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Abstract
Spherical harmonic expansions of the screened Coulomb interaction kernel involving the complementary error function are required in various problems in atomic, molecular and solid state physics, like for the evaluation of Ewald-type lattice sums or for range-separated hybrid density functionals. A general analytical expression is derived for the kernel, which is non-separable in the radial variables. With the help of series expansions a separable approximate form is proposed, which is in close analogy with the conventional multipole expansion of the Coulomb kernel in spherical harmonics. The convergence behaviour of these expansions is studied and illustrated by the electrostatic potential of an elementary charge distribution formed by products of Slater-type atomic orbitals.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Coulomb problem is at the heart of electronic structure calculations of molecules and solids. The classical electrostatic energy, due to the interaction of the electronic and nuclear charge distributions (Hartree and nuclear attraction), is one of the major components of the total energy. Furthermore, electrostatic repulsion of electrons is responsible for the electron correlation, which remains a major challenge for electronic structure theories. In both types of problems one is faced with conceptual and numerical difficulties raised by the handling of Coulomb interactions (CI).

The principal source of difficulties in the treatment of Coulomb interactions is the very nature of the $1/r$ function, which is singular at $r = 0$ and has a slow rate of decay at large

r, leading to convergence problems in both limits. A general strategy to handle this problem consists of splitting the $1/r$ function into a long- and a short-range components. The short-range component decays rapidly with increasing r, but it has a singularity at $r = 0$. The Fourier transform of the long-range component decays rapidly in reciprocal space, but it has a singularity at $k = 0$ (i.e. $r \to \infty$). An explicit separation of these two domains offers the possibility of treating both singularities separately, each with the most appropriate tool.

The archetypal example of this strategy is the Ewald technique to calculate Coulomb lattice sums. The conditionally convergent Coulomb lattice sum is replaced by the sum of two absolutely convergent sums of modified Coulomb interactions: one in the direct, the other in the reciprocal space (Ewald 1921, De Leeuw *et al* 1980a, 1980b, Toukmaji and Board 1996). The optimal decomposition of the Coulomb operator, $T(a) = 1/a$, would be the one that ensures the fastest decay rate of the two components in direct and in reciprocal spaces, respectively. Gill and his co-workers showed that the Ewald decomposition, i.e.

$$T(a) = S_\mu(a) + L_\mu(a) = \frac{\mathrm{erfc}(\mu a)}{a} + \frac{\mathrm{erf}(\mu a)}{a}, \tag{1}$$

widely used to accelerate the computation of electron interactions in extended systems (Dombroski *et al* 1996, Adamson *et al* 1996, Gill and Adamson 1996, Gill 1997, Lee 1998, Hetzer *et al* 2000), is very close to the optimal one in the above sense (Lee *et al* 1997). Here $S_\mu(a)$ and $L_\mu(a)$ stand for the short- and long-range components of the interaction, respectively. Numerous variants of the Ewald technique have been applied to accelerate the computation of the potential energy term in various electronic structure methods.

Another application of the split Coulomb operator consists in separating the treatment of short- and long-range correlations in the electronic Hamiltonian (Panas 1995, Patkowski *et al* 2001), in particular in the context of density functional theory (DFT). For instance in the DFT-CI method of Savin (Stoll and Savin 1985, Savin 1996, Toulouse *et al* 2004) as well as in similar approaches (Ángyán *et al* 2005, Gerber and Ángyán 2005a, 2005b, Goll *et al* 2005, Sato *et al* 2005, Tawada *et al* 2004, Yanai *et al* 2004, Kamiya *et al* 2002), it is supposed that the short-range electron correlation is essentially correctly described with local or semi-local density functionals, while the remaining long-range correlation effects can be efficiently treated by wavefunction methods. A somewhat different philosophy is followed in the case of screened Coulomb hybrid functional (HSE03) which is designed to circumvent the convergence problems in the Fock exchange component of hybrid functionals in solids. Here, the long-range part of the Fock exchange is replaced by an appropriately tailored long-range-only density functional (Heyd *et al* 2003, Heyd and Scuseria 2004), while the short-range component is calculated explicitly.

The computational implementation of the modified, short- and/or long-range electron interaction integrals is relatively easy in Gaussian basis sets (Panas 1995, Gill and Adamson 1996, Savin 1996), and requires only minor modifications in existing Gaussian-based quantum chemical codes. There is no problem for plane waves either, since the screened interaction function has a simple Fourier transform (Paier *et al* 2006).

However, there are many successful electronic structure codes that do not use Gaussian or plane wave basis functions. The basis set can be constituted of numerical (Velde *et al* 2001, Soler *et al* 2002) exponential (Delley 1990) or Bessel-type (Furthmüller *et al* 1994, Kresse and Joubert 1999, Blöchl *et al* 2004, Blaha *et al* 1999) radial functions, augmented by spherical harmonic angular components. In all these cases, the treatment of the electrostatic interactions can take advantage of the spherical harmonic decomposition of the Coulomb kernel. The interaction between two point charges situated at the points $\boldsymbol{R}$ and $\boldsymbol{r}$, expressed in

spherical polar coordinates $\{r, \theta, \phi\}$ and $\{R, \Theta, \Phi\}$, respectively, is described by the Coulomb kernel

$$T(R, r, \gamma) = \frac{1}{(R^2 + r^2 - 2Rr \cos \gamma)^{1/2}}, \tag{2}$$

where γ is the angle between $\boldsymbol{R}$ and $\boldsymbol{r}$. The corresponding Legendre expansion is

$$T(R, r, \gamma) = \sum_{l=0}^{\infty} \mathcal{G}_l(R, r) P_l(\cos \gamma). \tag{3}$$

$P_l(x)$ is the Legendre polynomial of order l, and the radial function $\mathcal{G}_l(R, r)$ is defined as

$$\mathcal{G}_l(R, r) = \frac{r_<^l}{R_>^{l+1}}, \tag{4}$$

where $r_<$ $(R_>)$ is the smaller (greater) of r and R. In order to obtain a fully separable expression, the addition theorem for spherical harmonics, $Y_{lm}(\theta, \phi) = Y_{lm}(\omega)$, can be used to write

$$T(\boldsymbol{R}, \boldsymbol{r}) = \sum_{l=0}^{\infty} \mathcal{G}_l(R, r) \left(\frac{4\pi}{2l+1}\right) \sum_{m=-l}^{l} Y_{lm}^*(\Omega) Y_{lm}(\omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathcal{I}_{lm}^*(\boldsymbol{R}) \mathcal{R}_{lm}(\boldsymbol{r}), \tag{5}$$

where the regular, $\mathcal{R}_{lm}(\boldsymbol{r})$, and irregular, $\mathcal{I}_{lm}(\boldsymbol{r})$, spherical harmonics are defined as

$$\mathcal{R}_{lm}(\boldsymbol{r}) = r^l \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\omega), \qquad \mathcal{I}_{lm}(\boldsymbol{r}) = r^{-l-1} \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\omega). \tag{6}$$

The final expression is the product of two functions, each depending exclusively either on $\boldsymbol{r}$ or on $\boldsymbol{R}$, making it possible to perform integrations over $\boldsymbol{R}$ and $\boldsymbol{r}$ separately.

In the present paper we address the question whether it is possible to obtain an analogous series expansion of the short-range screened interaction kernel,

$$S_\mu(R, r, \gamma) = \frac{\operatorname{erfc}(\mu(R^2 + r^2 - 2Rr \cos \gamma)^{1/2})}{(R^2 + r^2 - 2Rr \cos \gamma)^{1/2}}. \tag{7}$$

To answer this question we first seek a Legendre expansion

$$S_\mu(R, r, \gamma) = \sum_{l=0}^{\infty} \mathcal{F}_l(R, r, \mu) P_l(\cos \gamma), \tag{8}$$

where $\mathcal{F}_l(R, r, \mu)$ is the short-range generalization of the Coulomb radial function, $\mathcal{G}_l(R, r)$. Secondly, we will examine whether a further series expansion may bring it in a fully separable form, analogous to equation (5).

The question whether a Legendre expansion of the short-range screened interaction kernel does in fact exist need not concern us here; a general analytical expression for the Legendre expansion of the short-range (erfc) interaction has already been derived by Marshall (2002), by applying the Gegenbauer addition theorem to the Laplace transform of the screened interaction operator. Following the main lines of Marshall's procedure and using the facilities of the Mathematica program (Wolfram 2005), we have found an alternative expression for the radial functions of different orders, which could be further developed in a separable form, analogous to the spherical harmonic multipole expansion of the full Coulomb interaction.

In contrast to previous works on the series expansion of screened Coulomb interactions, which relied exclusively on Cartesian multipole components, the originality of our method resides in the consistent use of spherical harmonic functions. For instance, Gill (1997) showed

that the non-singular long-range (erf) interaction function can be expanded in the convergent Taylor series

$$L_\mu(R, r, \gamma) = \sum_{l=0}^{\infty} \frac{2\mu^{2l+1}}{\sqrt{\pi}} \frac{(-1)^l}{(2l+1)l} (R^2 + r^2 - 2Rr\cos\gamma)^l, \tag{9}$$

which can be written in terms of the Cartesian components of the vectors $r = \{x, y, z\}$ and $R = \{X, Y, Z\}$. Hetzer *et al* (2000) found that the numerical stability of such an expansion can be improved if the analytical Taylor expansion coefficients are replaced by optimized ones, obtained by a least-squares fitting procedure. These authors underlined correctly the importance of using an expansion in terms of a reducible set of traced Cartesian moments. In effect, the prerequisite for using an irreducible multipole expansion is that the interaction kernel should satisfy the Laplace equation, which is the case for the full Coulomb interaction, $\nabla^2(1/r) = 0$. The screened Coulomb kernel does not satisfy the Laplace equation; therefore, the use of traced Cartesian moments seems to be mandatory. However, this does not exclude the use of a spherical harmonic formulation of the angular part of the interaction, as will be demonstrated in the present work. Doing so, we gain the considerable advantage of exploiting directly the orthogonality of spherical harmonics.

This paper is organized as follows. The derivation of the Legendre expansion of the short-range (erfc) interaction function is outlined in section 2, followed by a discussion of the explicit analytical expressions for the corresponding radial functions of different orders. A separable form of the radial function $\mathcal{F}_l(R, r, \mu)$ is obtained by a Taylor expansion of the radial functions. In section 3 the behaviour of the radial function and its approximations is discussed in more detail. As an example, the details of the calculation of the screened electrostatic potential are treated in section 4. The possibility of particular physical applications is outlined in section 5, and we conclude in section 6, which summarizes the main results of the present work.

2. Theory

2.1. Legendre expansion of the short-range interaction

While the derivation of the Legendre expansion of the Coulomb operator, based on the application of the cosine rule and on the form of the generator function of the Legendre polynomials, is a standard textbook material (Jackson 1975), the analogous problem involving a short-range interaction function is much less obvious to solve. The approach followed by Marshall (2002) consists in taking the Laplace transform of the interaction kernel as

$$S_t(a) = \frac{\text{erfc}(a/2\sqrt{t})}{a}, \qquad \mathcal{L}[S_t(a)] = \frac{e^{-a\sqrt{s}}}{sa}, \tag{10}$$

where the range separation parameter is defined as $t = 1/4\mu^2$. Provided that $\cos\gamma \neq 1$, the Laplace transform can be expanded by the virtue of Gegenbauer's addition theorem (Watson 1944) in terms of Bessel functions, $i_n(z)$, $k_n(z)$, and Legendre polynomials, $P_n(\cos\gamma)$, as

$$\begin{aligned}
\mathcal{L}[S_t(R, r, \gamma)] &= \frac{\exp(-\sqrt{s}(R^2 + r^2 - 2Rr\cos\gamma)^{1/2})}{s(R^2 + r^2 - 2Rr\cos\gamma)^{1/2}} \\
&= \frac{2}{\pi} \sum_{n=0}^{\infty} (2n+1) \frac{i_n(r\sqrt{s})k_n(R\sqrt{s})}{\sqrt{s}} P_n(\cos\gamma).
\end{aligned} \tag{11}$$

The Bessel functions $i_n(z)$ and $k_n(z)$ are defined explicitly as

$$k_n(z) = \frac{\pi}{2z} e^{-z} \sum_{p=0}^{n} \frac{(n+p)!}{p!(n-p)!(2z)^p} \tag{12}$$

$$i_n(z) = \frac{1}{2z} \left(e^z \sum_{p=0}^{n} \frac{(-1)^p(n+p)!}{p!(n-p)!(2z)^p} + (-1)^{n+1} e^{-z} \sum_{p=0}^{n} \frac{(n+p)!}{p!(n-p)!(2z)^p} \right). \tag{13}$$

The inverse Laplace transform of the series expansion, equation (11), gives the short-range interaction function in the desired form

$$S_t(R, r, \gamma) = \sum_{n=0}^{\infty} \mathcal{F}_n(R, r; t) P_n(\cos \gamma), \tag{14}$$

where the nth-order radial function is defined by the inverse Laplace transform

$$\mathcal{F}_n(R, r; t) = \frac{2(2n+1)}{\pi} \mathcal{L}^{-1} \left[\frac{i_n(r_< \sqrt{s}) k_n(R_> \sqrt{s})}{\sqrt{s}} \right]. \tag{15}$$

As stressed by Marshall (2002), the necessary condition for the existence of the inverse Laplace transform is that equation (11) tends to zero with increasing s. In order to satisfy this condition it is required that the argument of the Bessel function k_n be greater than that of the Bessel function i_n, i.e. $R > r$, otherwise the two arguments should be interchanged, analogously to the convention used in the definition of the full Coulomb radial function, $\mathcal{G}_n(R, r)$, in equation (4). The details of the calculation of the radial function associated with the screened Coulomb interaction are to be discussed in the following subsection.

2.2. Short-range radial function

In order to simplify the analysis of its behaviour, the radial function, $\mathcal{F}_n(R, r; \mu)$, will be expressed in terms of the scaled variables, $\Xi = \mu R$ and $\xi = \mu r$, as

$$\mathcal{F}_n(R, r; \mu) = \mu \Phi_n(\Xi, \xi), \tag{16}$$

where $\Phi_n(\Xi, \xi)$ is the scaled radial function. Note that the full Coulomb radial function, equation (4), obeys a similar scaling relationship

$$\mathcal{G}_n(R, r) = \mu \mathcal{G}_n(\Xi, \xi). \tag{17}$$

By solving equation (15) explicitly, Marshall (2002) has derived three different closed expressions for the inverse Laplace transform. We have tested these analytical expressions against the numerical evaluation of the inverse Laplace transform integral, but were not able to confirm the validity of either the first or the third analytical evaluations, which used the incomplete and Euler gamma functions on the one hand and the error function integral, erfci, on the other. However, we succeeded in verifying numerically the second analytic evaluation, given by equation (A.27) of Marshall's paper, which was obtained by calculating the intermediary integral

$$\mathcal{F}_n(R, r; t) = (2n+1) \int_0^t d\tau \frac{e^{-(R^2+r^2)/4\tau}}{2\sqrt{\pi \tau^3}} i_n \left(\frac{rR}{2\tau} \right). \tag{18}$$

A transcription Marshall's result in our previously introduced scaled variables leads to the

expression

$$\Phi_n(\Xi, \xi) = (2n+1)\left(\frac{1}{\sqrt{2\pi\,\Xi\xi}}\sum_{p=0}^{n}\frac{(-1)^p(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{1}{2\Xi\xi}\right)^{p+1/2}E_{p+3/2}((\Xi-\xi)^2)\right.$$

$$\left.+\frac{(-1)^{n+1}}{\sqrt{2\pi\,\Xi\xi}}\sum_{p=0}^{n}\frac{(n+p)!}{p!(n-p)!2^{p+1}}\left(\frac{1}{2\Xi\xi}\right)^{p+1/2}E_{p+3/2}((\Xi+\xi)^2)\right), \tag{19}$$

where $E_n(z) = \int_1^\infty e^{-zt}/t^n\,dt$ is the exponential integral function of order n. This formula is symmetric in the variables Ξ and ξ, but indeterminate for $\Xi = \xi$.

In the present work we followed a strategy, which consists in performing an order by order determination of the inverse Laplace transform using the Mathematica package (Wolfram 2005), employing the explicit forms of the modified Bessel functions, $i_n(z)$ and $k_n(z)$, given by equations (12) and (13). For instance, at the zeroth order we obtain

$$\mathcal{L}^{-1}\left[\frac{(e^{-(R-r)\sqrt{s}} - e^{-(R+r)\sqrt{s}})\pi}{4Rrs^{3/2}}\right] = \frac{1}{2\sqrt{\pi}\xi\Xi}\{(e^{-(\Xi-\xi)^2} - e^{-(\Xi+\xi)^2})$$

$$+ \sqrt{\pi}((\Xi+\xi)\operatorname{erfc}(\Xi+\xi) - (\Xi-\xi)\operatorname{erfc}(\Xi-\xi))\}. \tag{20}$$

Analogous expressions are obtained for higher orders, containing an exponential and a complementary error function contribution.

After rearrangement of the lowest order results the following general expression can be established for the nth-order radial function:

$$\Phi_n(\Xi, \xi) = F_n(\Xi, \xi) + \sum_{m=1}^{n} F_{n-m}(\Xi, \xi)\frac{\Xi^{2m} + \xi^{2m}}{(\xi\Xi)^m} + H_n(\Xi, \xi), \tag{21}$$

where $F_n(\Xi, \xi)$ and $H_n(\Xi, \xi)$ are auxiliary functions. $F_n(\Xi, \xi)$ is symmetric with respect to the interchange of the two variables, i.e. $F_n(\Xi, \xi) = F_n(\xi, \Xi)$, and it is defined as

$$F_n(\Xi, \xi) = \frac{2}{\sqrt{\pi}}\sum_{p=1}^{n}\left(\frac{-1}{4\Xi\xi}\right)^{p+1}\frac{(n+p)!}{p!(n-p)!}((-1)^{n-p}e^{-(\xi+\Xi)^2} - e^{-(\xi-\Xi)^2}). \tag{22}$$

Note that $F_n(\Xi, \xi)$ can also be expressed with the help of the modified Bessel functions of the second kind, $K_n(z)$, as

$$F_n(\Xi, \xi) = \frac{e^{-(\xi^2+\Xi^2)}}{\pi\sqrt{\xi\Xi}}(\iota K_{-1/2-n}(-2\xi\Xi) - (-1)^n K_{-1/2-n}(2\xi\Xi)). \tag{23}$$

The auxiliary function $H_n(\Xi, \xi)$ is defined in terms of the complementary error function as

$$H_n(\Xi, \xi) = \frac{1}{2(\xi\Xi)^{n+1}}((\Xi^{2n+1} + \xi^{2n+1})\operatorname{erfc}(\Xi+\xi) - (\Xi^{2n+1} - \xi^{2n+1})\operatorname{erfc}(\Xi-\xi)). \tag{24}$$

$H_n(\Xi, \xi)$ is *not* symmetric with respect to the interchange of the variables and it is supposed that $\Xi \geqslant \xi$.

Explicit expressions for the lowest order radial functions in terms of reduced variables are given in the appendix. Only simple exponential and complementary error functions are needed to evaluate the radial function, $\Phi_n(\Xi, \xi)$.

Special care should be devoted to the handling of very small arguments where, due to numerical instabilities, $\Phi_n(\Xi, \xi)$ may show a strongly oscillatory behaviour. This can be avoided by the use of a series expansion of the auxiliary function, $F_n(\Xi, \xi)$, and of the

complementary error function. We use a smooth representation of the complementary error function $\mathrm{erfc}(x)$ for $x < 10^{-4}$ by the power series

$$\mathrm{erfc}(x) \approx 1 - \frac{2x}{\sqrt{\pi}} + \frac{2x^3}{3\sqrt{\pi}} - \frac{x^5}{\sqrt{5\pi}}. \tag{25}$$

At small values of ξ strong oscillations can be observed in the auxiliary function, $F_n(\Xi, \xi)$, which can be attributed mainly to the numerical instabilities in the evaluation of the sum of Bessel functions. One possibility of avoiding this inconvenience consists in expanding the Bessel function sum in power series in the variable $\xi \Xi$ up to order $(n + 2)$:

$$\frac{1}{\pi \sqrt{\xi \Xi}} \left(\iota K_{-1/2-n}(-2\xi \Xi) - (-1)^n K_{-1/2-n}(2\xi \Xi) \right)$$
$$\approx \frac{2^{n+1}(3 + 2n + 2\xi^2 \Xi^2)\xi^n \Xi^n}{\sqrt{\pi}(2n + 3)!} + \mathcal{O}^{n+4}(\xi \Xi). \tag{26}$$

An empirically established criterion for the use of the above power series is $(\xi \Xi)^{2n+1} \leqslant 10^{-6}$. Another, perhaps safer solution is to replace $\Phi_n(\Xi, \xi)$ by its power series, as detailed in the following subsection.

2.3. Series expansion of the radial function for $\Xi \gg \xi$

The general expression for the nth-order radial function, as $\mathcal{F}_n(R, r; \mu) = \mu \Phi_n(\Xi, \xi)$, offers the possibility of exploiting the orthogonality of the spherical harmonic angular functions, but it is not separable in the vector variables R and r. In order to arrive at a separable expression we proceed by a power series expansion of the radial function $\Phi_n(\Xi, \xi)$ in the smaller reduced variable, ξ.

As an example, let us take the series expansion of the zeroth-order radial function, $\Phi_0(\Xi, \xi)$, cf equation (A.1):

$$\Phi_0(\Xi, \xi) = \frac{\mathrm{erfc}(\Xi)}{\Xi} + \frac{2\,e^{-\Xi^2}}{3\sqrt{\pi}}\xi^2 + \frac{(2\Xi^2 - 3)\,e^{-\Xi^2}}{15\sqrt{\pi}}\xi^4 + \cdots. \tag{27}$$

The first contribution is a screened analogue of the $1/R$ potential of the charge, i.e. the zeroth-order multipole moment. While in the Coulomb case this would be the only contribution, for the screened short-range interaction we have further contributions, proportional to the higher order spherically symmetric moment functions, r^2, r^4, etc. The long-range decay of these latter terms is essentially of Gaussian shape in the Ξ variable.

This behaviour proves to be general for the higher order radial functions as well. One has a first contribution, proportional to ξ^n, decaying roughly as $\mathrm{erfc}(\Xi)/\Xi^n + e^{-\Xi^2}$, followed by a series of contributions with Gaussian decay, proportional to ξ^{n+2k}. Introducing the Ξ-dependent damping functions, $D_{n,k}(\Xi)$, associated with terms of order $n + 2k$ in the variable ξ,

$$D_{n,0}(\Xi) = \mathrm{erfc}(\Xi) + \frac{e^{-\Xi^2}}{\sqrt{\pi}} 2^{n+1} \Xi^{2n+1} \sum_{m=1}^{n} \frac{2^{-m} \Xi^{-2m}}{(2n - 2m + 1)!!} \quad (k = 0) \tag{28}$$

$$D_{n,k}(\Xi) = \frac{e^{-\Xi^2}}{\sqrt{\pi}} \frac{2^{n+1}(2n + 1)\Xi^{2n+1}}{k!(2n + 2k + 1)} \sum_{m=1}^{k} \binom{m - k - 1}{m - 1} \frac{2^{k-m} \Xi^{2(k-m)}}{(2n + 2k - 2m + 1)!!} \quad (k \geqslant 1), \tag{29}$$
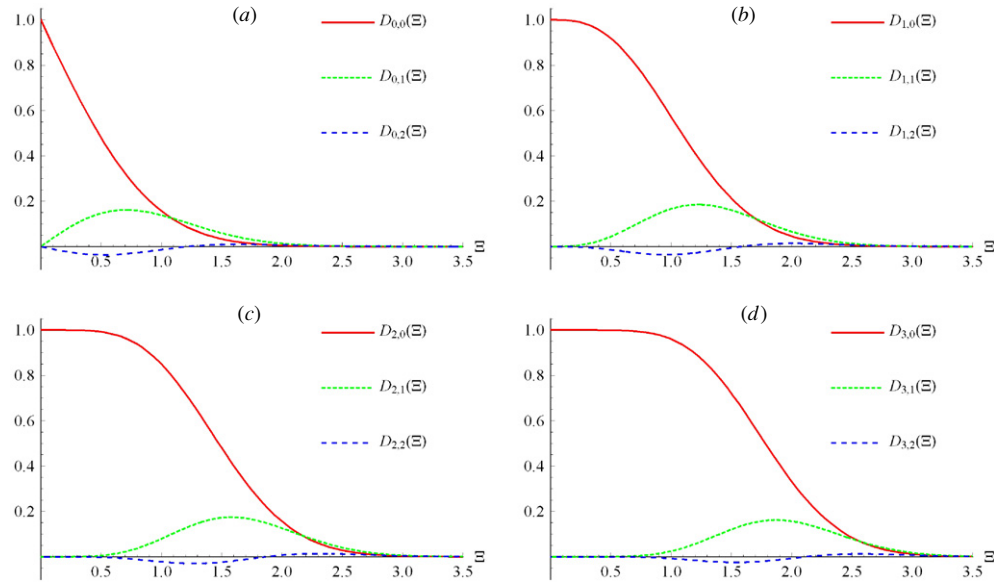
Figure 1. Damping functions of different orders, $D_{n,0}(\Xi)$, $D_{n,1}(\Xi)$ and $D_{n,2}(\Xi)$. Although higher order damping functions, $D_{n,k}(\Xi)$, are almost invisible on this scale, their contribution may be non-negligible once they are multiplied by ξ^{2k}.

the short-range radial interaction function can be written in a separable form using the scaled variables ξ and Ξ as

$$\Phi_n(\Xi, \xi) = \sum_{k=0}^{\infty} \frac{D_{n,k}(\Xi)}{\Xi^{n+1}} \xi^{n+2k}. \tag{30}$$

An insight into the shape of the screening factors of different orders is offered by figure 1. Note the dominating role of the $D_{n,0}(\Xi)$ term. The first-order correction, $D_{n,1}(\Xi)$, contributes mostly at a distance which shifts to larger and larger values with increasing n. The second-order correction, $D_{n,2}(\Xi)$, is negative first, acting against the first-order contribution, and becomes positive later.

Substitution of the power series expansion of $\Phi_n(\Xi, \xi)$ and using the spherical harmonics addition theorem leads to the following separable expansion of the short-range interaction function:

$$S_\mu(\boldsymbol{R}, \boldsymbol{r}) = \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} \mu^{2k} \frac{D_{l,k}(\mu R)}{R^{l+1}} r^{l+2k} \left(\frac{4\pi}{2l+1}\right) \sum_{m=-l}^{l} Y_{lm}^*(\Omega) Y_{lm}(\omega)$$

$$= \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{k=0}^{\infty} \mu^{2k} D_{l,k}(\mu R) \mathcal{I}_{lm}^*(\boldsymbol{R}) \mathcal{R}_{lm}(\boldsymbol{r}) r^{2k}. \tag{31}$$

Alternatively, it is possible to regroup terms according to the powers of r, leading to the following expansion:

$$S_\mu(\boldsymbol{R}, \boldsymbol{r}) = \sum_{p=0}^{\infty} \sum_{k=0}^{[p/2]} \sum_{m=2k-p}^{p-2k} \mu^{2k} D_{p-2k,k}(\mu R) \mathcal{I}_{p-2k,m}^*(\boldsymbol{R}) r^p \mathcal{C}_{p-2k,m}(\omega), \quad (32)$$

where the notation $[m]$ stands for the largest integer less than or equal to m and $\mathcal{C}_{l,m}(\omega) = (4\pi/(2l+1))^{1/2} Y_{lm}(\omega)$ is a modified spherical harmonic. This latter form of the expansion, equivalent to equation (31), shows that the screened Coulomb interaction needs to be expanded in terms of the full 'traced' multipole moments. For instance, in the case of $p = 2$, for $k = 0$ we have the five components of the irreducible spherical harmonic components of rank 2, while for $k = 1$ a further component, $r^2\mathcal{C}_{0,0}(\omega)$, appears, which is equivalent to the trace of the Cartesian quadrupole (second) moment. In the case of octupole contributions ($p = 3$), the seven irreducible spherical components are supplemented by three terms arising from $k = 1$ of the form $r^2\mathcal{C}_{1,m}(\omega)$.

Even if the present expansion contains the same kind of traced multipolar contributions as one would obtain by a direct Taylor expansion of the screened interaction function, the convergence properties of the two series are not necessarily the same. The relatively poor performance of the analytical Taylor expansion of the long-range interaction function has already been demonstrated by Hetzer $et\ al$, who showed that for $\mu = 0.15$ the analytical Taylor expansion of $L_\mu(r) = T(r) - S_\mu(r)$ starts to diverge at about $r = 15$ au. The long-range interaction function obtained from the present expansion shows no divergence at all. This can be easily understood, since, unlike the direct Taylor expansion of the long-range interaction, equation (9), our formulation leaves the error function intact, without developing it in a Taylor series which is at the origin of the divergence at larger distances.

Note that for (traceless) point multipole distributions only irreducible multipole components are needed. In the context of multipole lattice summations with the Ewald method, Cummins $et\ al$ (1976) published such interaction tensors in a traceless Cartesian formulation up to order 4 (field of octupole moments), as partial derivatives of the zeroth-order interaction function, $\mathrm{erfc}(\Xi)/\Xi$.

3. Numerical studies of the radial interaction function

In the limit of vanishingly small range separation parameter, i.e. for $\mu \to 0$, the short-range interaction function becomes identical to the usual Coulomb interaction and one has the physically expected limiting behaviour

$$\lim_{\mu \to 0} \Phi_n(\Xi, \xi) = \mathcal{G}_n(R, r). \tag{33}$$

It means that for very small values of μ the reach of the short-range interaction is very large, i.e. the short-range interaction coincides with the normal Coulomb interaction.

The radial interaction functions of a given order, $\Phi_n(\Xi, \xi)$, are two-variable quantities. In order to obtain quantitative insight into their shape, the following presents a series of representative cross-sections for the n-order radial functions, $\Phi_n(\Xi, \xi)$. For the sake of comparison the full Coulomb interaction functions, $\mathcal{G}_n(\Xi, \xi)$, are shown, as well as the k-order series expansions, $\tilde{\Phi}_{n,k}(\Xi, \xi)$, defined as

$$\tilde{\Phi}_{n,k}(\Xi, \xi) = \sum_{j=0}^{k} \frac{D_{n,j}(\Xi)}{\Xi^{n+1}} \xi^{n+2j}. \tag{34}$$

3.1. Range of validity

The range of validity of the series expansion for different orders can be estimated from the plot of $\Phi_n(\xi, \xi)$ and the expanded forms, $\tilde{\Phi}_{n,k}(\xi, \xi)$, as illustrated in figure 2. At higher orders and at small values of ξ the diagonal value of the radial function is almost identical with that of $\mathcal{G}_n(\xi, \xi)$. While the expanded short-range radial functions tend to zero too quickly,
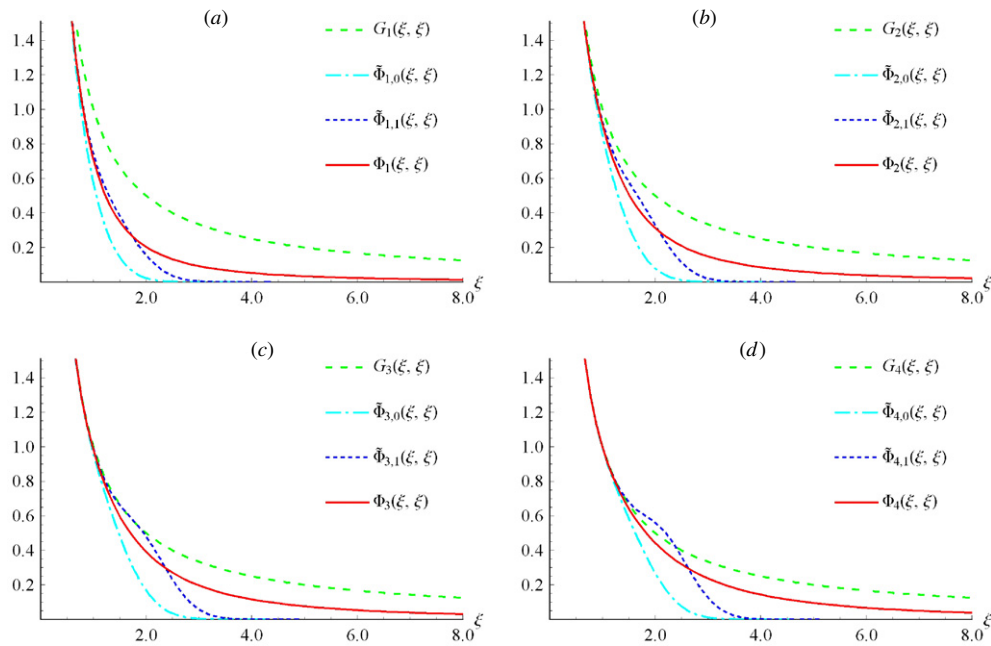
Figure 2. Radial interaction function of different orders at $\Xi = \xi$. The series expansion seems to be valid up to $\xi \approx 1.5/2.0$, depending on the order of the function.

the non-expanded form has a relatively long tail. The series expansion is correct roughly for $\xi < 1.5$. Higher order series expansions ($k > 2$) may lead to oscillations, as it is illustrated in figures 2(c) and (d).

3.2. Comparison of different orders

Cross-sections of the two-dimensional radial interaction functions of low order are plotted in figure 3 for a fixed value of $\Xi = 2.5$. In contrast to the full Coulomb interaction where the zeroth-order function is constant ($\mathcal{G}_0(\Xi, \xi) = 1/\Xi$ for $0 \leqslant \xi \leqslant \Xi$), the screened Coulomb interaction function grows roughly exponentially up to $\xi = \Xi$. For the relatively high value of $\Xi = 2.5$, the screened and full interaction functions are quite different over the whole range of the scaled variable ξ. Note that this difference between $\mathcal{G}_n(\Xi, \xi)$ and $\Phi_n(\Xi, \xi)$ persists for all but very small values of Ξ in the case of $n = 0$, but tends to become small for $n > 1$ up to relatively high values (about 0.5) of Ξ. It implies that for $\Xi < 0.5$ and $n > 1$, the screened interaction function can be replaced approximately by the full Coulomb interaction in the range of around $0 < \xi < 2\Xi$.

The series expansion of the screened interaction works better for the higher order radial interaction functions, but it is still not precise enough for the third-order radial function, as it can be seen from figure 3(d).

3.3. Comparison of the radial function for short-range and ordinary Coulomb interactions

Several cross-sections of the radial function of order 2 are illustrated in figure 4. At small values of Ξ the usual Coulomb, short-range and expanded forms are undistinguishable. For the
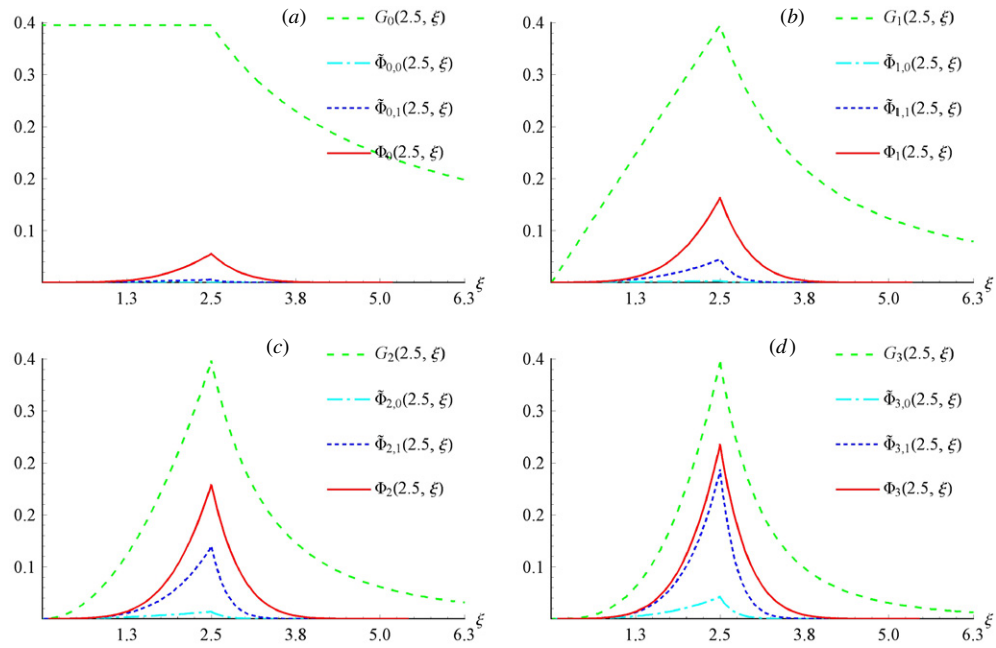
Figure 3. Radial interaction functions of different orders. All examples are presented for $\Xi = 2.5$.
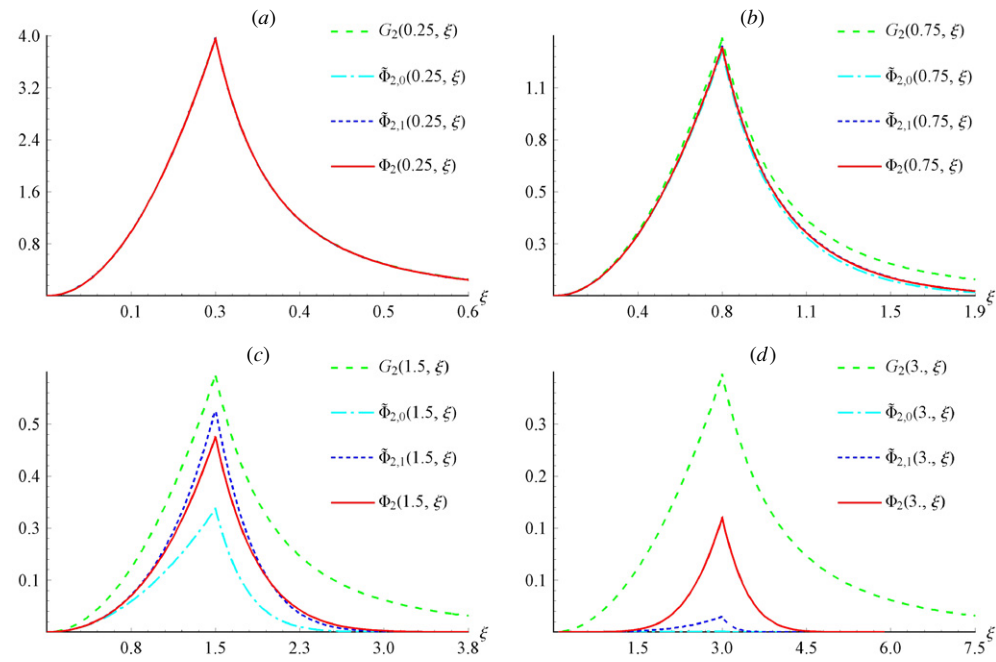
Figure 4. Comparison of radial functions of second order with normalized variables for the full Coulomb interaction $\mathcal{G}_2(\Xi, \xi)$ (broken line), for the short-range interaction in its complete form $\Phi_2(\Xi, \xi)$ (full line) and in its expanded forms $\tilde{\Phi}_{2,0}(\Xi, \xi)$ (dashed-dotted-line) and $\tilde{\Phi}_{2,0}(\Xi, \xi)$ (dotted line). (a)–(d) correspond to different choices of the variable $\Xi = 0.25$, 0.75, 1.5 and 3.0.

intermediate value of $\Xi = 0.75$ the large-ξ tail of the short-range function is slightly smaller than the full Coulomb function, but the expanded and non-expanded short-range functions are undistinguishable. At larger values of Ξ the non-expanded radial function must be used, since the expanded form is inexact.

In conclusion, a few practical rules can be established concerning the range of validity of the expanded forms of the screened short-range interaction. It turns out that for $\xi < 0.4$ the series expansion, $\tilde{\Phi}_{n,k}(\Xi, \xi)$, truncated at relatively low order ($k = 2$) can safely replace the full radial interaction function. Moreover, the use of the series expansion allows us to avoid numerical instabilities which may occur in this region. If both variables are below 0.5, or more precisely $0 < \xi < 2\Xi$ for $\Xi < 0.5$, the radial function associated with the screened interaction is very close to that of the full interaction. The convergence of the power series deteriorates for larger values of Ξ.

4. Potential of a charge distribution

In various applications concerning the electronic structure of molecules and solids, the treatment of Coulomb interactions involves the calculation of the electrostatic potential of a product of exponential basis functions, like

$$\langle n_1, l_1, m_1, \zeta_1 | \hat{V}^{sr,\mu}(R, \Theta, \Phi) | n_2, l_2, m_2, \zeta_2 \rangle, \tag{35}$$

where the $|n, l, m, \zeta\rangle$ stands for a Slater-type atomic orbital,

$$\chi_{nlm}(r, \theta, \phi) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} \, e^{-\zeta r} Y_{l,m}(\theta, \phi), \tag{36}$$

and $\langle n, l, m, \zeta |$ means its complex conjugate. The screened electrostatic potential operator can be expanded in spherical harmonics as

$$\hat{V}^{sr,\mu}(R, \Omega) = \int_0^\infty dr \, r^2 \int d\omega \, \hat{\rho}(r, \omega) \sum_{l=0}^{l} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \mathcal{F}_l(R, r, \mu)(-1)^m Y_{l,-m}(\omega) Y_{l,m}(\Omega), \tag{37}$$

where $\hat{\rho}(r, \omega)$ stands for the charge density operator in spherical coordinates, $\{r, \theta, \phi\} = \{r, \omega\}$. Using the product theorem of spherical harmonics, the charge density associated with the product of two orbitals can be expanded as

$$\langle n_1, l_1, m_1, \zeta_1 | \hat{\rho}(r, \theta, \phi) | n_2, l_2, m_2, \zeta_2 \rangle$$
$$= \sigma(n_1, \zeta_1, n_2, \zeta_2, r) \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{M=-L}^{L} C_{l_1 l_2 L}^{m_1 m_2 M} Y_{L,M}^*(\theta, \phi), \tag{38}$$

where the radial density function is

$$\sigma(n_1, \zeta_1, n_2, \zeta_2, r) = \frac{(2\zeta_1)^{n_1+1/2}(2\zeta_2)^{n_2+1/2}}{\sqrt{(2n_1)!(2n_2)!}} r^{n_1+n_2-2} \, e^{-(\zeta_1+\zeta_2)r}, \tag{39}$$

and the mixing coefficients can be given in terms of the Wigner $3j$-symbols as

$$C_{l_1 l_2 L}^{m_1 m_2 M} = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2L+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix}_{3j} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}_{3j}. \tag{40}$$

Combining these expressions and using the orthogonality of the spherical harmonics one obtains the screened short-range potential as

$$\langle n_1, l_1, m_1, \zeta_1 | \hat{V}^{sr,\mu}(R, \Theta, \Phi) | n_2, l_2, m_2, \zeta_2 \rangle$$
$$= \sum_{L=|l_1-l_2|}^{l_1+l_2} \frac{4\pi}{2L+1} W_L^{sr,\mu}(n_1, \zeta_1, n_2, \zeta_2, R) \sum_{M=-L}^{L} C_{l_1 l_2 L}^{m_1 m_2 M} Y_{L,M}^*(\Theta, \Phi). \tag{41}$$
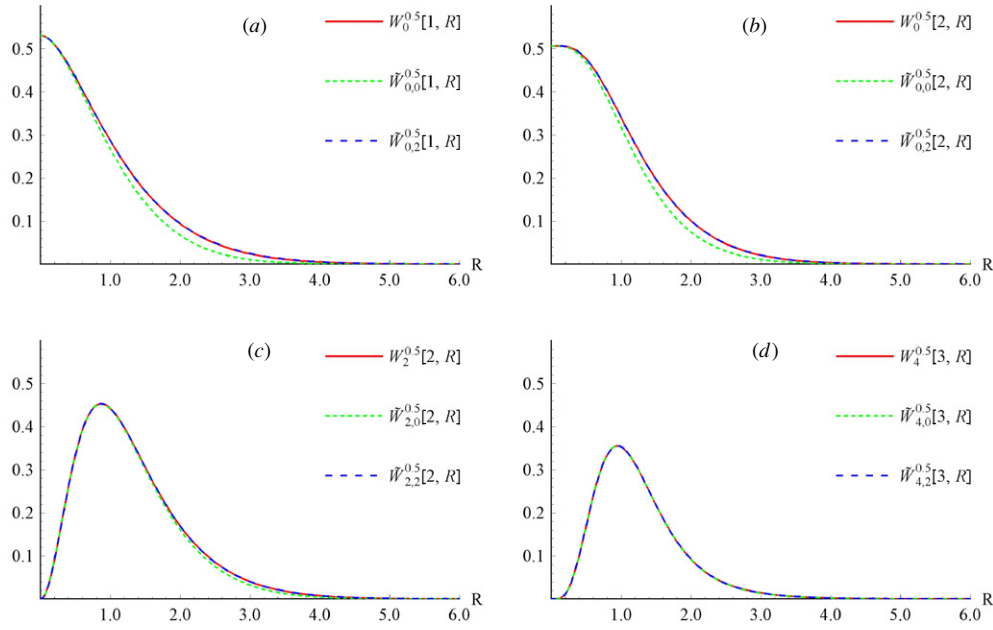
Figure 5. Short-range radial integrals for Slater functions, as described in the text.

The short-range radial integral of order L is defined as $W_L^{sr,\mu}(n_1, \zeta_1, n_2, \zeta_2, R)$ with

$$
\begin{aligned}
W_L^{sr,\mu}(n_1, \zeta_1, n_2, \zeta_2, R) = \mu \Bigg\{ & \int_0^R \mathrm{d}r\, r^2 \sigma(n_1, \zeta_1, n_2, \zeta_2, r) \Phi_L(\mu R, \mu r) \\
& + \int_R^\infty \mathrm{d}r\, r^2 \sigma(n_1, \zeta_1, n_2, \zeta_2, r) \Phi_L(\mu r, \mu R) \Bigg\},
\end{aligned}
\tag{42}
$$

where we have used the scaling relationship between $\mathcal{F}_L(R, r, \mu)$ and $\Phi(\Xi, \xi)$. This expression can be used to calculate the screened electrostatic potential over the whole range of distances.

For $R > r$, the short-range radial interaction function $\Phi(\Xi, \xi)$ can be replaced by its series expansion, leading to somewhat simpler integrals

$$
\begin{aligned}
\tilde{W}_{L,k}^{sr,\mu}(n_1, \zeta_1, n_2, \zeta_2, R) = \sum_{j=0}^{k} \mu^{2j} \Bigg\{ & D_{L,j}(\mu R) R^{-(L+1)} \int_0^R \mathrm{d}r\, r^2 \sigma(n_1, \zeta_1, n_2, \zeta_2, r) r^{L+2j} \\
& + R^{L+2j} \int_R^\infty \mathrm{d}r\, r^2 \sigma(n_1, \zeta_1, n_2, \zeta_2, r) D_{L,j}(\mu r) r^{-(L+1)} \Bigg\}.
\end{aligned}
\tag{43}
$$

The behaviour of the radial integrals has been studied for the simple case of radial densities obtained from the product of Slater functions of the form $\sigma_n(r) = \sigma(n, n, n, n, r)$, i.e. the exponents were taken to be equal to the principal quantum number. All of these radial functions have their maxima at $r = 1.0$.

Figure 5 shows the radial integrals, $W_L^{sr,\mu}(n, R)$ for $\mu = 0.5$, where n characterizes the order of the radial component, $\sigma_n(r)$, of the Slater function. It can be seen that the convergence of equation (43) with respect to k is slower for low principal quantum numbers and low values of L.

Table 1. Radial integrals of Slater-type orbitals, $\tilde{W}_L^{sr,0.5}(n, R = 2.0)$, as described in the text.

L	n	$k = 0$	$k = 2$	$k = 4$	$k = 6$	$k = \infty$
0	1	0.067 5648	0.094 338	0.094 173	0.094 165	0.094 165
0	2	0.075 2444	0.100 893	0.100 815	0.100 808	0.100 808
2	2	0.161 0200	0.169 164	0.169 417	0.169 419	0.169 419
0	3	0.077 4035	0.101 329	0.101 288	0.101 284	0.101 284
2	3	0.152 4000	0.158 921	0.159 100	0.159 102	0.159 102
4	3	0.092 1999	0.092 516	0.092 535	0.092 535	0.092 535
0	4	0.078 1516	0.100 734	0.100 710	0.100 707	0.100 707
2	4	0.144 4160	0.149 928	0.150 057	0.150 058	0.150 058

In order to provide a more precise idea about the convergence of the expanded form, equation (43), we show in table 1 the effect of including radial moments up to $k = 6$ (i.e. r^{12}) in the evaluation of radial integrals for $R = 2.0$ au. A six-digit agreement between the exact radial integral and its series expansion is obtained only for $k \geqslant 6$.

If the radial density $r^2\sigma(r)$ is sufficiently small for $r > R$, the second integral can, in principle, be neglected in equation (43) and by extending the upper limit of the first integral to infinity, one gets the following expansion:

$$\tilde{W}_L^{sr,\mu}(n_1, \zeta_1, n_2, \zeta_2, R) \approx \sum_{k=0}^{\infty} \frac{D_{L,k}(\mu R)}{R^{L+1}} \mu^{2k} M_{n_1,n_2}^{L+2k}(\zeta_1, \zeta_2), \tag{44}$$

where $M_{n_1,n_2}^{L+2k}(\zeta_1, \zeta_2)$ is the $(L + 2k)$-order moment of the radial charge distribution,

$$M_{n_1,n_2}^{L+2k}(\zeta_1, \zeta_2) = \int_0^{\infty} \mathrm{d}r\, r^2 \sigma(n_1, \zeta_1, n_2, \zeta_2, r) r^{L+2k}. \tag{45}$$

The convergence of these approximate radial integrals has been studied for the case of the radial densities $\sigma_n(r) = \sigma(n, n, n, n, r)$, described above. The radial integrals were evaluated at two characteristic distances. The first distance, R_1, is chosen such that $R_1^2\sigma_n(R_1) = \sigma_n(1)/2$, and it corresponds to the distance where the radial density is the half of the maximum. Another characteristic distance, R_2, is chosen such that $R_2^2\sigma_n(R_2) = 10^{-6}$, i.e. R_2 is a distance where the density begins to be negligibly small. As is shown in table 2 the expanded form of equation (43) is very precise: with the exception of the $n = 1$ and $L = 0$, the integrals are identical to the results of a full numerical integration of equation (42), to at least six digits. The approximate expansion of equation (44), using the explicit radial moments, is considerably less successful, even for large R.

5. Discussion

The main principles of two typical applications of the spherical harmonic expansion of the screened Coulomb interaction will be outlined in the following sections.

5.1. Electrostatic potential in crystals from experimental electron densities

As it has been stressed by Marshall (2002) one possible field of application of the screened interaction kernel concerns the calculation of the electrostatic potential in infinite periodic systems. While the determination of the potential from theoretical charge densities is relatively straightforward, only a few authors attempted to get converged electrostatic lattice potentials

Table 2. Comparison of typical radial integrals, $W_L^{sr,\mu}(n, R)$, for products of Slater orbitals $\sigma_n(r)$ for two characteristic distances, R_1 and R_2, described in the text. The parameter $\mu = 0.15$. Three alternative methods, corresponding to equations (42), (43) and (44), are compared. Numbers in parentheses indicate the powers of 10.

n	L	Equation (42)	Equation (43)	Equation (44)	Equation (42)	Equation (43)	Equation (44)
		$R_1 = 2.077\,96$			$R_2 = 9.892\,70$		
1	0	0.297 398	0.297 399	0.318 454	2.187 77 (−3)	2.187 71 (−3)	2.002 52 (−3)
1	2	0.188 098	0.188 098	0.334 084	9.384 01 (−4)	9.384 01 (−4)	8.815 57 (−4)
1	4	0.113 899	0.113 899	0.580 759	1.216 69 (−4)	1.216 69 (−4)	1.182 31 (−4)
		$R_1 = 1.709\,47$			$R_2 = 6.220\,00$		
2	0	0.402 003	0.402 003	0.420 538	1.813 20 (−2)	1.813 20 (−2)	1.779 15 (−2)
2	2	0.262 760	0.262 760	0.375 215	4.020 72 (−3)	4.020 72 (−3)	3.994 12 (−3)
2	4	0.162 929	0.162 929	0.449 533	3.297 83 (−4)	3.297 83 (−4)	3.294 62 (−4)
		$R_1 = 1.560\,59$			$R_2 = 4.881\,98$		
3	0	0.459 191	0.459 192	0.475 764	3.696 20 (−2)	3.696 20 (−2)	3.664 37 (−2)
3	2	0.313 732	0.313 732	0.409 200	6.950 65 (−3)	6.950 65 (−3)	6.937 53 (−3)
3	4	0.198 914	0.198 914	0.420 133	5.506 22 (−4)	5.506 22 (−4)	5.505 49 (−4)

from experimental charge densities. According to the current standards in the field, the experimental high-resolution (preferably low-temperature) data are fitted by some multipolar model (Stewart 1976, Hansen and Coppens 1978, Coppens and Volkov 2004).

A general multipolar model consists in an expansion of the density in terms of atomic charge distributions, $\rho(\boldsymbol{r}) = \sum_a \rho^a(\boldsymbol{r})$. An atomic distribution is composed of sum of radial Slater functions augmented by (real) spherical harmonic angular components:

$$\rho^a(\boldsymbol{r}) = \sum_{l=0}^{l_{\max}} \sum_i \sum_{m=-l}^{l} C_{lm}^{ai} \chi_l^{ai}(\boldsymbol{r}_a)$$
$$= \sum_{l=0}^{l_{\max}} \sum_i \sum_{m=-l}^{l} C_{lm}^{ai} R_l^{ai}(r_a) Y_{lm}(\theta_a, \phi_a), \tag{46}$$

where the argument $\boldsymbol{r}_a$ is the position vector with respect to the nuclear position of atom a, i.e. $\boldsymbol{r}_a = \boldsymbol{r} - \boldsymbol{R}_a$, $R_l^{ai}(r)$ is a radial function for the shell i of atom a, and C_{lm}^{ai} are linear expansion coefficients. The real spherical harmonics are given with the convention that for $l > 0$ and $l < 0$ one has the even and odd combinations, respectively. Note that equation (46) is mathematically equivalent with the conventional way of writing the Hansen–Coppens model (Hansen and Coppens 1978, Coppens and Volkov 2004).

The electrostatic potential,

$$V(\boldsymbol{R}) = \int_{\text{cell}} \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) \left(G(\boldsymbol{R}, \boldsymbol{r}) - \frac{2\pi}{3\Omega} \boldsymbol{r} \cdot \boldsymbol{r} \right), \tag{47}$$

and the corresponding periodic Coulomb kernel, $G(\boldsymbol{r}, \boldsymbol{r}')$,

$$G(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\boldsymbol{L}} \frac{\text{erfc}(\mu|\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{L}|)}{|\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{L}|} + \frac{4\pi}{\Omega} \sum_{\boldsymbol{k} \neq 0} \frac{\mathrm{e}^{-k^2/4\mu^2}}{k^2} \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r} - \boldsymbol{r}')}, \tag{48}$$

can be obtained on the basis of the Ewald method (Makov and Payne 1995, Marshall 2002). In the above expressions Ω is the unit cell volume.

While the full lattice sum is only conditionally convergent, the two contributions, one in the direct, the other in the reciprocal one, are both absolutely convergent by the virtue of the complementary error function and the Gaussian factors in the two terms, respectively. Therefore, the summation and integration can be interchanged in both components separately.

The long-range component of the periodic kernel involves a summation in the reciprocal space over the Fourier components of the charge distribution, while the short-range component corresponds to a summation in direct space. In the present context, we are mainly interested in this second component. Using the spherical harmonic expansion of the short-range kernel and the orthogonality of the spherical harmonics, the short-range direct-space contribution to the lattice sum is

$$\int_{\text{cell}} d\boldsymbol{r}\, \rho(\boldsymbol{r}) \sum_{\boldsymbol{L}} \frac{\text{erfc}(\mu|\boldsymbol{r} - \boldsymbol{R} + \boldsymbol{L}|)}{|\boldsymbol{r} - \boldsymbol{R} + \boldsymbol{L}|} = \sum_a \sum_i \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} C_{lm}^{ai} Y_{lm}^*(\Theta, \Phi)$$

$$\times \sum_{\boldsymbol{L}} \int dr_a\, r_a^2 R_l^{ai}(r_a) \mathcal{F}_l(|\boldsymbol{R} - \boldsymbol{R}_a + \boldsymbol{L}|, r_a, \mu). \tag{49}$$

The radial integral can be further simplified for most of the terms of the lattice sum. In fact, as far as $R_l^{ai}(r_a) \approx 0$, the separable series expansion of the radial part of the kernel applies, reducing the computational overhead considerably. Further details and numerical tests of this method will be published elsewhere.

5.2. Range-separated hybrid functionals in the PAW formalism

The implementation of the Fock exchange in a PAW (projector augmented wave) framework (Blöchl 1994, Kresse and Joubert 1999) has been described recently (Paier *et al* 2005) for the case of the full Coulomb interaction. In terms of the exchange integrals K_{abba}, given by

$$K_{abba} = \frac{1}{2} \iint d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \frac{\psi_a^*(\boldsymbol{r})\psi_b^*(\boldsymbol{r})\psi_b(\boldsymbol{r}')\psi_a(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{50}$$

the Fock exchange energy is $K = \frac{1}{2} \sum_{a,b} f_a f_b K_{abba}$, where f_i are the occupation numbers of the one-electron orbitals ψ_a. Introducing the standard definition of the overlap density $n_{ab}(\boldsymbol{r})$, and its PAW decomposition,

$$n_{ab}(\boldsymbol{r}) = \langle \psi_a | \hat{n}(\boldsymbol{r}) | \psi_b \rangle = \tilde{n}_{ab}(\boldsymbol{r}) + n_{ab}^1(\boldsymbol{r}) - \tilde{n}_{ab}^1(\boldsymbol{r}), \tag{51}$$

it can be seen that one needs three contributions to evaluate the Fock exchange energy: a pure plane-wave one $\widetilde{K}$, and two involving one-centre radial integrals over atomic radial functions, K^1 and $\widetilde{K}^1$, arising from the corresponding terms in the overlap density $\tilde{n}_{ab}, n_{ab}^1$ and $\tilde{n}_{ab}^1$, respectively. Typical radial integrals for the full Coulomb case (cf equations (38) and (40) in Paier *et al* (2005)) involve the kernel, $\mathcal{G}_L(R, r)$. For a short-ranged Fock exchange interaction, as employed in the HSE03 (Heyd *et al* 2003, Heyd and Scuseria 2004) functional for instance, $\mathcal{G}_L(R, r)$ has to be replaced by $\mathcal{F}_L(R, r; \mu)$ in the radial integrals:

$$S_{ijkl}^{L,\mu} = \frac{4\pi}{2L+1} \int_0^{r_c} dr\, u_i(r) u_j(r) \int_0^{r_c} dr'\, u_k(r') u_l(r') \mathcal{F}_L(r, r'; \mu). \tag{52}$$

6. Conclusions

In the present work a spherical harmonic expansion has been derived for the screened short- and long-range Coulomb interactions. This development takes full advantage of the orthogonality of spherical harmonics, especially when the angular component of the basis functions is

spherical harmonics themselves. A further series expansion in the variable r leads to a separable expression, which can be ordered either by the rank of the angular component or by increasing powers of r. The validity and the convergence properties of these expansions have been studied for numerical examples, in particular by computing the electrostatic potential of one-centre products of Slater-type atomic orbitals.

The principles of two different kinds of applications of the spherical harmonic expansion of the screened Coulomb interaction have been briefly presented and they are subject of ongoing work in our laboratories. We are convinced that the present formalism will find other applications in the field of electronic structure calculation of atoms, molecules and solids, or in problems of intermolecular forces in extended systems.

Acknowledgments

Appendix. Explicit low-order radial functions

$$\Phi_0(\Xi, \xi) = -\frac{1}{2\sqrt{\pi}\xi\,\Xi} \times \{(e^{-(\xi+\Xi)^2} - e^{-(\xi-\Xi)^2})$$
$$-\sqrt{\pi}((\xi - \Xi)\mathrm{erfc}(\Xi - \xi) + (\Xi + \xi)\mathrm{erfc}(\xi + \Xi))\} \tag{A.1}$$

$$\Phi_1(\Xi, \xi) = -\frac{1}{2\sqrt{\pi}\xi^2\,\Xi^2} \times \left\{ \frac{1}{2}((e^{-(\xi+\Xi)^2} - e^{-(\xi-\Xi)^2})(2\xi^2 + 2\xi\,\Xi - (1 - 2\Xi^2)) \right.$$
$$\left. -4\xi\,\Xi\,e^{-(\xi+\Xi)^2}) - \sqrt{\pi}((\xi^3 - \Xi^3)\,\mathrm{erfc}(\Xi - \xi) + (\xi^3 + \Xi^3)\mathrm{erfc}(\xi + \Xi)) \right\} \tag{A.2}$$

$$\Phi_2(\Xi, \xi) = -\frac{1}{2\sqrt{\pi}\xi^3\,\Xi^3} \times \left\{ \frac{1}{4}((e^{-(\xi+\Xi)^2} - e^{-(\xi-\Xi)^2})(4(\xi^4 + \xi^3\,\Xi + \Xi^4) \right.$$
$$-2\xi^2(1 - 2\Xi^2) + (1 - 2\xi\,\Xi)(3 - 2\Xi^2)) - 4\,e^{-(\xi+\Xi)^2}\xi\,\Xi(2\xi^2 - (3 - 2\Xi^2)))$$
$$\left. -\sqrt{\pi}((\xi^5 - \Xi^5)\,\mathrm{erfc}(\Xi - \xi) + (\xi^5 + \Xi^5)\,\mathrm{erfc}(\xi + \Xi)) \right\}. \tag{A.3}$$

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