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Chemistry without Coulomb tails

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Abstract

The theoretical model chemistry that results from a molecular Schrödinger equation in which the Coulomb terms are strongly attenuated is investigated for a range of molecules. Little deterioration is found and we propose that this represents a very natural approach to achieving linear cost scaling in quantum chemical calculations.

1. Introduction

In the last few years, interest has been kindled in the existence and implementation of algorithms that can compute the total Coulomb energy of a system of n localized distributions of charge at a computational cost that is only $O(n)$. The availability of such algorithms [1–5] has major consequences for many areas of computational physics but, in particular, it may serve to remove the notorious two-electron bottleneck of quantum chemistry.

The seminal breakthrough was made by Greengard and Rokhlin [1], who constructed an ingenious hierarchical algorithm, the fast multipole method (FMM), that was applicable to large systems of particles interacting through an inverse-square law. In 1994, a generalization of the FMM that is also valid for non-particulate charge distributions was published by White et al. [2]. These authors named their scheme the continuous fast multipole method (CFMM), but it has also latterly been termed the GMM [3] and the GvFMM [4] by other workers. The key feature of the FMM-based approaches is the assignment of the charge distributions to a nested tree-structure of computational boxes. Pairs of distributions that are in adjacent boxes are then treated by short-range techniques while all other pairs are handled using multipole expansions.

Very recently, Dombroski et al. [5] have introduced an alternative to the FMM schemes. The initial step of their KWIK algorithm is to separate the Coulomb operator into two pieces:

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

The first of these is singular but short-range while the second is non-singular but long-range. The parameter ω is chosen to minimize the total computational cost. Although many choices of the separator function are possible, the authors chose the error function and its complement because they yield both a very rapidly decaying short-range component and an exceptionally smooth long-range component (Fig. 1). The former minimizes the number of short-range interactions that must be considered while the latter facilitates an efficient Ewald-like treatment of the long-range interactions in Fourier space. We will refer to the long-range component $\mathrm{erf}(\omega r)/r$ as 'the background'.

Both the FMM and KWIK techniques achieve highly efficient solutions to the Coulomb problem by

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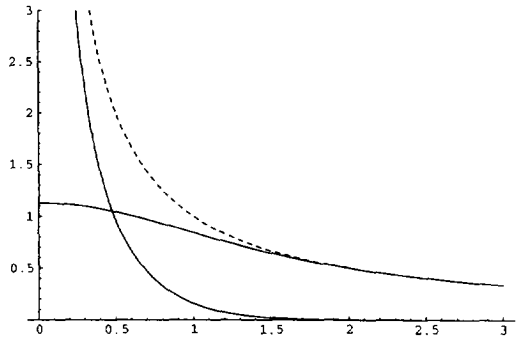

Fig. 1. Graphs of $1/r$ (dashed), $\mathrm{erfc}(r)/r$ and $\mathrm{erf}(r)/r$ illustrating Eq. (1) for $\omega = 1$. Note the rapid decay of $\mathrm{erfc}(r)/r$ and the smoothness of $\mathrm{erf}(r)/r$.

splitting the $1/r$ operator into short- and long-range parts. One may ask, however, whether both of these parts are then comparably important in determining chemical behavior. Specifically, since the background is extremely smooth, i.e. lacks high-frequency components, it is not unreasonable to hypothesize that it may be much less important than the short-range component and may, perhaps, be amenable to an approximate treatment.

In this Letter, we take this idea to its logical conclusion and explore the consequences of *completely neglecting* the background. This proposal is not as preposterous physically as it may appear mathematically. In fact, it is a constructive response to Bader's plea [6] that theoreticians should strive to introduce atoms and functional groups into ab initio calculations. It could also be viewed as a quantitative test of the short-sightedness of electrons [7].

2. A Coulomb-attenuated Hamiltonian

The Schrödinger equation $\hat{\mathbf{H}}\Psi = E\Psi$ for a molecule with M nuclei and N electrons involves the Hamiltonian operator

$$\hat{\mathbf{H}} = \sum_{i=1}^{N} \frac{-\nabla_i^2}{2} + \sum_{i=1}^{N} \sum_{j>i}^{N} f(r_{ij}) - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A f(r_{iA}) + \sum_{A=1}^{M} \sum_{B>A}^{M} Z_A Z_B f(r_{AB}), \tag{2}$$

and is found to be an extremely satisfactory foundation for quantum chemical calculations. The first term corresponds to the kinetic energy while the others represent the electron–electron, nuclear–electron and nuclear–nuclear energies, respectively. The interparticle energy function is traditionally given by the Coulomb form $f(r) = 1/r$.

Consider now the Coulomb-attenuated Schrödinger equation (CASE) defined by Eq. (2) but with the interparticle operator modified to exclude the background, i.e. $f(r) = \mathrm{erfc}(\omega r)/r$. At first glance, one might guess that the CASE could apply in a universe in which the Coulomb interaction decays very rapidly but would be totally inadequate elsewhere. After more careful reflection, however, that conclusion seems too hasty. Although it is not at all apparent from the Schrödinger equation itself, it is well known to theoreticians and non-theoreticians alike that molecules are essentially non-polar except on small distance scales and we ought therefore to expect that the attractive (nuclear–electron) and repulsive (electron–electron + nuclear–nuclear) Coulomb interactions between widely separated regions of a large molecule will approximately cancel. As Clementi has remarked [8], "the electrons on the nose of Professor Karplus do not interact with the electrons on the nose of Professor Eyring"...!

Of course, the CASE could also be employed as a zeroth-order approximation on which higher-order theories are constructed and we will pursue this possibility further elsewhere [9]. We should begin, however, by establishing the strengths and weaknesses of the CASE in its own right and this is the focus of the present work.

3. The hydrogen atom

Whenever introducing a new approximation, it is valuable to examine its performance on a simple model system. We have begun by solving the CASE of the H atom 1s state, viz.

$$\frac{1}{2}\frac{\mathrm{d}^2\Psi}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}\Psi}{\mathrm{d}r} + \frac{\mathrm{erfc}(\omega r)}{r}\Psi + E\Psi = 0. \tag{3}$$

At $\omega = 0$, the CASE becomes the traditional Schrödinger equation and we have $E_0^{1s} = -1/2$ and

$\Psi_0^{1s}(r) = \pi^{-1/2}\exp(-r)$. As ω increases, the attractive nuclear–electron potential rapidly attenuates and one would expect the energy E^{1s} to rise. The effect of ω on the wavefunction $\Psi^{1s}(r)$, however, is much less clear intuitively and we have found that first-order perturbation theory provides a convenient framework in which to investigate this quantitatively.

If we expand the CASE energy and wavefunction as

$$E^{1s} = E_0^{1s} + E_1^{1s} + E_2^{1s} + \cdots, \tag{4}$$

$$\Psi^{1s} = \Psi_0^{1s} + \Psi_1^{1s} + \Psi_2^{1s} + \cdots, \tag{5}$$

$$\Psi_1^{1s} = c_2\Psi_0^{2s} + c_3\Psi_0^{3s} + c_4\Psi_0^{4s} + \cdots, \tag{6}$$

where Ψ_0^{2s}, Ψ_0^{3s}, Ψ_0^{4s}, $\cdots$ are $\omega = 0$ excited-state wavefunctions, then the first-order correction to the energy is simply the expectation value of the background

$$\begin{aligned} E_1^{1s} &\approx \int \Psi_0^{1s}\hat{V}\Psi_0^{1s} \\ &= \int_0^\infty 4r^2\exp(-r)\frac{\mathrm{erf}(\omega r)}{r}\exp(-r)\mathrm{d}r \\ &= \frac{2}{\omega\sqrt{\pi}} + (1-2\omega^{-2})\exp(\omega^{-2})\mathrm{erfc}(\omega^{-1}), \end{aligned} \tag{7}$$

and the coefficients of the first-order correction to the wavefunction are given by

$$c_k = \frac{\int \Psi_0^{1s}V\Psi_0^{ks}}{E_0^{1s} - E_0^{ks}}. \tag{8}$$

The first-order energy $E_0^{1s} + E_1^{1s}$, and the exact energy E^{1s} obtained using Mathematica [10] to solve Eq. (3) numerically, are listed for various ω values in Table 1 and both confirm that E^{1s} rises linearly with ω. More interesting, however, is the astonishingly close agreement between the exact and first-order energies which suggests that, at least for fairly small ω values, Ψ_0^{1s} is an excellent approximation to Ψ^{1s}. This inference is supported by the small c_2 and c_3 values in Table 1 which indicate that the first-order correction to the wavefunction is almost negligible.

What can be learned from this very simple example of Coulomb attenuation? As Fig. 1 shows, the replacement of $1/r$ by $\mathrm{erfc}(\omega r)/r$ is a gross perturbation to the Schrödinger equation and might have been expected, a priori, to give rise to a radically altered mathematical model of chemistry. The truth, however, is much more subtle and interesting. While it is well known that a variational calculation will generally extract a good energy from a poor wavefunction, we observe the apparent converse, for the results in Table 1 show that Coulomb attenuation leads to poor energies and good wavefunctions. The resolution of this paradox lies in recognizing that, by virtue of its smoothness, the background is likely to have a very small effect on the wavefunction while, by virtue of its integrated magnitude, it is certain to have a large effect on the energy.

Is an approximation that has no effect on the wavefunction but a significant effect on the energy useful? If a wavefunction is the main goal of a calculation, the answer is affirmative. If a *total* energy is sought, the answer is negative. Nevertheless, if the goal of a calculation is a *relative* energy, it is not clear whether or not the background will have a substantial effect. It is conceivable that, by systematic cancellation, relative energies could be largely unaffected by the background and we investigate this possibility in the next Section.

Table 1
Results of first-order perturbation theory for the 1s state of the CASE hydrogen atom

ω	E^{1s}	$E_0^{1s} + E_1^{1s}$	c_2	c_3
0	−0.500000	−0.500000	0	0
0.001	−0.498872	−0.498872	3×10^{-9}	1×10^{-9}
0.01	−0.488717	−0.488717	3×10^{-6}	1×10^{-6}
0.1	−0.388270	−0.388266	3×10^{-3}	1×10^{-3}
0.2	−0.282838	−0.282631	2×10^{-2}	6×10^{-3}
0.5	−0.051071	−0.031011	1×10^{-1}	5×10^{-2}

4. Molecular results

All calculations were performed using the Q-Chem quantum chemistry program [11] and calculating any needed integrals over the $\mathrm{erfc}(\omega r)/r$ operator using the PRISM algorithm and related recent advances [12]. In the light of the Table 1 results, we chose $\omega = 1/10\ a_0^{-1}$.

To begin our study of CASE chemistry, we examined the effect of Coulomb attenuation on the molecular orbitals of the H_2O molecule at its MP2/6-31G* geometry. We performed HF/6-31G* calculations using $\omega = 0$ and $\omega = 1/10$ and obtained total energies of -76.00981 and -71.72696, respectively, a huge difference of more than 4 E_h. The corresponding MO energies, together with those from an LSDA/6-31G* (density functional) calculation, are shown in Fig. 2. Coulomb attenuation raises the occupied energies but has almost no effect on the others. The MO coefficients of the highest-occupied (HOMO) and lowest-unoccupied (LUMO) molecular orbitals are listed in Table 2 and typify the changes found for the occupied and unoccupied manifolds, respectively. It is clear that, despite its strong effect on the orbital energies, Coulomb attenuation at this level has a negligible effect on the orbitals themselves. We reiterate that this result is a consequence of the smoothness of the background.

Although molecular wavefunctions are very insensitive to Coulomb attenuation, it is by no means clear that chemical energetics will be similarly unaffected. Indeed, given the very large effects on total energy observed above for the hydrogen atom and water molecule, it might seem unlikely that bond dissociation energies, for example, could be reproduced well. In order to examine this question, we scanned the UHF/6-31G** potential curve of H_2 using both $\omega = 0$ and $\omega = 1/10$. The total energies obtained are listed in Table 3. Despite the fact that the $\omega = 1/10$ energies are 224 mE_h higher than their $\omega = 0$ counterparts, this difference is so constant over a wide range of bond distances that the spectroscopic parameters remain almost constant. Specifically, r_e increases from 0.7326 to 0.7338 Å, D_e falls from 354.1 to 353.5 kJ mol^{-1} and ν_e falls from 4635 to 4616 cm^{-1}. We ascribe this constancy

Table 2
MO coefficients and energies for the HOMO and LUMO of H_2O using HF/6-31G*

	HOMO (B_1)		LUMO (A_1)	
	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$
O (1s)	0	0	0.10002	0.09992
O (2s)	0	0	−0.05859	−0.05873
O ($2p_x$)	0	0	0	0
O ($2p_y$)	0.63998	0.63962	0	0
O ($2p_z$)	0	0	−0.22243	−0.22247
O (3s)	0	0	−1.38818	−1.38718
O ($3p_x$)	0	0	0	0
O ($3p_y$)	0.51110	0.51148	0	0
O ($3p_z$)	0	0	−0.51217	−0.51233
O ($3d_{xx}$)	0	0	0.05532	0.05519
O ($3d_{xy}$)	0	0	0	0
O ($3d_{yy}$)	0	0	0.07027	0.07016
O ($3d_{xz}$)	0	0	0	0
O ($3d_{yz}$)	0.03347	0.03334	0	0
O ($3d_{zz}$)	0	0	0.04191	0.04180
H_1 (1s)	0	0	0.05745	0.05744
H_1 (2s)	0	0	1.03009	1.02992
H_2 (1s)	0	0	0.05745	0.05744
H_2 (2s)	0	0	1.03009	1.02992
MO energy	−0.49736	−0.38174	+0.20821	+0.21353

to the inertness of the background, which seems blessed here with almost no bonding significance whatever.

In view of the discovery that Coulomb attenuation has an encouragingly small impact on the bonding in the prototypical H_2 molecule, it is reasonable to enquire whether or not this is also true of molecules with more complicated electronic structures. In order to investigate this, we calculated the HF/6-31G* atomization energies of 32 molecules using $\omega = 0$ and $\omega = 1/10$. The first five columns of Table 4 summarize our results. Zero-point vibrational corrections are not included. Once again, we observe that Coulomb attenuation gives rise to gross changes in total energies but almost imperceptible movement in relative (atomization) energies which are typically altered by 0–3 kJ mol^{-1}. The largest atomization error found is 6.4 kJ mol^{-1} for LiF. This ionic species is highly polar but the attenuated calculation fails to capture the full extent of the associated Coulombic stabilization and the atomization energy is underestimated as a result.

We have found that HF total energies are systematically underestimated by the CASE. The curious reader may be wondering (as we did) if it is possible to obtain useful *correlation* energies by developing CASE-based post-HF methods. The simplest such method yields the second-order Møller–Plesset perturbation (MP2) energy

$$E^{(2)} = \frac{1}{4} \sum_{abrs} \frac{\left| \left\langle \Psi_0 \left| \sum_{i<j} r_{ij}^{-1} \right| \Psi_{ab}^{rs} \right\rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}, \tag{9}$$

where we have used the notation of Szabo and Ostlund [13]. To investigate the effect of Coulomb attenuation on the numerators (which are antisymmetrized two-electron integrals), we have used the orbital energies from an $\omega = 0$ Hartree–Fock calculation. We have computed the MP2/6-31G* correlation energy for each of the 32 molecules studied earlier, both with and without Coulomb attenuation, and summarize the results in the last two columns of Table 4. An antisymmetrized integral is the *difference* between two integrals and the errors in the latter appear to cancel very well. The Coulomb-attenuated correlation energies are systematically lower

Table 3
UHF/6-31G** energies (E_h) of H_2 as a function of bond length R (Å)

R	$E(R)$		$E(R) - E(\infty)$	
	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$
0.4	−0.93620	−0.71184	+0.06027	+0.06107
0.5	−1.06148	−0.83730	−0.06502	−0.06439
0.6	−1.11393	−0.88993	−0.11747	−0.11702
0.7	−1.13050	−0.90667	−0.13403	−0.13376
0.8	−1.12843	−0.90479	−0.13197	−0.13188
0.9	−1.11652	−0.89305	−0.12005	−0.12014
1.0	−1.09947	−0.87619	−0.10301	−0.10329
1.1	−1.07994	−0.85685	−0.08348	−0.08394
1.2	−1.05940	−0.83649	−0.06293	−0.06359
1.3	−1.04147	−0.81847	−0.04501	−0.04556
1.4	−1.02864	−0.80553	−0.03217	−0.03262
1.5	−1.01950	−0.79631	−0.02303	−0.02340
1.6	−1.01299	−0.78974	−0.01653	−0.01683
1.7	−1.00836	−0.78505	−0.01189	−0.01214
1.8	−1.00505	−0.78169	−0.00858	−0.00878
1.9	−1.00267	−0.77928	−0.00621	−0.00637
2.0	−1.00097	−0.77754	−0.00450	−0.00464
∞	−0.99647	−0.77291	−0.00000	−0.00000

Table 4
HF/6-31G* total energies (E_h), HF/6-31G* atomization energies (kJ/mol) and MP2/6-31G* correlation energies (mE_h) of various molecules

Molecule	Total energy $\omega = 0$		Atomization energy		Correlation energy	
	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$
H_2	−1.12679	−0.90305	342.2	341.7	−17.4	−17.3
H_2CCH_2	−78.03107	−72.85255	1775.9	1776.1	−263.2	−261.7
H_2CO	−113.86372	−107.21602	1056.7	1058.9	−311.2	−309.9
H_2NNH_2	−111.16800	−104.40912	1061.2	1062.4	−336.4	−335.2
H_3CCH_3	−79.22854	−73.82606	2303.7	2302.8	−275.4	−274.0
H_3COH	−115.03419	−108.16217	1513.5	1513.7	−319.1	−318.0
HCCH	−76.81560	−71.86094	1200.9	1201.9	−260.6	−258.9
HCN	−92.87019	−87.23785	802.5	805.9	−296.8	−295.0
HCO	−113.24518	−106.70926	740.8	743.0	−295.2	−293.9
HOOH	−150.76012	−142.41897	514.0	516.4	−374.8	−373.7
Li_2	−14.86689	−13.52642	10.9	13.6	−20.0	−18.3
LiF	−106.93418	−101.18581	361.9	355.4	−195.3	−194.9
LiH	−7.98087	−7.19726	134.6	131.7	−15.6	−15.4
BeH	−15.14731	−13.91139	215.6	211.2	−24.1	−23.9
CH	−38.26485	−35.78739	225.1	225.3	−77.6	−77.2
CH_2 ($^1A_1$)	−38.87219	−36.28291	511.6	511.7	−101.8	−101.4
CH_2 ($^3B_1$)	−38.92142	−36.33159	640.9	639.5	−86.0	−85.7
CH_3	−39.55892	−36.85718	1006.5	1004.8	−114.1	−113.6
CH_4	−40.19507	−37.38157	1368.6	1366.9	−142.0	−141.3
CN	−92.17398	−86.65255	282.7	283.8	−220.8	−219.7
CO	−112.73448	−106.31014	708.1	709.7	−293.7	−292.4
CO_2	−187.62841	−177.14614	996.9	1002.0	−490.0	−487.9
N_2	−108.93540	−102.62432	431.9	434.9	−326.2	−324.4
NH	−54.95924	−51.69139	198.4	198.5	−102.2	−101.9
NH_2	−55.55731	−52.17765	460.5	460.5	−136.4	−136.0
NH_3	−56.18384	−52.69221	797.4	796.9	−173.5	−173.0
NO	−129.24730	−122.03288	204.6	207.0	−317.2	−315.9
O_2	−149.60681	−141.48969	102.3	105.8	−347.5	−346.2
OH	−75.38186	−71.21088	261.7	261.8	−141.3	−141.0
OH_2	−76.00981	−71.72696	602.3	602.2	−189.4	−189.0
F_2	−198.67283	−188.52364	−149.9	−146.9	−366.0	−365.1
FH	−100.00229	−94.81532	365.2	365.1	−181.9	−181.5

Table 5
UHF/6-31G* total energies (E_h) and ionization energies (eV)

Atom	Total energy (atom)		Total energy (cation)		Ionization energy		
	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$	$\omega = 0$	$\omega = 0.1$	Δ
H	−0.49823	−0.38645	−0.00000	−0.00000	13.56	10.52	3.04
He	−2.85516	−2.51752	−1.99362	−1.76853	23.44	20.38	3.06
Li	−7.43137	−6.76063	−7.23554	−6.67201	5.33	2.41	2.92
Be	−14.56694	−13.44452	−14.27552	−13.26483	7.93	4.89	3.04
B	−24.52204	−22.83410	−24.23406	−22.66026	7.84	4.73	3.11
C	−37.68086	−35.31512	−37.28708	−35.03592	10.72	7.60	3.12
N	−54.38544	−51.22933	−53.87220	−50.83083	13.97	10.84	3.12
O	−74.78393	−70.72469	−74.34264	−70.39817	12.01	8.89	3.12
F	−99.36496	−94.28980	−98.79206	−93.83177	15.59	12.46	3.13
Ne	−128.47441	−122.27059	−127.75171	−121.66270	19.67	16.54	3.12

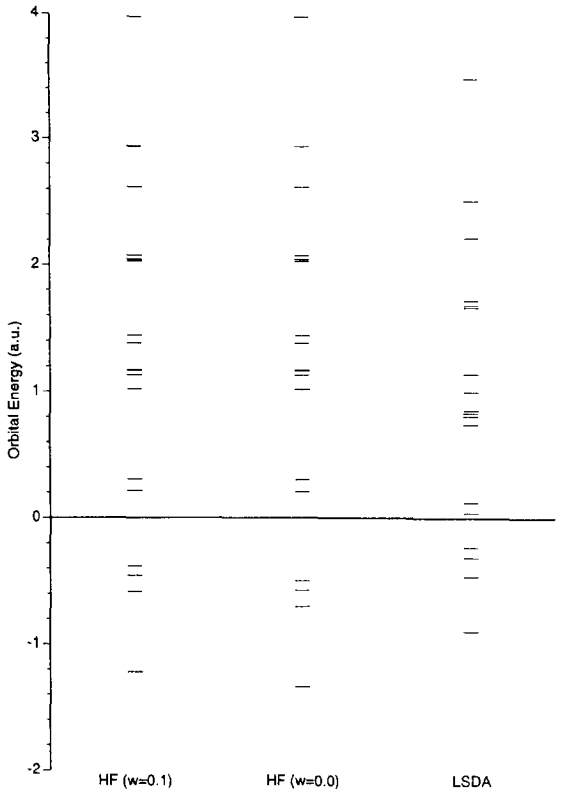

Fig. 2. Molecular orbital energies for H_2O using Coulomb-attenuated HF/6-31G*, traditional HF/6-31G* and traditional LSDA/6-31G*. (Core MO not shown.)

than the traditional values but the differences are slight in all cases. We infer from these results that the lifeless background seems to be unimportant for correlation energies.

Lest we leave the wrong impression, we hasten to point out that there *are* simple chemical problems in which the background plays an important role and Coulomb attenuation performs poorly. For example, the UHF/6-31G* atomic ionization energies listed in Table 5 are reduced markedly by Coulomb attenuation. Why is the background significant for ionization but not atomization energies? The explanation lies in the fact that, unlike the atomization $AB \rightarrow A + B$, the ionization $A \rightarrow A^+$ does not conserve particles – an electron is lost from the system – and, consequently, the expectation value of the background for A is very different from that for A^+. It is possible to predict theoretically [9] that this difference is 3.07 eV and this is obviously in good agreement with the differences observed in Table 5.

5. Concluding remarks

This Letter is a preliminary report and we have explored our new approach on only a few small systems. From the results obtained, we conclude that Coulomb attenuation:

1. Has a large effect on total energies;
2. Has a small effect on correlation energies;
3. Has a small effect on the relative energies (ionization energies are an exception);
4. Has a very small effect on molecular wavefunctions;
5. Yields a remarkably simple route to quantum chemical methods whose cost is $O(n)$.

It will be interesting to determine the extent to which the Coulomb and exchange-correlation holes are affected by attenuating the Coulomb operator. We also feel that Coulomb attenuation may offer a route to inexpensive correlation treatments and we are investigating extensions in which the background is treated as a correction, rather than being neglected completely [9].

That *wavefunctions are little affected by Coulomb attenuation* is a key result of this Letter and derives from the impressive blandness of the excluded background term $\mathrm{erf}(\omega r)/r$. This is significant, both conceptually and computationally, for it affirms the chemist's first article of faith – that the behaviour of an atom within a molecule is governed principally by its immediate vicinity – and then exploits it by facilitating the construction of new ab initio theories based on an entirely short-range molecular Hamiltonian.

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References

[1] L. Greengard and V. Rokhlin, J. Comput. Phys. 73 (1987) 325.
[2] C.A. White, B.G. Johnson, P.M.W. Gill and M. Head-Gordon, Chem. Phys. Letters 230 (1994) 8.
[3] R. Kutteh, E. Aprà and J. Nichols, Chem. Phys. Letters 238 (1995) 173.
[4] M.C. Strain, G.E. Scuseria and M.J. Frisch, Science, 271 (1996) 51.
[5] J.P. Dombroski, S.W. Taylor and P.M.W. Gill, J. Phys. Chem. in press.
[6] R.F.W. Bader, Chem. Rev. 91 (1991) 893.
[7] W. Kohn, Chem. Phys. Letters 208 (1993) 167.
[8] E. Clementi, in Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research, XVI, Theoretical Chemistry, Houston, 1972.
[9] J.P. Dombroski, R.D. Adamson and P.M.W. Gill, in preparation.
[10] S. Wolfram et al., Mathematica (Wolfram Research Inc., 1988).
[11] B.G. Johnson, P.M.W. Gill, M. Head-Gordon, C.A. White, D.R. Maurice, R.D. Adamson, T.R. Adams and M. Oumi, Q-Chem (Q-Chem Inc., Pittsburgh, PA, 1995).
[12] P.M.W. Gill, Advan. Quantum Chem. 25 (1994) 141; T.R. Adams, R.D. Adamson and P.M.W. Gill, J. Chem. Phys. in preparation.
[13] A. Szabo and N.S. Ostlund, Modern quantum chemistry: introduction to advanced electronic structure theory (McGraw-Hill, New York, 1989).