Electric Field Gradients in Point-Ion and Uniform-Background Lattices. II*

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The electric field gradients in point-charge lattices and the electric field in point-dipole lattices are given by the same lattice sums (dipole sums). Expressions for the electric field gradients in point-charge ionic crystals and metals of arbitrary symmetry are presented. Rapidly converging expressions for the dipole sums appearing in these expressions have been obtained in the preceding paper by the method of planewise summation.

I. INTRODUCTION

SOME years ago one of the authors (F. W. de W.) applied the method of planewise summation to the evaluation of the lattice contribution to the electric field gradients in point-charge ionic crystals and metals with hexagonal and tetragonal symmetry.[1] The lattice sums appearing in the expressions for the field gradients in point-charge lattices are exactly the same as those appearing in the expression for the electric field in point-dipole lattices. Since, in the preceding paper,[2] we have extended the method of planewise summation of dipole sums to lattices of arbitrary symmetry, we have at the same time obtained the necessary expressions for the field gradients in arbitrary point-charge lattices. In this paper we will indicate how the results of the preceding paper[2] can be used to evaluate the field gradients in ionic and metallic point-charge lattices of arbitrary symmetry.

At this point we mention one important difference between the electric field in dipole lattices and the electric field gradients in point-charge lattices; this concerns the question of shape dependence.[3] The lattice sums occurring in both problems are the same conditionally convergent sums (dipole sums), but whereas the electric field in a dipole lattice, as a consequence of the conditional convergence of the dipole sum, has a value that depends on the shape of the crystal, the field gradients in an ionic crystal or metallic point-charge lattice are independent of the crystal shape, as a result of the charge neutrality of the unit cell. Still, the shape dependence of the dipole sum has some practical importance for the evaluation of field gradients for the following reason: In an actual calculation the lattice is divided into sublattices each of which carries charges of the same sign. As a result, the field gradients due to each sublattice separately are shape-dependent and these sublattice field gradients can only be added together after they have been made to apply to the same crystal shape. This is of importance here because in the planewise summation method it may be advantageous to choose differently oriented sets of planes (i.e., different x, y, z axes) for the different sublattices. In such a case one has to add or subtract from the calculated sublattice field gradients the proper "depolarization fields," so that all results refer to the same x, y, z system before they can be added to give the total field gradients (cf. Ref. 2, Secs. I and VI).

We briefly recall the standard definitions of field gradients. The potential at a point $\mathbf{r}$ due to a charge distribution of density $\rho(\mathbf{r})$ is

$$V(\mathbf{r})=\int \frac{\rho(\mathbf{r}')d^3r'}{|\mathbf{r}-\mathbf{r}'|}. \tag{1}$$

The field-gradient tensor has the elements $\partial^2V(\mathbf{r})/\partial\kappa\partial\nu$, where κ and ν indicate x, y, z of the arbitrary coordinate system in which $\mathbf{r}(x,y,z)$ is defined. It is evident that the field-gradient tensor is symmetric, and it is therefore completely specified by six quantities. Since one of these quantities (the trace) is unobservable in nuclear resonance experiments, it is customary to consider the traceless tensor

$$V_{\kappa,\nu}(\mathbf{r})\equiv\partial^2V(\mathbf{r})/\partial\kappa\partial\nu-\tfrac{1}{3}\delta_{\kappa,\nu}\textstyle\sum_\kappa \partial^2V(\mathbf{r})/\partial\kappa^2 \tag{2}$$

($\delta_{\kappa,\nu}$ is the Kronecker symbol) which satisfies Laplace's equation and which is determined by five quantities. Henceforth we will use the name field-gradient tensor for the traceless tensor $V_{\kappa,\nu}$. With respect to its principle axes $V_{\kappa,\nu}$ is completely specified by two quantities. (The other three quantities specify the orientation of the principal axes.) Choosing the z' and x' directions along the directions of maximum and minimum field gradients, respectively, the customary choice for these two quantities is

$$eq\equiv V_{z'z'}, \tag{3}$$

$$\eta\equiv(V_{x'x'}-V_{y'y'})/V_{z'z'}. \tag{4}$$

η is called the "asymmetry parameter." To relate eq and η to the quantities $V_{\kappa,\nu}$ taken with respect to an arbitrary coordinate system x, y, z, one has to specify the three Eulerian angles of x', y', z' with respect to x, y, z.

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[1] F. W. de Wette, Phys. Rev. 123, 103 (1961).
[2] F. W. de Wette and G. E. Schacher, Phys. Rev. 137, A78 (1965), preceding paper.
[3] These questions of shape dependence have been discussed in more detail in Refs. 2 and 1, respectively.

In Ref. 2 we have indicated how, in the method of planewise summation, the choice of the x, y, z system is determined by the choice of the set of planes over which the planewise summation is carried out. For complex lattices of arbitrary symmetry it may be necessary to introduce a number of sublattices for which the x, y, z axes are not the same. Furthermore, none of these coordinate systems necessarily coincides with the principle axis system x', y', z' of the field-gradient tensor at a given reference point. The procedure to evaluate eq and η using the method of planewise summation is then the following: First, evaluate five independent field-gradient quantities $V_{\kappa,\nu}{}^{(i)}(\mathbf{r}_0)$ at the reference point $\mathbf{r}_0$ for each of the sublattices i. Second, if different x, y, z axes have been used for the evaluation of the $V_{\kappa,\nu}{}^{(i)}$ for different sublattices, refer all quantities to the same coordinate system by adding or subtracting the appropriate "depolarization fields." Third, add the $V_{\kappa,\nu}{}^{(i)}$'s so obtained to give the total field-gradient components in the reference point: $V_{\kappa,\nu}(\mathbf{r}_0)=\sum_i V_{\kappa,\nu}{}^{(i)}(\mathbf{r}_0)$. This completes the determination of the field-gradient tensor $V_{\kappa,\nu}(\mathbf{r}_0)$ with respect to the common coordinate system x, y, z. The fourth step consists of diagonalizing the matrix $V_{\kappa,\nu}$. The largest eigenvalue is by definition the quantity eq, and η is obtained from the three eigenvalues by the use of Eq. (4). The eigenvectors of the matrix $V_{\kappa,\nu}$ give the directions of the principle axes x', y', z' of the field-gradient tensor with respect to the x, y, z axes.

On the other hand, from experiments one directly derives the quantities eqQ (Q is the quadrupole moment of the nucleus under consideration) as well as η and the orientation of the principle axes system x', y', z' with respect to the crystal axes.[4] Discrepancies between the measured and the calculated quantities eq, η, and the $x'y'z'$ directions, may result from a number of causes such as neglect of covalency, failure of the point-charge model on other grounds, etc. In some circumstances it may be more useful to evaluate eq and η from the computed $V_{\kappa,\nu}$ by a transformation from the x, y, z coordinate system to the *experimentally* determined x', y', z' coordinate system. This avoids the diagonalization procedure of the matrix $V_{\kappa,\nu}$, but it requires a coordinate transformation. As an example we express the quantity $eq=V_{z',z'}(0)$ in terms of the dipole sums $S(\kappa,p_\nu)$ with respect to that coordinate system that is most convenient for carrying out the planewise summations. For an ionic crystal we have [cf. Sec. II, Eq. (11)]

$$eq=V_{z',z'}(0)=\sum_j \epsilon_j \sum_\lambda \{3z'_{\lambda,j}{}^2 r_{\lambda,j}{}^{-5}-r_{\lambda,j}{}^{-3}\}. \quad (5)$$

Let α, γ, β be the Eulerian angles of the principle axis system x', y', z' with respect to the system x, y, z used in calculating the lattice sums (cf. Fig. 1), then

$$z'_{\lambda,j}=\sin\alpha \sin\beta x_{\lambda,j}-\cos\alpha \sin\beta y_{\lambda,j}+\cos\beta z_{\lambda,j}. \quad (6)$$

Substitution of (6) into (5) leads to:

$$\begin{aligned} eq=V_{z',z'}(0)=\sum_j \epsilon_j\{&-\cos2\alpha \sin^2\beta S_{j_1,j_2,j_3}(x,p_x)\\ &+(\cos^2\beta-\sin^2\beta\cos^2\alpha)S_{j_1,j_2,j_3}(z,p_z)\\ &-\sin2\alpha \sin^2\beta S_{j_1,j_2,j_3}(x,p_y)\\ &+\sin\alpha \sin2\beta S_{j_1,j_2,j_3}(x,p_z)\\ &-\cos\alpha \sin2\beta S_{j_1,j_2,j_3}(y,p_z)\}, \end{aligned} \quad (7)$$

where we used the relation $S(x,p_x)+S(y,p_y)+S(z,p_z)=0$, which is equivalent to Laplace's equation [cf. Ref. 2, Eq. (64)]. Hence, if the Eulerian angles α, γ, β are known, eq can immediately be found from the values of the sums appearing in Eq. (7).

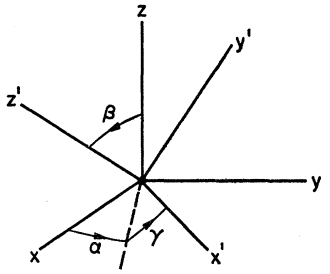

FIG. 1. Eulerian angles relating the x', y', z' axes to the x, y, z axes.

II. THE FIELD GRADIENT IN IONIC LATTICES

In this and the following section we adopt the notation of Ref. 2, Sec. III. We consider an ionic crystal made up of a number of sublattices j, containing the point charges[5] ϵ_j. The charge neutrality of the unit cell is expressed by $\sum_j \epsilon_j=0$. If we choose the origin 0 at the point at which we want to evaluate the field gradient, then the charge density in the lattice is (omitting the point charge at 0):

$$\rho(\mathbf{r})=\sum_j \epsilon_j \sum_\lambda \delta(\mathbf{r}-\mathbf{r}_{\lambda,j}), \quad (8)$$

where it is understood that for $j=0$ (i.e., $j_1=j_2=j_3=0$) the term $\lambda_1=\lambda_2=\lambda_3=0$ is excluded from the λ summation.

Since the charge density is zero at the origin and hence the trace vanishes, we have from (2): $V_{\kappa,\kappa}(0)=\partial^2 V(0)/\partial\kappa^2$. Furthermore, the differentiations may be carried out under the integral sign in (1). This gives

$$V_{\kappa,\kappa}(0)=\int \rho(\mathbf{r})\frac{3\kappa^2-r^2}{r^5}d^3r, \quad (9)$$

$$V_{\kappa,\nu}(0)=\int \rho(\mathbf{r})\frac{\kappa\nu}{r^5}d^3r. \quad (10)$$

Substitution of Eq. (8) into Eqs. (9) and (10) gives:

$$\begin{aligned} V_{\kappa,\kappa}(0)&=\sum_j \epsilon_j \sum_\lambda\{3\kappa_{\lambda,j}{}^2 r_{\lambda,j}{}^{-5}-r_{\lambda,j}{}^{-3}\}\\ &=\sum_j \epsilon_j S_{j_1,j_2,j_3}(\kappa,p_\kappa), \end{aligned} \quad (11)$$

[cf. Ref. 2, Eqs. (34)–(36)[6]], and

$$\begin{aligned} V_{\kappa,\nu}(0)&=\sum_j \epsilon_j \sum_\lambda 3\kappa_{\lambda,j}\nu_{\lambda,j}r_{\lambda,j}{}^{-5}\\ &=\sum_j \epsilon_j S_{j_1,j_2,j_3}(\kappa,p_\nu), \end{aligned} \quad (12)$$

[4] G. M. Volkoff, Can. J. Phys. **31**, 820 (1953).

[5] Some of the ϵ_j's may have the same value, but belong to different sublattices for convenience of the summation procedure.

[cf. Ref. 2, Eqs. (37)–(39)[6]]. κ and ν indicate x, y, or z. The appropriate summation formulas for $S_{j_1,j_2,j_3}(\kappa,p_\kappa)$ and $S_{j_1,j_2,j_3}(\kappa,p_\nu)$ are given in Sec. IV of Ref. 2; the special formulas applying for the cases $j_3=0$, and $j_1=j_2=j_3=0$, given in Ref. 2, are equally valid here.

III. THE FIELD GRADIENT IN UNIFORM-BACKGROUND LATTICES

A uniform-background lattice is a simple model for a metal. The conduction electrons are considered to be free, giving rise to a uniform negative charge distribution, and the positive ionic cores are considered as point charges. We consider a monatomic lattice of this kind, but of arbitrary structure, so that a number of different sublattices may be required to cover all lattice points. The charge density in such a lattice is

$$\rho(\mathbf{r})=\rho_{\rm el}+\rho_{\rm ion}=-Ze/v+Ze\sum_{\lambda,j}\delta(\mathbf{r}-\mathbf{r}_{\lambda,j}), \quad (13)$$

where $\rho_{\rm el}$ is the electron charge density and $\rho_{\rm ion}$ is the charge density of the positive point ions. Charge neutrality requires that $\rho_{\rm el}=-Ze/v$, where Ze is the net charge of the ionic cores and v is the volume per ion. For $j_1=j_2=j_3=0$ the term $\lambda_1=\lambda_2=\lambda_3=0$ is excluded from the λ summation.

To evaluate $\partial^2V(0)/\partial\kappa^2$ and $\partial^2V(0)/\partial\kappa\partial\nu$ we cannot simply substitute (13) into integrals of the form (9) and (10), because $\rho_{\rm el}$ is different from zero at the origin and this causes the integrals to diverge. However, this difficulty can be avoided in the following way: We first evaluate the contributions to $\partial^2V(0)/\partial\kappa^2$ and $\partial^2V(0)/\partial\kappa\partial\nu$ resulting from the charge inside a small spherical region around the origin, which is chosen such that it does not contain any of the positive ionic point charges. Since this sphere only contains the uniform electronic charge distribution with density $\rho_{\rm el}$, it follows from Poisson's equation (viz., $\sum_\kappa \partial^2V(0)/\partial\kappa^2=-4\pi\rho_{\rm el}$) in combination with the spherical symmetry that

$$(\partial^2V(0)/\partial\kappa^2)_{\rm sphere}=-(4\pi/3)\rho_{\rm el}. \quad (14)$$

But if we now consider Eq. (2) we see that $(\partial^2V(0)/\partial\kappa^2)_{\rm sphere}$ will just be cancelled by the term $\frac{1}{3}\sum_\kappa \partial^2V(0)/\partial\kappa^2$ when all contributions to $V_{\kappa,\kappa}(0)$ are added together. In other words, in the case of uniform background lattices, the expression for $V_{\kappa,\kappa}(0)$ can again be obtained from (9), provided an arbitrarily small spherical region around the origin is excluded from the integration. Furthermore, since it immediately follows from (14) that $(\partial^2V(0)/\partial\kappa\partial\nu)_{\rm sphere}=0$, $V_{\kappa,\nu}(0)$ can in a similar fashion be obtained from (10). Keeping these restrictions in mind the expressions for $V_{\kappa,\kappa}(0)$ and $V_{\kappa,\nu}(0)$ follow directly from the substitution of (13) into (9) and (10), respectively,

$$V_{\kappa,\kappa}(0)=-\frac{Ze}{v}\int_{r>R}(3\kappa^2-r^2)r^{-5}d^3r + Ze\sum_{\lambda,j}\{3\kappa_{\lambda,j}{}^2r_{\lambda,j}{}^{-5}-r_{\lambda,j}{}^{-3}\}, \quad (15)$$

$$V_{\kappa,\nu}(0)=-\frac{Ze}{v}\int_{r>R}3\kappa\nu r^{-5}d^3r + Ze\sum_{\lambda,j}3\kappa_{\lambda,j}\nu_{\lambda,j}r_{\lambda,j}{}^{-5}. \quad (16)$$

κ, ν indicate x, y, or z and R is the radius of the small sphere. At this point we have to recall that the quantities $V_{\kappa,\kappa}(0)$ and $V_{\kappa,\nu}(0)$ are independent of the crystal shape as a result of the over-all charge neutrality of the crystal. However, in Eqs. (15) and (16) we have separated the contribution due to the negative background (in the integrals) from that due to the positive ionic cores (in the sums). Since each of these contributions by itself is shape-dependent, we have to be sure to evaluate the integral and the sum for the same crystal shape. Since we evaluate the sums by planewise summation, in which the planes are perpendicular to the z axis, we must evaluate the integrals for a slab-shaped region of integration perpendicular to the z axis. A straightforward integration gives:

$$\int_{\substack{\text{slab}\perp z\text{ axis}\\ r>R}}\frac{3z^2-r^2}{r^5}d^3r=\int\frac{2P_2(\cos\theta)}{r^5}d^3r=-\frac{8\pi}{3}. \quad (17)$$

Furthermore, from the fact that $\sum_\kappa(3\kappa^2-r^2)=0$ (κ is x, y, z) and that the x and y directions in the slab are equivalent, it follows immediately from (17) that

$$\int_{\substack{\text{slab}\perp z\text{ axis}\\ r>R}}\frac{3\kappa^2-r^2}{r^5}=\frac{4\pi}{3} \quad (18)$$

for κ is x or y. Finally

$$\int_{\substack{\text{slab}\perp z\text{ axis}\\ r>R}}\frac{\kappa\nu}{r^5}d^3r=0 \quad (\kappa,\nu\text{ indicate }x,y,\text{ or }z). \quad (19)$$

Notice that the results (17), (18), and (19) are independent of the radius R as well as of the thickness of the slab. Substituting these results in (15) and (16) and using for the sums the notation which was introduced in Eqs. (34)–(39) of Ref. 2, we have

$$V_{z,z}(0)=\frac{8\pi}{3}\frac{Ze}{v}+Ze\sum_j S_{j_1,j_2,j_3}(z,p_z), \quad (20)$$

$$V_{\kappa,\kappa}(0)=-\frac{4\pi}{3}\frac{Ze}{v}+Ze\sum_j S_{j_1,j_2,j_3}(\kappa,p_\kappa) \quad (21)$$

for κ is x or y, and

$$V_{\kappa,\nu}(0)=Ze\sum_j S_{j_1,j_2,j_3}(\kappa,p_\nu), \quad (22)$$

where κ, ν indicate x, y, or z. The appropriate summation formulas for the sums S_{j_1,j_2,j_3} are given in Sec. IV of Ref. 2.

[6] For the sake of brevity the present notation is slightly different from that of Ref. 2. To make a comparison with Eqs. (34)–(39) of Ref. 2, one should make the following identifications:

$$\kappa_{\lambda,j}=a_1(\sigma_{\lambda,j})_\kappa, \quad \text{if } \kappa \text{ is } x \text{ or } y$$
$$\kappa_{\lambda,j},\nu_{\lambda,j}=(\lambda_3+j_3)a_3\cos\delta, \quad \text{if } \kappa,\nu \text{ is } z.$$