Elementary function expansions for Madelung constants

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Abstract. The Madelung constant—essentially the Coulomb energy density of a crystal—is usually calculated via Ewald error function expansions or, for the simpler cubic structures, by the 'cosech' series of modern vintage. By considering generalised functional equations for multidimensional zeta functions, we provide explicit expansions for the spatial potential and energy density of three-dimensional periodic structures. These formulae, involving only elementary functions, are suitable for systematic calculation of Madelung constants of arbitrary point-charge crystals. We indicate how zeta function relations may be used for dimensional reduction of certain multiple sums arising in the special cubic cases.

1. Introduction

The problem of computing the electrostatic potential energy density of a crystal has occupied researchers for over seventy years (Madelung 1918, Sherman 1932, Born and Huang 1954, Hautot 1975, Zucker 1976, Glasser and Zucker 1980, Borwein *et al* 1985). Closed form evaluations of the triple sums that define the Madelung constants of crystals are perhaps out of the question. The most common method of computer calculation of these numbers is due to Ewald (1921) and involves rapidly converging triple sums of error function terms. More recently Hautot (1975) and Zucker (1976) have established elementary 'cosech' double sums for cubic crystals. Crandall and Delord (1987) provide generalised double sums for arbitrary point-charge crystals and non-alternating summations suitable for deriving bounds on Madelung constants.

Both the Ewald triple sums and cosech double sums have drawbacks for actual calculation for general crystals. The Ewald sums use various error functions whose computation can be unwieldy, especially if high precision is desired. The double sums for cubic crystals can be quickly implemented, but for general crystals these formulae are complex. In the present paper we develop triple sums for the spatial potentials and Madelung constants of arbitrary crystals. These arise from generalisation of the functional equation approach implicit in Ewald's work and in much of the literature. This analysis will, for arbitrary three-dimensional crystals, provide expressions that converge rapidly, are easy to implement and involve only elementary functions.

The celebrated Madelung constant for the NaCl crystal is given formally by a triple sum of Coulomb terms. If the charge at a lattice point (u, v, w) of integers is $(-1)^{u+v+w}$ then the Madelung constant is

$$M_{\text{NaCl}} = \sum_{u,v,w \in Z}' \frac{(-1)^{u+v+w}}{(u^2 + v^2 + w^2)^{1/2}} = -1.747\,564\,594\,633\,182\,190\,636\ldots \tag{1.1}$$

where the prime on the summation signifies that the singularity at $(0, 0, 0)$ is avoided. The spatial potential $V(x, y, z)$ is given by a similar formula, with denominator $[(u - x)^2 + (v - y)^2 + (w - z)^2]^{1/2}$ and prime removed. The number M_{NaCl} thus represents the potential seen by the origin charge with self-potential removed.

The convergence of such sums is problematic. The sum (1.1) clearly does not converge absolutely and, in fact, is not convergent if the summation is done by taking all terms within a given radius and then letting the radius go to infinity. Although the summation can be defined rigorously (Borwein *et al* 1985, Crandall and Buhler 1987) the sum then converges far too slowly for practical purposes. It is standard to apply certain integral transformations to this sum to get multidimensional zeta functions. We shall generalise the usual functional equation for these zeta functions; this gives an expression for the Madelung constant of an arbitrary crystal as a sum of quantities J (coming from the 'jellium' potential), with J having the general form

$$J = P + \Sigma_F + \Sigma_G \tag{1.2}$$

where P involves 'polar' terms. The sums Σ_F and Σ_G are similar to the original sum for M except that each term contains a multiplier involving a function F or a function G that guarantees rapid convergence. The function G is a cosine transform of the derivative of F. The choice of F, subject to certain general properties, is arbitrary. If F is an error function then the classical Ewald sum is obtained. By trying other expressions for F we obtain formulae involving only elementary functions. For instance, in the NaCl case a certain choice for F will yield

$$M_{NaCl} = -\lambda + \sum_{v \in Z^3}{}' \frac{(-1)^{\Sigma v_i}(1 - \tanh \lambda |v|)}{|v|}$$
$$+ \frac{2\pi}{\lambda} \sum_{v \in O^3} \frac{\mathrm{cosech}(\pi^2|v|/2\lambda)}{|v|} \tag{1.3}$$

where O^3 denotes all triples of odd integers, λ is an arbitrary positive real number and $|v|$ is the length of a 3-vector v. In the limit of vanishing λ we obtain the original form (1.1). The sums for arbitrary crystals are not substantially more difficult. This means that relatively simple programs, requiring only the input of fundamental crystal parameters, can quickly calculate arbitrary Madelung constants. The corresponding expression for the spatial potential at a point $V(x, y, z)$ within the NaCl crystal is somewhat more complicated than (1.3) but still involves the same elementary F and G functions.

It should be mentioned that various cosech sums as in (1.3) for certain values of the free parameter λ are known in closed form, or at least as one-dimensional cosech sums. Such evaluations present some hope for sharper approximation methods in the Madelung problem. We take up this subject within the context of dimensional reduction of zeta functions.

2. Crystal nomenclature

We shall take the general point-charge crystal to be defined by a 3×3 real matrix $\mathbf{A}$ such that the general lattice site is

$$p = \mathbf{A}v \qquad v \in Z^3. \tag{2.1}$$

The volume of one lattice cell is det $\mathbf{A}$. We denote the reciprocal lattice matrix $\mathbf{B} = \mathbf{A}^{-T}$ (where $-T$ is the inverse transpose). At each lattice site we assume there is an assembly of m point charges. Thus there is a collection of distinct offset vectors $\mathbf{d}_j$ such that the point charges in our crystal may be denoted q_j, residing at positions

$$\mathbf{p} + \mathbf{d}_j \tag{2.2}$$

for $j = 0, 1, \ldots, m - 1$. In order to obtain finite Madelung sums we must assume that the overall crystal is neutral, i.e. that $\Sigma\, q_j = 0$.

In summary, our crystal is defined by a matrix $\mathbf{A}$, a collection of offsets $\mathbf{d}_0, \ldots, \mathbf{d}_{m-1}$ and a collection of charges $q_0, \ldots, q_{m-1}$, subject to the conditions that the $\mathbf{d}_j$ be distinct and the sum of the q_j is 0.

Some examples for common crystal structures are as follows.

CsCl: $m = 2$, $\mathbf{A}$ is the identity matrix, the offsets are $\mathbf{d}_0 = 0$, $\mathbf{d}_1 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the charges are $q_0 = 1$, $q_1 = -1$.

ZnS: $m = 2$,

$$\mathbf{A} = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$$

the offsets are $\mathbf{d}_0 = 0$, $\mathbf{d}_1 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the charges are $q_0 = 1$, $q_1 = -1$.

NaCl: $m = 2$, $\mathbf{A}$ is the same as for ZnS, the offsets are $\mathbf{d}_0 = 0$, $\mathbf{d}_1 = (1, 1, 1)$ and the charges are $q_0 = 1$, $q_1 = -1$.

In fact this representation of a crystal is not unique. For instance, in the case of NaCl one may devise a representation in which $m = 8$, $\mathbf{A}$ is twice the identity matrix, and the offsets are eight binary vectors, ordered lexicographically, with corresponding q_j: $(1, -1, -1, 1, -1, 1, 1, -1)$. This $m = 8$ representation is often the easiest to work with, chiefly because the $\mathbf{A}$ matrix is so simple. In fact, results such as (1.3) can be derived by summing eight values of a J function, as we shall see.

We formally define the Madelung constant for a general crystal to be

$$M = \frac{1}{\det \mathbf{A}} \sum_{j,k} q_j q_k \sum_{v \in Z^3}' \frac{1}{|\mathbf{A}v + \mathbf{d}_k - \mathbf{d}_j|} \tag{2.3}$$

while the spatial potential at a vector x is

$$V(x) = \sum_k q_k \sum_{v \in Z^3} \frac{1}{|\mathbf{A}v + \mathbf{d}_k - x|}. \tag{2.4}$$

We shall consistently use a prime on summations such as (2.3) to denote that any infinite summands are ignored. This rule is not equivalent to simple removal of $v = 0$ terms. The sum for M has the natural physical interpretation as the electrostatic potential energy density of the crystal. (Note that this explains the denominator det $\mathbf{A}$.) Other definitions of M, such as Sherman's (1932), are consistent with (2.3) for simpler crystals, and in any case are proportional to M for more complex structures as discussed in Crandall and Delord (1987).

3. Zeta functions

In order to give a more workable definition of M (i.e. as a quickly convergent sum) we employ the usual technique of analytic continuation.

The core of the above expression for M is the function

$$J_{\mathbf{A}}(x) = \sum'_{v \in Z^3} \frac{1}{|\mathbf{A}v - x|}. \tag{3.1}$$

For x not equal to any d_k, this function may also be used to calculate (the finite value of) $V(x)$. This potential $J_{\mathbf{A}}$ arises from a charge of $+1$ at each lattice site $\mathbf{A}v$ and clearly cannot converge. However, the sum

$$\sum'_{v \in Z^3} |\mathbf{A}v - x|^{-s} \tag{3.2}$$

converges for complex numbers s whose real part is larger than 3. It turns out that this sum has an analytic continuation to all complex numbers $s \neq 3$. Thus we have a function defined by

$$J_{\mathbf{A}}(x) = \sum'_{v \in Z^3} |\mathbf{A}v - x|^{-s}|_{s=1} \tag{3.3}$$

where | denotes the analytic continuation. This function will turn out to have physical significance.

More generally, we consider multidimensional zeta functions (Glasser 1973, Zucker 1976, Terras 1985). Let s be a complex variable, $\mathbf{A}$ a non-singular real $n \times n$ matrix, and c and d be real n-vectors. Define

$$Z_{\mathbf{A}}(s) = Z_{\mathbf{A}}(s; c, d) = \sum'_{v \in Z^n} \exp(2\pi i c \cdot \mathbf{A}v)|\mathbf{A}v - d|^{-s}. \tag{3.4}$$

We adopt the convention that if the $\mathbf{A}$ is omitted from the notation then it is taken to be the identity matrix. Ultimately we shall be interested in the physical case $n = 3$ but the general theory is uniform for arbitrary n. Also we note in passing that for $n = 1$ the usual Riemann zeta function is given by $\zeta(s) = \frac{1}{2}Z(s; 0, 0)$. Finally, we should warn the reader that many treatments have a $-2s$ term where we have chosen to use $-s$.

The sum (3.4) is absolutely convergent for $\mathrm{Re}(s) > n$ as can be seen by bounding the sum by an integral over $\mathbf{R}^n$. Define an extended zeta function by

$$\Lambda_{\mathbf{A}}(s; c, d) = \Lambda_{\mathbf{A}}(s) = (\det \mathbf{A})^{1/2} \exp(-\pi i c \cdot d)\pi^{-s/2}\Gamma(\tfrac{1}{2}s)Z_{\mathbf{A}}(s; c, d). \tag{3.5}$$

It is a standard fact in analytic number theory that this function has an analytic continuation to a function that is analytic on the entire complex plane, except for simple poles at $s = 0$ and $s = n$. In addition, the 'functional equation'

$$\Lambda_{\mathbf{A}}(s; c, d) = \Lambda_{\mathbf{B}}(n - s; -d, c) \tag{3.6}$$

holds. This famous relation was discovered by Riemann in the case of the usual zeta function and was extended to more general contexts by Hecke and others. The analytic continuation and functional equation will be seen to be special cases of results given below.

The Madelung constant can be rigorously defined in terms of the function $Z_{\mathbf{A}}$. As an example of the functional equation we note that

$$M_{\mathrm{NaCl}} = Z(1; (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}), 0) = \pi^{-1}Z(2; 0, (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})) \tag{3.7}$$

where the matrix $\mathbf{A}$ is understood to be the identity matrix. Thus the constant can be cast in the form

$$M_{\mathrm{NaCl}} = 4\pi^{-1} \sum_{v \in O^3} v^{-s}|_{s=2} \tag{3.8}$$

where O^3 denotes the set of 3-tuples of odd integers. Although $s = 2$ is closer to the half-plane $\mathrm{Re}(s) > 3$ of absolute convergence than $s = 1$ this sum still cannot be used to calculate M_{NaCl}—direct summation is not convergent.

4. Jellium

Recall that the formal sum for the function $J_\mathbf{A}(x)$ was obtained by considering the Coulomb potential at a location x when each lattice point $\mathbf{A}v$ has a point charge of $+1$. It turns out that the analytic continuation

$$J_\mathbf{A}(x) = \sum_{v \in Z^3}' |\mathbf{A}v - x|^{-s}|_{s=1}$$
$$= Z_\mathbf{A}(1; 0, x) \tag{4.1}$$

corresponds to the physical situation in which, in addition to the point charges at the lattice points, all of 3-space is filled with a jelly of uniform charge density

$$\rho^- = -(\det \mathbf{A})^{-1}. \tag{4.2}$$

It is precisely this charge density which gives an overall neutral charge; this combination of point charges and uniform charge density is called jellium.

One way to proceed is to solve the Poisson equation

$$\nabla^2 J_\mathbf{A}(x) = -4\pi[\rho^+(x) + \rho^-] \tag{4.3}$$

where ρ^+ is the charge density of all the positive site charges (i.e. a triple sum of delta functions). The electrostatic solution is, for x not in the lattice $\mathbf{A}Z^3$, given by (Crandall and Delord 1987)

$$J_\mathbf{A}(x) = (\pi \det \mathbf{A})^{-1} \sum_{v \in Z^3}' \exp(2\pi i x \cdot \mathbf{B}v)|\mathbf{B}v|^{-2}. \tag{4.4}$$

The corresponding special case of the general functional equation (3.6) then shows that when x is not in the lattice $\mathbf{A}Z^3$ then (4.4) and (4.1) are identical. If x is not in the lattice $\mathbf{A}Z^3$ then the sum (4.4) is oscillatory and can be verified to converge in some appropriate sense (Crandall and Buhler 1987). If x is in the lattice $\mathbf{A}Z^3$ then (4.1) is taken to be the definition of the jellium potential. (The apparent contradiction between the non-convergence of (4.4) in the limit as x approaches 0 and the smooth behaviour of the analytic continuation (4.1) is spurious; the summation and limit operations do not commute!) The value when x is in the lattice represents the potential as seen by the charge at the lattice point x with self-potential removed. In a curious fashion the zeta-function analytic continuation machinery removes the singularity resulting from the self-potential.

Recall that the general Madelung constant (2.3) is a superposition of jellium potentials:

$$M = (\det \mathbf{A})^{-1} \sum_{j,k} q_j q_k J_\mathbf{A}(d_j - d_k) \tag{4.5}$$

while the spatial potential is a similar superposition:

$$V(x) = \sum_k q_k J_\mathbf{A}(x - d_k) \qquad x \neq \text{any } d_k. \tag{4.6}$$

This is reasonable—the Madelung constant is essentially a sum over one charge assembly of the potential energy binding that charge to the rest of the lattice. Since

each charge sees a finite superposition of m jellium constructs, the binding potential will be a superposition of jellium potentials. The introduction of the uniform charge jelly does not matter in the final analysis, since the neutrality condition on the crystal charges implies that the sum of the m signed jellies vanishes.

5. The functional equation

The goal of this section is to derive a generalised form of the functional equation that is suitable for efficient computation of the Madelung constants. We will consider the zeta functions defined above and will later consider the special cases relevant to the Madelung problem. Though much of the following treatment is reminiscent of previous work (Glasser and Zucker 1980, Nijboer and de Wette 1957, 1958, Chaba and Pathria 1975, 1976a, b), we have included details in order to motivate our generalisation of the standard analysis.

Let $\mathbf{A}$ be a non-singular $n \times n$ real matrix and let $\mathbf{B}$ be its inverse transpose. These matrices will play a dual role throughout; the functional equation relates a zeta function attached to $\mathbf{A}$ to a zeta function attached to $\mathbf{B}$ evaluated at a mirror image point. Fix real n-vectors c and d; these will also play a dual role and will sometimes be omitted from the notation. Define, as above, the zeta function of $\mathbf{A}$ to be a function of the complex variable s by

$$Z_{\mathbf{A}}(s; c, d) = Z_{\mathbf{A}}(s) = \sum_{v \in Z^n}{}' \exp(2\pi i c \cdot \mathbf{A}v)|\mathbf{A}v - d|^{-s}. \tag{5.1}$$

The prime on the summation of course just means that the vector v (if any) with $\mathbf{A}v = d$ is omitted from the summation. It is a standard fact that this converges to an analytic function for $\text{Re}(s) > n$.

The central idea of the proof of the functional equation is to realise the zeta function as a Mellin transform of a theta function and to apply Poisson summation to the theta function. The generalised theta function that we need to consider is

$$\Theta_{\mathbf{A}}(t) = \sum_{v \in Z^n}{}' \exp(2\pi i c \cdot \mathbf{A}v) f(t|\mathbf{A}v - d|) \tag{5.2}$$

where t is a positive real number and f is a smooth real-valued function that decreases exponentially so that the sum converges for all t. The usual theta function considered in this context is $f(t) = \exp(-\pi t^2)$. Later we will see that other f can be useful. The idea of allowing arbitrary 'Schwarz–Bruhat' functions f is certainly not new; a very general formulation in a number theoretic context is given by Tate (1968).

The last function that we shall need is the partial Mellin transform of f

$$F(s, x) = \int_x^\infty f(t) t^{s-1} \, dt \tag{5.3}$$

where x is a non-negative real number. If x is positive then the exponential decrease of f guarantees that F exists for all complex s and that it is exponentially decreasing as a function of x; if $x = 0$ then the integral converges at least for $\text{Re}(s) > 0$.

By interchanging integration and summation one easily shows that the Mellin transform of the theta function is essentially the zeta function:

$$\int_0^\infty \Theta_{\mathbf{A}}(t) t^{s-1} \, dt = \sum_{v \in Z^n}{}' \exp(2\pi i c \cdot \mathbf{A}v) \int_0^\infty f(t|\mathbf{A}v - d|) t^{s-1} \, dt$$

$$= \sum_{v \in Z^n}{}' \exp(2\pi i c \cdot \mathbf{A}v)|\mathbf{A}v - d|^{-s} \int_0^\infty f(t) t^{s-1} \, dt = F(s, 0) Z_{\mathbf{A}}(s). \tag{5.4}$$

Our general strategy is to choose an arbitrary positive number λ and to write the integral on the left as

$$\int_0^\lambda \Theta_{\mathbf{A}}(t)t^{s-1}\,\mathrm{d}t + \int_\lambda^\infty \Theta_{\mathbf{A}}(t)t^{s-1}\,\mathrm{d}t. \tag{5.5}$$

This fundamental idea is due to Riemann. The second integral is straightforward; interchanging the summation and integration as above gives

$$\int_\lambda^\infty \Theta_{\mathbf{A}}(t)t^{s-1}\,\mathrm{d}t = \sum_{v\in Z^n}{}' \exp(2\pi i c\cdot \mathbf{A}v)|\mathbf{A}v - d|^{-s}F(s,\lambda|\mathbf{A}v - d|). \tag{5.6}$$

This is identical to the original summation (5.1) except that an exponential decreasing 'convergence factor' has been introduced.

The next step is to derive a similar expression for the first integral in (5.5). The general idea is to change variables in the integral by replacing t by t^{-1} and to use Poisson summation in the summation defining $\Theta_{\mathbf{A}}(t)$.

In the following let δ_1 be 1 if the vector d lies in the lattice $\mathbf{A}Z^n$ and 0 otherwise. In order to apply a Poisson summation it is necessary to have an unprimed sum

$$\Theta_{\mathbf{A}}(t) = -f(0)\exp(2\pi i c\cdot d)\delta_1 + \sum_{v\in Z^n}\exp(2\pi i c\cdot \mathbf{A}v)f(t|\mathbf{A}v - d|). \tag{5.7}$$

Applying Poisson summation and writing the Fourier coefficients out explicitly gives

$$\Theta_{\mathbf{A}}(t) = -f(0)\exp(2\pi i c\cdot d)\delta_1 + \det\mathbf{B}\exp(2\pi i c\cdot d)t^{-n}\sum_{w\in Z^n}\exp(-2\pi i d\cdot \mathbf{B}w)$$

$$\times \int_{R^n}\exp[2\pi i t^{-1}u\cdot(-\mathbf{B}w + c)]f(|u|)\,\mathrm{d}^n u. \tag{5.8}$$

To simplify the notation define a function g by

$$g(|u|) = \int_{R^n} f(|v|)\exp(2\pi i v\cdot u)\,\mathrm{d}v. \tag{5.9}$$

Since the integral on the right only depends on $|u|$ this is valid; by standard arguments g is in fact a Bessel transform of f. The expression (5.8) can now be rewritten

$$\Theta_{\mathbf{A}}(t) = -f(0)\exp(2\pi i c\cdot d)\delta_1 + \det\mathbf{B}\exp(2\pi i c\cdot d)t^{-n}$$

$$\times \sum_{w\in Z^n}\exp(-2\pi i\mathbf{B}w\cdot d)g(t^{-1}|\mathbf{B}w - c|). \tag{5.10}$$

In order to integrate this we need summands that decrease exponentially in t; to ensure this the possibility $\mathbf{B}w = c$ has to be handled separately:

$$\Theta_{\mathbf{A}}(t) = -f(0)\exp(2\pi i c\cdot d)\delta_1 + g(0)t^{-n}\det\mathbf{B}\delta_2\exp(2\pi i c\cdot d)$$

$$+ \det\mathbf{B}\exp(2\pi i c\cdot d)t^{-n}\sum_{w\in Z^n}{}'\exp(-2\pi i\mathbf{B}w\cdot d)g(t^{-1}|\mathbf{B}w - c|) \tag{5.11}$$

where δ_2 is 1 if the vector c is in $\mathbf{B}Z^n$ and 0 otherwise.

Now we can calculate the first integral in (5.5) by changing variables and applying (5.11):

$$\int_0^\lambda \Theta_{\mathbf{A}}(t)t^{s-1}\,\mathrm{d}t = \int_{\lambda^{-1}}^\infty \Theta_{\mathbf{A}}(t^{-1})t^{-s-1}\,\mathrm{d}t$$

$$= -f(0)\exp(\pi i c\cdot d)\delta_1\frac{\lambda^s}{s} + g(0)\det\mathbf{B}\delta_2\frac{\lambda^{s-n}}{s-n}\exp(2\pi i c\cdot d)$$

$$+ \det\mathbf{B}\exp(2\pi i c\cdot d)\sum_{w\in Z^n}{}'\exp(-2\pi i\mathbf{B}w\cdot d)\int_{\lambda^{-1}}^\infty g(t|\mathbf{B}w - c|)t^{n-s-1}\,\mathrm{d}t. \tag{5.12}$$

Note that the integrals in the polar terms were explicitly evaluated using $\int_a^\infty t^{-s-1}\,dt = a^{-s}/s$ which is valid for $\mathrm{Re}(s) > 0$; it follows that the preceding formula is valid for all s with $\mathrm{Re}(s) > n$.

Now let G be the partial Mellin transform of g. A simple change of variables in (5.12) together with (5.4)–(5.6) gives us our central formula

$$F(s, 0)Z_\mathbf{A}(s) = -f(0) \exp(2\pi i\mathbf{c} \cdot \mathbf{d})\delta_1 \frac{\lambda^s}{s} - g(0) \det \mathbf{B}\delta_2 \frac{\lambda^{s-n}}{n-s} \exp(2\pi i\mathbf{c} \cdot \mathbf{d})$$

$$+ \sum_{v \in Z''}{}' \exp(2\pi i\mathbf{c} \cdot \mathbf{A}v)|\mathbf{A}v - \mathbf{d}|^{-s} F(s, \lambda|\mathbf{A}v - \mathbf{d}|)$$

$$+ \det \mathbf{B} \exp(2\pi i\mathbf{c} \cdot \mathbf{d}) \sum_{w \in Z''}{}' \exp(-2\pi i\mathbf{d} \cdot \mathbf{B}w)|\mathbf{B}w - \mathbf{c}|^{-(n-s)}$$

$$\times G(n - s, \lambda^{-1}|\mathbf{B}w - \mathbf{c}|). \tag{5.13}$$

Note that although the left-hand side has only been defined for $\mathrm{Re}(s) > n$ the right-hand side is an analytic function for *all* complex s except $s = 0$ and $s = n$. This provides the analytic continuation of $Z_\mathbf{A}$ promised earlier.

Observe that there is a certain duality between the two sums. The first is formed from f and $\mathbf{A}$ and the second is formed from g and $\mathbf{B}$ after also interchanging $\mathbf{c}$ and $-\mathbf{d}$, s and $n - s$, and λ and λ^{-1}. To exploit the duality further let us take the special case in which $\lambda = 1$, $f(x) = \exp(-\pi x^2)$. An easy calculation shows that $F(s, 0) = \pi^{-s/2}\Gamma(s/2)$ and that in general F is an incomplete gamma function. A somewhat harder calculation shows that in this case $g(x) = f(x)$. Now multiply both sides of (5.13) by $(\det \mathbf{A})^{1/2} \exp(-\pi i\mathbf{c} \cdot \mathbf{d})$. The left-hand side is then

$$\Lambda_\mathbf{A}(s; \mathbf{c}, \mathbf{d}) = (\det \mathbf{A})^{1/2} \exp(-\pi i\mathbf{c} \cdot \mathbf{d})\pi^{-s/2}\Gamma(s/2)Z_\mathbf{A}(s; \mathbf{c}, \mathbf{d}). \tag{5.14}$$

Upon examination one finds that the resulting right-hand side is

$$\Lambda_\mathbf{B}(n - s; -\mathbf{d}, \mathbf{c}). \tag{5.15}$$

This establishes the functional equation (3.6) stated above. From the simple pole structure of (5.13) when $s = 0$, one may infer the exact value $Z_\mathbf{A}(0; \mathbf{c}, \mathbf{d}) = -\delta_1$. For the Riemann zeta function in particular, this gives the value $\zeta(0) = -\frac{1}{2}$.

The Gaussian $f(x) = \exp(-\pi x^2)$ is the only function that we know for which the formula (5.13) can be made reasonably explicit for arbitrary n and s. In the next section we will see that for $n = 3$ and $s = 1$ there are other useful f to be considered.

6. Explicit formulae for the Madelung constants and spatial potentials

Now we return to the jellium potential for the physical case $s = 1$ in $n = 3$ dimensions

$$J_\mathbf{A}(x) = Z_\mathbf{A}(1; 0, x). \tag{6.1}$$

In formula (5.13) take $n = 3$, $\mathbf{c} = 0$, $\mathbf{d} = x$, and $s = 1$. Since s is fixed we shall write $F(1, x) = F(x)$ and $G(2, x) = G(x)$ for the sake of simplicity. The result is

$$F(0)J_\mathbf{A}(x) = -\lambda f(0)\delta_1 - \tfrac{1}{2}\lambda^{-2} \det \mathbf{B}g(0) + \sum_{v \in Z^3}{}' \frac{F(\lambda|\mathbf{A}v - \mathbf{d}|)}{|\mathbf{A}v - \mathbf{d}|}$$

$$+ \det \mathbf{B} \sum_{w \in Z'}{}' \frac{\exp(-2\pi i\mathbf{d} \cdot \mathbf{B}w)G(\lambda^{-1}|\mathbf{B}w|)}{|\mathbf{B}w|} \tag{6.2}$$

where the function F is

$$F(x) = \int_x^\infty f(t)\, dt. \tag{6.3}$$

The calculation of G is more involved; convert the integral in the definition of g to spherical coordinates and use the Riemann–Lebesgue lemma to evaluate the integral

$$G(x) = \lim_{A \to \infty} \int_x^A g(t)\, dt. \tag{6.4}$$

The result is that G is essentially the cosine transform of f:

$$G(x) = \pi^{-1} \int_0^\infty f(r) \cos(2\pi rx)\, dr. \tag{6.5}$$

If f is chosen to be of the Gaussian form $\exp(-cx^2)$ then it can be checked that F is an incomplete gamma function and that G is also Gaussian. We would like to find f such that both F and G can be evaluated explicitly in terms of elementary functions. There seems to be a number of such f. Two examples are

$$f(x) = \text{sech}(x) \qquad f(x) = \text{sech}^2(x). \tag{6.6}$$

The resulting functions decay exponentially and give expansions for the jellium potential, and hence arbitrary Madelung constants, entirely in terms of elementary functions.

The second choice of f seems to be slightly better in practical terms. Simple calculations then show that

$$F(x) = 1 - \tanh(x) \tag{6.7}$$

and

$$G(x) = \pi x \, \text{cosech}(\pi^2 x). \tag{6.8}$$

Now an explicit version of the jellium representation (1.2) may be written as

$$J_\mathbf{A}(\boldsymbol{d}) = -\lambda \delta_1 - \frac{\pi^3}{6\lambda^2} \det \mathbf{B} + \sum_{\boldsymbol{v} \in Z^3}{}' \frac{1 - \tanh(\lambda |\mathbf{A}\boldsymbol{v} - \boldsymbol{d}|)}{|\mathbf{A}\boldsymbol{v} - \boldsymbol{d}|}$$
$$+ \frac{\pi}{\lambda} \det \mathbf{B} \sum_{\boldsymbol{w} \in Z^3}{}' \frac{\exp(-2\pi i \boldsymbol{d} \cdot \mathbf{B}\boldsymbol{w}) \, \text{cosech}(\lambda^{-1} |\mathbf{B}\boldsymbol{w}| \pi^2)}{|\mathbf{B}\boldsymbol{w}|}. \tag{6.9}$$

One may use this expansion together with (4.5) and (4.6) in practical computations. When using this general prescription for Madelung constants or spatial potentials, one may simplify by exploiting certain symmetries. For example, the second polar term amounts to a correction for the negative jelly, independent of any $\boldsymbol{d}$ or q values. Either sum (4.5) or (4.6) will, as indicated previously, receive no net contribution from the term. Similarly, the first polar term vanishes for any computation of the spatial potential, since the argument of J is to be non-zero in such cases.

This unified computational scheme requires only the crystal parameters as input. Moreover the freedom to vary the parameter λ has been found to be very useful; if a program generates the same numerical value for two different values of λ this is strong evidence that it is working correctly. The parameter can be interpreted as an inverse length scale, and as an empirical matter the scheme (6.9) converges most quickly when

$$\lambda \simeq (\det \mathbf{A})^{-1/3}. \tag{6.10}$$

Both limits $\lambda \to 0$ and $\lambda \to \infty$ are interesting in (6.9). For small λ the tanh sum blows up (being, in the limit, the formal defining sum for J_A with self-potential intact) and the cosech sum becomes negligible. However, the divergence is cancelled by the second polar term. Similarly, for large λ the tanh sum is negligible and the cosech sum blows up; the resulting singularity is cancelled by the first polar term. Such behaviour may be verified by approximating the sums with integrals in the appropriate limits (Gradshteyn and Rhyzik 1965).

We also note that this uniform method of calculating Madelung constants and spatial potentials does not suffer from the complexity of the double sum cosech expansions in Crandall and Delord (1987) which, for complicated crystals, can involve extensive combinatorics and matrix algebra. The double sums converge more quickly but (6.9) is easier to program.

Note also that the scaling behaviour of the jellium potential is correct. The relation (6.9) is invariant under replacement of $\mathbf{A}$ by $k\mathbf{A}$, d by kd, λ by $k^{-1}\lambda$, and J_A by $k^{-1}J_A$. But this is reasonable: the Coulomb energy must scale as k^{-1} if all distances are scaled by k.

Observe that (6.9) explains how analytic continuation removes singularities due to self-potential. Indeed, if we consider (6.9) in the limit as $d \to 0$ then there is a leading term $-\lambda + |d|^{-1}$ arising from the tanh sum. But when $d = 0$ the tanh sum avoids the Coulomb singularity, while the polar term $-\lambda\delta_1$ appears. This verifies what one expects of the jellium potential in the vicinity of, but not at, the origin:

$$J_A(d) = \pi^{-1} \det \mathbf{B} \sum_{v \in Z^3}{}' \frac{\exp(2\pi i d \cdot \mathbf{B}v)}{|\mathbf{B}v|^2}$$

$$\sim |d|^{-1} + \pi^{-1} \det \mathbf{B} \sum_{v \in Z^3}{}' |\mathbf{B}v|^{-s}\big|_{s=2} = |d|^{-1} + J_A(0). \tag{6.11}$$

These manipulations show explicitly that, whereas $J_A(d)$, $d \neq 0$ is the jellium potential with origin charge included, $J_A(0)$ is the (finite) Madelung constant for the jellium construct.

When the crystal has special symmetries, one may further reduce sums of J_A terms in the representation (4.5). For NaCl one finds that for any suitable function F having $F(0) = 1$, the three-dimensional result (6.2) yields

$$M_{\text{NaCl}} = \lambda F'(0) + \sum_{m \in Z^3}{}' \frac{(-1)^{\sum m_i}}{|m|} F(m\lambda) + 4 \sum_{v \in O^3} \frac{G(|v|/2\lambda)}{|v|^2} \tag{6.12}$$

of which (1.3) is the special case arising from the choice (6.7). The arbitrary nature of F is tantalising—one is tempted to find better examples of F, G pairs to approach the celebrated problem of closed form evaluation of M.

It is even possible to choose discontinuous F functions if singular terms are properly handled. From the choice $F(x) = 1$ on $x \in [0, \varepsilon)$ and $F(x) = 0$ on $x \in [\varepsilon, \infty)$ we obtain

$$M_{\text{NaCl}} = \frac{4}{\pi} \sum_{v \in O^3} \frac{\cos(\pi\varepsilon|v|)}{|v|^2} \qquad 0 < \varepsilon < 1. \tag{6.13}$$

This sum, whose small ε limit can be interpreted as (3.8), can be used to analyse the convergence of spherical lattice sums (Crandall and Buhler 1987). Such ε-independent expansions also give rise to the non-alternating 'sine' series of Crandall and Delord (1987).

7. Dimensional reduction and cosech sums

Our general prescription embodied in (4.5), (4.6) and (6.9) still involves triple summations. Various authors have shown how Madelung sums for cubic crystals can be reduced to double sums. For instance, the formulae of Hautot (1975) for NaCl, ZnS and CsCl crystals involve only the cosech function. When $\mathbf{A}$ is the identity matrix, one may use a key identity, valid for $|x| < 1$,

$$\sum_{m \in Z}{}' \exp(2\pi imx)/(m^2 + a^2) = (\pi/a) \cosh(\pi a(1 - 2|x|)) \operatorname{cosech} \pi a \quad (7.1)$$

applied to a single integer summand, to reduce an n-dimensional zeta function $Z(2; c, 0)$ to an $(n-1)$-fold sum. More complex identities required for general matrices $\mathbf{A}$ are given by Crandall and Delord (1987) and may be used to reduce arbitrary three-dimensional Madelung sums to double form. In the present section we concentrate on the simple cubic cases to indicate how various Madelung sums may be reduced by one dimension.

Cubic Madelung constants, as in (3.7), are characterised by $\mathbf{A} = 1$ and $c_i = 0$ or $\frac{1}{2}$. The constant will be $Z(1; c, 0)$ which is proportional to $Z(2; 0, c)$. Neither of these is quite the same as $Z(2; c, 0)$ which can be reduced through use of (7.1). We shall derive some additional zeta function relations connecting these various Z sums. Heretofore let c or d denote a *binary* vector consisting of zeros and ones. Then the extra relations may be used to reduce any of the following n-fold sums to $(n-1)$-fold cosech sums:

$$
\begin{aligned}
&Z(n-2; 0, d/2) \\[4pt]
&Z(2; c/2, 0) \\[4pt]
&Z(n-2; c/2, 0) \\[4pt]
&Z(2; 0, d/2).
\end{aligned}
\qquad (7.2)
$$

The first two forms will reduce directly by virtue of (7.1) and the functional relation, with the last two reducible via the new relations. The treatment is a generalisation of the work of Zucker (1976). As examples of the reduction we shall derive Hautot's NaCl formula and various cosech triple sum relations.

Suppose that d is a binary vector. Then

$$
\begin{aligned}
Z(s; 0, d/2) &= \sum_{v \in Z^n}{}' \frac{1}{|v + d/2|^s} = 2^s \sum_{v \in Z^n}{}' \frac{1}{|2v + d|^s} \\[6pt]
&= 2^s \sum_{w \in Z^n}{}' \frac{a_w}{|w|^s}
\end{aligned}
\qquad (7.3)
$$

where the coefficient a_w is 0 or 1 according as to whether the vector $w - d$ has all even components. In fact

$$a_w = \frac{1}{2^n} \sum_c \exp[\pi i c \cdot (w - d)] \qquad (7.4)$$

where the summation is over all 2^n binary vectors c. Using this (7.3) can be rewritten, after a little manipulation, in the form

$$Z(s; 0, d/2) = 2^{s-n} \sum_c \exp(-\pi i c \cdot d) Z(s; c/2, 0). \qquad (7.5)$$

This sum can be further reduced by using the $d = 0$ case to obtain a formula for $Z(s; 0, 0)$ that can be substituted in the right-hand side of (7.5). The resulting formula is

$$Z(s; 0, d/2) = 2^{s-n} \sum_{c \neq 0} \left(\exp(-\pi ic \cdot d) + \frac{1}{2^{n-s} - 1} \right) Z(s; c/2, 0). \qquad (7.6)$$

It is evident that the last two forms of (7.2) may now be cast into $(n-1)$-fold cosech forms. Noting that $M_{\mathrm{NaCl}} = \pi^{-1} Z(2; 0, (1, 1, 1)/2)$ with $n = 3$, we obtain from (7.6) Zucker's formula

$$M = \frac{3}{\pi} \sum_{(u,v,w) \in Z^3}' \frac{(-1)^{v+w}}{u^2 + v^2 + w^2}. \qquad (7.7)$$

Finally we apply (7.1) to the w summation to get Hautot's formula, essentially

$$M = -\frac{\pi}{2} + 3 \sum_{(u,v) \in Z^2}' \frac{(-1)^v \operatorname{cosech} \pi r}{r} \qquad (7.8)$$

where $r = (u^2 + v^2)^{1/2}$.

As a second example of dimensional reduction, we may consider $n = 4$ dimensions and define the sum U_k, $0 \leq k \leq 4$, to be the zeta function $Z(2; c/2, 0)$ where the binary vector c has exactly k ones. Then the cosech formula (7.1) may be applied directly, for example,

$$U_1 = Z(2; (0001)/2, 0) = \sum_{(a,b,c,d) \in Z^4}' \frac{(-1)^a}{a^2 + b^2 + c^2 + d^2}$$

$$= -\tfrac{1}{6} \pi^2 + \pi \sum_{u \in Z^3}' \frac{\operatorname{cosech} \pi |u|}{|u|} \qquad (7.9)$$

with similar expressions arising for the other U functions. On the other hand, one may apply the reduction formula (7.6) with $s = 2$, $n = 4$ to obtain relations

$$U_0 = \tfrac{4}{3} U_1 + 2 U_2 + \tfrac{4}{3} U_3 + \tfrac{1}{3} U_4$$
$$3 U_2 = U_1 + U_3 + U_4. \qquad (7.10)$$

The second of these yields a curious and apparently non-trivial identity

$$\sum_{(u,v,w) \in Z^3}' [1 - 3(-1)^u + (-1)^{u+v} + (-1)^{u+v+w}] \frac{\operatorname{cosech} \pi r}{r} = 0 \qquad (7.11)$$

where $r^2 = u^2 + v^2 + w^2$. It turns out that all five U sums can be evaluated exactly, using previous results together with the relations (7.10). Zucker (1974, 1975, 1984) established that

$$U_0 = -8 \ln 2$$
$$U_2 = -2 \ln 2$$
$$U_4 = -4 \ln 2 \qquad (7.12)$$
$$U_1 = \pi/2 - \ln 2.$$

In fact the last three of these can be used with the relations to obtain U_0 and U_3, the latter taking the value

$$U_3 = -\pi/2 - \ln 2. \qquad (7.13)$$

One may now derive directly an important triple cosech identity of Zucker (1984). Define the general cosech sum

$$S(x) = \sum_{u \in O^3}' \frac{\text{cosech } \pi x |u|}{|u|}. \tag{7.14}$$

Then manipulation of the odd integer indices results in the evaluation

$$S(1) = (U_1 - 3U_2 + 3U_3 - U_4)/8\pi = -\tfrac{1}{8} + (3 \ln 2)/4\pi. \tag{7.15}$$

This evaluation is important in the present context because it removes one of the summations in the NaCl Madelung expression (1.3) if we set the free parameter $\lambda = \pi/2$.

One might look longingly at the cosech sum $S(x)$ and observe from the elementary function expansion (1.3) that

$$M_{\text{NaCl}} = \lim_{\lambda \to \infty} (-\lambda + (2\pi/\lambda)S(\pi/2\lambda)). \tag{7.16}$$

Such an expression is perhaps a starting point for sharp representations of M_{NaCl}. As $S(x)$ is evaluated for smaller x, one has a more rapidly converging tanh sum in (1.3). It is possible to do better than (7.15); for example, Zucker (1984) has derived

$$S(\tfrac{1}{2}) = 1/\sqrt{2} \tag{7.17}$$

on the basis of Jacobi theta function analysis. We have been able to carry the analysis a little further, using the theta function identities of Glasser and Zucker (1980) to obtain closed-form evaluations

$$S(1/\sqrt{8}) = \sqrt{8} \sum_{m=0}^{\infty} (-1)^m \text{ cosech}[\pi(m+\tfrac{1}{2})/\sqrt{2}] = \sqrt{2}\theta_2^2(x) \tag{7.18}$$

$$S(\tfrac{1}{4}) = \sqrt{32} \sum_{m=0}^{\infty} L_m \text{ cosech}[\pi(m+\tfrac{1}{2})/\sqrt{2}] = \sqrt{32}\theta_2(x^2)\theta_3(x) \tag{7.19}$$

where $x = \exp(-\pi/\sqrt{2})$ and L_m is the sequence $(1, 1, -1, -1, \ldots)$ arising in the definition of the θ_6' function. Furthermore, these two S evaluations can be cast in the form of elliptic integrals, expressible in terms of such oddities as $\Gamma(\tfrac{1}{4})$ (Zucker 1984). The approximation to M_{NaCl} arising from (7.19) thus has a triple tanh sum component of magnitude of the order of 4×10^{-5}.

8. Open questions

Presumably it is possible to use zeta function relations such as (7.6), but for more general **A** matrices and **c, d** vectors, in order to obtain general two-dimensional sums similar to those of Crandall and Delord (1987). The relevant formulae will be very intricate and the difficulties to be overcome in developing a unified treatment of dimensional reduction remain unclear.

As for the triple elementary function sum (6.9), there are natural questions concerning the rate of convergence. The basic formula (5.13) becomes the classical Ewald expansion if f is chosen to be a Gaussian $f(x) = \exp(-\pi x^2)$. In this case both F and G decay 'doubly exponentially', i.e. as $\exp(-Cx^2)$, with the constant C depending on the free parameter.

Our elementary function expansions such as (1.3) decay only as $\exp(-Cx)$. This leads us to ask whether there is a function f giving rise to *elementary* F and G but with more rapid decay. For ease of programming it would be useful to find a pair F, G such that

$$F(x) = P(x) * G(x) \tag{8.1}$$

where P is some polynomial. If this is possible, then one would expect optimal or near-optimal decay. Since G is essentially a cosine transform of F', typical 'uncertainty principle' arguments may well apply, and we expect that rapid decay in F will generally give rise to rapid decay in the transform G.

Acknowledgments

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