

## Electrostatic potentials using direct-lattice summations

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A direct-lattice summation scheme is described which is completely general for one-, two-, and three-dimensional periodic arrays of point charges. This scheme is based on a proper rearrangement of terms within the lattice sum. Rapid convergence is achieved by appropriate cancellation of multipolar terms.

Since the first calculation of the electrostatic potential in a crystal by Madelung<sup>1</sup> several other methods have been proposed to perform lattice summations. The classical methods are those of Ewald<sup>2</sup> and the direct-lattice summation techniques given by Evjen<sup>3</sup> and Frank.<sup>4</sup> Another procedure has been developed by Bertaut.<sup>5</sup> All these methods have been reviewed by Tosi.<sup>6</sup> Recently, the implications of the classical methods have been pointed out by Harris,<sup>7</sup> and the Fourier-transform method to evaluate the electrostatic potential in crystals was introduced.<sup>7</sup> If for any reason (for example, because of the complexity of integrals in reciprocal space) direct-lattice summation techniques are desired, no general way of performing the lattice summation is existent so far.

In this Communication we want to show that it is possible to formulate a direct-lattice summation scheme, which is completely general, and which is applicable to three-dimensional (3D) as well as to 2D and 1D problems. We also demonstrate how, in practical calculations, the speed to achieve convergence can be increased. First we introduce some definitions and then we discuss the implications of the classical summation techniques. We then describe the direct-lattice summation scheme.

The calculation of the electrostatic (Madelung) potential in a crystal involves lattice summations of the type

$$\Phi_{ij} = \frac{1}{|\vec{r}_j - \vec{r}_i|} + \sum_{i \neq 0} \left( \frac{1}{|\vec{R}_i + \vec{r}_j - \vec{r}_i|} - \frac{1}{|\vec{R}_i|} \right), \quad (1)$$

$i \neq j$  .

$\vec{R}_i$  is a lattice translation vector, and  $\vec{r}_i$  and  $\vec{r}_j$  refer to the location of point charges  $q_i$  and  $q_j$  in a primitive basis. The Madelung potential  $V_i$  at an atomic site  $i$  is then given as

$$V_i = \sum_{j \neq i} \Phi_{ij} q_j, \quad (2)$$

with the summation being carried out over all atoms  $j$  in the basis. The dimensionless Madelung constant  $\alpha_R$ , which is generally referred to a characteristic

length  $R$  (next-neighbor distance, lattice parameter, etc.), is connected to  $V_i$  by

$$\alpha_R = -\frac{R}{2n} \sum_i V_i q_i, \quad (3)$$

where  $n$  denotes the number of molecules in the unit cell, and the summation includes all atoms in the basis.

Because of the conditional convergence of the series in Eq. (1) the value of  $\Phi_{ij}$  will depend upon grouping the terms and truncating the series, unless a certain set of basic conditions is imposed. It has been recognized<sup>7,8</sup> that in 3D all lattice summation methods are based on repeating units with vanishing moments up to the second order. This condition is fulfilled in the lattice summation methods implicitly, and we may call it the Ewald condition. In 2D the Ewald condition requires only vanishing moments up to the first order,<sup>7</sup> while in 1D charge-neutral-repeating units are sufficient to arrive at the unique Ewald result.<sup>7</sup> Using such repeating units and summing over a sufficiently large number of them, we were able to reproduce reported Ewald results. However, convergence of this summation is achieved relatively slowly because the Ewald condition does not imply optimization of convergence. This situation can be improved if the repeating units are chosen such that, additional to the Ewald condition, higher-order moments are zero. This we demonstrate for a linear chain of equal point charges with alternating sign (Fig. 1). From inspection of Table I it is obvious that the lattice sum based on only charge-neutral-repeating units (BC) converges much more slowly than the lattice sum based on repeating units including zero moments up to the second order (SC).

The procedure which was described for a 1D example in Fig. 1 can be easily generalized to 2D and 3D, and to any order of vanishing moments. This leads to a system of linear equations for the fractional charges [Fig. 1(b)] within the repeating unit. Thus, similar to the situation shown in Fig. 1(c), "bulk" contributions (BC) and "surface" corrections (SC) to the Madelung potential are obtained. Since in 3D the

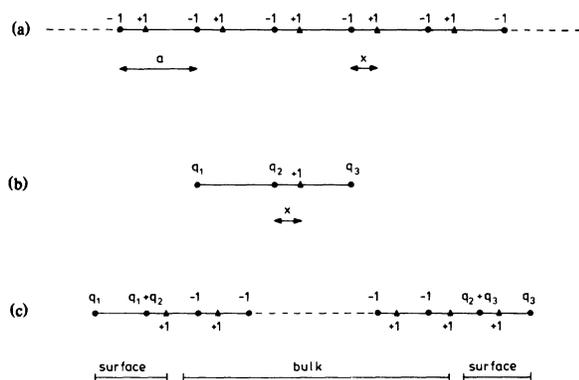


FIG. 1. (a) Linear chain of point unit charges with alternating sign and lattice parameter  $a = 1$ . The distance  $x$  denotes the fractional coordinate of a positive charge relative to its next-neighbor negative charge. (b) Repeating unit with vanishing charge and vanishing first- and second-order moments. If the fractional charges  $q_1$ ,  $q_2$ , and  $q_3$  are chosen such that the conditions  $q_1 + q_2 + q_3 + 1 = 0$ ,  $-q_1 + q_3 + x = 0$ , and  $q_1 + q_3 + x^2 = 0$  are fulfilled, the repeating unit has zero moments up to the second order. This is achieved by using fractional charges  $q_1 = (x - x^2)/2$ ,  $q_2 = -1 + x^2$ , and  $q_3 = (-x - x^2)/2$ . (c) One-dimensional crystal sample which results from the translation of the repeating units, defined in (b) according to the lattice translation  $R_l = la$ . Inside this crystal sample ("bulk") the sequence of charges  $(-1 + 1 \dots -1 + 1)$  corresponds to the actual situation (a), while at the "surfaces" of this crystal sample, fractional charges are created, which are necessary to correct for the vanishing moments. If the summation in Eq. (1) is performed from  $l = -N$  to  $l = +N$  the total surface correction to the Madelung potential is given by  $x^2/N(N+1)$ .

fractional charges are located on planes, edges, and corners of the surface of the crystal sample, we term the corresponding surface corrections according to their location as planar (PC), edge (EC), and corner (CC) corrections. Only edge and corner corrections in 2D and only edge corrections in 1D have to be considered.

TABLE I. Madelung constant  $\alpha_R$  for a linear chain of unit charges with alternating sign and equal distances. If  $\alpha_R$  is given in units of the next-neighbor distance, the well-known result is  $2 \ln 2 = 1.386 294 \dots$  (Ref. 9). The entries in the table are as follows:  $N$  denotes the limits of the lattice sum in Eq. (1) from  $l = -N$  to  $l = +N$ . The abbreviations BC and SC refer to the "bulk" contribution and to the "surface" correction as indicated in Fig. 1(c).

$N$	BC	SC	$\alpha_R$
1	1.333 333	0.062 500	1.395 833
2	1.366 667	0.020 833	1.387 500
4	1.380 159	0.006 250	1.386 409
8	1.384 567	0.001 736	1.386 303
16	1.385 835	0.000 460	1.386 295
32	1.386 176	0.000 118	1.386 294

For actual 3D cases we have constructed repeating units with vanishing moments up to the fourth order. The result for NaCl (with primitive nonorthogonal lattice translation vectors) is shown in Table II. It is interesting to note that the converged BC value is far off from the correct Madelung potential, and that PC and EC values are leading terms, while the CC value is small but important to achieve fast convergence. Additional examples for the efficiency of the method are given in Table III.

In 2D the Ewald condition requires vanishing zeroth- and first-order moments; however, if second- and higher-order moments additionally are zero, convergence is achieved faster. 2D in this context means that the point charges are located exactly within the  $x$ - $y$  plane. If thin films with point charges outside the  $x$ - $y$  plane, and hence with nonvanishing  $z$  components of the second- and higher-order moments, are considered, an alternative criterion has to be fulfilled in order to achieve fast convergence for the Madelung potential. For example, it is possible to regroup the charges within the  $x$ - $y$  plane such that

TABLE II. Madelung constant  $\alpha_R$  for NaCl. The reported literature value is 3.495 130 (Ref. 9), with  $\alpha_R$  given in units of the lattice constant. (See text for abbreviations for BC, PC, EC, and CC.)

$N_1 = N_2 = N_3$	BC	PC	EC	CC	$\alpha_R$
2	-0.302 957	2.552 392	1.279 952	-0.022 538	3.506 849
4	-0.330 722	2.536 540	1.297 848	-0.007 318	3.496 348
8	-0.339 619	2.532 044	1.304 889	-0.002 083	3.495 231
16	-0.342 162	2.530 796	1.307 058	-0.000 555	3.495 136
32	-0.342 843	2.530 464	1.307 653	-0.000 143	3.495 130

TABLE III. Madelung constants  $\alpha_R$  for CsCl, ZnS, BaTiO<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The entries in the table are identical to those in Table II. The reported literature values are  $\alpha(\text{CsCl}) = 2.035\,362$  (Ref. 9),  $\alpha(\text{ZnS}) = 3.7830$  (Ref. 9),  $\alpha(\text{BaTiO}_3) = 49.510$  (Ref. 10),  $\alpha(\alpha\text{-Al}_2\text{O}_3) = 24.242$  (Ref. 10). For CsCl and ZnS the Madelung constants are given in units of the lattice parameter, while for BaTiO<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> the shortest next-neighbor distance has been used as the characteristic length.

System	$N_1 = N_2 = N_3$	BC	PC	EC	CC	$\alpha_R$
CsCl <sup>a</sup>	32	0.464 656	1.570 842	-0.000 137	0.0	2.035 362
ZnS <sup>b</sup>	32	2.823 344	0.632 605	0.326 986	-0.000 009	3.782 926
BaTiO <sub>3</sub> <sup>a</sup>	16	49.505 631	0.0	0.004 241	0.0	49.509 872
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> <sup>b,c</sup>	4	29.949	-1.468	-4.257	0.019	24.243

<sup>a</sup>Orthogonal lattice translation vectors.

<sup>b</sup>Nonorthogonal lattice translation vectors.

<sup>c</sup>The hexagonal unit cell with 6 molecules and 30 atoms has been used as well as the rhombohedral unit cell with only 2 molecules and 10 atoms to verify that both examples yield the same result.

the electric field gradient at the center of the repeating unit is zero. An example for this situation is given in Table IV for a double layer of cubic unit cells of BaTiO<sub>3</sub>.<sup>10,11</sup>

As a technical remark it should be mentioned that the calculational procedure becomes straightforward if, first, the quantities  $\Phi_{ij}$  are evaluated by regrouping the charges on the sublattice  $i, j$ , and then by summing up the contributions from the various sublattices. In addition, convergence is achieved faster if the atomic positions of the basis atoms are used as the smallest possible fractional coordinates.

We have introduced in this Communication a direct-lattice summation scheme which is completely general for 1D, 2D, and 3D periodic arrays of point charges, which matches the requirements of the

Ewald conditions, and which has the merit of simple mathematical formalism. It was shown that the convergence of lattice summations can be accelerated, in principle, to any desired degree by canceling higher-order moments as compared to the Ewald conditions. The direct-lattice summation scheme being proposed here is of particular interest if reciprocal-lattice techniques are not practical, for example, because of the complexity of reciprocal-space integrals.

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TABLE IV. Madelung constant  $\alpha_R$  for a double layer of BaTiO<sub>3</sub> consisting of TiO<sub>2</sub>-BaO-TiO<sub>2</sub>-BaO-TiO<sub>2</sub> planes, given in units of the lattice parameter. The entries in the table correspond to those used in Table II. The reported literature value is  $\alpha_R = 134.117$  (Ref. 10).

$N$	BC <sup>a</sup>	EC	CC	$\alpha_R$
1	132.495 653	2.039 573	0.0	134.535 226
2	133.193 326	1.162 090	0.0	134.355 416
4	133.554 375	0.633 741	0.0	134.188 116
8	133.796 849	0.333 525	0.0	134.130 373
16	133.947 594	0.171 525	0.0	134.119 119
32	134.030 400	0.087 042	0.0	134.117 442
64	134.073 364	0.043 853	0.0	134.117 217

<sup>a</sup> The BC value converges in this specific 2D case to the correct Madelung constant only because the lattice sum has been carried out in a symmetric way, i.e., contributions from a repeating unit at position  $R_j$  have been simultaneously summed up with contributions from a repeating unit at position  $-R_j$ , thus matching the 2D Ewald condition for vanishing first-order moments.

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