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Direct Sum of Coulomb Potential without Ambiguities of Conditionally Convergent Series

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We propose a definitive expression to evaluate electrostatic energies under periodic conditions, starting from the Yukawa potential with a finite range and summing up positive and negative contributions separately. We find a dimension-dependent function that can be used to solve problems concerning divergences and ambiguities in the direct sum of Coulomb potentials. The infinite-range limit of this function leads to a universal constant independent of lattice structure, which reveals the origin of ambiguities from conditionally convergent series in the sum of Coulomb potentials.

§1. Introduction

In the theory of ionic crystals, as well as in molecular dynamics simulations, the Coulomb interaction is of fundamental importance. However, the evaluation of electrostatic energies for an aggregate with an infinite number of point charges under periodic conditions encounters inevitable difficulties, namely, the conditionally and slowly convergent problem, owing to the long-range property of the Coulomb interaction. The original calculation of the electrostatic energy of an ionic crystal was made by Madelung.[1] The classical methods to sum up Coulomb potentials are those of Evjen[2] and Ewald.[3] The sums of Madelung and Evjen are carried out using the rearrangement procedure based on charge neutrality. The Ewald sum is an integral representation with two parts, each of which has a summation with more rapid convergence than the original one. Therefore, the Ewald sum has often been applied to molecular dynamics and Monte Carlo simulations in various fields, such as liquid-state physics,[4] plasma physics,[5)–7)] and astrophysics.[8] In addition to the Ewald sum, there is a Fourier representation as another mathematical transformation method.[9)–11)] The Fourier representation has the advantage that it can be applied to quantum systems,[12] and Harris et al. have performed Hartree-Fock calculations for ideal crystals using this representation.[13]

In spite of these methods, computing the sum of Coulomb potentials on a reference charge coming from all other point charges is very cumbersome, due to the conditionally convergent series. In particular, different methods used to compute this sum can be lead to different values, and even within the same method, the value to which the sum converges can depend on the order in which contributions of the charges are taken. Redlack and Grindlay considered ellipsoidal systems, and

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analyzed the above four methods.[14] Their analyses indicate that the specific way in which a primitive cell is chosen for a given crystal structure and the shape of the array of replications can affect the result. De Leeuw et al.[15] succeeded in applying the Ewald sum to molecular dynamics simulations without ambiguities due to the conditionally convergent series. They introduced a mathematical convergence factor related to the spherical surface for adding series of spherical shells and found a term lacking in the Ewald sum used previously in molecular dynamics and Monte Carlo simulations. Their term contains information of surface, and compensates for the differences among the characteristics of the surface in specifying a primitive cell.

In this paper we aim at overcoming the difficulty arising from the conditionally convergent series by starting with the Yukawa potential whose series is absolutely convergent. It is called a screening Coulomb potential, and it is fundamental in various fields, such as liquid-state physics,[16)–18)] plasma physics[19)–21)] and astrophysics.[22),23)] We define the electrostatic energy as the static energy of the Yukawa potential with an infinite-limit range. Another essential point is that we sum up positive and negative contributions separately, in contrast to the conventional methods, such as the Ewald sum. As a matter of course, each sum of the Coulomb potentials has a divergent term. The main subject of this paper is to show how to eliminate this divergent term and to show that this elimination enables us to naturally remove ambiguities in conditionally convergent series. Our expression for the sum of Coulomb potentials on a reference charge is divided into three terms as follows:

$$U_{\mathrm{Coul}}^{(3)} = U_{\mathrm{Coul}}^{\mathrm{in}} + U_{\mathrm{Coul}}^{\mathrm{env}} + U_{\mathrm{Coul}}^{\mathrm{coup}}. \tag{1·1}$$

The first term here represents the internal energy of a unit cell, the second term represents the energy stemming from all the environmental cells, and the third term is the coupling term between the lattice structure of the crystal and the unit-cell structure. The superscript "(3)" means that the expression (1·1) is applicable only for crystals with "three"-dimensional periodicity.

In §2, we start with the direct sum of Coulomb potentials and give expressions for the first and second terms in Eq. (1·1). Divergent terms appear in our method because positive and negative contributions are summed separately. In this section, we assume that positive and negative divergent terms cancel because positive and negative point charges have the same periodicity. We show that this assumption is appropriate for crystals with one- and two-dimensional periodicity and that it leads to ambiguities in the sum of Coulomb potentials under three-dimensional periodic conditions. In §3, we give the expression for the direct sum of Yukawa potentials, and we show that the static energy smoothly connects to an empirical electrostatic energy for a given crystal structure in the limit of an infinite range. In §4, we define the dimension-dependent function that reveals how ambiguities arise in electrostatic energies depending on the dimension of periodicity. This leads us to a definitive expression for the sum of Coulomb potentials. Finally, we close this paper by giving a summary and concluding remarks in §5. In this paper, we employ the CGS system of units, and the elementary electric charge e is set to unity.

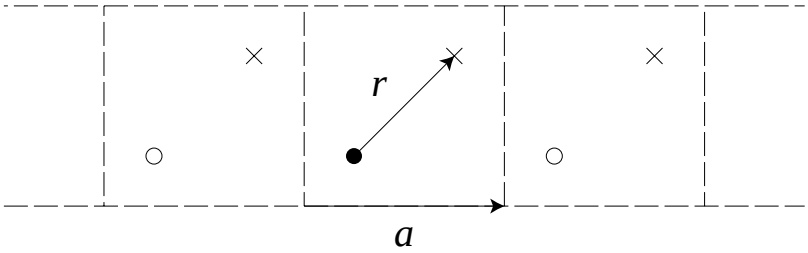

Fig. 1. Charge distribution of an ionic crystal with one-dimensional periodicity. Two point particles with different charges separated by the vector $\boldsymbol{r}$ are within a cubic cell, and the same placement is repeated periodically with the primitive vector $\boldsymbol{a}$. The circles represent positive or negative charges, and the crosses represent charges opposite to those of the circles. The solid circle represents the reference charge.

§2. Intuitive method to sum Coulomb potentials under periodic conditions

Let us start with the direct sum of Coulomb potentials. To give the mathematical foundation of this computation, we consider the one-dimensional periodic ionic crystal shown in Fig. 1. The sum of Coulomb potentials on a reference charge at the origin (the solid circle in Fig. 1) is given by

$$U_{\mathrm{Coul}} = -\sum_{n=-\infty}^{\infty} \frac{1}{|\boldsymbol{r} - n\boldsymbol{a}|} + 2\sum_{n=1}^{\infty} \frac{1}{na}. \tag{2·1}$$

This expression implies that the positive (the first terms) and negative (the second terms) contributions are summed up separately. Each term in the first sum, except $1/r$ for $n = 0$, is the generating function of a Legendre polynomial P_m. Equation (2·1) can be rewritten as

$$U_{\mathrm{Coul}} = -\frac{1}{r} - \frac{2}{a}\sum_{m=1}^{\infty} \left(\frac{r}{a}\right)^{2m} \zeta(2m+1) P_{2m}(\cos\theta) - \frac{2}{a}\zeta(1) + \frac{2}{a}\zeta(1), \tag{2·2}$$

where

$$\cos\theta = \frac{\boldsymbol{r}\cdot\boldsymbol{a}}{ra}, \quad \left[\frac{r}{a} < 1\right]. \tag{2·3}$$

The Riemann ζ-function,

$$\zeta(z) = \sum_{n=1}^{\infty} \frac{1}{n^z}, \tag{2·4}$$

is convergent under the condition $\mathcal{R}z > 1$. The divergent terms in Eq. (2·1) appear as $\pm\zeta(1)$.

Here, we assume that $\pm\zeta(1)$ are canceled out, because the periodic distributions of the positive and negative point charges are the same. The general expression is given by

$$U_{\mathrm{Coul}}^{(1,2)} = U_{\mathrm{Coul}}^{\mathrm{in}} + U_{\mathrm{Coul}}^{\mathrm{env}}, \tag{2·5}$$

$$U_{\mathrm{Coul}}^{\mathrm{in}} = \sum_{j}^{N-1} \frac{1}{r_j} - \sum_{j'}^{N} \frac{1}{r_{j'}}, \tag{2·6}$$

and

$$U_{\mathrm{Coul}}^{\mathrm{env}} = \sum_{\mathbf{a}} \frac{2}{a} \sum_{m=1}^{\infty} \zeta\left(2m+1\right) \times \left[\sum_{j}^{N-1} P_{2m}\left(\cos\theta_j\right) \left(\frac{r_j}{a}\right)^{2m} - \sum_{j'}^{N} P_{2m}\left(\cos\theta_{j'}\right) \left(\frac{r_{j'}}{a}\right)^{2m} \right], \tag{2·7}$$

where a primitive cell includes N pairs of positive and negative point charges. The reference charge is at the origin, and the charges in a given cell with the same sign as the reference and the opposite sign of the reference are at the positions $\boldsymbol{r}_j$ and $\boldsymbol{r}_{j'}$, respectively. For two- and three-dimensional periodic crystals, we have to sum up the lattice vectors $\boldsymbol{a}$.*) The angles θ_j and $\theta_{j'}$ are those between $\boldsymbol{a}$ and $\boldsymbol{r}_j$ and between $\boldsymbol{a}$ and $\boldsymbol{r}_{j'}$. The superscript "(1,2)" indicates that the expression (2·5) is applicable for "one"- and "two"-dimensional periodic crystals, as is shown in §4, where we verify the cancellation of $\pm\zeta(1)$ for one- and two-dimensional periodicity.

For a one-dimensional periodic crystal in which positive and negative charges are alternatively placed on a linear chain with unit nearest-neighbor distance, the expression (2·5) with no summation of $\boldsymbol{a}$ gives -1.386 as the electrostatic energy, which is equal to $-2\log 2$, obtained by summing up positive and negative contributions alternatively. For a two-dimensional periodic crystal with an alternating square lattice, the expression (2·5) gives -1.615, independent of the choice of the primitive cell.

For three-dimensional periodic crystals, the expression (2·5) leads to ambiguities in electrostatic energies, depending on the choice of the primitive cell, due to the lack of the coupling term compared with Eq. (1·1), resulting from the cancellation of $\pm\zeta(1)$. For instance, the expression (2·5) gives three different values of the electrostatic energy for CsCl-type ionic crystals, -0.402, -3.123 and -1.762, depending on the choice of the primitive cell shown in Figs. 2 (a)–(c), respectively. The values in Cases (a) and (b) are also obtained from the Evjen sum, and he regarded the average of the two values, which is equal to the value in Case (c), as the physical value for CsCl-type ionic crystals.[2] In the next section we give an expression for the direct sum of Yukawa potentials with a finite range, and in §4 we derive a definitive expression for the sum of Coulomb potentials by regarding it as a sum of Yukawa potentials with the infinite-limit range.

*) The lattice vectors are represented as $\boldsymbol{a} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2$ for two dimensions, and $\boldsymbol{a} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$ for three dimensions, where $(\boldsymbol{a}_1, \boldsymbol{a}_2)$ and $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ are the primitive vectors characterizing the periodicity of the crystal. There are an infinite number of choices, including oblique coordinates. The greatest common divisor of the set (n_1, n_2) or (n_1, n_2, n_3) should be unity to avoid over-counting on the same line. Here, n_1 and n_2 are integers, and n_3 is a non-negative integer. (n_1 or n_2 is restricted to a positive integer value if $n_3 = 0$. This is also the case for two dimensions.) If one integer is zero, the greatest common divisor of the other integers should be unity, and if two integers are zero, the remaining one should be unity.

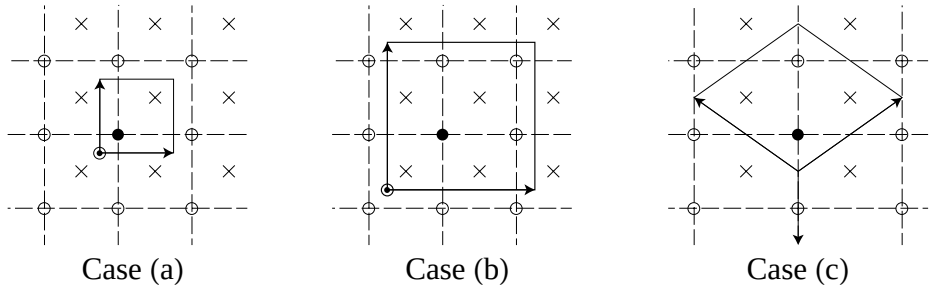

Fig. 2. Three different choices of the primitive cell for CsCl-type crystals. Case (a): $\boldsymbol{a}_1 = (2/\sqrt{3}, 0, 0)$, $\boldsymbol{a}_2 = (0, 2/\sqrt{3}, 0)$, $\boldsymbol{a}_3 = (0, 0, 2/\sqrt{3})$. Case (b): $\boldsymbol{a}_1 = (4/\sqrt{3}, 0, 0)$, $\boldsymbol{a}_2 = (0, 4/\sqrt{3}, 0)$, $\boldsymbol{a}_3 = (0, 0, 4/\sqrt{3})$. Case (c): $\boldsymbol{a}_1 = (2/\sqrt{3}, 2/\sqrt{3}, -2/\sqrt{3})$, $\boldsymbol{a}_2 = (2/\sqrt{3}, -2/\sqrt{3}, 2/\sqrt{3})$, $\boldsymbol{a}_3 = (-2/\sqrt{3}, 2/\sqrt{3}, 2/\sqrt{3})$. Cases (a) and (b) correspond to orthogonal coordinates, and Case (c) to oblique coordinates. The primitive cells include one, eight and four pairs of positive and negative charges in Cases (a), (b) and (c), respectively.

§3. Expression for sum of Yukawa potentials under periodic conditions

We now turn to the subject of the sum of Yukawa potentials with a finite range. In this case, in contrast to the conditionally convergent series (2·1), the series is absolutely convergent:

$$U(\mu) = -\sum_{n=-\infty}^{\infty} \frac{e^{-|\boldsymbol{r}-n\boldsymbol{a}|/\mu}}{|\boldsymbol{r}-n\boldsymbol{a}|} + 2\sum_{n=1}^{\infty} \frac{e^{-na/\mu}}{na}. \tag{3·1}$$

Each term in the first summation, except the term $\exp(-r/\mu)/r$ for $n = 0$, can be expanded by using the modified spherical Bessel function i_m and the modified spherical Hankel function k_m. The general expression for the sum of Yukawa potentials on a reference charge at the origin is given as follows:

$$U(\mu) = U^{\mathrm{in}}(\mu) + U^{\mathrm{env}}(\mu) + U^{\mathrm{coup}}(\mu), \tag{3·2}$$

$$U^{\mathrm{in}}(\mu) = \frac{1}{\mu}\left[\sum_{j}^{N-1} \frac{e^{-\tilde{r}_j}}{\tilde{r}_j} - \sum_{j'}^{N} \frac{e^{-\tilde{r}_{j'}}}{\tilde{r}_{j'}}\right], \tag{3·3}$$

$$\begin{aligned} U^{\mathrm{env}}(\mu) = \frac{2}{\mu} &\sum_{\tilde{\boldsymbol{a}}} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} k_{2m}(n\tilde{a})\,(4m+1) \\ &\times \left[\sum_{j}^{N-1} P_{2m}\left(\cos\theta_j\right) i_{2m}(\tilde{r}_j) - \sum_{j'}^{N} P_{2m}\left(\cos\theta_{j'}\right) i_{2m}(\tilde{r}_{j'})\right], \end{aligned} \tag{3·4}$$

and

$$U^{\mathrm{coup}}(\mu) = \frac{2}{\mu}\left(1 + \sum_{j}^{N-1} \frac{\sinh\tilde{r}_j}{\tilde{r}_j} - \sum_{j'}^{N} \frac{\sinh\tilde{r}_{j'}}{\tilde{r}_{j'}}\right) \sum_{\tilde{\boldsymbol{a}}} \frac{1}{\tilde{a}} \phi(1, s_{\tilde{a}}), \tag{3·5}$$

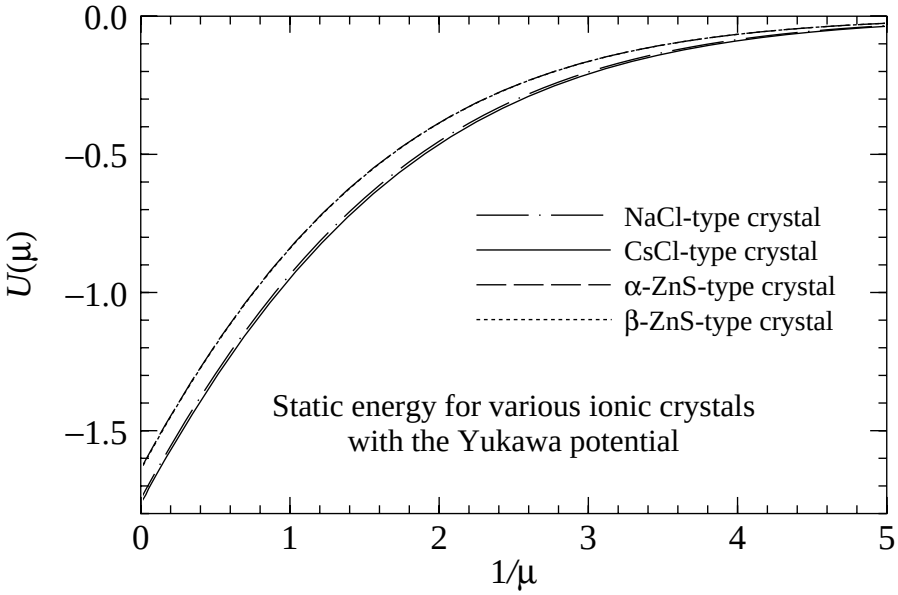

Fig. 3. The $1/\mu$-dependence of $U(\mu)$ for various crystals with unit nearest-neighbor distance. Those for the NaCl-type, CsCl-type, α-ZnS-type and β-ZnS-type ionic crystals are indicated by the dotted-dashed, solid, dashed and dotted curves, respectively.

where $\phi(z, s)$ is the Appell function,

$$\phi(z, s) = \sum_{n=1}^{\infty} \frac{s^n}{n^z}, \tag{3·6}$$

which becomes the Riemann ζ-function (2·4) when s is equal to unity. Here $\tilde{r} = r/\mu$ and $\tilde{a} = a/\mu$ are dimensionless variables ($r/a < 1$), and $s_{\tilde{a}} = \exp(-\tilde{a})$.

We apply the expressions (3·2)–(3·5) to NaCl-, CsCl-, α-ZnS- and β-ZnS-type crystals. The behavior of $U(\mu)$ with respect to $1/\mu$ is displayed in Fig. 3 in the case that the nearest-neighbor distance is unity. In contrast to the expression (2·5) for a sum of Coulomb potentials, the expression (3·2) gives a definitive curve to a given crystal structure, independent of the choice of the primitive cell, even in the case of three-dimensional periodicity. As μ goes to infinity, each $|U(\mu)|$ approaches the corresponding Madelung constant for the given crystal structure, 1.747, 1.762, 1.638 and 1.641 for NaCl-type (dashed-dotted curve), CsCl-type (solid curve), α-ZnS-type (dashed curve) and β-ZnS-type (dotted curve) crystals, respectively. In the limit of an infinite range, we easily prove that the internal term (3·3) and environmental term (3·4) coincide with Eqs. (2·6) and (2·7) in the previous section. Nevertheless, the coupling term is lacking in the expression (2·5) for the sum of Coulomb potentials, corresponding to Eq. (3·5), due to the cancellation of $\pm\zeta(1)$. In the next section we verify this cancellation for one- and two-dimensional periodicity but not for three-dimensional periodicity, by introducing a dimension-dependent function with respect to the range of the Yukawa potential. Its infinite range limit gives the expression for the coupling term in the direct sum of Coulomb potentials under three-dimensional

periodic conditions.

§4. Definitive expression for the direct sum of Coulomb potentials

4.1. *Dimension-dependent function to eliminate ambiguities and divergences in the sum of Coulomb potentials*

Let us scrutinize the ambiguities and divergences inherent in the sum of Coulomb potentials. To go more deeply into the core of the matter, we define a dimension-dependent function as

$$F_k(\mu) = \tilde{V}_{\text{cell}}^{(k)} \sum_{\tilde{\mathbf{a}}}^{(k\text{-dim})} \frac{1}{\tilde{a}} \phi(1, s_{\tilde{a}}), \tag{4·1}$$

where k represents the number of dimensions of the periodicity, and dimensionless scales are introduced by

$$\tilde{V}_{\text{cell}}^{(1)} = L_{\text{cell}}/\mu, \quad \tilde{V}_{\text{cell}}^{(2)} = S_{\text{cell}}/\mu^2, \quad \tilde{V}_{\text{cell}}^{(3)} = V_{\text{cell}}/\mu^3. \tag{4·2}$$

Here L_{cell}, S_{cell} and V_{cell} are the length, area and volume of a primitive cell, respectively. Using this function, we define the coupling term in the sum of Coulomb potentials as follows:

$$U_{\text{Coul}}^{\text{coup}} \equiv \lim_{\mu\to\infty} \frac{2}{\mu} \left(\sum_{j}^{N-1} \frac{\tilde{r}_j^2}{6} - \sum_{j'}^{N} \frac{\tilde{r}_{j'}^2}{6} \right) \frac{1}{\tilde{V}_{\text{cell}}^{(k)}} F_k(\mu). \tag{4·3}$$

The coupling term (4·3) is well-behaved in the limit of an infinite range as the form $\lim_{\mu\to\infty} \mu^{k-3} F_k(\mu)$.

For one dimension, there is no summation with respect to $\boldsymbol{a}$, and we find immediately that $F_1(\mu)$ diverges logarithmically. For two and three dimensions, we found numerically that $F_2(\mu)$ and $F_3(\mu)$ converge to π and 2π, for any choice of the primitive cell, as shown in Fig. 4. Therefore, in one and two dimensions, the coupling term (4·3) gives no contribution to the sum of Coulomb potentials, because $\lim_{\mu\to\infty} \mu^{-2} F_1(\mu) = 0$ and $\lim_{\mu\to\infty} \mu^{-1} F_2(\mu) = 0$; hence, the cancellation of $\pm\zeta(1)$ in §2 is verified for one- and two-dimensional periodic crystals. Contrastingly, in three dimensions, the coupling term gives contribution to the sum of Coulomb potentials proportional to 2π. This is why the expression (2·5) causes ambiguities in electrostatic energies for three-dimensional periodic crystals due to the lack of a coupling term.

4.2. *Mathematical expression for electrostatic energies without ambiguities from conditionally convergent series*

The dimension-dependent function leads us to the following definitive expression for the direct sum of Coulomb potentials under three-dimensional periodic condition:

$$U_{\text{Coul}} = U_{\text{Coul}}^{\text{in}} + U_{\text{Coul}}^{\text{env}} + U_{\text{Coul}}^{\text{coup}}, \tag{4·4}$$

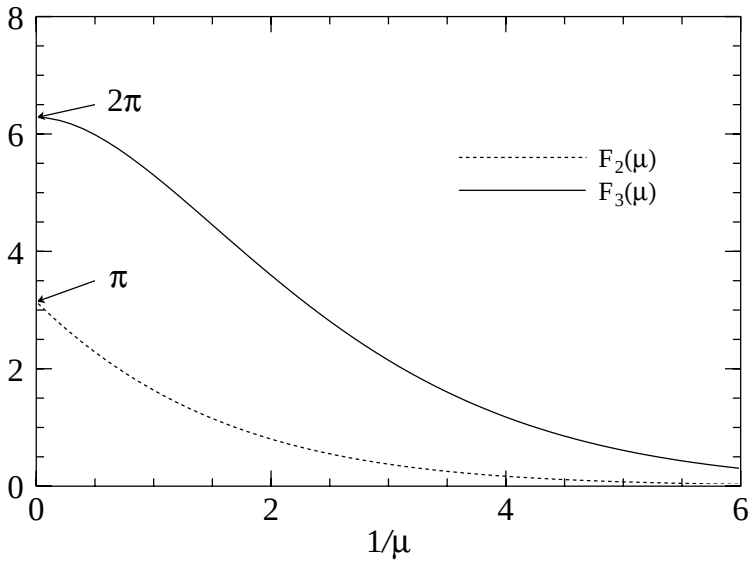

Fig. 4. The behavior of the functions $F_2(\mu)$ and $F_3(\mu)$ with respect to $1/\mu$, which are indicated by the dotted and solid curves, respectively.

where

$$U_{\mathrm{Coul}}^{\mathrm{in}} = \sum_{j}^{N-1} \frac{1}{r_j} - \sum_{j'}^{N} \frac{1}{r_{j'}}, \tag{4·5}$$

$$U_{\mathrm{Coul}}^{\mathrm{env}} = \sum_{\boldsymbol{a}} \frac{2}{a} \sum_{m=1}^{\infty} \zeta\left(2m+1\right) \times \left[\sum_{j}^{N-1} P_{2m}\left(\cos\theta_j\right) \left(\frac{r_j}{a}\right)^{2m} - \sum_{j'}^{N} P_{2m}\left(\cos\theta_{j'}\right) \left(\frac{r_{j'}}{a}\right)^{2m} \right], \tag{4·6}$$

and

$$U_{\mathrm{Coul}}^{\mathrm{coup}} = \frac{1}{V_{\mathrm{cell}}} \frac{2\pi}{3} \left(\sum_{j}^{N-1} r_j^2 - \sum_{j'}^{N} r_{j'}^2 \right). \tag{4·7}$$

It should be noted here that the summation with respect to $\boldsymbol{a}$ must be taken as spherical shells, because we regarded the direct sum of Coulomb potentials as that of Yukawa potentials with an infinite-limit range; that is, taking the infinite limit of the range is equivalent to taking the infinite limit of the surface with a spherical boundary. In this sense, the coupling term (4·7) is similar to that in Ref. 15), but its origin is different. Our coupling term originates in the character of the potential, while their term comes from the spherical boundary condition. In addition, the contribution from our coupling term to the electrostatic energy has the opposite sign of that from their term, because the summation with respect to $\boldsymbol{a}$ in our method acts to plug up a hole on the spherical surface successively.

Table I. The electrostatic energy for CsCl-type ionic crystals with unit nearest-neighbor distance evaluated using the expressions (4·4)–(4·7) in the cases that the primitive cell is chosen as in (a), (b) and (c) in Fig. 2. The first column indicates the electrostatic energy, and the second, third and fourth columns represent the internal, environmental and coupling terms evaluated using Eqs. (4·5), (4·6) and (4·7), respectively.

	$U_{\rm Coul}$	$U_{\rm Coul}^{\rm in}$	$U_{\rm Coul}^{\rm env}$	$U_{\rm Coul}^{\rm coup}$
Case (a)	−1.762675	−1.000000	0.597675	−1.360350
Case (b)	−1.762675	−3.064807	−0.058214	1.360350
Case (c)	−1.762675	−1.401924	−0.360741	0.000000

Table II. The Madelung constants for typical ionic crystals. The Madelung constants evaluated using Eqs. (4·4)–(4·7) in the present work (first row) are compared with empirical values listed in Kittel's[24] (second row) and Lee's[25] (third row) textbooks.

	CsCl type	NaCl type	α-ZnS type	β-ZnS type
Present work	1.762675	1.747565	1.638055	1.64132
Kittel[24]	1.762675	1.747565	1.6381	-
Lee[25]	1.76267	1.74756	1.63806	1.64132

It is certain that the expressions (4·4)–(4·7) can remove ambiguities in the electrostatic energy for CsCl-type ionic crystals depending on the choice of the primitive cell. Table I lists the electrostatic energy for CsCl-type ionic crystals with unit nearest-neighbor distance in the cases that the primitive cell is chosen as in (a), (b) and (c) in Fig. 2. The expressions (4·4)–(4·7) also give an ordinary Madelung constant for other typical ionic crystals independent of the choice of the primitive cell, which are compared with those given in textbooks[24),25)] in Table II.

§5. Summary and concluding remarks

We succeeded in deriving a definitive expression for the direct sum of Coulomb potentials given in (2·5)–(2·7) in one- and two-dimensional periodic crystals, and (4·4)–(4·7) in three-dimensional ones by regarding it as a sum of Yukawa potentials with an infinite-limit range. In this paper, we applied our expression only to ideal ionic crystals, but it can also be applied to molecular dynamics simulations used in liquid-state physics, plasma physics and astrophysics. The electrostatic energy per unit cell, which includes N charges, with the charge q_i at $\boldsymbol{r}_i$, is given as follows under the condition of charge neutrality of a unit cell, $\sum_i^N q_i = 0$:

$$E_{\rm Coul} = E_{\rm Coul}^{\rm in} + E_{\rm Coul}^{\rm env} + E_{\rm Coul}^{\rm coup}, \tag{5·1}$$

$$E_{\rm Coul}^{\rm in} = \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{q_i q_j}{r_{ij}}, \tag{5·2}$$

$$E_{\rm Coul}^{\rm env} = \sum_{i}^{N}\sum_{j\neq i}^{N}\sum_{\boldsymbol{a}}\frac{q_i q_j}{a}\sum_{m=1}^{\infty}\zeta(2m+1)\left(\frac{r_{ij}}{a}\right)^{2m}P_{2m}(\cos\theta_{\boldsymbol{a}}), \tag{5·3}$$

and

$$E_{\mathrm{Coul}}^{\mathrm{coup}} = \frac{1}{V_{\mathrm{cell}}} \frac{\pi}{3} \sum_{i}^{N} \sum_{j \neq i}^{N} q_i q_j r_{ij}^2. \tag{5·4}$$

Here, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ $(r_{ij}/a < 1)$ and $\theta_{\boldsymbol{a}}$ is the angle between $\boldsymbol{r}_{ij}$ and $\boldsymbol{a}$. These expressions are applicable only for simulations under three-dimensional periodic conditions, and the coupling term (5·4) should be zero for the cases of one- and two-dimensional periodicity. We can also write down the static energy per unit cell for Yukawa potentials, (3·2)–(3·5), in the similar way.

In our derivation, the dimension-dependent function (4·1) with respect to the range parameter of the Yukawa potential plays an essential role in removing ambiguities inherent in electrostatic energies, especially in three-dimensional periodic crystals. It converges to constants in the infinite range limit, namely, π and 2π for two- and three-dimensional lattices, independent of the lattice structure. We can naturally extend the dimension-dependent function to dimensions higher than three. We also numerically checked that it converges to constants proportional to π^2, π^2 and π^3 in four, five and six dimensions, respectively. These constants are related to the solid angles of the corresponding dimensions, because this function includes information of an infinite spherical surface. Accordingly, the coupling term (4·3) seems to give infinite electrostatic energies for crystals in dimensions higher than three, but the environmental term for the Yukawa potentials, Eq. (3·4), also has divergent components in the infinite range limit, and the sum of Coulomb potentials has a finite value. Our approach starting with the Yukawa potential is useful point of view that can be extended to crystals in multi-dimensional space. This subject is currently under study. We remark that our expression can be extended to crystals with surfaces and/or defects in solid state physics.

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