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The potential within a crystal lattice

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Abstract. The generalised Madelung problem, that of finding the spatial electric potential within a crystal lattice, is often approached via analytic function theory. But new results can be achieved through careful application of standard theorems from classical electrostatics. In this way we show that the celebrated Madelung constant for the NaCl crystal can be rigorously bounded through symmetry arguments devoid of summations. We derive new expansions for Madelung constants of general crystals: an absolutely convergent 'sine' series which has the advantage of non-alternating summands, and an 'exponential' series which agrees in the simple cubic cases with the 'cosech' expansions of previous authors. Finally, we show how the NaCl Coulomb singularity may be removed to yield a regular power series expansion for the potential well at the origin.

1. Introduction

The electrostatic potential at a vector \mathbf{x} within a periodic point structured crystal is given formally by a sum over Coulomb terms

$$V(\mathbf{x}) = \sum_{\mathbf{p}} q(\mathbf{p}) |\mathbf{p} - \mathbf{x}|^{-1} \quad (1.1)$$

where \mathbf{p} generally denotes the location of point charge $q(\mathbf{p})$. We shall call this simply the *crystal potential*. A closely related construct describes the potential well in which a particular charge resides. This *Madelung potential*, indexed by some point charge location \mathbf{r} , is given formally by a sum in which the self-potential of the reference charge is removed:

$$V_r(\mathbf{x}) = V(\mathbf{x}) - q(\mathbf{r}) |\mathbf{r} - \mathbf{x}|^{-1}. \quad (1.2)$$

The electrostatic energy binding a particular site to the rest of the crystal is thus $q(\mathbf{r}) V_r(\mathbf{r})$. This potential can be used to determine the electrostatic potential energy of the crystal. When the crystal is structured generally as a periodic lattice with identical charge assemblies at each lattice site, a *Madelung constant* can be determined by summing and normalising the potential energies associated with a single cell:

$$M = v^{-1} \sum_{\mathbf{r}} q(\mathbf{r}) V_r(\mathbf{r}) \quad (1.3)$$

where v is the volume of a lattice cell and \mathbf{r} runs over the charge sites associated with one cell. This definition of the Madelung constant is consistent with traditional dimensionless ones (Sherman 1932), provided some lattice constant, such as unit nearest-neighbour separation, is enforced. We discuss later the relation of M to total cell energy and other crystal energy measures.

In the case of the simple cubic crystal NaCl we adopt the common convention that nearest-neighbour separation is unity. For this and other highly symmetric crystals, M turns out to be the potential energy in which a unit origin charge resides. The Madelung constant in this case is just $V_0(0)$, and can be written out as a Coulomb sum over integer triplets, with the origin taken as reference site:

$$M_{\text{NaCl}} = \sum_{m,n,p \neq 0} (-1)^{m+n+p} (m^2 + n^2 + p^2)^{-1/2}. \quad (1.4)$$

The difficulty in performing this and similar sums is well known, having occupied various researchers for more than seventy years (Madelung 1918, Ewald 1921, Born and Goppert-Mayer 1933, Born and Huang 1954, Glasser and Zucker 1980). Numerical values can be computed from transformations of (1.4) having exponentially decaying summands involving only elementary functions (Hautot 1975, Zucker 1976). General crystal sums suitable for computer work will appear later in this treatment. We compute the NaCl case as

$$M_{\text{NaCl}} = -1.747\ 564\ 594\ 633\ 182\ 190\ 636 \\ 212\ 035\ 544\ 397\ 403\ 485\ 161\ 436\ 624\ 741\ 758\ 152\ 672 \dots \quad (1.5)$$

presumed correct to 50, and possibly 60, places.

A simple thought experiment using fundamental electrostatic principles can relegate the NaCl Madelung problem to the confines of a finite space. We shall find that a bound on the Madelung constant M for this problem

$$-2 < M < -(4/3)^{1/2} \quad (1.6)$$

can be obtained 'in one's head', without recourse to infinite summations. Using the principles in conjunction with a previous result for the NaCl crystal potential, namely (Forrester and Glasser 1982)

$$V(\frac{1}{6}, \frac{1}{6}, \frac{1}{6}) = \sqrt{3} \quad (1.7)$$

one can obtain, again with virtually no calculation, a fair estimate

$$M \sim -\sqrt{3} \quad (1.8)$$

which is in error by only one per cent of the value (1.5).

Using such principles with proper precision we can deduce some striking exact relations. We shall show that for any t in the interval $(0, 1)$, the Madelung constant M for the NaCl crystal can be obtained from a non-alternating absolutely convergent series

$$8\pi^{-3} \sum_{r \in \mathcal{O}^3} \sin^2(\pi r t / 2) / r^4 = t + M t^2 / 2 \quad (1.9)$$

where the sum is taken over all distances r from the origin to odd integer triplets. We still do not know just how much one may discover about M by exploiting the free parameter t . But certainly this kind of series, with its lack of alternating signs, can be used to provide rigorous bounds tighter than (1.6).

We eventually arrive at efficient expansions for the various electrostatic quantities. These expansions are reminiscent of previous work (Zucker 1975, Glasser and Zucker 1980) on cubic crystals but can handle general crystals. In particular we derive the spatial behaviour of the potential well $V_0(x)$ in which the (positive) origin charge of NaCl sits. We provide formal expressions for the coefficients of the axial expansion

$$V_0(x, 0, 0) = M + ax^4 + bx^6 + \dots \quad (1.10)$$

It is interesting that there is no quadratic term, as will follow again from electrostatic principles, so that the origin charge of NaCl sees at least a quartic, not a harmonic electrostatic well.

We have used such expansions in computer programs which will compute general crystal potentials and Madelung constants. Besides generating values such as (1.5), we have confirmed previous work (Hajj 1972) and discovered, by numerical accident, some provable theorems concerning exact potential values. For the CsCl crystal, an exact value similar to the previous (1.7) for NaCl can be given at a particular point in space:

$$V_{\text{CsCl}}(\frac{1}{4}, 0, 0) = 2. \quad (1.11)$$

We were given pause upon receiving the computed value 1.999 999 999 . . . , and indeed the exact value can be proved. There is also a similar result for a crystal consisting of parallel planes of like charge, i.e. the charge at (m, n, p) is given by $(-1)^m$. For this case it turns out that

$$V(0, 0, \frac{1}{2}) = 2. \quad (1.12)$$

A method for establishing such particular potential values depends upon previous applications of Jacobi theta functions, as discussed in § 7.

2. Crystal nomenclature

Our general crystal is taken to be built upon a periodic Bravais site lattice generated by replicated non-coplanar basis vectors $\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$ such that the position vector for a lattice site (not necessarily a charge site) has three components

$$\mathbf{p}_i = m_1 \mathbf{A}_{1i} + m_2 \mathbf{A}_{2i} + m_3 \mathbf{A}_{3i} \quad m_j \in \mathbb{Z}. \quad (2.1)$$

Denote by \mathbf{A} the matrix collection of all nine basis components. These components can be thought of either as spatial lengths, or dimensionless multiples of some lattice constant. Then for three columns \mathbf{m} of integers we can write the general site column vector as

$$\mathbf{p} = \mathbf{A}\mathbf{m} \quad \mathbf{m} \in \mathbb{Z}^3. \quad (2.2)$$

It should be noted that the volume of one Bravais cell is given by the determinant, $\det \mathbf{A}$. It will be convenient to define the reciprocal crystal matrix whose basis components are essentially those of the reciprocal lattice:

$$\mathbf{B} = \mathbf{A}^{-\text{T}} \quad (2.3)$$

where $-\text{T}$ refers to inverse transpose. Having defined the lattice, it remains to place at every site an assembly of point charges. We shall assume a neutral crystal, where at each site \mathbf{p} we assemble n charges q_j at positions determined by *distinct* fixed offset vectors \mathbf{d}_j :

$$\mathbf{p} + \mathbf{d}_j \quad j = 0, \dots, n-1 \quad (2.4)$$

where the neutrality condition is

$$\sum q_j = 0. \quad (2.5)$$

The general crystal is thus defined by the quantities

$$\mathbf{A}, n, \{ \mathbf{d}_j : j = 0, \dots, n-1 \}, \{ q_j : j = 0, \dots, n-1 \} \quad (2.6)$$

together with the constraint (2.5) and the distinctness of the d_j . Examples of this nomenclature for common crystal structures are

$$\text{CsCl: } n = 2, \mathbf{d}_0 = 0, \mathbf{d}_1 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right), q_0 = 1, q_1 = -1 \quad (2.7)$$

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

$$\text{ZnS: } n = 2, \mathbf{d}_0 = 0, \mathbf{d}_1 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right), q_0 = 1, q_1 = -1$$

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

$$\text{NaCl: } n = 2, \mathbf{d}_0 = 0, \mathbf{d}_1 = (1, 1, 1), q_0 = 1, q_1 = -1$$

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

Equivalent form:

$$n = 8, \{d_j: n = 0, \dots, 7\} = \text{ordered set of eight binary triplets}$$

$$\{q_j: n = 0, \dots, 7\} = \{+1, -1, -1, +1, -1, +1, +1, -1\}$$

$$\mathbf{A} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

The second form for NaCl may seem unwieldy, but the simplicity of the \mathbf{A} matrix represents a certain advantage in the analysis.

The extension of the ideas herein to handle charge distributions, such as electron orbitals combined with point nuclei, is straightforward. Though our treatment does not go beyond the generality of the point-charge crystal, we shall indicate in what follows those junctures where charge distributions would be appropriate to introduce.

We shall often perform summations where some singularity must be avoided. A symbol such as

$$\sum'_{m \in S} \quad (2.8)$$

means to sum over all vectors m in the set S except to allow only finite summands (because of the ' superscript). Note that ' does *not* mean simply to avoid the zero element of S . A simple example of this singularity removal is as follows. Let

$$g(u) = \sum'_{m \in \mathbb{Z}} (m - u)^{-2} \quad (2.9)$$

be defined for real u , and denote by $f(u)$ the same sum but without the ' superscript. Now almost everywhere $f = g$, but whereas $f(u)$ diverges for any integer value of u , the sum for g becomes just $\pi^2/3$ at such u , because the diverging term 0^{-2} is to be removed.

At several points in our analysis we shall use the Poisson transformation method, which has enjoyed wide use in lattice summation problems (Hautot 1975, Zucker 1976). For suitable complex valued functions f defined on R^3 , the transformation is

$$\sum_{\mathbf{m} \in Z^3} f(\mathbf{m}) = \sum_{\mathbf{u} \in Z^3} \int f(\mathbf{m}) \exp(2\pi i \mathbf{m} \cdot \mathbf{u}) d^3 \mathbf{m}. \tag{2.10}$$

The integral is performed over a continuous 3-vector \mathbf{m} even though the left-hand sum is over integer triplets. Here and elsewhere, a form such as $\mathbf{m} \cdot \mathbf{u}$ is interpreted as a dot product.

3. Electrostatics

The above nomenclature will now be used to establish various electrostatic quantities. The *crystal potential* at any point \mathbf{x} is obtained by summing Coulomb terms over each charge in the crystal, knowing that the vector from \mathbf{x} to the j th charge at site (m_1, m_2, m_3) is $\mathbf{A}\mathbf{m} + \mathbf{d}_j - \mathbf{x}$:

$$V(\mathbf{x}) = \sum_{\mathbf{m} \in Z^3} \sum_{j=0}^{n-1} q_j |\mathbf{A}\mathbf{m} + \mathbf{d}_j - \mathbf{x}|^{-1}. \tag{3.1}$$

The question of convergence naturally arises, since for no crystal is the sum absolutely convergent. We do not handle such questions here, referring the reader to other work on convergence theorems over polyhedral domains (Borwein *et al* 1985) and Coulombic convergence corrections for spherical domains (Crandall and Buhler 1987b). At this point we indicate that if the charges were more general than mere points, the relevant spatial integrals must be used in place of the q_j . This crystal potential V diverges naturally as the position \mathbf{x} approaches any charge location $\mathbf{r} = \mathbf{A}\mathbf{m} + \mathbf{d}_j$, with behaviour

$$V(\mathbf{x}) \sim q_j |\mathbf{r} - \mathbf{x}|^{-1}. \tag{3.2}$$

It is now evident that the Madelung potential (1.2) at any site is just the sum (3.1) with the first summation given a prime superscript. Accordingly, the energy density for the crystal is

$$\begin{aligned} M &= (\det \mathbf{A})^{-1} \sum'_{\mathbf{m} \in Z^3} \sum_{k=0}^{n-1} \sum_{j=0}^{n-1} q_k q_j |\mathbf{A}\mathbf{m} + \mathbf{d}_j - \mathbf{d}_k|^{-1} \\ &= (\det \mathbf{A})^{-1} \sum_{k=0}^{n-1} M_k \end{aligned} \tag{3.3}$$

where $M_k = q_k V_{\mathbf{d}_k}(\mathbf{d}_k)$ represents the building energy for the k th charge of the cell. Expression (1.4) for the NaCl constant can be obtained directly from (3.3) together with the second definition in (2.7) for the crystal.

The constant M is not to be confused with the total electrostatic energy per cell, which is given by

$$U = \frac{1}{2} \sum_{k=0}^{n-1} q_k V_{\mathbf{d}_k}(\mathbf{d}_k) \tag{3.4}$$

$$= \frac{1}{2} \sum_{k=0}^{n-1} M_k \tag{3.5}$$

with the factor of $\frac{1}{2}$ arising from pairwise combinations for the Coulomb energy. The energy U depends via the \mathbf{A} matrix upon the definition of the unit cell, whereas M is independent of the choice of \mathbf{A} as long as the crystal structure is unchanged. Yet another measure of crystal energy is Sherman's (1932) per ion measure, namely $E = (2*U)/n$. For example, across the two definitions of the same NaCl crystal in (2.7), U varies but M and E do not. Whether to use U , E or $M = 2U/\det \mathbf{A} = nE/\det \mathbf{A}$ depends upon context. For NaCl, using the first definition (2.7), we have $n = \det \mathbf{A} = 2$, so $M = U = E$ in this case. If the second representation for NaCl is adopted, however, the cell has become larger since $n = \det \mathbf{A} = 8$, and we have $M = E = U/4$. For general crystals, one may avoid the issue of what measure is best by reverting to calculation of the separate 'Madelung constants' M_k to settle any energy problem involving the crystal.

The electrostatic analysis begins with consideration of the exact charge density of the crystal, keeping in mind the potential law:

$$\nabla^2 V(\mathbf{x}) = -4\pi\rho(\mathbf{x}). \tag{3.6}$$

The charge density is given formally by placing delta functions at all sites:

$$\rho(\mathbf{x}) = \sum_j q_j \sum_{\mathbf{m} \in \mathbf{Z}^3} \delta^3(\mathbf{A}\mathbf{m} + \mathbf{d}_j - \mathbf{x}). \tag{3.7}$$

This can be immediately Poisson transformed to give

$$\rho(\mathbf{x}) = (\det \mathbf{A})^{-1} \sum_j q_j \sum_{\mathbf{u} \in \mathbf{Z}^3} \exp[-2\pi i(\mathbf{B}\mathbf{u})(\mathbf{d}_j - \mathbf{x})]. \tag{3.8}$$

Note that if the charges were spatially distributed and not mere points, then the transform can still be performed in principle, with a Fourier transform of the site charge density appearing in (3.8).

Now the Poisson equation (3.6) can be solved by finding that summation whose Laplacian in \mathbf{x} is proportional to (3.8). The difficulty is that in the resulting sum for V a denominator $|\mathbf{B}\mathbf{u}|^2$ causes the \mathbf{u} sum to diverge at $\mathbf{u} = (0, 0, 0)$. This can be traced to the requirement of crystal neutrality: the constraint (2.5) on the total charge actually removes this divergence. A way to solve this is to place a primed sum as the second summation in (3.8). This can be done with impunity, again because of the constraint $\sum q_j = 0$.

Yet another equivalent way to cancel the infinity is to note that (3.6) can only be solved up to the ambiguity of an additive constant for V . As the 'infinite constant' obtained by direct solution is devoid of any crystal structure details, it can safely be removed. In any case we obtain a legitimate expression for the crystal potential:

$$V(\mathbf{x}) = (\pi \det \mathbf{A})^{-1} \sum_j q_j \sum'_{\mathbf{u} \in \mathbf{Z}^3} |\mathbf{B}\mathbf{u}|^{-2} \exp[-2\pi i(\mathbf{B}\mathbf{u})(\mathbf{d}_j - \mathbf{x})]. \tag{3.9}$$

This is valid for the general crystal, and forms the basis of many useful expansions. Such formulae are often derived in the literature by analytic continuation of Epstein zeta functions (Emersleben 1923), of which (3.1) and (3.9) are complementary special cases. Such analytic methods give us (3.9) from (3.1) directly, but already in passing through the electrostatic considerations we see a portent of simple physical arguments to come. For the moment, we write out some examples of (3.9). For NaCl one obtains

$$V_{\text{NaCl}}(\mathbf{x}) = 4\pi^{-1} \sum_{\mathbf{u} \in \mathbf{O}^3} \exp(\pi i \mathbf{u}\mathbf{x})/u^2. \tag{3.10}$$

This being a sum over odd triplets, the prime notation has been safely removed. For the CsCl crystal, the potential is

$$V_{\text{CsCl}}(\mathbf{x}) = 2\pi^{-1} \sum_{u_1+u_2+u_3 \text{ odd}} \exp(2\pi i \mathbf{u} \mathbf{x}) / u^2 \tag{3.11}$$

where, again, the prime notation is not required since the \mathbf{u} origin is ruled out.

We shall make use of another principle of electrostatics as embodied in the Green theorem (Griffiths 1981) that for suitable functions V and W defined on and inside a closed surface S ,

$$\int_{\text{volume}} (V \nabla^2 W - W \nabla^2 V) d^3 R = \int_{\text{surface}} (V \nabla W - W \nabla V) d^2 R. \tag{3.12}$$

If V describes an electrostatic potential within a sphere S which happens to be devoid of interior and surface charge, then the choice $W = 1/R$ gives the familiar result that the value of V at the centre of S equals the average of V over the surface of S . Recall that the Madelung potential V_r , referring to charge site \mathbf{r} is computed by ignoring $q(\mathbf{r})$, so we conclude that V_r may in general be computed as an average over a sufficiently small sphere centred at \mathbf{r} . This principle will be used to derive formulae such as (1.9).

4. Direct bounds

Symmetry principles are directly applicable to simple crystals such as NaCl. As suggested by (1.4) or (2.7) the charge at a lattice point \mathbf{m} is

$$q(\mathbf{m}) = (-1)^{m_1+m_2+m_3}. \tag{4.1}$$

It is easy to see that each of the infinite planes $x = \frac{1}{2}$, $y = \frac{1}{2}$, or $z = \frac{1}{2}$ is a surface of zero potential, for charge values are antisymmetric when reflected through such planes. Looked at from the point of view of the expansion (3.10), this phenomenon follows from the observation that the real part of $\exp(\pi i k/2)$ vanishes for odd integers k . Therefore the unit cube centred at the origin with vertices $(\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2})$ is a closed surface of zero potential. This 'neutral cube' therefore represents a finite domain with known boundary conditions for which a complete solution to the electrostatic problem would yield also the Madelung constant for NaCl.

The constant M_{NaCl} can now be estimated in many ways. One has only to solve this problem: a solitary +1 charge resides at the centre of a grounded unit cube. What is the electrostatic energy of the configuration? This will be the Madelung constant. An equivalent question is: what is the interior surface charge density of the cube? Let σ represent said density. Then clearly the surface integral of σ will balance the origin charge:

$$\int_{\text{cube}} \sigma d^2 a = -1 \tag{4.2}$$

while the Madelung constant will be the potential seen by the origin charge

$$\int_{\text{cube}} (\sigma/r) d^2 a = M. \tag{4.3}$$

Evidently, then, M is bounded by the extreme possibilities for the integral (4.3), namely

$$-1/r_{\text{min}} < M < -1/r_{\text{max}} \tag{4.4}$$

where r_{\min} , r_{\max} are the minimum and maximum distances, respectively, from the origin to the cube surface. Immediate calculation of these radii gives the bound (1.6).

A second way of analysing the neutral cube problem is to attempt to solve the Laplace equation for the Madelung potential

$$\nabla^2 V_0(\mathbf{x}) = 0 \quad (4.5)$$

subject to the boundary condition that the potential at a point on the cube surface is $1/r$. If one attempts an eigenfunction expansion solution, one obtains the sum (3.10) or a transformation of same. But there are numerical methods for solving the Laplace equation. Performing a standard neighbour-relaxation pass of a $31 \times 31 \times 31$ point cube yields a stable estimate at the origin of

$$M_{\text{NaCl}} \sim -1.748\,79 \dots \quad (4.6)$$

Unfortunately such a method does not converge nearly as fast as the best exponential sums for M .

Still another approximation method for NaCl is to recall the sphere-averaging theorem discussed after (3.12). Note on the basis of (1.7) and the coordinate symmetry of the crystal that the eight points $(\pm\frac{1}{6}, \pm\frac{1}{6}, \pm\frac{1}{6})$ all sit at the potential $\sqrt{3}$. It is reasonable to estimate that the crystal potential on the sphere of radius $1/\sqrt{12}$, which passes through all eight points, is roughly $\sqrt{3}$. Thus for points \mathbf{x} lying on that sphere, the Madelung potential is roughly

$$V_0(\mathbf{x}) \sim \sqrt{3} - |\mathbf{x}|^{-1} = -\sqrt{3} \quad (4.7)$$

and we obtain the estimate (1.8) for M_{NaCl} .

It is interesting that these arguments for the NaCl crystal appear not to extend readily to any other structure, not even the simple CsCl crystal. As in (2.7) we assume a positive origin charge. Analysis of the problem indicates that there is no finite neutral surface enclosing this charge. All that we have been able to show is that the crystal potential for CsCl vanishes on the six squares (thought of as wire frames and hence one dimensional):

$$x = \pm\frac{1}{4} \quad |y| + |z| = \frac{1}{2} \quad (4.8)$$

with the remaining four obtained by permuting coordinates. This follows from symmetry considerations applied to the sum (3.11). It is true that all points on all squares lie on the Wigner-Seitz polyhedron for the crystal, but alas that polyhedron is not a neutral surface. The result (1.11) was prompted by the numerical results obtained in the course of the futile search for a closed neutral surface.

The NaCl estimate arising from (4.3) can be made more precise through more knowledge of the surface density σ . Later results, such as formula (7.1) for the exact Coulombic potential, yield an exact description of the density on the neutral cube surface, where we may take $x = \frac{1}{2}$, y and z ranging from $-\frac{1}{2}$ to $+\frac{1}{2}$:

$$\sigma(y, z) = -\frac{1}{2} \sum_{n, p \text{ odd}} \operatorname{sech} \pi R/2 \cos \pi n y \cos \pi p z \quad (4.9)$$

where $R = (n^2 + p^2)^{1/2}$. Application of the integral in (4.3) yields then a representation for the Madelung constant reminiscent of the Benson-Mackenzie sech^2 form (Glasser and Zucker 1980).

5. Sine series for general crystals

We may apply the sphere-averaging principle, as a special case of (3.12), to obtain an expression for the general Madelung potential at a charge site \mathbf{r} . In fact, if S is a sphere centred at \mathbf{r} with radius t , and there is no other point charge in S , then the Madelung potential is given by the surface average:

$$V_r(\mathbf{r}) = (4\pi t^2)^{-1} \int_S V_r(\mathbf{x}) d^2\mathbf{x}. \tag{5.1}$$

Inserting the expansion (3.9) for the crystal potential we find

$$V_r(\mathbf{r}) = -q(\mathbf{r})/t + (2\pi^2 t \det \mathbf{A})^{-1} \sum_j q_j \sum_{\mathbf{u} \in \mathbf{Z}^3} \frac{\exp[-2\pi i(\mathbf{B}\mathbf{u})(\mathbf{d}_j - \mathbf{r})] \sin 2\pi t |\mathbf{B}\mathbf{u}|}{|\mathbf{B}\mathbf{u}|^3}. \tag{5.2}$$

This 'sine series' can be used to calculate Madelung constants via (1.3), although faster convergence can be realised by exploiting the freedom to choose t as long as t lies between 0 and the distance from site \mathbf{r} to nearest neighbour. Formal integration of (5.2) yields an absolutely convergent series:

$$tq(\mathbf{r}) + V_r(\mathbf{r})t^2/2 = (2\pi^3 \det \mathbf{A})^{-1} \sum_j q_j \sum_{\mathbf{u} \in \mathbf{Z}^3} \frac{\exp[-2\pi i(\mathbf{B}\mathbf{u})(\mathbf{d}_j - \mathbf{r})] \sin^2 \pi t |\mathbf{B}\mathbf{u}|}{|\mathbf{B}\mathbf{u}|^4}. \tag{5.3}$$

The formal integration has not been justified, but (5.3) can be verified independently by Poisson transformation of the inverse quartic sum. The Madelung constant may now be obtained from the definition (1.3). Define, for a 3-vector $\mathbf{m} \in \mathbf{B}\mathbf{Z}^3$, the Fourier transform of one charge assembly

$$h(\mathbf{m}) = \sum_j q_j \exp(2\pi i \mathbf{m} \mathbf{d}_j). \tag{5.4}$$

For highly symmetric crystals, h tends to have a simple evaluation. For the second definition of NaCl (2.7), $h(\mathbf{m}) = 8$ if $\mathbf{m} \in \mathbf{B}\mathbf{O}^3$, otherwise $h(\mathbf{m}) = 0$. Then for any t such that

$$0 \leq t < \min_{j \neq k} |\mathbf{d}_j - \mathbf{d}_k| \tag{5.5}$$

the Madelung constant M satisfies

$$t \det \mathbf{B} \sum_k q_k^2 + Mt^2/2 = (2\pi^3 \det \mathbf{A}^2)^{-1} \sum_{\mathbf{u} \in \mathbf{Z}^3} \frac{|h(\mathbf{B}\mathbf{u})|^2 \sin^2 \pi t |\mathbf{B}\mathbf{u}|}{|\mathbf{B}\mathbf{u}|^4}. \tag{5.6}$$

This general formula has the advantage of non-alternating summands. This means that during calculations one may always use the current partial sum to establish a bound on M . It is tempting to integrate further, perhaps even arbitrarily, exploiting to the fullest the free parameter t . This idea is best demonstrated by analysing the special case of the NaCl crystal. In that case, (5.2) reduces to

$$\pi^2(1 + tM) = 4 \sum_{\mathbf{u} \in \mathbf{O}^3} \sin \pi t \mathbf{u} / \mathbf{u}^3 \tag{5.7}$$

valid for $0 < t < 1$. It may seem at first that (5.7) is impossible, since the limiting value of the right-hand sum appears to vanish as t approaches zero. This is not so—the sum approaches $\pi^2/4$ in the small t limit, a phenomenon not uncommon in the world of Fourier series. Integration of (5.7) gives the claim (1.9), which is the NaCl form of (5.6).

By manipulating further integrals of (5.7) one can derive some interesting expressions, such as

$$\pi^4(Mt^3/4 + 3t^2/16) = \sum_{\mathbf{u} \in \mathbb{O}^3} \sin^3 \pi t \mathbf{u} / \mathbf{u}^5 \tag{5.8}$$

valid for all $0 \leq t < \frac{1}{3}$. This sine series converges yet more rapidly than (1.9), but we do not yet know how much information about the Madelung constant can be gleaned with such techniques. Still, one advantage of the general crystal expansion (5.6) is that, in spite of its formidable appearance and non-optimal convergence, it is the simplest formula we know of for reasonable computer calculation. Much more convergent formulae we describe later are harder to program.

One may take advantage also of the positive definiteness of the summands in (1.9). If we take $t = 1/\sqrt{3}$, for example, then (1.9) gives on the basis of the first summand alone

$$M > 6(64\pi^{-3}/9 - 1/\sqrt{3}) \sim -2.088 \dots \tag{5.9}$$

and for the other direction,

$$t + Mt^2/2 < 8\pi^{-3} \sum_{\mathbf{u} \in \mathbb{O}^3} \mathbf{u}^{-4} \tag{5.10}$$

which when extremised in t gives $M < -1.318 \dots$. Of course, tighter bounds result upon more complicated analysis of the summands of (1.9).

Bounds for general crystals can likewise be obtained from (5.6). For lower bounds, one may choose an integer triplet such that $t = (2|\mathbf{B}\mathbf{u}|)^{-1}$ satisfies the constraint (5.5). Then the right-hand side of (5.6) can be bounded below by a finite set of summands in the spirit of (5.9).

6. Exponential series for general crystals

Previous authors have found rapidly convergent ‘cosech’ series for the Madelung constants of cubic crystals (Hautot 1975, Zucker 1975, Glasser and Zucker 1980). We have extended this work to the general case, starting with the crystal potential (3.9). Transformation of this potential to an exponential sum is somewhat tedious, involving a straightforward geometrical series identity valid for positive $y < 1$:

$$\begin{aligned} f(y) &= \sum_{q \in \mathbb{Z}} \exp[2\pi(it(q+y) - s|q+y|)] \\ &= \frac{\sinh(2\pi sy) \exp[2\pi it(y-1)] + \sinh[2\pi s(1-y)] \exp(2\pi ity)}{2(\sinh^2 \pi s + \sin^2 \pi t)} \end{aligned} \tag{6.1}$$

where s, t are positive reals. The function f can be continued for negative $y > -1$ from the relation $f(y) = f^*(-y)$. The idea is to use this one-dimensional sum for just one of the components of the \mathbf{u} triplet in (3.9), to obtain a two-dimensional sum having the exponential convergence properties.

One hesitates to carry out the fundamentally asymmetrical calculations, especially when the lattice-defining matrix A enjoys no particular symmetry. But once a general formula is obtained, computer programs can take care of the numerical aspect. To this end we have worked out the generalised two-dimensional sum which agrees with

previous authors for the simple cubic structures. The result is as follows. Define a matrix \mathbf{D} and, for a given 3-vector \mathbf{x} , define a 3-vector \mathbf{h} by

$$\begin{aligned} \mathbf{D} &= \mathbf{B}^T \mathbf{B} \\ \mathbf{h} &= \mathbf{B} \mathbf{x}. \end{aligned} \tag{6.2}$$

Now choose some component of \mathbf{h} , say h_i , which is non-zero. There will be at least one such since the crystal potential will turn out to diverge if $\mathbf{h} = (0, 0, 0)$. Define a positive quadratic form R^2 acting on a select pair of components of a 3-vector \mathbf{m} by

$$(R(\mathbf{m}))^2 = \sum_{j, k \neq i} (D_{jk}/D_{ii} - D_{ij}D_{ik}/D_{ii}^2) m_j m_k. \tag{6.3}$$

The two components of \mathbf{m} which appear in this form will be the summation indices for the final two-dimensional potential sum. Next, define 2-vectors \mathbf{c} , \mathbf{H} having components

$$\begin{aligned} \mathbf{c} &= (D_{ij}/D_{ii}, D_{ik}/D_{ii}) \\ \mathbf{H} &= (h_j, h_k) \end{aligned} \tag{6.4}$$

where j, k are chosen here such that i, j, k is a cyclic ordering of 1, 2, 3. Now consider the function defined for 3-vectors \mathbf{x} :

$$J(\mathbf{x}) = (\pi \det \mathbf{A})^{-1} \sum_{\mathbf{u} \in \mathbb{Z}^3} \exp[2\pi i(\mathbf{B}\mathbf{u})\mathbf{x}] |\mathbf{B}\mathbf{u}|^{-2}. \tag{6.5}$$

This function can be Poisson transformed via the identity (6.1) to give

$$\begin{aligned} D_{ii} \det \mathbf{A} J(\mathbf{x}) &= \pi(2h_i^2 - 2|h_i| + \frac{1}{2}) \\ &+ \sum'_{N \in \mathbb{Z}_2} \frac{\sinh(2\pi R|h_i|) \cos\{2\pi N[\mathbf{H} - (|h_i| - 1) \operatorname{sgn}(h_i)\mathbf{c}]\} + \sinh[2\pi R(1 - |h_i|)] \cos[2\pi N(\mathbf{H} - \mathbf{c}h_i)]}{2R(\sin^2 \pi N\mathbf{c} + \sinh^2 \pi R)} \end{aligned} \tag{6.6}$$

where $R = R(N_1, N_2)$. This expansion is valid for all \mathbf{x} such that $0 < |h_i| < 1$. The final step in calculating the crystal potential is to observe that

$$V(\mathbf{x}) = \sum_{j=0}^{n-1} q_j J(\mathbf{x} - \mathbf{d}_j). \tag{6.7}$$

In spite of the cumbersome notation, it should be clear that assignments (6.2)-(6.7) can be programmed with knowledge of the crystal parameters in (2.6). It is also evident that the summation in (6.6) has terms decreasing exponentially in either component of N . One may compute the crystal potential efficiently in this way, noting that in (6.7) the vector \mathbf{x} should be taken to lie in the origin cell without loss of generality.

To obtain the Madelung potential in reference to a site \mathbf{d}_k lying in the origin cell, one may subtract from $V(\mathbf{x})$ the Coulomb term $q_k |\mathbf{x} - \mathbf{d}_k|^{-1}$. If, however, one wishes to compute the limiting value of the Madelung potential as \mathbf{x} approaches \mathbf{d}_k , it is necessary to perform further analysis. We shall not pursue the analytic theory for the J function here, but it is possible to establish an analytic continuation of J for zero argument (Zucker 1976, Glasser and Zucker 1980, Crandall and Buhler 1987a), giving a workable formula for the Madelung potential at site \mathbf{d}_k

$$\begin{aligned} V_{d_k}(\mathbf{d}_k) &= \lim_{\mathbf{x} \rightarrow \mathbf{d}_k} (V(\mathbf{x}) - q_k |\mathbf{x} - \mathbf{d}_k|^{-1}) \\ &= \sum'_j q_j J(\mathbf{d}_k - \mathbf{d}_j) + q_k \sum'_\delta J(\mathbf{A}\delta/2) \end{aligned} \tag{6.8}$$

where δ runs over binary triples. Note that the prime superscript for the first sum rules out $j = k$, while the prime in the second rules out $\delta = (0, 0, 0)$. Thus the sums have $n - 1$ and 7 terms, respectively.

General calculation of crystal potentials and Madelung constants is now possible with (6.2)-(6.8) and (1.3). We have used programs which accept numerical input of the general parameters (2.6) and have obtained precision such as that of (1.5) in this fashion. In addition, one may obtain the 'cosech' series formulae previously discovered (Hautot 1975) by algebraic manipulation of (6.8) and (6.6).

The Madelung constant itself, which arises from (6.8) via (1.3), can be obtained in certain cases by appeal to a different method of subtracting the singularity in the limit of site approach. This is the method which will yield a power series expansion for the NaCl Madelung potential, and to which we now turn.

7. The problem of the Coulomb singularity

A method of handling the Coulomb singularity without recourse to analytic function theory is most easily demonstrated for the NaCl structure. The method yields a regular power series expansion for the Madelung potential near the origin. From the general formulae (6.6) and (6.7) for the crystal potential, one may deduce that for NaCl

$$V(x, y, z) = 2 \sum_{n,p \text{ odd}} \frac{\sinh \pi R(1/2 - |x|) \cos \pi n y \cos \pi p z}{R \cosh \pi R/2} \tag{7.1}$$

where $R = (n^2 + p^2)^{1/2}$. This expansion is valid everywhere within the (0, 0, 0) lattice cell. Note that this exponentially convergent expression reveals immediately many of the properties we have discussed. For example, if any coordinate $x, y,$ or z is $\pm \frac{1}{2}$ then $V = 0$. It is not so clear that V is completely symmetric under permutation of the coordinates, but such is true on the basis of the original sum (1.1).

The Coulomb singularity is evident upon the observation that if (x, y, z) represents a charge site, then the sinh/cosh ratio is not exponentially damped and the sum diverges. To obtain the Madelung potential, therefore, we must find an effective way to subtract from the sum (7.1) a Coulomb term. This can be effected with a useful Poisson identity. Let \mathbf{w} be the 2-vector (y, z) . Then

$$2 \sum_{\mathbf{u} \in \mathbb{O}^2} \mathbf{u}^{-1} \exp(-\pi \mathbf{x}|\mathbf{u}| + i\pi \mathbf{u}\mathbf{w}) = (\mathbf{x}^2 + \mathbf{w}^2)^{-1} + \sum_{\substack{\mathbf{a} \in \mathbb{Z}^2 \\ \mathbf{a} \neq (0,0)}} (-1)^{a_1+a_2} (\mathbf{x}^2 + |\mathbf{a} + \mathbf{w}|^2)^{-1/2}. \tag{7.2}$$

The first term on the right-hand side is a Coulomb term which has been separated off the right-hand sum; hence the omission of the \mathbf{a} origin. If we identify the 2-vector \mathbf{u} with the pair (n, p) from (7.1) we obtain an expression for the Madelung potential referred to the NaCl origin:

$$V_0(x, y, z) = \sum_{\substack{\mathbf{a} \in \mathbb{Z}^2 \\ \mathbf{a} \neq (0,0)}} (-1)^{a_1+a_2} (\mathbf{x}^2 + |\mathbf{a} + \mathbf{w}|^2)^{-1/2} - 4 \sum_{n,p \text{ odd}} \frac{\cosh \pi R x \cos \pi n y \cos \pi p z}{R [1 + \exp(\pi R)]}. \tag{7.3}$$

Evaluating this expression at the NaCl origin yields a previously known expansion for the Madelung constant (Hautot 1975):

$$M_{\text{NaCl}} = 4(1 - \sqrt{2})\zeta(\frac{1}{2})\beta(\frac{1}{2}) - 4 \sum_{n,p \text{ odd}} R^{-1} [1 + \exp(\pi R)]^{-1}. \tag{7.4}$$

Here, the Riemann zeta and beta functions appear due to the identity (Glasser 1973)

$$\sum'_{a \in \mathbb{Z}^2} (-1)^{a_1+a_2} a^{-2s} = 4\zeta(s)\beta(s)(-1+2^{1-s}). \tag{7.5}$$

But (7.3) contains information also about the regular behaviour of the Madelung potential near the origin. In fact, one may use (7.5) and a binomial square root expansion to deduce an axial series. Define the coefficients

$$C_k = 4(-\frac{1}{2})^k (2k-1)!! (-1+2^{1/2-k}) \zeta(k+\frac{1}{2}) \beta(k+\frac{1}{2}) / k! - \frac{4\pi^{2k}}{(2k)!} \sum_{n,p \text{ odd}} R^{2k-i} [1 + \exp(\pi R)]^{-1}. \tag{7.6}$$

Then the Madelung potential along the x axis can be written in a power series

$$V_0(x, 0, 0) = \sum_{k=0}^{\infty} C_k x^{2k} = -1.747\ 564\ 59 - 3.578\ 582x^4 - 0.989\ 4995x^6 - 2.942\ 158x^8 - 1.010\ 713x^{10} - 2.914\ 156x^{12} - 1.171\ 4335x^{14} - \dots \tag{7.7}$$

The coefficient C_0 is just M_{NaCl} as in (7.4). The coefficient C_1 is interesting: it must vanish. This is because $\nabla^2 V$ must vanish everywhere, and formally equals $3C_1$ at the origin. This in turn provides an interesting identity when we evaluate (7.6) for $k=1$:

$$\zeta(\frac{3}{2})\beta(\frac{3}{2}) = \pi^2(1-1/\sqrt{2})^{-1} \sum_{n=2 \bmod 8} r_2(n)\sqrt{n}[1 + \exp(\pi\sqrt{n})]^{-1} \tag{7.8}$$

where $r_2(n)$ is the number of representations of integer n as the sum of two squares. This result for the zeta-beta product at $\frac{3}{2}$ has been derived previously (Zucker 1984).

The coefficients C_k for $k > 1$ are all negative and tend to the value -2 . This asymptotic value -2 is interesting in that it suggests a rough model for the NaCl Madelung potential in the form

$$V_0(x, 0, 0) \sim M - 2x^4 - 2x^6 - \dots = M - 2x^4/(1-x^2) \tag{7.9}$$

which, although only an approximate formula, shows the proper quartic behaviour as well as the required Coulomb poles at $x = \pm 1$.

As a final note we refer to the exact special values (1.11) and (1.12). One may follow the arguments of Forrester and Glasser (1982) and Glasser and Zucker (1980) using Jacobi identities (Whittaker and Watson 1973) to obtain some useful formulae, for example:

$$\sum_{m,n,p \in \mathbb{Z}} (-1)^{n+p} [(m-\frac{1}{4})^2 + n^2/2 + p^2/2]^{-s} = 16^s \beta(2s-1) \tag{7.10}$$

$$\sum_{m,n,p \in \mathbb{Z}} (-1)^m [m^2 + n^2 + (p-\frac{1}{2})^2]^{-s} = 2^{2s+1} \beta(2s-1). \tag{7.11}$$

Expression (7.10) is an equivalent form of the CsCl crystal potential when $s = \frac{1}{2}$. Since $\beta(0) = \frac{1}{2}$, we immediately obtain $V_{\text{CsCl}}(\frac{1}{4}, 0, 0) = 2$. For the crystal defined

$$n = 2; \mathbf{d}_0 = (0, 0, 0); \mathbf{d}_1 = (1, 0, 0)$$

$$q_0 = +1; q_1 = -1$$

$$\mathbf{A} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7.12}$$

which amounts to parallel planes of like charge, the crystal potential is given by (7.11) as

$$V(0, 0, \frac{1}{2}) = 2. \quad (7.13)$$

As mentioned in § 1, our computer programs, which use the general prescription (6.2)–(6.8) with (1.3), verify these exact results and the previous (1.7) numerically. One good feature of exact potential results is that they may act as a sharp test of any programming effort.

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