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OPTIMUM ATOMIC SHAPE FOR BERTAUT SERIES

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ABSTRACT

Calculations are made of the error in the Madelung constant when computed by Bertaut's method with a finite number of terms and with various shapes for the charge distribution within the atoms. A charge density which is proportional to the distance from the edge of the spherical atom gives most rapid convergence for the range of accuracy one percent to 0.003 percent. For higher accuracy a better shape is charge density proportional to the square of the distance from the edge. If Gaussian atoms are used and overlap neglected, no choice of parameter allows an accuracy for a given number of terms as great as for the above functions. If the overlap effect is included by a second series (double series of Ewald) the convergence can be made more rapid than for any of the single series methods, but at the price of a more complicated program.

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INTRODUCTION

If the atoms of an ionic crystal are replaced by spherically symmetric charge distributions which do not overlap, the Coulomb interaction energy can be calculated by a single absolutely convergent infinite series whose terms are a function of the lattice vectors in reciprocal space. Bertaut[1, 2] developed this theory and has given the form of the terms for a few simple shapes of the charge density as a function of distance from the atomic center. An estimate of the rate of convergence of the series has been given for the case of uniform charge distribution within the spherical atom.[3] The present paper reports similar estimates for several other shapes. It is found that some of these are substantially superior to the uniform distribution for accurate computations.

POWER DISTRIBUTIONS

Each ionic charge is distributed within a sphere of radius R so that the charge density is proportional to a normalized distribution function f(r), where r is the distance from the atomic center. We have considered cases where $f(r) = a(R-r)^n$, with n zero or a positive integer. Then the Madelung constant A can be expressed:

$$A = -\frac{WL}{\epsilon^2} = \frac{gL}{RZ}\sum_j Z_j^2 - \frac{\pi R^2 L}{ZV}\sum_h |F|^2 \phi(\alpha), \quad \alpha = 2\pi hR \qquad (1)$$

The notation is the same as in the previous paper[3] except that g is a constant and ϕ is a function which depend on the choice of f(r), as listed in Table I.

Table I

Functions and Constants for Eq. (1)

Atomic shape	f(r), r<R	g	ϕ (a)
uniform	$\frac{3}{4\pi R^3}$	3/5	$\frac{18(\sin a - a\cos a)^2}{a^8}$
linear	$\frac{3(R-r)}{\pi R^4}$	26/35	$\frac{288(a\sin a + 2\cos a - 2)^2}{a^{10}}$
parabolic	$\frac{15(R-r)^2}{2\pi R^5}$	25/28	$\frac{7200(a\cos a - 3\sin a + 2a)^2}{a^{12}}$
cubic	$\frac{15(R-r)^3}{\pi R^6}$	23/22	$\frac{259200(a^2 + a\sin a + 4\cos a - 4)^2}{a^{14}}$

The error in Eq. (1) when the series includes only terms for a less than a limiting value has been estimated as in the previous work[3] by replacing the sum by an integral of the average value of the terms. The results are plotted in Fig. 1. Table II lists selected values of the integral Q ($Q = \Delta ARZ/L\Sigma Z^2$). It is seen that initially the uniform case gives the best approximation because of the smaller self-energy term, but at about one percent accuracy the linear case series becomes better. For the range one percent to 0.003 percent, which is likely to include most problems of practical interest, the linear case is as good as or better than any other. Beyond 0.003 percent, the parabolic series is better. The cubic or higher

powers are not likely ever to be better because g is always greater and the asymptotic form of ϕ is proportional to the same power of α.

Table II

Q vs. α for Series Types

α/π	Uniform	Linear	Parabolic	Cubic
0.5	0.1726643	0.2931046	0.4295580	0.5732962
1.0	0.0159921	0.0586987	0.1374429	0.2390632
1.5	0.0047134	0.0036371	0.0258938	0.0731344
2.0	0.0019496	0.0003013	0.0024336	0.0163946
2.5	0.0009964	0.0001357	0.0001883	0.0030793
3.0	0.0005739	0.0000903	0.0000902	0.0007350
3.5	0.0003612	0.0000329	0.0000554	0.0002801
4.0	0.0002414	0.0000123	0.0000164	0.0001223
4.5	0.0001697	0.0000081	0.0000041	0.0000512
5.0	0.0001234	0.0000057	0.0000031	0.0000240

The number of terms in the series is roughly proportional to α^3. Thus to reduce the error to 0.1 percent, if x terms are required in the linear series, about 2.1x, 5.6x, and 6.2x terms would be required respectively in the parabolic, uniform, and cubic cases.

GAUSSIAN DISTRIBUTIONS

If $f(r) = k^3 e^{-k^2 \pi r^2}$, a normalized Gaussian function, Eq. (1) must be corrected for the overlap of the atoms. In this case, as shown by Bertaut,[1,2]

$$A = \frac{kL}{Z}\sum_j Z_j^2 - \frac{L}{2\pi ZV}\sum_h \frac{|F|^2}{h^2}\exp(-\pi h^2/k^2) - \frac{L}{2Z}\sum_{i,\ell}\frac{Z_i Z_\ell}{r_{i,\ell}}\operatorname{erfc}(\sqrt{\pi}\,k r_{i,\ell} \qquad (2)$$

This expression is equivalent to the double series of Ewald.[4] The choice of k is arbitrary. If it is small enough, the sum over h converges rapidly, but the sum over $r_{i,\ell}$ is large. If k is large enough, the second sum is negligible, but the first sum converges slowly.

Estimates have been made by integration of the convergence of the sum over h for three values of k. The results are shown in Fig. 2. For four nearest neighbors and kR = 1, 2/3, or 1/2, the first term of the second series is respectively 0.10, 4.5, or 19 percent of A, with R taken as half the nearest neighbor distance. These values are included in the plot to show approximately the limit of accuracy if the second series is neglected. It is seen that in the interval considered here, the Ewald method with neglect of the second series is not competitive with the best single series function. On the other hand, the exponential functions ultimately converge much more rapidly than the power functions. For very high accuracy the Ewald method with both series and judicious choice of k is likely to involve much less computation than any of our single series, assuming sufficiently accurate values of the error function are available. It should be pointed out that in general it is much simpler to compute the reciprocal lattice vectors than the interatomic distances. The choice of the best method in a particular case will depend on the accuracy desired and the relative inconvenience of many terms or more complicated program.

We thank Dr. Bertaut for calling our attention to his unpublished report[2] and for suggesting that we investigate this problem.

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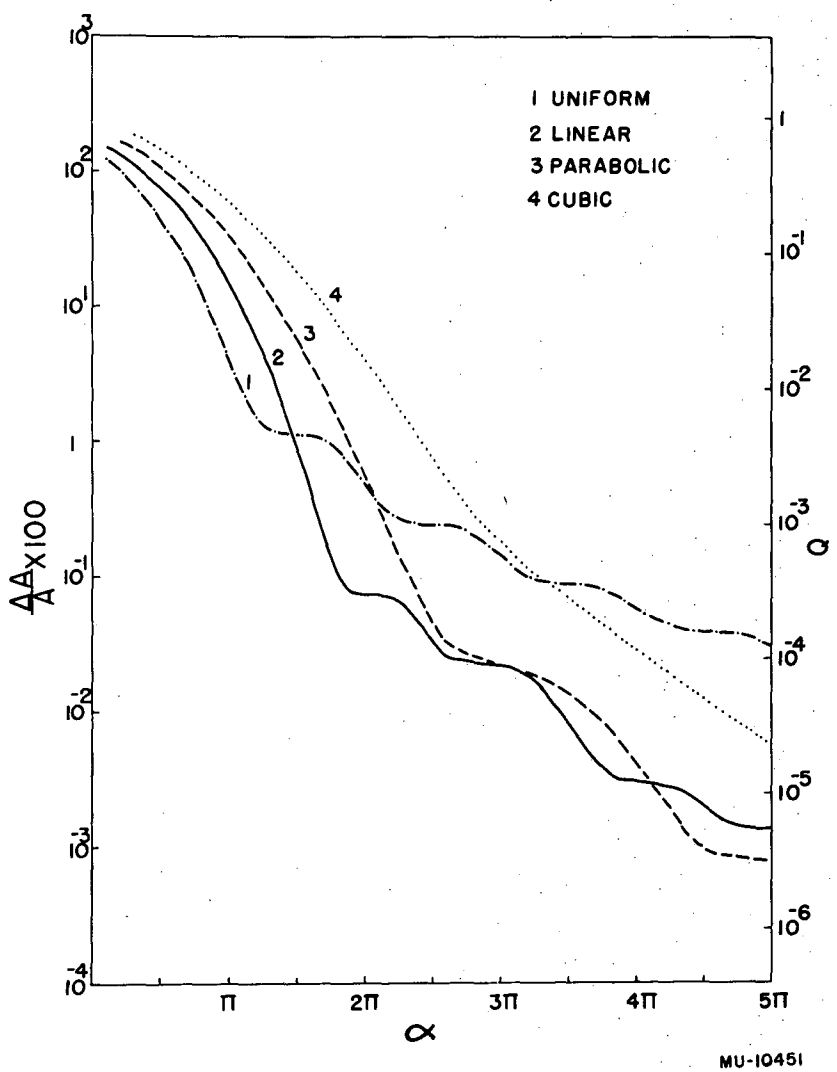

Fig. 1. Percentage error of Madelung constant for power distributions.

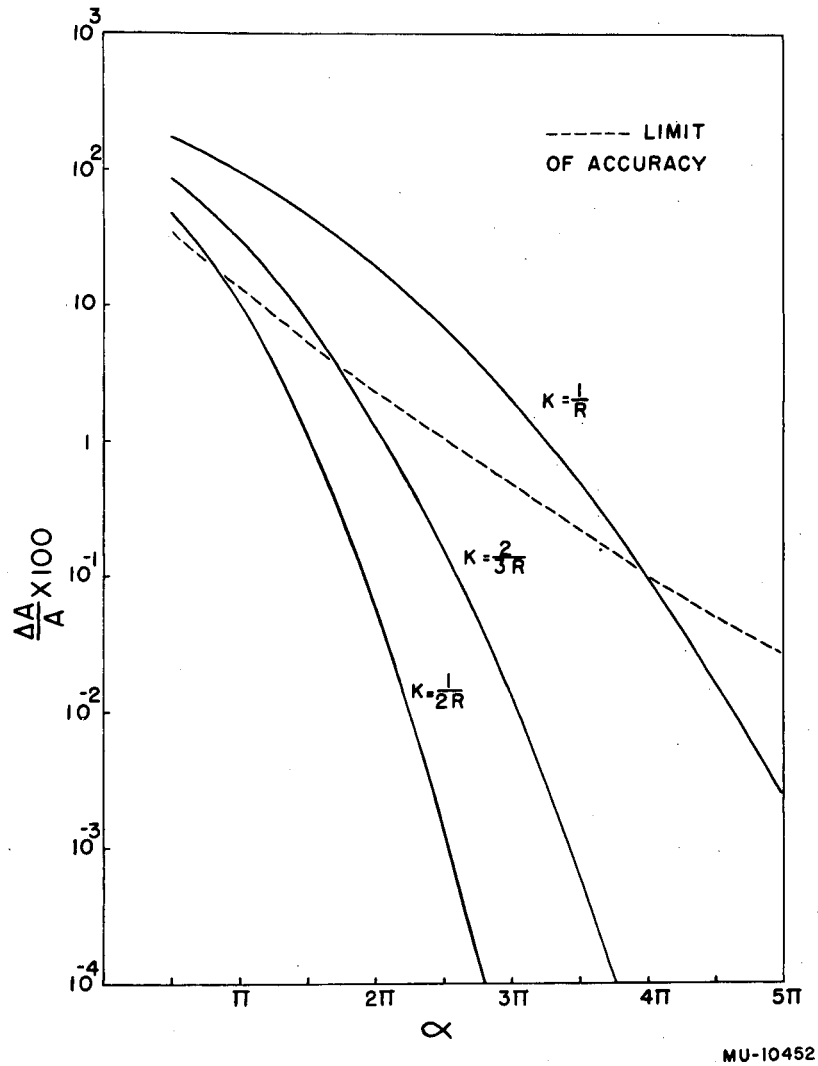

Fig. 2. Percentage error of Madelung constant for Gaussian distributions.