Clifford boundary conditions: a simple direct-sum evaluation of Madelung constants

Nicolas Tavernier, Gian Luigi Bendazzoli, Véronique Brumas, Stefano Evangelisti, and J. A. Berger

1Laboratoire de Chimie et Physique Quantiques, IRSAMC, CNRS, Université de Toulouse, UPS, France
2Università di Bologna, Bologna, Italy
3European Theoretical Spectroscopy Facility (ETSF)

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We propose a simple direct-sum method for the efficient evaluation of lattice sums in periodic solids. It consists of two main principles: i) the creation of a supercell that has the topology of a Clifford torus, which is a flat, finite and border-less manifold; ii) the renormalization of the distance between two points on the Clifford torus by defining it as the Euclidean distance in the embedding space of the Clifford torus. Our approach does not require any integral transformations nor any renormalization of the charges. We illustrate our approach by applying it to the calculation of the Madelung constants of ionic crystals. We show that the convergence towards the system of infinite size is monotonic, which allows for a straightforward extrapolation of the Madelung constant. We are able to recover the Madelung constants with a remarkable accuracy, and at an almost negligible computational cost.

To describe properties of regular crystalline systems it is convenient to use periodic boundary conditions (PBC). Indeed PBC are widely used in solid-state physics and chemistry as well as in material sciences. In the case of short-range interactions PBC can be imposed via the Born-Von Kármán (BvK) boundary conditions. However, often long-range interactions are present due to the long-range nature of the Coulomb potential, the resulting sums are conceptually difficult due to the fact that, because of the long-range nature of the Coulomb potential, the resulting series is conditionally convergent. For this reason, special care must be taken to perform such a summation, since the result depends on the order in which the summation is carried out.

Madelung sums are a special type of lattice sums which can be performed either by direct summations or indirectly by integral transformations. In the case of direct summations it has been shown that neutrality of the supercell is required to accelerate convergence, and sometimes even to ensure convergence at all. Therefore, fractional charges are sometimes needed in order to ensure convergence. Two early methods of this type have been proposed by Evjen and by Højendahl.

In Evjen’s approach, for example, the surface charges are renormalized by applying weights equal to 1/8, 1/4, and 1/2 for charges on the corners, edges, and faces,
the parallelepiped generated by the vectors $v_\alpha$, \( \alpha = 1, \ldots, K \) with \( 0 \leq \alpha \leq 1 \). In this way, by imposing a number of vanishing moments in the cell, exponential convergence can be achieved \cite{9,11}. However, the main drawback of these approaches is that they require the renormalization of a large number of charges in the supercell.

The most commonly used integral-transformation method, on the other hand, was proposed by Ewald \cite{12}, and several related methods have been proposed in the literature. \cite{13,14} These approaches generally converge to the correct values. However, these approaches are also more cumbersome to implement and can, therefore, not always be applied. \cite{9} Therefore, an accurate and numerically efficient direct-sum approach would be desirable.

We will show below that our approach based on a Clifford torus allows for a simple direct-sum approach yielding converged results. No renormalization of the charges is required. Instead we use a simple renormalization of the distance between ions. We note that, thanks to the PBC, all moments vanish by definition.

Let us consider a Bravais lattice in \( d \) dimensions. Let \( v_j \) be the generator vectors of a unit cell (not necessarily a primitive unit cell). A generic vector \( |u\rangle \) belonging to the unit cell is given by the vector

$$|u\rangle = \sum_{j=1}^{d} \alpha_j |v_j\rangle,$$

with \( 0 \leq \alpha_j < 1 \). Given a set of positive integers \( K_1, \ldots, K_d \), we define the Euclidean supercell (ESC) as the parallelepiped generated by the vectors

$$|V_j\rangle = K_j |v_j\rangle.$$

The ESC thus consists of \( \prod_{j=1}^{d} K_j \) replicas of the unit cell. A generic vector \( |W^{ESC}\rangle \) in the ESC is given by

$$|W^{ESC}\rangle = |u\rangle + \sum_{j=1}^{d} K_j |v_j\rangle = \sum_{j=1}^{d} x_j |v_j\rangle,$$

where \( x_j = \alpha_j + k_j \), with \( 0 \leq k_j \leq K_j - 1 \).

In a completely analogous way, we define the Clifford supercell (CSC) as the Clifford torus associated to the ESC, obtained by joining the opposite edges of the corresponding ESC. A generic point in the CSC is thus given by

$$|W^{CSC}\rangle = \sum_{j=1}^{d} \frac{K_j}{2\pi} e^{i2\pi x_j/K_j} |v_j\rangle.$$

The factor \( K_j/2\pi \) ensures that the circumference of a circle with such a radius coincides with the length of the corresponding edge of the ESC. We remind the reader that a \( d \)-torus is the product of \( d \) circles. We note that, since the ESC and the corresponding CSC are built with the same unit vectors \( v_j \), the two supercells are locally isometric.

To treat Coulomb potentials we have to define the distance between two points on the torus. Since the CSC is embedded in \( \mathbb{C}^d \), we define the distance between the two points \( A \) and \( B \) as the usual norm, in \( \mathbb{C}^d \), of the difference \( |R^{CSC}_{AB}\rangle = |W^{CSC}_B\rangle - |W^{CSC}_A\rangle \) of the two corresponding position vectors,

$$|R^{CSC}_{AB}\rangle = \sum_{j=1}^{d} \frac{K_j}{2\pi} (e^{i2\pi x_j^B/K_j} - e^{i2\pi x_j^A/K_j}) |v_j\rangle.$$

Therefore, the distance \( R^{CSC}_{AB} = \|R^{CSC}_{AB}\| \) between \( A \) and \( B \) is given by

$$R^{CSC}_{AB} = \left[ \sum_{j=1}^{d} \frac{K_j^2}{2\pi^2} \left[ 1 - \cos \left( \frac{2\pi}{K_j} [x_j^B - x_j^A] \right) \right] \|v_j\|^2 \right]^{1/2},$$

where for simplicity we assumed that \( \langle v_i | v_j \rangle = \delta_{ij} \), since in practice one can often choose a supercell with orth-
onal edges. We note that this definition of the distance between two points is closely related to the modified position operator that we recently proposed for electrons in periodic systems. [4]. In Fig. 1 we show an illustration of a CSC for a 2-dimensional NaCl structure and the renormalized distance between the ions.

Let us now consider the following general double lattice sum \( S = \sum_A \sum_B f(R^{ESC}_{AB}) \) where both \( A \) and \( B \) run over two sets of equivalent points in the CSC, and \( f \) is an arbitrary real function. We note that the two sets, \( A \) and \( B \), could coincide. More precisely, using Eq. (6), we can express this sum as

\[
S = \sum_{k_j=0}^{K_j-1} \sum_{k_d=0}^{K_d-1} f \left( \left[ \sum_{j=1}^d K_j^2 2\pi^2 \right]^{-1/2} \cos \left( \frac{2\pi}{K_j} (\alpha_j^B - \alpha_j^A + k_j) \right) \right) \|v_j\|^2^{1/2}. 
\]  
(7)

It is important to note that, thanks to the periodicity of the CSC, each double sum over \( k_j^A \) and \( k_j^B \) can be reduced to a single sum by the substitution \( k_j = k_j^B - k_j^A \). We finally obtain

\[
S = \sum_{k_j=0}^{K_j-1} \sum_{k_d=0}^{K_d-1} f \left( \left[ \sum_{j=1}^d K_j^2 2\pi^2 \right]^{-1/2} \cos \left( \frac{2\pi}{K_j} (\alpha_j^B - \alpha_j^A + k_j) \right) \right) \|v_j\|^2^{1/2}. 
\]  
(8)

Therefore, a sum over all the atom pairs, needed to compute the Madelung constant, reduces to a sum over the individual atoms only.

The Madelung constant \( M_A \) is the electrostatic potential felt by an ion \( A \) due to all other ions in the crystal. It can be expressed as a lattice sum and its standard definition is given by

\[
M_A = \sum_{B \neq A} \frac{z_B}{R^{ESC}_{AB}/R^{ESC}_0}, 
\]  
(9)

where \( z_A \) is the valency of ion \( A \), \( R^{ESC}_{AB} \) is the distance between ions \( A \) and \( B \) in the ESC and \( R^{ESC}_0 \) is the nearest-neighbor distance in the ESC. Instead, in terms of the renormalized distance the Madelung constant of ion \( A \) is redefined in our approach as

\[
M_A = \sum_{B \neq A} \frac{z_B}{R^{ESC}_{AB}/R^{ESC}_0}, 
\]  
(10)

\[
\frac{R^{ESC}_{AB}}{R^{ESC}_0} = \sum_{B \neq A} z_B \sum_{k_j=0}^{K_j-1} \sum_{k_d=0}^{K_d-1} \left[ \sum_{j=1}^d \frac{K_j^2}{2\pi^2} \left[ \frac{1}{2} - \cos \left( \frac{2\pi}{K_j} (\alpha_j^B - \alpha_j^A + k_j) \right) \right] \|v_j\|^2 \right]^{-1/2}, 
\]  
(11)

where we used Eq. (8). Here \( R^{ESC}_0 \) is nearest-neighbour renormalized distance in the embedding space of the CSC. Equation (11) is the main result of this work. We note that the cohesion energy \( E_{coh} \) can be obtained from the knowledge of the Madelung constants of the ions in the lattice according to

\[
E_{coh} = \sum_A z_A M_A. 
\]  
(12)

We now compare the following three approaches to calculate Madelung sums,

1. The plain sum over the ESC of increasing size according to Eq. (6). This approach gives in general non-converging sums, and is added for completeness. We note that the supercell is not electrically neutral in this approach.

2. The sum over the ESC with surface-weighted charges according to Evjen’s method, i.e.,

\[
M_A = \sum_{B \neq A} w_B \frac{x_B}{R^{ESC}_{AB}/R^{ESC}_0}, 
\]  
(13)

where the weight \( w_B \) is equal to 1/2, 1/4, and 1/8 for an ion on the face, edge, and summit of the ESC, respectively; \( w_B = 1 \) for all ions inside the ESC.

3. The sum over the CSC with renormalized distance according to Eq. (11), which is the method proposed in the present work.

We limit ourselves to these three methods since they are of similar simplicity. We note that since the numerical precision is a key issue in order to obtain a large number of significant digits, all our results have been obtained using quadruple precision.

We consider here three types of crystal structures, namely NaCl, CsCl, and ZnS, which represent, the rock-salt, the CsCl, and the zincblende structures, respectively. In Tables I, II, and III we report the Madelung constants computed for a set of cubic supercells (\( K = K_1 = K_2 = K_3 \)) of increasing size for NaCl, CsCl, and
TABLE I. The Madelung constant of Na\textsuperscript{+} in NaCl for various values of \(K\), the number of unit cells per side. The extrapolated \(K \to \infty\) value has been obtained through a linear fit in \(K^{-2}\) according to Eq. (14) using the CSC results that correspond to the two largest \(K\) values.

\[
\begin{array}{cccc}
K & ESC & Evjen & CSC \\
40 & -1.7333900325 & -1.7475646102 & -1.7479830134 \\
41 & -1.7614766492 & -1.7475645804 & -1.749628535 \\
42 & -1.7339798824 & -1.7475646075 & -1.749441161 \\
43 & -1.7608370145 & -1.7475645829 & -1.749266706 \\
60 & -1.7380216149 & -1.7475645977 & -1.7475055682 \\
80 & -1.7403925416 & -1.7475645956 & -1.7476692067 \\
100 & -1.7418198158 & -1.7475645950 & -1.7476315469 \\
120 & -1.7427733060 & -1.7475645948 & -1.7476110895 \\
\infty & & -1.7475645953 & \\
\end{array}
\]

Reference value: \[17\] -1.7475645946

TABLE II. The Madelung constant of Cs\textsuperscript{+} in CsCl for various values of \(K\), the number of unit cells per side. The extrapolated \(K \to \infty\) value has been obtained through a linear fit in \(K^{-2}\) according to Eq. (14) using the CSC results that correspond to the two largest \(K\) values.

\[
\begin{array}{cccc}
K & ESC & Evjen & CSC \\
40 & -165.1951301706 & -3.1228159774 & -1.761329129 \\
41 & -172.8429845898 & -0.402535314 & -1.7613786888 \\
42 & -173.4399599212 & -3.1228354346 & -1.761398086 \\
43 & -181.0877243486 & -0.4025555166 & -1.7614967019 \\
60 & -247.6434281092 & -3.1229317065 & -1.7620703281 \\
80 & -330.0917264008 & -3.1229722138 & -1.7623349348 \\
100 & -412.5400247666 & -3.1229990632 & -1.7624573245 \\
120 & -494.9883231553 & -3.1230011482 & -1.7625237851 \\
\infty & & -1.7626748322 & \\
\end{array}
\]

Reference value: \[18\] -1.7626747731

ZnS, respectively. For simplicity \(K\) will denote the number of unit cells per side in the following. We see that, while the ESC and Evjen approaches only converge for NaCl, our CSC approach converges for all three structures. More importantly, the CSC Madelung sum converges to the reference values. Let us briefly discuss the three crystal structures in more detail.

\textbf{NaCl}: The Madelung constant for the NaCl crystal has been evaluated with high accuracy. Its fifteen-digits approximate value is -1.7475645946318 [17]. The plain sum over ESC of increasing size converges extremely slowly to this limit with a series of alternating values that are above and below the exact value, depending on the total charge of the supercell. In the case of NaCl the Evjen method converges extremely fast to the reference value. Finally, the Clifford series converges to the reference value with a convergence rate in between that of the ESC and Evjen approaches. As can be seen in Fig. 2, the convergence of the NaCl Madelung constant is monotonic in the CSC approach. Thanks to this monotonicity we can extrapolate the finite-size results to that corresponding to the infinite-size CSC. In Table I we also report this extrapolated CSC value, which coincides with the exact result up to the ninth decimal digit using just 120 unit cells per side. We will discuss the details of our extrapolation method below.

\textbf{CsCl}: The case of CsCl is well known, since by performing Evjen’s approach one gets two different limits, i.e., one limit for \(K\) even and another limit for \(K\) odd. The reason, as already discussed by Evjen himself in his paper, is because the surface of the supercell contains either only cations or only anions. The commonly accepted value for the Madelung constant of this crystal is the average between the two limiting values, i.e., -1.76267477307098 [18]. The values obtained with the plain ESC method are wildly oscillating. Instead, our CSC approach is the only one that converges to the reference value. Again, the convergence is monotonic (see Fig. 2) and by extrapolating the values of the finite-size CSC we obtain a correspondence with the reference value up to the seventh decimal digit using just 120 unit cells per side.

\textbf{ZnS}: As in the previous case of the CsCl crystal, also for the ZnS crystal structure, only charges with the same sign are located on the faces of the ESC. However, in this case Evjen’s approach converges to the same incorrect limit for both even and odd numbers of unit cells on each side of the supercell. We note that a different limit could be obtained if instead of an integer number of unit cells per side one would use a half-integer number of unit cells on each side of the supercell. The value for the Madelung constant of the ZnS crystal turns out to be the average of the two limiting values. It is given by -1.6380550533 [19]. The sum over a plain ESC does not appear to converge, similarly to what happens in the CsCl case, because the supercells are highly charged. Again, our CSC method is the only one that converges to the reference bulk limit. Moreover, the convergence is monotonic (see Fig. 2) and by extrapolating the values of the finite-size CSC we obtain a correspondence with the reference value up to the seventh decimal digit using just 120 unit cells per side.

As can be seen from the tables above, the calculation of the Madelung constant from a single CSC, even of large size (\(K \approx 100\)), yields an approximation of the exact value, corresponding to the system of infinite size, up to four or five digits. An important advantage of our CSC approach is that we can obtain a much better approximation of the exact value by extrapolating the Madelung constants computed for the finite-size CSC’s to the infinite-size limit. It turns out that the CSC Madelung constants follows the following inverse power law as a function of the system size \(K\),

\[
M(K) = M_\infty + CK^{-2},
\]
where $M_\infty$ is the Madelung constant of the infinite crystal and $C$ is a constant. In Fig. 2, we used this inverse-power law to fit the computed Madelung constants of the finite systems. We observe an almost perfect linearity of the curves for all three crystal structures. Therefore, in practice, we used just the two largest values of $K$ in Eq. (14) to obtain $M_\infty$. The extrapolated values in the tables were obtained in this way. As can be seen from those results the inverse-power law yields very accurate results for $M_\infty$, increasing the correspondence with the reference values to seven, eight or even nine digits.

In conclusion, we presented a formalism suitable for the computation of lattice sums of ionic crystals. The general strategy of our approach consists in transforming a supercell of a periodic system into a Clifford torus, and then renormalizing the distance between two points on the torus as the Euclidean distance between these points in the embedding space of the torus. In this way, a lattice sum on an infinite periodic system is replaced by a sequence of sums over finite periodic systems, and the value for the infinite crystal is then obtained by extrapolating to the infinite-size limit. As a numerical illustration, we computed the Madelung constants of ionic crystals. The values we obtain are in excellent agreement with the available reference data. Finally, we note that the same formalism can be applied to calculate the properties of electronic systems, e.g., Wigner crystals [20].

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### TABLE III. The Madelung constant of Zn$^{2+}$ in ZnS for various values of $K$, the number of unit cells per side. The extrapolated $K \to \infty$ value has been obtained through a linear fit in $K^{-2}$ according to Eq. (14) using the CSC results that correspond to the two largest $K$ values (both corresponding to $K$ even).

| $K$ | ESC | Evjen | CSC |
|-----|-----|-------|-----|
| 40  | 164.295318 | -2.3182037805 | -1.6380663149 |
| 41  | 168.405536 | -2.3182050224 | -1.6380657779 |
| 42  | 172.539858 | -2.3182062003 | -1.6380652782 |
| 43  | 176.650643 | -2.3182072755 | -1.6380648124 |
| 60  | 246.741576 | -2.3182182423 | -1.6380600884 |
| 80  | 329.188848 | -2.3182233050 | -1.6380578914 |
| 100 | 411.636528 | -2.3182256484 | -1.6380568714 |
| 120 | 494.084414 | -2.3182269215 | -1.6380563166 |
| $\infty$ | | | -1.6380550555 |

Reference value: [19] -1.6380550533

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