Crystal potentials under invariant periodic boundary conditions at infinity

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The definiteness of bulk electrostatic potentials in solids under periodic boundary conditions defined in an invariant manner has been proved in the general case of triclinic symmetry. Some principal consequences following from the universal potential correction arising are discussed briefly.

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I. INTRODUCTION

The summation of Coulomb potentials over crystal lattices is a classical problem [1] important for determining the cohesive energy in crystals [2] as well as for describing electronic properties there [3,4]. Despite a long history of this subject ([1] and references therein) the question about the uniqueness of electrostatic properties in the bulk remains controversial. Indeed, it is well-known that every electrostatic task is defined by boundary conditions [5] and periodic boundary conditions are appropriate to the solution in the bulk [6]. As a result, any electric field generated by polar unit cells is to be excluded as irrelevant to the bulk state [7]. Notwithstanding, as far as electrostatic potentials are concerned, an arbitrary constant potential could be formally added as an available electrostatic potentials are well defined by boundary conditions on open surfaces of crystals, but these potentials are undetermined to an additive constant in infinite crystals [8]. This claim is, however, at variance with the wide-spread standpoint that the electrostatic potentials are definite in the bulk [9]. The approach of Ewald [10] is often treated as optional [3], whereas the wide-spread standpoint is that the electrostatic potentials are concerned, an arbitrary constant potential could be formally added as an available arbitrary unit vectors, with the products ($b = ae_i + be_j + ce_k$) attributed to necessary points charges $\rho'(r')$ located in the vicinity of the origin, $r = 0$, at points $r_j$ connected by admissible lattice translations. The values of $q_j$ are constrained by

$$\sum_j q_j = 0$$

so as to exclude the contribution of $q_j$ to the overall initial charge distribution upon combining $\rho(r)$ attributed to neighbouring unit cells. It is significant that ten different charge species among $q_j$ are sufficient to fulfill (3)–(5) and (9). Thus, $H$ remains optional in (9).

It is advantageous to consider a unit cell with the origin in its geometric centre. Then a compact distribution of $q_j$ is supplied by $r_j$ belonging to the following set of vectors: $0$, $\pm a$, $\pm b$, $\pm c$, $\pm a \pm b$, $\pm b \pm c$ and $\pm c \pm a$. Keeping

In the present paper we show that periodic boundary conditions defined properly are sufficient to make electrostatic potentials definite in the bulk. It means that periodic boundary conditions are as effective as boundary conditions on surfaces are. Moreover, the latter ones can then be reconstructed as relevant to real surfaces consistent with bulk states [11].
in mind that \( \rho^{\text{ini}}(r) \) is still contained in the unit-cell parallelepiped, \( \rho(r) \) can be connected with a parallelepiped that is the same in shape, but twice as large in size. It is convenient to adopt this parallelepiped as a new unit cell. Being additive, the potential of interest is then described by the sum of independent contributions of eight interpenetrating lattices composed of new unit cells. Thus, it is conceptually sufficient to discuss the potential effect generated by a single lattice specified by \([\parallel A, B, C] \), provided that this lattice is still determined by the lattice parameters \( a, b, c \) at

\[
A/a = B/b = C/c \gg 1,
\]

so that the uniformity along each crystallographic direction is maintained. Periodic boundary conditions are then readily involved as imposed in such a way that each couple of remote parallel restricting planes merges, so that equal number of complete unit cells occur along each direction of \( e_a, e_b \) and \( e_c \). In this event, the invariant character of periodic boundary conditions implies that each plane of merging may also occur somewhere within boundary unit cells, without changing the result. It is important that if planes of merging happen in intermediate positions specified by 0 \( \leq f \leq 1 \) within boundary unit cells, without loss of generality, some instantaneous charge distributions are to be introduced on those planes so as to fulfill conditions (2) and (3) furnishing the convergence of the surface potential contributions. As a result, the contribution of any dipolar polarization along those planes can be eliminated, but dipolar moments normal to the planes in question are inevitable and contribute to the potential value in the interior \([19,24–26]\). In the particular case of the \( +A \) plane one can show that the corresponding potential contribution takes the form

\[
\Phi_A(f) = \frac{\Omega}{\sin \beta} \int \frac{dv/2}{-b/2} \int \frac{du/2}{-c/2} \rho(t, p, u)
\]

\[
\times \left[ t(f) - \frac{1}{2} \right] \sum_{i \in \{A\}} \frac{R_{iA}^A}{R_i^2},
\]

where in the triclinic co-ordinates \( r = te_a + pe_b + ue_c, t(f) = af - a/2, i \) runs over unit cells truncated by the boundary plane, with \( R_{iA}^A \), the component of \( R_i \) along an outward normal to this plane, \( \Omega = [1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{1/2} \). Upon merging the \( \pm A \) planes, auxiliary charges on those planes cancel each other at a given \( f \), but the aforementioned invariance of the boundary conditions is based on \([\parallel 1 \] averaged over \( f \), so that the effective potential generated by that couple of planes is to be specified as

\[
\Phi_A = \int_0^1 \left[ \Phi_A(f) + \Phi_{-A}(1 - f) \right] df,
\]

where \( \Phi_{-A}(f) \) follows from \([2] \) upon inversion of the coordinate system. Carrying out the integration over \( f \) in \([11] \) and utilizing \([5] \), we obtain

\[
\Phi_A = \frac{H \sin \beta}{a \Omega} \sum_{i \in \{A\}} \frac{R_i^A}{R_i^2}. \tag{12}
\]

### III. INVARIANCE OF PERIODIC BOUNDARY CONDITIONS

To make the solution of interest determinate, we assume that the overall structure is composed of an integral number of unit cells restricted by planes which are parallel to the unit-cell faces and are specified by the vectors \( \pm A, \pm B \) and \( \pm C \) relative to a central unit cell, where \( A = A e_a, B = B e_b \) and \( C = C e_c \). This is convenient to adopt this parallelepiped as a new unit cell, without loss of generality, some instantaneous potential contribution takes the form

\[
\Phi_{\pm A} = \frac{H \sin \beta}{a \Omega} \sum_{i \in \{A\}} \frac{R_i^A}{R_i^2}. \tag{12}
\]

### IV. UNIQUENESS OF BULK POTENTIALS

The structural factor described by the sum in \([12] \) determines the potential at a large distance from the plane at hand. Therefore, it is independent of the discrete character of that sum \([11,13,22,25] \) and so can be represented in the following integral form

\[
\Phi_{\pm A} = \frac{H \sin \beta}{a \Omega} \sum_{i \in \{A\}} \frac{R_i^A}{R_i^2}. \tag{12}
\]

where the scale transformation to the parameters of a unit cell is performed in agreement with \([\parallel 5] \).

\[
W(a, b, c) = (a^2 + b^2 + c^2 + 2ab \cos \alpha + 2bc \cos \beta + 2ca \cos \gamma)^{1/2}. \tag{14}
\]

Carrying out the integration in \([13] \) and substituting the result into \([12] \), we derive

\[
\Phi_A = \frac{H}{\nu} \left[ Y(a, b, c|\alpha, \beta, \gamma) - Y(-a, b, c|\alpha, \beta, \gamma) - Y(a, -b, c|\alpha, \beta, \gamma) - Y(a, b, -c|\alpha, \beta, \gamma) \right], \tag{15}
\]

where \( \nu = abc \Omega \) is the volume of the unit cell,

\[
Y(a, b, c|\alpha, \beta, \gamma) = \tan^{-1} \left\{ \left[ b\sin^2 \beta + ab \Gamma(\gamma) + ca \Gamma(\alpha) - a^2 \Gamma(\beta) \right] [a \Omega W(a, b, c)]^{-1} \right\}, \tag{16}
\]

\[
\Gamma(\phi_1) = \cos \phi_1 - \cos \phi_2 \cos \phi_3, \tag{17}
\]

the parameters \( \phi_i \) are the angles \( \alpha, \beta \) and \( \gamma \) in an arbitrary combination.

As a generalization of \([24] \), the total potential contribution associated with the \( \pm A, \pm B \) and \( \pm C \) boundary planes after their merging takes the form
\[ \Phi_{\text{top}} = \Phi_A + \Phi_B + \Phi_C, \]

where \( \Phi_B \) and \( \Phi_C \) are obtained from (15)–(17) upon the cyclic interchanges \( A \rightarrow B \rightarrow C \), \( a \rightarrow b \rightarrow c \rightarrow a \) and \( \alpha \rightarrow \beta \rightarrow \gamma \rightarrow \alpha \) there. To proceed further, we remark that the angles \( Y(a,b,c|\alpha,\beta,\gamma) \), \( Y(b,c,a|\beta,\gamma,\alpha) \) and \( Y(c,a,b|\alpha,\beta,\gamma) \) associated with \( W(+a,+b,+c) \) and denoted as \( \chi_j \) form a closed set with the property

\[ \tan(\chi_1 + \chi_2) \tan \chi_3 = 1, \quad |\chi_j| < \pi/2. \]

One can readily prove therefrom that

\[ \chi^{+++} = \chi^+ + \chi^+ = \pi \]

where the sign combination specifying the arguments of \( W(+a,+b,+c) \) is indicated as a superscript. Likewise, for the angles associated with \( W(-a,+b,+c) \), \( W(+a,-b,+c) \) and \( W(+a,+b,-c) \) we get

\[ \chi^{-++} = \chi^- + \chi^- = \frac{\pi}{2}. \]

Substituting (21) and (20) into (18), we finally reach

\[ \Phi_{\text{top}} = \frac{2\pi H}{U_v}. \]

On combining (19) and (22), the definite bulk potential field takes the form

\[ U_b(r) = U_{\text{Coul}}(r) + \Phi_{\text{top}}. \]

Following Bethe (23), one can see that the value of \( U_{\text{Coul}}(r) \) averaged over a unit cell cancels the last term on the right-hand side of (23), so that for the mean bulk potential we obtain

\[ \bar{U}_b = 0. \]

Hence, the bulk potential field \( U_b(r) \) is independent of an optional parameter \( H \) and has no uniform component, in agreement with the result of Ewald (13).

V. DISCUSSION

It is significant that in a general case of (1) the effect of eight sublattices mentioned above on the resulting \( \Phi_{\text{top}} \) just compensates the increase of the unit-cell volume in each of them, so that relation (22) is reproduced with the parameters attributed to the initial unit cell. It is also clear that the auxiliary fictitious charges introduced in (1) vanish under periodic boundary conditions, so that real structural charges are of importance altogether. On the other hand, according to the above procedure of averaging, the issue (2) turns out to be indifferent to the particular definition of a unit cell. As discussed in (3), the foregoing result may also be associated with the translational invariance as an integral property of the direct lattice sum (1) within a special mode of summation. This circumstance was stressed by Ewald (13) as desirable upon the definition of lattice sums as such.

Note that the potential \( U_{\text{Coul}}(r) \) as a function of \( r \) is asymmetric if \( H \neq 0 \). This is especially prominent in diatomic structures composed of point charges (21,28), but relation (23) retrieves the symmetric result there.

For completeness, one can show that, in terms of (23), the bulk Coulomb energy per unit cell takes the form

\[ \mathcal{E}_b = \frac{1}{2} \int_{V_{\text{ini}}} \rho_{\text{ini}}(r) U_b(r) \, dr, \]

which is invariant, though \( \rho_{\text{ini}}(r) \) occupying a volume \( V_{\text{ini}} \) remains optional. According to (23), the variational derivative of \( \mathcal{E}_b \) with respect to \( \rho_{\text{ini}}(r) \) is then equal to

\[ \frac{\delta \mathcal{E}_b}{\delta \rho_{\text{ini}}(r)} = U_b(r) \]

that is the basic statement for determining \( \rho_{\text{ini}}(r) \) in a self-consistent manner (13).

It is worth noting that relations (23) and (22) also describe the potential effect exerted by extended charges even if we deal with spherical electronic distributions in ions (3). As a result, the potential asymmetry beyond the potential contribution of a point-charge lattice takes place as well. According to (23), this fact results in the asymmetry of the concentration of vacancies of different ionic species (29) and so explains the n-type conductivity in intrinsic semiconductors such as ZnO or GaAs (30,31).

Note that the description based on (1)–(6) and (22)–(26) is quite general, with including the effect of the Lorentz field for polar unit cells as a particular case (32). A subtle problem associated with the definition of a local polarization in ferroelectrics (33,34) can also be elucidated therefrom, as will be discussed elsewhere.

VI. CONCLUSION

Without loss of generality, the problem of summation of Coulomb potentials over crystal lattices is investigated in terms of absolutely convergent sums with an arbitrary choice of the charge distribution in a unit cell. The principle case of triclinic symmetry is considered. It is shown that periodic boundary conditions imposed in an invariant manner so as to exclude the influence of the particular choice of a unit cell are sufficient for determining the electrostatic potentials in the bulk as uniquely defined, with zero mean bulk potential value. A few direct consequences of the results obtained are pointed out.

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