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Direct Computation of Madelung Constants

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An algorithm is proposed by which the Madelung constants can be computed by direct summation with any precision given by that of the computer used. The necessary program can be made very simple, requiring acceptable computation times due to a small number of necessary lattice points. The algorithm is based on the calculation of arithmetical means of higher order of partial sums of infinite alternating convergent series equal to the Madelung constants. As an example, the Madelung constant of cubic lattice was computed using only 21, 18, 16 members in the axes, coordination planes and the space volume respectively. The obtained value was $MC = 1.74756\,460 + \delta$, with an estimated error of $-5 \times 10^{-9} < \delta < 1 \times 10^{-8}$.

INTRODUCTION

In solid state physics the lattice energies of crystals are of greatest importance. The interaction energy of two points charges z_+e and z_-e, r_{+-} apart, is $z_+z_-e^2/r_{+-}$. Similarly, the total electrostatic energy U_m of n such point charges of magnitude z_i ($i = 1, 2, 3, \ldots, n$) is

$$U_m = \sum_{\text{pair}} z_1 z_2 e^2/r_{ij} \tag{1}$$

in which the summation extends over all pairs of charges, each pair being considered. This may also be written in the form

$$U_m = (1/2) \sum_{i\,j}{}' z_i z_j e^2/r_{ij} \tag{2}$$

where the summation is now a double sum over all charges and the superscript prime indicates that the cases $i = j$ are to be excluded. For binary crystals such as sodium chloride, sodium nitrate, and calcium fluoride, the results can always be expressed in the simple form

$$U_m = N_A MC (z_+ e z_- e)/l \tag{3}$$

Here U_m is the molar energy; $z_+ e$ and $z_- e$ are the absolute values of the charges on the positive and negative ions; l is one of the characteristic crystal dimensions: N_A is the Avogadro constant and MC is the Madelung constant, a pure number independent of the dimensions of the lattice. The series

$$MC = \sum_{i\,j} l/r_{ij} \tag{4}$$

cannot be evaluated by uncritical summation because it converges with extreme slowness. Up to 1959, two methods were available for summing the Madelung series; the first was to replace the point charges with a distributed charge and then use a mathematical manipulation to obtain a quickly convergent series; the second method was to arrange the terms so that summation takes place over electrostatically neutral layers.[6] In a series of papers Sakamoto[5] calculated Madelung constants for several lattices, using a method based on the previously calculated Born's »Grundpotential«-s. The first mentioned method gives values of limited accuracy, due to extremely slow convergence, while remaining methods, being theoretical, need an independent check of the values obtained. Since all Madelung terms were reported in the literature as constants one should conclude that the series by which they are defined, converge. The purpose of present paper is to describe a method of direct computation of Madelung constants based on an algorithm by which the alternating infinite series is transformed into a monotonically descreasing series whose rate of convergence is increased for many orders of magnitude. Any Madelung constant can be defined as a sum of several alternating infinite convergent series. It will be demostrated that the use of the proposed algorithm permits the calculation of Madelung constant of the example cubic lattice (with reciprocal distances of 21, 18, 16 lattice points in the axes, coordination planes and space volume, respectively) with a precision of 9 significant figures in several minutes with a common desk computer. We expect that the same principle can be applied for the calculation of the Madelung constant of any other binary crystal lattice. The algorithm is based on the calculation of arithmetical means of the order equal to the number of lattice points in the axes, planes and space volume, respectively (*e. g.* 21, 18, 16 for the cubic lattice as example). The derivation of the algorithm will also be represented.

THEORETICAL

The principle of the derivation of the algorithm can be explained as follows:[4]

A convergent, alternating, infinite series can be represented by:

$$S_{\infty} = a_0 - a_1 + \ldots \pm a_i \pm \ldots = \sum_{i=0}^{\infty} (-1)^i a_i \ (a_i > 0). \tag{5}$$

In the case of convergence it is valid (S_{∞} = const.):

$$\lim_{n \to \infty} S_n = S_{\infty}. \tag{6}$$

The partial sum of the series reads

$$S_n = a_0 - a_1 \pm \ldots \pm a_n = \sum_{i=0}^{n} (-1)^i a_i. \tag{7}$$

The series of the first arithmetical mean sum, $S(1, n)$, between S_{n+1} and S_{n+2} reads

$$S(1, n) = (S_{n+1} + S_{n+2})/2 = S_n + 2^{-1}(2a_{n+1} - a_{n+2}). \quad (8)$$

The series of the third arithmetical mean sum, $S(2, n)$ reads

$$S(2, n) = [S(1, n+1) + S(1, n+2)]/2 = S_n + 2^{-2}[2^2 a_{n+1} - (2+1) a_{n+2} + a_{n+3}]. \quad (9)$$

The series of the third arithmetical mean sum, $S(3, n)$ reads

$$S(3, n) = [S(2, n+2) + S(2, n+3)]/2 =$$
$$= S_n + 2^{-3}[2^3 a_{n+1} - (2^2 + 2 + 1) a_{n+2} + (2 + 1 + 1) a_{n+3} - a_{n+4}]. \quad (10)$$

It follows therefrom that the series of the e-th arithmetical mean sum, $S(e, n)$ is [4]

$$S(e, n) = [S(e-1, n+e-1) + (S(e-1, n+e)]/2 =$$
$$S_n + 2^{-e} \sum_{i=n+1}^{n+e+1} (-1)^{i+1} k(e, i-n-1)\, a_i. \quad (11)$$

The coefficients for $1 \leq e$ are:

$$k(e, 0) = 2^e \quad (12)$$

$$k(e, e) = 1 \quad (13)$$

The remaining coefficients can be calculated for $2 \leq e$ and $1 \leq i \leq e-1$ by the recursive formula

$$k(e, i) = k(e-1, i-1) + k(e-1, i) \quad (14)$$

Then the scheme of calculation of the coefficients is as follows

$k(e, 0) = 2^2$	$k(e, i) = k(e-1, i-1) + k(e-1, i)$	$k(1, 1) = 1$
$k(1, 0) = 2^1$		$k(e, e) = 1$
$k(2, 0) = 2^2$	$k(2, 1) = k(1, 0) + k(1, 1)$	$k(2, 2) = 1$
$k(3, 0) = 2^3$	$k(3, 1) = k(2, 0) + k(2, 1)$	
	$k(3, 2) = k(2, 1) + k(2, 2)$	$k(3, 3) = 1$
$k(4, 0) = 2^4$	$k(4, 1) = k(3, 0) + k(3, 1)$	
	$k(4, 2) = k(3, 1) + k(3, 2)$	
	$k(4. 3) = k(3, 2) + k(3, 3)$	$k(4, 4) = 1$

and so on.

Then it can be written

$$\lim_{n = \text{const},\ e \to \infty} (S(e, n) = S_\infty \quad (15)$$

and

$$\lim_{n,\ e \to \infty} (S(e, n) = S_\infty \quad (16)$$

The method of averaging is already known.[1,2] However, according to the author's knowledge, it was not used in the form of an algorithm with high order of averaging as here, *i. e.* with high e values.

The difference $D(e, n)$ between two computed values $S(e, n)$ is

$$D(e, n) = S(e-1, n) - S(e, n) \quad (17)$$

and the quotient, $Q(e, n)$, of two neighbouring differences

$$Q(e, n) = D(e, n)/D(e-1, n). \quad (18)$$

Then the infinite sum S_∞ equals to its computed part S (e, n) minus its not-computed part, *i. e.* it can be defined by

$$S_\infty = S(e, n) - \sum_{i=1}^{\infty} D(e+i, n). \quad (19)$$

The not computed values of $D(e = i, n)$ for $i \geq 1$ are

$$D(e+i, n) = D(e+i-1, n)\, Q(e+i, n). \quad (20)$$

The condition of convergence of the series is $D(e+1, n) < D(e, n)$ and, also, $Q(e+1, n) < Q(e, n) < 1$. Consequently, the sum of all not computed differences is

$$\sum_{i=1}^{\infty} D(e+i, n) < D(e, n)\, Q(e, n) \sum_{i=0}^{\infty} Q(e, n)^i \quad (21)$$

Since the right hand sum is a geometrical series with $Q(e, n) < 1$ it also holds:

$$\sum_{i=1}^{\infty} D(e+i, n) < D(e, n)\, Q(e, n)/[1 - Q(e, n)]. \quad (22)$$

The following sum $SE(e, n)$ can be defined:

$$SE(e, n) = S(e, n) - D(e, n)\, Q(e, n)/[1 - Q(e, n)] \quad (23)$$

which represents a better approximation to S_∞ than S (e, n) because the not computed part of the sum was estimated and subtracted from the computed sum $S(e, n)$. The difference, $\delta(e, n)$ is the error of computation, *i. e.*

$$\delta(e, n) = SE(e, n) - S_\infty. \quad (24)$$

If p and s are of the order magnitude of δ (e, n) and SE (e, n) (and S_∞) then

$$\delta(e, n) = \delta(e, n)'\, 10^{-p}\ (1 < \delta(e, n)' < 10) \quad (25)$$

and

$$SE(e, n) = SE(e, n)'\, 10^{-s}\ (1 < SE(e, n)' < 10). \quad (26)$$

If the computation with a given e_{max} gives the result $SE(e_{max}, n)$ and if the following condition is fulfilled ($e < e_{max}$)

$$SE(e, n) - 5 \cdot 10^{-p} < SE(e_{max}, n) < SE(e, n), \quad (27)$$

then also $\delta(e, n) < 5 \cdot 10^{-p}$ and $SE(e, n)$ is calculated with p—s significant figures. The deviation of $SE(e_{max}, n)$ from S_∞ can be estimated from the following inequality:

$$SE(e_{max} - i, n) - 5 \cdot 10^{-p} < SE(e_{max}, n) < SE(e_{max} - i, n)\ (i \geq 1). \quad (28)$$

Then it is also

$$\delta(e_{max}, n) = SE(e_{max}, n) - S_\infty < 5 \cdot 10^{-p}. \quad (29)$$

THE COMPUTATION OF MADELUNG COSTANTS

The Madelung constant, MC_∞, is defined by the sum of reciprocal distances of all lattice points from the point (0, 0, 0). *E. g.* for the cubic lattice it can be defined by

$$MC_\infty = \sum_{\pm\infty}^{z=\pm\infty} \{ \sum_{\pm\infty}^{y=\pm\infty} [\sum_{\pm\infty}^{x=\pm\infty} (-1)^{z+y+x+1}/R(z, y, x)] \}, \tag{30}$$

excluding the case when $z = y = x = 0$; z, y, x are integers and

$$R(z, y, x) = \sqrt{z^2 + y^2 + x^2}. \tag{31}$$

Mathematically, the series of this type are relatively convergent. Since the Madelung terms were always reported as constants it can be concluded that the same series for binary lattices always converge.

Due to the symmetry, in order to avoid repetitive calculation of the same distances, the sum MC_∞ can be decomposed into three summands SX, SY, SZ:

$$SX = 6 \sum_{x=1}^{\infty} (-1)^{x+1}/x \tag{32}$$

$$SY = \sum_{y=1}^{\infty} \sum_{x=y}^{\infty} (-1)^{y+x+1} F/\sqrt{y^2 + x^2}, \tag{33}$$

where $F = 12$ for $y = x$ and $F = 24$ for $y < x$. The third summand can be defined by

$$SZ = \sum_{z=1}^{\infty} \sum_{y=z}^{\infty} \sum_{x=y}^{\infty} (-1)^{z+y+x+1} F/\sqrt{z^2 + y^2 + x^2}. \tag{34}$$

here $F = 8$ for $z = y = x$, $F = 24$ for $z = y < x$ and for $z < y = x$, while $F = 48$ for $z < y < x$. Then the Madelung constant is the sum

$$MC_\infty = SZ + SY + SX. \tag{35}$$

In analogy to *e. g.* (27) the three summands are defined by [$SX(e)$, $SY(e)$, $SZ(e) = SE(e, n)$, $S(e, n) = 0$, $n = 0$, $Q(e) = Q(e, n)$, $D(e) = D\,e, n)$, the computation was performed for $n = 0$ for reasons of simplicity].

$$SX(e) = 2^{-e} \sum_{x=1}^{\infty} (-1))^{x+1} F\,k(e, x-1)/x - D(e)\,Q(e)/[1 - Q(e)] \tag{36}$$

$$SY(e) = 2^{-e} \sum_{y=1}^{e+1} \sum_{x=y}^{e+1} (-1)^{y+x+1} F\,k(e, y-1)\,k(e, x-1)/\sqrt{y^2 + x^2} -$$

$$- D(e)\,Q(e)/[1 - Q(e)]. \tag{37}$$

$$SZ(e) = 2^{-e} \sum_{y=1}^{e+1} \sum_{y=z}^{e+1} \sum_{x=y}^{e+1} (-1)^{z+y+x+1} F\,k(e), z-1)\,k(e, y-1)\,k(e, x-1/$$

$$/\sqrt{z^2 + y^2 + x^2} - D(e)\,Q(e)/[1 - Q(e)]. \tag{38}$$

The values of F are the same as for the infinite series.

Then the computed Madelung constant reads

$$MC = SZ(e_{max}) + SY(e_{max}) + SX(e_{max}). \tag{39}$$

The computation performed for p = 9 and s = 0 gives the following values of the three summands

$$SX\,(21) = 4.158\,883\,08 - < 5 \times 10^{-9} \qquad (40)$$

$$SY\,(18) = -3.471\,138\,29 + < 5 \times 10^{-9} \qquad (41)$$

$$SZ\,(16) = 1.059\,819\,81 - < 5 \times 10^{-9} \qquad (42)$$

and the Madelung constant

$$MC = SX\,(21) + SY\,(18) + SZ\,(16) = 1.747\,564\,60 + \delta - 5 \times 10^{-9} < \delta < 1 \times 10^{-8} \qquad (43)$$

The most accurate value known to the author was published by Sakamoto[5]

$$MC = 1.747\,564\,594\,633\,182\,2. \qquad (44)$$

It was calculated by using the previously calculated Born's »Grundpotential«, not by direct summation. The difference of $\sim 5 \times 10^{-9}$ between both values indicates the basic correctness of the direct method of computation proposed in the present note. It is obvious that the precision of the computation can be increased up to any higher precision, within the limits imposed by the accuracy of the computer used. Also, Callara and Miller[3] published a method of calculation of the same Madelung constant. However, their value differed from both cited values by -8.5×10^{-6}.

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SAŽETAK

Izravno računanje Madelungovih konstanti

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Izveden je algoritam kojim je moguće izravnim zbrajanjem izračunati Madelungove konstante raznih binarnih kristalnih sustava s preciznošću koju omogućuje upotrijebljeno računalo. Potreban program može se načiniti vrlo jednostavnim tako da su vremena računanja prihvatljiva, jer je potreban malen broj prostornih parametara. Algoritam se temelji na računanju aritmetičkih sredina višeg reda alternirajućih beskonačnih konvergirajućih redova kojima se mogu definirati Madelungove konstante. Kao primjer izračunana je Madelungova konstanta za kubičnu rešetku sa svega 21, 18, 16 članova u osima, u plohama osi i u prostoru između njih. Dobivena vrijednost iznosi 1,74756 460 + δ, s procijenjenom vrijednošću pogreške $-5 \times 10^{-9} < \delta < 1 \times 10^{-8}$. Direktnim sumiranjem za istu preciznost bilo bi potrebno računati s oko 10^9 članova u osima.