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A simple approach to evaluation of lattice sums

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Abstract. It is shown that starting from a Fourier transform relation one can derive, in a surprisingly simple manner, all the well-known results of lattice summation, that have been obtained so far by a complicated use of the Ewald theta transformation. We show that the Ewald transformation follows directly from the Fourier transform relation.

Keywords. Lattice sum; Ewald transformation; Fourier transformation.

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1. Introduction

The evaluation of a long-range lattice sum arising usually from Coulomb interaction, is essential in the theory of crystalline solids. Such lattice sums involve conditionally convergent series with a slow rate of convergence. Among the many methods in vogue (Tosi 1964; Glasser and Zucker 1980) for transforming such series into a rapidly convergent one, the method using Ewald theta transformation (Born and Huang 1954; Slater 1967) is probably the most powerful. It also finds application in another important situation, namely the separation of macroscopic electric field from an indeterminate lattice sum involving Coulomb coefficients (Born and Huang 1954). Unfortunately however, the deduction of Ewald transformation and the subsequent manipulations are quite lengthy and complicated in all cases.

We present in this paper an alternative transformation, which is basically a Fourier transform relationship and from which all the different types of lattice sums can be evaluated. The important point is that, the whole derivation in each and every case is surprisingly simple and concise. We shall present first the proposed transformation (§2), and then discuss some applications (§3).

2. The transformation

We propose the transformation

$$\exp(-r^2\sigma^2) = (4\pi\sigma^2)^{-3/2} \int \exp(-q^2/(4\sigma^2) + i\mathbf{q}\cdot\mathbf{r})\mathrm{d}\mathbf{q}, \tag{1}$$

where σ is an arbitrary real parameter, and the integration extends over the entire $\mathbf{q}$-space. This equation is a well-known Fourier transformation and can be readily verified by direct integration. Another useful form of this equation is obtained by integrating it

with respect to σ:

$$(1/r)\,\mathrm{erf}(r\sigma) = (1/2\pi^2)\int (1/q^2)\exp(-q^2/(4\sigma^2) + i\mathbf{q}\cdot\mathbf{r})\,d\mathbf{q}, \tag{2}$$

where erf(x) is the error function.

The basic difference between the Ewald theta transformation and the proposed transformation is that, while the former involves only lattice vectors, the latter involves arbitrary position vectors. (This property has been used in the development of a pseudopotential theory of effective interaction in metals by Sarkar *et al* (1983).) Ewald transformation can be obtained directly from (1) for a particular choice of $\mathbf{r}$, as will be shown below. In this sense, the new transformation seems to be more fundamental than Ewald's.

We mention here that, throughout this paper we shall make the following assumptions. (i) Our sample has the shape of a parallelopiped whose edges are parallel to the three basis vectors of direct lattice and (ii) all relevant physical properties satisfy periodic boundary condition. The limit of an infinite lattice is achieved by maintaining these assumptions. One obtains therefore the well-known equalities (Ziman 1972),

$$\sum_l \exp(i\mathbf{q}\cdot\mathbf{r}_l) = N\sum_{\mathbf{G}} \delta_{\mathbf{q},\mathbf{G}} \tag{3}$$

and in the limit of an infinite lattice,

$$\sum_{\mathbf{q}} \equiv \frac{Nv}{8\pi^3}\int d\mathbf{q}. \tag{4}$$

Here, $\mathbf{r}_l$ is the position of l-th lattice site, N is the number of unit cells in the lattice, $\mathbf{G}$ is a reciprocal lattice vector, v is the volume of a unit cell, and $\mathbf{q}$ is a member of the quasi-continuous space of the allowed wave-vectors.

We can now obtain Ewald transformation from (1), by putting $\mathbf{r} = \mathbf{r}_l - \mathbf{r}_0$ there, multiplying both sides by $\exp i\mathbf{q}_0\cdot(\mathbf{r}_l - \mathbf{r}_0)$, ($\mathbf{r}_0$ and $\mathbf{q}_0$ being arbitrary vectors), summing over l, and using (3) and (4). This gives

$$\sum_l \exp[-(\mathbf{r}_l - \mathbf{r}_0)^2\sigma^2 + i\mathbf{q}_0\cdot(\mathbf{r}_l - \mathbf{r}_0)] = \pi^{3/2}/(v\sigma^3)\sum_{\mathbf{G}} \exp[-(\mathbf{G} - \mathbf{q}_0)^2/4\sigma^2 - i\mathbf{G}\cdot\mathbf{r}_0], \tag{5}$$

which is identical with the most general form of Ewald transformation (Born and Huang 1954).

3. Applications

3.1 *Madelung energy for ionic crystals*

Madelung energy (Coulomb part of cohesive energy per unit cell) for ionic crystals is given by

$$U = \tfrac{1}{2}\sum_k e_k \mathscr{S}_1(k), \qquad \mathscr{S}_1(k) = \sum_{l'k'}{}' \frac{e_{k'}}{r}, \tag{6}$$

where prime over Σ implies omission of the $lk = l'k'$ term, and $\mathbf{r} = \mathbf{r}_{l'k'} - \mathbf{r}_{lk}$, lk denoting the kth particle in lth unit cell, and e_k is charge of kth particle. In the expression for $\mathscr{S}_1(k)$

we write $(1/r)$ as $(1/r)\,\mathrm{erf}(r\sigma) + (1/r)\,\mathrm{erfc}(r\sigma)$, and use the transformation in (2) to obtain

$$\mathscr{S}_1(k) = \sum_{l'k'}{}' e_{k'}(1/r)\,\mathrm{erfc}\,(r\sigma) + \sum_{l'k'}{}' e_{k'}/(2\pi^2) \times \int (1/q^2)\exp(-q^2/(4\sigma^2) + i\mathbf{q}\cdot\mathbf{r})\,\mathrm{d}\mathbf{q}. \tag{7}$$

On the second term in the right side we perform the following operations: (i) add and subtract the $lk = l'k'$ term, which is easily seen to be $(2/\sqrt{\pi})e_k\sigma$; (ii) exchange the order of summation and integration to obtain a factor $\sum_{l'} \exp(i\mathbf{q}\cdot\mathbf{r})$ and rewrite this factor as $\exp(i\mathbf{q}\cdot\mathbf{u})\sum_{l'} \exp(i\mathbf{q}\cdot\mathbf{r}_{l'})$, with the choice $\mathbf{r}_l = 0$ ($\mathbf{u}$ being $\mathbf{r}(lk') - \mathbf{r}(lk)$); (iii) use eqs (3) and (4) in order. The final result is

$$\mathscr{S}_1(k) = \sum_{l'k'}{}' e_{k'}(1/r)\,\mathrm{erfc}\,(r\sigma) - (2/\sqrt{\pi})e_k\sigma + \sum_{\mathbf{G},k'} (4\pi e_{k'}/v)(1/G^2) \times \exp(-G^2/(4\sigma^2) + i\mathbf{G}\cdot\mathbf{u}). \tag{8}$$

In the last summation, $\mathbf{G} = 0$ term vanishes in view of charge neutrality in an ionic crystal. Equation (8) is the well-known expression obtained in connection with Madelung sum by Ewald transformation (Born and Huang 1954; Tosi 1964).

3.2 *Coulomb dynamical matrix*

The Coulomb part of dynamical matrix is given by

$$D\begin{pmatrix} \mathbf{q} & \\ k & k' \\ \alpha & \beta \end{pmatrix} = \sum_{l'} \Phi_2^C \begin{pmatrix} l & l' \\ k & k' \\ \alpha & \beta \end{pmatrix} \exp(-i\mathbf{q}\cdot\mathbf{r}) = -\sum_{l'} \exp(-i\mathbf{q}\cdot\mathbf{r}) \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\left(\frac{e_k e_{k'}}{r}\right), \tag{9}$$

where Φ_2^C is the Coulomb part of second order force constant matrix. One may follow here exactly the same procedure as for the previous case (we take first the $k \neq k'$ case); only, due to the presence of $\partial^2/\partial r_\alpha \partial r_\beta$ operator, corresponding to (7) we get here,

$$D\begin{pmatrix} \mathbf{q} & \\ k & k' \\ \alpha & \beta \end{pmatrix} = -\sum_{l'} e_k e_{k'} \exp(-i\mathbf{q}\cdot\mathbf{r}) \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\left(\frac{1}{r}\,\mathrm{erfc}\,(r\sigma)\right) + \sum_{l'} (e_k e_{k'}/2\pi^2) \int (1/Q^2) Q_\alpha Q_\beta \exp\{-Q^2/(4\sigma^2) + i(\mathbf{Q}-\mathbf{q})\cdot\mathbf{r}\}\,\mathrm{d}\mathbf{Q}. \tag{10}$$

One may obtain without much difficulty the final result,

$$D\begin{pmatrix} \mathbf{q} & \\ k & k' \\ \alpha & \beta \end{pmatrix} = -\sum_{l'} e_k e_{k'} \exp(-i\mathbf{q}\cdot\mathbf{r}) \cdot [(4\sigma^3/\sqrt{\pi})(r_\alpha r_\beta/r^2)\exp(-r^2\sigma^2) + (3r_\alpha r_\beta/r^2 - \delta_{\alpha\beta})\{(1/r^3)\,\mathrm{erfc}\,(r\sigma) + (2\sigma/\sqrt{\pi})(1/r^2)\exp(-r^2\sigma^2)\}] + \sum_{\mathbf{G}} (4\pi/v) e_k e_{k'} (G_\alpha + q_\alpha)(G_\beta + q_\beta)(\mathbf{G}+\mathbf{q})^{-2} \exp\{i\mathbf{G}\cdot\mathbf{u} - (\mathbf{G}+\mathbf{q})^2/(4\sigma^2)\}. \tag{11}$$

This result is identical with that obtained by Kellerman (1940) by a lengthy application of Ewald method. One should note here that for $k = k'$, the above result has to be augmented by terms so as to maintain the translational symmetry relation

$$\sum_{k'} D\begin{pmatrix} \mathbf{q}=0 \\ k & k' \\ \alpha & \beta \end{pmatrix} = 0.$$

3.3 *A general lattice sum*

Let us consider a more general type of lattice sum, that involves phases of the waves:

$$\mathscr{S}_n^{kk'}(\mathbf{a}) = \sum_{l'} (1/r^n)\exp(-i\mathbf{a}\ \mathbf{r}), \tag{12}$$

where n is any positive number. We shall again treat here only the case of $k \neq k'$, a generalisation being straightforward.

Firstly, we substitute the well-known Euler's integral representation formula

$$1/r^n = [1/\Gamma(n/2)]\int_0^\infty \beta^{n/2-1}\exp(-r^2\beta)\,d\beta,$$

in (12), break up the integral into two parts $\int_0^{\sigma^2} + \int_{\sigma^2}^\infty$ and introduce a new variable $t = \beta/\sigma^2$ to obtain,

$$\mathscr{S}_n^{kk'}(\mathbf{a}) = [\sigma^n/\Gamma(n/2)]\sum_{l'}\exp(-i\mathbf{a}\cdot\mathbf{r})\left[\int_0^1 + \int_1^\infty\right] t^{n/2-1}\exp(-r^2\sigma^2 t)\,dt.$$

In the right side, while the part $\int_1^\infty$ is retained as such, on the part $\int_0^1$ we perform these operations: (i) use the transformation of (1); (ii) separate out as before, the factor $\sum_{l'}\exp i(\mathbf{q}-\mathbf{a})\cdot\mathbf{r}$ and use (3); (iii) convert $\int d\mathbf{q}$ to $\sum_{\mathbf{q}}$ by (4) and change variable to $1/t$. The final result can be written as

$$\mathscr{S}_n^{kk'}(\mathbf{a}) = [\sigma^n/\Gamma(n/2)]\Bigg[\sum_{l'}\{\Phi_{n/2-1}(r^2\sigma^2)\}\exp(-i\mathbf{a}\cdot\mathbf{r}) + (\pi^{3/2}/v\sigma^3)\sum_{\mathbf{G}}\{\Phi_{-n/2+1/2}((\mathbf{G}+\mathbf{a})^2/4\sigma^2)\}\exp(i\mathbf{G}\cdot\mathbf{u})\Bigg], \tag{14}$$

where we have introduced the function (Born and Huang 1954; Misra 1940)

$$\Phi_n(x) = \int_1^\infty t^n\exp(-tx)\,dt.$$

Equation (14) is the result obtained by Born and Bradburn (1943) using Ewald theta transformation.

3.4 *Fuchs, formula for electrostatic energy in metals*

So far we have been dealing with the conversion of a slowly and conditionally convergent series to one converging fast. We now go over to a different situation, where the transformation of (2) extracts from a divergent sum, a convergent part which has some physical significance. Thus, consider a monatomic lattice, each ion of which has a charge $+e$. A uniform electron charge density of amount $-e/v$ is smeared out in the background ($-$ the 'jellium model'). The ion-ion interaction energy per unit volume

$$U_{ii} = (1/2v)\sum_{l'}' e^2/r$$

involves a sum that resembles $\mathscr{S}_1(k)$. Making use of (2), one may proceed therefore as for $\mathscr{S}_1(k)$ and obtain corresponding to (8), a relationship that involves a divergent term.

$$U_{ii} = \sum_{i'}' (e^2/2v)(1/r)\,\mathrm{erfc}(r\sigma) - (e^2\sigma/v\sqrt{\pi}) - (e^2\pi/2\sigma^2v^2)$$
$$+ \sum_{\mathbf{G}}' (2\pi e^2/v^2)(1/G^2)\exp(-G^2/4\sigma^2) + (2\pi e^2/v^2)\lim_{q\to 0}(1/q^2).$$

The last term is really the potential energy per unit volume due to a uniform charge density e/v and is cancelled by the effect of the negatively charged background. Omitting this term we get the well-known result of Fuchs for cohesive energy in a metal.

It will be shown elsewhere that the present method of lattice summation can also be successfully applied in the homogeneous deformation theory of piezoelectric crystals. In that case, (2) serves to separate out macroscopic electric field from an indeterminate lattice sum, leaving a convergent quantity (Dasgupta and Sengupta 1985).

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Note added in proof:

We would like to mention that a generalised form of the transformation in (1) has been successfully applied to evaluate a new lattice sum (Dasgupta S and Sengupta S 1985 *J. Phys.* **C18** L47).