ANALYTICAL TWO- AND THREE-DIMENSIONAL LATTICE SUMS
FOR GENERAL MULTIPOLAR INTERACTIONS

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We present a rapidly convergent analytical Fourier expansion of the interaction between an electrostatic multipole moment and a two-dimensional lattice of multipoles, which is a generalisation of two-dimensional monopole-monopole and dipole-dipole lattice sums. Three-dimensional lattice sums can be obtained via analytical planewise summation.

1. Introduction

Lattice sums of pairwise interactions occur in many branches of solid state physics. A textbook example is the calculation of the cohesion energy of an ionic crystal [1]. Because of the crystal symmetry, it is sufficient to consider only the total interaction between an ion at a specific lattice site and the ions at all other lattice sites. Thus, the electrostatic cohesion energy can be written as a three-dimensional lattice sum of pairwise Coulomb potentials. In lattice dynamics calculations on ionic crystals, the Coulomb potential is expanded with respect to charge displacements, which, within the harmonic approximation, results in lattice sums of electrostatic dipole-dipole interactions for the force constants. Similar dipole-dipole sums occur in the dielectric theory of solids; for example, in calculations of the macroscopic polarisation of a dielectric material. Lattice sums of higher-order multipole-multipole interactions are important for anharmonic lattice dynamics calculations, where the Coulomb potential is expanded beyond the harmonic approximation. They are also needed in lattice energy and dynamics calculations of molecular crystals with intrinsic higher-order molecular multipole moments.

Often, special techniques are used to evaluate lattice sums of electrostatic multipole-multipole interactions, because the direct summation is either slowly or conditionally convergent [2-5]. Two classic examples are the treatment of Madelung [6] (for the Madelung constant) and the Ewald method [1,7], which can be applied to three-dimensional lattice sums of pairwise dipole-dipole interactions. Nijboer and de Wette [2] have developed an elegant and efficient method of evaluating three-dimensional lattice sums of general multipole-multipole interactions, which decay faster than the dipole-dipole interaction with increasing distance. It was first used in connection with the theory of neutron scattering in dense systems [8].

Nijboer and de Wette [3] have also derived an expansion for the interaction between a dipole and a two-dimensional lattice of parallel dipoles, which are oriented perpendicularly to the lattice plane. Because of the two-dimensional translation symmetry, the sum over pairwise dipole-dipole potentials can be replaced by a rapidly convergent Fourier series. They have used this expansion to evaluate the electric field within a slab of dielectric material via planewise summation. Steele [9] has derived a similar Fourier expansion for the interaction between an atom and a two-dimensional lattice of substrate atoms, adopting a Lennard-Jones 12-6 atom-atom potential model. This expansion has proved to be valuable in various dynamics calculations of molecules adsorbed or scattered on a surface. Steele has also given an explicit formula for the Fourier transform in the case of a Coulomb potential. This result was first derived, via direct solution of the Poisson equation,
by Lennard-Jones and Dent [10]. Moreover, Steele has analytically evaluated, via planewise summation, the interaction of a charge with a semi-infinite three-dimensional ionic substrate.

In the present paper, we show that for general multipole–multipole interactions the occurring two- and three-dimensional lattice sums can also be evaluated analytically. Thus we extend the electrostatic monopole–monopole expansion of Steele [9] and the dipole–dipole expansion of Nijboer and de Wette [3] to a general multipole–multipole Fourier series which, to our knowledge, has not been derived before.

2. Derivation of the lattice sums

The electrostatic multipole moments \( Q^{(l_A)} \) of a charge cloud \( A \) are defined as spherical tensors with components [11,12]

\[
Q^{(l_A)}_{m_A} = \sum_{l_A=1}^{N_A} Z_{l_A} u_{l_A} C^{(l_A)}_{m_A} (\theta_{l_A}, \varphi_{l_A}) .
\]

The polar coordinates \( u_{l_A}, \theta_{l_A} \) and \( \varphi_{l_A} \) denote the positions of the charges \( Z_{l_A} \) with respect to a local coordinate system, which is centered at position \( r_A \) and which is chosen to be parallel to a global frame. The function \( C^{(l_A)}_{m_A} \) is a Racah spherical harmonic [13].

Consider the interaction of these multipole moments localised at \( r_A \) with a two-dimensional lattice of multipole moments \( Q^{(l_B)} \) at positions

\[
r_B = k_1 a_1 + k_2 a_2
\]

in the \( xy \) plane of the global reference frame. Here, \( a_1 \) and \( a_2 \) are two-dimensional lattice vectors, \( k_1 \) and \( k_2 \) are integers. The pair interaction between the multipoles \( Q^{(l_A)} \) and \( Q^{(l_B)} \), at positions \( r_A \) and \( r_B \), is written in the well-known spherical expansion [11,12]

\[
V(Q^{(l_A)}, Q^{(l_B)}, r_A, r_B) = \sum_{m_A = -l_A}^{l_A} \sum_{m_B = -l_B}^{l_B} C^{(l_A)}_{m_A m_B} Q^{(l_A)}_{m_A} Q^{(l_B)}_{m_B} \gamma^{(l_B + l_A)}_{-m_A - m_B} (r_A - r_B)
\]

with coefficients

\[
c^{(l_A)}_{m_A m_B} = (-1)^{l_B} \left( \frac{(2l_A + 2l_B + 1)!}{(2l_A)! (2l_B)!} \right)^{1/2} \begin{pmatrix} l_A & l_B & l_A + l_B \\ m_A & m_B & -m_A - m_B \end{pmatrix},
\]

which comprise a Wigner 3j-symbol. The function \( \gamma^{(l)}_{m} \), occurring in eq. (3), represents an irregular solid Racah harmonic [13]

\[
\gamma^{(l)}_{m} (r) = r^{-l - 1} C^{(l)}_{m} (\theta, \varphi),
\]

where \( \theta \) and \( \varphi \) denote the polar angles of the vector \( r \). From eqs. (2) and (3) it follows directly that the total interaction between a single multipole \( Q^{(l_A)} \) and a two-dimensional lattice of identical multipoles \( Q^{(l_B)} \) contains a lattice sum

\[
S^{(l_A)}_{m_A} (r_A) = \sum_{k_1 = -\infty}^{+\infty} \sum_{k_2 = -\infty}^{+\infty} \gamma^{(l_A)}_{m_A} (r_A - k_1 a_1 - k_2 a_2),
\]

of pairwise irregular solid harmonics.

Because of the two-dimensional periodicity this lattice sum can be Fourier expanded as follows [9]

\[
S^{(l_A)}_{m_A} (r) = \sum_{g} \tilde{S}^{(l_A)}_{m_A} (g|z) \exp(i g \cdot r),
\]

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with reciprocal lattice vectors
\[ g = n_1 b_1 + n_2 b_2 \quad (a_i \cdot b_j = 2\pi \delta_{ij}) . \] (8)

In eq. (7), the vector \( r = r_A \) is decomposed into its projection \( \tau \) on the \( xy \) plane and its component \( z e_z \) along the \( z \) axis. The Fourier coefficients are given by the Fourier transform [9]

\[ \mathcal{S}_m^{(l)}(g \mid z) = \frac{1}{\sigma_c} \int_{xy} \mathcal{Y}_m^{(l)}(\tau + z e_z) \exp(-ig \cdot \tau) \, d\tau \quad (z \neq 0) , \] (9)

where \( \sigma_c \) is the area of the two-dimensional unit cell and the integration has to be performed over the entire \( xy \) plane. We will derive an analytical expression for the two-dimensional integral of eq. (9). To this end, we use the following cylindrical expansion of a two-dimensional plane wave

\[ \exp(-ig \cdot \tau) = \sum_{n=-\infty}^{\infty} (-i)^n J_n(g \tau) \exp(i\varphi_\tau) \exp(-in\varphi) , \] (10)

which comprises Bessel functions \( J_n \) of the first kind [14]. The symbols \( \varphi_\tau \) and \( \varphi \) denote the angles of the vectors \( g \) and \( \tau \) with respect to the \( x \) axis, \( g \) and \( \tau \) are the lengths of these vectors. The irregular solid harmonic is written in terms of associated Legendre functions \( P^m_l \) as [13]

\[ \mathcal{Y}_m^{(l)}(\tau + z e_z) = (-1)^m \left( \frac{(l-m)!}{(l+m)!} \right)^{1/2} \frac{1}{\sqrt{z^2 + \tau^2}} \left( \frac{z}{\sqrt{z^2 + \tau^2}} \right)^{l+1} P^m_l \left( \frac{z}{\sqrt{z^2 + \tau^2}} \right) \exp(i\varphi) . \] (11)

After substitution of eqs. (10) and (11) into eq. (9) and performing the integration over \( \varphi \), we obtain

\[ \mathcal{S}_m^{(l)}(g \mid z) = \frac{2\pi}{\sigma_c} \left( \frac{(l-m)!}{(l+m)!} \right)^{1/2} i^m f_m^{(l)}(g \mid z) \exp(i\varphi) , \] (12)

with radial integrals

\[ f_m^{(l)}(g \mid z) = \int_0^\infty \left( \frac{1}{\sqrt{z^2 + \tau^2}} \right)^{l+1} P^m_l \left( \frac{z}{\sqrt{z^2 + \tau^2}} \right) J_m(g \tau) \, \tau \, d\tau . \] (13)

The integrals of eq. (13) are relatively simple in the case \( g = 0 \). Because of the property [14]

\[ J_m(0) = \delta_{m0} , \] (14)

they reduce to

\[ f_m^{(l)}(0 \mid z) = \delta_{m0} z^{-l+1} \int_0^1 \rho^{l-2} P_l(\rho) \, d\rho = \delta_{l1} \delta_{m0} \quad (l \geq 1) \] (15)

with \( \rho = z/\sqrt{z^2 + \tau^2} \). We observe that the integral of eq. (15) does not exist for the monopole–monopole interaction \( (l=0) \).

Although the radial Fourier integrals of eq. (13) are much more complicated for \( g > 0 \), an analytical solution is also possible in this case. These integrals are closely connected to specific Hankel transforms which are tabulated in ref. [15]. Alternatively, they can all be derived from the well-known isotropic \( (l=0) \) integral

\[ f_0^{(l)}(g \mid z) = g^{-1} \exp(-gz) \] (16)

given in ref. [9], with the aid of the relation

\[ f_m^{(l)}(g \mid z) = g^m(-1)^{l-m} \frac{1}{(l-m)!} \frac{d^{l-m}}{dz^{l-m}} f_0^{(l)}(g \mid z) \quad (m \geq 0) . \] (17)
This relation is derived in two steps. First, it can be proved, using partial integration and some properties of the associated Legendre and Bessel functions \[14\], that the indices \(l\) and \(m\) of \(f^{(l)}_m\) can be raised simultaneously for \(l=m\) using

\[
f^{(m)}_m(g|z) = g f^{(m-1)}_{m-1}(g|z) \quad (m \geq 1).
\]  

(18)

Secondly, from the derivative of eq. (13) with respect to \(z\), it follows that

\[
f^{(l)}_m(g|z) = -\frac{1}{l-m} \frac{\partial}{\partial z} f^{(l-1)}_{m-1}(g|z) \quad (l \geq 1),
\]  

(19)

which can be used to raise the index \(l\) for fixed \(m\). After successive application of eqs. (18) and (19) to the monopole integral we arrive at eq. (17), which is not directly applicable for negative values of the index \(m\). In that case, however, the symmetry property

\[
f^{-l}_m(g|z) = (-1)^l f^{-l}_{m-l}(g|z)
\]  

(20)

can be used as an intermediate step. The combination of eqs. (16), (17) and (20) results in the desired analytical expression

\[
f^{(l)}_m(g|z) = \frac{1}{(l-m)!} g^{l-1} \exp(-gz) \quad (g > 0),
\]  

(21)

which is surprisingly simple. This expression, which is also given in ref. [15], is valid for all relevant \(m\) values. After substitution of eqs. (15) and (21) into (12) we obtain the final result

\[
S^{(l)}_m(g|z) = \frac{2\pi}{\sigma_c} \delta_{l1} \delta_{m0} \quad (g=0, l \geq 1),
\]  

(22)

We have now transformed the sum over pair interactions, occurring in eq. (6), into a two-dimensional Fourier series (7) with coefficients that can be calculated with the aid of eq. (22). Thus, the two-dimensional lattice sum has been written analytically. Eq. (22) is not valid if \(z=0\), i.e. if the single multipole lies in the lattice plane. A method of evaluating the two-dimensional lattice sum for that case can be found in ref. [2].

The analytical two-dimensional Fourier series derived above is also convenient to evaluate three-dimensional lattice sums of general multipole–multipole interactions for semi-infinite and infinite crystals, via planewise summation. For a semi-infinite three-dimensional lattice we replace eq. (2) by

\[
r_B = k_1 a_1 + k_2 a_2 - k_3 a_3 \quad (k_3 \geq 0)
\]  

(23)

and substitute this into eq. (6). If we then write the interlayer translation \(a_3\) as \(\Delta r = \Delta \tau + \Delta z e_3\), the summation over the layers can be performed analytically with the aid of the rapidly converging series

\[
\sum_{k_3=0}^{\infty} \exp[k_3 (-g \Delta z + ig \cdot \Delta \tau)] = \frac{1}{1 - \exp(-g \Delta z + ig \cdot \Delta \tau)},
\]  

(24)

which yields

\[
\sum_{k_3=0}^{\infty} S^{(l)}_m(r + k_3 \Delta r) = \frac{2\pi}{\sigma_c} \frac{\delta_{l1} \delta_{m0}}{[(l-m)!(l+m)!]^{-1/2} i^m g^{l-1} \exp(-gz+im \varphi_e) \exp(im \varphi_e)}
\]  

(25)

The combination of two of these semi-infinite lattice sums with the two-dimensional lattice sum for \(z=0\) [2]...
gives the three-dimensional lattice sum for an infinite crystal. One has to be careful, however, if \( l \leq 2 \), because in that case the original three-dimensional lattice sum of irregular solid harmonics is conditionally convergent, i.e. the result depends on the order of summation which is prescribed by the macroscopic shape of the crystal [2-5]. As pointed out by Nijboer and De Wette [3] this implies that for \( l \leq 2 \) the layerwise summation is only correct for slablike materials. For \( l \geq 3 \) the lattice sum is absolutely convergent, i.e. independent of the crystal shape, so that a planewise summation may always be applied.

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References