

Resolutions of the Coulomb Operator: IV. The Spherical Bessel Quasi-Resolution

Taweetham Limpanuparb,* Andrew T. B. Gilbert, and Peter M. W. Gill

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

ABSTRACT: We show that the Coulomb operator can be resolved as $r_{12}^{-1} = \sum_{nlm} \phi_{nlm}(r_1) \phi_{nlm}(r_2)$ where $\phi_{nlm}(r)$ is proportional to the product of a spherical Bessel function and a spherical harmonic, provided that $r_1 + r_2 < 2\pi$. The resolution reduces Coulomb matrix elements to Cholesky-like sums of products of auxiliary integrals. We find that these sums converge rapidly for four prototypical electron densities. To demonstrate its viability in large-scale quantum chemical calculations, we also use a truncated resolution to calculate the Coulomb energy of the nanodiamond crystallite $C_{84}H_{64}$.

The apparently innocuous Coulomb operator

$$r_{12}^{-1} \equiv |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \quad (1)$$

lies at the heart of many of challenging problems in contemporary quantum chemistry, and many ingenious schemes have been devised^{1–17} to treat it efficiently and accurately. In most cases, the full complexity of the operator is avoided by partially decoupling it^{1–3} and employing multipole expansions,^{4–7} Fourier transforms,⁸ Cholesky decomposition,^{9–12} density fitting,^{13–15} or other such methods.^{16,17}

Our contributions^{18–20} employ Coulomb resolutions

$$r_{12}^{-1} = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^l \phi_{nlm}(r_1) \phi_{nlm}(r_2) \quad (2)$$

where the one-particle functions

$$\phi_{nlm}(\mathbf{r}) = V_{nl}(r) Y_{lm}(\mathbf{r}) \quad (3)$$

involve a radial function $V_{nl}(r)$ and a real spherical harmonic Y_{lm} .²¹ Such resolutions reduce Coulomb matrix elements to sums of auxiliary integrals

$$\langle a | r_{12}^{-1} | b \rangle = \sum_{nlm} \langle a | \phi_{nlm} \rangle \langle \phi_{nlm} | b \rangle \quad (4)$$

and thus formally resemble Cholesky schemes.^{9–12} However, our approach forms the “Cholesky triangle” directly, without computing the matrix elements.

To construct a Coulomb resolution, one combines the Legendre expansion and the Addition Theorem²¹ to obtain the well-known²¹ angular resolution

$$r_{12}^{-1} = \sum_{lm} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(r_1) Y_{lm}(r_2) \quad (5)$$

where $r_{<}$ and $r_{>}$ are the smaller and larger of r_1 and r_2 .

To achieve a radial resolution

$$\frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} = \sum_n V_{nl}(r_1) V_{nl}(r_2) \quad (6)$$

one possibility^{18–20} is to choose

$$V_{nl}(r) = 2\sqrt{2} \int_0^{\infty} h_n(x) j_l(xr) dx \quad (7)$$

where the j_l are spherical Bessel functions²¹ and the h_n are any functions that form a complete and orthonormal set on $[0, \infty)$. We chose the Hermite functions

$$h_n(x) = \frac{(2/\pi)^{1/4}}{2^n \sqrt{(2n)!}} H_{2n}(x/\sqrt{2}) \exp(-x^2/4) \quad (8)$$

in our first work¹⁸ but adopted the Laguerre functions

$$h_n(x) = \sqrt{2} L_n(2x) \exp(-x) \quad (9)$$

in later studies.^{19,20} This approach to the radial resolution is theoretically attractive, but unfortunately, the radial functions V_{nl} that emerge from such “natural” choices for the h_n are often computationally expensive.^{18–20} This has led us to explore alternative schemes.

In the present letter, we offer a route based on the recently proven identity²²

$$\int_0^{\infty} j_l(nx) j_l(ny) dn \stackrel{\circ}{=} \frac{\delta_{l,0}}{2} + \sum_{n=1}^{\infty} j_l(nx) j_l(ny) \quad (10)$$

where $l = 0, 1, 2, \dots$ and $|x| + |y| < 2\pi$. We use the symbol $\stackrel{\circ}{=}$ to remind us of this domain restriction.

If we begin with the integral representation²³ of the left-hand side of eq 6

$$\frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} = 8 \int_0^{\infty} j_l(xr_1) j_l(xr_2) dx \quad (11)$$

and apply eq 10, we obtain the radial quasi-resolution

$$\frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \stackrel{\circ}{=} 8 \left[\frac{\delta_{l,0}}{2} + \sum_{n=1}^{\infty} j_l(nr_1) j_l(nr_2) \right] \quad (12)$$

Published: March 16, 2011

Table 1. Coulomb Energies E , Components $\Delta\tilde{E}^{(n)}$, and Domain-Violation Errors^a E_{DVE} of Four Radial Charge Densities^b $\rho(r)$

	uniform density ^c	exponential density	rational density	Gaussian density
$R^3 \times \rho(r)$	$3/(4\pi) H(R-r)$	$\exp(-r/R)/(8\pi)$	$(1+(r/R)^2)^{-2}/\pi^2$	$\exp(-r^2/R^2)/\pi^{3/2}$
nonanalyticity	discontinuity at $r=R$	cusp at $r=0$	poles at $r=\pm iR$	no singularities
$R \times E$	3/5	5/32	$1/(2\pi)$	$1/(2\pi)^{1/2}$
$\Delta\tilde{E}^{(n)}$	$9j_1^2(nR)/(nR)^2$	$(1+n^2R^2)^{-4}$	$\exp(-2nR)$	$\exp(-n^2R^2/2)$
convergence	$O[(nR)^{-4}]$	$O[(nR)^{-8}]$	$O[\exp(-2nR)]$	$O[\exp(-n^2R^2/2)]$
$R \times E_{\text{DVE}}$	$6(1-\theta)^3 H(1-\theta)/\theta^4$	$1/6(\theta+1)^3 \exp(-2\theta)$	$1/(6\theta)$	$(2/\pi)^{1/2} \exp(-2\theta^2)$

^a $\theta = \pi/R$. ^b R is a parameter that characterizes the radial extent of the density. ^c H is the Heaviside step function.²¹

and then the spherical Bessel quasi-resolution

$$r_{12}^{-1} = \sum_{nlm} \phi_{nlm}(r_1) \phi_{nlm}(r_2) \quad (13)$$

where the one-particle functions are

$$\phi_{nlm}(r) = 2\sqrt{2 - \delta_{n,0}} j_l(nr) Y_{lm}(r) \quad (14)$$

This is the key result of our letter. As the prefix “quasi” and the symbol = emphasize, it is valid only for $r_1 + r_2 < 2\pi$. The quasi-resolution, unlike our previous resolutions,^{18–20} requires only the calculation of spherical Bessel functions²⁴ and spherical harmonics,²⁵ which is efficient and stable even for large n , l , and m .

Replacing r_{12}^{-1} with the quasi-resolution directly yields the Cholesky-like decomposition

$$\langle a|r_{12}^{-1}|b\rangle = \sum_{nlm} \langle a|\phi_{nlm}\rangle \langle \phi_{nlm}|b\rangle \quad (15)$$

but without the need to compute the $\langle a|r_{12}^{-1}|b\rangle$ integrals. The auxiliary integrals

$$\langle a|\phi_{nlm}\rangle = 2\sqrt{2 - \delta_{n,0}} \int a(r) j_l(nr) Y_{lm}(r) dr \quad (16)$$

are easily found if the Fourier transform of $a(r)$ is known. For example, if $a(r)$ is the Gaussian

$$a(r) = (\alpha/\pi)^{3/2} \exp(-\alpha|r-R|^2) \quad (17)$$

we have

$$\langle a|\phi_{nlm}\rangle = \exp\left(-\frac{n^2}{4\alpha}\right) \phi_{nlm}(R) \quad (18)$$

If $a(r)$ is sufficiently smooth, then, by Darboux’s principle,²⁶ the $\langle a|\phi_{nlm}\rangle$ will decay quickly for large n , l , and m , leading to rapid convergence of the sum in eq 15. We see from eq 18, for example, that small α yield fast decay with n , and small R yield fast decay with l .

One elementary use of the quasi-resolution is to find the Coulomb self-interaction energy:

$$E = \frac{1}{2} \langle \rho|r_{12}^{-1}|\rho\rangle \quad (19)$$

of a given charge density $\rho(r)$. If the density $\rho(r) \equiv \rho(r)$ is a normalized, origin-centered radial function, one finds

$$\tilde{E} = \frac{1}{2} \sum_{nlm} \langle \rho|\phi_{nlm}\rangle \langle \phi_{nlm}|\rho\rangle = \frac{1}{2\pi} + \frac{1}{\pi} \sum_n \Delta\tilde{E}^{(n)} \quad (20)$$

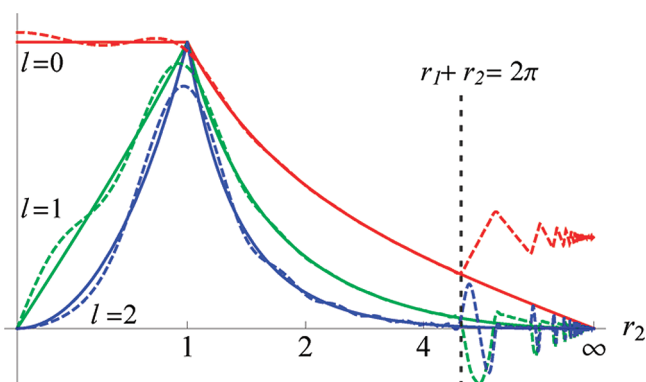


Figure 1. The left-hand side (solid) and right-hand side (dashed) of eq 12 for $l=0, 1$, and 2 when $r_1=1$ and the sum is truncated after $n=10$. Plots are scaled so that the left-hand sides coincide at $r_2=1$.

and results for four such densities are given in Table 1. These densities consist of a uniform ball (which is discontinuous on its boundary), an exponential (which has a cusp at a point), a rational function (which has poles in the complex plane), and a Gaussian (which is entire). Consistent with Darboux’s principle,²⁶ the results in the penultimate row of Table 1 confirm that the convergence of the resolution eq 20 is algebraic if $\rho(r)$ has a singularity in real space, exponential if it has a singularity in the complex plane, and superexponential if $\rho(r)$ is entire.

The key weakness of the quasi-resolution is the domain restriction $r_1 + r_2 < 2\pi$. If the quasi-resolution is applied to a density that extends beyond $r = \pi$, it introduces a domain-violation error

$$E_{\text{DVE}} = \tilde{E} - E \quad (21)$$

and the final row of Table 1 illustrates this. The message is clear: in practical applications, one should scale the system so that the DVE is acceptably small.

We begin our numerical assessment by truncating the radial resolution eq 12 after N terms. The truncated sums are useful approximations to the left-hand side, and Figure 1 illustrates this for $l=0, 1$, and 2 with $r_1=1$ and $N=10$. It confirms that the approximations are satisfactory when $r_1 + r_2 < 2\pi$ but erratic outside that domain. We note however that, even there, the errors are bounded.

Truncating the quasi-resolution eq 13 at $n=N$ and $l=L$ yields well-defined approximations to both the operator and its matrix elements. For example, the approximation

$$\tilde{E}^{(N,L)} = \frac{1}{2} \sum_{n=0}^N \sum_{l=0}^L \sum_{m=-l}^l \langle \rho|\phi_{nlm}\rangle \langle \phi_{nlm}|\rho\rangle \quad (22)$$

Table 2. Stewart parameters for atoms

hydrogen		carbon	
c_i	α_i	c_i	α_i
0.29449	0.21	1.71581	0.29
0.63550	0.88	2.54666	0.82
0.05859	3.73	-0.18334	2.31
0.01253	15.90	0.26810	6.50
-0.00111	67.73	1.09048	18.31
		0.45570	51.55
		0.09106	145.16
		0.01337	408.75
		0.00195	1150.99
		0.00016	3241.06
		0.00005	9126.48

has the truncation error

$$E_{TE} = \tilde{E}^{(N,L)} - \tilde{E} \quad (23)$$

Is such a truncation useful in practice? To explore this question, we used eq 22 to calculate the Coulomb self-interaction energy of the electrons in the octahedral nanodiamond $C_{84}H_{64}$ crystallite.²⁷ This molecule has a diamond-like structure with T_d symmetry, and for the sake of simplicity, we have used C–C and C–H bond lengths of 154 and 109 pm, respectively. The electron density

$$\rho(\mathbf{r}) = \sum_{A=1}^{148} \rho_A(\mathbf{r}) \quad (24)$$

is the sum of the Stewart atomic densities^{28–30}

$$\rho_A(\mathbf{r}) = \sum_{i=1}^{D_A} c_i (\alpha_i/\pi)^{3/2} \exp(-\alpha_i |\mathbf{r} - \mathbf{R}_A|^2) \quad (25)$$

generated from the UHF/6-311G densities of isolated 3P carbon and 2S hydrogen atoms. The Stewart parameters are given in Table 2 and yield $E = 20511.5578014$ au.

We have written a C program to compute eq 22, and we use the relative error

$$\varepsilon \equiv \left| \frac{\tilde{E}^{(N,L)} - E}{E} \right| = \left| \frac{E_{DVE} + E_{TE}}{E} \right| \quad (26)$$

to measure the accuracy of the approximation eq 22 for different (N,L) . The molecule's center of mass is placed at the origin, but most of its nuclei still lie outside the allowed domain (i.e., $|\mathbf{R}_A| > \pi$). We therefore compress the entire system by a scale factor s , perform the Coulomb calculation, and then unscale the resulting energy. The relationship between scaled and unscaled systems is described by the following equations

$$\mathbf{R}'_A = s^{-1} \mathbf{R}_A \quad (27)$$

$$\alpha'_i = s^2 \alpha_i \quad (28)$$

$$\rho'(\mathbf{r}') = s^3 \rho(\mathbf{r}) \quad (29)$$

$$E' = sE \quad (30)$$

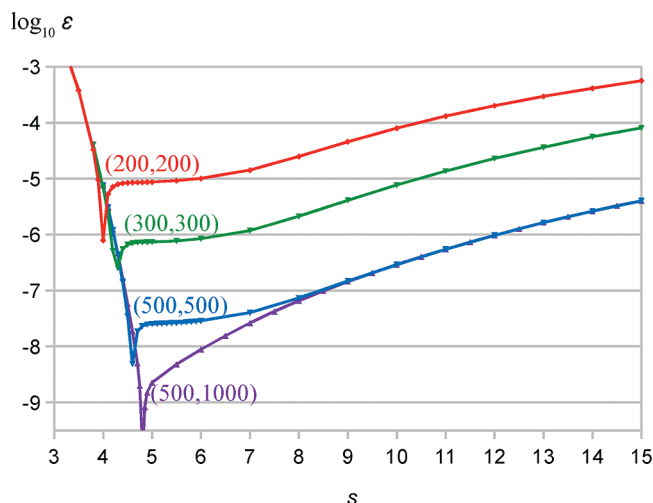


Figure 2. Relative error, eq 26, of $E^{(N,L)}$ for $3 \leq s \leq 15$.

A scaled system described by \mathbf{R}'_i , α'_i , and $\rho'(\mathbf{r}')$ is mathematically equivalent to the unscaled one. Thus, in theory, this scheme is exact and works for any kind of energies or molecular properties. However, when we use scaling in conjunction with truncated resolution, the compression increases the exponents α'_i . As a result, the auxiliary integrals eq 18 decay more slowly, reducing the rate of convergence of eq 22 and increasing the truncation error eq 23.

Figure 2 reveals that there is a DVE-dominated region ($s \lesssim 4$) and a TE-dominated region ($s \gtrsim 5$). The results show that the truncation error grows slowly as s is increased, but that the domain-violation error grows rapidly as s is decreased. It is therefore important to scale the system to fit in the domain, but moderate overcompression does not magnify the error by very much. For $N = 500$ and $L = 1000$, the lowest errors arise near $s = 4.8$, but any s from 4.5 to 12 leads to $\varepsilon < 10^{-6}$.

In summary, we have derived a quasi-resolution of the Coulomb operator that allows it to be expressed in terms of products of one-particle functions. Unlike earlier resolutions, the quasi-resolution is based on simple mathematical functions and is well suited for computational purposes. Our numerical study indicates that the quasi-resolution is useful for computing the Coulomb energy, which is an important bottleneck in DFT calculations. However, the potential scope of the quasi-resolution is much wider than this, and there are significant possibilities for applications to other operators and to exchange and correlation energies. We are currently investigating these and will report results elsewhere.

AUTHOR INFORMATION

Corresponding Author

*E-mail: taweetham.limpanuparb@anu.edu.au.

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). We thank NCI National Facility for a generous allocation of supercomputer resources.

■ REFERENCES

- (1) Gill, P. M. W.; Adamson, R. D. *Chem. Phys. Lett.* **1996**, *261*, 105–110.
- (2) Dombroski, J. P.; Taylor, S. W.; Gill, P. M. W. *J. Phys. Chem.* **1996**, *100*, 6272–6276.
- (3) Adamson, R. D.; Dombroski, J. P.; Gill, P. M. W. *Chem. Phys. Lett.* **1996**, *254*, 329–336.
- (4) Rokhlin, V. J. *Comput. Phys.* **1985**, *60*, 187–207.
- (5) Appel, A. W. *SIAM J. Sci. Stat. Comput.* **1985**, *6*, 85–103.
- (6) Greengard, L. *The rapid evaluation of potential fields in particle systems*; MIT Press: Cambridge, MA, 1987.
- (7) White, C. A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M. *Chem. Phys. Lett.* **1996**, *253*, 268–278.
- (8) Fusti-Molnar, L.; Pulay, P. *J. Chem. Phys.* **2002**, *117*, 7827–7835.
- (9) Beebe, N. H. F.; Linderberg, J. *Int. J. Quantum Chem.* **1977**, *12*, 683–705.
- (10) Koch, H.; Sanchez de Meras, A.; Pedersen, T. B. *J. Chem. Phys.* **2003**, *118*, 9481–9484.
- (11) Aquilante, F.; Lindh, R.; Pedersen, T. B. *J. Chem. Phys.* **2007**, *127*, 114107.
- (12) Weigend, F.; Kattannek, M.; Ahlrichs, R. *J. Chem. Phys.* **2009**, *130*, 164106.
- (13) Vahtras, O.; Almlöf, J.; Feyereisen, M. *Chem. Phys. Lett.* **1993**, *213*, 514–518.
- (14) Jung, Y.; Sodt, A.; Gill, P. M. W.; Head-Gordon, M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6692–6697.
- (15) Chinnamsetty, S. R.; Espig, M.; Khoromskij, B. N.; Hackbusch, W.; Flad, H.-J. *J. Chem. Phys.* **2007**, *127*, 084110.
- (16) Kinoshita, T.; Hino, O.; Bartlett, R. J. *J. Chem. Phys.* **2003**, *119*, 7756–7762.
- (17) Hino, O.; Kinoshita, T.; Bartlett, R. J. *J. Chem. Phys.* **2004**, *121*, 1206–1213.
- (18) Varganov, S. A.; Gilbert, A. T. B.; Deplazes, E.; Gill, P. M. W. *J. Chem. Phys.* **2008**, *128*, 201104.
- (19) Gill, P. M. W.; Gilbert, A. T. B. *Chem. Phys.* **2009**, *356*, 86–90.
- (20) Limpanuparb, T.; Gill, P. M. W. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9176–9181.
- (21) Olver, F. W. J.; Lozier, D. W.; Boisvert, R. F.; Clark, C. W. *NIST Handbook of Mathematical Functions*; Cambridge University Press: New York, 2010.
- (22) Dominici, D. E.; Gill, P. M. W.; Limpanuparb, T. A Remarkable Identity Involving Bessel Functions, arXiv:1103.0058. arXiv.org ePrint archive. <http://arxiv.org/abs/1103.0058> (accessed Mar 1, 2011).
- (23) Gradshteyn, I. S.; Ryzhik, I. M. *Table of Integrals, Series and Products*; Academic: London, 2007; pp 683–684.
- (24) R: *A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2010.
- (25) Smith, J. M.; Olver, F. W. J.; Lozier, D. W. *ACM Trans. Math. Software* **1981**, *7*, 93–105.
- (26) Boyd, J. P. *Chebyshev and Fourier Spectral Methods*, 2nd ed.; Dover: New York, 2000; pp 32–35.
- (27) Filik, J.; Harvey, J. N.; Allan, N. L.; May, P. W.; Dahl, J. E. P.; Liu, S.; Carlson, R. M. K. *Phys. Rev. B* **2006**, *74*, 035423.
- (28) Gill, P. M. W. *J. Phys. Chem.* **1996**, *100*, 15421–15427.
- (29) Lee, A. M.; Gill, P. M. W. *Chem. Phys. Lett.* **1998**, *286*, 226–232.
- (30) Gilbert, A. T. B.; Gill, P. M. W.; Taylor, S. W. *J. Chem. Phys.* **2004**, *120*, 7887–7893.

■ NOTE ADDED AFTER ASAP PUBLICATION

This Letter was published ASAP on March 16, 2011. A correction has been made to equation 26. The correct version was published on March 21, 2011.