

Madelung Constants of NaCl and CsCl Structures Using Screened Coloumb Potential

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Abstract

A simple, direct, and easily computable and convergent series obtained from the screened Coulomb potential is used to calculate the Madelung constants of the NaCl and CsCl ionic crystals structures. Two FORTRAN codes were written and executed, the first, to obtain the series and the second to fit the series to a quadratic polynomial from which the Madelung constant is obtained. The Madelung constants are found to be 1.746941 and 1.761997 for the NaCl and CsCl structures respectively.

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Introduction:

The Madelung constant, one of the important constants in condensed matter physics, is physically related to the electrostatic interaction of an ion with all other ions in a perfect ionic crystal and it depends on the geometric arrangement of constituent ions in the crystal structure. It is named after Erwin Madelung, a German physicist [1]. The coulombic electrostatic energy, U between two ions of opposite charge is given by the relation

$$U = - \frac{Z^2 e^2}{4\pi\epsilon_0 r}, \quad (1)$$

where Z is the number of 'charges' in each of the ions, e is the electronic charge, ϵ_0 is the permittivity of free space and r is the inter-ionic distance. For more than one ionic pair of charges, and in particular for one mole of the ionic pair, the electrostatic energy depends on the number of ions and also on A , their geometrical arrangement in space [2], and is given by

$$U = - \frac{NZ^2 A e^2}{4\pi\epsilon_0 r}, \quad (2)$$

where N is the Avogadro number and A is the dimensionless constant known as the Madelung constant.

For ions in linear arrangement (one dimensional lattice) A can be written as [3]

$$A = \sum_{-\infty}^{+\infty} \frac{(-1)^{|x-1|}}{|x|}; x \neq 0, \quad (3)$$

where x is distance of respective ions along the x -axis from the reference ion. Assigning Cartesian coordinates to the points, the expression becomes:

$$A = \sum_{i=-\infty}^{+\infty} \sum_{j=0}^0 \sum_{k=0}^0 \frac{(-1)^{|i+j+k-1|}}{\sqrt{i^2+j^2+k^2}}; i \neq 0.$$

For a three dimensional distribution of charges the Madelung constant is given as [4]

$$A = \sum_{i=-\infty}^{+\infty} \sum_{j=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \frac{(-1)^{|i+j+k-1|}}{\sqrt{i^2+j^2+k^2}}; (i, j, k) \neq (0,0,0).$$

However, it has been shown [5] that A can be expressed as

$$A = \sum_j \frac{(\pm)}{p_{ij}}, \quad (4a)$$

where p_{ij} is the nearest-neighbour distance. Another equivalent definition is

$$\frac{A}{r} = \sum_j \frac{(\pm)}{r_j}, \quad (4b)$$

where, r_j is the distance of the j th ion from the reference ion and r is the nearest-neighbour distance. It must be emphasized that the value of A depend on whether it is defined in terms of the nearest-neighbour distance r or in terms of the lattice constant a or in terms of some other relevant length [6].

In 1921, Ewald worked out a convergent series expansion for A applicable to arbitrary crystals. For the rest of the 20th century, new computational representations such as the Riemann, Benson-Mackenzie and the Hautot formulae have arisen, in the form of convergent series [7]. For crystals in particular, the Riemann approach gives rise to what is known in condensed matter physics as the Ewald expansion [8].

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The Riemann formula for A takes the form of a rapidly convergent expansion

$$\frac{\Gamma(s)}{\pi^2} A(s) = -\frac{1}{s} + \sum'_{x,y,z \in Z} \frac{\Gamma(s, \pi r^2) (-1)^{x+y+z}}{(\pi r^2)^s} + \sum_{k \in Z^3} \frac{\Gamma(\frac{3}{2} - s, \pi |k-c|^2)}{(\pi |k-c|^2)^{\frac{3}{2}-s}}, \tag{5}$$

where r denotes the lattice radius $\sqrt{x^2 + y^2 + z^2}$, c is the vector $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$, and $\Gamma(s, \pi r^2)$ is the standard incomplete gamma function. The Ewald expansion is essentially the physical case $s = 1/2$ for this convergent formula [9].

A more elegant expansion for A started in the 1950s with the Benson-Mackenzie attractive two-dimensional formula

$$A = -12\pi \sum'_{x,y \in O^+} \text{sech}^2 \frac{\pi r}{2}, \tag{6}$$

where the summation is over positive odd integers, and $r = \sqrt{x^2 + y^2}$ is the two-dimensional lattice radius. Later, in 1975, emerged the Hautot formula

$$A = -\frac{\pi}{2} + 3 \sum'_{x,y \in Z} \frac{(-1)^x \text{cosech}(\pi r)}{r}, \tag{7}$$

where $r = \sqrt{x^2 + y^2}$ is also the two-dimensional lattice radius. The summands in these elegant formulae converge less rapidly [10].

Although Eqs (5), (6) and (7) and other representations not given here have been used to calculate Madelung constants [7, 8], they are to say the least indirect and difficult to compute. Such representations are often in reciprocal space, require the implementation of Fast Fourier Transforms (FFT), and employ complicated mathematical functions such as the gamma function. In this work, a simple, direct, and more easily computable and convergent series obtained from the screened Coulomb potential is used, to calculate the Madelung constants of the NaCl and CsCl structures.

2. The Screened Coulomb Potential

The screened Coulomb potential, Φ_{ij} can be used to calculate the Madelung constants for ionic crystals with arbitrary number of charges in a neutral cubic unit cell. It can be expressed as^[11]

$$\Phi_{ij} = \frac{\pm e^2}{4\pi\epsilon_0 r_{ij}} \exp(-\alpha r_{ij}), \tag{8}$$

where α is a damping factor, $r_{ij} = r p_{ij}$ and p_{ij} is the length of the lattice vector in terms of the nearest-neighbour distance. Choosing α to have the unit of r the above equation can be written as

$$\Phi_{ij} = \frac{\pm e^2}{4\pi\epsilon_0 r p_{ij}} \exp(-\alpha p_{ij}). \tag{9}$$

Let a hypothetical sum be defined as

$$D = \sum_{i \neq j \neq k} \frac{\pm \exp(-\alpha p_{ij})}{p_{ij}}. \tag{10}$$

Therefore Eq (9) becomes $\Phi = \frac{\pm e^2}{4\pi\epsilon_0 r} D$. If $\exp(-\alpha p_{ij}) = 1$ in Eq (10), D converges to the Madelung constant.

For the NaCl ionic crystal structure, the primitive lattice vectors are [12]

$$a_1 = \frac{x}{2}, a_2 = \frac{y}{2}, a_3 = \frac{z}{2}. \tag{11}$$

The length of the vector is $(i a_1 + j a_2 + k a_3)$, therefore the length of the vector p_{ij} in terms of the nearest-neighbour distance in the NaCl structure is therefore given by

$$p_{ij} = \sqrt{i^2 + j^2 + k^2}. \tag{12}$$

For the CsCl ionic crystal structure, the primitive lattice vectors are^[12]:

$$a_1 = \frac{(x+y-z)}{2}, a_2 = \frac{(-x+y+z)}{2}, a_3 = \frac{(x-y-z)}{2}. \tag{13}$$

Therefore the length of the vector p_{ij} in terms of the nearest-neighbour distance is therefore given by

$$p_{ij} = \frac{\sqrt{(i-j+k)^2 + (i+j-k)^2 + (-i+j+k)^2}}{\sqrt{3.0}}. \tag{14}$$

3 Procedure

Two FORTRAN programs were written. The first program evaluates D , the hypothetical sum and employs the appropriate lattice vector p_{ij} as in Eqs (12) and (14) for NaCl and CsCl ionic structures respectively. The hypothetical sum is evaluated for different values of the damping factor α : $0 > \alpha \geq 1$. The program prompts for the number of iterations for the evaluation of the sum; and the results is printed out in a file.

As stated above, if $\exp(-\alpha p_{ij}) = 1$, in Eq (10), D converges to the Madelung constant. It should, however, be noted that even though $\exp(-\alpha p_{ij}) = 1$ only if α is equal to zero, the Madelung constant can not be directly obtained from Eq (10) because D vanishes at $\alpha = 0$. Thus the value of D as α approaches zero can only be obtained numerically by extrapolation. The data generated was used to plot a graph D versus α . The form of the curve obtained suggests that it can be approximated by a polynomial of degree two. The second program written fits the curve with a polynomial of degree two (i.e. $y = ax^2 + bx + c$) using Discrete Least-Square Approximation. The intercept on the vertical axis (i.e. c), which is an extrapolated value of D at $\alpha = 0$ is the Madelung constant of the ionic crystal structure under investigation.

4 Result

Table 1 below, contains the computed values of *D* for various α for both NaCl and CsCl. The variation of *D* with α are shown in Figures 1 and 2 for NaCl and CsCl respectively.

Table 1 Values of α and *D* obtained.

Alpha α	D	
	NaCl	CsCl
0.1000000	1.649507	1.664694
0.2000000	1.555181	1.570164
0.3000000	1.464720	1.479652
0.4000000	1.378054	1.392856
0.5000000	1.295092	1.309733
0.6000000	1.215860	1.230313
0.7000000	1.140266	1.154916
0.8000001	1.068238	1.082315
0.9000001	0.9997624	1.014162
1.000000	0.9346342	0.9478924

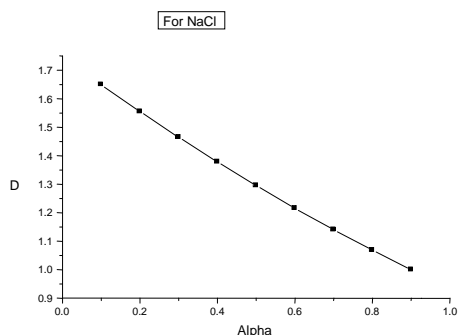


Fig. 1 D against Alpha for NaCl Structure.

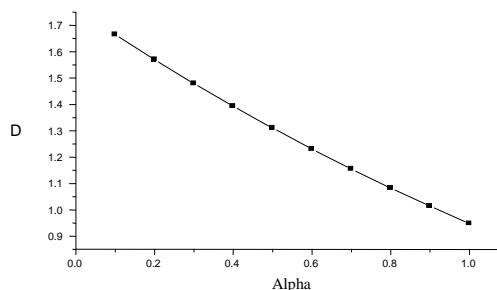


Fig. 2 D against Alpha for CsCl Structure.

For NaCl structure, the polynomial is,

$$P_{NaCl}(x) = 0.182952295568833 x^2 - 0.994992200199242 x + 1.74694054260560$$

The calculated Madelung constant for NaCl ionic crystal structure, i.e. the intercept on the vertical axis, $c = 1.74694054260560$

For CsCl structure the polynomial is,

$$P_{CsCl}(x) = 0.181316307799206 x^2 - 0.994789824771478 x + 1.76199732916432$$

The intercept on the vertical axis $c = 1.76199732916432$. The calculated Madelung constant for CsCl ionic crystal structure is therefore 1.76199732916432

TABLE 2 Madelung constant of NaCl and CsCl structures.

Crystal Structure	This work	Other work
NaCl	1.746941	1.74756[13], 1.7476[14], 1.747558[2], 1.747564594633.....[8]
CsCl	1.761997	1.76267[13], 1.7627[14], 1.762670[2], 1.76267477[15]

5. Conclusion

The Madelung constant is found to be 1.746941 for the NaCl structure and 1.761997 for the CsCl structure. These are in good agreement with values reported in the literature. The difference between our value of *A* for the NaCl structure and the most precise and hopefully most accurate value[8] is -6.24×10^{-4} . In the case of the CsCl structure, the difference between the value of our computed *A* and the most accurate value[15] is -6.78×10^{-4} . Thus the absolute percentage errors in our Madelung constants are 0.0357% and 0.0385% for the NaCl and CsCl structures respectively. The novelty of our work is its ability to produce the achieved accuracy considering the little computational effort it requires.

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