JCTC Journal of Chemical Theory and Computation

LETTER

pubs.acs.org/JCTC

Resolutions of the Coulomb Operator: V. The Long-Range Ewald Operator

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ABSTRACT: We show that the long-range Ewald operator can be resolved as $\mathrm{erf}(\omega r_{12})/r_{12} = \Sigma_k \phi_k^*(\mathbf{r}_1)\,\phi_k(\mathbf{r}_2)$, where ϕ_k is proportional to the product of a spherical Bessel function and a spherical harmonic. We demonstrate the use of this new resolution by calculating the long-range Coulomb energy of the nanodiamond crystallite $C_{84}H_{64}$ and the long-range exchange energy of the graphene $C_{96}H_{24}$. The resolution appears particularly effective for long-range exchange calculations.

1. INTRODUCTION

We have recently published a series of papers[1−5] concerned with resolving the Coulomb operator

$$r_{12}^{-1} \equiv |\mathbf{r}_1 - \mathbf{r}_2|^{-1} = \sum_{k=1}^{\infty} |\phi_k\rangle\langle\phi_k| \tag{1}$$

into one-particle functions, where $|\phi_k\rangle$ and $\langle\phi_k|$ are functions of $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Such resolutions factorize a Coulomb integral into a sum of products of auxiliary integrals

$$\langle a|r_{12}^{-1}|b\rangle = \sum_{k=1}^{\infty} \langle a|\phi_k\rangle\langle\phi_k|b\rangle \tag{2}$$

and thereby offer the computational benefits of Cholesky decomposition[6−9] and density fitting,[10−12] but without the need to solve Cholesky or fitting equations.

In our most recent work,[4,5] we have shown that the one-particle functions can take the form

$$\phi_k(\mathbf{r}) \equiv \phi_{nlm}(\mathbf{r}) = 2\sqrt{2-\delta_{n,0}}\; j_l(nr)Y_{lm}(\mathbf{r}) \tag{3}$$

where j_l is a spherical Bessel function and Y_{lm} is a complex spherical harmonic.[13] Although this resolution is valid only for $r_1 + r_2 < 2\pi$, we have shown that this weakness can be overcome by a suitable prescaling of the system under study.

There is considerable contemporary interest[14−36] in partitioning the Coulomb operator as

$$r_{12}^{-1} \equiv S(r_{12}) + L(r_{12}) \tag{4}$$

where S is a singular short-range operator and L is a smooth long-range operator, and then treating the short-range and long-range subproblems separately. Ewald introduced this to chemistry to compute Madelung constants,[37] but it can be traced, in the mathematics literature, to Riemann.[38]

The partition strategy is now employed in many quantum chemical methods. It is particularly prominent in hybrid methodologies, wherein wavefunction-based and density-based approaches are carefully combined to exploit their respective strengths. This has led, for example, to the popular HSE,[21−24] CAM-B3LYP,[25] LC-ωPBE,[30] LCgau-BOP,[34] and ωB97XD[35] methods.

The short-range operator S can be treated efficiently by the use of boxing schemes[22,39−43] that exploit spatial locality. However, the long-range operator L is more computationally difficult, and it is natural to ask whether a resolution analogous to eq 1 can be constructed for it.

It turns out that there are many ways to resolve such operators, and we will consider several. Our approaches are general, but in this Letter, we focus on the long-range Ewald operator

$$L(r_{12}) = \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} \tag{5}$$

The partition parameter ω can take any positive value (the limit $\omega \to \infty$ recovers the Coulomb operator) but, in practice, often lies between 0.1 and 1. We use atomic units throughout.

2. RESOLUTIONS OF THE EWALD OPERATOR

We have investigated five approaches for resolving the Ewald operator: orthonormal expansion, Taylor expansion, Gaussian expansion, Bessel expansion, and Hermite quadrature. The first four are outlined in the Appendix, but we describe the fifth and most promising here.

If we apply $2N$-point Gauss−Hermite quadrature[13,44] to the integral representation

$$L(r_{12}) = \frac{2\omega}{\pi}\int_{-\infty}^{\infty} j_0(2\beta\omega r_{12})\,\exp(-\beta^2)\,\mathrm{d}\beta \tag{6}$$

we obtain the spherical Bessel expansion:

$$L(r_{12}) = \frac{4\omega}{\pi}\left[\sum_{n=1}^{N} b_n j_0(2\beta_n\omega r_{12}) + \varepsilon_N(\omega r_{12})\right] \tag{7}$$

where β_n and b_n are the (positive) Hermite roots and weights.

How accurate are these Bessel expansions? The quadrature error $\varepsilon_N(\omega r_{12})$ for $N = 2$, 4, 6, 8, and 10 is shown in Figure 1. It is initially tiny, indicating that the expansions are accurate for small ωr_{12}, but eventually breaks away from the axis when the expansion becomes unsatisfactory. (We note, however, that the error is bounded for all ωr_{12}.) It is encouraging to observe that the breakaway point moves rapidly to the right as N is increased,

Published: June 21, 2011

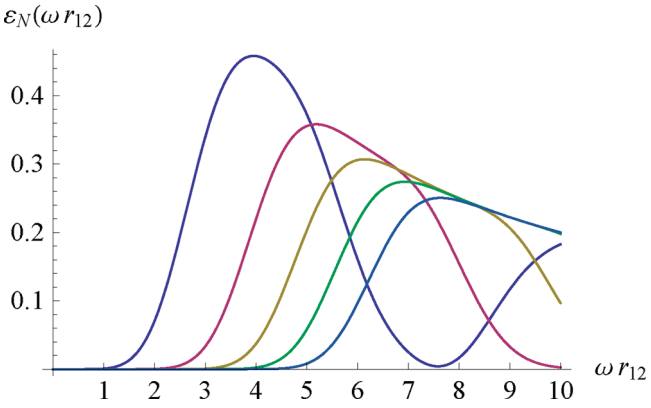

Figure 1. Quadrature error $\varepsilon_N(\omega r_{12})$ in eq 7 for $N = 2$ (left-most), 4, 6, 8, and 10 (right-most).

Table 1. N and N' such that $\varepsilon_N(\omega r_{12}) < \varepsilon$ for $0 \le \omega r_{12} \le R$

	$R = 10$		$R = 20$		$R = 30$		$R = 40$		$R = 50$	
$-\log_{10}\varepsilon$	N	N'	N	N'	N	N'	N	N'	N	N'
2	31	8	108	13	235	19	410	25	634	30
3	35	10	117	17	248	25	428	32	658	39
4	38	12	122	21	257	29	441	38	674	47
5	40	14	127	24	264	34	450	43	687	53
6	42	16	132	27	270	37	459	48	697	59
7	44	17	135	29	276	41	467	53	707	65
8	46	19	139	32	281	44	473	57	715	70
9	48	20	142	34	286	48	480	61	723	75
10	50	22	145	36	291	51	486	65	731	80
11	51	23	148	38	295	54	491	69	738	84
12	53	24	151	41	299	57	497	73	744	89

suggesting that even modest values of N yield Bessel expansions that are useful over large domains of ωr_{12}.

In principle, all N terms in eq 7 must be included. However, because $|j_0(x)| \le 1$ and the Hermite weights b_n decay extremely rapidly, it is possible to truncate eq 7 at $n = N' \ll N$ with a negligible loss of accuracy. The minimum N and N' that guarantee that the quadrature error is below ε over the domain $0 \le \omega r_{12} \le R$ are shown in Table 1. This Table reveals that, in a molecule where $\max(r_{12}) \approx 30$ (for example, taxol $C_{47}H_{51}NO_{14}$), an accuracy of 10^{-10} requires only $N' = 51$ terms for $\omega = 1$ or only $N' = 22$ terms for $\omega = 1/3$.

To resolve the j_0 functions in eq 7, we start with the spherical Bessel addition theorem[13]

$$j_0(\lambda r_{12}) = \sum_{l=0}^{\infty} (2l+1)\, j_l(\lambda r_1)\, j_l(\lambda r_2)\, P_l(\cos\theta_{12}) \tag{8}$$

and apply the Legendre addition theorem[13] to find

$$j_0(\lambda r_{12}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} j_l(\lambda r_1)\, j_l(\lambda r_2)\, Y_{lm}^*(\mathbf{r}_1)\, Y_{lm}(\mathbf{r}_2) \tag{9}$$

Substituting eq 9 into eq 7 then yields our key result—the Ewald resolution:

$$L^{(N,L)}(r_{12}) = \sum_{n=1}^{N} \sum_{l=0}^{L} \sum_{m=-l}^{l} |\phi_{nlm}\rangle\langle\phi_{nlm}| \tag{10a}$$

$$\phi_{nlm}(\mathbf{r}) = 4\sqrt{b_n\omega}\, j_l(2\beta_n\omega r)\, Y_{lm}(\mathbf{r}) \tag{10b}$$

3. COMPUTATIONAL CONSIDERATIONS

It is essential to be able to determine *a priori* the minimum values of N and N' that will guarantee that eq 7 is accurate to within ε over the domain of important ωr_{12} values in one's system. By examining the values of N in Table 1, we have devised the simple quadratic estimate

$$N \approx R^2/4 + (\sqrt{-\log_{10}\varepsilon} - 1)R + 3 \tag{11}$$

and it is then easy to show from the asymptotic behavior of the Hermite roots and weights that

$$N' \approx \frac{2}{\pi}\sqrt{-N \ln \varepsilon} \tag{12}$$

To use the Ewald resolution, eq 10, to find long-range energies, we need the auxiliary integrals

$$\langle ab|\phi_{nlm}\rangle = \int a(\mathbf{r})\, b(\mathbf{r})\, \phi_{nlm}(\mathbf{r})\, d\mathbf{r} \tag{13}$$

where we will assume that a and b are Gaussian basis functions centered at **A** and **B**, respectively. Because the Gaussian product rule allows $a(\mathbf{r})\, b(\mathbf{r})$ to be expanded as a finite linear combination[45] of Gaussians with a centroid **P** on the line between **A** and **B**, the problem reduces to finding two-center integrals of the form

$$\langle G_{n'l'm'}|\phi_{nlm}\rangle = \int r^{n'} \exp(-\zeta r^2)\, Y_{l'm'}(\mathbf{r})\, \phi_{nlm}(\mathbf{r}+\mathbf{P})\, d\mathbf{r} \tag{14}$$

These can be solved in closed form, and we will discuss elsewhere[46] an efficient algorithm for Gaussians of arbitrary angular momentum. However, in a basis that contains only s and p functions, the only necessary formulas are

$$\langle G_{000}|\phi_{nlm}\rangle = c_n C_l^{lm00} j_l Y_{lm} \tag{15a}$$

$$\langle G_{200}|\phi_{nlm}\rangle = c_n C_l^{lm00}[3/(2\zeta) - x_n^2] j_l Y_{lm} \tag{15b}$$

$$\langle G_{11m'}|\phi_{nlm}\rangle = c_n x_n [C_{l-1}^{lm1m'} j_{l-1} Y_{l-1,m-m'} - C_{l+1}^{lm1m'} j_{l+1} Y_{l+1,m-m'}] \tag{15c}$$

$$\langle G_{22m'}|\phi_{nlm}\rangle = c_n x_n^2 [C_{l-2}^{lm2m'} j_{l-2} Y_{l-2,m-m'} - C_l^{lm2m'} j_l Y_{l,m-m'} + C_{l+2}^{lm2m'} j_{l+2} Y_{l+2,m-m'}] \tag{15d}$$

where $x_n \equiv \beta_n\omega/\zeta$, $j_l \equiv j_l(2\beta_n\omega P)$, and $Y_{lm} \equiv Y_{lm}(\mathbf{P})$

$$c_n = 4\sqrt{b_n\omega}(\pi/\zeta)^{3/2} \exp(-\zeta x_n^2) \tag{16}$$

$$C_{l'}^{lm l'm'} = (-1)^{m'} \sqrt{\frac{(2l+1)(2l'+1)}{4\pi(2l'+1)}} \langle ll'00|ll'l'0\rangle \langle ll'm(-m')|ll'l'(m-m')\rangle \tag{17}$$

and the final two factors in eq 17 are Clebsch−Gordan coefficients.[13] We note that $C_l^{lm00} = Y_{00} = 1/(4\pi)^{1/2}$, and thus, eq 15a is analogous to eq 18 of our previous work.[4]

dx.doi.org/10.1021/ct200305n |J. Chem. Theory Comput. 2011, 7, 2353–2357

Table 2. (*N*,*L*) Pairs Required in Long-Range Coulomb and Exchange Calculations

	long-range Coulomb energy of the nanodiamond $C_{84}H_{64}$			long-range exchange energy of the graphene $C_{96}H_{24}$		
	$\omega = 0.1$	$\omega = 0.5$	$\omega = 1.0$	$\omega = 0.1$	$\omega = 0.5$	$\omega = 1.0$
$\varepsilon = 10^{-3}$	(3,0)	(30,13)	(114,24)	(1,4)	(2,27)	(5,45)
$\varepsilon = 10^{-6}$	(5,4)	(49,23)	(181,50)	(2,9)	(4,44)	(8,85)
$\varepsilon = 10^{-9}$	(7,8)	(65,36)	(241,68)	(3,13)	(6,58)	(12,99)

We have implemented the Ewald resolution in a stand-alone C program which precomputes the required Hermite roots and weights,[44] along with the Clebsch−Gordan coefficients.[13] The j_l and Y_{lm} are calculated recursively, as in our previous work.[4] We use the relative error

$$\varepsilon = \left| \frac{E^{(N,L)} - E}{E} \right| \tag{18}$$

to measure the accuracy of the approximate energies afforded by eq 10.

4. NUMERICAL RESULTS

The long-range Coulomb energy of a density $\rho(\mathbf{r})$ is

$$E_J = \frac{1}{2}\langle \rho | L(r_{12}) | \rho \rangle \tag{19}$$

and applying the Ewald resolution eq 10 to this yields the approximation

$$E_J^{(N,L)} = \frac{1}{2}\sum_{n=1}^{N}\sum_{l=0}^{L}\sum_{m=-l}^{l} \langle \rho | \phi_{nlm} \rangle^2 \tag{20}$$

We have applied eq 20 to the electron density in the nanodiamond $C_{84}H_{64}$, which is described in our previous paper.[4] The (*N*,*L*) pairs that yield various relative errors ε for various attenuation parameters ω are shown in the middle columns of Table 2.

The long-range exchange energy is

$$E_K = -\frac{1}{2}\sum_{ij}^{occ} \langle \psi_i \psi_j | L(r_{12}) | \psi_i \psi_j \rangle \tag{21}$$

and applying the Ewald resolution (eq 10) to this yields the approximation

$$E_K^{(N,L)} = -\frac{1}{2}\sum_{n=1}^{N}\sum_{l=0}^{L}\sum_{m=-l}^{l}\sum_{ij}^{occ} \langle \psi_i \psi_j | \phi_{nlm} \rangle^2 \tag{22}$$

Diamond has a large bandgap, and its exchange interactions decay rapidly with distance. We therefore chose to apply eq 22 to the more interesting π system of the $C_{96}H_{24}$ graphene,[47] placing a unit exponent p_π Gaussian on each C atom and using its Hückel orbitals.[48] The (*N*,*L*) pairs that yield various relative errors ε for various ω are shown in the final columns of Table 2.

Because the Ewald operator eq 5 is smooth, the (*N*,*L*) pairs required for the long-range Coulomb energies are much smaller than for the total Coulomb energies.[4] Moreover, we find that long-range exchange energies require surprisingly small *N* values, reflecting that, even in the highly delocalized graphene system, the exchange interaction decays fairly quickly with distance.[47,49,50]

5. CONCLUDING REMARKS

There are a number of ways to resolve the long-range Coulomb (Ewald) operator into products of one-particle functions. Our favorite resolution eq 10 employs a spherical Bessel expansion of the Ewald operator and thereby generalizes our earlier quasi-resolution of the Coulomb operator. Numerical results indicate that this Ewald resolution converges rapidly and may be useful in a range of quantum chemical contexts. It looks particularly promising for the efficient calculation of long-range exchange energies. We are implementing the resolution in the Q-Chem package,[51] and we will discuss the efficient evaluation of the auxiliary integrals eq 14 and present timing comparisons elsewhere.[46]

We note finally that the Bessel expansion method is easy to extend to the erfgau operator[16,34,52]

$$L_1(r_{12}) = \frac{\mathrm{erf}(\omega r_{12})}{r_{12}} - \frac{2\omega}{\sqrt{\pi}}\exp\left(-\frac{\omega^2 r_{12}^2}{3}\right) \tag{23}$$

Applying Gauss−Hermite quadrature as for the Ewald operator yields

$$\frac{2\omega}{\sqrt{\pi}}\exp\left(-\frac{\omega^2 r_{12}^2}{3}\right) = \frac{4\omega}{\pi}\int_{-\infty}^{\infty} \beta^2 j_0\left(\frac{2}{\sqrt{3}}\beta\omega r_{12}\right)\exp(-\beta^2)\,\mathrm{d}\beta \approx \frac{8\omega}{\pi}\sum_{n=1}^{N} b_n \beta_n^2 j_0\left(\frac{2}{\sqrt{3}}\beta_n \omega r_{12}\right) \tag{24}$$

where β_n and b_n have the same meanings as in eq 7.

APPENDIX

Orthonormal Expansion. One way to resolve $L(r_{12})$ is to find functions f_k that are complete and Ewald-orthonormal, i.e.

$$\langle f_k | L(r_{12}) | f_{k'} \rangle = \delta_{k,k'} \tag{25}$$

If these f_k are known, one can show[1] that

$$\phi_k(\mathbf{r}_1) = \int L(r_{12})\, f_k(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_2 \tag{26}$$

If f_k is chosen to be a product of Y_{lm} and a radial function, one eventually obtains

$$\phi_k(\mathbf{r}) = \sqrt{2/\pi}Y_{lm}(r)\int_0^\infty p_n(x)\, j_l(rx)\, \hat{L}^{1/2}(x) x\,\mathrm{d}x = 2\sqrt{2}Y_{lm}(\mathbf{r})\int_0^\infty p_n(x)\, j_l(rx)\exp\left(-\frac{x^2}{8\omega^2}\right)\mathrm{d}x \tag{27}$$

where $\hat{L}$ is the Fourier transform of L and the p_n are any functions that form a complete and orthonormal set on $[0,\infty)$. Unfortunately, this approach is thwarted by the difficulty of selecting p_n that yield tractable integrals.

Taylor Expansion. The Taylor expansion of the Ewald operator

$$L(r_{12}) = \frac{2\omega}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-\omega^2 r_{12}^2)^n}{n!(2n+1)} \tag{28}$$

converges for all r_{12}. Because $(r_{12}^2)^n$ expands naturally[18] into a finite sum for any *n*, it is easy to construct a resolution from eq 28. However, when truncated after $n = N$, the series eq 28 behaves as $(-r_{12}^2)^N$ and is therefore worthless at large r_{12}.

Gaussian Expansion. If we apply $2N$-point Gauss−Legendre quadrature[13] to the Ewald integral representation

$$L(r_{12}) = \frac{\omega}{\sqrt{\pi}}\int_{-1}^{1} \exp(-\omega^2\gamma^2 r_{12}^2)\, \mathrm{d}\gamma \tag{29}$$

we obtain the Gaussian expansion[16]

$$L(r_{12}) \approx \frac{2\omega}{\sqrt{\pi}} \sum_{n=1}^{N} g_n \exp(-\omega^2\gamma_n^2 r_{12}^2) \tag{30}$$

where the γ_n and g_n are the (positive) Legendre roots and weights. The function $\exp(-\lambda r_{12}^2)$ can be partially resolved, using the exponential and Legendre addition theorems[13] to find

$$\begin{aligned}\frac{\exp(-\lambda r_{12}^2)}{\exp(-\lambda r_1^2 - \lambda r_2^2)} &= \sum_{l=0}^{\infty} (2l+1)\, i_l(\lambda r_1 r_2)\, P_l(\cos\theta_{12}) \\ &= 4\pi \sum_{l=0}^{\infty}\sum_{m=-l}^{l} i_l(\lambda r_1 r_2)\, Y_{lm}^*(\mathbf{r}_1)\, Y_{lm}(\mathbf{r}_2)\end{aligned} \tag{31}$$

where i_l is a modified spherical Bessel function.[13] However, this does not mirror the form of eq 1 because we cannot resolve $i_l(\lambda r_1 r_2)$.

Bessel Expansion. The Fourier−Bessel expansion[13,53]

$$\begin{aligned}L(r_{12}) &= \frac{2}{\pi}\sum_{n=1}^{\infty} j_0(nr_{12}) \int_0^{\pi} L(x)\, j_0(nx)\, n^2 x^2\, \mathrm{d}x \\ &= \frac{2}{\pi}\sum_{n=1}^{\infty}\left[(-1)^{n+1}\mathrm{erf}(\omega\pi) + \exp\left(-\frac{n^2}{4\omega^2}\right)\mathscr{R}\left\{\mathrm{erf}\left(\omega\pi + \frac{n}{2\omega}\iota\right)\right\}\right] j_0(nr_{12}) \\ &= L(\pi) + \frac{2}{\pi}\sum_{n=1}^{\infty}\exp\left(-\frac{n^2}{4\omega^2}\right)\mathscr{R}\left\{\mathrm{erf}\left(\omega\pi + \frac{n}{2\omega}\iota\right)\right\} j_0(nr_{12})\end{aligned} \tag{32}$$

converges rapidly, but unfortunately, it is valid only on the finite domain $0 \le r_{12} \le \pi$. As a consequence, it yields what we have previously termed a "quasi-resolution",[4] and to use it in practice, one would need to scale the system to fit within this domain.

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ACKNOWLEDGMENT

T.L. thanks the Development and Promotion of Science and Technology Talents Project for a Royal Thai Government Ph.D. scholarship. P.M.W.G. thanks the Australian Research Council for funding (DP0984806 and DP1094170) and the NCI National Facility for supercomputer resources.

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