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Note

AN AVERAGING PROCESS FOR CALCULATING THE MADELUNG CONSTANT FROM THE ION GROUPING METHOD

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In our previous paper, it was shown that an ion grouping method provides terms for a Madelung constant summation for the sodium chloride lattice [1]. In that procedure, a reference ion is chosen and the other ions surrounding it are grouped into one of seven groups. In considering a number of cubic shells around the reference ion, an oscillating series of values is obtained [1]. This series converges slowly and an average value must be obtained based on the computed value for several cubic shells. A graphical method was developed that gave the approximate Madelung constant. We describe here another process for finding the value of the series that provides increased accuracy.

METHOD

An alternate method of obtaining the value of the Madelung constant is based on averaging the Madelung constants for adjacent shells and then using adjacent pairs of the new averages to obtain additional averages [2]. The process is repeated until only one value remains. The Madelung values for the successive shells are represented as $A_S^{(0)}$ ($S = 1$—29 in this case). Then, the average values are obtained, $A_S^{(1)}$, where

$$A_S^{(k+1)} = \tfrac{1}{2}(A_{S+1}^{(k)} + A_S^{(k)})$$

This process is repeated to find the successive averages $A_S^{(1)}$, $A_S^{(2)}$, ..., until only $A_1^{(S-1)}$ remains. Using this technique, rapid convergence is obtained. A program was written to carry out this procedure using a Texas Instruments Programmable TI-59 calculator in which the initial data are entered.

Using the shell-by-shell Madelung constants presented in our earlier paper, the convergence is obtained at $A_S^{(22)}$ where six averages remain. At this point, the value obtained is 1.74756495 for all of the six values. This is the correct Madelung constant for the sodium chloride lattice to nine decimal places. It is likely that the value of $A_S^{(28)}$ would be accurate to 10 or 11 deci-

TABLE 1

Successive averaging of Madelung constants from shells of ions in the sodium chloride lattice

S	$A_S^{(0)}$ *	$A_S^{(1)}$	$A_S^{(2)}$	$A_S^{(3)}$	$A_S^{(22)}$
1	2.13352078	1.82508356	1.76982936	1.755030178 . . .	1.747564595
2	1.51664634	1.71457516	1.74023099	.	
3	1.91250398	1.76588683	.	.	
4	1.61926968	.	.	.	
.	.	.	.		
.	.	.			
.	.				

* A complete list of the Madelung constants including effects of 29 successive shells can be found in ref. 1.

mal places. The procedure is outlined in Table 1.

The results shown here indicate that an accurate value of the Madelung constant for the sodium chloride lattice can be obtained from this averaging technique. In fact, even five or six shells can yield a value correct to two or three decimal places. Using all 29 shells, the Madelung constant is accurate to nine decimal places. Clearly, this method is a successful means of obtaining the Madelung constant from the slowly converging series.

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REFERENCES

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