AN ION GROUPING METHOD FOR CALCULATING THE MADELUNG CONSTANT FOR THE SODIUM CHLORIDE LATTICE

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ABSTRACT

A method has been developed for calculating the Madelung constant for a sodium chloride lattice. In this method, a reference ion is selected and all other ions are placed in groups around the reference ion. To include ions in all locations, seven types of groups are necessary. Recursion formulas are obtained to compute the effect of each group of ions and the Madelung constant is computed from the total effect produced by all the groups. A total of 29 cubical shells of ions around the reference ion were used in the calculation. The computation produces an oscillating function which alternately goes above and below the actual Madelung constant as the computation is expanded to include each successive shell of ions. A numerical method is described to obtain the average value of the oscillating function. A value of the Madelung constant of 1.74759 results from the abbreviated calculation.

INTRODUCTION

The Madelung constant, A, is of fundamental importance in considering the factors affecting lattice energies in crystals. That parameter takes into account the geometrical arrangement of ions in the lattice. The Madelung constant is a function only of the geometry of the crystal. However, some authors also include a factor to correct for a different ratio of cations to anions in the formula[1]. As a physical quantity, the Madelung constant for a 1 : 1 salt gives the ratio of the energy released when 1 mole of lattice is formed to that released when 1 mole of ion pairs is formed from the gaseous ions.

Evaluation of the Madelung constant is, in principle, a straightforward procedure[2, 3]. The usual way is to consider the electrical potential generated at a reference ion in the crystal and then arriving at a series of terms which take into account the number of ions and their respective distances from the reference ion. For the sodium chloride structure, such a series of terms has as the first few members

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - 3 + \dots$$

This series converges only very slowly. Various techniques for obtaining the sum have been employed[4-6].

However, a major difficulty arises when a large number of ions is considered as to how to derive all the terms necessary to evaluate the Madelung constant. In one method, a Gaussian distribution of charge is considered to reside at each lattice point and these Gaussian distributions are combined to produce the potential[4, 7]. However, this combination of overlapping Gaussian distributions is complex and involves a choice of the ratio of the width to height of the Gaussian.

In the present paper, we present a geometrical approach to calculating the Madelung constant for the sodium chloride lattice which makes use of the fact that all the ions in this type of lattice can be grouped into a limited number of areas within the overall lattice. Thus, it is possible to generate recursion relationships to take into account the effect of each area upon the summation.

METHOD

The procedure used for evaluation of the Madelung constant consists of choosing a reference ion (RI) of positive charge around which cubical shells of ions are considered. Figure 1 shows the arrangement of ions in a layer of such a crystal. The value of A depends on the arrangement and respective distance of ions from the RI. The Madelung constant for a particular structure is the summation of series of terms which are functions of the numbers of ions and the reciprocal of the distance of separation.

If one starts with the RI at the center and constructs the first cubical shell ($S = 1$), that shell contains three ions along each edge. It therefore contains a total of 27 ions (26 plus RI). However, it contains 12 positive ions but 14 negative ions. Similarly, the second shell ($S = 2$) is a cube having five ions on an edge with RI at the center and it contains 125 ions. The number of ions in any cubic shell is computed
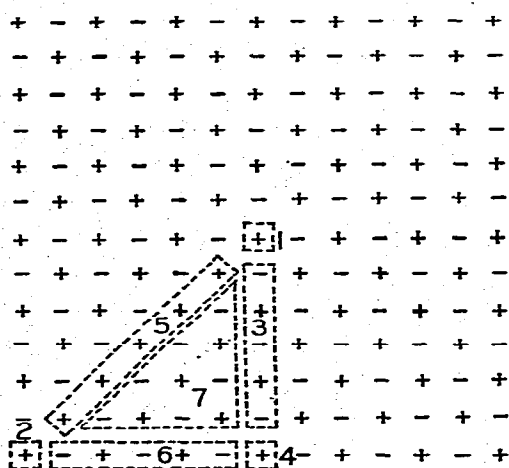

Fig. 1. A layer in the NaCl lattice. The numbered areas refer to eqns. (1–7) which give the contributions to the Madelung constant from ions in each region, respectively.

TABLE 1

IONIC COMPOSITION OF SHELLS AROUND THE REFERENCE ION, RI

Shell, S	No. of ions on edge, n	No. of ions in		No. of positive ions	No. of negative ions	Difference
		Cube	Outer shell			
1	3	27	26	12	14	2
2	5	125	98	50	48	2
3	7	343	218	108	110	2
4	9	729	386	174	172	2
5	11	1331	602	300	302	2

by cubing the number of ions, n, on an edge and subtracting from this the number of ions in all the inner shells. This number of ions in the inner shells is given by $(n - 2)^3$. These results, as well as the numbers of ions of each charge, are summarized in Table 1 for the first few shells. From the results given in Table 1, it is readily apparent that in successive shells the number of positive and negative ions differs by two and that the ion present in the majority alternates in successive shells.

Although the species in the majority depends upon the specific shell, the pattern of charge distribution can be predicted for any shell. The following method was developed utilizing cubical symmetry which makes it possible to consider one face of a cube and extend the results to three dimensions. The RI was chosen to be of unit positive charge although a negatively charged ion could also be used with modification of the equations. In the equations developed, the denominators represent the distances from the RI to specific locations on cubical shells surrounding the RI in units of the length of a unit cell. The numerators of the equations include the sign of the charge on the ions and the number of equivalent ions on any particular shell. All ions in the crystal are assigned to one of seven regions and an equation is developed to express the contribution of the ions each region. Then, the Madelung constant is the sum of all these contributions. Equations to compute all the necessary terms in the Madelung expression are derived as follows.

Figure 1 shows an extended array of ions in a sodium chloride lattice. On each of the six faces of a cubical shell there is a central ion and there are six equivalent central ions in each shell. These are labeled as area 1 in Fig. 1. The electrostatic charge alternates in sign for each successive shell. Equation (1) represents the contribution of the six equivalent ions for any shell, S.

$$A_1 = \sum_{S=1}^{\infty} \frac{6(-1)^S}{S} \tag{1}$$

Since every cubic shell has eight corners, there are eight ions on the corners of each cubic shell (area 2 in Fig. 1). Equation (2) represents this contribution to the Madelung constant.

$$A_2 = \sum_{S=1}^{\infty} \frac{8(-1)^S}{S\sqrt{3}} \tag{2}$$

Suppose a line is drawn from the center of any edge of a cubic shell to an ion on the center of that face. Along that line are ions of alternating sign of charge (area 3 in Fig. 1). The number of such ions in each shell is a function of S and the contribution to A from these ions is given by eqn. (3).

$$A_3 = \sum_{S=1}^{\infty} \sum_{a=1}^{(S-1)} \frac{24(-1)^{S+a}}{\sqrt{S^2 + a^2}} \tag{3}$$

Each cubic shell has twelve edges. There are twelve equivalent ions in each shell that are situated at the midpoints of the edges between any two adjacent corners (area 4 in Fig. 1). The contribution of these twelve ions in each shell is given by eqn. (4)

$$A_4 = \sum_{S=1}^{\infty} \frac{12}{S\sqrt{2}} \tag{4}$$

Along a diagonal line from the center of any face of a cube to any corner on that face there are ions whose charge depends only on the shell, S. For one shell they are all positive and for the next they are all negative (area 5 in Fig. 1). Equation (5) gives the contribution of the ions in this area of the cubic shells.

$$A_5 = \sum_{S=1}^{\infty} \sum_{a=1}^{(S-1)} \frac{24(-1)^{S}}{\sqrt{S^2 + 2a^2}} \tag{5}$$

Along the edge of a cube from the midpoint of the edge to either adjacent corner there are ions of alternating charge sign (area 6 in Fig. 1). Equation (6) gives the contribution of these ions to the Madelung constant.

$$A_6 = \sum_{S=1}^{\infty} \sum_{a=1}^{(S-1)} \frac{24(-1)^{a}}{\sqrt{2S^2 + a^2}} \tag{6}$$

Beginning with the shell $S = 3$, and for all subsequent shells, ions of alternating charges appear in the four quadrants of each face of the cube, both above and below the diagonals of those faces (area 7 in Fig. 1). The contribution from such ions becomes important for large values of S, and eqn. (7) takes into account these contributions to A.

$$A_7 = \sum_{S=1}^{\infty} \sum_{b=1}^{(S-2)} \sum_{a=(b+1)}^{(S-1)} \frac{48(-1)^{(S+a+b)}}{\sqrt{S^2 + a^2 + b^2}} \tag{7}$$

The Madelung constant is the sum of the contributions from ions in these seven areas of the lattice, each summed over an infinite number of cubic shells.

$$A = \sum_{i=1}^{7} A_i \tag{8}$$

RESULTS AND DISCUSSION

The Madelung constant for the sodium chloride structure was computed using eqns. (1–7). In the present work, the first 29 cubic shells were included in the calcula-

TABLE 2

CALCULATED VALUES OF THE MADELUNG CONSTANT FOR SUCCESSIVE SHELLS[a]

Shell, S	A	Shell, S	A
1	2.13352078	16	1.71257368
2	1.51664634	17	1.78055603
3	1.91250398	18	1.71635648
4	1.61926968	19	1.77717230
5	1.85253549	20	1.71940117
6	1.65874229	21	1.77441809
7	1.82454423	22	1.72190458
8	1.67964125	23	1.77213269
9	1.80833819	24	1.72399928
10	1.69257893	25	1.77020578
11	1.79776892	26	1.72577779
12	1.70137660	27	1.76855915
13	1.79033126	28	1.72730669
14	1.70774735	29	1.76713579
15	1.78481299		

[a] The value for a given shell includes the contribution from all shells of lower S.

tion which thus takes into account the interactions of 24389 ions. The results obtained are shown in Table 2. It is apparent that this summation of interactions to obtain the Madelung constant is convergent. As each successive shell is included in the calculation, the approximate Madelung constant alternates from a value above to a value below the correct one. It can be shown by the ratio test that the series is absolutely convergent.

As the number of shells becomes large, the computation becomes so slow that the computation was truncated. Figure 2 shows the variation in the computed value
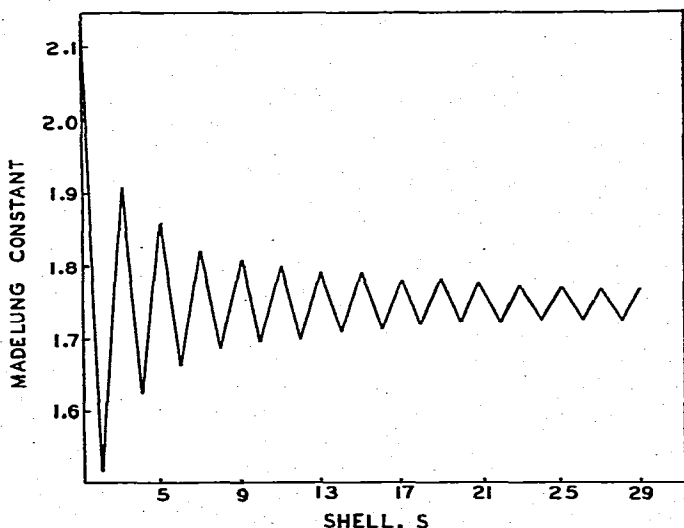

Fig. 2. The approximate Madelung constant obtained by summing the contributions of succeeding shells of ions. The contribution from all inner shells is cumulative.
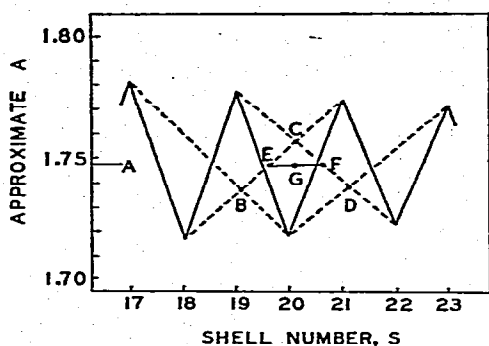
Fig. 3. Graphical method for determining the mean values of the oscillating function.

of the Madelung constant as the number of shells increases. Although the summation is convergent, the rate at which it converges is far too slow to be a practical method. The problem then is to determine the average value of this oscillating function. An attempt was made to represent the data points on either side of the true value by an exponentially decaying sine wave. This attempt, however, was not successful. A second attempt, also unsuccessful, was to take an arithmetic average of these points. This procedure yields a value of 1.7565, the correct value being 1.7476 to the same number of decimal places.

The most successful method we have found to obtain the asymptotic value of the oscillating function is a numerical one utilizing the point-slope equation of a linear function and arithmetic averaging. To illustrate the method, a group of seven approximate values for the Madelung constant were chosen. The values arbitrarily chosen were those obtained from the computation for the 17th through the 23rd shells ($S = 17$ to $S = 23$). Figure 3 shows the necessary geometrical reference for this technique. The point-slope method for determining the equation of a line was used to calculate the X and Y coordinates of the points B, C, and D. Next, the Y coordinate for point E was calculated by averaging the Y coordinates of points B and C and that of point F by averaging those of C and D. Finally, point G was determined by averaging points E and F. Table 3 shows the numerical values obtained for these points with G representing the Madelung constant. The average value of the

TABLE 3

DATA USED IN THE CALCULATION OF THE AVERAGE VALUE OF THE OSCILLATING FUNCTION FOR SHELLS 17 THROUGH 23

Point	X Coordinate	Y Coordinate
B	19.1024	1.73770
C	20.0974	1.75696
D	21.0931	1.73862
E		1.74733
F		1.74779
G		1.74759

Y coordinate obtained in this way is 1.74759 while the true Madelung constant is 1.74756 to the same number of decimal places. It is readily apparent that the use of a limited number of approximate values of the Madelung constant obtained by considering a limited number of cubic shells can lead to an accurate value of the Madelung constant. It is also possible to use a smaller number of approximate solutions or to use shells of smaller S. For example, if the calculated values for shells $S = 3$ to $S = 9$ are used, an average value of 1.74721 results. This value is within 0.02% of the correct value and is obtained by considering only 729 ions instead of the 24389 ions considered in the first 29 shells. However, if shells $S = 1$ to $S = 7$ are used, the average value obtained is 1.78749. Obviously more accurate values are obtained by considering larger shells where the convergence is more rapid.

The method described in this work appears to be capable of providing accurate values for Madelung constants with less computation than previous methods. We are currently extending this method to lattices of lower symmetry.

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