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A family of attenuated Coulomb operators

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Abstract

We discuss a family of computationally useful approximations to the Coulomb operator. These operators, which we term CAP(m), are systematic improvements to our earlier CASE operator. In particular, we have CAP(0) ≡ CASE and CAP(∞) ≡ $1/r$. Because the CAP(m) approximations are all short-ranged, the computational cost of using one to compute the Coulomb energy of N localized charge distributions scales linearly with N. To investigate their accuracy, we have applied a number of CAP(m) approximations to the computation of the hydrogen atom energy and the NaCl Madelung constant. We find that the higher approximations model the original Coulomb operator quite well and the half-integer approximations, though non-vanishing at infinity, are especially accurate.

1. Introduction

All of chemistry is determined by the Coulomb force. Indeed, the electronic structure of any system, however complex, is simply the result of minimizing its Coulomb energy while ensuring that its wavefunction remains antisymmetric and of minimal curvature. It is therefore not surprising that the treatment of Coulomb interactions, particularly between electrons, has consistently emerged as a topic of central importance throughout the history of computational ab initio chemistry. The pioneering work of Heitler and London [1] for example, while often discussed in terms of the 'exchange phenomenon', may just as accurately be described as the first occasion on which the Coulomb energy in a molecule was treated properly.

For several decades thereafter, the Coulomb problem resurfaced in various guises. In the early days of quantum chemistry, a major obstacle was simply the intractability of the integrals that arise in the computation of the Coulomb energy of polyatomic molecules when exponential basis functions are employed. Although this was overcome by Boys's introduction [2] of the much more tractable Gaussian basis function in 1950, the very large number of Gaussians that are required leads to a major computational bottleneck even using modern computing hardware and the latest, highly efficient algorithms [3,4]. The fundamental difficulty is that the Coulomb interaction involves *pairs* of particles and the cost of evaluating the Coulomb energy, if treated in the most obvious way, naturally scales quadratically with the size of the system.

In recent years, a number of workers have suggested that such quadratic scaling may be avoidable and the important work of White and coworkers [5,6], which generalizes the approach of Greengard and Rokhlin [7], introduced to quantum chemistry the first Coulomb algorithm whose cost scales only

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linearly with the system size. Other research groups quickly followed.

The CFMM approach of White and coworkers achieves linear scaling by the Greengard partitioning of physical space into regions, all pairs of which are then classified as either 'well-separated' or 'not well-separated'. The Coulomb problem then falls easily into two parts. Inspired by this, we have recently introduced a second linear Coulomb scheme, the KWIK algorithm [8], wherein the Coulomb operator (rather than physical space) is partitioned into two parts, one singular and short-ranged and the other non-singular and smooth. This splits the Coulomb problem into two Ewald-like subproblems, a short-range one that is handled in real space and a long-range one that is treated in Fourier space. Each can be shown to scale linearly.

Subsequently [9], we enquired whether or not chemical properties depend equally on the short- and long-range KWIK components and were intrigued to find that properties such as atomization energies and electron and proton affinities are remarkably insensitive to the latter. This led us to the CASE (Coulomb-attenuated Schrödinger equation) approximation wherein the long-range KWIK component is systematically omitted from every Coulomb term in the Schrödinger equation. CASE is a purely short-range and thereby intrinsically linear approach.

It is not trivial to apply a theory that is based upon a modified Coulomb operator within the context of density functional theory (DFT). All of the standard density functionals have been derived on the assumption that the interelectronic interaction is $1/r$ and it is hopelessly inconsistent to treat the Coulomb and exchange–correlation energies using different operators. Therefore, in a recent paper [10], we rederived the Dirac/Slater exchange functional under the assumption that the Coulomb operator had been replaced by the short-range CASE operator. Our derivation yields the Coulomb-attenuated Dirac (CAD) exchange functional and has enabled us to perform Coulomb-attenuated Hartree–Fock–Slater (HFS) calculations.

Although we found that the original CASE approximation has surprisingly little effect on many chemical properties, there are certain properties (ionization energies, for example) that are strongly affected. Obviously therefore, it is desirable to devise a mechanism by which CASE results can be systematically improved toward exactitude. In the following Section, we show that the original CASE approximation may be regarded as the first member of a family of approximations, CAP(m), that bridge the gap between the CASE and Coulomb potentials.

Efficient practical implementations of the CAP(m) approximations require specialized numerical techniques. Because the present paper is concerned principally with the accuracy of the approximations, rather than their efficiency, we defer discussion of implementational details to another paper [11].

Finally, we should mention that our ultimate goal is to use the CAP(m) approximations as good starting points for an exact treatment of the Coulomb operator. Of course, in order to achieve this, we must reintroduce the omitted long-range Coulomb component in some form. KWIK itself can be viewed as one scheme for accomplishing this but we are also developing a number of others and these are described elsewhere [12,13].

2. CAP(m) approximations

We begin with the exact KWIK partitioning [8] of the Coulomb operator

$$\frac{1}{r} = \frac{\mathrm{erfc}(\omega r)}{r} + \frac{\mathrm{erf}(\omega r)}{r} \tag{1}$$

into parts termed 'short-range' and 'background', respectively. Choosing the error function and its complement to achieve this partition ensures that the short-range part decays as fast as a Gaussian while the background is smooth (in the sense that its Fourier transform $F(k)$ decays as fast as a Gaussian). The parameter ω determines how rapidly the short-range part decays.

In the KWIK approach [8], we replace the background by its exact Fourier representation

$$\frac{1}{r} = \frac{\mathrm{erfc}(\omega r)}{r} + \omega \int F(k) \exp(\mathrm{i}\omega \boldsymbol{k} \cdot \boldsymbol{r})\, \mathrm{d}\boldsymbol{k}, \tag{2}$$

whereas, in the original CASE approximation [9], we neglect the background entirely to obtain

$$\frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r}. \tag{3}$$

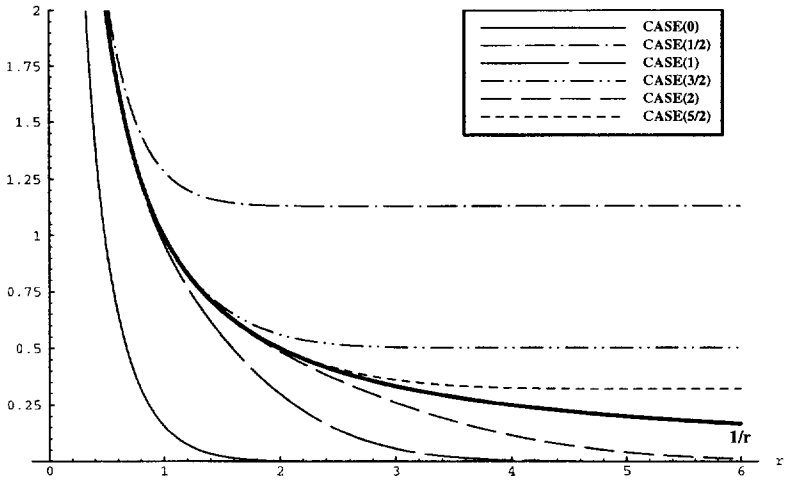

Fig. 1. The first six CAP(m) approximations ($\omega = 1$).

Between (2) and (3), however, lies a family of approximations of intermediate accuracy

$$\frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \sum_{j=1}^{[m+1/2]} a_{mj} \exp\left(-\omega^2 \alpha_{mj}^2 r^2\right), \qquad (4)$$

and we call these the Coulomb-attenuated potentials or CAP(m) approximations. We confine our attention to integer and half-integer values of m stipulating that, in the half-integer cases, $\alpha_{m1} = 0$. We note that CAP(0) is simply the potential from the CASE approximation (3) and, furthermore, that the Fourier transform of the error of any CAP(m) approximation decays as fast as a Gaussian.

We choose the roots (α_{mj}) and weights (a_{mj}) of the Gaussians in (4) to reproduce the background and its first $4m-2$ derivatives at $r = 0$. In this way, the CAP(m) approximations afford progressively more accurate models of the Coulomb singularity and its neighbourhood.

The Taylor series for the background is

$$\frac{\mathrm{erf}(\omega r)}{r} = \frac{2\omega}{\sqrt{\pi}} \left(1 - \frac{\omega^2 r^2}{3 \cdot 1!} + \frac{\omega^4 r^4}{5 \cdot 2!} - \frac{\omega^6 r^6}{7 \cdot 3!} + \ldots\right), \qquad (5)$$

while that for a single Gaussian is given by

$$\exp(-\omega^2 \alpha^2 r^2) = 1 - \frac{\omega^2 \alpha^2 r^2}{1!} + \frac{\omega^4 \alpha^4 r^4}{2!} - \frac{\omega^6 \alpha^6 r^6}{3!} + \ldots. \qquad (6)$$

Equating the leading terms in the background to those in a sum of Gaussians leads to a system of equations in the α_{mj} and a_{mj} that is familiar from Gauss–Legendre quadrature theory. The roots and weights are tabulated elsewhere [14] but the simplest approximations turn out to be

$$\text{CAP(0)} \quad \frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r}, \qquad (7)$$

$$\text{CAP(1/2)} \quad \frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}}, \qquad (8)$$

$$\text{CAP(1)} \quad \frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \exp\left(\frac{-\omega^2 r^2}{3}\right), \qquad (9)$$

$$\text{CAP(3/2)} \quad \frac{1}{r} \approx \frac{\mathrm{erfc}(\omega r)}{r} + \frac{2\omega}{\sqrt{\pi}} \left[\frac{4}{9} + \frac{5}{9} \exp\left(\frac{-3\omega^2 r^2}{5}\right)\right]. \qquad (10)$$

The first few CAP(m) approximations ($\omega = 1$) are illustrated in Fig. 1. The crudest approximation, CAP(0), is not equal to $1/r$ at any point. By adding an appropriate constant, we produce CAP(1/2) which is equal to $1/r$ at the origin but overshoots thereafter. The higher CAP(m) remain faithful to $1/r$ over larger and larger intervals but all eventually decay quickly either to zero (when m is an integer) or to a non-zero constant (when m is a half-integer). The integer approximations are all *lower* bounds and the half-integer approximations are all *upper* bounds to $1/r$. Aside from a trivial constant, the CAP(m) are all short-range approximations.

3. Two-electron integrals

One of the most time-consuming tasks in an ab initio molecular orbital calculation is the generation of the required two-electron repulsion integrals. In conventional calculations, where the molecular orbitals are expanded in a Gaussian basis, the fundamental integral that arises is

$$\left(\frac{\zeta\eta}{\pi^2}\right)^{3/2}\int\int \exp\left(-\zeta r_1^2\right)\left(\frac{1}{r_{12}}\right) \times \exp\left(-\eta|\boldsymbol{r}_2-\boldsymbol{R}|^2\right)\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 = R^{-1}\,\mathrm{erf}\left(R\Big/\sqrt{\frac{1}{\zeta}+\frac{1}{\eta}}\right) \tag{11}$$

and represents the energy between two normalized Gaussian charge distributions. The formula (11) has been known since the work of Boys [2] and the extensive literature concerned with the evaluation of such integrals has been reviewed [3]. However, in a CAP(m) calculation, the $1/r$ potential is modelled by a linear combination of $\mathrm{erfc}(\omega r)/r$ and $\exp(-\omega^2\alpha^2 r^2)$ and appropriate analogues of (11) must therefore be sought. Fortunately, the corresponding integrals are easily handled by the standard Fourier convolution technique [2] and one finds that

$$\left(\frac{\zeta\eta}{\pi^2}\right)^{3/2}\int\int \exp\left(-\zeta r_1^2\right)\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} \times\exp\left(-\eta|\boldsymbol{r}_2-\boldsymbol{R}|^2\right)\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

$$= R^{-1}\left[\mathrm{erf}\left(R\Big/\sqrt{\frac{1}{\zeta}+\frac{1}{\eta}}\right) -\mathrm{erf}\left(R\Big/\sqrt{\frac{1}{\zeta}+\frac{1}{\eta}+\frac{1}{\omega^2}}\right)\right]. \tag{12}$$

$$\left(\frac{\zeta\eta}{\pi^2}\right)^{3/2}\int\int \exp\left(-\zeta r_1^2\right)\exp\left(-\omega^2\alpha^2 r_{12}^2\right) \times\exp\left(-\eta|\boldsymbol{r}_2-\boldsymbol{R}|^2\right)\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

$$= \left[\omega^2\alpha^2\left(\frac{1}{\zeta}+\frac{1}{\eta}+\frac{1}{\omega^2\alpha^2}\right)\right]^{-3/2} \times\exp\left[-R^2\Big/\left(\frac{1}{\zeta}+\frac{1}{\eta}+\frac{1}{\omega^2\alpha^2}\right)\right]. \tag{13}$$

Eq. (12) is related to integrals that have recently been considered by Panas [15] and, although it can be cast into forms that are more efficient for actual computation [11], that above highlights its similarity to (11). When used in conjunction with standard recurrence relations [3,4], the formulae (12) and (13) are sufficient for all integrals arising in a CAP(m) calculation.

4. Results and discussion

4.1. Energy of the hydrogen atom

How accurate are the CAP(m) approximations in practice? To begin to answer this, we have used them to compute the total energy of the ground state of the hydrogen atom using its exact wavefunction. It can be shown that, using the operator (4), this energy is given by

$$E = -\frac{1}{2}+\frac{2}{\omega\sqrt{\pi}}-(2\omega^{-2}-1)\exp(\omega^{-2}) \times\mathrm{erfc}(\omega^{-1})+\frac{2}{\omega^2}\sum_{j=1}^{[m+1/2]}\frac{a_{mj}}{\alpha_{mj}^3}\left[\frac{2}{\alpha_{mj}\omega\sqrt{\pi}} -\left(2\alpha_{mj}^{-2}\omega^{-2}+1\right)\exp\left(\alpha_{mj}^{-2}\omega^{-2}\right) \times\mathrm{erfc}\left(\alpha_{mj}^{-1}\omega^{-1}\right)\right]. \tag{14}$$

Table 1
Errors [a] in the energy of the H atom ground state, $\psi(r) = e^{-r}$, computed using CAP(m)

m	$\omega = 0.5$	$\omega = 0.4$	$\omega = 0.3$	$\omega = 0.2$	$\omega = 0.1$
0	0.468989	0.396675	0.312866	0.217369	0.111734
1/2	−0.095201	−0.054677	−0.025648	−0.008307	−0.001104
1	0.013634	0.005886	0.001803	0.000295	0.000011
3/2	−0.002336	−0.000744	−0.000148	−0.000012	−0.000000
2	0.000429	0.000103	0.000014	0.000001	0.000000
5/2	−0.000086	−0.000016	−0.000001	−0.000000	−0.000000
3	0.000018	0.000003	0.000000	0.000000	0.000000
7/2	−0.000004	−0.000000	−0.000000	−0.000000	−0.000000

[a] CAP(m) − Exact.

The magnitude of the total energy of the hydrogen atom is equal to its ionization energy and, in our earlier work [9], we observed that CASE significantly underestimates this. We note that ionizations are a very demanding test of a Coulomb-attenuated approximation because they lack the felicitous cancellations of error that typify atomization processes and electron or proton additions. Unlike these, ionization energies and total energies directly reflect the quality of the underlying approximation.

In Table 1, we present the CAP(m) errors for the hydrogen atom using a variety of m and ω values. As we found earlier [9], CAP(0) performs poorly for all values of ω studied: even for $\omega = 0.1$, the error is more than 100 mh. However, in proceeding to CAP(1/2), we observe a dramatic improvement. The errors are now negative but are as much as two orders of magnitude smaller than for CAP(0). Evidently, the constant term in (8) is very important.

As m increases further, the errors continue to fall quickly, especially when ω is small. Because CAP(m) bounds $1/r$ below or above (depending upon whether or not m is an integer) and the hydrogen atom involves only a single Coulomb potential, the CAP(m) errors are consistently positive when m is an integer and negative when m is a half-integer. That CAP($m + 1/2$) yields smaller errors than CAP(m) is noteworthy because, computationally, they are virtually identical: the constant terms in (8), (10), etc. incur almost no cost.

4.2. Madelung constant of NaCl

It might be argued that, because it is very small and lacks important long-range effects, the hydrogen atom is not a very demanding test of CAP(m). Accordingly, we have next applied CAP(m) to find the Madelung constant (the potential of an ion in the

Table 2
Errors [a] in the Madelung constant of NaCl [b] computed using CAP(m)

m	$\omega = 0.5$	$\omega = 0.4$	$\omega = 0.3$	$\omega = 0.2$	$\omega = 0.1$
0	−0.327689	−0.325013	−0.303278	−0.224731	−0.112838
1/2	0.236501	0.126338	0.035236	0.000944	0.000000
1	−0.066350	0.044884	0.031996	0.000944	0.000000
3/2	−0.051156	−0.038349	−0.000148	0.000753	0.000000
2	0.043585	−0.000494	−0.005272	0.000252	0.000000
5/2	−0.006689	0.010898	0.000139	−0.000004	0.000000
3	−0.012523	−0.004867	0.001190	−0.000037	0.000000
7/2	0.011127	−0.000771	−0.000313	−0.000006	0.000000

[a] CAP(m) − Exact.
[b] Lattice spacing = 5.33 bohr.

field of all others) of NaCl with a lattice spacing of 5.33 au. This represents a much harsher test since the system involved is of infinite size and the property sought includes very long-range contributions. The exact value [16] of the Madelung constant is 0.327873 but it is impossible to determine this by straightforward summation because of the painfully slow convergence of the associated harmonic series. In contrast, due to their short-range character, the CAP(m) approximations give rapidly converging sums. The errors in the resulting estimates are shown in Table 2.

It is clear that the CAP(0) Madelung estimates are poor: as for the hydrogen atom, the error exceeds 100 mh even for $\omega = 0.1$. The errors are markedly smaller, however, for the higher CAP(m) approximations, especially when ω is small. Patterns in these errors are less obvious than in Table 1, principally because the Madelung constant results from large numbers of positive and negative Coulomb interactions that almost cancel.

With only one exception (which is fortuitous), we observe that CAP($m + 1/2$) is superior to CAP(m). Given that these are equally demanding computationally, we are led to conclude (as we did from the hydrogen atom results) that the integer approximations are relatively inefficient and probably less useful than their half-integer counterparts.

5. Concluding remarks

The CAP(m) operators are a well-defined and systematic family of approximations to the Coulomb operator $1/r$. When used in quantum chemical calculations employing a Gaussian basis set, they yield analytically evaluable integrals. Unlike the Coulomb operator, CAP(m) operators are short-range and therefore computationally inexpensive.

In the preliminary studies presented here, we have found the half-integer CAP(m) approximations to be particularly accurate. It appears that the constant terms in (8), (10), etc. are valuable assets that enhance the quality of the approximations more than might have been anticipated. We note, however, that these terms can become liabilities in certain circumstances. Within any of the half-integer approximations, two infinitely separated charged moieties have a non-zero interaction energy: this is obviously non-physical.

It is next of interest to study the effects of the CAP(m) approximations on the chemical properties of a wide range of molecules. We have therefore implemented CAP(m) within the Q-Chem computer program [17] and we will report Coulomb-attenuated HF, HFS and MP2 results in the near future [18].

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