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Note

Depolarization Correction for Coulomb Lattice Sums

Two main approaches have been developed for calculating the Coulomb potential at a point inside a perfect crystal (the Madelung sum). The first, which is associated with the name of Evjen [1], is a direct summation (or integration) over whole unit-cells, with an expanding outer boundary that tends to a particular shape. In the second method (Ewald [2]), part of the series which is slowly convergent is transformed into reciprocal space so that it converges rapidly. The former method has the advantage of conceptual simplicity which, despite the disadvantage of poor convergence, recommends it to the computer programmer. But it is well known that the series for the potential is only semi-convergent, so that the limiting value of a direct sum depends on the choice of building-block and the shape of the boundary. The Ewald sums, on the other hand, are absolutely convergent and so define a *principal value* of the potential, called the intrinsic potential, which is characterized by two important properties [3–6]: (i) it displays the period of the crystal, and (ii) it averages to zero over the unit-cell. The difference between the potential represented by a direct sum and the Ewald value is called the extrinsic potential [6]. It is the potential due to the "macroscopic" or smoothed crystal [3], a distribution of charge which (if the crystal is electrically neutral) is concentrated near the surface and is known as the polarization charge. Thus, while the direct method applies to a perfectly regular crystal which is insulated from all foreign influence, the Ewald method corresponds to the case of a superficially distorting or uninsulated crystal which surrounds itself if required with a film of neutralizing charge. Any calculation that employs the direct method generally has to be corrected in order to recover the intrinsic value. The problem of determining the extrinsic potential was solved by Laue and others [7, 6], who showed it to be the product of the second moment of the crystallographic basis with the depolarization tensor from dielectric theory. Although it often vanishes by symmetry, this *depolarization correction* must be considered in the case of the general crystal.

One of the most practical versions of the direct method is the one propounded by Wood and others [8–10], in which the crystal is built up successively from similar shells of unit-cells. It is the purpose of the present note to describe a computational procedure, which implements the Laue formulas for the depolarization correction in the case of the Wood mode of direct summation. The summation itself will not be discussed.

Perhaps the main use to which the program has been put is for computing the electric field due to a lattice of dipoles, a problem which arises in exploring the effect of polarizability in ionic crystals.

Since the Laue derivation [7] is not widely known, it is worth while to reassert it

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here, leading us to Eqs. (5) and (6) below. The charge density $\rho_{\text{mac}}(\mathbf{r})$ of the "macroscopic crystal" is the convolution $s * \rho_1/v$ between the shape function $s(\mathbf{r})$, which defines the occupied region of the crystal, and the charge density $\rho_1(\mathbf{r})$ of the crystallographic basis or building-block, divided by the volume v of the unit-cell. This generates a field of macroscopic and extrinsic potential, $\phi_{\text{ex}} = \rho_{\text{mac}} * r^{-1}$, which relates the intrinsic potential ϕ_{in} to the direct summation ϕ_{ds} in the limit of the infinite crystal:

$$\phi_{\text{ds}} \rightarrow \phi_{\text{in}} + \phi_{\text{ex}} . \tag{1}$$

Microscopic and macroscopic quantities can be disentangled from each other by expanding one of the convolutions as a Taylor series, whose terms are the scalar product of a moment and a gradient, and by introducing λ as a scaling-parameter of the shape function and a measure of the size of the crystal. If the shape function is standardized by means of a macroscopic coordinate $\mathbf{R}$, one can write $s(\lambda\mathbf{R}) = s_1(\mathbf{R})$, and so obtain

$$\nabla_{\mathbf{r}}{}^{L}\phi_{\text{ex}}(\mathbf{r} + \lambda\mathbf{R}) = \sum_{n} \left[\frac{1}{v}\,\rho_1(\mathbf{r}) * \nabla_{\mathbf{r}}{}^{L}\frac{1}{n!}\,\mathbf{r}^{n}\right] \cdot \nabla_{\mathbf{R}}{}^{n}[s_1(\mathbf{R}) * R^{-1}]\,\lambda^{2-n}. \tag{2}$$

For the limit of the infinite crystal one need only consider the process, $\lambda \rightarrow \infty$, which represents the geometrically congruent expansion of the boundary about the origin. Equation (2) shows that in this limit the terms of the series having $n > 2$ vanish. The terms $n < 2$ then provide the conditions of convergence of the direct sum in the limit process:

$$\rho_1(\mathbf{r}) * 1 = 0 \qquad (L = 0), \tag{3}$$

$$[\rho_1(\mathbf{r}) * \nabla_{\mathbf{r}}{}^{L}\mathbf{r}] \cdot \nabla_{\mathbf{R}}[s_1(\mathbf{R}) * R^{-1}] = 0 \qquad (L = 0, 1). \tag{4}$$

Condition (3) requires the basis to be electrically neutral. Condition (4) is always satisfied in the Wood mode, because the shape function is centrosymmetric about the macroscopic field-point $\mathbf{R} = \mathbf{0}$. Under these conditions, then, only the term $n = 2$ remains, so that the limiting value of the expression (2) can be written as

$$\nabla_{\mathbf{r}}{}^{L}\phi_{\text{ex}}(\mathbf{r}, \mathbf{R} \mid \rho_1, s_1) = \left[\frac{1}{v}\,\rho_1(\mathbf{r}) * \nabla_{\mathbf{r}}{}^{L}\,\tfrac{1}{2}\mathbf{r}^{2}\right] \cdot \nabla_{\mathbf{R}}{}^{2}[s_1(\mathbf{R}) * R^{-1}]. \tag{5}$$

This factorization displays properties of the basis separately from properties of the shape function.

From the first factor in Eq. (5) some simple properties of the different gradients of the extrinsic potential may be observed. The potential itself ($L = 0$) depends on the quadrupole and dipole moments of the basis, the electric field ($L = 1$) depends on its dipole moment and charge, the electric field gradient ($L = 2$) depends on its charge, while gradients of higher order vanish identically. It may be noted that, if the dipole moment and the irreducible quadrupole moment both vanish, ϕ_{ex} becomes independent of $\mathbf{r}$ and of the shape of s_1, and reduces to the mean potential of Bethe [11].

The second factor in Eq. (5) is the classical depolarization tensor. In the Wood mode, one sets $s_1 = 1$ within a central parallelepiped congruent with the Bravais unit-cell, and $s_1 = 0$ outside it. Then $\nabla_{\mathbf{R}} s_1(\mathbf{R})$ vanishes everywhere except on the surface, where one may resolve $\nabla_{\mathbf{R}} R^{-1}$ into components across a face and within it, using a vector cross product. Thus,

$$\begin{aligned} \int d^3\mathbf{R}[\nabla_{\mathbf{R}} s_1(\mathbf{R})][\nabla_{\mathbf{R}} R^{-1}] &= \sum_i^6 \left[\hat{\mathbf{n}}_i \hat{\mathbf{n}}_i \Omega_i + \hat{\mathbf{n}}_i \hat{\mathbf{n}}_i \times \oint_i d\mathbf{R}\, R^{-1}\right] \\ &\equiv 4\pi[\mathbf{D}(\text{faces}) + \mathbf{D}(\text{edges})]. \end{aligned} \tag{6}$$

Here $\hat{\mathbf{n}}_i$ is the unit-normal of the face i. In the first term Ω denotes the solid angle that a face subtends at the origin, a quantity representing the potential due to a uniform double layer. Such an effect was remarked by Evjen in his original paper [1], and it was also derived by Dahl [10]. The second term in Eq. (6) contains the potential due to a uniform line source, and was unfortunately neglected in the work of Dahl.

Details of the trigonometry needed to compute the depolarization tensor (6) may now be stated. The Bravais unit-cell is generated by three vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, forming a right-handed system, and the volume v is their scalar triple product $[\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3]$. We generate vectors normal to each face, $\mathbf{n}_i = \mathbf{a}_j \times \mathbf{a}_k$, where (ijk) is understood to be cyclic, and we define $\hat{\mathbf{n}}_i = \mathbf{n}_i/n_i$ and $\mathbf{b}_i = \hat{\mathbf{n}}_i/n_i$ for $i = 1, 2, 3$. The vertices of the central parallelepiped lie at the points, $\mathbf{c}_0 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$, $\mathbf{c}_i = \mathbf{c}_0 - \mathbf{a}_i$, and their reflexion through the origin. First let us consider the face terms. To compute the solid angle Ω_i of the face $(0j\bar{i}k)$ we divide it into two triangles $(0jk)$ and $(\bar{i}jk)$. Instead of L'Huilier's theorem for the spherical excess ϵ of a spherical triangle we use a more direct formula [12],

$$\begin{aligned} t(0jk) &\equiv \tan \tfrac{1}{2}\epsilon(0jk) = \tfrac{1}{2}v/(c_0c_jc_k + c_0C_{jk} + c_jC_{k0} + c_kC_{0j}), \\ t(\bar{i}jk) &\equiv \tan \tfrac{1}{2}\epsilon(\bar{i}jk) = \tfrac{1}{2}v/(c_ic_jc_k + c_iC_{jk} - c_jC_{ki} - c_kC_{ij}), \end{aligned} \tag{7}$$

in which $C_{ij} = \mathbf{c}_i \cdot \mathbf{c}_j$. The compound tangent formula then gives

$$\frac{\Omega_i}{2\pi} = \frac{1}{\pi} \operatorname{artan} \left[\frac{t(0jk) + t(\bar{i}jk)}{1 - t(0jk)\, t(\bar{i}jk)}\right]. \tag{8}$$

If this comes out to be negative, unity is added to ensure a positive solid angle. The face contributions to the depolarization tensor appear as the cyclic sum,

$$\mathbf{D}(\text{faces}) = \sum_i^3 \hat{\mathbf{n}}_i \hat{\mathbf{n}}_i \Omega_i / 2\pi. \tag{9}$$

Next is the edge effect, which rests on the result that the straight line integral of R^{-1} between $\mathbf{c}_j$ and $\mathbf{c}_k$ with length a_i has the magnitude,

$$\ln\left(\frac{c_j + c_k + a_i}{c_j + c_k - a_i}\right).$$

Consequently the edge contributions to the depolarization tensor are a cyclic sum,

$$\mathbf{D}(\text{edges}) = \sum_i^3 \ln\left(\frac{c_0 + c_i + a_i}{c_0 + c_i - a_i} \times \frac{c_j + c_k - a_i}{c_j + c_k + a_i}\right)$$

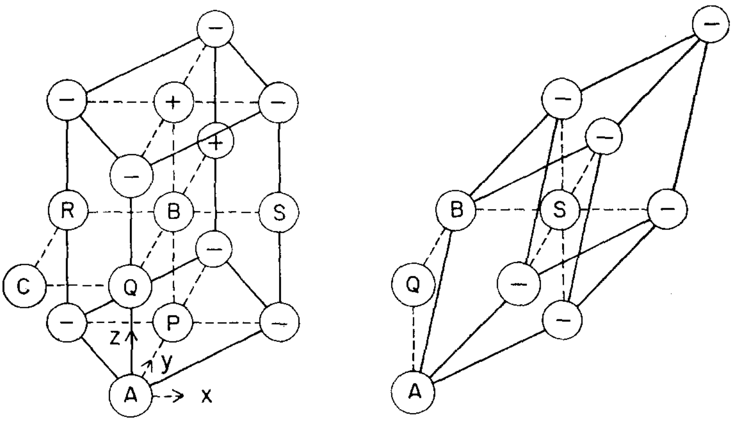
$$\times \frac{1}{2\pi}\,[\mathbf{b}_j(\mathbf{a}_i A_{ik}/a_i - \mathbf{a}_k a_i) + \mathbf{b}_k(\mathbf{a}_i A_{ij}/a_i - \mathbf{a}_j a_i)], \tag{10}$$

in which $A_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$.

The computer program has been organized in the following manner. To a main program which computes the direct sum, $(\hat{\mathbf{a}} \cdot \nabla)^L \phi_{\text{ds}}(\mathbf{r}, \mathbf{0} \mid \rho_1, s_1)$, two subroutines have been added which compute the depolarization correction, so that the intrinsic value is obtained according to Eq. (1). In the main program the user has already defined the crystal by specifying the unit-cell of the Bravais lattice (which is not necessarily the primitive unit-cell of the crystal) and by furnishing it with a basis consisting of point charges q_l at position $\mathbf{r}_l$. No restrictions are made on the crystal class. When the first of the subroutines, BASMOM, is called, the basis moments are evaluated at the field-point $\mathbf{r}$,

$$\nabla^{2-\nu}\rho_1 * \tfrac{1}{2}\mathbf{r}^2 = \sum_l q_l \frac{1}{\nu!}(\mathbf{r} - \mathbf{r}_l)^\nu \equiv \mathbf{M}_\nu \qquad (\nu = 0, 1, 2).$$

If these are not all zero, the lowest order N of nonzero moment is determined. The main program, after performing the direct summation over a given number of shells, forms an index of convergence, $I = L + N$. Then if $I > 2$, absolute convergence is



(a) (b)

FIG. 1. In the crystal structure of rocksalt, negative ions A, B, C, etc. alternate with positive ions P, Q, R, S, etc. on a unit cubic lattice, shown here by dashed lines. The same periodic structure can be built up using (a) a tetragonal unit-cell of volume $v = 4$, or (b) the primitive rhombohedral cell of $v = 2$.

indicated; if $I = 0$, there is divergence; while if $I = 1$ or 2, there is conditional convergence, and the second subroutine, MACCOR, is activated. MACCOR computes the elements of the depolarization tensor according to Eqs. (7)–(10), brings in the above moments to compute the scalar product (5), and finally returns the value, $\mathrm{SMAC} = -(\hat{\mathbf{a}} \cdot \nabla)^L \phi_{\mathrm{ex}}(\mathbf{r}, \mathbf{0} \mid \rho_1, s_1)$, as the depolarization correction which is required.

The program is designed to reproduce the same intrinsic value, no matter what periodically equivalent definition of the crystal is used for the direct summation. While the choice of Bravais lattice corresponds, through its unit-cell, to a choice in the shape of the crystal, and while the selection of ions for the basis affects the surface composition of the crystal, the direct and extrinsic contributions to the potential should vary equally with these parameters. Some instructive tests of this intrinsic invariance are offered by the rocksalt structure shown in Fig. 1, and here the program has indeed reproduced the standard Madelung constant (i.e., the intrinsic potential at a negative-

TABLE I

Potential contributions, using some alternative parameters of shape and basis, evaluated at a negative-ion site (A) in rocksalt (see Fig. 1 for geometry).[a]

Bravais cell	Tetragonal		Rhombohedral	
$\mathbf{D}$(faces); $\mathbf{D}$(edges)	$\frac{1}{\pi}\arccos\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{7}{9} \end{pmatrix}$; 0		$\frac{1}{9}\begin{pmatrix} 3 & -1 & -1 \\ -1 & 3 & -1 \\ -1 & -1 & 3 \end{pmatrix}$; $\frac{0.14532}{\pi}\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$	
Basis	$APBQ$	$APCR$	AQ	AS
$\mathbf{M}_2$	$\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 0 & -1 & 0 \\ -1 & 2 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$
ϕ_{ds}	1.74756	0.51661	0.70037	−0.17154
ϕ_{ex}(faces)	0	−1.23096	−1.04720	−1.04720
ϕ_{ex}(edges)	0	0	0	−0.87191
ϕ_{in}	1.74756	1.74757	1.74756	1.74756

[a] Face and edge contributions to the depolarization tensor $\mathbf{D}$, and the second moment $\mathbf{M}_2$ of the basis about A, are given in cartesian components. The potential terms are ϕ_{ds}, computed as the limit of a direct sum over a greater unit-cell (Wood mode); the face and edge contributions to the extrinsic potential, $\phi_{\mathrm{ex}} = -(4\pi/v)\,\mathbf{M}_2 \cdot \mathbf{D}$ [Eq. (5)]; and the intrinsic resultant, $\phi_{\mathrm{in}} = \phi_{\mathrm{ds}} - \phi_{\mathrm{ex}}$.

ion site) [4] with an accuracy of one part in 10^5. Details of the computations are given in Table I. Thus, when the tetragonal cell is chosen [Fig. 1a] with a basis consisting of a nearest-neighbor square of ions, the direct sum converges to the intrinsic value; but if a different quadrupole is taken as the basis, there is a different ϕ_{ds}, and a nonzero ϕ_{ex} arising from face contributions. When the primitive rhombohedral cell is chosen [Fig. 1b] with a pair of nearest neighbors as the basis, the resulting ϕ_{ex} comes from face contributions; but if the third-neighbor pair on the body diagonal is selected, there are edge contributions as well, so that ϕ_{ds} and ϕ_{in} have opposite sign.

The subroutines described here are available in the form of FORTRAN source listings from the author.

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