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A new expansion of the Coulomb interaction

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Abstract

An expansion for the Coulomb $1/r_{12}$ interaction is derived which, unlike the classical multipole expansion, converges for all r_1 and r_2. It allows the long-range component of the total Coulomb energy of a system to be written as an infinite series involving the system's multipole moments. The series is convergent if the system is of finite extent and is asymptotically convergent otherwise.

There is much current research interest in linear solutions to the Coulomb problem [1–10]. Such approaches, called $O(n)$ methods, yield the Coulomb energy of a system of n localized charge distributions in computational work that scales only linearly, rather than quadratically, with n. Since the Coulomb problem is the bottleneck in ab initio quantum chemical calculations using Hartree–Fock or density functional theories, $O(n)$ methods appear poised to revolutionize the range of applicability of these approaches.

The difficult features of the Coulomb operator $1/r$ are its singularity at $r=0$ and its slow rate of decay at large r and these conspire to render a *unified* $O(n)$ algorithm almost impossible. Consequently, all the linear algorithms that have been proposed abandon the unified treatment and begin by dividing the Coulomb interaction into a short-range and a long-range part. Because each of these inherits only one of the difficulties present in the original problem, each can be solved relatively efficiently.

In the Fast Multipole Method and its variants [1–5], every Coulomb interaction in the system is classified as either near-field (if the interacting distributions are physically close) or far-field (otherwise). Far-field interactions are treated using the Legendre expansion [11]

$$r_{12}^{-1} = \frac{1}{r_1} \sum_{k=0}^{\infty} \left(\frac{r_2}{r_1} \right)^k P_k \left(\frac{\boldsymbol{r}_1 \cdot \boldsymbol{r}_2}{r_1 r_2} \right) \tag{1}$$

where P_k is the kth Legendre polynomial. This series is convergent only if $r_1 > r_2$, that is, for parts of the system that can be enclosed in non-overlapping spheres. Nonetheless, if applied to parts of the system that overlap slightly, it can still yield a useful asymptotic series.

In the KWIK method and its variants [6–10], the function r_{12}^{-1} is partitioned as

$$r_{12}^{-1} \equiv S(r_{12}) + L(r_{12}) \equiv \frac{f(r_{12})}{r_{12}} + \frac{1-f(r_{12})}{r_{12}} \tag{2}$$

using a rapidly decaying separator f with $f(0)=1$. This splits r_{12}^{-1} into a singular short-range function $S(r_{12})$ and a non-singular long-range function $L(r_{12})$. The separator is chosen carefully to ensure that S decays rapidly and that L is nearly flat. Long-range interactions can be treated by Fourier transformation

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[6], by orthogonal polynomials [7] or by simple neglect [8,9].

However, if f is chosen such that $L(r_{12})$ is even and has a convergent Taylor series, we can resolve $L(r_{12})$ into a sum of products of one-particle functions thus

$$L(r_{12}) \equiv \sum_{k=0}^{\infty} \frac{L^{(2k)}(0)}{(2k)!}\left(r_1^2 + r_2^2 - 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_2\right)^k \tag{3}$$

This is the multipole expansion of $L(r_{12})$ but, unlike (1), it is valid for all $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

We would like to apply the new expansion in the evaluation of the total Coulomb energy

$$E_J = \tfrac{1}{2}\langle \rho(\boldsymbol{r}_1)|r_{12}^{-1}|\rho(\boldsymbol{r}_2)\rangle_{\neq} \tag{4}$$

of a system with total (electronic + nuclear) charge density $\rho(\boldsymbol{r})$. (The subscript $\neq$ indicates that nuclear self-interactions are excluded.) Substituting (2) and (3) into (4) and inverting the order of integration and summation yields

$$E_J = \tfrac{1}{2}\langle \rho|S|\rho\rangle_{\neq} + \sum_{k=0}^{\infty} \frac{L^{(2k)}(0)}{(2k)} W_{2k} \tag{5}$$

$$W_\lambda = \tfrac{1}{2}\langle \rho|r_{12}^{\lambda}|\rho\rangle_{\neq} \tag{6}$$

The W_{2k} factorize into multipole moment integrals and it is not hard to show, for example, that

$$W_0 = \left(\boldsymbol{M}_0^2 - \Sigma Z_I^2\right)/2 \tag{7a}$$

$$W_2 = \boldsymbol{M}_0\boldsymbol{M}_{ii} - \boldsymbol{M}_i\boldsymbol{M}_i \tag{7b}$$

$$W_4 = \boldsymbol{M}_0\boldsymbol{M}_{iijj} - 4\boldsymbol{M}_i\boldsymbol{M}_{ijj} + \boldsymbol{M}_{ii}\boldsymbol{M}_{jj} + 2\boldsymbol{M}_{ij}\boldsymbol{M}_{ij} \tag{7c}$$

$$W_6 = \boldsymbol{M}_0\boldsymbol{M}_{iijjkk} - 6\boldsymbol{M}_i\boldsymbol{M}_{ijjkk} + 3\boldsymbol{M}_{ii}\boldsymbol{M}_{jjkk} + 12\boldsymbol{M}_{ij}\boldsymbol{M}_{ijkk} - 6\boldsymbol{M}_{iij}\boldsymbol{M}_{jkk} - 4\boldsymbol{M}_{ijk}\boldsymbol{M}_{ijk} \tag{7d}$$

$$W_{2k} = \tfrac{1}{2}\sum_{p=0}^{k}\sum_{q=0}^{k-p} \frac{(-2)^p k!}{p!q!(k-p-q)!} \times \langle r^{2(k-p-q)}(r_\alpha r_\beta \ldots)_p\rangle\langle r^{2q}(r_\alpha r_\beta \ldots)_p\rangle \tag{7e}$$

where the Z_I are nuclear charges and the $\boldsymbol{M}$ are Cartesian multipole moment tensors of $\rho(\boldsymbol{r})$, e.g.

$$\boldsymbol{M}_0 = \int \rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{8a}$$

$$\boldsymbol{M}_i = \int r_i \rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{8b}$$

$$\boldsymbol{M}_{ij} = \int r_i r_j \rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{8c}$$

where r_i is the ith Cartesian component of $\boldsymbol{r}$. The W_{2k}, of course, are independent of the origin and we also note that W_{2k} vanishes if the system's multipole moments up to order k vanish.

Eq. (5) is theoretically significant for it demonstrates constructively that E_J can be found from knowledge of only its short-range component and the system's multipole moments. The W_0 term, which corrects for the fact that $S(r_{12})$ underestimates r_{12}^{-1} at $r_{12} = 0$, contains a negative correction $(-Z_I^2)$ for each nucleus in the system and a positive correction $(\boldsymbol{M}_0^2)$ for the self-interaction of the system's overall charge. The W_2 term corrects for charge–quadrupole and dipole–dipole self-interactions of the system, the W_4 term for charge–hexadecapole, dipole–octopole and quadrupole–quadrupole interactions, and so forth.

Suppose now that, following our earlier work [6–8], we choose the separator

$$f(r) = \mathrm{erfc}(\omega r) \tag{9}$$

where ω is a tunable decay parameter. This leads to an even $L(r_{12})$ and reduces (5) to

$$E_J = \tfrac{1}{2}\langle \rho|\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}|\rho\rangle_{\neq} + \frac{2\omega}{\sqrt{\pi}}\sum_{k=0}^{\infty}\frac{(-1)^k\omega^{2k}}{k!(2k+1)}W_{2k} \tag{10}$$

If the system is of finite extent, the W_{2k} increase exponentially and (10) is a convergent series; if the system is unbounded, the W_{2k} increase factorially and (10) is an asymptotic series in $1/\omega$.

Well-defined approximations to E_J can be obtained by truncating (10) at various points. Inclusion of only the first term is equivalent to the CASE approximation [8]

$$E_J^{(S)} = \tfrac{1}{2}\langle \rho|\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}|\rho\rangle_{\neq} \tag{11}$$

addition of the second term is equivalent to the CAP(1/2) approximation [9]

$$E_J^{(0)} = \tfrac{1}{2}\langle \rho|\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}|\rho\rangle_{\neq} + \frac{2\omega}{\sqrt{\pi}}W_0 \tag{12}$$

and further addition of the third term yields the intriguing dipole-corrected approximation

$$E_J^{(2)} = \tfrac{1}{2}\langle \rho | \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} | \rho \rangle_{\neq} + \frac{2\omega}{\sqrt{\pi}}\left(W_0 - \frac{\omega^2}{3}W_2\right) \tag{13}$$

In general, we define the $E_J^{(2k)}$ approximation by truncation after the term involving W_{2k}.

In order to determine the practical usefulness of (10) and its various truncations, it will be necessary to apply them to the calculation of Coulomb energies in a wide variety of systems. We are currently doing so and will report results in a forthcoming paper. However, the ground state of the H atom is a sufficiently illuminating yet simple case that we consider it here. Eq. (10) is an asymptotic expansion for this system and it can be shown that

$$\tfrac{1}{2}\langle \rho | \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} | \rho \rangle_{\neq} = -\frac{11}{16} + \frac{32}{\pi}\int_0^{\infty} \frac{k^4 + 8k^2 + 8}{(k^2+4)^4} \exp\left(\frac{-k^2}{4\omega^2}\right) \mathrm{d}k \tag{14}$$

$$W_\lambda = \frac{(\lambda - 2)(\lambda + 12)\Gamma(\lambda + 3)2^{-\lambda}}{96} \quad (\lambda > -3) \tag{15}$$

Because the H atom possesses no net charge or dipole moment, W_2 vanishes and $E_J^{(2)} \equiv E_J^{(0)}$. Deviations from the exact value $E_J = -11/16$ are given in Table 1 for various values of ω and $2k$. It is clear that the $E_J^{(S)}$ approximation (which we have previously [8] called CASE) introduces significant errors even for small ω values and that $E_J^{(0)}$ and $E_J^{(2)}$ are very much more accurate. The higher corrections yield useful improvements for small ω values but obviously diverge for $\omega \geqslant 0.4$. We have observed similar patterns of behaviour in other larger systems.

Table 1
Coulomb energy errors[a] of the H atom using various $E_J^{(2k)}$ approximations

ω	$E_J^{(S)}$	$E_J^{(0)}$	$E_J^{(2)}$	$E_J^{(4)}$	$E_J^{(6)}$	$E_J^{(8)}$
0.1	+56.40	−0.02	−0.02	+0.00	−0.00	+0.00
0.2	+112.42	−0.42	−0.42	+0.13	−0.04	+0.01
0.3	+166.84	−2.42	−2.42	+1.69	−1.08	+0.74
0.4	+218.12	−7.56	−7.56	+9.78	−11.02	+13.24
0.5	+265.17	−16.93	−16.93	+35.96	−63.21	+117.58

[a] Defined as $E_J^{(2k)} + 11/16$ and given in millihartree.

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