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2002 J. Phys.: Condens. Matter 14 3175

(http://iopscience.iop.org/0953-8984/14/12/308)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 3175–3198 PII: S0953-8984(02)27281-1

Calculation of coulombic lattice potentials: II. Spherical harmonic expansion of the Green function

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Received 27 July 2001, in final form 16 January 2002
Published 15 March 2002
Online at stacks.iop.org/JPhysCM/14/3175

Abstract

The modified Green function appropriate for calculation of coulombic lattice potentials is developed in a spherical harmonic expansion. This is derived from the corresponding Ewald sum in Cartesian coordinates, by applying Gegenbauer's addition theorem for modified spherical Bessel functions to the screened Coulomb potentials resulting from Laplace transformation with respect to the scalar convergence parameter, and Bauer's expansion to the plane waves. It is useful where the charge-density distribution about each nucleus is represented by a spherical harmonic expansion. Radial coefficients of the spherical harmonics are attenuated exponentially, and orthogonality reduces determination of electrostatic lattice potentials to one-dimensional quadratures. This use of the Green function is contrasted with conventional approaches based on point-multipole representations, in which important information on the diffuseness of electronic charge density around the nuclei may be lost in the calculation of multipole coefficients. Possible applications of this result in electronic structure calculations are briefly discussed.

1. Introduction

The physical properties of solids are all ultimately determined by the manner in which the electrons are distributed around nuclei, and the extent to which this distribution is affected, at short and long distances, by surrounding atoms in the lattice. The calculation of the potential energy associated with long-range coulombic forces is an interesting problem, with a long history dating back to the work of Madelung (1918) on the cohesive energy of ionic lattices. The numerous treatments that have been published since then can be divided into two broad groups: those that approximate the crystal as a collection of point charges, and those where electronic structure is also considered.

The first category, which includes the celebrated Ewald (1921) method, focuses on the evaluation of lattice sums for the Coulomb potential. These involve replacement of the reciprocal distance with its representation as a Gaussian integral (Ewald 1921, Chaba and Pathria 1975, 1976a, 1976b), a gamma function integral (van der Hoff and Benson 1953,

Lekner 1991, 1998, Grønbech-Jensen *et al* 1997), or various types of Fourier–Bessel integral (Hautot 1974, Macdonald and Barlow 1966, Marshall and Conway 1992a, 1992b, Miller 1995). Other approaches have relied on the connection between lattice sums and multi-dimensional generalizations of the Riemann zeta function (Lennard-Jones and Ingham 1925, Topping 1927, Glasser 1973a, 1973b, Zucker 1974–6).

The second category of methods, which have arisen from solid-state electronic structure calculations, involves representation of the charge density by multipole expansions within spherical regions centred at the nuclear positions and by a plane-wave expansion in the interstitial regions (Rudge 1969a, Weinert 1981, Herzig 1985, Krasovskii *et al* 1999), or bipolar spherical harmonic expansion of the periodic Green function for Poisson's equation (Schadler 1992, Oh *et al* 1992, Zhang *et al* 1994). The resulting expressions for the potential involve doubly infinite series of spherical harmonics, which are often conditionally convergent.

Recently (Marshall (2000); hereinafter referred to as part I), I showed that point-charge lattice sums could be efficiently evaluated by use of a periodic Green function for Poisson's equation, represented either as a Fourier series involving modified Bessel functions of the second kind (cf Lekner 1991, 1998) resulting from application of the Poisson summation formula (cf Marshall 1998a, 1998b, 1999), or as an Ewald expansion in Gaussian exponentials and complementary error functions; the Bessel function series is the more rapidly convergent. Two salient advantages of using Green functions can be identified:

(1) the potential due to a periodic charge distribution is given explicitly as the integral of the product of the charge density and the Green function over the volume of the unit cell; and
(2) numerical ambiguities associated with the conditional convergence of Coulomb lattice sums are avoided.

Although the use of the Green function to determine the potential in this manner is in principle equally applicable to continuous or discrete charge-density distributions, the representations derived in part I are not necessarily in the most convenient form for performing the required integrations. The purpose of the present paper is to describe a spherical harmonic representation of the Green function, and to demonstrate how this enables the above two advantages to be realized for a periodic charge density in the form resulting from solid-state electronic structure calculations. The principal motivation for this work was the problem of calculating the electrostatic potential due to water molecules in crystalline gas clathrate hydrates.

2. Overview

In the following sections, the simple physical model used to represent the charge density of a crystal is described, and the relevant geometrical variables defined. Following this, the three groups of terms that make up the Green function are in turn expanded in spherical harmonics, in which the coefficient radial parts are expressed in terms of a Gaussian integral involving a modified spherical Bessel function, or as a series of complementary error function integrals. An expression is also given for the non-singular part of the Green function. Finally, calculation of lattice potentials by use of the Green function is contrasted with conventional approaches based on multipole expansions.

3. Analysis

3.1. Definition of geometrical variables

A representation of a crystal as spherical charge distributions arranged in a lattice generated by an orthogonal basis of primitive translation vectors is depicted in figure 1. The potential

is required at a field point $\boldsymbol{r}$, due to a distribution centred at $\boldsymbol{r_0}$, and its repetitions centred at $\boldsymbol{r_0} + \boldsymbol{R_K}$, where

$$\boldsymbol{R_K} = (Na, Mb, Kc), \tag{1}$$

N, M, and K are integers, and a, b, and c are lattice parameters. The charge density within each sphere can be regarded as a distribution of point charges, whose spherical polar coordinates are expressed relative to the centre, with a polar axis parallel to one of the lattice coordinates:

$$\boldsymbol{r}' = \boldsymbol{r_0} + \boldsymbol{\rho}' \qquad \boldsymbol{\rho}' = (\rho' \sin\theta' \cos\phi', \rho' \sin\theta' \sin\phi', \rho' \cos\theta'). \tag{2}$$

The source points in each of the repeated spheres occupy the same positions with respect to the centres. It proves more convenient to specify the position of the field point in terms of the same coordinate system than with respect to the origin of the central unit cell, by means of the vector

$$\boldsymbol{\rho_K} = \boldsymbol{r} - \boldsymbol{r_0} - \boldsymbol{R_K}, \tag{3}$$

whose spherical polar coordinates are

$$\rho_K = \sqrt{(x - x_0 - Na)^2 + (y - y_0 - Mb)^2 + (z - z_0 - Kc)^2} \tag{4a}$$

$$\theta_K = \arccos\left(\frac{z - z_0 - Kc}{\rho_K}\right) \tag{4b}$$

$$\phi_K = \arctan\left(\frac{y - y_0 - Mb}{x - x_0 - Na}\right). \tag{4c}$$

The spherical harmonic expansion of the complementary error function terms in the Green function relies on the relation between the displacement from the source point in each sphere to the field point, the magnitudes of the vectors $\boldsymbol{\rho_K}$ and $\boldsymbol{\rho}'$, and the angle γ_K between them, which is

$$|\boldsymbol{\rho_K} - \boldsymbol{\rho}'| = \sqrt{\rho_K^2 + \rho'^2 - 2\rho_K \rho' \cos\gamma_K}; \tag{5}$$

the angle γ_K can in turn be related to the spherical polar coordinates of these two vectors:

$$\cos\gamma_K = \cos\theta_K \cos\theta' + \sin\theta_K \sin\theta' \cos(\phi_K - \phi'). \tag{6}$$

3.2. The periodic Green function: plane-wave expansion and Ewald sum

The periodic Green function P_{222} for the lattice is represented by the plane-wave expansion

$$P_{222}(\boldsymbol{r}|\boldsymbol{r}') = \frac{1}{abc}\sum_{\boldsymbol{k}}{}' \frac{e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{|\boldsymbol{k}|^2} \qquad \boldsymbol{r} = (x, y, z) \qquad \boldsymbol{k} = \left(\frac{2n\pi}{a}, \frac{2m\pi}{b}, \frac{2k\pi}{c}\right), \tag{7}$$

in which the lattice parameters in the x-, y-, and z-directions are a, b, and c, respectively, and the summation extends over all $\boldsymbol{k}$-space points except the origin $n = m = k = 0$. (The subscripts 2 signify that each coordinate axis is intersected by two planar boundaries.) Physically, this function gives the potential at $\boldsymbol{r}$ due to a unit positive point charge at $\boldsymbol{r}'$, a superimposed unit negative charge distributed uniformly over the entire unit cell, and infinite periodic repetitions of this arrangement in three directions. Decomposition of equation (7) into one-, two-, and three-dimensional contributions and application of the Poisson summation formula gives a series of two-dimensional logarithmic potentials plus a Fourier series containing modified Bessel functions of the second kind. Ewald summation results in a series of complementary error functions and an attenuated Fourier series:

$$P_{222}(\boldsymbol{r}|\boldsymbol{r}') = \frac{1}{4\pi}\sum_{\boldsymbol{K}} \frac{\operatorname{erfc}(|\boldsymbol{r} - \boldsymbol{r}' - \boldsymbol{R_K}|/2\sqrt{t})}{|\boldsymbol{r} - \boldsymbol{r}' - \boldsymbol{R_K}|} - \frac{t}{abc} + \frac{1}{abc}\sum_{\boldsymbol{K}}{}' \frac{e^{-t|\boldsymbol{k}|^2 + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{|\boldsymbol{k}|^2} \tag{8}$$

$\boldsymbol{R_K} = (Na, Mb, Kc)$.

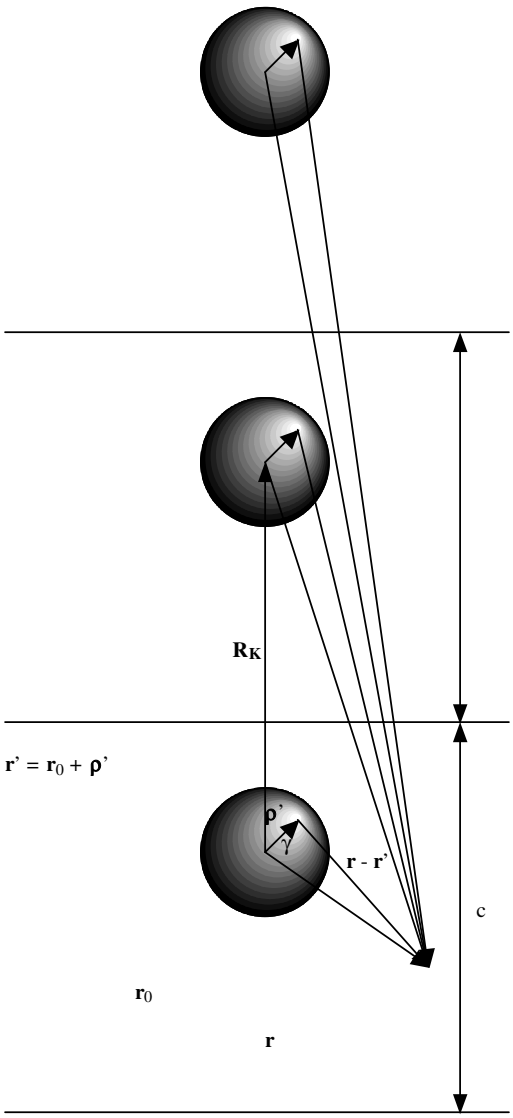

Figure 1. Definition of the geometrical variables and coordinates.

The first summation extends over all values of the indices K, M, and N, and each term can be regarded as expressing the effect of a repetition of the source in neighbouring cells. The value of the scalar convergence parameter t determines the contributions of the Fourier (reciprocal-space) and Coulomb (real-space) sums to the final result; its value can be chosen such that the same number of terms are required for convergent estimates of each series. As shown in part I, the Bessel function expansion converges considerably more rapidly than the Ewald sum, and is therefore to be preferred if the charge distribution in the unit cell can be accurately represented as a discrete set of points. Since for any charge distribution σ satisfying the electroneutrality condition

$$\int_{\Omega} \sigma(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}' = 0 \tag{9}$$

the potential is given by

$$V(\boldsymbol{r}) = 4\pi \int_{\Omega} \sigma(\boldsymbol{r}') P_{222}(\boldsymbol{r}|\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}', \tag{10}$$

determination of the potential reduces in principle to numerical quadratures, for which either representation of the Green function would be suitable. 'Brute-force' application of multidimensional quadrature methods is almost certainly impractical: a relatively coarse mesh consisting of 10 nodes on each axis would require 1000 function evaluations, and the concentration of most of the electron density in relatively small volumes about the nuclei would require that the nodes be much more numerous and closely spaced in these regions. But if the charge density about each nucleus can be expanded in a series of normalized spherical harmonics

$$\sigma(\rho, \theta, \phi) = \sum_{p=0}^{\infty} \sum_{q=-p}^{p} \sigma_{pq}(\rho) Y_p^q(\theta, \phi) \tag{11}$$

and the Green function can be similarly represented, most of the terms in the integrand vanish by orthonormality on integration with respect to the angular coordinates, leaving a series of one-dimensional integrals that can be evaluated numerically, or in favourable cases, analytically.

3.3. Transformation of the complementary error function terms

To construct a spherical harmonic expansion of the first series on the right-hand side of equation (8), namely

$$S_1 = \frac{1}{4\pi} \sum_{\boldsymbol{K}} \frac{\operatorname{erfc}(|\boldsymbol{r} - \boldsymbol{r}' - \boldsymbol{R}_{\boldsymbol{K}}|/2\sqrt{t})}{|\boldsymbol{r} - \boldsymbol{r}' - \boldsymbol{R}_{\boldsymbol{K}}|}, \tag{12}$$

the coordinates of the field and source point vectors are expressed in terms of the spherical coordinates about the $\boldsymbol{K}$th repeated sphere, as defined in equations (3)–(6):

$$S_1 = \frac{1}{4\pi} \sum_{\boldsymbol{K}} \frac{\operatorname{erfc}(|\boldsymbol{\rho}_{\boldsymbol{K}} - \boldsymbol{\rho}'|/2\sqrt{t})}{|\rho_{\boldsymbol{K}} - \rho'|} = \frac{1}{4\pi} \sum_{\boldsymbol{K}} \frac{\operatorname{erfc}\left(\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}/2\sqrt{t}\right)}{\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}}; \tag{13}$$

taking the Laplace transform with respect to t gives (Erdélyi *et al* 1954, p 177, formula (11))

$$\bar{S}_1 = \frac{1}{4\pi} \sum_{\boldsymbol{K}} \frac{\exp\left(-s^{1/2}\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}\right)}{s\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}}. \tag{14}$$

This transformed series of error functions can now be expanded in Legendre polynomials by use of Gegenbauer's addition theorem for modified spherical Bessel functions (Watson 1944, p 366):

$$\frac{\exp\left(-s^{1/2}\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}\right)}{s\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho' \cos\gamma_{\boldsymbol{K}}}} = \sum_{n=0}^{\infty} (2n+1) \frac{I_{n+1/2}(\rho'\sqrt{s}) K_{n+1/2}(\rho_{\boldsymbol{K}}\sqrt{s})}{s\sqrt{\rho'\rho_{\boldsymbol{K}}}} P_n(\cos\gamma_{\boldsymbol{K}}) \tag{15}$$

or, somewhat more simply,

$$\frac{\exp\left(-s^{1/2}\sqrt{\rho_K^2+\rho'^2-2\rho_K\rho'\cos\gamma_K}\right)}{s\sqrt{\rho_K^2+\rho'^2-2\rho_K\rho'\cos\gamma_K}}=\frac{2}{\pi}\sum_{n=0}^{\infty}(2n+1)\frac{i_n(\rho'\sqrt{s})k_n(\rho_K\sqrt{s})}{\sqrt{s}}P_n(\cos\gamma_K) \tag{16}$$

where

$$i_n(z)=\sqrt{\frac{\pi}{2z}}I_{n+1/2}(z)\qquad k_n(z)=\sqrt{\frac{\pi}{2z}}K_{n+1/2}(z). \tag{17}$$

From the closed-form representations (Watson 1944, p 80) of the i and k Bessel functions

$$i_n(z)=\frac{1}{2z}\left[\mathrm{e}^z\sum_{p=1}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!(2z)^p}+(-1)^{n+1}\mathrm{e}^{-z}\sum_{p=1}^{n}\frac{(n+p)!}{p!(n-p)!(2z)^p}\right] \tag{18a}$$

and

$$k_n(z)=\frac{\pi}{2z}\mathrm{e}^{-z}\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!(2z)^p}, \tag{18b}$$

it is clear that the Laplace transform represented by equation (16) will tend to zero with increasing s only if the argument of the k Bessel function is greater than the argument of the i Bessel function: this condition is necessary for the existence of the inverse Laplace transform. If this condition is not satisfied, convergence can be ensured simply by interchanging the two arguments. The limiting form of equation (16) obtained when the two radial arguments are both equal to ρ is

$$\frac{\mathrm{e}^{-\rho\sqrt{2s(1-\cos\gamma_K)}}}{s\rho\sqrt{2(1-\cos\gamma_K)}}=\frac{2}{\pi}\sum_{n=0}^{\infty}(2n+1)\frac{i_n(\rho\sqrt{s})k_n(\rho\sqrt{s})}{\sqrt{s}}P_n(\cos\gamma_K); \tag{16a}$$

the sum of Legendre functions on the right-hand side does not seem to be otherwise expressible in closed form, but it is finite if the cosine of the angle gamma is different from 1. The expression necessarily becomes singular as the $\cos\gamma_K$ approaches 1—this singularity is identical to that possessed by the well-known expansion of the free-space Green function in Legendre functions (Barton 1989, p 384), and is just the polar-coordinate counterpart of that shown by the $\boldsymbol{K}=\boldsymbol{0}$ error function term in the original form of the Ewald sum. The Legendre functions can be expanded further by applying the addition theorem for spherical harmonics (Morse and Feshbach 1953, p 1274):

$$P_n(\cos\gamma_K)=\frac{4\pi}{2n+1}\sum_{m=-n}^{n}Y_n^m(\theta_K,\phi_K)Y_n^{m*}(\theta',\phi'). \tag{19}$$

Combining equations (14), (16), and (18),

$$\bar{S}_i=\frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\frac{i_n(\rho'\sqrt{s})k_n(\rho_K\sqrt{s})}{\sqrt{s}}\left\{\sum_{m=-n}^{n}Y_n^m(\theta_K,\phi_K)Y_n^{m^*}(\theta',\phi')\right\}. \tag{20}$$

As shown in the appendix, the required inverse Laplace transform is

$$\mathrm{L}^{-1}\left[\frac{i_n(\rho'\sqrt{s})k_n(\rho_K\sqrt{s})}{\sqrt{s}}\right]=\int_0^t\frac{\mathrm{e}^{-(\rho_K^2+\rho'^2)/4t}}{2\sqrt{\pi t^3}}i_n\left(\frac{\rho_K\rho'}{2t}\right)\mathrm{d}t. \tag{21}$$

An alternative representation, which is more convenient for some purposes, follows by expanding the Bessel functions according to equations (18a) and (18b), and noting that the inverse Laplace transform of each term is a repeated integral of the complementary error

function (*Handbook of Mathematical Functions* 1964, p 1026, formula 29.3.86). The required result can therefore be written as

$$S_1 = \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\left\{\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}A_{pq}\frac{(2\sqrt{t})^{p+q+1}}{\rho_{\boldsymbol{K}}^{p+1}\rho'^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{\rho_{\boldsymbol{K}}-\rho'}{2\sqrt{t}}\right)\right.$$
$$\left.+(-1)^{n+1}\sum_{p=0}^{n}\sum_{q=0}^{n}B_{pq}\frac{(2\sqrt{t})^{p+q+1}}{\rho_{\boldsymbol{K}}^{p+1}\rho'^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{\rho_{\boldsymbol{K}}-\rho'}{2\sqrt{t}}\right)\right\}$$
$$\times\left\{\sum_{m=-n}^{n}Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}})Y_n^{m^*}(\theta',\phi')\right\} \tag{22a}$$

where as shown in the appendix, the coefficients are complicated products of factorials and

$$\operatorname{erfci}_n(z) \equiv \mathrm{i}^n\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{(t-z)^n}{n!}\mathrm{e}^{-t^2}\,\mathrm{d}t,$$

or more compactly as

$$S_1 = \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\left\{\int_0^t\frac{\mathrm{e}^{-(\rho_{\boldsymbol{K}}^2+\rho'^2)/4t}}{2\sqrt{\pi t^3}}i_n\left(\frac{\rho_{\boldsymbol{K}}\rho'}{2t}\right)\mathrm{d}t\right\}\left\{\sum_{m=-n}^{n}Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}})Y_n^{m^*}(\theta',\phi')\right\}. \tag{22b}$$

3.4. Transformation of the constant term

The second term on the right-hand side of equation (8) corresponds physically to the effect of the uniform neutralizing background charge that ensures the convergence of the Green function. This is

$$S_2 = -\frac{t}{abc}, \tag{23}$$

and since the first of the normalized spherical harmonics is

$$Y_0^0(\theta',\phi') = Y_0^{0^*}(\theta',\phi') = \frac{1}{\sqrt{4\pi}}, \tag{24}$$

$$S_2 = -\frac{t\sqrt{4\pi}}{abc}Y_0^{0^*}(\theta',\phi'). \tag{25}$$

3.5. Transformation of the Fourier series

The development of the plane-wave terms in spherical harmonics can be achieved by application of Bauer's (1859) formulae (cf Watson (1944, p 368), Morse and Feshbach (1953, p 1466)):

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi\sum_{n'=0}^{\infty}\mathrm{i}^n j_n(kr)\sum_{m=-n}^{n}Y_n^m(\theta,\phi)Y_n^{m^*}(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}) \tag{26a}$$

$$\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi\sum_{n'=0}^{\infty}\mathrm{i}^{-n} j_n(kr)\sum_{m=-n}^{n}Y_n^{m^*}(\theta,\phi)Y_n^{m}(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}) \tag{26b}$$

where θ, ϕ and $\theta_{\boldsymbol{K}}, \phi_{\boldsymbol{K}}$ are the polar angles associated with the vectors $\boldsymbol{r}$ and $\boldsymbol{k}$, respectively, and j_n is the spherical Bessel function of order n. In the present context, the vector $\boldsymbol{r}-\boldsymbol{r}'$ appearing in equation (8) can be written as

$$\boldsymbol{r}-\boldsymbol{r}' = \boldsymbol{r}-\boldsymbol{r}_0-\boldsymbol{\rho}', \tag{27}$$

so that

$$\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}'}. \tag{28}$$

The plane-wave series can therefore be written as

$$S_3 = \frac{1}{abc}\sum_{k}{}' \frac{\mathrm{e}^{-t|\boldsymbol{k}|^2 - \mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2} \sum_{n=0}^{\infty} \mathrm{i}^{-n} j_n(k\rho') \sum_{m=-n}^{n} Y_n^{m^*}(\theta', \phi') Y_n^m(\theta_{\boldsymbol{K}}, \phi_{\boldsymbol{K}}). \tag{29}$$

3.6. The periodic Green function: spherical harmonic expansion

The required representation of the periodic Green function follows by combining the expressions given in equations (22), (25) and (29):

$$\begin{aligned} P_{222}(\boldsymbol{r}|\boldsymbol{r}') = {} & \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\left\{\int_0^t \frac{\mathrm{e}^{-(\rho_{\boldsymbol{K}}^2+\rho'^2)/4t}}{2\sqrt{\pi t^3}} i_n\left(\frac{\rho_{\boldsymbol{K}}\rho'}{2t}\right)\mathrm{d}t\right\}\left\{\sum_{m=-n}^{n} Y_n^m(\theta_{\boldsymbol{K}}, \phi_{\boldsymbol{K}}) Y_n^{m^*}(\theta', \phi')\right\} \\ & - \frac{t\sqrt{4\pi}}{abc} Y_0^{0^*}(\theta', \phi') + \frac{1}{abc}\sum_{\boldsymbol{k}}{}' \frac{\mathrm{e}^{-t|\boldsymbol{k}|^2 - \mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2} \sum_{n=0}^{\infty} \mathrm{i}^{-n} j_n(k\rho') \\ & \times \sum_{m=-n}^{n} Y_n^{m^*}(\theta', \phi') Y_n^m(\theta_{\boldsymbol{K}}, \phi_{\boldsymbol{K}}). \end{aligned} \tag{30}$$

The dependence of the terms in this expression on the radial variables is qualitatively similar to that in the Cartesian form, equation (8). Thus, the coefficients of the spherical harmonics decay exponentially to zero when summed over the real and reciprocal lattices; the rapidity of attenuation of the real-space terms depends inversely on the value of t, whereas that of the reciprocal-space terms depends directly on the value of t. The significance of this is that the conditional convergence arising in earlier treatments (Herzig 1985, Schadler 1992, Zhang *et al* 1994) is eliminated. The behaviour of this (or any) Green function as the field and source points approach each other is of particular interest. From equation (8), the singularity is clearly localized in the error function term with $\boldsymbol{K} = \boldsymbol{0}$; that the singularity in equation (30) is similarly localized in the $\boldsymbol{K} = \boldsymbol{0}$ term of the real-space sum is easily seen by expanding the exponential on the left-hand side of equation (16):

$$\begin{aligned} & \frac{\exp\left(-s^{1/2}\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho'\cos\gamma_{\boldsymbol{K}}}\right)}{s\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho'\cos\gamma_{\boldsymbol{K}}}} \\ & \qquad = \frac{1}{s}\sum_{p=0}^{\infty} \frac{(-1)^p s^{p/2}}{p!} [\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho'\cos\gamma_{\boldsymbol{K}}]^{(p-1)/2}. \end{aligned} \tag{31}$$

As $\rho_{\boldsymbol{K}}$ tends to ρ' and $\gamma_{\boldsymbol{K}}$ tends to zero, all terms vanish except the first, for which

$$\lim_{\rho_{\boldsymbol{K}}\to\rho', \gamma_{\boldsymbol{K}}\to 0} \frac{1}{s\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho'\cos\gamma_{\boldsymbol{K}}}} = \infty. \tag{32}$$

The non-singular part can be isolated by subtraction of the free-space Green function

$$G_{000}(\boldsymbol{r}|\boldsymbol{r}') = \frac{1}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|} = \frac{1}{4\pi\sqrt{\rho_{\boldsymbol{K}}^2 + \rho'^2 - 2\rho_{\boldsymbol{K}}\rho'\cos\gamma_{\boldsymbol{K}}}}. \tag{33}$$

Assuming that $\rho_{\boldsymbol{K}} > \rho'$, this can be expanded in Legendre functions (Barton 1989, p 384):

$$G_{000}(\boldsymbol{r}|\boldsymbol{r}') = \frac{1}{4\pi\rho_{\boldsymbol{K}}}\sum_{n=0}^{\infty}\left(\frac{\rho'}{\rho_{\boldsymbol{K}}}\right)^n P_n(\cos\gamma_{\boldsymbol{K}}), \tag{34}$$

with the result that

$$Q_{222}(\boldsymbol{r}|\boldsymbol{r}') \equiv P_{222}(\boldsymbol{r}|\boldsymbol{r}') - G_{000}(\boldsymbol{r}|\boldsymbol{r}')$$
$$= \sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\left\{\frac{2}{\pi}\int_0^t \frac{\mathrm{e}^{-(\rho_{\boldsymbol{K}}^2+\rho'^2)/4t}}{2\sqrt{\pi t^3}} i_n\left(\frac{\rho_{\boldsymbol{K}}\rho'}{2t}\right)\mathrm{d}t - \frac{1}{(2n+1)\rho_{\boldsymbol{K}}}\left(\frac{\rho'}{\rho_{\boldsymbol{K}}}\right)^n\right\}$$
$$\times\left\{\sum_{m=-n}^{n} Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}})Y_n^{m^*}(\theta',\phi')\right\} - \frac{t\sqrt{4\pi}}{abc}Y_0^{0^*}(\theta',\phi')$$
$$+ \frac{1}{abc}{\sum_{\boldsymbol{k}}}' \frac{\mathrm{e}^{-t|\boldsymbol{k}|^2-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\sum_{n=0}^{\infty}\mathrm{i}^{-n}j_n(k\rho')\sum_{m=-n}^{n}Y_n^{m^*}(\theta',\phi')Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}). \quad (35)$$

3.7. Determination of the potential

The potential at $\boldsymbol{r}$ due to a charge distribution about $\boldsymbol{r}_0$ given by equation (11) is given by the integral

$$V(\boldsymbol{r}) = 4\pi\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')P_{222}(\boldsymbol{r}|\boldsymbol{r}')\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$= 4\pi\int_{\rho'=0}^{r_1}\int_{\theta'=0}^{\pi}\int_{\phi'=0}^{2\pi}\left\{\sum_{n=0}^{\infty}\sum_{m=-n}^{n}\sigma_{mn}(\rho')Y_n^m(\theta',\phi')\right\}$$
$$\times P_{222}(\boldsymbol{r}|\boldsymbol{r}')\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'. \quad (36)$$

The operations of Laplace transformation and integration with respect to the radial coordinate are interchangeable, subject to relatively mild restrictions on the radial coefficient functions. Assuming that these conditions are satisfied, the contribution of the real-space sum to the potential can be evaluated either by integrating the Laplace transform times each σ-component (defined in equation (11)) and inverting the result, or by integrating the σ-component times the original function given by equation (20). Thus, proceeding in the first way, the integral of σ times the Laplace transform of S_1 is

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')\bar{S}_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$= \frac{2}{\pi}\int_{\rho'=0}^{r_1}\int_{\theta'=0}^{\pi}\int_{\phi'=0}^{2\pi}\left\{\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sigma_{pq}(\rho')Y_p^q(\theta',\phi')\right\}\sum_{\boldsymbol{K}}\sum_{n=0}^{\infty}\frac{i_n(\rho'\sqrt{s})k_n(\rho_{\boldsymbol{K}}\sqrt{s})}{\sqrt{s}}$$
$$\times\left\{\sum_{m=-n}^{n}Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}})Y_n^{m^*}(\theta',\phi')\right\}\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'. \quad (37)$$

The integrals of all products of the spherical harmonics vanish by orthonormality except that for which $n = p$ and $m = q$, which is unity, so

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')\bar{S}_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$= \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\left\{\int_{\rho'=0}^{r_1}\sigma_{pq}(\rho')\frac{i_n(\rho'\sqrt{s})k_n(\rho_{\boldsymbol{K}}\sqrt{s})}{\sqrt{s}}\rho'^2\,\mathrm{d}\rho'\right\}Y_p^q(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}). \quad (38)$$

Taking the inverse Laplace transform of equation (37),

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')S_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$= \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\mathrm{L}^{-1}\left\{\int_{\rho'=0}^{r_1}\sigma_{pq}(\rho')\frac{i_n(\rho'\sqrt{s})k_n(\rho_{\boldsymbol{K}}\sqrt{s})}{\sqrt{s}}\rho'^2\,\mathrm{d}\rho'\right\}Y_p^q(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}). \quad (39)$$

The orthonormality of the spherical harmonics is not affected by the interchange of Laplace transformation and radial integration. Thus, for example, it follows from equation (22*a*) that

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')S_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi' = \frac{2}{\pi}\sum_{\boldsymbol{K}}\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\int_{\rho'=0}^{r_1}\sigma_{pq}(\rho')$$
$$\times\left\{\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}A_{pq}\frac{(2\sqrt{t})^{p+q+1}}{\rho_{\boldsymbol{K}}^{p+1}\rho'^{q+1}}\,\mathrm{erfci}_{p+q+1}\left(\frac{\rho_{\boldsymbol{K}}-\rho'}{2\sqrt{t}}\right)\right.$$
$$\left.+\sum_{p=0}^{n}\sum_{q=0}^{n}B_{pq}\frac{(2\sqrt{t})^{p+q+1}}{\rho_{\boldsymbol{K}}^{p+1}\rho'^{q+1}}\,\mathrm{erfci}_{p+q+1}\left(\frac{\rho_{\boldsymbol{K}}+\rho'}{2\sqrt{t}}\right)\right\}\rho'^2\,\mathrm{d}\rho'\,Y_p^q(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}). \tag{40}$$

Integration of S_2 times σ selects the zeroth term:

$$\int_{\rho'=0}^{r_1}\int_{\theta'=0}^{\pi}\int_{\phi'=0}^{2\pi}\left\{\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sigma_{pq}(\rho')Y_p^q(\theta',\phi')\right\}\left\{-\frac{t\sqrt{4\pi}}{abc}Y_0^{0^*}(\theta',\phi')\right\}\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$=-\frac{t\sqrt{4\pi}}{abc}\left\{\int_0^{r_1}\sigma_{00}(\rho')\rho'^2\,\mathrm{d}\rho'\right\}, \tag{41}$$

and similarly, integration of S_3 produces

$$\int_{\rho'=0}^{r_1}\int_{\theta'=0}^{\pi}\int_{\phi'=0}^{2\pi}\left\{\sum_{p=0}^{\infty}\sum_{q=-p}^{p}\sigma_{pq}(\rho')Y_p^q(\theta',\phi')\right\}\left\{\frac{1}{abc}{\sum_{\boldsymbol{k}}}'\frac{\mathrm{e}^{-t|\boldsymbol{k}|^2-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\sum_{n=0}^{\infty}\mathrm{i}^{-n}j_n(k\rho')\right.$$
$$\left.\times\sum_{m=-n}^{n}Y_n^{m^*}(\theta',\phi')Y_n^m(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}})\right\}\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$=\frac{1}{abc}{\sum_{\boldsymbol{k}}}'\frac{\mathrm{e}^{-t|\boldsymbol{k}|^2-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\sum_{p=0}^{\infty}\mathrm{i}^{-p}$$
$$\times\sum_{q=-p}^{p}\left\{\int_{\rho'=0}^{r_1}\sigma_{pq}(\rho')j_p(k\rho')\rho'^2\,\mathrm{d}\rho'\right\}Y_p^q(\theta_{\boldsymbol{K}},\phi_{\boldsymbol{K}}). \tag{42}$$

Combining these results, it is seen that the potential at the field point is the sum of terms that are equivalent to distributed monopole, dipole, quadrupole, ..., densities about each nucleus.

The relative merits of the two representations of the real-space sum in the Green function given by equations (20) and (21) can be demonstrated most clearly by considering in more detail the evaluation of the integrals appearing in the foregoing general expressions for the potential. Equation (21) has the obvious advantage of compactness, and as shown in the appendix can be evaluated in terms of incomplete gamma functions or exponential integrals. The complementary error function expansion appears somewhat unwieldy, but it possesses the great advantage that its dependence on each radial coordinate can be separated in a way that is apparently not possible for equation (21). Assuming again that the operations of integration with respect to the radial coordinate and Laplace transformation with respect to t are interchangeable, this separability proves valuable in the evaluation of integrals of the form

$$I=\int_0^{r_1}(2\sqrt{t})^n\,\mathrm{erfci}_n\left(\frac{R\pm r}{2\sqrt{t}}\right)f(r)\,\mathrm{d}r, \tag{43}$$

where $R>r_1$ and f represents the product of a radial coefficient function and some inverse power of r. Taking Laplace transforms by application of equation (A.14),

$$\bar{I}=\int_0^{r_1}\frac{\mathrm{e}^{-(R\pm r)\sqrt{s}}}{s^{1+n/2}}f(r)\,\mathrm{d}r=\frac{\mathrm{e}^{-R\sqrt{s}}}{s^{1+n/2}}\int_0^{r_1}\mathrm{e}^{\mp r\sqrt{s}}f(r)\,\mathrm{d}r. \tag{44}$$

Since this integral is over a finite interval, it can be equally well evaluated if the argument of the exponential is of either sign. If the radial functions are determined from a numerical solution of the Schrödinger equation, a numerical quadrature rule with nodes r_p and weights w_p can be applied:

$$\int_0^{r_1} \mathrm{e}^{\mp r\sqrt{s}} f(r)\,\mathrm{d}r \approx \sum_{p=1}^{P} w_p \mathrm{e}^{\mp r_p\sqrt{s}} f(r_p), \tag{45}$$

so one has

$$\bar{I} \approx \frac{\mathrm{e}^{-R\sqrt{s}}}{S^{1+n/2}} \sum_{p=1}^{P} w_p \mathrm{e}^{\mp r_p\sqrt{s}} f(r_p) = \sum_{p=1}^{P} w_p \frac{\mathrm{e}^{(-R\pm r_p)\sqrt{s}}}{s^{1+n/2}} f(r_p) \tag{46}$$

and

$$I \approx \sum_{p=1}^{P} w_p (2\sqrt{t})^n \operatorname{erfci}_n\left(\frac{R \pm r_p}{2\sqrt{t}}\right) f(r_p). \tag{47}$$

If the charge density is uniform throughout the spheres, all terms in equation (11) are zero except that corresponding to $p = q = 0$, which is assumed to be a constant, σ. This model can be regarded as the degenerate limiting case of the spherical atom or 'promolecule' approximation of atomic charge-density distributions, which is used in the refinement of single-crystal x-ray diffraction data and their use in the calculation of properties such as molecular moments (Spackman 1992) and cohesive energies (Trefry *et al* (1987); see also Gibbs *et al* (1992), Feth *et al* (2000), Spackman and Maslen (1987)). On integration with respect to the angular coordinates, all but one of the terms of equation (38) likewise vanish, and applying equations (18*a*) and (18*b*) for $n = 0$, the modified spherical Bessel function product is

$$\frac{k_0(\rho_K\sqrt{s})i_0(\rho'\sqrt{s})}{\sqrt{s}} = \frac{\pi}{4\rho_K\rho' s}[\mathrm{e}^{-(\rho_K-\rho')\sqrt{s}} - \mathrm{e}^{-(\rho_K+\rho')\sqrt{s}}]. \tag{48}$$

The non-vanishing term therefore involves the integral

$$\int_0^{r_1} \frac{k_0(\rho_K\sqrt{s})i_0(\rho'\sqrt{s})}{\sqrt{s}}\sigma_{00}(\rho')\rho'^2\,\mathrm{d}\rho' = \frac{\pi\sigma}{4\rho_K\rho' s^{3/2}}\left[\mathrm{e}^{-\rho_K\sqrt{s}}\int_0^{r_1}\mathrm{e}^{+\rho'\sqrt{s}}\rho'\,\mathrm{d}\rho' - \mathrm{e}^{-\rho_K\sqrt{s}}\int_0^{r_1}\mathrm{e}^{-\rho'\sqrt{s}}\,\mathrm{d}\rho'\right]. \tag{49}$$

Substituting the elementary results

$$\int_0^{r_1}\mathrm{e}^{+\rho'\sqrt{s}}\rho'\,\mathrm{d}\rho' = \frac{r_1\mathrm{e}^{+r_1\sqrt{s}}}{\sqrt{s}} - \frac{\mathrm{e}^{+r_1\sqrt{s}}}{s} + \frac{1}{s} \tag{50a}$$

$$\int_0^{r_1}\mathrm{e}^{-\rho'\sqrt{s}}\rho'\mathrm{d}\rho' = -\frac{r_1\mathrm{e}^{-r_1\sqrt{s}}}{\sqrt{s}} - \frac{\mathrm{e}^{-r_1\sqrt{s}}}{s} + \frac{1}{s} \tag{50b}$$

results in

$$\int_0^{r_1} \frac{k_0(\rho_K\sqrt{s})i_0(\rho'\sqrt{s})}{\sqrt{s}}\sigma_{00}(\rho')\rho'^2\,\mathrm{d}\rho' = \frac{\pi\sigma}{4\rho_K}\left[r_1\frac{\mathrm{e}^{-(\rho_K-r_1)\sqrt{s}} + \mathrm{e}^{-(\rho_K+r_1)\sqrt{s}}}{s^2} - \frac{\mathrm{e}^{-(\rho_K-r_1)\sqrt{s}} - \mathrm{e}^{-(\rho_K+r_1)\sqrt{s}}}{s^{5/2}}\right], \tag{51}$$

which on application of equation (A.14) gives

$$\mathrm{L}^{-1}\left\{\int_0^{r_1}\frac{k_0(\rho_{\boldsymbol{K}}\sqrt{s})i_0(\rho'\sqrt{s})}{\sqrt{s}}\sigma_{00}(\rho')\rho'^2\,\mathrm{d}\rho'\right\}$$
$$=\frac{\pi\sigma}{4\rho_{\boldsymbol{K}}}\left[r_1(2\sqrt{t})^2\,\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)+r_1(2\sqrt{t})^2\,\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}+r_1}{2\sqrt{t}}\right)\right.$$
$$\left.-(2\sqrt{t})^3\,\mathrm{erfci}_3\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)+(2\sqrt{t})^3\,\mathrm{erfci}_3\left(\frac{\rho_{\boldsymbol{K}}+r_1}{2\sqrt{t}}\right)\right]. \tag{52}$$

Therefore,

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')S_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$=\frac{\sigma}{2}\sum_{\boldsymbol{K}}\frac{1}{\rho_{\boldsymbol{K}}}\left[r_1(2\sqrt{t})^2\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)+\ r_1(2\sqrt{t})^2\,\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}+r_1}{2\sqrt{t}}\right)\right.$$
$$\left.-(2\sqrt{t})^3\,\mathrm{erfci}_3\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)+\ (2\sqrt{t})^3\,\mathrm{erfci}_3\left(\frac{\rho_{\boldsymbol{K}}+r_1}{2\sqrt{t}}\right)\right]. \tag{53}$$

Integration of the constant term is straightforward:

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')S_2\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$=-\frac{t\sqrt{4\pi}}{abc}\left\{\int_0^{r_1}\sigma_{00}(\rho')\rho'^2\,\mathrm{d}\rho'\right\}=-\frac{t\sqrt{4\pi}}{abc}\frac{r_1^3\sigma}{3}. \tag{54}$$

The contribution of the plane-wave expansion can be evaluated by making use of the representation

$$j_0(z)=\frac{\sin z}{z}; \tag{55}$$

thus, by orthonormality,

$$\int_{\rho=0}^{r_1}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sigma(\rho',\theta',\phi')S_1\rho'^2\sin\theta'\,\mathrm{d}\rho'\,\mathrm{d}\theta'\,\mathrm{d}\phi'$$
$$=\frac{1}{abc}{\sum_{\boldsymbol{k}}}'\frac{\mathrm{e}^{-t|\boldsymbol{k}|^2-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\int_{\rho'=0}^{r_1}\sigma_{00}(\rho')j_0(k\rho')\rho'^2\,\mathrm{d}\rho'$$
$$=\frac{\sigma}{abc}{\sum_{\boldsymbol{k}}}'\frac{\mathrm{e}^{-t|\boldsymbol{k}|^2-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\int_{\rho'=0}^{r_1}\frac{\sin k\rho'}{k\rho'}\rho'^2\,\mathrm{d}\rho'. \tag{56}$$

The potential at the field point due to the infinite periodic repetitions of a uniformly charged sphere and its neutralizing background charge density is therefore 4π times the sum of the expressions given in equations (53), (54), and (56). But to apply these results to crystalline arrays of ions, it is necessary to take into account that the net charge on the ion is the sum of the nuclear charge (concentrated at the centre) and the combined electronic charge. Since the potential due to the nuclear charge and its periodic repetitions is given by the appropriate multiple of the Green function, the potential at $\boldsymbol{r}$ due to periodic repetitions of an ion i and its uniform neutralizing background, with nuclear and electronic charge numbers $Z_{+,i}$ and $Z_{-,i}$, centred at $\boldsymbol{r}_{0,i}$, is

$$V_i(\boldsymbol{r}|\boldsymbol{r}_{0,i})=4\pi Z_{+,i}P_{222}(\boldsymbol{r}|\boldsymbol{r}_{0,i})-4\pi|Z_{-,i}|\left\{\frac{\sigma}{2}\sum_{\boldsymbol{K}}\frac{1}{\rho_{\boldsymbol{K}}}\left[r_1(2\sqrt{t})^2\,\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)\right.\right.$$
$$\left.\left.+\,r_1(2\sqrt{t})^2\,\mathrm{erfci}_2\left(\frac{\rho_{\boldsymbol{K}}+r_1}{2\sqrt{t}}\right)-(2\sqrt{t})^3\,\mathrm{erfci}_3\left(\frac{\rho_{\boldsymbol{K}}-r_1}{2\sqrt{t}}\right)\right.\right.$$

$$+ (2\sqrt{t})^3 \operatorname{erfci}_3\left(\frac{\rho_K + r_1}{2\sqrt{t}}\right)\Bigg] - \frac{t\sqrt{4\pi}}{abc}\frac{r_1^3\sigma}{3}$$
$$+ \frac{\sigma}{abc}\sum_{\boldsymbol{k}}{}' \frac{\mathrm{e}^{-t|\boldsymbol{k}|^2 - \mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}}{|\boldsymbol{k}|^2}\int_{\rho'=0}^{r_1}\frac{\sin k\rho'}{k\rho'}\rho'^2\,\mathrm{d}\rho'\Bigg\}. \tag{57}$$

In a real system, an expression of this type applies to each ion in the unit cell; the total potential is that due to an electroneutral combination of such ionic potentials. Thus,

$$V(\boldsymbol{r}) = \sum_i V_i(\boldsymbol{r}|\boldsymbol{r}_{0,i}). \tag{58}$$

Of course, the charge density about each nucleus is *not* uniform, but must be obtained from a solution of the Schrödinger equation with self-consistent inclusion of the coulombic lattice potential. But consideration of this crude model in the present context is of interest in that the expression for the real-space sum in the potential can be derived *without* use of the spherical harmonic expansion, thereby providing a check on the consistency of the analysis presented here. Denoting by r the distance between the field point and the source points in each sphere,

$$r = \sqrt{\rho_K^2 + \rho'^2 - 2\rho_K\rho'\cos\gamma_K} \tag{59}$$

from which it is clear that

$$\frac{\mathrm{d}r}{\mathrm{d}\gamma_K} = \frac{1}{2}\frac{-2R\rho'(-\sin\gamma_K)}{\sqrt{\rho_K^2 + \rho'^2 - 2\rho_K\rho'\cos\gamma_K}} = \frac{\rho_K\rho'\sin\gamma_K}{r}. \tag{60}$$

This result is useful in the derivation of a general expression for the integral:

$$I = 2\pi\int_{\rho'=0}^{r_1}\rho'^2\sigma(\rho')\left\{\int_{r_1=0}^{\pi}\frac{f\left(\sqrt{\rho_K^2 + \rho'^2 - 2\rho_K\rho'\cos\gamma_K}\right)}{\sqrt{\rho_K^2 + \rho'^2 - 2\rho_K\rho'\cos\gamma_K}}\sin\gamma_K\,\mathrm{d}\gamma_K\right\}\mathrm{d}\rho'$$
$$= \frac{2\pi}{\rho_K}\int_0^{r_1}\rho'\sigma(\rho')\left\{\int_0^{\pi} f(r)\frac{\mathrm{d}r}{\mathrm{d}\gamma_K}\,\mathrm{d}\gamma_K\right\}\mathrm{d}\rho'$$
$$= \frac{2\pi}{\rho_K}\int_0^{r_1}\rho'\sigma(\rho')\left\{\int_{\rho_K - r_1}^{\rho_K + r_1} f(r)\,\mathrm{d}r\right\}\mathrm{d}\rho'. \tag{61}$$

If σ is constant and the indefinite integral of the function f is represented by F,

$$I = \frac{2\pi\sigma}{\rho_K}\int_0^{r_1}\rho'[F(\rho_K + \rho') - F(\rho_K + \rho')]\,\mathrm{d}\rho',$$
$$= \frac{2\pi\sigma}{\rho_K}\int_0^{r_1}\rho' F(\rho_K + \rho')\,\mathrm{d}\rho' - \frac{2\pi\sigma}{\rho_K}\int_0^{r_1}\rho' F(\rho_K - \rho')\,\mathrm{d}\rho'$$
$$= \frac{2\pi\sigma}{\rho_K}\int_{\rho_K - r_1}^{\rho_K + r_1}(u - \rho_K)F(u)\,\mathrm{d}u, \tag{62}$$

and integration by parts gives

$$I = \frac{2\pi\sigma}{\rho_K}\{r_1[G(\rho_K + r_1) + G(\rho_K - r_1)] + H(\rho_K - r_1) - H(\rho_K + r_1)\}, \tag{63}$$

where

$$G'(z) = F(z) \qquad H'(z) = G(z).$$

With $f = 1$,

$$F(z) = z \qquad G(z) = \frac{z^2}{2} \qquad H(z) = \frac{z^3}{6},$$

and it can easily be verified that

$$I = \frac{2\pi\sigma}{\rho_K}\left\{r_1\left[\frac{(\rho_K + r_1)^2 + (\rho_K - r_1)^2}{2}\right] + \frac{(\rho_K - r_1)^3 - (\rho_K + r_1)^3}{6}\right\} = \frac{4\pi\sigma r_1^3}{3\rho_K}, \tag{64}$$

which expresses the result of classical field theory that the potential due to a uniformly charged sphere in free space is equal to that due to the entire sphere concentrated at the centre. Now if

$$f(z) = \operatorname{erfc}\left(\frac{z}{2\sqrt{t}}\right),$$

it follows from the properties of the erfci_n functions (*Handbook of Mathematical Functions* 1964) that

$$\begin{aligned} F(z) &= -(2\sqrt{t})\operatorname{erfci}_1\left(\frac{z}{2\sqrt{t}}\right) \qquad G(z) = (2\sqrt{t})^2\operatorname{erfci}_2\left(\frac{z}{2\sqrt{t}}\right) \\ H(z) &= -(2\sqrt{t})^3\operatorname{erfci}_3\left(\frac{z}{2\sqrt{t}}\right). \end{aligned} \tag{65}$$

Use of these results in equation (63) gives

$$\begin{aligned} I = \frac{2\pi\sigma}{\rho_K}\Bigg[& r_1(2\sqrt{t})^2\operatorname{erfci}_2\left(\frac{\rho_K + r_1}{2\sqrt{t}}\right) + r_1(2\sqrt{t})^2\operatorname{erfci}_2\left(\frac{\rho_K - r_1}{2\sqrt{t}}\right) \\ & + (2\sqrt{t})^3\operatorname{erfci}_3\left(\frac{\rho_K - r_1}{2\sqrt{t}}\right) - (2\sqrt{t})^3\operatorname{erfci}_3\left(\frac{\rho_K + r_1}{2\sqrt{t}}\right)\Bigg]. \end{aligned} \tag{66}$$

This is evidently identical to the part of equation (57) that is due to the negative charge density.

4. Discussion

The spherical harmonic expansion of the periodic Green function as developed in the present paper provides a solution of the 'generalized Ewald potential problem' that arises in the development of self-consistent electronic structure calculations for crystals, based, for example, on the augmented-plane-wave (APW) formalism (Slater 1937, 1972) incorporating the use of more general potentials that do not conform to the radially symmetric 'muffin-tin' model. Published treatments of the generalized Ewald potential all involve multipole expansions, by means of which a charge density distributed throughout a finite spherical volume is replaced by an equivalent arrangement of point multipoles located at the centre of the sphere. The potential due to the infinite periodic repetition of these multipoles is then obtained by use of an appropriate lattice summation procedure, such as that described by Hama (1982). From the computational viewpoint, the multipole method and the use of the Green function as described here would be roughly equivalent—each term in the spherical harmonic expansion requires evaluation of an integral over the radial coordinate which can be achieved by application of an appropriate one-dimensional numerical quadrature formula. The additional overhead associated with the presence of the modified spherical Bessel functions could be mitigated to some extent by use of the recurrence formulae.

But the multipole and Green function methods differ in a more fundamental and significant sense. The calculation of the multipole moments involves the loss of important information on the diffuseness—the spatial extent—of the charge distribution; this information is experimentally available through high-resolution single-crystal x-ray diffractometry. Application of the multipole moment approach would result in identical potentials for two periodic charge distributions with identical multipole components distributed over different volumes, unless the lattice parameters of the periodic arrangements were correspondingly

different. In particular, an array of spherically symmetric non-fluctuating neutral objects (for example, in a model representing an atomic crystal) would have zero potential in the interstitial regions. In contrast, the Green function method, which uses the components of the charge density directly, i.e., without replacing them with equivalent point multipoles, *does* imply the existence of a non-vanishing interstitial potential. That the Green function method predicts a finite interstitial potential while the multipole expansion method does not results on the one hand from the imposition of periodic boundary conditions, and on the other from the fact that the multipole method involves replacing a charge distribution of finite spatial extent with one that is concentrated at a point. Replacing a finite neutral object by its zeroth-order multipole moment (i.e., a zero charge) is equivalent to shrinking the radius of the diffuse charge in equation (57) to zero. It is also equivalent to keeping the positions of the charges and field point constant, and allowing the lattice parameters to tend to infinity. In this limit the periodic Green function correctly approaches the free-space Green function, as shown in part I, and the spherical symmetry destroyed by imposition of periodic boundary conditions is recovered. It is this symmetry that causes the electrostatic potential due to a neutral spherical object in free space to vanish.

The idea that an array of spherically symmetric neutral objects should give rise to a finite potential is somewhat counter-intuitive, but it is to be observed that the physical properties of such a system are determined not by the potential alone, but by the interaction energy. This is obtained from the potential by integrating the product of the potential and the atomic charge densities over the volumes of the appropriate atomic spheres, and summing over all distinguishable pairs of objects in the unit cell. This integration, which is enormously simplified if the objects are spherically symmetrical, contains terms resulting from attractive interactions between nuclei and diffuse electronic charges and repulsive interactions of the nuclei and the charge clouds with each other. For neutral objects, extensive cancellation occurs when these contributions are added. This treatment closely parallels the analysis of atomic interactions presented by Gordon and Kim (1972); the difference is that the free-space Green function used there is replaced by one satisfying periodic boundary conditions.

The limitations of the spherical-atom approximation were recognized many years ago in the context of the refinement of crystal structures deduced from single-crystal x-ray diffraction measurements. Hansen and Coppens (1978) described an improved analysis involving parameterization of atomic charge densities by a spherical harmonic expansion in which the distributed multipole densities are represented by Slater-type functions. Although such charge-density models can in principle be combined with experimental x-ray scattering data to estimate the electrostatic potential within the lattice, the success of such calculations is limited on the one hand by the extreme slowness of the convergence of the appropriate reciprocal-space summation, and on the other hand by the finite resolution of diffractometers. In this regard it is to be observed that use of the rapidly converging Green function described in the present work extends the accuracy of potential calculations based on such aspherical-atom refinement models, since all finite spatial frequencies are automatically included—the truncation of the Fourier series resulting from finite resolution is not necessary.

From the theoretical viewpoint, the distributed multipole density functions used in the aspherical-atom refinement models can be regarded as arising from solution of the Schrödinger equation with self-consistent inclusion of exchange and electrostatic lattice energies. While the details of such calculations are clearly beyond the scope of the present paper, it seems appropriate to conclude the discussion by commenting, in general terms, on the significance of the present results in this connection. In the APW method the electronic wavefunction to be determined is expanded in terms of basis functions represented as spherical harmonic series within spheres about the nuclei, and as plane waves in the interstitial regions. The radial

factors in the spherical harmonic representation are determined by numerical solution of a radial Schrödinger equation with a muffin-tin potential (Loucks 1967, pp 47–55) that incorporates the coulombic potential associated with the electronic distribution, obtained by numerical solution of the radial Poisson equation. The evaluation of matrix elements in the secular determinant is greatly facilitated if the combined exchange–electrostatic lattice potential is expanded in spherical harmonics within the atomic spheres. In the scheme proposed by Rudge (1969b), this representation was constructed by use of a multipole expansion for the electrostatic component (Rudge 1969a) and linearization of the non-linear function relating the exchange energy to the electron density. A more rigorous procedure would involve determination of the electrostatic lattice potential by use of the Green function, addition of the exchange energy determined from some non-linear function of the electron density, and numerical resolution of the total potential into spherical harmonics. Several highly efficient algorithms based on fast Fourier transformation are available for this purpose (Dilts 1985, Elowitz *et al* 1989, Alpert and Rokhlin 1991, Potts *et al* 1998).

An alternative approach to electronic structure calculations is the Hartree–Fock method, which involves calculation of (numerous) integrals that represent interactions between charge distributions. In adaptations of this method to polar molecular crystals (Panas 1992), it is necessary to calculate the interactions between one charge distribution and infinite repetitions of another: since integrations over two sets of polar coordinates are involved, use of the results in this paper would not be practical, since each integral would require that the potential be expanded in spherical harmonics of the field point coordinates. For solution of this problem, and the related general problem of calculating the lattice energy of polar molecular crystals, it is preferable to use a bipolar spherical harmonic expansion of the periodic Green function. Application of the general method described in the present paper would require a bipolar expansion of the screened Coulomb potential.

5. Conclusions

The Ewald sum of the periodic Green function for Poisson's equation has been developed in a spherical harmonic expansion. In the real-space part of the Ewald sum, the dependence on the radial coordinates is expressed by an integral of a modified spherical Bessel function; the latter is in turn expressible in terms of exponential integrals, repeated integrals of the complementary error function, or incomplete gamma functions. The terms in the sum over lattice points are attenuated exponentially, resulting in improved convergence properties compared with previous treatments based on spherical harmonics.

Acknowledgments

The present work was carried out as part of a project on the application of neutron scattering measurements to determine the physical and thermodynamic properties of clathrate hydrates, recently established in the Solid-State Division of Oak Ridge National Laboratory, and supported by the Laboratory Director's Research and Development fund. I am also grateful to an anonymous reviewer for helpful comments.

Appendix. Inversion of the Laplace transform and evaluation of the integral

Here, the details of the derivation of equation (20) are given. It is also shown that the integral can be evaluated analytically in several alternative forms, all of which are amenable to efficient computation.

A.1. Bessel function integral

The inverse Laplace transform of the product of the modified spherical Bessel functions appearing in equation (16) follows from the following result, due to van der Pol and Bremmer (1950, p 394)

$$\mathrm{L}_2\left\{\frac{\mathrm{e}^{-(a+b)/t}}{t} I_\nu\left(\frac{2\sqrt{ab}}{t}\right) U(t)\right\} = 2pI_\nu(2\sqrt{ap})K_\nu(2\sqrt{bp}), \tag{A.1}$$

where $a < b$, $U(t)$ is the unit step function and the two-sided Laplace transform with parameter p is

$$g(p) \equiv \mathrm{L}_2\{f(t)\} = p\int_{-\infty}^{\infty} \mathrm{e}^{-pt} f(t)\,\mathrm{d}t. \tag{A.2}$$

In terms of the more usual definition of the one-sided Laplace transform with parameter s, namely

$$g(s) \equiv \mathrm{L}\{fg(t)\} = \int_0^{\infty} \mathrm{e}^{-st} f(t)\,\mathrm{d}t, \tag{A.3}$$

equation (A.1) is evidently equivalent to

$$\mathrm{L}\left\{\frac{\mathrm{e}^{-(a+b)/t}}{t} I_\nu\left(\frac{2\sqrt{ab}}{t}\right)\right\} = 2I_\nu(2\sqrt{as})K_\nu(2\sqrt{bs}). \tag{A.4}$$

To apply equation (A.4), it is convenient to simplify the notation by representing the greater and lesser of the two radial variables by R and r, respectively, and to make the substitutions

$$a = \frac{r^2}{4} \qquad b = \frac{R^2}{4}; \tag{A.5}$$

$$\mathrm{L}\left\{\frac{\mathrm{e}^{-(r^2+R^2)/4t}}{2t} I_\nu\left(\frac{Rr}{2t}\right)\right\} = I_\nu(r\sqrt{s})K_\nu(2R\sqrt{s}). \tag{A.6}$$

But the expression that appears in the spherical harmonic expansion is

$$\begin{aligned}\frac{2}{\pi}\frac{i_n(r\sqrt{s})k_n(R\sqrt{s})}{\sqrt{s}} &= \frac{2}{\pi\sqrt{s}}\sqrt{\frac{\pi}{2r\sqrt{s}}} I_{n+1/2}(r\sqrt{s})\sqrt{\frac{\pi}{2R\sqrt{s}}} K_{n+1/2}(R\sqrt{s}) \\ &= \frac{I_{n+1/2}(r\sqrt{s})K_{n+1/2}(R\sqrt{s})}{s\sqrt{Rr}};\end{aligned} \tag{A.7}$$

since from equation (A.6)

$$\mathrm{L}\left\{\frac{\mathrm{e}^{-(r^2+R^2)/4t}}{2t} I_{n+1/2}\left(\frac{Rr}{2t}\right)\right\} = I_{n+1/2}(r\sqrt{s})K_{n+1/2}(2R\sqrt{s}), \tag{A.8}$$

it follows from elementary properties of Laplace transforms that

$$\frac{I_{n+1/2}(r\sqrt{s})K_{n+1/2}(2R\sqrt{s})}{s\sqrt{Rr}} = \mathrm{L}\left\{\int_o^t \frac{\mathrm{e}^{-(r^2+R^2)/4t}}{2t\sqrt{Rr}} I_{n+1/2}\left(\frac{Rr}{2t}\right)\mathrm{d}t\right\}. \tag{A.9}$$

Finally, making use of the definition of the modified spherical Bessel functions (equation (17)) leads to equation (20), since

$$\frac{1}{2t\sqrt{Rr}}\sqrt{\frac{2Rr}{2\pi t}}i_n\left(\frac{Rr}{2t}\right)=\frac{1}{2\sqrt{\pi t^3}}i_n\left(\frac{Rr}{2t}\right). \tag{A.10}$$

Analytical evaluation of the integral can be achieved in two ways. The first makes use of the ascending power series expansion for the spherical modified Bessel function, which follows from combination of the result

$$I_\nu(z)=\left(\frac{z}{2}\right)^\nu\sum_{p=0}^{\infty}\frac{1}{p!\Gamma(\nu+p+1)}\left(\frac{z}{2}\right)^{2p} \tag{A.11}$$

with the definition in equation (17), after setting $\nu=n+1/2$:

$$i_n(z)=\frac{\sqrt{\pi}}{2}\left(\frac{z}{2}\right)^n\sum_{p=0}^{\infty}\frac{1}{p!\Gamma(n+p+3/2)}\left(\frac{z}{2}\right)^{2p}. \tag{A.12}$$

Applying the elementary substitution

$$\int_0^t\frac{\mathrm{e}^{-(R^2+r^2)/4t}}{2\sqrt{\pi t^3}}i_n\left(\frac{Rr}{2t}\right)\mathrm{d}t\xrightarrow[u=Rr/2t,\ \mathrm{d}t=-(Rr/2u^2)\,\mathrm{d}u]{}\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u, \tag{A.13}$$

expanding the modified spherical Bessel function according to equation (A.12), and integrating termwise results in a series of terms of the form

$$\begin{aligned}\sqrt{\frac{2}{Rr}}\int_{Rr/2t}^{\infty}\mathrm{e}^{-([R^2+r^2]/2Rr)u}u^{2p+n-1/2}\,\mathrm{d}u&\xrightarrow[\nu=([R^2+r^2]/4Rr)u]{}\sqrt{\frac{2}{Rr}}\left(\frac{2Rr}{R^2+r^2}\right)^{2p+n+1/2}\\&\quad\times\int_{(R^2+r^2)/4t}^{\infty}\mathrm{e}^{-\nu}\nu^{2p+n-1/2}\,\mathrm{d}\nu\\&=\frac{1}{\sqrt{Rr}}\left(\frac{2Rr}{R^2+r^2}\right)^{2p+n+1/2}\Gamma\left(2p+n+\frac{1}{2},\frac{R^2+r^2}{4t}\right),\end{aligned} \tag{A.14}$$

where

$$\Gamma(z,z)\equiv\int_z^{\infty}t^{a-1}\mathrm{e}^{-t}\,\mathrm{d}t$$

is the complementary incomplete gamma function, but the sum of these terms over p does not converge. This problem can, however, be overcome by observing that

$$\begin{aligned}\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u&=\frac{1}{\sqrt{2\pi Rr}}\left[\int_0^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u\right.\\&\quad\left.-\int_0^{Rr/2t}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u\right],\end{aligned} \tag{A.15}$$

and applying the same termwise integration method to the second integral on the right-hand side. The first integral can be determined in closed form by making use of the Laplace transform pair

$$\int_0^{\infty}\mathrm{e}^{-su}\frac{I_\nu(au)}{u}\,\mathrm{d}u=\frac{a^\nu}{\nu}\frac{1}{\left[s+\sqrt{s^2-a^2}\right]^\nu}. \tag{A.16}$$

(Erdélyi *et al* 1954 (p 196); cf Watson 1944 (p 388)), which is valid if $\mathrm{Re}(s)>a$ and $\mathrm{Re}(\nu)>0$. With $a=1$ and $\nu=n+1/2$, this becomes

$$\int_0^\infty \mathrm{e}^{-su}\frac{I_{n+1/2}(u)}{u}\,\mathrm{d}u = \sqrt{\frac{2}{\pi}}\int_0^\infty \mathrm{e}^{-su}\frac{i_n(u)}{\sqrt{u}}\,\mathrm{d}u = \sqrt{\frac{2}{\pi}}\frac{1}{(n+1/2)\left[s+\sqrt{s^2-1}\right]^{n+1/2}}, \tag{A.17}$$

and setting

$$s = \frac{R^2+r^2}{2Rr},$$

$$\frac{1}{\sqrt{2\pi Rr}}\int_0^\infty \mathrm{e}^{-([R^2+r^2]/2Rr)u}\frac{i_n(u)}{\sqrt{u}}\,\mathrm{d}u \tag{A.18}$$
$$= \frac{1}{\pi\sqrt{Rr}}\left(\left(n+\frac{1}{2}\right)\left[\frac{R^2+r^2}{2Rr}+\sqrt{\left(\frac{R^2+r^2}{2Rr}\right)^2-1}\right]^{n+1/2}\right)^{-1}.$$

Now termwise integration of the other integral gives

$$\begin{aligned}\frac{1}{\sqrt{2\pi Rr}}\int_0^{Rr/2t}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u &= \frac{1}{2\sqrt{Rr}}\int_0^{Rr/2t}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{u}I_{n+1/2}(u)\,\mathrm{d}u\\ &= \frac{1}{2\sqrt{Rr}}\sum_{p=0}^\infty\frac{1}{p!\Gamma(n+p+3/2)2^{2p+n+1/2}}\int_0^{Rr/2t}\mathrm{e}^{-([R^2+r^2]/2Rr)u}u^{2p+n-1/2}\,\mathrm{d}u\\ &\quad\times\xrightarrow[v=([R^2+r^2]/2Rr)u]{}\frac{1}{2\sqrt{Rr}}\sum_{p=0}^\infty\frac{1}{p!\Gamma(n+p+3/2)2^{2p+n+1/2}}\left(\frac{2Rr}{R^2+r^2}\right)^{2p+n+1/2}\\ &\quad\times\int_0^{[R^2+r^2]/4t}\mathrm{e}^{-v}v^{2p+n-1/2}\,\mathrm{d}v\\ &= \frac{1}{2\sqrt{R^2+r^2}}\sum_{p=0}^\infty\frac{\gamma\left(2p+n+1/2,[R^2+r^2]/4t\right)}{p!\Gamma(n+p+3/2)}\left(\frac{Rr}{R^2+r^2}\right)^{2p+n},\end{aligned} \tag{A.19}$$

where

$$\begin{aligned}\gamma(a,z) \equiv \int_0^z t^{a-1}\mathrm{e}^{-t}\,\mathrm{d}t &= \mathrm{e}^{-z}z^a\sum_{p=0}^\infty\frac{\Gamma(a)}{\Gamma(a+1+p)}z^n\\ &= \mathrm{e}^{-z}z^a\sum_{p=0}^\infty\frac{1}{(a+p)(a+p-1)\cdots(a-1)a}z^p\end{aligned}$$

is the incomplete gamma function. From the cancellation of the gamma functions in the general term of the power series

$$\gamma(a,z) = \mathrm{e}^{-z}z^a\sum_{p=0}^\infty\frac{\Gamma(a)}{\Gamma(a+1+p)}z^n = \mathrm{e}^{-z}z^a\sum_{p=0}^\infty\frac{1}{(a+p)(a+p-1)\cdots(a-1)a}z^p, \tag{A.20}$$

it is clear that the above expression for the second integral of equation (A.15) is convergent. The required integral is therefore

$$\begin{aligned}\int_0^t\frac{\mathrm{e}^{-(R^2+r^2)/4t}}{2\sqrt{\pi t^3}}i_n\left(\frac{Rr}{2t}\right)\mathrm{d}t &= \frac{1}{\pi\sqrt{Rr}}\left(\left(n+\frac{1}{2}\right)\left[\frac{R^2+r^2}{2Rr}+\sqrt{\left(\frac{R^2+r^2}{2Rr}\right)^2-1}\right]^{n+1/2}\right)^{-1}\\ &\quad-\frac{1}{2\sqrt{R^2+r^2}}\sum_{p=0}^\infty\frac{\gamma(2p+n+1/2,[R^2+r^2]/4t)}{p!\Gamma(n+p+3/2)}\left(\frac{Rr}{R^2+r^2}\right)^{2p+n}.\end{aligned} \tag{A.21}$$

The convergence of the series can be expected to be slowest when R and r are very nearly equal, but even in this case, convergence is reasonably fast. For example, with $n = 0$, $r = 1$, $R = 1.01$, and $t = 0.1$, the terms in the series are as follows:

p	$\gamma\left(2p+n+\frac{1}{2}, \frac{R^2+r^2}{4t}\right)$	$\Gamma\left(n+p+\frac{3}{2}\right)$	$\left(\frac{Rr}{R^2+r^2}\right)^{2p}$	Term
0	0.1769826558487914E+01	0.8862269254527573E+00	0.1000000000000000E+01	1.9970354179701117
1	0.1233046701261864E+01	0.1329340388179136E+01	0.2499752493626863E+00	0.2318677438560125
2	0.7648900863180841E+01	0.3323350970447840E+01	0.6248762529393718E−01	0.0719095959618898
3	0.9048343757676601E+02	0.1163172839656744E+02	0.1562035971493405E−01	0.0202518461430885
4	0.1412662037116506E+04	0.5234277778455348E+02	0.3904703314875497E−02	0.0043909481344239
5	0.2541113695430869E+05	0.2878852778150441E+03	0.9760791848233101E−03	0.0007179735515956
6	0.4962579872993717E+06	0.1871254305797787E+04	0.2439956376239345E−03	0.0000898719701761
7	0.1021345744914883E+08	0.1403440729348340E+05	0.6099287035845065E−04	0.0000088069847305
8	0.2178928035968024E+09	0.1192924619946089E+06	0.1524670797719970E−04	0.0000006906936193
9	0.4770776590390331E+10	0.1133278388948785E+07	0.3811299628560552E−05	0.0000000442142774
10	0.1065190194176059E+12	0.1189942308396224E+08	0.9527305750453375E−06	0.0000000023502189
11	0.2414751274202015E+13	0.1368433654655657E+09	0.2381590630724137E−06	0.0000000001052834
12	0.5541089526835874E+14	0.1710542068319572E+10	0.5953387117951035E−07	0.0000000000040261
13	0.1284177533786036E+16	0.2309231792231422E+11	0.1488199429362414E−07	0.0000000000001329
14	0.3000776555496798E+17	0.3348386098735562E+12	0.3720130234562768E−08	0.0000000000000038
15	0.7060914397927304E+18	0.5189998453040121E+13	0.9299404830464965E−09	0.0000000000000001

Thus, the computational effort required to evaluate the integral is not great, and is probably comparable with that required to evaluate the error functions in a conventional Ewald summation. The second analytical evaluation applies the same transformation as was used in equation (A.13), but then uses the closed-form representation given by equation (18*a*):

$$\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}i_n(u)\,\mathrm{d}u = \frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}} \times \frac{1}{2u}\left[\mathrm{e}^{u}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!(2u)^p} + (-1)^{n+1}\mathrm{e}^{-u}\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!(2u)^p}\right]\mathrm{d}u. \tag{A.22}$$

The order of integration and summation in the first sum can be interchanged:

$$\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}\frac{\mathrm{e}^{u}}{2u}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!(2u)^p}\,\mathrm{d}u = \frac{1}{\sqrt{2\pi Rr}}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!2^{p+1}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr-1)u}}{u^{p+3/2}}\,\mathrm{d}u \tag{A.23}$$

and the integral further transformed:

$$\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{u^{p+3/2}}\,\mathrm{d}u \xrightarrow{v=([R^2+r^2]/2Rr-1)u} \left(\frac{R^2+r^2}{2Rr}-1\right)^{p+1/2}\int_{([R^2+r^2]/4t-Rr/2t)}^{\infty}\frac{\mathrm{e}^{-v}}{v^{p+3/2}}\,\mathrm{d}v = \left(\frac{R^2+r^2}{2Rr}-1\right)^{p+1/2}E_{p+3/2}\left[\frac{(R-r)^2}{4t}\right], \tag{A.24}$$

where

$$E_n(z) \equiv \int_z^{\infty}\frac{\mathrm{e}^{-t}}{t^n}\,\mathrm{d}t$$

is the exponential integral function of order n. Therefore,

$$\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}\frac{1}{2u}\left[\mathrm{e}^{u}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!(2u)^p}\right]\mathrm{d}u$$
$$=\frac{1}{\sqrt{2\pi Rr}}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{R^2+r^2}{2rr}-1\right)^{p+1/2}E_{p+3/2}\left[\frac{(R-r)^2}{4t}\right]. \quad (A.25)$$

Proceeding similarly for the other sum,

$$\frac{1}{\sqrt{2\pi Rr}}\int_{Rr/2t}^{\infty}\frac{\mathrm{e}^{-([R^2+r^2]/2Rr)u}}{\sqrt{u}}\frac{\mathrm{e}^{-u}}{2u}\sum_{p=0}^{t}\frac{(n+p)!}{p!(n-p)!(2u)^p}\,\mathrm{d}u$$
$$=\frac{1}{\sqrt{2\pi Rr}}\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{R^2+r^2}{2Rr}+1\right)^{p+1/2}E_{p+3/2}\left[\frac{(R+r)^2}{4t}\right], \quad (A.26)$$

and forming the appropriate combination of equations (A.25) and (A.26) results in

$$\int_0^t\frac{\mathrm{e}^{-(R^2+r^2)/4t}}{2\sqrt{\pi t^3}}i_n\left(\frac{Rr}{2t}\right)\mathrm{d}t$$
$$=\frac{1}{\sqrt{2\pi Rr}}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{R^2+r^2}{2Rr}-1\right)^{p+1/2}E_{p+3/2}\left[\frac{(R-r)^2}{4t}\right]$$
$$+\frac{(-1)^{n+1}}{\sqrt{2\pi Rr}}\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{R^2+r^2}{4Rr}+1\right)^{p+1/2}E_{p+3/2}\left[\frac{(R+r)^2}{4t}\right]. \quad (A.27)$$

It is to be observed that the effort involved in the implementation of this closed-form result is not great if the exponential integral functions are evaluated by means of the recursion schemes developed by Gautschi (1961) and Amos (1980). Thus, since the integrals required in each sum all have the same argument, they can be determined by a single call to a subroutine based on these methods.

A.2. Error function integral representation

The third alternative expression follows by first making use of equation (18*b*):

$$\frac{k_n(R\sqrt{s})i_n(r\sqrt{s})}{\sqrt{s}}=\left[\pi\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!(2R)^{p+1}}\frac{\mathrm{e}^{-R\sqrt{s}}}{s^{1+p/2}}\right]i_n(r\sqrt{s}). \quad (A.28)$$

Now from equation (18*a*),

$$i_n(r\sqrt{s})=\frac{1}{2r\sqrt{s}}\left[\mathrm{e}^{r\sqrt{s}}\sum_{q=0}^{n}\frac{(-1)^p(n+q)!}{q!(n-q)!(2r\sqrt{s})^q}+(-1)^{n+1}\mathrm{e}^{-r\sqrt{s}}\sum_{q=0}^{n}\frac{(n+q)!}{q!(n-p)!(2r\sqrt{s})^p}\right] \quad (A.29)$$

which when substituted into equation (39) yields, after straightforward algebra,

$$\frac{k_n(R\sqrt{s})i_n(r\sqrt{s})}{\sqrt{s}}=\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}\frac{(n+p)!(n+q)!(-1)^q}{p!q!(n-p)!(n-q)!2^{p+q}}\frac{\mathrm{e}^{-(R-r)\sqrt{s}}}{R^{p+1}r^{q+1}s^{1+(p+q+1)/2}}$$
$$+(-1)^{n+1}\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}\frac{(n+p)!(n+q)!}{p!q!(n-p)!(n-q)!2^{p+q}}\frac{\mathrm{e}^{-(R+r)\sqrt{s}}}{R^{p+1}r^{q+1}s^{1+(p+q+1)/2}}. \quad (A.30)$$

The inverse Laplace transform of this involves the n-fold repeated integral of the complementary error function, erfci_n, defined immediately following equation (21):

$$\mathrm{L}^{-1}\left[\frac{\mathrm{e}^{-k\sqrt{s}}}{s^{1+n/2}}\right]=2(\sqrt{t})^n\,\mathrm{erfci}_n\left(\frac{k}{2\sqrt{t}}\right). \quad (A.31)$$

(*Handbook of Mathematical Functions* 1964, p 299, formula 2.7.3). Thus,

$$\begin{aligned}\frac{2}{\pi}\mathrm{L}^{-1}\left[\frac{k_n(R\sqrt{s})i_n(r\sqrt{s})}{\sqrt{s}}\right] &= \frac{1}{2}\sum_{p=0}^{n}\sum_{q=0}^{n}\frac{(n+p)!(n+q)!(-1)^q}{p!q!(n-p)!(n-q)!2^{p+q}}\\ &\quad\times\frac{(2\sqrt{t})^{p+q+1}}{R^{p+1}r^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{R-r}{2\sqrt{t}}\right)\\ &\quad+(-1)^{n+1}\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}\frac{(n+p)!(n+q)!}{p!q!(n-p)!(n-q)!2^{p+q}}\\ &\quad\times\frac{(2\sqrt{t})^{p+q+1}}{R^{p+1}r^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{R-r}{2\sqrt{t}}\right)\\ &\equiv\frac{\pi}{4}\sum_{p=0}^{n}\sum_{q=0}^{n}A_{pq}\frac{(2\sqrt{t})^{p+q+1}}{R^{p+1}r^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{R-r}{2\sqrt{t}}\right)\\ &\quad+(-1)^{n+1}\sum_{p=0}^{n}\sum_{q=0}^{n}B_{pq}\frac{(2\sqrt{t})^{p+q+1}}{R^{p+1}r^{q+1}}\operatorname{erfci}_{p+q+1}\left(\frac{R+r}{2\sqrt{t}}\right)\end{aligned}\tag{A.32}$$

$$A_{pq}=\frac{(n+p)!(n+q)!(-1)^q}{p!q!(n-p)!(n-q)!2^{p+q}}\qquad B_{pq}=\frac{(n+p)!(n+q)!}{p!q!(n-p)!(n-q)!2^{p+q}}.\tag{A.33}$$

Although twice as many erfci functions are present in each sum as there are exponential integrals in equation (A.23), these functions are also amenable to efficient recursive computation (Gautschi 1960). Thus, all the error functions of each argument can be determined by one call to a subroutine implementing this algorithm.

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