Physics Letters A 375 (2011) 1281–1285

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Convergence analysis of the Wolf method for Coulombic interactions

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ARTICLE INFO

Article history:
Received 7 July 2010
Received in revised form 20 January 2011
Accepted 24 January 2011
Available online 2 February 2011
Communicated by A.P. Fordy

Keywords:
Lattice sums
Wolf method
Ewald method

ABSTRACT

A rigorous proof for convergence of the Wolf method (Wolf et al., 1999 [9]) for calculating electrostatic energy of a periodic lattice is presented. In particular, we show that for an arbitrary lattice of unit cells, the lattice sum obtained via Wolf method converges to the one obtained via Ewald method.

1. Introduction

The classical Madelung problem [1] has an important role in atomic and molecular simulations involving electrostatic interactions. Consider an arbitrary lattice with a unit cell that is composed of N charges $\{q_1,\dots,q_N\}$ and let linearly independent vectors $\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3\in\mathbb{R}^3$ denote the lattice vectors. We assume the charge neutrality condition for the unit cell, i.e., $\sum_{i=1}^{N} q_i = 0$. Then the Madelung problem for calculation of the total electrostatic energy of the unit cell located at the origin can be expressed as

$$\mathcal{E}_{\text{cell}} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' |\mathbf{V}\mathbf{n}+\mathbf{r}_{ij}|^{-1}, \tag{1}$$

where $\mathbf{V}=[\mathbf{e}_1\mathbf{e}_2\mathbf{e}_3]\in\mathbb{R}^{3\times 3}$ (the matrix with lattice vectors as its columns) and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, where $\mathbf{r}_i$ denotes the atomic position within the unit cell. The prime on the summation emphasizes that we exclude self-energy, i.e., for $\mathbf{n}=\mathbf{0}$ the term $i=j$ is omitted. In order to be able to use the well-established theory of multi-dimensional zeta functions [2], we introduce the following non-standard representation of electrostatic energy of a unit cell in an arbitrary lattice:

$$\mathcal{E}_{\text{cell}} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})\right]^{-1/2}, \tag{2}$$

where T stands for matrix transport and $Q_{ij}=2\mathbf{e}_i\cdot\mathbf{e}_j$ is a positive-definite matrix (twice the metric tensor), $\mathbf{p}_{ij}=\mathbf{U}\mathbf{r}_{ij}$ with $\mathbf{U}=\mathbf{V}^{-1}$ and the prime on the summation denotes the exclusion of the self-energy. For example, for an orthorhombic lattice with lattice parameters $a=|\mathbf{e}_1|$, $b=|\mathbf{e}_2|$ and $c=|\mathbf{e}_3|$ we have

$$\mathbf{Q}=\begin{pmatrix} 2a^2 & 0 & 0\\ 0 & 2b^2 & 0\\ 0 & 0 & 2c^2\end{pmatrix},\qquad \mathbf{U}=\begin{pmatrix} \frac{1}{a} & 0 & 0\\ 0 & \frac{1}{b} & 0\\ 0 & 0 & \frac{1}{c}\end{pmatrix}. \tag{3}$$

For a hexagonal lattice with unit cell vectors

$$\mathbf{e}_1=\begin{pmatrix} a\\ 0\\ 0\end{pmatrix},\qquad \mathbf{e}_2=\begin{pmatrix} \frac{1}{2}a\\ \frac{\sqrt{3}}{2}a\\ 0\end{pmatrix},\qquad \mathbf{e}_3=\begin{pmatrix} 0\\ 0\\ c\end{pmatrix}, \tag{4}$$

where a and c are unit cell parameters, we have

$$\mathbf{Q}=\begin{pmatrix} 2a^2 & a^2 & 0\\ a^2 & 2a^2 & 0\\ 0 & 0 & 2c^2\end{pmatrix},\qquad \mathbf{U}=\begin{pmatrix} \frac{1}{a} & -\frac{1}{\sqrt{3}a} & 0\\ 0 & \frac{2}{\sqrt{3}a} & 0\\ 0 & 0 & \frac{1}{c}\end{pmatrix}. \tag{5}$$

One method of calculating the above lattice sum is to use direct sums. However, it is a well-known fact that (2) is a conditionally convergent series, which means that (2) is meaningless unless the order of summation of the terms is specified. It is interesting to note that summation over regions that may seem to be natural can diverge. As an example, for a 3-dimensional NaCl-type ionic crystal, it was shown that this lattice sum does not converge over expanding spheres [3], expanding ellipsoids, and some specific expanding polygons [4], but it would converge for expanding cubes [3]. The direct summation method is not practical due to the slow rate of convergence.

Another method for dealing with (2) is to find some analytic continuation for this expression over the complex plane and then

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0375-9601/$ – see front matter
doi:10.1016/j.physleta.2011.01.048

to find some fast converging series to evaluate this analytic continuation. The celebrated Ewald method [5] uses this procedure. One can write $\mathcal{E}_{\text{cell}}$ as

$$\mathcal{E}_{\text{cell}} = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j Z_{\mathbf{Q}}(1, \mathbf{p}_{ij}), \tag{6}$$

with

$$Z_{\mathbf{Q}}(s, \mathbf{p}) = \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2}(\mathbf{n}+\mathbf{p})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p})\right]^{-s/2}, \tag{7}$$

where again the prime denotes the exclusion of any infinite summands. $Z_{\mathbf{Q}}(s, \mathbf{p})$ is a special case of the general Epstein zeta functions [2,6]. It is known that $Z_{\mathbf{Q}}(s, \mathbf{p})$ is uniformly and absolutely convergent for any complex number s with $\mathfrak{Re}(s) > 3$ and it has a meromorphic continuation to the whole complex s-plane [6,2,7]. From here on, by $Z_{\mathbf{Q}}(s, \mathbf{p})$ we mean its analytic continuation. $Z_{\mathbf{Q}}(s, \mathbf{p})$ is analytic everywhere except for the simple pole at $s = 3$ with the residue [2]

$$\operatorname*{Res}_{s=3} Z_{\mathbf{Q}}(s, \mathbf{p}) = \frac{(2\pi)^{3/2}}{\Gamma(3/2)\sqrt{\det \mathbf{Q}}} = \frac{2^{5/2}\pi}{\sqrt{\det \mathbf{Q}}}. \tag{8}$$

Using some special functions, it is possible to write $Z_{\mathbf{Q}}(s, \mathbf{p})$ and thus $\mathcal{E}_{\text{cell}}$ in terms of a rapidly converging series that recovers the standard Ewald method [8,6].

Determining the relation between the above-mentioned two methods is not a straightforward task. Specifically, in what order one should sum the terms of the series (2) to obtain the Ewald's result? Borwein et al. [3] showed that for NaCl-type crystals, summing over cubes would yield the Ewald result. It is interesting to note that $\sum'_{\mathbf{n}\in\mathbb{Z}^3} |\mathbf{n}+\mathbf{r}|^{-1}$ is not a convergent series and since all of the summands are positive, partial sums of this series would be unbounded. Thus, it is meaningless to expect to find $Z_{\mathbf{Q}}(1, \mathbf{p})$ using direct sums.

As we mentioned earlier, for NaCl-type crystals direct summation over expanding cubes converges while summation over expanding spheres diverges. One may guess that what makes the expanding cubes to converge is that, unlike expanding spheres, each cube is charge neutral, and thus it may be possible to obtain a converging sequence over spheres if one somehow converts the regular spheres to charge neutral ones. This is the main idea of the Wolf method [9] and the earlier work of Buhler and Crandall [10]. In particular, for a general lattice of charges, Wolf et al. [9] suggested that putting a mirror charge on the surface of sphere for each charge inside the sphere and neglecting the charges outside the sphere results in a convergent sequence that converges to the result obtained via Ewald method. Although they verified their method by considering several numerical examples, they did not present a rigorous proof.

In this Letter, we present the missing proof of the convergence of Wolf's method for calculating electrostatic energy of an arbitrary lattice of charges. We should mention that Buhler and Crandall [10] presented a proof for NaCl lattice with unit charges. Here we generalize their proof to arbitrary lattices. Note that Wolf et al. [9] presented two different methods, namely, damped and undamped methods. Here by Wolf method we mean the undamped method. In Section 2 we present the proof and in Section 3 we mention some concluding remarks and future directions.

2. Proof of the convergence of Wolf's method

We use the contour integral method of [10] to prove the convergence of Wolf's method. Let us first review the required preliminaries. We consider the following analytic continuation of (2)

$$\begin{aligned} E(\mathbf{Q}, s) &= \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})\right]^{-s/2} \\ &= \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j Z_{\mathbf{Q}}(s, \mathbf{p}_{ij}). \end{aligned} \tag{9}$$

Note that $E(\mathbf{Q}, 1) = \mathcal{E}_{\text{Ewald}} = \mathcal{E}_{\text{cell}}$. Let $\Psi(x)$ denote the function

$$\Psi(x) = \begin{cases} 0, & x < 1, \\ \frac{1}{2}, & x = 1, \\ 1, & x > 1. \end{cases} \tag{10}$$

Then, for $R \in \mathbb{R}^+$, where $\mathbb{R}^+$ is the set of the positive real numbers, define the spherically truncated (finite) sum

$$\begin{aligned} E_R(\mathbf{Q}, s) = \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \Bigg\{ &\Psi\left(\frac{R}{[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})]^{1/2}}\right) \\ &\times \left[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})\right]^{-s/2}\Bigg\}. \end{aligned} \tag{11}$$

Note that $E_R(\mathbf{Q}, s)$ roughly denotes the direct sum of (2) over spheres centered at charges in the unit cell located at the origin with radius R. From (10) one can see that if

$$R = \mathcal{R}(\mathbf{n}, \mathbf{p}_{ij}) := \left[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})\right]^{1/2}, \tag{12}$$

for some values of i, j, and $\mathbf{n}$, then the charges located on the surface of the sphere would have the additional weight of 1/2. But this would be irrelevant in our analysis because as we will see in the sequel, we are interested in the behavior of a continues function of R as $R \to \infty$. This can be expressed in term of $E_R(\mathbf{Q}, s)$ if R does not take the discrete values $\mathcal{R}(\mathbf{n}, \mathbf{p}_{ij})$ for $\mathbf{n} \in \mathbb{Z}^3$ and $i, j = 1, \ldots, N$, and so we can exclude those values.

In the Wolf method one considers spheres with radii R centered at each charge of the unit cell at the origin and puts a mirror charge on the surface of the sphere for each charge inside the sphere including center charges. Then energy of the unit cell, $\mathcal{E}_{\text{Wolf}}$, is calculated using only charges located on and inside these spheres. This can be written as

$$\mathcal{E}_{\text{Wolf}} = \lim_{R\to\infty}\left[E_R(\mathbf{Q}, 1) - \frac{1}{R}E_R(\mathbf{Q}, 0) - \frac{1}{R}\sum_{i=1}^{N} q_i^2\right]. \tag{13}$$

But for a lattice with N charges in its unit cell, the term $\sum_{i=1}^{N} q_i^2$ is bounded, and thus we have

$$\mathcal{E}_{\text{Wolf}} = \lim_{R\to\infty}\left[E_R(\mathbf{Q}, 1) - \frac{1}{R}E_R(\mathbf{Q}, 0)\right]. \tag{14}$$

For $c \in \mathbb{R}^+$, Perron's formula states that [11]

$$\frac{1}{2\pi\mathbb{i}}\int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} \frac{R^s}{s}\,ds = \Psi(R). \tag{15}$$

Finally, for any $c, T \in \mathbb{R}^+$ with $c > 3$ let $\alpha_{c,T}$ be the contour in the complex s-plane depicted in Fig. 1. Also let $\mathcal{S}_T = \{s \in \mathbb{C} \mid 0 < \mathfrak{Re}(s) < 3 \text{ and } |\mathfrak{Im}(s)| < T\}$. Then, the following Lemma holds.

Lemma. *Let $\epsilon \in \mathbb{R}^+$. Then there exist $c, T \in \mathbb{R}^+$ with $c > 3$, such that for any $w \in \mathcal{S}_T$ the following relation holds as $R \to \infty$:*

$$I_\alpha = \frac{1}{2\pi\mathbb{i}}\int_{\alpha_{c,T}} \frac{Z_{\mathbf{Q}}(s, \mathbf{p})R^s}{s(s-w)}\,ds = O\left(R^{\epsilon}\right). \tag{16}$$

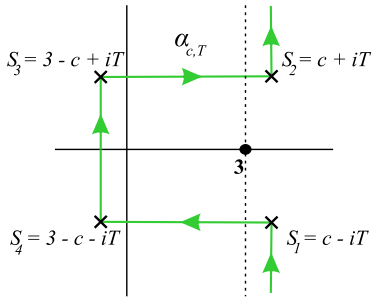

Fig. 1. The contour $\alpha_{c,T}$ in the complex s-plane.

Proof. Let $s = \sigma + \mathbb{i}t$ and $I_\alpha = \sum_{i=1}^{5} I_i$, where

$$I_1 = \frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c-\mathbb{i}T} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds,$$

$$I_2 = \frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}T}^{3-c-\mathbb{i}T} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds,$$

$$I_3 = \frac{1}{2\pi\mathbb{i}} \int_{3-c-\mathbb{i}T}^{3-c+\mathbb{i}T} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds,$$

$$I_4 = \frac{1}{2\pi\mathbb{i}} \int_{3-c+\mathbb{i}T}^{c+\mathbb{i}T} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds,$$

$$I_5 = \frac{1}{2\pi\mathbb{i}} \int_{c+\mathbb{i}T}^{c+\mathbb{i}\infty} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds. \tag{17}$$

We are going to show that all of the above integrals are bounded. For I_1 and I_5 we have $|Z_{\mathbf{Q}}(s,\mathbf{p})| = |Z_{\mathbf{Q}}(c,\mathbf{p})|$, $|R^s| = R^c$ and $[s(s-w)]^{-1} = O(t^{-2})$. Thus, these integrals are $O(R^c T^{-1})$.

Using the standard methods of analytic number theory and the Phragmén–Lindelöf theorem [12,11], we find that $|Z_{\mathbf{Q}}(s,\mathbf{p})| = O(t^{c-3/2})$ for $3-c<\sigma<c$, and hence I_2 and I_4 are $O(R^c T^{c-7/2})$. If $3<c<7/2$ and $T = R^{7/(7-2c)}$, we can conclude that I_1, I_2, I_4 and I_5 are $O(R^\epsilon)$ for any $\epsilon > 0$.

Next, note that [2]

$$Z_{\mathbf{Q}}(s,\mathbf{p}) = \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2}(\mathbf{n}+\mathbf{p})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p})\right]^{-s/2} = \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' |\mathbf{A}\mathbf{n}-\mathbf{d}|^{-s} =: \zeta_{\mathbf{A}}(s,\mathbf{d}), \tag{18}$$

where $\mathbf{A}$ is a matrix with nonzero determinant. Define

$$\Lambda_{\mathbf{A}}(s,\mathbf{d}) = \sqrt{\det\mathbf{A}}\,\pi^{-s/2}\Gamma\left(\frac{s}{2}\right)\zeta_{\mathbf{A}}(s,\mathbf{d}). \tag{19}$$

Then, we have the following functional equation [7]

$$\Lambda_{\mathbf{A}}(s,\mathbf{d}) = e^{\pi|\mathbf{d}|^2\mathbb{i}}\Lambda_{\mathbf{B}}(3-s,\mathbf{0}), \tag{20}$$

where $\mathbf{B} = \mathbf{A}^{-\mathsf{T}}$ with $-\mathsf{T}$ denoting the inverse transpose. Substituting (19) into (20) yields

$$\zeta_{\mathbf{A}}(s,\mathbf{d}) = \frac{e^{\pi|\mathbf{d}|^2\mathbb{i}}\pi^{s-3/2}\Gamma[\frac{1}{2}(3-s)]}{\det\mathbf{A}\,\Gamma(\frac{s}{2})}\zeta_{\mathbf{B}}(3-s,\mathbf{0}). \tag{21}$$

Now we replace s by $3-s$ in I_3 and use (18) and (21) to write the integral over the upper half segment as

$$\begin{aligned}
&\frac{1}{2\pi\mathbb{i}} \int_{3-c}^{3-c+\mathbb{i}T} \frac{Z_{\mathbf{Q}}(s,\mathbf{p})R^s}{s(s-w)}\,ds \\
&= \frac{1}{2\pi\mathbb{i}} \int_{c}^{c+\mathbb{i}T} \frac{Z_{\mathbf{Q}}(3-s,\mathbf{p})R^{3-s}}{(s-3)(s+w-3)}\,ds \\
&= \frac{1}{2\pi\mathbb{i}} \int_{c}^{c+\mathbb{i}T} \frac{\zeta_{\mathbf{A}}(3-s,\mathbf{d})R^{3-s}}{(s-3)(s+w-3)}\,ds \\
&= \frac{e^{\pi|\mathbf{d}|^2\mathbb{i}}\pi^{1/2}}{2(\det\mathbf{A})\mathbb{i}} \int_{c}^{c+\mathbb{i}T} \frac{\pi^{-s}\Gamma(\frac{s}{2})\zeta_{\mathbf{B}}(s,\mathbf{0})R^{3-s}\,ds}{\Gamma[\frac{1}{2}(3-s)](s-3)(s+w-3)} \\
&= \frac{e^{\pi|\mathbf{d}|^2\mathbb{i}}\pi^{1/2}}{2(\det\mathbf{A})\mathbb{i}} \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \int_{c}^{c+\mathbb{i}T} \frac{\pi^{-s}\Gamma(\frac{s}{2})|\mathbf{A}\mathbf{n}|^{-s}R^{3-s}\,ds}{\Gamma[\frac{1}{2}(3-s)](s-3)(s+w-3)},
\end{aligned} \tag{22}$$

where in the last step, since $c>3$, we use the fact that $\zeta_{\mathbf{B}}(s,\mathbf{0})$ is uniformly and absolutely convergent over the integration path. Stirling's formula states that for any fixed strip $\alpha \leqslant \sigma \leqslant \beta$, as $t\to\infty$ [11]

$$\log\left[\Gamma(\sigma+\mathbb{i}t)\right] = \left(\sigma+\mathbb{i}t-\frac{1}{2}\right)\log(\mathbb{i}t) - \mathbb{i}t + \frac{1}{2}\log(2\pi) + O\left(t^{-1}\right). \tag{23}$$

Using (23), we conclude that to bound (22) one needs to bound

$$R^{3-c}\sum_{\mathbf{n}\in\mathbb{Z}^3}|\mathbf{A}\mathbf{n}|^{-c}\int_{t_0}^{T} t^{c-7/2}e^{\mathbb{i}[t\log(t)-t-t\log(\pi R|\mathbf{A}\mathbf{n}|)]}\,ds, \tag{24}$$

where $t_0>0$ is an arbitrary constant. But using the method of stationary phase [13], it can be shown that this integral is $O(\log R)$ [10] and so I_3 is $O(R^\epsilon)$ for $\epsilon>0$. To summarize, we have proved that $I_1,\dots,I_5$ are $O(R^\epsilon)$ for $\epsilon>0$ and hence (16) holds. □

Now we state the main result of this Letter.

Theorem. *There exists $T\in\mathbb{R}^+$ such that if $s\in\mathcal{S}_T$ then*

$$E(\mathbf{Q},s) = \lim_{R\to\infty}\left[E_R(\mathbf{Q},s) - \frac{1}{R^s}E_R(\mathbf{Q},0)\right]. \tag{25}$$

In particular, setting $s=1$ yields

$$\begin{aligned}
\mathcal{E}_{\text{cell}} &= E(\mathbf{Q},1) \\
&= \lim_{R\to\infty}\left[E_R(\mathbf{Q},1) - \frac{1}{R}E_R(\mathbf{Q},0)\right] \\
&= \mathcal{E}_{\text{Wolf}}.
\end{aligned} \tag{26}$$

Proof. Choose $c, T\in\mathbb{R}^+$ in accordance with the previous Lemma and let $w\in\mathcal{S}_T$. Consider the integral

$$\begin{aligned}
I &= \frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} \frac{E(\mathbf{Q},s)R^s}{s-w}\,ds \\
&= \frac{1}{2\pi\mathbb{i}} \int_{c-\Re\mathrm{e}(w)-\mathbb{i}\infty}^{c-\Re\mathrm{e}(w)+\mathbb{i}\infty} \frac{E(\mathbf{Q},s+w)R^{s+w}}{s}\,ds.
\end{aligned} \tag{27}$$

Note that since $c > 3$, the contour of the integral is in the region of the uniform and absolute convergence of (2). Also $c - \mathfrak{Re}(w) > 0$, and hence using (15) one can write (27) as

$$\begin{aligned} I &= \frac{1}{2\pi\mathbb{i}} \int_{c-\mathfrak{Re}(w)-\mathbb{i}\infty}^{c-\mathfrak{Re}(w)+\mathbb{i}\infty} \left\{ \frac{R^{s+w}}{s} \right. \\ &\quad \left. \times \frac{1}{2} \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2} (\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}} \mathbf{Q} (\mathbf{n}+\mathbf{p}_{ij}) \right]^{-(s+w)/2} \right\} ds \\ &= \frac{R^w}{2} \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2} (\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}} \mathbf{Q} (\mathbf{n}+\mathbf{p}_{ij}) \right]^{-w/2} \\ &\quad \times \frac{1}{2\pi\mathbb{i}} \int_{c-\mathfrak{Re}(w)-\mathbb{i}\infty}^{c-\mathfrak{Re}(w)+\mathbb{i}\infty} \left(\frac{R}{[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}} \mathbf{Q} (\mathbf{n}+\mathbf{p}_{ij})]^{1/2}} \right)^s \frac{ds}{s} \\ &= \frac{R^w}{2} \sum_{i,j=1}^{N} q_i q_j \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \left[\frac{1}{2} (\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}} \mathbf{Q} (\mathbf{n}+\mathbf{p}_{ij}) \right]^{-w/2} \\ &\quad \times \Psi \left(\frac{R}{[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}} \mathbf{Q} (\mathbf{n}+\mathbf{p}_{ij})]^{1/2}} \right) \\ &= R^w E_R(\mathbf{Q}, w). \end{aligned} \tag{28}$$

Let

$$F_w(\mathbf{Q}, s) = \frac{E(\mathbf{Q}, s) R^s}{s(s-w)}. \tag{29}$$

Then, we use (28) to write

$$\begin{aligned} &\frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} F_w(\mathbf{Q}, s)\, ds \\ &= \frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} \left[\frac{E(\mathbf{Q}, s) R^s}{w} \left(\frac{1}{s-w} - \frac{1}{s} \right) \right] ds \\ &= \frac{1}{w} \left[R^w E_R(\mathbf{Q}, w) - E_R(\mathbf{Q}, 0) \right], \end{aligned} \tag{30}$$

or equivalently

$$\frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} F_w(\mathbf{Q}, s)\, ds = \frac{R^w}{w} \left[E_R(\mathbf{Q}, w) - \frac{1}{R^w} E_R(\mathbf{Q}, 0) \right]. \tag{31}$$

Next we choose the contour $\alpha_{c,T}$ as in Fig. 1. Let β denote the rectangle with vertices S_1, S_2, S_3 and S_4 (see Fig. 1). We have

$$\begin{aligned} &\frac{1}{2\pi\mathbb{i}} \int_{c-\mathbb{i}\infty}^{c+\mathbb{i}\infty} F_w(\mathbf{Q}, s)\, ds - \frac{1}{2\pi\mathbb{i}} \int_{\alpha_{c,T}} F_w(\mathbf{Q}, s)\, ds \\ &= \frac{1}{2\pi\mathbb{i}} \int_{\beta} F_w(\mathbf{Q}, s)\, ds. \end{aligned} \tag{32}$$

One can use Cauchy's Residue Theorem to calculate the right side of (32). Referring to (29), it is evident that $F_w(\mathbf{Q}, s)$ has simple poles at $s = 0$ and $s = w$ and may have a simple pole at $s = 3$. Since $E(\mathbf{Q}, s)$ is analytic at $s = 0$ and $s = w$, we obtain

$$\operatorname*{Res}_{s=0} F_w(\mathbf{Q}, s) = -w^{-1} E(\mathbf{Q}, 0), \tag{33}$$

$$\operatorname*{Res}_{s=w} F_w(\mathbf{Q}, s) = w^{-1} R^w E(\mathbf{Q}, w). \tag{34}$$

To calculate the residue at $s = 3$ we use (29) and (8) to write

$$\begin{aligned} \operatorname*{Res}_{s=3} F_w(\mathbf{Q}, s) &= \frac{R^3}{3(3-w)} \operatorname*{Res}_{s=3} E(\mathbf{Q}, s) \\ &= \frac{R^3}{6(3-w)} \sum_{i,j=1}^{N} q_i q_j \left[\operatorname*{Res}_{s=3} Z_{\mathbf{Q}}(s, \mathbf{p}_{ij}) \right] \\ &= \frac{2^{3/2} \pi R^3}{3(3-w)\sqrt{\det \mathbf{Q}}} \sum_{i,j=1}^{N} q_i q_j \\ &= \frac{2^{3/2} \pi R^3}{3(3-w)\sqrt{\det \mathbf{Q}}} \left(\sum_{i=1}^{N} q_i \right)^2 = 0, \end{aligned} \tag{35}$$

where we used the charge neutrality condition for the unit cell in the last step. Thus, we have shown that although $Z_{\mathbf{Q}}(s, \mathbf{p})$ has a simple pole at $s = 3$, charge neutrality implies that residue of $F_w(\mathbf{Q}, s)$ at $s = 3$ vanishes. Therefore, using Cauchy's Residue Theorem and Eqs. (33), (34), and (35) we conclude that

$$\frac{1}{2\pi\mathbb{i}} \int_{\beta} F_w(\mathbf{Q}, s)\, ds = -w^{-1} E(\mathbf{Q}, 0) + w^{-1} R^w E(\mathbf{Q}, w). \tag{36}$$

Substituting (31) and (36) into (32) results in

$$\begin{aligned} &\frac{1}{2\pi\mathbb{i}} \int_{\alpha_{c,T}} F_w(\mathbf{Q}, s)\, ds \\ &= \frac{R^w}{w} \left[E_R(\mathbf{Q}, w) - \frac{1}{R^w} E_R(\mathbf{Q}, 0) \right] + w^{-1} E(\mathbf{Q}, 0) \\ &\quad - w^{-1} R^w E(\mathbf{Q}, w). \end{aligned} \tag{37}$$

On the other hand, with the aid of (9), (16), and (29) the left side of (37) can be written as

$$\begin{aligned} \frac{1}{2\pi\mathbb{i}} \int_{\alpha_{c,T}} F_w(\mathbf{Q}, s)\, ds &= \frac{1}{2} \sum_{i,j=1}^{N} q_i q_j \frac{1}{2\pi\mathbb{i}} \int_{\alpha_{c,T}} \frac{Z_{\mathbf{Q}}(s, \mathbf{p}_{ij}) R^s}{s(s-w)}\, ds \\ &= O\left(R^{\epsilon}\right), \end{aligned} \tag{38}$$

for an arbitrary $\epsilon > 0$. Thus, (37) becomes

$$\begin{aligned} &E_R(\mathbf{Q}, w) - \frac{1}{R^w} E_R(\mathbf{Q}, 0) \\ &= -\frac{1}{R^w} E(\mathbf{Q}, 0) + E(\mathbf{Q}, w) + R^{-w} O\left(R^{\epsilon}\right). \end{aligned} \tag{39}$$

Since $\mathfrak{Re}(w) > 0$, upon taking the limit of (39) as $R \to \infty$ and replacing w with s, we obtain (25). This completes the proof. □

3. Concluding remarks

A rigorous proof for the Wolf method is given in this Letter. However, there are still some open questions. As we mentioned earlier, we prove that the undamped Wolf method converges to the Ewald sum. But usually the undamped method converges very slowly and this makes it unfavorable in practice. To resolve this issue, Wolf et al. [9] modified their method and introduced the damped method. The electrostatic energy computed via damped method, $\mathcal{E}^D_{\text{Wolf}}$, is

$$\mathcal{E}^D_{\text{Wolf}} = \lim_{R\to\infty} E^D_R(\mathbf{Q}, 1), \tag{40}$$

where

$$E_R^D(\mathbf{Q},s)=\frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \times {\sum_{\mathbf{n}\in\mathbb{Z}^3,\,\mathcal{R}(\mathbf{n},\mathbf{p}_{ij})\leqslant R}}' \left\{ \frac{\operatorname{erfc}(\alpha[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})]^{1/2})}{[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})]^{s/2}} - \frac{\operatorname{erfc}(\alpha R)}{R} \right\} - \left(\frac{\operatorname{erfc}(\alpha R)}{2R} + \frac{\alpha}{\sqrt{\pi}} \right) \sum_{i=1}^{N} q_i^2, \tag{41}$$

with

$$\operatorname{erfc}(x)=1-\operatorname{erf}(x), \quad \operatorname{erf}(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt. \tag{42}$$

Since $\lim_{x\to\infty}\operatorname{erfc}(x)=0$, using (26) we obtain

$$\mathcal{E}^D_{\text{Wolf}}-\mathcal{E}_{\text{cell}} = -\lim_{R\to\infty}\left\{ \frac{1}{2}\sum_{i,j=1}^{N} q_i q_j \times {\sum_{\mathbf{n}\in\mathbb{Z}^3,\,\mathcal{R}(\mathbf{n},\mathbf{p}_{ij})\leqslant R}}' \left[\frac{\operatorname{erf}(\alpha[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})]^{1/2})}{[\frac{1}{2}(\mathbf{n}+\mathbf{p}_{ij})^{\mathsf{T}}\mathbf{Q}(\mathbf{n}+\mathbf{p}_{ij})]^{1/2}} - \frac{\operatorname{erf}(\alpha R)}{R} \right] \right\} - \frac{\alpha}{\sqrt{\pi}}\sum_{i=1}^{N} q_i^2. \tag{43}$$

Although the damped method converges fast, it converges to values that depend on the damping parameter and crystal structure [9,14]. This means that the right side of (43) converges to values that depend on α. Thus, it does not seem that one can prove a theorem counterpart to the one presented here for the undamped method. But one may find an interval(s) for the values of the damping parameter to control the error of the damped method. Also it is interesting to note that the variation of the calculated energy versus the radius of the charge natural sphere depends on the crystal structure: it may have an oscillatory behavior as for NaCl crystal [9] or non-oscillatory behavior as for $PbTiO_3$ crystal [14].

We saw that the charge neutralization idea works for spherical expanding domains. One may want to see if this idea would work for other (convex) domains as well. Answer to this question can help to justify the use of the Wolf method for other geometries like free surfaces, slabs and regions near crystal defects. Besides calculating energy, Wolf et al. [9] proposed a method for obtaining forces exerted on charges again without a rigorous proof. As force is a vector quantity, there is an ambiguity on how one should project mirror charges on the surface of the sphere. Since energy only depends on the distance between charges such ambiguity does not arise in the calculation of energy. A rigorous study of the above questions will be a very interesting extension of the present work.

References

[1] E. Madelung, Physikalische Zeitschrift 19 (1918) 524.
[2] E. Elizalde, Comm. Math. Phys. 198 (1998) 83.
[3] D. Borwein, J.M. Borwein, K.F. Taylor, J. Math. Phys. 26 (1985) 2999.
[4] D. Borwein, J.M. Borwein, C. Pinner, Trans. American Math. Soc. 350 (1998) 3131.
[5] P.P. Ewald, Annalen der Physik 64 (1921) 253.
[6] A. Terras, Harmonic Analysis on Symmetric Spaces and Applications I, Springer-Verlag, Berlin, 1985.
[7] R.E. Crandall, J.P. Buhler, J. Phys. A: Math. Gen. 20 (1987) 5497.
[8] K. Fuchizaki, J. Phys. Soc. Japan 63 (1994) 4051.
[9] D.P. Wolf, P. Keblinski, S.R. Phillpot, J. Eggebrecht, J. Chem. Phys. 110 (1999) 8254.
[10] J.P. Buhler, R.E. Crandall, J. Phys. A: Math. Gen. 23 (1990) 2523.
[11] E.C. Titchmarsh, The Theory of the Riemann Zeta-Function, Oxford University Press, Oxford, 1986.
[12] A. Ivić, The Riemann Zeta Function: Theory and Applications, Wiley, New York, 1985.
[13] J.D. Murray, Asymptotic Analysis, Springer-Verlag, New York, 1984.
[14] A. Yavari, M. Ortiz, K. Bhattacharya, Philos. Mag. 87 (2007) 3997.