Calculations of Electrostatic Potential in Ionic Crystals with Direct Summation of the Coulomb Potentials of Point Charges

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Electrostatic potentials in ionic crystals have been calculated with direct summation of the Coulomb potential of point charges by the Coker's method. The self-potentials for the lattice ions and the Madelung constants are obtained in high precision and accuracy for several compounds : NaCl, CsCl, CaF$_2$, ZnS, Cu$_2$O, 2-4 and 3-3 perovskites. The self-potentials and the Madelung constants for these compounds are consistent with each other and the electrostatic potentials at lattice interstitial points are checked.

KEY WORDS: Electrostatic potential/ Madelung constant/ Self-potential/ Coker's method/ Ionic crystal

I. INTRODUCTION

To understand the chemical bond and the electronic structure of ionic crystals, estimation of electrostatic potentials in the periodic arrangement of the ions is an inevitable task. There are two kinds of methods which carry out the estimation. Direct summation of electrostatic potentials due to the lattice ions is a straightforward method. Several methods have been proposed by Evjen,[1] Frank[2] and the others. However, most of the methods are applicable for only special cases. The direct sums are conditionally convergent. For the lattice self-potential for CsCl, for example, the Evjen's method approached to double limits erroneously, as mentioned in the original paper.[1] Moreover, most of the direct-summation methods provide the potentials only at the lattice sites, not at the interstitial sites of the lattice, because these methods depend on symmetries about the sites of consideration. Generally applied methods[3,4] are on the basis of the indirect method of Ewald.[5] The ionic charges are distributed in the Gaussian form and the Poisson's equation is solved for the generated potential. Although some parameters are optimized for acceleration of convergence, the indirect methods require great effort and much time of computation.

As the Ewald's method is successful, there must exist an equivalent direct-summation method. A point charge produces the equal potential to that of corresponding ionic charge distribution at positions outside the ion. Hajj has proposed a direct-summation method along with an acceleration procedure of convergence which is applicable to the interstitial sites because of an appropriate symmetric property.[6] Averaging the potentials which are calculated for some different unit cells are necessary to cancel out the potential due to the surface of the finite

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crystallites. The Hajj's method is universal but the averaging procedure depends on the crystal structure. Coker has reported a simple and universal method for the electrostatic potentials in the crystals with direct summation.[7] He has discussed that the residual potential due to the surface structure of the finite crystallite causes the trouble in the previous direct-summation methods. He uses asymmetric crystallites where the surface potential at one end cancels out that at the opposite end. The remaining field due to the dipoles lying around the asymmetric point is estimated separately and removed from the lattice sums. Coker has analyzed the convergence polynomials which express the difference between the sums for the finite crystallite and for the infinite crystal. Removal of some lower order terms from the polynomials accelerates the convergence.

The purpose of the present work is to study the Coker's direct-summation method whose implementation is intended in a molecular orbital computational code. This method is applied to calculations of the self-potentials, the Madelung constants and the electrostatic potential at the interstitial positions of the lattice. The results are examined whether systematic errors occur among the values of several compounds.

II. COMPUTATIONAL METHOD

The lattice self-potential ϕ_i for the ith ion in the reference cell is

$$\phi_i = \frac{1}{2} \sum_l \sum_j Z_j e / |r_l + r_j - r_i| , \tag{1}$$

where the Coulomb interactions with the jth ion owning $Z_j e$ charges in the lth unit cell are summed up. The total electrostatic energy U per mole is expressed as

$$U = (N_A e^2 / 2\varkappa) \sum_i Z_i \phi_i , \tag{2}$$

where N_A is the Avogadro number and $\varkappa$ is the total number of molecules in the unit cell. The Madelung constant M_R is connected with U by a characteristic length R of the crystal structure :

$$U = -N_A (e^2 / R) M_R . \tag{3}$$

The dimensionless quantity M_R is calculated with the following equation:

$$M_R = -(R/2\varkappa) \sum_i Z_i \phi_i . \tag{4}$$

In the original definition by Madelung, the largest common factor of Z_i's is extracted from the Madelung constant in Eq. (4). This factor is included here for the convenience of comparison of the Madelung constant with the self-potential and between the compounds.

The direct-summation method by Coker[7] is briefly summarized. For the unit cell shown in Fig. 1, component ions are a cation and an anion. A space filling procedure using the translational vectors generates crystallites. An asymmetric point with a null electrostatic potential resides at the midpoint between these ions. The pair of ions makes up a dipole and then the method is called the dipolar-addition method. The potential due to the surface structure is cancelled out because of the asymmetric property. The field produced by the dipole μ at a distant point r is expressed as follows:

$$dE = \sigma r / r^3 dv , \tag{5}$$
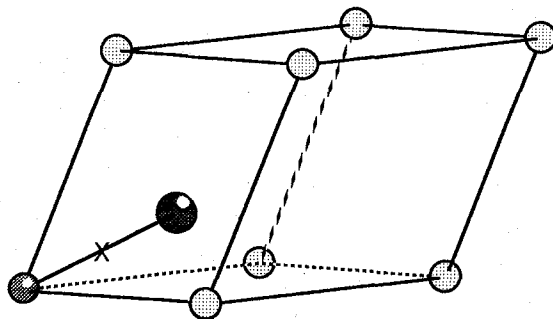
$$\sigma = \mu \cdot n / \text{abc} , \tag{6}$$

Fig. 1.   Unit cell for the dipolar-addition method.   White
colored atoms belong to the adjacent cells.

where a, b and c are the lattice parameters for an orthorhombic crystal.   Coker has obtained the
solutions of the total field in the crystallites for all the crystal systems.[7]   The field for the
orthorhombic crystal is estimated as

$$E_x = (8\mu_x/\text{abc}) \tan^{-1}(\text{bc}/a\sqrt{a^2+b^2+c^2}) . \tag{7}$$

E_y and E_z are obtained from E_x by cyclic permutation.   Coker has found that the convergence
polynomials for all the crystal symmetries include only even reciprocal powers beginning with the
inverse quadratic.   Elimination of some lower order terms among successive sums of the
crystallites accelerates the convergence.

III.   RESULTS AND DISCUSSION

The self-potentials and the Madelung constants for several compounds are summarized in
Table I.   In the present calculations, 14 shells around the central unit cell are included.   The
results contain the decimal figures unchanged between calculations of 14 shells and 15 shells.
The first two terms of the convergence polynomial were removed among three successive
crystallite sums.   For NaCl and CsCl, the Madelung constants in high precision have been
reported.[6,7]   The present results agree with them within the significant decimal figures.   For
simple structures such as NaCl and CsCl, the Madelung constants Ma is equal to the absolute
value of the self-potential for the cation and the anion in units of e/a, where the lattice parameter a
is adopted as the characteristic length for the Madelung constant.   These values agree in high
precision with each other.   No surface potentials contribute to the Madelung constants for these
structures because the contribution to the cation site cancels out that to the anion site.   The
agreement between the Madelung constant and the self-potentials in the present work means that
the surface contribution to the potentials at the lattice sites is throughly removed.

For ZnS, Cu_2O, CaF_2, $SrTO_3$ and $LaAlO_3$, the Madelung constants and the self-potentials
agree with the reported values and the higher precision is achieved.   For comparison of the
values among these compounds, alternative estimation was also made.   The self-potentials for a
compound relate to the Madelung constants for other compounds.   For CaF_2, these relation-
ships are[11]

$$\phi(\text{Ca}) = \text{Ma}(\text{ZnS})/2 , \tag{8}$$
$$= 2\text{Ma}(\text{CsCl}) + \text{Ma}(\text{NaCl}) , \tag{9}$$

$$\phi(F) \;\; = Ma(ZnS)/2 - Ma(NaCl),\tag{10}$$
$$= 2Ma(CsCl).\tag{11}$$

For the perovskite structure of $A^{+z}B^{+(3-z)}X_3{}^{-1}$, they are[12]

$$\phi(A) = z\,a_0 - 3a_2 + (3-z)a_3,\tag{12}$$
$$\phi(B) = (3-z)a_0 - 3a_1 + z\,a_3,\tag{13}$$
$$\phi(X) = -a_0 + (3-z)a_1 + (z-2)a_2,\tag{14}$$
$$a_0 = 3a_1 + 3a_2 + a_3,\tag{15}$$
$$a_1 = [Ma(NaCl) - 2Ma(CsCl)]/6a,\tag{16}$$
$$a_2 = -Ma(NaCl)/6a,\tag{17}$$
$$a_3 = [Ma(NaCl) + 6Ma(CsCl) - 2Ma(Cu_2O)]/6a.\tag{18}$$

These equations relate all the values in Table I. The solutions with the direct summation completely agree with the values derived with the above relations. It is proved that the present values are in high accuracy and precision.

Table I. Self-potentials and Madelung constants for several compounds.

Compound	Ref.*	Potential (e/a)		Ref.*	Madelung constant (Ma**)
		Cation site	Anion site		
NaCl	TW	− 3.49512918927	3.49512918927	TW	3.49512918927
				6	3.495129189266
CsCl	TW	− 2.035361509	2.035361509	TW	2.035361509
				7	2.035361509426
ZnS	TW	− 7.565852208	7.565852208	TW	15.131704417
				8	15.13168
Cu$_2$O	TW	− 3.782926104	6.476530930	TW	10.259457034
	9	− 3.78	6.477	10	10.25946
CaF$_2$	TW	− 7.565852208	4.070723019	TW	11.636575227
	TW1	− 7.565852208	4.070723019	TW1	11.636575227
	TW2	− 7.565852208	4.070723019	TW2	11.636575227
	9	− 7.566	4.07	8	11.63656
SrTiO$_3$	TW	− 5.387209651 Sr^{+2}	6.455908803	TW	49.50987212
		−12.377468029 Ti^{+4}			
	TW3	− 5.387209651 Sr^{+2}	6.455908803	TW3	49.50987212
		−12.377468030 Ti^{+4}			
	9	− 5.389 Sr^{+2}	6.455	10	49.509872
		−12.38 Ti^{+4}			
LaAlO$_3$	TW	− 7.422571160 La^{+3}	5.969319576	TW	44.55497525
		−10.342106520 Al^{+3}			
	TW3	− 7.422571160 La^{+3}	5.969319576	TW3	44.55497525
		−10.342106520 Al^{+3}			
	9	− 7.424 La^{+3}	5.969	10	44.55489
		−10.34 Al^{+3}			

* Numbers indicate the reference number, TW: this work with the direct summation, TW1: this work using Eq. (8), (10), TW2: this work using Eq. (9), (11), TW3: this work using Eq. (12)~(18).
** The lattice parameter a is the characteristic length for the Madelung constant.

Three kinds of unit cells for CsCl were used to examine the present computational code for the consistency among different crystal systems. The lattice parameters and the atomic positions are as follows.

Cubic

$a=b=c=1$ Cs : 1/2 1/2 1/2   Cl : 0   0   0

Tetragonal

$a=b=\sqrt{2}$ Cs : 0   0   1/2   Cl : 1/2 0   0

$c=1$ Cs : 1/2 1/2 1/2   Cl : 0   1/2 0

Orthorhombic

$a=2\sqrt{2}$ Cs : 0   0   1/2   Cl : 1/4 0   0

$b=\sqrt{2}$ Cs : 1/4 1/2 1/2   Cl : 0   1/2 0

$c=1$ Cs : 1/2 0   1/2   Cl : 3/4 0   0

               Cs : 3/4 1/2 1/2   Cl : 1/2 1/2 0

The self-potentials agree with each other as shown in Table II.

To provide an implement of the present code for molecular orbital calculations, rapid execution is preferable. The self-potentials were obtained with two shells around the central unit cell. The first term of the convergence polynomial expressing the difference between the

Table II. Consistency of self-potentials for CsCl in different crystal systems.

Crystal system	Potential (e/a)	
	Cation site	Anion site
Cubic	2.035361509_2	2.035361509_2
Tetragonal	2.035361509_5	2.035361509_5
Orthorhombic	2.035361509_4	2.035361509_4

Table III. Comparison in precision of self-potential calculations between crystallites with 14 shells and 2 shells around the central unit cell.

Compound	Site	Potential (e/a)		diff. %
		14 shells	2 shells	
NaCl	Cl^-	3.49512918927	3.4955	0.01
CsCl	Cl^-	2.035361509	2.0350	-0.02
ZnS	S^{-2}	7.565852208	7.5648	-0.01
Cu_2O	Cu^+	$-$ 3.782926104	$-$ 3.7831	0.00
	O^{-2}	6.476530930	6.4791	0.04
CaF_2	Ca^{+2}	$-$ 7.565852208	$-$ 7.5676	0.02
	F^-	4.070723019	4.0707	0.00
$SrTiO_3$	Sr^{+2}	$-$ 5.387209651	$-$ 5.3878	0.01
	Ti^{+4}	-12.377468029	-12.3788	0.01
	O^{-2}	6.455908803	6.4566	0.01
$LaAlO_3$	La^{+3}	$-$ 7.422571160	$-$ 7.4228	0.00
	Al^{+3}	-10.342106520	-10.3438	0.02
	O^{-2}	5.969319576	5.9698	0.01

Table IV. Electrostatic potentials at interstitials in the CsCl crystal.

Positions			Potential (e/a)		
x/a	y/a	z/a	15 shells	2 shells	Hajj*
0.0	0.25	0.0	−2.0000000001	−2.00022	−2.0000000001
0.05	0.25	0.0	−1.9183377003	−1.91853	−1.9183377003
0.10	0.25	0.0	−1.6988081207	−1.69897	−1.6988081207
0.15	0.25	0.0	−1.3991350747	−1.39927	−1.3991350747
0.20	0.25	0.0	−1.0763748116	−1.07647	−1.0763748116
0.25	0.25	0.0	−0.7700854509	−0.77015	−0.7700854509
0.30	0.25	0.0	−0.5029159551	−0.50294	−0.5029159551
0.35	0.25	0.0	−0.2869294567	−0.28693	−0.2869294567
0.40	0.25	0.0	−0.1287699935	−0.12876	−0.1287699935
0.45	0.25	0.0	−0.0323793066	−0.032365	−0.0323793066
0.50	0.25	0.0	0.0000000000	0.000000	0.0000000000

* Ref. 6.

sums for the finite crystallite and for the infinite crystal was eliminated. The precision is better than 0.04% as shown in Table III. This percentage roughly corresponds to 0.01 eV of the self-potential for real compounds.

For interstitial positions of the lattice, the electrostatic potentials calculated with the present procedure is compared with those obtained with another direct-summation method by Hajj[6] (Table IV). Complete agreement is achieved between two methods. The evaluation with two shells around the central unit cell is found enough for the present requirement for the electronic structure calculations. Contours of the electrostatic potential are plotted in the (100) cross section of the CaF$_2$ structure as shown in Fig. 2. This figure has no fault in the symmetrical
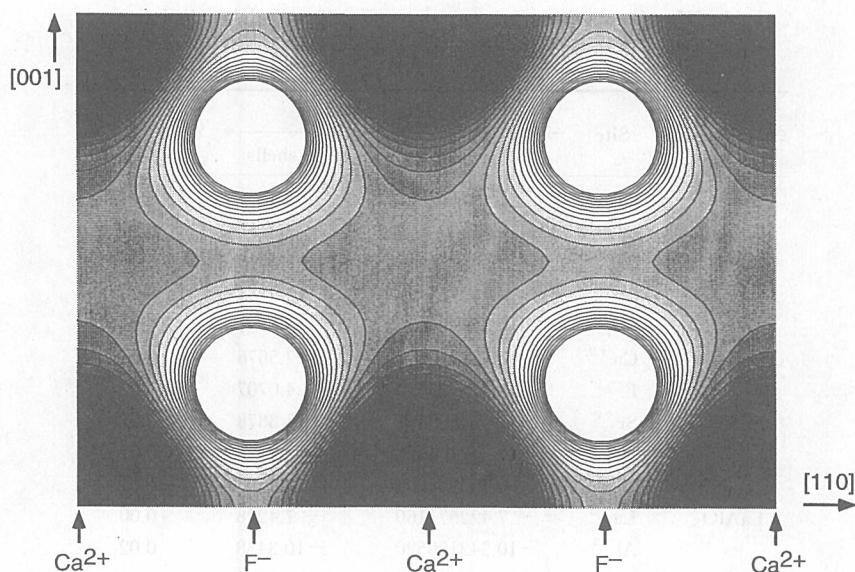
Fig. 2. Electrostatic potential of the (100) plain for CaF$_2$.

property in contrast to that by the Evjen's method. As an additional remark connecting with the property of this structure, a region of low gradient electric field spreads around the center of the cross section.

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