

# Improvement of Bertaut's Method for Calculating Electric Field Gradient \*

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Bertaut's method for calculating the electric field and its gradient is analyzed. The formula for the electric field is always valid, whereas that for the electric field gradient holds only for an infinitely large unit cell. We present a practical method to use the formulae.

**Key words:** Electric field gradient, Electrostatic potential, Electrostatic field, Lattice sum, Bertaut's method.

## Introduction

Summation over the sites of an infinite lattice appears frequently in many fields of solid state physics. One of the most representative example of such a summation is the calculation of the lattice energy of an ionic crystal.

A great difficulty arises if the convergency of the summation is slow. This trouble is inevitable when the interaction decreases slowly with increasing interaction distance. Indeed, in the case of the Coulomb interaction, it is practically impossible to obtain reliable values by performing term-by-term summation.

Previously, two methods were published for evaluating the lattice sum. The first method was given by Ewald [1], who introduced an auxiliary function  $G(n)$ . The sum consists of two terms:

$$S = \sum_n f(n) = \sum_n f(n) G(n) + \sum_n f(n)(1 - G(n)). \quad (1)$$

The second term is then converted to a sum in reciprocal space. The auxiliary function  $G(n)$  is usually chosen as an incomplete gamma function to facilitate the convergence of both terms. This method can readily be

extended to a wide class of lattice sums [2–6]. The calculation, however, is rather complicated.

The second method, developed by Bertaut [7, 8], introduces the concept of “non-overlapping charge”  $q(r)$ , i.e.,

$$S = \sum_n f(n) = \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q(r_i) q(r_j)}{|r_i - r_j|}. \quad (2)$$

The sum in real space is converted to that in reciprocal space. This method is applicable only in case of Coulomb interaction. However, the sum is represented by one convergent series in reciprocal space instead of two series in the Ewald method. The expression is simple.

These two methods were first applied to the calculation of lattice energies and electric potentials [1, 2], and later to the evaluation of electric field gradients (EFG's) [9, 10]. We have recently calculated the EFG's at bromine sites in  $\text{Cs}_2\text{CdBr}_4$  [11] by using Bertaut's method [10] and found out the imperfection of the method. In this paper, the method is analyzed in order to clarify the origin of the deficiency. A practical way to use the method will be proposed.

## Results and Discussion

### 1) Deficiency of Bertaut's Method

Consider for example a crystal consisting of two atomic species. The lattice is orthorhombic with the cell dimensions  $a=0.40$  nm,  $b=0.42$  nm,  $c=0.44$  nm. An atom A is located at (0, 0, 0) (in reduced coordinates) with an electric charge  $+e$ . Another atom B is located at (0.4, 0.4, 0.4) with negative charge  $-e$ . The

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Table 1. Cell dependence of potential, electric field and electric gradient for an orthorhombic cell.

Cell dimension	Potential $\bar{V}$	Electric field			Electric field gradient		
		$\frac{E_x \cdot 10^{-9}}{\text{V m}^{-1}}$	$\frac{E_y \cdot 10^{-9}}{\text{V m}^{-1}}$	$\frac{E_z \cdot 10^{-9}}{\text{V m}^{-1}}$	$\frac{Q_{xx} \cdot 10^{-19}}{\text{V m}^{-2}}$	$\frac{Q_{yy} \cdot 10^{-19}}{\text{V m}^{-2}}$	$\frac{Q_{zz} \cdot 10^{-19}}{\text{V m}^{-2}}$
$a \times b \times c$	7.177	3.066	3.855	4.756	1.415	-0.041	-1.456
$2a \times 2b \times 2c$	7.177	3.066	3.855	4.756	3.011	-0.029	-2.982
$3a \times 3b \times 3c$	7.177	3.066	3.855	4.756	3.173	-0.036	-3.137
$4a \times 4b \times 4c$	7.177	3.066	3.855	4.756	3.212	-0.038	-3.174
$5a \times 5b \times 5c$	7.177	3.066	3.855	4.756	3.225	-0.037	-3.219

EFG produced at the position of the atom B is calculated.

The procedure requires to introduce a structure factor

$$F(h) = \sum_j q_j \exp(2\pi i h r_j), \quad (3)$$

where the summation  $\sum_j$  is taken over the charges in a unit cell. The selection of the unit cell is arbitrary. From the physical point of view, the calculated EFG should not be affected by the arbitrariness of the unit cell adoption. However, Table 1 shows that, although the electric potential and field are independent of the unit cell size, those of the EFG turn out to depend on the unit cell size.

In order to reveal the cause for this curious result, we first follow Bertaut's method [10]. The electrostatic interaction energy per unit cell can be expressed by the sum in reciprocal space:

$$\begin{aligned} W_{\text{int}} &= \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \\ &= (2V)^{-1} \frac{1}{4\pi\epsilon_0} \sum_h \frac{|F(h)|^2 |\phi(h)|^2}{|h|^2} \\ &\quad - (2\pi)^{-1} \frac{1}{4\pi\epsilon_0} \int \frac{|\phi(h)|^2}{|h|^2} d^3h \sum_j q_j^2, \end{aligned} \quad (4)$$

where the notation is the same as in the cited papers [5, 8]. The potential is, therefore

$$\begin{aligned} V_B(r_j) &= (\pi V)^{-1} \frac{1}{4\pi\epsilon_0} \sum_h' F(h) \frac{|\phi(h)|^2}{|h|^2} \exp(-2\pi i h r_j) \\ &\quad - q_j (\pi)^{-1} \frac{1}{4\pi\epsilon_0} \int \frac{|\phi(h)|^2}{|h|^2} d^3h, \end{aligned} \quad (5)$$

of which the first and the second derivatives are obtained as the electric field and its gradient;

$$\begin{aligned} E(r_j) &= 2iV^{-1} \frac{1}{4\pi\epsilon_0} \sum_h F(h) \Phi(h) h \exp(-2\pi i h r_j) \\ &\quad - 2iV^{-1} \frac{1}{4\pi\epsilon_0} \sum_h q_j \Phi(h) h, \end{aligned} \quad (6)$$

and

$$\begin{aligned} \theta_{\alpha\beta}(r_j) &= 4\pi(V)^{-1} \frac{1}{4\pi\epsilon_0} \sum_h F(h) \Phi(h) \exp(-2\pi i h r_j) h_\alpha h_\beta \\ &\quad - 4\pi(V)^{-1} q_j \frac{1}{4\pi\epsilon_0} \sum_h \Phi(h) h_\alpha h_\beta. \end{aligned} \quad (7)$$

The second terms in (6) and (7), which only arise through the differentiation of  $F(h)$  with respect to  $r_j$  (and not  $r$ ), are very complicated and, in order to understand why these terms are wrong, we will now consider a simple system (shown in Figure 1). If the dimension of the unit cell is  $a$ , the structure factor  $F(h)$  ( $h=n/a$ ) becomes

$$F(n) = e(1 - \exp(2\pi i n(x/a))). \quad (8)$$

If the dimension of the unit cell is  $2a$ , the structure factor  $F(m)$  ( $h=m/2a$ ) becomes

$$\begin{aligned} F(m) &= e(1 + \exp(\pi i(m/2a)a) \\ &\quad - \exp(\pi i(m/2a)x) - \exp(\pi i(m/2a)x')). \end{aligned} \quad (9)$$

Here, for convenience, we denote the coordinate of the neighboring equivalent atom by  $x'$ , though  $x' = x + a$  in fact.  $F(m)$  becomes zero if  $m$  is odd. In case  $m = 2n$ ,  $F(m)$  is given by

$$F(m) = e(1 - \exp(2\pi i n(x/a))). \quad (10)$$

This is the same as (8). Namely, the summation, which contains the structure factor, over  $h$  (i.e.  $n$  or  $m$ ) gives the same value independently of the unit cell size. This

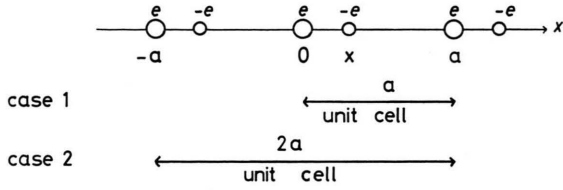


Fig. 1. Model systems to analyze Bertaut's formula: Case 1: cell size =  $a$ . Case 2: cell size =  $2a$ .

means that the values of the electric field and the first term of the field gradient in (7) do not depend on the unit cell size.

On the other hand, the second term of the EFG depends on the unit cell size:

if  $m = 2n$ ,

$$\sum_h \Phi(h) |h|^2 = \sum \Phi(n/a) (n/a)^2, \quad \text{and} \quad (11)$$

if  $m = \text{odd}$ ,

$$\sum_h \Phi(h) |h|^2 = \sum \Phi(m/2a) (m/2a)^2. \quad (12)$$

Consequently, the terms containing odd  $m$ 's are larger than those for the unit cell dimension  $a$ . These terms appear through differentiating  $F(h)$  with respect to  $r_j$ ; the derivative operation produces the wrong expression for the EFG. In the case of the electric field, although the term which contains the derivative of  $F(h)$  on  $r_j$  also exists, it is always zero.

Now, we consider the differential operation on the structure factor  $F(h)$  in more detail in order to know why this operation done in Bertaut's paper gives wrong results. We return to the simple one-dimensional system in Figure 1. If the structure factor is given by (8), differentiation of this equation with respect to  $x$  gives

$$\frac{\partial F(n)}{\partial x} = -e 2\pi i n(1/a) \exp(2\pi i n(x/a)). \quad (13)$$

If the structure factor is represented by (9), differentiation of (9) with respect to  $x$ , ignoring  $x' = x + a$ , gives

$$\frac{\partial F(m)}{\partial x} = -e 2\pi i m(1/2a) \exp(-2\pi i m(x/2a)). \quad (14)$$

Equation (14) becomes identical with (13) if  $m = 2n$ , whilst  $\partial F(m)/\partial x$  does not vanish if  $m$  is odd. Therefore, the sum including  $\partial F/\partial x$  depends on the unit cell size. Taking into account the fact that  $x' = x + a$ , on the

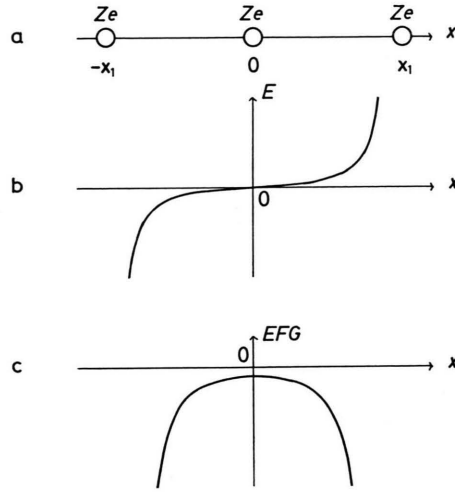


Fig. 2. The electric field and electric field gradient for the system a are shown in b and c, respectively.

other hand, differentiation gives

$$\frac{\partial F(m)}{\partial x} = -e (1 + \exp(\pi i m)) \cdot 2\pi i m(1/2a) \exp(-2\pi i m(x/2a)). \quad (15)$$

Equation (15) is, of course, equivalent to (13):

$\partial F(m)/\partial x = 0$  if  $m$  is odd, and  $F(m)/x$  is given by (13) if  $m = 2n$ .

From the comparison of (13) and (14) it is clear that the differentiation giving (13) ignores the contribution from the atom at  $x' = x + a$ . In fact, differentiation on  $F(h)$  corresponds to simultaneous displacement of the equivalent atoms concerned. However, the differentiation should be made only at the position considered. The values of the electric field and the EFG's based on (13) do not include the contributions from all the equivalent atoms (i.e. atoms at  $x + na$ ), and those from (14) do not include the contributions from atoms at  $x + (2n + 1)a$ . Hence, (6) and (7) hold only if the infinitely large unit cell is assumed.

Finally we consider the reason why the formula for the electric field gives the same value, whereas that for the EFG gives different values depending on the unit cell size. The above analysis shows that the effect of the equivalent atoms concerned is the key to solve the problem. Consider the system shown in Figure 2a. The electric field and its gradient are expressed as

$$E(x) = \frac{Ze}{4\pi\epsilon_0} \left( \frac{x - x_1}{|x - x_1|^3} + \frac{x + x_1}{|x + x_1|^3} \right), \quad (16)$$

Table 2a. Cell parameters used for the calculation.

Lattice	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
Cubic	4.2	4.2	4.2	90.0	90.0	90.0
Orthorhombic	4.0	4.2	4.4	90.0	90.0	90.0
Triclinic	4.0	4.2	4.4	70.0	85.0	100.0

Table 2b. Atomic coordinates and charges used for the calculation.

Lattice	Atom	Atomic coordinate			Charge/ <i>e</i>
		<i>x/a</i>	<i>x/b</i>	<i>z/c</i>	
Cubic	A	0.0	0.0	0.0	1.0
	B	0.4	0.4	0.4	−1.0
Orthorhombic	A	0.0	0.0	0.0	1.0
	B	0.4	0.4	0.4	−1.0
Triclinic	A	0.0	0.0	0.0	1.0
	B	0.4	0.4	0.4	−1.0

and

$$\theta_{xx}(x) = \frac{-2Ze}{4\pi\epsilon_0} \left( \frac{1}{|x-x_1|^3} + \frac{1}{|x+x_1|^3} \right). \quad (17)$$

These equations are plotted in Figs. 2b and 2c. The electric field at the position of the center atom vanishes because the electric fields generated by the atoms at sites 1 and −1 are opposite in sign and the sum of these two cancels: no effect of the equivalent atoms exists. This is the reason why the formula for the electric field is correct in spite of the incorrect derivation of the formula. On the other hand, the contributions from the equivalent atoms have the same sign in case of the EFG, which makes the formula for the EFG incorrect.

In conclusion, we must not differentiate the electrostatic potential expressed as (5), once the sum is converted to that in reciprocal space. In the case of the electric field, however, the formula derived through differentiation is valid because of symmetry.

## 2) Practical Method

For a simple lattice, the formula has been obtained by applying the Ewald method to the sum of derivatives of the electric field in real space [2]. It is not easy to derive formulae generalized for complex lattices. This difficulty requires to devise a practical method for estimating EFG's.

Table 3a. Cell size dependence of  $V_{zz}$  and  $\eta$  for a cubic lattice.

Cell dimension	$V_{zz}/\text{Vm}^{-2}$	$\eta$
$a \times a \times a$	$3.362 \cdot 10^{19}$	0
$2a \times 2a \times 2a$	$3.362 \cdot 10^{19}$	0
$3a \times 3a \times 3a$	$3.362 \cdot 10^{19}$	0
$4a \times 4a \times 4a$	$3.362 \cdot 10^{19}$	0
$5a \times 5a \times 5a$	$3.362 \cdot 10^{19}$	0

Table 3b. Cell size dependence of  $V_{zz}$  and  $\eta$  for a orthorhombic lattice.

Cell dimension	$V_{zz}/\text{Vm}^{-2}$	$\eta$
$a \times b \times c$	$3.697 \cdot 10^{19}$	0.289
$2a \times 2b \times 2c$	$4.531 \cdot 10^{19}$	0.635
$3a \times 3b \times 3c$	$4.634 \cdot 10^{19}$	0.660
$4a \times 4b \times 4c$	$4.659 \cdot 10^{19}$	0.665
$5a \times 5b \times 5c$	$4.668 \cdot 10^{19}$	0.667

Table 3c. Cell size dependence of  $V_{zz}$  and  $\eta$  for a triclinic lattice.

Cell dimension	$V_{zz}/\text{Vm}^{-2}$	$\eta$
$a \times b \times c$	$1.131 \cdot 10^{20}$	0.328
$2a \times 2b \times 2c$	$1.292 \cdot 10^{20}$	0.369
$3a \times 3b \times 3c$	$1.308 \cdot 10^{20}$	0.372
$4a \times 4b \times 4c$	$1.312 \cdot 10^{20}$	0.373
$5a \times 5b \times 5c$	$1.314 \cdot 10^{20}$	0.373

The direct summation in real space is also possible because the series for the electric field gradient is absolutely convergent.

As stated in the preceding section, (7) in Bertaut's method is valid for an infinitely large unit cell. The summation converges monotonously. Therefore, we examined this convergency, considering the dependence of the EFG on the unit cell size. The unit cell sizes examined are tabulated in Tables 2a and b. For the cubic case, no dependence on the cell size exists because of the symmetry. The results of the calculation are shown in Tables 3a, b and c. These results show that the EFG can be calculated within the accuracy of  $\pm 0.1\%$  if the unit cell is larger than  $(2 \times 2 \times 2) \text{ nm}^3$ . This accuracy will be enough for many purposes.

Equation (7) does not include the contribution from a primitive lattice composed of the equivalent atoms. Thus, in cases where the change of the EFG upon translation and/or rotation of molecules is dealt with, it is necessary to calculate the contribution from the primitive lattice only once.

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