S. N. & Rozova, M. N. (1967). *Sov. Phys. Solid State*, **8**, 2319–2324.

Leech, J. W. & Pawley, G. S. (1975). *Phys. Stat. Sol.* (*b*). Submitted for publication.

Mahan, G. D. & Obermair, G. (1969). *Phys. Rev.* **183**, 834–841.

Munn, R. W. & Newham, R. J. (1976). *Chem. Phys.* In the press.

Newham, R. J. (1975). Ph.D. Thesis, UMIST.

Philpott, M. R. (1972). *J. Chem. Phys.* **56**, 996–997.

Philpott, M. R. (1973). *J. Chem. Phys.* **58**, 588–594.

Philpott, M. R. & Lee, J. W. (1973). *J. Chem. Phys.* **58**, 595–602.

Philpott, M. R. & Mahan, G. D. (1973). *J. Chem. Phys.* **59**, 445–446.

Rae, A. I. M. (1969). *Mol. Phys.* **16**, 257–273.

Robinson, F. N. H. (1973). *Macroscopic Electromagnetism.* Oxford Univ. Press.

Sinha, S. K., Gupta, R. P. & Price, D. L. (1974). *Phys. Rev.* (*B*), **9**, 2564–2572.

Temple, G. (1967). *Cartesian Tensors.* London: Methuen.

Tessman, J. R., Kahn, A. H. & Shockley, W. (1953). *Phys. Rev.* **92**, 890–895.