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ORIGINAL PAPER

# Corner ion, edge-center ion, and face-center ion Madelung expressions for sodium chloride

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**Abstract** Building on work of Tyagi (Progr Theor Phys 114(3):517–521, 2005), we present expressions for calculating the corner ion, edge-center ion, and face-center ion Madelung constants for bulk sodium chloride crystals.

**Keywords** Madelung constant · Corner ion · Edge-center ion · Face-center ion · NaCl

In [1], Crandall gives a historical overview of attempts to evaluate the Madelung constant for bulk ionic crystals. For sodium chloride he gave an expression for this in terms of the following series.

$$\sum_{x,y,z}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \approx -1.74756459463\ldots. \tag{1}$$

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The prime denotes that the sum is over all triples $(x, y, z)$ that are not identically zero. This sum represents the charge on an ion in an infinite cubic lattice. In [2], Tyagi gives a representation of the Madelung constant that is the sum of a rapidly converging series and the fundamental constant

$$-\frac{1}{8}-\frac{\ln 2}{4\pi}-\frac{4\pi}{3}+\frac{1}{2\sqrt{2}}+\frac{\Gamma\left(\frac{1}{8}\right)\left(\frac{3}{8}\right)}{\pi^{3/2}\sqrt{2}}\approx -1.74756459\underline{78}\ldots, \tag{2}$$

which alone agrees with the Madelung constant to ten decimal places.

Madelung constants are defined as single ion values, relating to individual ions in a crystal lattice [3]. Only in a bulk (infinitely large) crystal can all the single ion values be considered to be equal, calculable by evaluating Coulombic lattice sums. However, in any real (non-infinite) crystal the single-ion Madelung Constants for surface ions differ significantly from those within the bulk of the crystal. Taylor [4] shows that in a finite crystal, the error between the bulk Madelung constant and an ion's Madelung constant is inversely proportional to the distance between the ion and the closest face of the crystal.

In the spirit of Crandall's work the surface Madelung constants can also be determined using series expansions. In assembling these series it is important that each Coulombic interaction is counted once only. The determination of surface Madelung constants may be of practical interest as it is at the surface where many important and useful reactions occur.

We will consider three different situations related to the cubic lattice—corner ion, edge-center ion, and face-center ion. In this article, we wish the provide evaluated expressions for approximations to $M_{\text{corner}}$, $M_{\text{edge}}$, and $M_{\text{face}}$. As in Crandall's overview, we take a number to be "evaluated" when it can be written as a numerical combination of fundamental numbers including evaluations of Dirichlet $L$-series.

We are interested in the three infinite sums

$$\begin{gathered} M_{\text{corner}}={\sum_{x,y,z\geq 0}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \\ M_{\text{edge}}={\sum_{\substack{-\infty<x<+\infty\\ y,z\geq 0}}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \qquad M_{\text{face}}={\sum_{\substack{-\infty<x,y<+\infty\\ z\geq 0}}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}. \end{gathered} \tag{3}$$

Again, the prime excludes the case when $x$, $y$, and $z$ are all zero. As discussed in Borwein, Borwein, and Taylor [5], it is not evident that the infinite sum of Eq. (1) converges. An easy-to-read discussion of this non-eventuality is given by Burrows and Kettle in [6]. In fact, the authors of [5] revisit a proof of Emersleben which shows that when Eq. (1) is summed by a method of expanding spheres, the sum in question diverges. As such, it must not be taken for granted that the sums in Eq. (3) converge; we prove that they do in Theorems 8–10. Our argument incorporates lattice sums in three dimensions, two dimensions, and one dimension; define

$$M_3={\sum_{x,y,z}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \qquad M_2={\sum_{x,y}}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} \qquad M_1={\sum_{x}}' \frac{(-1)^{x}}{\sqrt{x^2}}. \tag{4}$$

In addition, we will refer repeatedly to two convergence results from [5]; we state these results for completeness after a few definitions.

**Definition 1** For every positive integer $n$, define three finite sums $S_3(n)$, $S_2(n)$, and $S_1(n)$ as follows:

$$S_3(n) = \sum_{-n\le x,y,z\le n}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \qquad S_2(n) = \sum_{-n\le x,y\le n}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}$$
$$S_1(n) = \sum_{-n\le x\le n}' \frac{(-1)^{x}}{\sqrt{x^2}}.$$

**Theorem 2** (Theorem 4 in [5]) $\lim_{n\to+\infty} S_3(n)$ *exists.*

**Theorem 3** (Theorem 2 in [5]) $\lim_{n\to+\infty} S_2(n)$ *exists.*

*Remark 4* It is also well known that the doubly infinite alternating harmonic series $\lim_{n\to+\infty} S_1(n)$ converges and evaluates to $-2\ln 2$.

The significance of these theorems is that the sums in Eq. (4) converge when the terms in the sums are grouped in expanding cubes from the origin. Therefore, it makes sense to discuss these sums and calculate the appropriate limits. We use a similar strategy to prove the convergence of the sums in Eq. (3).

As these latter sums are subsets of the three-dimensional lattice, it is natural that in addition to convergence results in the three-dimensional lattice, we will need convergence results for subsets of the two-dimensional lattices as well. We will make use of the following definitions.

**Definition 5** For every positive integer $n$, define $S_2^+(n)$, $S_2^{++}(n)$, $S_3^+(n)$, $S_3^{++}(n)$, and $S_3^{+++}(n)$ as follows:

$$S_1^+(n) = \sum_{0\le y\le n}' \frac{(-1)^y}{y} \qquad S_2^+(n) = \sum_{\substack{-n\le x\le n\\ 0\le y\le n}}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} \qquad S_2^{++}(n) = \sum_{0\le x,y\le n}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}$$
$$S_3^+(n) = \sum_{\substack{-n\le x,y\le n\\ 0\le z\le n}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} \qquad S_3^{++}(n) = \sum_{\substack{-n\le x\le n\\ 0\le y,z\le n}}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}$$
$$S_3^{+++}(n) = \sum_{0\le x,y,z\le n}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}$$

We use a convention that the number of plus signs in the superscript corresponds to how many coordinates are restricted to be non-negative.

Note that the alternating harmonic series $\lim_{n\to+\infty} S_1^+(n)$ converges and has limit $M_1/2 = -\ln 2$. In addition, the series $M_2 = \lim_{n\to+\infty} S_2(n)$ is studied in many places including [7]; we have

$$M_2 = 4\left(\sqrt{2}-1\right)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right) \approx -1.61554262671\ldots,$$

where $\zeta(s)$ is the Riemann zeta function, and $L_{-4}(s) = \sum_{x\geq 0}(-1)^x(2x+1)^{-s}$ is a Dirichlet $L$-function.

We prove each of the following theorems by repartitioning two halves of a lattice into a lattice of full dimension and a lattice of one smaller dimension. For example, in Theorem 6, summing over the upper half of the $xy$-plane and the lower half of the $xy$-plane is the same as summing over the whole $xy$-plane and over the $x$-axis.

**Theorem 6** $\lim_{n\to+\infty} S_2^+(n)$ *exists and equals* $2\left(\sqrt{2}-1\right)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right) - \ln 2.$

*Proof* We have that

$$\begin{aligned}
S_2^+(n) &= \frac{1}{2}\left[\sum_{\substack{-n\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{\substack{-n\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}\right]\\
&= \frac{1}{2}\left[\sum_{\substack{-n\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{\substack{-n\leq x\leq n\\ -n\leq y\leq 0}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}\right]\\
&= \frac{1}{2}\left[\sum_{-n\leq x,y\leq n}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{-n\leq x\leq n}{}' \frac{(-1)^{x+0}}{\sqrt{x^2+0^2}}\right]\\
&= \frac{1}{2}\left[S_2(n) + S_1(n)\right].
\end{aligned}$$

The limit $\lim_{n\to+\infty}\frac{1}{2}\left[S_2(n)+S_1(n)\right]$ exists and equals $\frac{1}{2}M_2 + \frac{1}{2}M_1$. Averaging the exact values for $M_2$ and $M_1$ completes the proof. □

**Theorem 7** $\lim_{n\to+\infty} S_2^{++}(n)$ *exists and equals* $\left(\sqrt{2}-1\right)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right) - \frac{3}{2}\ln 2.$

*Proof* We have that

$$\begin{aligned}
S_2^{++}(n) &= \frac{1}{2}\left[\sum_{\substack{0\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{\substack{0\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}\right]\\
&= \frac{1}{2}\left[\sum_{\substack{0\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{\substack{-n\leq x\leq 0\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}}\right]\\
&= \frac{1}{2}\left[\sum_{\substack{-n\leq x\leq n\\ 0\leq y\leq n}}{}' \frac{(-1)^{x+y}}{\sqrt{x^2+y^2}} + \sum_{0\leq y\leq n}{}' \frac{(-1)^{y}}{y}\right]\\
&= \frac{1}{2}\left[S_2^+(n) + S_1^+(n)\right].
\end{aligned}$$

The limit $\lim_{n\to+\infty}\frac{1}{2}\left[S_2^+(n)+S_1^+(n)\right]$ exists and equals $\frac{1}{4}M_2+\frac{1}{2}M_1$. □

By a similar technique, we prove the convergence of the sums in Eq. (3).

**Theorem 8** $M_{\text{face}}=\lim_{n\to+\infty}S_3^+(n)$ *exists and is approximately equal to*

$$M_{\text{face}}\approx-\frac{1}{16}-\frac{\ln 2}{8\pi}-\frac{2\pi}{3}+\frac{1}{4\sqrt{2}}+\frac{\Gamma\left(\frac{1}{8}\right)\left(\frac{3}{8}\right)}{2\pi^{3/2}\sqrt{2}}+2(\sqrt{2}-1)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right).$$

*Proof*

$$\begin{aligned}
S_3^+(n)&=\frac{1}{2}\left[\sideset{}{'}\sum_{\substack{-n\le x,y\le n\\0\le z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}+\sideset{}{'}\sum_{\substack{-n\le x,y\le n\\0\le z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]\\
&=\frac{1}{2}\left[\sideset{}{'}\sum_{\substack{-n\le x,y\le n\\0\le z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}+\sideset{}{'}\sum_{\substack{-n\le x,y\le n\\-n\le z\le 0}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]\\
&=\frac{1}{2}\left[\sideset{}{'}\sum_{-n\le x,y,z\le n}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}+\sideset{}{'}\sum_{-n\le x,y\le n}\frac{(-1)^{x+y+0}}{\sqrt{x^2+y^2+0^2}}\right]\\
&=\frac{1}{2}[S_3(n)+S_2(n)].
\end{aligned}$$

The limit $\lim_{n\to+\infty}\frac{1}{2}\left[S_3(n)+S_2(n)\right]$ exists and equals $\frac{1}{2}M_3+\frac{1}{2}M_2$. Averaging the exact value for $M_2$ with the approximate value for $M_3$ given by Eq. (2) completes the proof. □

**Theorem 9** $M_{\text{edge}}=\lim_{n\to+\infty}S_3^{++}(n)$ *exists and is approximately equal to*

$$M_{\text{edge}}\approx-\frac{1}{32}-\frac{\ln 2}{16\pi}-\frac{\pi}{3}+\frac{1}{8\sqrt{2}}+\frac{\Gamma\left(\frac{1}{8}\right)\left(\frac{3}{8}\right)}{4\pi^{3/2}\sqrt{2}}+2(\sqrt{2}-1)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right)-\frac{1}{2}\ln 2.$$

*Proof*

$$\begin{aligned}
S_3^{++}(n)&=\frac{1}{2}\left[\sideset{}{'}\sum_{\substack{-n\le x\le n\\0\le y,z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}+\sideset{}{'}\sum_{\substack{-n\le x\le n\\0\le y,z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]\\
&=\frac{1}{2}\left[\sideset{}{'}\sum_{\substack{-n\le x\le n\\0\le y,z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}+\sideset{}{'}\sum_{\substack{-n\le x\le n\\-n\le y\le 0\\0\le z\le n}}\frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]
\end{aligned}$$

$$= \frac{1}{2}\left[\sum_{\substack{-n\le x,y\le n\\0\le z\le n}}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} + \sum_{\substack{-n\le x\le n\\0\le z\le n}}{}' \frac{(-1)^{x+0+z}}{\sqrt{x^2+0^2+z^2}}\right]$$
$$= \frac{1}{2}[S_3^+(n) + S_2^+(n)].$$

The limit $\lim_{n\to+\infty}\frac{1}{2}\left[S_3^+(n)+S_2^+(n)\right]$ exists and equals $\frac{1}{4}M_3+\frac{1}{2}M_2+\frac{1}{4}M_1$. □

**Theorem 10** $M_{\text{corner}} = \lim_{n\to+\infty} S_3^{+++}(n)$ *exists and is approximately equal to*

$$M_{\text{corner}} \approx -\frac{1}{64} - \frac{\ln 2}{32\pi} - \frac{\pi}{6} + \frac{1}{16\sqrt{2}} + \frac{\Gamma\left(\frac{1}{8}\right)\left(\frac{3}{8}\right)}{8\pi^{3/2}\sqrt{2}}$$
$$+\frac{3}{2}(\sqrt{2}-1)\zeta\left(\frac{1}{2}\right)L_{-4}\left(\frac{1}{2}\right) - \frac{3}{4}\ln 2.$$

*Proof*

$$S_3^{+++}(n) = \frac{1}{2}\left[\sum_{0\le x,y,z\le n}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} + \sum_{0\le x,y,z\le n}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]$$
$$= \frac{1}{2}\left[\sum_{0\le x,y,z\le n}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} + \sum_{\substack{-n\le x\le 0\\0\le y,z\le n}}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}}\right]$$
$$= \frac{1}{2}\left[\sum_{\substack{-n\le x\le n\\0\le y,z\le n}}{}' \frac{(-1)^{x+y+z}}{\sqrt{x^2+y^2+z^2}} + \sum_{0\le y,z\le n}{}' \frac{(-1)^{0+y+z}}{\sqrt{0^2+y^2+z^2}}\right]$$
$$= \frac{1}{2}[S_3^{++}(n) + S_2^{++}(n)].$$

The limit $\lim_{n\to+\infty}\frac{1}{2}\left[S_3^{++}(n)+S_2^{++}(n)\right]$ exists and equals $\frac{1}{8}M_3+\frac{3}{8}M_2+\frac{3}{8}M_1$. □

Just as in [2], the fundamental constants $M_{\text{corner}}$, $M_{\text{edge}}$, and $M_{\text{face}}$ agree to ten digits with the true values, as shown here.

| | True value | Approximation |
|---|---|---|
| $M_{\text{corner}}$ | −1.34413444476 ... | −1.3441344447$\underline{8}$ ... |
| $M_{\text{edge}}$ | −1.59123605229 ... | −1.59123605$\underline{233}$ ... |
| $M_{\text{face}}$ | −1.68155361067 ... | −1.68155361$\underline{075}$ ... |

This paper describes the evaluation of Madelung constant for corner, edge-center, and face-center ions for bulk NaCl crystals using appropriate convergent series. The method produces an overall series sum for the entire crystal lattice by breaking apart and reassembling larger lattices. The values generated by this approach are in excellent agreement with literature values. The methodology can be extended to determine bulk Madelung constants for crystal types other than sodium chloride, and to nanoparticles, including determinations of the surface electrostatic mapping of crystals cleaved so as to expose various planes.

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