Resolutions of the Coulomb operator

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We discuss a generalization of the resolution of the identity by considering one-body resolutions of two-body operators, with particular emphasis on the Coulomb operator. We introduce a set of functions that are orthonormal with respect to $1/r_{12}$ and propose that the resulting "resolution of the Coulomb operator," $r_{12}^{-1} = |\phi_i\rangle\langle\phi_i|$, may be useful for the treatment of large systems due to the separation of two-body interactions. We validate our approach by using it to compute the Coulomb energy of large systems of point charges. © *2008 American Institute of Physics.*
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I. RESOLUTIONS OF TWO-BODY OPERATORS

The resolution of the identity is a powerful tool that is widely used in quantum chemistry. It is a statement about the completeness of a set of functions $\{f_i\}$ and, adopting the summation convention, can be written

$$|f_i\rangle\langle f_i| = \hat{I}, \tag{1}$$

where $\hat{I}$ is the identity operator and the f_i satisfy the orthonormality property

$$\langle f_i|f_j\rangle = \delta_{ij}. \tag{2}$$

Equivalently, we can view this as a resolution of the Dirac delta function,

$$f_i(\mathbf{r}_1)f_i(\mathbf{r}_2) = \delta(r_{12}). \tag{3}$$

Equation (3) is an example of resolving a coupled two-particle function into one-particle functions.

More generally, we can replace the orthonormality condition (2) by

$$\langle f_i|\hat{T}|f_j\rangle = \delta_{ij}, \tag{4}$$

where $\hat{T}$ is an operator of the form

$$\hat{T}[f_i(\mathbf{r})] = \int f_i(\mathbf{r}')T(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}' = \phi_i(\mathbf{r}), \tag{5}$$

which defines the potentials $\phi_i(\mathbf{r})$ of the functions $f_i(\mathbf{r})$. If the set $\{f_i\}$ is complete, we can expand arbitrary functions $a(\mathbf{r})$ and $b(\mathbf{r})$ as

$$\langle a| = \langle a|\hat{T}|f_i\rangle\langle f_i|, \tag{6}$$

$$|b\rangle = |f_j\rangle\langle f_j|\hat{T}|b\rangle. \tag{7}$$

By combining Eqs. (4), (6), and (7), we can write

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$$\langle a|\hat{T}|b\rangle = \langle a|\hat{T}|f_i\rangle\langle f_i|\hat{T}|f_j\rangle\langle f_j|\hat{T}|b\rangle = \langle a|\hat{T}|f_i\rangle\langle f_i|\hat{T}|b\rangle$$
$$= \langle a|\phi_i\rangle\langle\phi_i|b\rangle, \tag{8}$$

where $\langle a|\phi_i\rangle$ and $\langle\phi_i|b\rangle$ are one-particle overlap integrals that we call "auxiliaries." Inspection of Eq.(8) yields the one-body resolution,

$$|\phi_i\rangle\langle\phi_i| = \hat{T}, \tag{9}$$

which induces an equivalent resolution of the kernel

$$\phi_i(\mathbf{r}_1)\phi_i(\mathbf{r}_2) = T(r_{12}), \tag{10}$$

of which Eq. (3) is a special case.

Equation (10) is related to Mercer's theorem,[1] but incorporates cases where the $\phi_i(\mathbf{r})$ are not necessarily eigenfunctions of the operator $\hat{T}$ and thus provides an infinite number of representations of $T(r_{12})$.

The expansion (8) decouples the two-body interactions associated with calculating $\langle a|\hat{T}|b\rangle$ and may be computationally advantageous if $\langle a|\hat{T}|b\rangle$ is relatively expensive, the auxiliaries are relatively cheap, and the auxiliaries decay rapidly as $i \to \infty$. The third condition ensures that the series (8) converges rapidly. In this Communication, we discuss an important special case, namely, $T(r_{12}) = r_{12}^{-1}$.

II. RESOLUTIONS OF THE COULOMB OPERATOR

The Coulomb repulsion energy between two charge distributions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ is

$$J_{12} = \langle\rho_1|r_{12}^{-1}|\rho_2\rangle. \tag{11}$$

If each distribution is composed of $K \gg 1$ elements, the evaluation of J_{12} is computationally expensive because the Coulomb operator is not separable and therefore many pairwise interactions must be computed. Nonetheless, several linear-scaling methods have been proposed. Some exploit the fact that the function is almost separable when r_{12} is large,[2–5] others use the fact that its Fourier representation is diagonal,[6,7] or harness the Legendre expansion.[8] Alternatively, one can retain the Coulomb operator but expand the charge distributions in an auxiliary basis set $\{\chi_i(\mathbf{r})\}$ to obtain[9–18]

$$J_{12} = \langle \rho_1 | r_{12}^{-1} | \chi_i \rangle (X^{-1})_{ij} \langle \chi_j | r_{12}^{-1} | \rho_2 \rangle, \tag{12}$$

where X is the matrix with elements $\langle \chi_i | r_{12}^{-1} | \chi_j \rangle$.

Motivated by the obvious simplifications if X is the identity matrix, we now consider a one-body resolution of the Coulomb operator (RC),

$$r_{12}^{-1} = | \phi_i \rangle \langle \phi_i | \tag{13}$$

that allows us to write

$$J_{12} = \langle \rho_1 | \phi_i \rangle \langle \phi_i | \rho_2 \rangle. \tag{14}$$

This is related to the KWIK method,[6] in which the long-range part of r_{12}^{-1} is expanded in a similar way, and there are also some connections to the Cholesky decomposition of Beebe and Linderberg.[19]

To resolve the Coulomb operator, we must find a set of functions f_i that are complete and satisfy the orthonormality condition

$$\langle f_i | r_{12}^{-1} | f_j \rangle = \delta_{ij}. \tag{15}$$

For practical reasons, we seek functions that factorize in spherical polar coordinates and, in Appendix A, we show that

$$f_i(\mathbf{r}) \equiv f_{nlm}(\mathbf{r}) = \frac{Y_{lm}(\theta, \phi)}{\pi \sqrt{2}} \int_0^\infty x^2 h_n(x) j_l(xr) dx \tag{16}$$

possess these properties and have the potentials

$$\phi_i(\mathbf{r}) \equiv \phi_{nlm}(\mathbf{r}) = 2\sqrt{2} Y_{lm}(\theta, \phi) V_{nl}(r), \tag{17}$$

where we have introduced the radial potentials

$$V_{nl}(r) = \int_0^\infty h_n(x) j_l(xr) dx. \tag{18}$$

The $j_l(xr)$ are spherical Bessel functions and the $Y_{lm}(\theta, \phi)$ are real spherical harmonics.[20] The $h_n(x)$ are any set of functions that are complete and orthonormal on $[0, \infty)$.

III. A PARTICULAR CHOICE FOR THE $h_n(x)$

There are many sets of functions that are complete and orthonormal on $[0, \infty)$, but the even-order Hermite functions (parabolic cylinder functions),

$$h_n(x) = \frac{(2/\pi)^{1/4}}{2^n \sqrt{(2n)!}} H_{2n}\left(\frac{x}{\sqrt{2}}\right) \exp\left(-\frac{x^2}{4}\right), \tag{19}$$

are convenient and we adopt these henceforth.

By substituting Eq. (19) into Eq. (18) and integrating the terms in the Hermite polynomial, one finds that

$$V_{nl}(r) = \frac{(-1)^n}{2^{3/4}} \sqrt{\frac{\Gamma\left(n + \frac{1}{2}\right)}{\Gamma(n+1)} \frac{\Gamma\left(\frac{l+1}{2}\right)}{\Gamma\left(l + \frac{3}{2}\right)}} r^l$$

$$\times \sum_{i=0}^n \frac{(-n)_i \left(\frac{l+1}{2}\right)_i 2^i}{\left(\frac{1}{2}\right)_i i!} M\left(\frac{l+1}{2} + i, l + \frac{3}{2}, -r^2\right), \tag{20}$$

where $(a)_b$ is a Pochhammer symbol and $M(a,b,x)$ is the confluent hypergeometric function.[20]

For a given l, the potentials $V_{nl}(r)$ possess n interleaving positive roots. Each potential is a finite combination of error functions and Gaussians, but such formulas become unwieldy when n or l are large, and it is preferable to construct the $V_{nl}(r)$ recursively (see Appendix B).

IV. EXAMPLE

The new resolution (13) has many possible applications but, as a simple illustration, we use it to compute the Coulomb self-repulsion of a system of K point charges with spherical polar coordinates $\mathbf{P}_k = (P_k, \theta_k, \phi_k)$. The classical formula, of course, is

$$J = \frac{1}{2} \sum_{i=1}^K \sum_{j \neq i}^K \frac{q_i q_j}{|\mathbf{P}_i - \mathbf{P}_j|}, \tag{21}$$

where q_i is the charge on particle i and the restriction $j \neq i$ ensures that the self-interaction energy (SIE) of each point charge is excluded. The computational cost of this expression is $O(K^2)$.

Alternatively, using the Coulomb resolution, we have

$$J = \frac{1}{2} \sum_{nlm} \langle \rho | \phi_{nlm} \rangle \langle \phi_{nlm} | \rho \rangle - \text{SIE}$$

$$= \frac{1}{2} \sum_{nlm} \left[\left| \sum_k Y_{lm}^k V_{nl}^k \right|^2 - \frac{1}{4\pi} \sum_k (q_k V_{nl}^k)^2 \right], \tag{22}$$

where

$$Y_{lm}^k = 2\sqrt{2} q_k Y_{lm}(\theta_k, \phi_k), \tag{23}$$

$$V_{nl}^k = V_{nl}(P_k). \tag{24}$$

The Y_{lm}^k can be generated efficiently by recursion[21] but the V_{nl}^k are more complicated. In our program the set of V_{nl}^k ($0 \leq n \leq N$, $0 \leq l \leq L$ and $1 \leq k \leq K$) is formed by computing boundary values and then solving a pentadiagonal linear system at a cost of $19KLN$ floating-point operations. Details are given in Appendix B.

Pseudocode to compute the Coulomb energy in this way is shown in Table I. (For clarity, we have dropped the relatively trivial self-interaction correction.) By having an outer loop over l, only two-dimensional arrays (Y, V, and A) are required and the most expensive step (the construction of the auxiliaries from the spherical harmonics and the radial integrals) can be accomplished by the highly optimized matrix

TABLE I. Pseudocode for computing J via Eq. (22).

	Method	Flop cost
$J=0$		
loop over l		
$\quad$ Y(k,m)=Y_{lm}^k	Ref. 21	$9KLM$
$\quad$ V(k,n)=V_{nl}^k	Appendix B	$19KLN$
$\quad$ A(m,n)=Σ_kY(k,m)V(k,n)	DGEMM[a]	$2KLMN$
$\quad$ $J=J+\Sigma_{m,n}|\text{A}(m,n)|^2$	DDOT[b]	$2LMN$
next l		

[a]Reference 22.
[b]Reference 23.

multiplication subroutine DGEMM.[22] For fixed values of N and L the computational cost of this method is $O(K)$.

We used this algorithm to calculate the Coulomb energy of K unit point charges randomly distributed inside a cube of length $\sqrt{N}$. This dimension was chosen to ensure a reasonable coverage of the point charges by the radial basis functions. The origin was placed at the center of charge of the system. For simplicity, the maximum angular momentum L was chosen to be the same as the number N of radial basis functions.

Figure 1 shows the variation of CPU time with K for the classical particle-particle (PP) and resolution of the Coulomb operator methods. The RC times are shown for basis sets with $N=20$, 60, and 100. The times for the PP method exhibit the expected quadratic scaling with K, whereas, for fixed N, the RC times scale linearly. Using our current implementation, RC is faster than PP for K values larger than 8000, 50 000, and 150 000 for $N=20$, 60, and 100, respectively. Direct comparisons with other fast Coulomb methods are difficult due to implementation details. However, the results of Schmidt and Lee[24] indicate crossover points for the fast multipole method (FMM), when applied to three-dimensional systems, are around 80 000 point charges for 10^{-5} accuracy, making our initial implementation competitive with the FMM.

Figure 2 shows how the relative error ϵ varies with the number of basis functions for three values of K. The initial convergence with respect to basis set size is very rapid and almost independent of K. For larger N the convergence becomes slower and appears smoother for larger values of K. This behavior is similar to that observed for the KWIK method.[6]
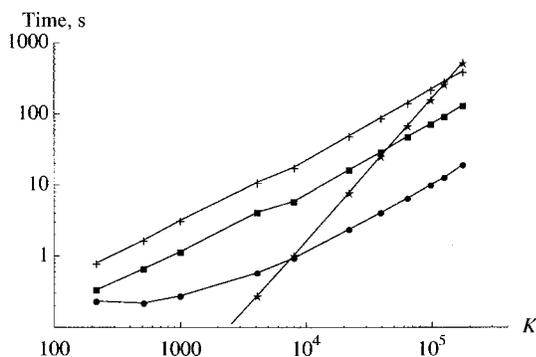

FIG. 1. CPU time (s) with number of point charges K for PP ($*$) and RC methods for $N=L=20$ ($\bullet$), 60 ($\blacksquare$), and 100 (+).
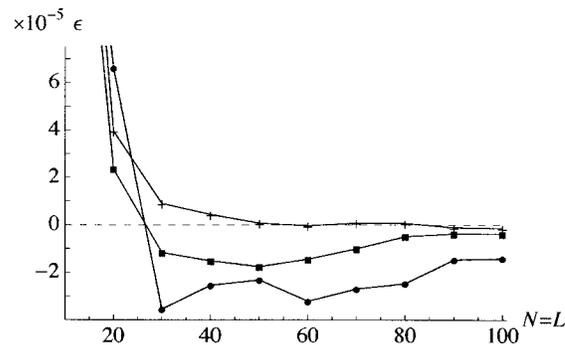

FIG. 2. Relative error ϵ with number of basis functions $N=L$ for $K=8000$ ($\bullet$), 20 000 ($\blacksquare$), and 64 000 (+).

V. CONCLUSION

We have shown how to resolve the Coulomb operator using one-particle functions, thus factorizing Coulomb interactions into one-particle contributions, and we have illustrated this factorization by calculating the Coulomb energy of a system of point charges. However, our approach can be applied to any problem where the Coulomb operator appears, and we will report applications to post–Hartree–Fock correlation methods in a future publication.

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APPENDIX A: POTENTIALS AND ORTHONORMALITY

In spherical coordinates, the functions[8]

$$\Phi_{lm}(\boldsymbol{r}) = Y_{lm}(\theta,\phi)j_l(xr) \tag{A1}$$

and

$$F_{lm}(\boldsymbol{r}) = \frac{Y_{lm}(\theta,\phi)}{4\pi}x^2 j_l(xr) \tag{A2}$$

satisfy the Poisson equation

$$\nabla^2\Phi = -4\pi F. \tag{A3}$$

Thus, by the superposition principle,

$$\phi_{nlm}(\boldsymbol{r}) = 2\sqrt{2}Y_{lm}(\theta,\phi)\int_0^\infty h_n(x)j_l(xr)dx \tag{A4}$$

are the Coulomb potentials of

$$f_{nlm}(\boldsymbol{r}) = \frac{Y_{lm}(\theta,\phi)}{\pi\sqrt{2}}\int_0^\infty x^2 h_n(x)j_l(xr)dx, \tag{A5}$$

which are complete if the $h_n(x)$ are. Finally, Coulomb orthonormality follows because

$$\langle f_{nlm}|r_{12}^{-1}|f_{n'l'm'}\rangle = \langle f_{nlm}|\phi_{n'l'm'}\rangle = \frac{2}{\pi}\int\left[\int_0^\infty x^2 h_n(x)j_l(xr)dx\right]\left[\int_0^\infty h_{n'}(y)j_{l'}(yr)dy\right]Y_{lm}(\theta,\phi)Y_{l'm'}(\theta,\phi)d\boldsymbol{r}$$

$$= \frac{2}{\pi}\int_0^\infty\int_0^\infty\int_0^\infty x^2 h_n(x)h_{n'}(y)j_l(xr)j_l(yr)r^2 drdydx\,\delta_{ll'}\delta_{mm'} = \delta_{ll'}\delta_{mm'}\int_0^\infty\int_0^\infty x^2 h_n(x)h_{n'}(y)\frac{\delta(x-y)}{xy}dydx$$

$$= \delta_{ll'}\delta_{mm'}\int_0^\infty h_n(x)h_{n'}(x)dx = \delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{A6}$$

The last line requires simple orthonormality of the $h_n(x)$. In this Communication, we chose to use the even Hermite functions (19) but we could have chosen any set of functions that is complete and orthonormal on $[0,\infty)$.

APPENDIX B: RECURRENCE RELATIONS

The $V_{n,l}(r)$ satisfy the following recurrence relations:

$$V_{0,l} = V_{0,l+2}\left(\frac{2}{2l+7}+\frac{2l+3}{r^2}\right)\frac{2l+5}{2l+2}$$
$$+ V_{0,l+4}\frac{(2l+3)(2l+8)}{(2l+2)(2l+7)}, \tag{B1}$$

$$V_{n,l} = -V_{n-1,l}\frac{4r^2}{\sqrt{2n(2n-1)}}$$
$$-V_{n-2,l}\frac{4(4n-7)r^2-(8n^2-28n+27)-4l(l+1)}{\sqrt{2n(2n-1)(2n-2)(2n-3)}}$$
$$-V_{n-3,l}\frac{\sqrt{(2n-4)(2n-5)}4r^2}{\sqrt{2n(2n-1)(2n-2)(2n-3)}}$$
$$-V_{n-4,l}\frac{\sqrt{(2n-4)(2n-5)(2n-6)(2n-7)}}{\sqrt{2n(2n-1)(2n-2)(2n-3)}}. \tag{B2}$$

In our program the $V_{0,l}$ are computed using Eq. (B1) in the backward direction. The starting values $V_{0,L}$ and $V_{0,L-1}$ are calculated using a modified confluent hypergeometric function subroutine from Ref. 25. Since Eq. (B2) is unstable in both the forward and backward directions, we compute $V_{n,l}$ from $V_{-2,l}$, $V_{-1,l}$ (which are both identically zero), $V_{0,l}$, and $V_{N,l}$ by solving a pentadiagonal system of $N-1$ linear equations. To compute $V_{N,l}$ we use cubic Chebyshev polynomial interpolation with the coefficients read from a binary file.

The coefficients are precomputed using Eq. (B2) in the forward direction with extended precision.

[1] J. Mercer, Philos. Trans. R. Soc. London **209**, 415 (1909).
[2] A. W. Appel, SIAM (Soc. Ind. Appl. Math.) J. Sci. Stat. Comput. **6**, 85 (1985).
[3] V. Rokhlin, J. Comput. Phys. **60**, 187 (1985).
[4] L. Greengard, *The Rapid Evaluation of Potential Fields in Particle Systems* (MIT Press, Cambridge, 1987).
[5] C. A. White, B. G. Johnson, P. M. W. Gill, and M. Head-Gordon, Chem. Phys. Lett. **230**, 8 (1994).
[6] J. P. Dombroski, S. W. Taylor, and P. M. W. Gill, J. Phys. Chem. **100**, 6272 (1996).
[7] L. Fusti-Molnar and P. Pulay, J. Chem. Phys. **117**, 7827 (2002).
[8] O. D. Kellogg, *Foundations of Potential Theory* (Ungar, New York, 1929).
[9] J. Whitten, J. Chem. Phys. **58**, 4496 (1973).
[10] H. Sambe and R. H. Felton, J. Chem. Phys. **62**, 1122 (1975).
[11] B. I. Dunlap, J. Connolly, and J. Sabin, J. Chem. Phys. **71**, 3396 (1979).
[12] P. M. W. Gill, B. G. Johnson, J. A. Pople, and S. W. Taylor, J. Chem. Phys. **96**, 7178 (1992).
[13] M. Feyereisen, G. Fitzgerald, and A. Komornicki, Chem. Phys. Lett. **208**, 359 (1993).
[14] O. Vahtras, J. Almlöf, and M. Feyereisen, Chem. Phys. Lett. **213**, 514 (1993).
[15] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, Chem. Phys. Lett. **240**, 283 (1995).
[16] A. M. Lee and P. M. W. Gill, Chem. Phys. Lett. **286**, 226 (1998).
[17] Y. Jung, A. Sodt, P. M. W. Gill, and M. Head-Gordon, Proc. Natl. Acad. Sci. U.S.A. **102**, 6692 (2005).
[18] P. M. W. Gill, A. T. B. Gilbert, S. W. Taylor, G. Friesecke, and M. Head-Gordon, J. Chem. Phys. **123**, 061101 (2005).
[19] N. H. F. Beebe and J. Linderberg, Int. J. Quantum Chem. **12**, 683 (1977).
[20] M. Abramowitz and I. E. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[21] K. G. Libbrecht, Sol. Phys. **99**, 371 (1985).
[22] J. J. Dongarra, J. du Croz, S. Hammarling, and I. Duff, ACM Trans. Math. Softw. **16**, 1 (1990).
[23] C. L. Lawson, R. J. Hanson, D. R. Kincaid, and F. T. Krogh, ACM Trans. Math. Softw. **5**, 308 (1979).
[24] K. E. Schmidt and M. A. Lee, J. Stat. Phys. **63**, 1223 (1991).
[25] W. J. Thompson, *Atlas for Computing Mathematical Functions* (Wiley, New York, 1997).