

Evaluation of Electrostatic Potentials and Madelung Constants in Ionic Crystals by the Method of Spherically Symmetric Equivalent Charges

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Abstract

A simple derivation is given of the electrostatic potential in a periodic three-dimensional array of spherically symmetric charge distributions. By noting the equivalence in electrostatic calculations of point charges and suitably chosen spherical charge distributions, this leads to expressions for electrostatic potentials and (Madelung) interaction energies in ionic crystals. The expressions involve sums in reciprocal space only. The approach is illustrated by the calculation of Madelung constants for NaCl and CaF₂, and the electrostatic interaction energy of TiO₂ (rutile). A previous controversy is resolved by showing that the two expressions for the electrostatic potential, which are apparently different, under certain conditions give the same result.

1. Introduction

In the simplest theory of cohesion in ionic crystals, the ions are regarded as positively and negatively charged entities, held together by Coulomb attraction and prevented from collapsing by strong short-range repulsive forces (Kittel 1976). The total energy is then the sum of an attractive electrostatic term and a repulsive term. In the calculation of the latter term, the short range of the repulsive forces means only near neighbour interactions need be considered, and for that reason the calculation is relatively straightforward. The Coulomb interaction is by contrast a long-range interaction, so the calculation of the electrostatic (Madelung) energy involves a summation extending over the whole crystal. The series to be summed is, moreover, only conditionally convergent, so the summation must be performed with particular care (Ashcroft and Mermin 1976). Although the simple model may be dated (Ashcroft and Mermin 1976), it accounts for the cohesive energies of most ionic crystals to within a few per cent. Indeed, the Madelung energy alone represents the major part (about 90 per cent) of the cohesive energy in these crystals. The evaluation of electrostatic potentials and energy in ionic crystals remains therefore a subject of interest and importance.

In the idealised picture, the ionic crystal is regarded as composed of spherical non-overlapping ions, bearing net charges of integral amount (Tosi 1964). For the evaluation of the electrostatic potential or energy, these may be considered as fixed point charges (see the later discussion and Appendix). The different methods for evaluating the relevant sums have been reviewed at length by Tosi (1964).

The sums may be carried out in direct space or, since the charge distributions in crystals are periodic and thus can be expanded in Fourier series, in reciprocal space. The original work by Madelung (1918), relating to the NaCl structure, invoked both direct and reciprocal space summations. Madelung calculated the potential at a selected ion site as the sum of contributions from planes and lines not containing the selected site (evaluated by reciprocal space methods) and a directly summed contribution from the line of ions containing the site in question. In direct summation methods, convergence problems quickly become apparent. Convergence can be aided by arranging charges, or fractions of charges, in groups which are electrically neutral. Evjen (1932) and Hojendahl (1938) achieved convergence in some cases by working with concentric electrically neutral blocks, and Frank (1950) introduced fictitious cancelling charges to produce electrically neutral cells. The accepted general method for evaluating the required sums is that due to Ewald (1921). In this method a neutralised array of point charges is represented as the sum of an array of point charges neutralised by Gaussian charge distributions, and an array of equal Gaussians of opposite sign neutralised by a uniform charge density. The contribution of the first array is summed directly, and that from the second array in reciprocal space. With a suitable choice for the width of the Gaussian, both direct and reciprocal space sums show good convergence. The Ewald method is a proven general method, which achieves rapid convergence, but conceptually it is far from simple!

There is another approach to the evaluation of electrostatic energies due to Bertaut (1952) who noted that, for the evaluation of electrostatic interaction energies, point charges and non-overlapping spherically symmetric charge distributions (with the same centres and same net charges) are equivalent. He proceeded to evaluate the electrostatic interaction energy for a crystal composed of non-overlapping spherical equivalent charges. The method is mentioned only briefly by Tosi (1964). It has the advantages, nevertheless, that the expressions obtained involve sums in reciprocal space only (cf. the Ewald method which involves direct sums as well), and good convergence can be achieved. The method has been employed on many occasions (see e.g. Calage and Pannetier 1977; Pilati *et al.* 1990; Groult *et al.* 1982), and extended by Bertaut (1978*a*) himself for the calculation of the electrostatic energy of charges and multipoles. The method might have found even wider application, but for a certain complexity in the derivation of the required formulae (Bertaut 1952), and a more recent unresolved controversy (Weenk and Harwig 1975; Bertaut 1978*b*). Weenk and Harwig (1975) followed a Bertaut-style approach to evaluate the electrostatic potentials in a crystal composed of non-overlapping spherical equivalent charges. The expressions obtained for the potential and energy were evidently different from those given earlier by Bertaut (1952), and the response from Bertaut (1978*b*) did little to resolve these differences.

In this paper, we provide a formally very simple derivation of the potential in a crystal composed of spherical equivalent charges. The result can be recognised immediately as the expression for potential given by Weenk and Harwig. The expression for the interaction energy follows. We discuss the convergence of the series obtained, and its dependence on, among other things, the detail of the radial dependence in the charge distributions used. The convergence will be illustrated through a number of example applications. Finally, we examine closely the relationship of the Weenk and Harwig to the Bertaut series, and show that under certain conditions these two apparently different results are identical.

2. Theory

We adopt the model of an ionic crystal in which the charges are taken as point charges, but for the purposes of the calculation of the potential we replace the point charges by suitably chosen spherically symmetric equivalent charges. The potential is evaluated with the aid of Poisson's equation, and the interaction energy is derived in a straightforward manner.

(a) Charge Density

The charge density in a crystal comprising point charges is

$$\rho(\mathbf{r}) = \sum_j q_j \delta(\mathbf{r} - \mathbf{r}_j), \quad (1)$$

where charge q_j is located at site \mathbf{r}_j , and the sum extends over all the ionic sites in the crystal. Replacing the point charges by spherically symmetric equivalent charges, we have

$$\rho'(\mathbf{r}) = \sum_j q_j \sigma(\mathbf{r} - \mathbf{r}_j), \quad (2)$$

where $\sigma(\mathbf{r})$ is a spherically symmetric distribution, centred on the origin, of finite radius, and normalised to make

$$\int \sigma(\mathbf{r}) d^3r = 1. \quad (3)$$

In the calculation of potential, we shall in due course invoke the result (see the Appendix) that the potential on the surface or outside of a spherically symmetric charge distribution is the same as would be produced if the total charge were located at a point at its centre.

The charge density (2) has the periodicity of the crystal, and as such can be expanded in the Fourier series

$$\rho'(\mathbf{r}) = \sum_{\mathbf{h}} A_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (4)$$

where the sum is over all the vectors \mathbf{h} of the reciprocal lattice, and the coefficients $A_{\mathbf{h}}$ are given by

$$A_{\mathbf{h}} = \frac{1}{v} \int_C \rho'(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3r. \quad (5)$$

The integration here is over the unit cell C , which is taken to have volume v . The condition of electrical neutrality implies $A_0 = 0$. For $\mathbf{h} \neq 0$, we have

$$\begin{aligned} A_{\mathbf{h}} &= \frac{1}{v} \sum_i q_i \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_i) \int \sigma(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3r \\ &= \frac{1}{v} F(\mathbf{h}) \phi(\mathbf{h}), \end{aligned} \quad (6)$$

where

$$F(\mathbf{h}) = \sum_i q_i \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_i), \quad (7)$$

with the sum now running over the ions in one unit cell, is the 'structure factor of the point charges', and

$$\phi(\mathbf{h}) = \int \sigma(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3r. \quad (8)$$

The Fourier series (4) can thus be written as

$$\rho'(\mathbf{r}) = \frac{1}{v} \sum_{\mathbf{h} \neq 0} F(\mathbf{h}) \phi(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (9)$$

(b) *Electrostatic Potential and Poisson's Equation*

The electrostatic potential $V(\mathbf{r})$ within the array of spherical equivalent charges also has the periodicity of the crystal, so it too can be expanded in the Fourier series

$$V(\mathbf{r}) = \sum_{\mathbf{h}} B_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}). \quad (10)$$

This potential is related to the charge distribution (2) by Poisson's equation

$$\nabla^2 V(\mathbf{r}) = -4\pi \rho'(\mathbf{r}). \quad (11)$$

Substituting the series (10) and (9) into (11), then equating the coefficients of corresponding terms, we find that $B_0 = 0$ and, for $\mathbf{h} \neq 0$,

$$B_{\mathbf{h}} = \frac{1}{\pi v} \frac{F(\mathbf{h}) \phi(\mathbf{h})}{|\mathbf{h}|^2}. \quad (12)$$

This means the Fourier series expansion for the potential can be rewritten as

$$V_{\text{tot}}(\mathbf{r}) = \frac{1}{\pi v} \sum_{\mathbf{h} \neq 0} \frac{F(\mathbf{h}) \phi(\mathbf{h})}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}), \quad (13)$$

which is the first term in the Weenk and Harwig (1975, equation 14) expression for the potential.

(c) *Potential at the Site of One Ion due to All Other Ions in the Crystal*

In most applications, the quantity required is the potential at the site of one ion due to all the other ions in the crystal. In particular, this is what is needed for the evaluation of the electrostatic interaction (Madelung) energy. To proceed, we focus attention on a particular site, at position \mathbf{r}_i . The expression (13) gives a potential $V_{\text{tot}}(\mathbf{r}_i)$ which includes a contribution from the ion located at this site. We shall evaluate and subtract this contribution, which leaves $V_{\text{int}}(\mathbf{r}_i)$, the potential at \mathbf{r}_i due to the other ions in the crystal. By virtue of the result (A1), and provided that the site \mathbf{r}_i does not fall within the charge distribution centred on one of the other ionic sites in the crystal [it is sufficient to assume that the radius of the charge distribution $\sigma(\mathbf{r})$ does not exceed the

nearest neighbour separation], the result for $V_{\text{int}}(\mathbf{r}_i)$ is unaffected by the use of spherically symmetric equivalent charges in place of point charges. The approach outlined in the introduction to this theory is thereby justified.

It remains to evaluate the contribution at a particular site from the ion located at that site. This involves the potential $V_{\text{sn}}(\mathbf{r})$ at the origin due to the normalised, spherically symmetric charge distribution $\sigma(\mathbf{r})$:

$$V_{\text{sn}}(0) = \int \frac{\sigma(\mathbf{r})}{|\mathbf{r}|} d^3r. \quad (14)$$

The integration extends only over the finite volume in which $\sigma(\mathbf{r}) \neq 0$, and can be evaluated easily (see pp. 57–8 in Kellogg 1920). For an atom with a charge q_i the ‘self potential’ is $V_s(\mathbf{r}_i) = q_i V_{\text{sn}}(\mathbf{r}_i)$. Both Bertaut (1952, 1978*b*) and Weenk and Harwig (1975) chose to express their results in terms of $\phi(\mathbf{h})$, though it does not appear to be advantageous to do so. We also derive an alternative expression for $V_{\text{sn}}(0)$ by a procedure very similar to that used in equations (9) to (13). Inverting (8) to express $\sigma(\mathbf{r})$ as a Fourier transform of $\phi(\mathbf{h})$, expressing $V_{\text{sn}}(\mathbf{r})$ also as a Fourier transform, and noting that $V_{\text{sn}}(\mathbf{r})$ is related to $\sigma(\mathbf{r})$ by Poisson’s equation, we can show that

$$V_{\text{sn}}(\mathbf{r}) = \frac{1}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d^3h, \quad (15)$$

whence

$$V_{\text{sn}}(0) = \frac{1}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} d^3h. \quad (16)$$

Subtracting from (13) the self-potential based on (16), we find the potential at \mathbf{r}_i due to the other ions in the crystal is

$$V_{\text{int}}(\mathbf{r}_i) = \frac{1}{\pi v} \sum_{\mathbf{h} \neq 0} \frac{F(\mathbf{h}) \phi(\mathbf{h})}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i) - \frac{q_i}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} d^3h, \quad (17)$$

which is now exactly the Weenk and Harwig (1975) equation (14).

In the debate between Weenk and Harwig (1975) and Bertaut (1978*b*) there has been some discussion on Poisson’s equation. We do not wish to comment on the detail of this discussion. We remark, however, that the potential $V_{\text{tot}}(\mathbf{r})$ in (13) has been constructed here to satisfy Poisson’s equation (11) in the crystal composed of spherical equivalent charges. The potential $V_{\text{int}}(\mathbf{r}_i)$ in (17), on the other hand, is the potential at site \mathbf{r}_i when there is no longer charge at that site (ion removed from site, no overlap from other sites), so $V_{\text{int}}(\mathbf{r})$ satisfies Laplace’s equation at all the ion sites.

(d) *Electrostatic Interaction (Madelung) Energy*

The total electrostatic interaction energy of an array of point charges is (see p. 80 in Kellogg 1920)

$$W = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}, \quad (18)$$

where point charges q_i and q_j are at a separation r_{ij} . The interaction energy per unit cell (the Madelung energy) is therefore

$$W_{\text{int}} = \frac{1}{2} \sum_i q_i \sum_{i \neq j} \frac{q_j}{r_{ij}} = \frac{1}{2} \sum_i q_i V_{\text{int}}(\mathbf{r}_i), \quad (19)$$

wherein the sum in i runs over the ions in one unit cell. In this we have recognised $\sum q_j/r_{ij}$ as the potential at the site i due to all the other ions in the crystal. Equation (19) here is identical with the Bertaut (1978*b*) equation (1.4).

Substituting for $V_{\text{int}}(\mathbf{r}_i)$ from our equation (17), we have finally for the Madelung energy

$$W_{\text{int}} = \frac{1}{\pi v} \sum_{\mathbf{h} \neq 0} \frac{|F(\mathbf{h})|^2 \phi(\mathbf{h})}{|\mathbf{h}|^2} - \frac{1}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} d^3 h \sum_i q_i^2. \quad (20)$$

(e) *General Remarks on Convergence*

Since the matter of convergence is critical in the calculations described here, a few general remarks are in order. To discuss the convergence of the sums appearing in (17) and (20) we consider that the sums in reciprocal space are approximated by integrals. Since the magnitude of $F(\mathbf{h})$ (from equation 7) shows no systematic trend with the magnitude of \mathbf{h} , the behaviour is determined by $\phi(\mathbf{h})/|\mathbf{h}|^2$. In fact if the integral

$$\int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} d^3 h \quad (21)$$

which appears in (17) and (20) is absolutely convergent, so too are the sums appearing in these expressions. Provided $\phi(\mathbf{h}) \sim |\mathbf{h}|^n$ with $n < -1$, the convergence of the sums and the integrals is assured.

In the point charge model of the ionic crystal we have $\sigma(\mathbf{r}) = \delta(\mathbf{r})$ and, from (8), $\phi(\mathbf{h}) = 1$. The sums and integrals are divergent. Replacement of the point charges by spherically symmetric equivalent charges leads to $\phi(\mathbf{h}) \sim |\mathbf{h}|^n$ with $n < -1$, which makes (21) convergent. The replacement of point charges by spherically symmetric equivalent charges can thus be regarded as a device for ensuring the absolute convergence of the sums and integrals involved.

Subject to conditions already outlined, the extent and form of $\sigma(\mathbf{r})$ should be chosen to make $\rho'(\mathbf{r})$ as 'smooth' as possible, so as to reduce the importance in its Fourier expansion (9) of the higher terms. This point is illustrated in the examples which follow.

Table 1. Spherically symmetric charge distributions and related functions

Charge distribution	$\sigma(\mathbf{r})$ for $r < R$ [$\sigma(\mathbf{r}) = 0$ for $r > R$]	$\phi(\mathbf{h})$ ($\omega = 2\pi \mathbf{h} R$)	$V_{\text{sn}}(0)$	$V_{\text{sn}}(0)^A$ (Bertaut series)
Uniform	$3/4\pi R^3$	$3(\sin\omega - \omega\cos\omega)/\omega^3$	$3/2R$	$6/5R$
Polynomial	$(15/4\pi R^3)[1 - 3(\tau/R)^2 + 2(\tau/R)^3]$	$90(8 - 8\cos\omega - 5\omega \sin\omega + \omega^2 \cos\omega)/\omega^6$	$9/4R$	$513/308R$

^A See examples for CaF₂ and TiO₂.

3. Applications of the Method

The method is illustrated by using it to calculate the Madelung constants or Madelung energies in a few common ionic crystals. The calculations involve the evaluation of the expressions (17) and (20). The form of $\phi(\mathbf{h})$ in these expressions is determined by our choice for $\sigma(\mathbf{r})$. For purposes of illustration, we take this function to correspond to (1) a uniform charge density or (2) a smoothly varying third-degree polynomial in r . The polynomial has been tailored to have a zero derivative at the centre ($r = 0$) and boundary ($r = R$). The detailed form of these charge distributions, including expressions for the corresponding $\phi(\mathbf{h})$ (equation 8) and $V_{\text{sn}}(0)$ (equation 14) are collected in Table 1. Note that the uniform and polynomial choices for $\sigma(\mathbf{r})$ give $\phi(\mathbf{h}) \sim |\mathbf{h}|^n$ with $n = -2$ and $n = -4$ respectively.* The sums in (17) and (20) have been estimated using a limited number of terms, as detailed below. All calculations were carried out on a PC spreadsheet (Microsoft Excel).

Table 2. Crystallographic data for NaCl

Cubic, $a = 5.45 \text{ \AA}$	
Na ⁺ , ($q_{\text{Na}} = +e$) at $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$; $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{1}{2})$	
Cl ⁻ , ($q_{\text{Cl}} = -e$) at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; $(0, 0, \frac{1}{2})$; $(\frac{1}{2}, 0, 0)$; $(0, \frac{1}{2}, 0)$	
$F(\mathbf{h}) = 8e$ for h, k, l all odd = 0 otherwise	
Nearest neighbour distance $a/2$.	

Table 3. Evaluation of electrostatic potential of NaCl at Na site

h	k	l	m	$ \mathbf{h} $	$F(\mathbf{h})$	$\phi(\mathbf{h})^A$	$V(\text{Na})^A$	$\phi(\mathbf{h})^B$	$V(\text{Na})^B$	$\phi(\mathbf{h})^C$	$V(\text{Na})^C$
1	1	1	8	1.732	8	0.431	-3.07477	-0.081	-3.55263	0.1480	-3.49498
3	1	1	24	3.317	8	-0.071	-3.47136	0.013	-3.48134	-0.0002	-3.49619
3	3	1	24	4.359	8	-0.049	-3.62928	-0.006	-3.50003	0.0003	-3.49517
5	1	1	32	5.196	8	0.019	-3.57219	0.009	-3.47350	-0.0007	-3.49741
1	3	5	48	5.916	8	0.035	-3.45021	-0.009	-3.50321	0.0008	-3.49468

^A Uniform charge distribution, $R = a/4$. ^B Uniform charge distribution, $R = a/2$.

^C Polynomial charge distribution, $R = a/2$.

(a) NaCl

Every method for the calculation of electrostatic potential and energy is illustrated by application to the calculation of the Madelung constant in NaCl. The basic crystallographic data, along with the structure factors of the point charges from equation (7), are recorded in Table 2.

For NaCl, the Madelung constant is in fact simply

$$\alpha = -\frac{a}{2e} V_{\text{int}}(\text{Na}^+), \quad (22)$$

* Integration of (8), including successive integration by parts, leads to the following general result: If a radial distribution $\sigma(r)$ and its first n derivatives vanish at $r = R$, and if also the odd derivatives up to the $(n-1)$ th vanish at $r = 0$, then $\phi(\mathbf{h}) \sim |\mathbf{h}|^{-(n+3)}$.

where $V_{\text{int}}(\text{Na}^+)$ is the potential at a Na^+ site due to all the other ions in the crystal. We shall use (17) to evaluate V_{int} at the origin; the results are in units of e/a .

The effect of charge distribution will be illustrated with three different choices for $\sigma(\mathbf{r})$, hence $\phi(\mathbf{h})$. These are (1) uniform density of radius $R = a/4$, (2) uniform density of radius $R = a/2$, this being the nearest neighbour separation and the maximum radius available in the theory, and (3) the 'polynomial' charge density with $R = a/2$. In (17), the calculation of the sum proceeds after arranging the contributing reciprocal lattice vectors in sets with equal $|\mathbf{h}|$ (number in set equals multiplicity), then adding these sets in order of increasing $|\mathbf{h}|$. Note that the only nonzero terms are those with h, k, l all odd. The progress of the calculation is recorded in Table 3, which shows the indices (and modulus) of the last added set of reciprocal lattice vectors, the multiplicity in this set, the structure factor of the point charges, and the progressive result for V_{int} for each of the choices for $\sigma(\mathbf{r})$ just described.

The accepted value for the Madelung constant for NaCl (Kittel 1976) is $\alpha = 1.747565$, which from equation (22) gives $V_{\text{int}}(\text{Na}^+)$ as $3.49512e/a$. In every case the result converges towards this value. Comparing the two uniform distributions, it is apparent that the distribution with the larger radius gives the faster convergence. The convergence is very much faster again when the polynomial charge distribution is used. This faster convergence is due to the faster fall-off of $\phi(\mathbf{h})$ with $|\mathbf{h}|$ for the polynomial distribution selected.

Table 4. Crystallographic data for CaF_2

Cubic, $a = 5.65 \text{ \AA}$	
$\left. \begin{array}{l} \text{Ca}^{2+}, (q_{\text{Ca}} = +2e) \text{ at } (0, 0, 0) \\ \text{F}^-, (q_{\text{F}} = -e) \text{ at } \pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \end{array} \right\}$	plus fcc positions
$F(\mathbf{h}) = 0$ unless h, k, l all odd or all even	
= $16e$ for $4n+2$, $n = h+k+l$	
= $8e$ for $4n \pm 1$	
= 0 for $4n$	
Nearest neighbour distance $\sqrt{3}a/2$	

Table 6. Crystallographic data for TiO_2

Tetragonal, $a = 4.592 \text{ \AA}$, $c = 2.959 \text{ \AA}$	
$\text{Ti}^{4+}, (q_{\text{Ti}} = +4e) \text{ at } (0, 0, 0); (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	
$\text{O}^{2-}, (q_{\text{O}} = -2e) \text{ at } (x, x, 0); (-x, -x, 0);$	
$(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}); (\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}); x = 0.305$	
$F(\mathbf{h}) = q_{\text{Ti}}(1+(-1)^n) + 2q_{\text{O}}(\cos\lambda + (-1)^n \sin\mu)$	
$n = h+k+l; \lambda = 2\pi(h+k)x; \mu = 2\pi(h-k)x$	
Nearest neighbour distance (NND) 1.946 \AA	

(b) CaF_2

The Madelung constant for CaF_2 is calculated using (20). The crystallographic data for CaF_2 are given in Table 4 and the progress of the calculation is

Table 5. Evaluation of the Madelung constant for CaF₂
 Calculation includes 27 independent reciprocal lattice vectors. Shown are details of the summation for the first four and last three

h	k	l	m	$ h $	$F(h)$	$\phi(h)^A$	α^A	$\phi(h)^B$	α^B	$\phi(h)^C$	α^C
1	1	1	8	1.732	8	-0.02865	-1.52813	0.25942	-1.99580	0.73684	-2.79912
2	0	0	6	2.000	16	-0.08138	-1.70759	0.14802	-1.66936	0.66296	-1.82985
3	1	1	24	3.317	8	0.03551	-1.67911	-0.01287	-1.67969	0.29498	-1.76007
2	2	2	8	3.464	16	0.03378	-1.64600	-0.00935	-1.68886	0.25942	-1.69411
9	3	1	48	9.539	8	-0.00291	-1.68473	0.00011	-1.67939	0.00244	-1.67963
9	5	1	48	10.344	8	0.00377	-1.68411	-0.00014	-1.67942	-0.00058	-1.67963
8	8	2	24	11.489	16	-0.00305	-1.68493	0.00010	-1.67939	-0.00144	-1.67963

^A Uniform charge distribution, $R = \sqrt{3}a/4$. ^B Polynomial charge distribution, $R = \sqrt{3}a/4$. ^C Polynomial charge distribution, Bertaut series, $R = \sqrt{3}a/8$.

Table 7. Evaluation of the electrostatic interaction energy W_i for TiO₂
 Calculation includes 65 independent reciprocal lattice vectors. Shown are details of the summation for the first four and last three

h	k	l	m	$ h $	$F(h)$	$\phi(h)^A$	W_i^A	$\phi(h)^B$	W_i^B	$\phi(h)^C$	W_i^C
1	1	0	4	0.308	7.082	0.13887	-17.74999	0.44149	-25.36638	0.82440	-37.41512
0	1	1	8	0.402	10.710	-0.04992	-18.47273	0.22520	-22.10578	0.71654	-29.98122
0	2	0	4	0.436	14.164	-0.07711	-19.30505	0.16372	-20.33851	0.67497	-25.06347
1	1	1	8	0.457	7.082	-0.08485	-19.72043	0.12883	-19.70784	0.64726	-23.01254
0	2	4	8	1.421	14.164	-0.00148	-19.61921	0.00040	-19.61650	-0.01490	-19.61579
1	2	4	8	1.437	-4.798	-0.00335	-19.61997	-0.00055	-19.61638	-0.01442	-19.61574
2	2	4	8	1.486	3.250	-0.00738	-19.62069	0.00079	-19.61630	-0.01240	-19.61572

^A Uniform charge distribution, $R = \text{NND}$. ^B Polynomial charge distribution, $R = \text{NND}$. ^C Polynomial charge distribution, Bertaut series, $R = \text{NND}/2$, with W_i in units of $e^2 \text{Å}^{-1}$.

indicated in Table 5. In this example we have used a uniform charge distribution with $R = \sqrt{3}a/4$, and the polynomial charge distribution with $R = \sqrt{3}a/4$ and $R = \sqrt{3}a/8$. The last calculation was performed using a Bertaut series (see Section 4).

To obtain the Madelung constant from (20), W_i must be scaled by twice the nearest neighbour distance ($\sqrt{3}a/4$), and normalised by dividing by Σq_i^2 , the summation being over the unit cell. The values of the Madelung constant obtained here should be compared with the one obtained using the Ewald method, that is $\alpha = 1.67960$. As in the case of NaCl the series utilising the polynomial charge distribution converges faster and gives a more accurate result.

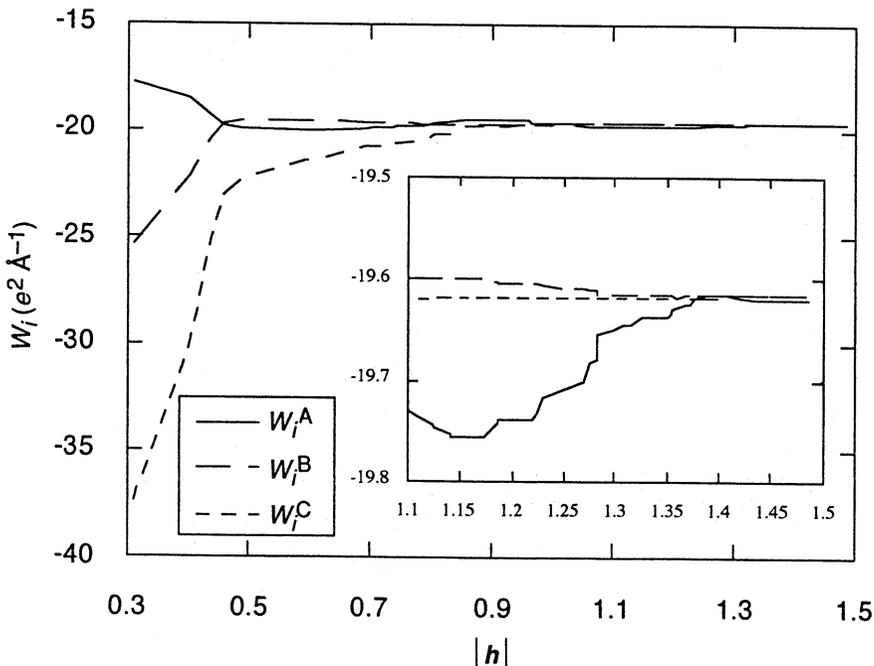


Fig. 1. Convergence of the progressive sums for TiO_2 for a uniform charge distribution, a polynomial charge distribution and a polynomial charge distribution using a Bertaut series, as a function of increasing $|h|$ (in \AA^{-1}). The insert shows the behaviour of the summation near the final result.

(c) TiO_2

The calculation of the Madelung constant is particularly significant in cubic structures. However, for more complicated structures the utility of the Madelung constant is diminished. Under this circumstance it is better to calculate the electrostatic interaction energy W_i (equation 20). This is demonstrated for rutile (TiO_2). Its crystallographic data are given in Table 6 and the progress of the calculation is shown in Table 7. The same three choices for charge distribution and R have been made as for CaF_2 . We carried the calculation to 65 reciprocal lattice vectors (see Fig. 1), producing values of $W_i^A = -19.55007 e^2 \text{\AA}^{-1}$, $W_i^B = -19.62680 e^2 \text{\AA}^{-1}$ and $W_i^C = -19.62104 e^2 \text{\AA}^{-1}$. These values should be

compared with $W_i = -19.61519 e^2 \text{ \AA}^{-1}$ calculated using the Ewald method. We note here that the progressive sums of series A and B oscillate about the final result. This is in contrast to the Bertaut series C which always approaches from the one side.

4. The Bertaut Expressions

Bertaut (1952, 1978*b*) obtained expressions for the electrostatic potential and energy which are of the same form as (17) and (20), but differ in that $\phi(\mathbf{h})$ in these expressions is replaced by $|\phi(\mathbf{h})|^2$. Weenk and Harwig (1975) noted the difference and attributed it to difficulties in evaluating certain infinite integrals.

In fact, the apparently different expressions can be reconciled by comparing the energy of a unit point charge placed at site \mathbf{r}_i with the energy of the spherically symmetric distribution $\sigma(\mathbf{r}-\mathbf{r}_i)$ centred on \mathbf{r}_i . By the theorems of electrostatics (see the Appendix), these energies are equal provided the spherically symmetric equivalent charges do not overlap. Specifically, from equation (A3), we have

$$\int V_{\text{int}}(\mathbf{r}) \sigma(\mathbf{r} - \mathbf{r}_i) d^3r = \int V_{\text{int}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) d^3r = V_{\text{int}}(\mathbf{r}_i). \quad (23)$$

To evaluate the left-hand side we need an expression for $V_{\text{int}}(\mathbf{r})$ valid in the vicinity of \mathbf{r}_i . We subtract (15) from (13) to obtain (analogous to 17) for the region around \mathbf{r}_i , not within the charge distributions associated with other ions,

$$\begin{aligned} V_{\text{int}}(\mathbf{r}) = \frac{1}{\pi\nu} \sum_{\mathbf{h} \neq 0} \frac{F(\mathbf{h}) \phi(\mathbf{h})}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \\ - \frac{q_i}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} \exp[-2\pi i \mathbf{h} \cdot (\mathbf{r} - \mathbf{r}_i)] d^3h. \end{aligned} \quad (24)$$

Noting that

$$\int \sigma(\mathbf{r} - \mathbf{r}_i) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d^3r = \phi(-\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i), \quad (25)$$

we can evaluate the left-hand side of (23), obtaining finally

$$\begin{aligned} \frac{1}{\pi\nu} \sum_{\mathbf{h} \neq 0} \frac{F(\mathbf{h}) |\phi(\mathbf{h})|^2}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i) - \frac{q_i}{\pi} \int \frac{|\phi(\mathbf{h})|^2}{|\mathbf{h}|^2} d^3h \\ = \frac{1}{\pi\nu} \sum_{\mathbf{h} \neq 0} \frac{F(\mathbf{h}) \phi(\mathbf{h})}{|\mathbf{h}|^2} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i) - \frac{q_i}{\pi} \int \frac{\phi(\mathbf{h})}{|\mathbf{h}|^2} d^3h, \end{aligned} \quad (26)$$

which is the equality showing that the Bertaut and the expressions given here (and by Weenk and Harwig) have the same value. The required conditions are satisfied provided the radius of the charge distribution $\sigma(\mathbf{r})$ does not exceed one-half of the nearest neighbour distance.

The equality of the Bertaut expressions and those given here can also be seen by noting that the Bertaut expressions with charge distribution $\sigma_{\text{B}}(\mathbf{r})$ are *identical* with our (17) and (20) with charge distribution

$$\sigma(\mathbf{r}) = \int |\phi(\mathbf{h})|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) d^3h, \quad (27)$$

where

$$\phi(\mathbf{h}) = \int \sigma_{\text{B}}(\mathbf{r}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}) d^3r. \quad (28)$$

Provided the radius of $\sigma(\mathbf{r})$ does not exceed the nearest neighbour distance, $\sigma(\mathbf{r})$ is an acceptable charge distribution, so (17) and (20) converge to the required results. Bertaut (1978*b*) himself compared the reach of functions related by (27) and (28) and concluded that the 'reach' of $\sigma(\mathbf{r})$ is twice that of $\sigma_{\text{B}}(\mathbf{r})$. It follows (again) that provided the radius of $\sigma_{\text{B}}(\mathbf{r})$ does not exceed one-half of the nearest neighbour distance the Bertaut expressions may be used.

Although the expressions (17) and (20) have been shown to provide the same end results as the corresponding Bertaut series, the convergence behaviour [for the same $\sigma(\mathbf{r})$] may be different. This has already been illustrated in Tables 5 and 7 (see the comments on rutile in particular). We reiterate that exactly the same behaviour could be achieved with (17) and (20) by using the charge density generated by (27) and (28).

5. Summary and Discussion

The method of spherically symmetric equivalent charges provides the electrostatic potential and Madelung energy in terms of summations in reciprocal space. The derivation is straightforward, depending on the calculation of the potential in a periodic array of spherical charges, and the subtraction of the potential due to a single spherical charge. The sums obtained are absolutely convergent, the rate of convergence being determined by the detail of the charge distribution assumed.

The discussion includes the explanation and removal of a previous controversy, by showing two apparently different expressions to be equal. Since the derivation is simple and the controversy surrounding the method resolved, there is a sound basis for its continued use.

The illustrations given here concern the evaluation of electrostatic potential and energy. The method has been used for the calculation of electric fields and field gradients (Bertaut 1978*b*; Weenk and Harwig 1975). It has also been extended to the case in which the charge distribution in the crystal is modelled using dipoles and, more generally, multipoles as well as the point charges considered here (Bertaut 1978*a*).

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References

- Ashcroft, N. W., and Mermin, N. D. (1976). 'Solid State Physics' (Saunders College: Philadelphia).
- Bertaut, E. F. (1952). *J. Phys. Radium* **13**, 499.
- Bertaut, E. F. (1978a). *J. Phys. (Paris)* **39**, 1331.
- Bertaut, E. F. (1978b). *J. Phys. Chem. Solids* **39**, 97.
- Calage, Y., and Pannetier, J. (1977). *J. Phys. Chem. Solids* **38**, 711.
- Evjen, H. M. (1932). *Phys. Rev.* **39**, 675.
- Ewald, P. P. (1921). *Ann. Phys. (Leipzig)* **64**, 253.
- Frank, F. C. (1950). *Philos. Mag.* **41**, 1287.
- Groult, D., Pannetier, J., and Raveau, B. (1982). *J. Solid State Chem.* **41**, 277.
- Hojendahl, K. (1938). *Math-Fys. Mag.* **16**, 138.
- Kellogg, O. D. (1920). 'Foundations of Potential Theory' (Frederick Ungar: New York).
- Kittel, C. (1976). 'Introduction to Solid State Physics', 5th edn (Wiley: New York).
- Madelung, E. (1918). *Z. Phys.* **19**, 524.
- Pilati, T., Bianchi, R., and Gramaccioli, C. M. (1990). *Acta Crystallogr. A* **46**, 309.
- Tosi, M. P. (1964). *Solid State Phys.* **16**, 1.
- Weenk, J. W., and Harwig, H. A. (1975). *J. Phys. Chem. Solids* **36**, 783.

Appendix

Two results on the electrostatics of spherically symmetric charge distributions are given here. These results are crucial to the arguments presented in the text, and are therefore recorded here. Our reference on potential theory is Kellogg (1920).

(1) *The potential on the surface or outside of a spherically symmetric charge distribution is the same as would be produced if the total charge were located at a point at its centre.*

This is a well known result which can be established by direct integration of the expression for potential (see Kellogg p. 57, Exercise 11; also pp. 6–8). For a spherically symmetric charge distribution $\sigma(\mathbf{r})$ centred on the origin carrying total charge of one, the potential at position \mathbf{R} on the surface or outside the distribution can be written as

$$\int_{\text{sphere}} \frac{\sigma(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|} d^3r = \frac{1}{|\mathbf{R}|} = \int_{\text{sphere}} \frac{\delta(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|} d^3r. \quad (\text{A1})$$

This form of the result proves useful below.

(2) *The energy of a spherically symmetric charge distribution placed in the potential due to an array of point charges is the same as if the total charge is located at its centre. This result holds provided none of the point charges producing the potential falls within the spherical charge distribution under consideration.*

This result depends on the evaluation of similar integrals. We suppose we have an array of point charges, charge q_j being located at \mathbf{R}_j , and we calculate the energy of the spherical charge distribution $\sigma(\mathbf{r})$, carrying unit total charge, centred on the origin. The potential at \mathbf{r} due to the array of charges is

$$V'(\mathbf{r}) = \sum_j \frac{q_j}{|\mathbf{R}_j - \mathbf{r}|}, \quad (\text{A2})$$

so the interaction energy of $\sigma(\mathbf{r})$ with this potential is (from A2)

$$\begin{aligned}
 \int_{\text{sphere}} V'(\mathbf{r}) \sigma(\mathbf{r}) d^3r &= \sum_j q_j \int_{\text{sphere}} \frac{\sigma(\mathbf{r})}{|\mathbf{R}_j - \mathbf{r}|} d^3r \\
 &= \sum_j q_j \int \frac{\delta(\mathbf{r})}{|\mathbf{R}_j - \mathbf{r}|} d^3r \\
 &\quad [\text{from A1 since all the } \mathbf{R}_j \text{ are outside } \sigma(\mathbf{r})] \\
 &= \int V'(\mathbf{r}) \delta(\mathbf{r}) d^3r, \tag{A3}
 \end{aligned}$$

which is the required result.

It follows that *the interaction energy of an array of point charges is the same as for an array of non-overlapping spherically symmetric equivalent charge distributions*. For from (1), the potential at any one site due to other charges is the same for point charges as for spherically symmetric equivalent charges and from (2) the energy of a charge at this site is the same for a point charge as for its spherically symmetric equivalent.