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RATE OF CONVERGENCE OF MADELUNG SERIES BY THE METHOD OF BERTAUT

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ABSTRACT

A calculation is made of the correction to be applied to the Madelung constant when computed by a method given by Bertaut with a finite number of terms. Some advantages of this method are discussed.

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There are many problems in crystal chemistry in which it is of interest to consider the electrostatic energy of a crystal resulting from the interaction of the ions considered as point charges. This energy is given by the sum of an infinite series which converges slowly and conditionally. Considerable effort has been devoted to methods of carrying out this computation.

Bertaut[1] noticed the connection between the terms of this series and the Patterson function of the charge distribution. He showed how the calculation could be carried out if the point charges are replaced by spherically symmetrical charges of various shapes. If the charge of each ion is spread uniformly over the volume of a sphere of radius R, with R no greater than the shortest interionic distance, an expression results which has several advantages for numerical work:

$$A = -\frac{WL}{\epsilon^2} = \frac{3L}{5RZ}\sum_j z_j^2 - \frac{18\pi R^2 L}{ZV}\sum_h |F|^2 \frac{(\sin\alpha - \alpha\cos\alpha)^2}{\alpha^8} \tag{1}$$

where

$$\alpha = 2\pi hR \tag{2}$$

1. F. Bertaut, J. Phys. Radium, 13, 499 (1952)

and

$$F = \sum_j z_j e^{2\pi i(h_1 x_{1j} + h_2 x_{2j} + h_3 x_{3j})} \tag{3}$$

Equation (1) is Bertaut's equation (41) with slight changes of notation. Here A is the Madelung constant based on L as unit distance, W is the electrostatic energy per molecule, ϵ is the electronic charge, Z is the number of molecules in the unit cell, z_j is the charge number of atom j, V is the volume of the unit cell, and h is the magnitude of the vector $(h_1\ h_2\ h_3)$ in reciprocal space or the reciprocal of the spacing d of the planes $(h_1\ h_2\ h_3)$. The coordinates of atom j are x_{1j}, x_{2j}, x_{3j}. The sum over h in Eq. (1) includes the infinite number of reciprocal vectors corresponding to all combinations of integral values of h_1, h_2 and h_3, positive, zero, and negative. It is convenient to insert a factor p, the multiplicity of the form $(h_1\ h_2\ h_3)$ for the crystal under consideration, and to include in the sum only one term for each group of equivalent terms. Since F(000) = 0 for an electrically neutral crystal, there is no difficulty with singularities. The sums over j in Eqs. (1) and (3) include the atoms of one unit cell. The structure factor F is the ordinary X-ray structure factor with charge numbers in place of atomic form factors. The value used for R is arbitrary, as long as it is less than half the smallest interionic distance, but the convergence is more rapid the larger its value.

The convergence of the series in Eq. (1) is reasonably rapid, but the work involved is not trivial except for the most simple structures. A special advantage, at least for crystallographers, is that the geometrical part of the calculations is reduced to the familiar structure

factors and vectors in reciprocal space. It is simple to arrange the terms in order of increasing h and to check that none has been omitted. Full use of the symmetry may be made to combine like terms. The geometry of the unit cell is separated from that of the atomic coordinates in this calculation. Thus it is possible to calculate the energies of several arrangements of the atoms in unit cells of a given shape with much less effort than that required to carry out an equal number of separate calculations.

In the application of Eq. (1) it is advantageous to know the error introduced if the sum over h includes only those values of h not greater than some quantity m. This becomes especially of interest when the number of terms in a small interval of h becomes large. Under this condition $|F|^2$ may be replaced by its average value[2] $\sum_j z_j^2$. The density of terms in reciprocal space is V. Therefore the error, ΔA,

$$\Delta A = \frac{18\pi R^2 L}{ZV} \sum_{h>m} |F|^2 \frac{(\sin \alpha - \alpha \cos \alpha)^2}{\alpha^8} \tag{4}$$

is approximated by an integral:

$$\Delta A = \frac{18\pi R^2 L}{ZV} \int_m^\infty \sum_j z_j^2 \frac{(\sin \alpha - \alpha \cos \alpha)^2}{\alpha^8} 4\pi h^2 V dh \tag{5}$$

$$= \frac{9L\Sigma z^2}{\pi R Z} \int_\beta^\infty \frac{(\sin \alpha - \alpha \cos \alpha)^2}{\alpha^6} d\alpha \tag{6}$$

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2. The derivation given by H. Lipson and W. Cochran (The determination of crystal structures, G. Bell and Sons, Ltd., London, 1953, p. 134) applies equally well when some of the z's are negative.

where

$$\beta = 2\pi Rm. \tag{7}$$

The integral in Eq. (6) can be reduced by five successive integrations by parts to the form

$$\Delta A = \frac{3L\Sigma z^2}{5\pi RZ}\left\{\frac{3\sin^2\beta}{\beta^5} - \frac{6\sin\beta\cos\beta}{\beta^4} + \frac{2+\cos^2\beta}{\beta^3} - \frac{\sin\beta\cos\beta}{\beta^2} - \frac{1-2\sin^2\beta}{\beta} + \pi - 2Si(2\beta)\right\} \tag{8}$$

where

$$Si(2\beta) = \int_0^{2\beta} \frac{\sin t}{t}\, dt. \tag{9}$$

The function Si(x) can be found in tables[3]. The error may be written as:

$$Q = \frac{\Delta ARZ}{L\Sigma z^2} = \frac{-\Delta WRZ}{\epsilon^2 \Sigma z^2}. \tag{10}$$

Selected values of Q are tabulated in Table I. It so happens[4] that the value of $ARZ/L\Sigma z^2$ is always of the order of 0.4 if R is half the shortest interionic distance. Therefore we can also list in Table I approximately the percentage error in A if the series is terminated at $\alpha = \beta$.

If the calculated errors listed in Table I are applied as corrections to the computed series, then the accuracy of the result

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3. Work Projects Administration, Tables of sine, cosine and exponential integrals, New York, 1940. Two volumes.

4. This can be shown by a simple extension (unpublished) of the generalizations of A. Kapustinsky, Z. phys. Chem. B22, 257 (1933) and D. H. Templeton, J. Chem. Phys. 21, 2097 (1953).

is an order of magnitude better than without the correction. This table is also very useful for planning the work so that enough but only enough terms are included to obtain the desired accuracy.

One should not interpolate in Table I, because the function $Q(\beta)$, though monotonic, has zero slope at certain points near those where β is a half integral multiple of π.

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Table I

Corrections for termination of the series

β/π	Q	$100\ \Delta A/A$
0.5	0.172664	43
1.0	.015992	4
1.5	.004715	1
2.0	.001950	0.5
2.5	.000996	.2
3.0	.000574	.1
3.5	.000362	.09
4.0	.000242	.06
4.5	.000170	.04
5.0	.000123	.03