Optimal partition of the Coulomb operator

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We set up and solve the problem of optimally partitioning the Coulomb operator $1/r$ into a sum of two functions $f_1(r)$ and $f_2(r)$ such that both f_1 and the Fourier transform of f_2 decay as quickly as possible. The rigorous solution involves a Hermite function, but we find that the conventional Ewald-KWIK partition appears to be only slightly inferior. [S1050-2947(97)05604-7]

There has been considerable recent interest in the development of linear solutions to the Coulomb problem [1–10]. Such approaches, often 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 has generally been the bottleneck in *ab initio* quantum chemical calculations using Hartree-Fock or density-functional theories, $O(n)$ methods are poised to revolutionize the range of applicability of these theories.

The first step in all of the linear methods that have been proposed hitherto is to partition the Coulomb problem into two subproblems and solve each using an appropriate methodology. The fast multipole method was introduced a decade ago by Greengard and Rokhlin [1] and, more recently, has been generalized for use in a quantum chemical context and implemented by a number of groups [2–7]. Its linear cost is achieved by partitioning the physical space around a charge distribution into a small ''neighboring'' region and an infinite ''well-separated'' region whose distributions are treated by an ingenious hierarchical multipole expansion technique.

In the KWIK approach and related treatments [8–11] rather than splitting physical space, one partitions the Coulomb operator itself by writing

$$\frac{1}{r} \equiv S(r) + L(r) \equiv \frac{f(r)}{r} + \frac{1-f(r)}{r}, \qquad (1)$$

where the separator $f(r)$ decays rapidly and $f(0)=1$. This splits $1/r$ into a singular short-range function $S(r)$ and a nonsingular long-range function $L(r)$. The first can be treated in real space and, because it is negligible for large r, needs to be applied only to neighboring distributions. The second can be treated in Fourier space [8,11] or, in some cases, ignored completely [9].

For the KWIK partition to work efficiently, it is essential that the function $f(r)$ be chosen carefully. Ideally, we would like to abandon the last term in Eq. (1) entirely but, even if this does not prove feasible in general, it would certainly be convenient to be able to justify treating it approximately and we would therefore like it to be as physically insignificant as possible. Although this requirement is not mathematically well defined as it stands, we have found that it is roughly equivalent to the requirement that its Fourier transform decay as rapidly as possible. This makes sense intuitively since a function with a rapidly decaying Fourier transform must be slowly varying and a component of the Coulomb potential that is slowly varying can do little more than shift the energy origin: it cannot give rise to large forces.

We therefore seek the separator $f(r)$ in Eq. (1) that makes both the first term and the Fourier transform of the second term decay as fast as possible. There are many possible ways in which the decay rate of a function $g(r)$ can be quantified, but it is convenient for our purposes to use the second moment of $g^2(r)$. We therefore seek the $f(r)$ that minimizes

$$Z[f] = \int f^2(r)d\mathbf{r} + \int k^2 |\hat{L}(k)|^2 d\mathbf{k}, \qquad (2)$$

where $\hat{L}(k)$ is the Fourier transform of $L(r)$. Using Parseval's identity, this becomes

$$Z[f] = \int f^2(r) + |\mathbf{\nabla}[1/r - f(r)/r]|^2 d\mathbf{r}, \qquad (3)$$

and minimizing this using the calculus of variations yields the elegant Euler equation
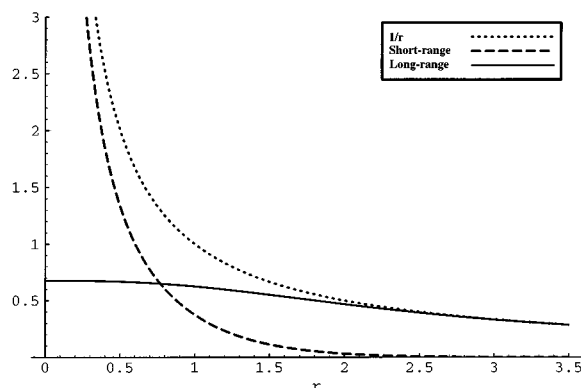
$$f''(r) = r^2 f(r). \qquad (4)$$

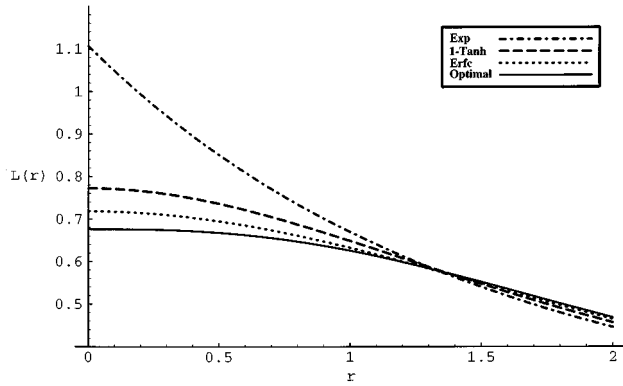FIG. 1. Optimal partition of the Coulomb operator.

FIG. 2. Long-range part of the Coulomb operator for various separators (see the text).

The solution of Eq. (4) is

$$f(r) = A\left[1 + \frac{r^4}{3.4} + \frac{r^8}{3.4.7.8} + \cdots\right]$$
$$+ B\left[r + \frac{r^5}{4.5} + \frac{r^9}{4.5.8.9} + \cdots\right] \quad (5)$$

and the boundary conditions $f(0)=1$ and $f(\infty)=0$ imply that $A=1$ and $B=-2\Gamma(\frac{3}{4})/\Gamma(\frac{1}{4})$. The resulting series for the optimal separator can be expressed in terms of modified Bessel, Hermite, or parabolic cylinder functions [12]. In terms of the latter, it is simply

$$f(r) = U(0, r\sqrt{2})/U(0,0). \quad (6)$$

This function decays asymptotically as $r^{-1/2}\exp(-r^2/2)$, i.e., slightly faster than a Gaussian.

Expressing the second term of Eq. (1) as a Fourier integral yields the optimal partition

$$\frac{1}{r} \equiv \frac{U(0, r\sqrt{2})}{r U(0,0)} + \frac{1}{2\pi^2}\int \frac{1}{k^2}\left\{1 - \Gamma\left(\frac{3}{4}\right)\sqrt{\pi}\left(\frac{k}{2}\right)^{3/2}\left[I_{1/4}\left(\frac{k^2}{2}\right)\right.\right.$$
$$\left.\left. - \mathbf{L}_{1/4}\left(\frac{k^2}{2}\right)\right]\right\}e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k} \quad (7)$$

($\mathbf{L}$ is a modified Struve function [12]), which may be contrasted with other partitions such as

$$\frac{1}{r} \equiv \frac{\mathrm{erfc}(\omega r)}{r} + \frac{1}{2\pi^2}\int\frac{1}{k^2}\exp\left(\frac{-k^2}{4\omega^2}\right)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}, \quad (8)$$

$$\frac{1}{r} \equiv \frac{1-\tanh(\omega r)}{r} + \frac{1}{4\pi\omega}\int\frac{1}{k}\,\mathrm{csch}\left(\frac{k\pi}{2\omega}\right)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}, \quad (9)$$

TABLE I. Optimized ω, Z, and α values for various separators $\phi(r)$.

$\phi(r)$	ω	$Z[\phi]$	α
1		∞	1.6875
$\exp(-\omega r)$	1.107	9.271	1.405
$1-\tanh(\omega r)$	0.772	8.627	1.543
$\mathrm{erfc}(\omega r)$	0.637	8.510	1.580
$U(0,r\sqrt{2})/U(0,0)$		8.495	1.606

$$\frac{1}{r} \equiv \frac{\exp(-\omega r)}{r} + \frac{1}{2\pi^2}\int\frac{1}{k^2}\left(\frac{\omega^2}{\omega^2+k^2}\right)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}. \quad (10)$$

The optimal partition is shown in Fig. 1 and its long-range part $L(r)$ is contrasted with the long-range parts of Eqs. (8)–(10) in Fig. 2. The optimal $L(r)$ is evidently flatter at the origin than the others. In fact, it is easy to show that the long-range parts of Eqs. (7)–(10) are cubic, quadratic, quadratic, and linear, respectively, at $r=0$.

How much better is the optimal partition (7) than the partitions (8)–(10)? One way to answer this question is to evaluate the functional (3) for the various separators employing, in each case, the value of ω that yields the smallest Z. Table I lists the resulting ω and Z values. The Z values are surprisingly insensitive to the separator and the choice $\phi(r) = \mathrm{erfc}(\omega r)$, which is used in the Ewald and KWIK-based algorithms [8–11], appears to perform well.

In the CASE approximation [9], one neglects the long-range part of the Coulomb operator completely and, naturally, the success of such an approach depends critically on the flatness of the neglected function. It is not possible to infer quantitatively from the Z values in Table I the effects on CASE calculations of using the various separators in Eqs. (7)–(10). As a very preliminary investigation of this, however, we have replaced the Coulomb operator in the Schrödinger equation for a helium atom by the attenuated operator $\phi(r)/r$ and used the variational method to find the optimal exponent α in the elementary wavefunction $\Psi(r_1, r_2) = \exp[-\alpha(r_1+r_2)]$. The α values obtained are given in the final column of Table I and we conclude that the wavefunction from the optimal separator is significantly, but not overwhelmingly, better than that from the Ewald separator.

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