Theor Chem Acc (1997) 97:232–239

Theoretical
Chemistry Accounts

Effective dynamic correlation in multiconfigurational wave-function calculations on atoms and molecules

Itai Panas, Anders Snis

Department of Inorganic Chemistry, Goteborg University, S-412 96 Goteborg, Sweden

Received: 26 November 1996 / Accepted: 21 April 1997

Abstract. An intuitive understanding of dynamic correlation in terms of a regularized electron repulsion expression is outlined. Expressions for cusp kinetic energy corrected regularized electron repulsion integrals are deduced and implemented in a multiconfigurational wave-function framework. A regularized complete active space self-consistent field (reg-CASSCF) technique is suggested and tested on atomic total energies, molecular structures and binding energies.

Key words: Effective dynamic correlation – Multiconfigurational wave-function calculations – Atoms – Molecules

1 Introduction

The procedure to obtain the correct electronic wave function for molecular systems is contained in the ab initio quantum chemistry formulations of quantum mechanics. The existence of such efficient computational tools is invaluable as intuitive effective understanding can be tested for consistency against Dirac's quantum mechanics machine [1]. The drawback of the ab initio approach is the well-known slow convergence of the wave-function description, which originates from the two singular preconditions to take the electrostatic Green's function for the electron-electron interaction, and to insist on an explicit independent fermion basis. It becomes the task of the wave function alone to describe the detailed correlation between electrons, which is necessary (1) to avoid the $r_{12} = 0$ singularity, and (2) to fulfil the Pauli exclusion principle. Fortunately, although the latter is correct and proper, in many cases accurate wave functions are not the central issue. Modern density functional theory (DFT) is the quintessence of this understanding. In the Kohn-Sham formulation of DFT [2], complex properties of the wave function are absorbed in an effective density-dependent functional, the existence of which is the subject of the Hohenberg-Kohn theorem [3]. Thus, the probability density corresponding to an independent particle wave function is shown to contain sufficient information to describe the ground state of a many-electron system.

The impressive performance of DFT has been demonstrated for a number of exchange-correlation functionals and has made a significant lasting impact on computational chemistry in expanding the domain of systems that can be addressed by means of theory. Maybe the single most important contribution was the Becke gradient correction to the Slater exchange functional [4, 5]. Nevertheless, the class of problems that address properties other than the ground state, i.e. electron spectroscopy and bond-breaking regions on potential energy surfaces, remain outside the programme of molecular DFT. It may be argued that a working strategy to provide such reliable functionals is lacking within the Kohn-Sham formulation.

It is natural to seek forms that describe non-local correlation explicitly, and treat dynamic correlation effectively. Thus, the purpose of the present paper is threefold. It aims to: (1) present the flow of ideas that point to certain simple mathematical and physical structures to describe the so-called Coulomb hole, (2) discuss some particular formulations, and (3) test their performance in single- and multi-configurational calculations on atoms and molecules.

An intuitive basis for the possible existence of a simple regularized electron repulsion description of the Coulomb hole is provided below. It comprises the background to a recently suggested regularized Hartee-Fock (HF) scheme [6]. Being closely related to the understandings of Wigner [7], it bears a great resemblance to the Coulomb hole approach of Clementi et al. [8–11], and the MGVB approach of Goodgame and Goddard [12]. A major source of inspiration to our effort has been the approximate separability of static and dynamic correlations, demonstrated in the performance of the CAS-PT2 method [13].

---

e-mail: itai.panas@inoc.chalmers.se
Correspondence to: I. Panas

2 Method

The particular mathematical form for removing the singular behaviour of the Coulomb interaction is understood to benefit from structural similarities between the Gaussian electron repulsion integrals and the Ewald expression [14] for Coulomb interactions on a lattice [15]

$$\sum_{\mathbf{i}} \frac{1}{r_{oi}} = C + \sum_{\mathbf{k}} \frac{1}{k^2} \exp\left[-\frac{k^2}{4x^2} + i\mathbf{k} \cdot \mathbf{r}_o\right] + \sum_{\mathbf{i}} \left\{\frac{1}{r_{oi}} - \frac{2}{\sqrt{\pi}} \int_0^x \exp\left[-s^2 r_{oi}^2\right] \mathrm{d}s\right\}. \tag{1}$$

This expression is compared with the basic structure of the Gaussian [ss|ss] integral

$$\int\int \frac{\exp(-\kappa \cdot r_{P1}^2)\ \exp(-\xi \cdot r_{Q2}^2)}{r_{12}} \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \propto \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{k^2} \exp\left[-\frac{k^2}{4}\left\{\frac{1}{\kappa} + \frac{1}{\xi}\right\} + i\mathbf{k} \cdot \mathbf{R}_{PQ}\right] \mathrm{d}k_x\, \mathrm{d}k_y\, \mathrm{d}k_z. \tag{2}$$

The straightforward interpretation of the right-hand side of Eq. (2) would be to imply cancellation in Eq.(1) of the direct-space summation, as it would represent self-interaction. An extension of this understanding suggests that the Coulomb hole is an additional damping factor in Eq. (2), i.e. $\{\frac{1}{\kappa} + \frac{1}{\xi}\} \rightarrow \{\frac{1}{\kappa} + \frac{1}{\xi} + \frac{1}{\chi^2}\}$, as the hole implies omission of "self-interaction" in a third "void". It is suggested that the interpretation of this third void to describe the effect of a Coulomb hole is precisely what the present paper sets out to investigate.

The structural understanding of Eq. (1) implies obtaining the resulting interaction by truncation of the equivalent expressions

$$\frac{1}{r_{12}} = \lim_{\chi\rightarrow\infty} \frac{1}{2\pi^2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{k^2} \exp\left[-\frac{k^2}{4\chi^2} + i\mathbf{k} \cdot \mathbf{r}_{12}\right] \mathrm{d}k_x\, \mathrm{d}k_y\, \mathrm{d}k_z \tag{3}$$

and

$$\frac{1}{r_{12}} = \lim_{\chi\rightarrow\infty} \frac{2}{\sqrt{\pi}} \int_0^{\chi} \exp\left[-s^2 r_{12}^2\right] \mathrm{d}s. \tag{4}$$

An effective separation between local and non-local correlation is sought in Sect. 2.1, where the role of the truncated integral representation of r_{12}^{-1} will also be formulated. In Sect. 2.2 it is shown how an electron repulsion integral (ERI) is modified by introducing the cut-off χ. An expression for χ in terms of primitive Gaussian basis function exponents is arrived at in Sect. 2.3. Interpretation of the cut-off in terms of a maximum reciprocal length, and analogy to the indeterminacy principle are made in Sect. 2.4. Finally, a cusp kinetic energy interpretation of the Coulomb singularity is deduced in Sect. 2.5, and employed to produce a parametrized electron-electron cusp kinetic energy augmented Coulomb hole description. Implementation is also discussed in this section.

2.1 Separation of local and non-local correlation

Guided by Becke's discussion [16] on the exact electron-electron interaction contributions to the total energy of a molecule in terms of the two-particle density matrix $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$, we write

$$V_{ee}[\rho] = \int\int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{5}$$

and

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\ [1 + h(\mathbf{r}_1, \mathbf{r}_2)]. \tag{6}$$

It becomes formally necessary for the pair-correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$ to produce the non-local exchange interaction, introduced in order that the wave function of N-independent electrons satisfies Fermi-Dirac statistics. There is also the need for a correlation hole description to mimic the correlated motions of electrons, as such dynamics cannot be displayed in an independent electron wave function description. The simplest way to satisfy these two physical requirements for electron correlation is to assume they factorize. Thus, we formally rewrite Eq. (6) as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\ (1 + h^x(\mathbf{r}_1, \mathbf{r}_2))\ (1 + h^c(\mathbf{r}_1 - \mathbf{r}_2)). \tag{7}$$

A special case is presented here and in [6]. As the particularly simple correlation hole expression

$$h^c(\mathbf{r}_1 - \mathbf{r}_2) = -\frac{2r_{12}}{\sqrt{\pi}} \int_{\chi}^{\infty} \exp\left[-s^2 r_{12}^2\right] \mathrm{d}s \tag{8}$$

is explored, it produces

$$1 + h^c(\mathbf{r}_1 - \mathbf{r}_2) = r_{12}\left\{\frac{1}{r_{12}} - \frac{2}{\sqrt{\pi}} \int_{\chi}^{\infty} \exp\left[-s^2 r_{12}^2\right] \mathrm{d}s\right\} \tag{9}$$

or equivalently

$$1 + h^c(\mathbf{r}_1 - \mathbf{r}_2) = \frac{2r_{12}}{\sqrt{\pi}} \int_0^{\chi} \exp\left[-s^2 r_{12}^2\right] \mathrm{d}s. \tag{10}$$

Equation (10) forces the reduced two-particle density matrix to take the form

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\ (1 + h^x(\mathbf{r}_1, \mathbf{r}_2))\, r_{12} G(\chi; r_{12}) \tag{11}$$

where

$$G(\chi; r_{12}) = \frac{2}{\sqrt{\pi}} \int_0^{\chi} \exp[-s^2 r_{12}^2]\, \mathrm{d}s. \tag{12}$$

We obtain the sought expression

$$V_{ee}[\rho] = \frac{1}{2}\int\int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)(1 + h^x(\mathbf{r}_1, \mathbf{r}_2))G(\chi; r_{12})\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2. \tag{13}$$

The main achievement above is to make Eq. (13) take the same form as Eq. (5) and Eq. (6), i.e. h^x is kept explicit and local correlation is treated effectively. This is a necessary prerequisite for incorporation of the Coulomb hole in an ab initio framework. It is clear that χ must display a complicated density dependence. Below, it is suggested that an expansion of the two-particle density matrix in a product of four Gaussians simplifies the functional form of χ.

2.2 Solving for the $[ss|ss]$ ERI

An expression for the χ dependence of a general $[s_\alpha s_\beta|s_\gamma s_\delta]$ integral is sought. We replace the Coulomb-Green's function by

$$G_o(|\mathbf{r}_1-\mathbf{r}_2|;\chi)=\frac{2}{\sqrt{\pi}}\int_0^{\chi}\exp\left(-s^2r_{12}^2\right)\mathrm{d}s$$
$$=\frac{1}{\sqrt{\pi}}\int_0^{\chi^2}\exp\left(-tr_{12}^2\right)\frac{\mathrm{d}t}{\sqrt{t}}. \tag{14}$$

This produces (see, e.g. [17])

$$\text{reg-ERI}=K_{\alpha\beta}K_{\gamma\delta}\,\pi^{5/2}(\kappa+\xi)^{-3/2}$$
$$\times\int_0^{\chi^2}\frac{\exp[-ctR_{PQ}^2/(c+t)]}{(c+t)^{3/2}\sqrt{t}}\,\mathrm{d}t \tag{15}$$

where

$$K_{\alpha\beta}=\exp\left[-\frac{\alpha\beta}{\alpha+\beta}|\mathbf{r}_A-\mathbf{r}_B|^2\right];\ \kappa=\alpha+\beta;\ \xi=\gamma+\delta,$$
$$c=\frac{\kappa\cdot\xi}{\kappa+\xi}.$$

Substituting

$$s^2=\frac{t}{c+t}\Rightarrow 2s\mathrm{d}s=\frac{c}{(c+t)^2}\mathrm{d}t\Rightarrow\frac{2}{c}\,\mathrm{d}s=\frac{\mathrm{d}t}{\sqrt{t}(c+t)^{3/2}}$$

and writing $\theta=\dfrac{\chi}{(c+\chi^2)^{1/2}}$,
we obtain

$$\text{reg-ERI}=2K_{\alpha\beta}\ K_{\gamma\delta}\frac{\pi^{5/2}}{(\kappa\cdot\xi)^{3/2}}\ \sqrt{c}\int_0^{\theta}\exp\left[-cR_{PQ}^2s^2\right]\mathrm{d}s. \tag{16}$$

By writing

$$\tau=c\theta^2=\frac{1}{\frac{1}{c}+\frac{1}{\chi^2}}=\frac{1}{\frac{1}{\kappa}+\frac{1}{\xi}+\frac{1}{\chi^2}}, \tag{17}$$

the sought expression becomes

$$\text{reg-ERI}=2K_{\alpha\beta}K_{\gamma\delta}\frac{\pi^{5/2}}{(\kappa\cdot\xi)^{3/2}}\ \sqrt{\tau}\int_0^1\exp[-\tau R_{PQ}^2u^2]\,\mathrm{d}u \tag{18}$$

or equivalently

$$\text{reg-ERI}=2K_{\alpha\beta}K_{\gamma\delta}\frac{\pi^{5/2}}{(\kappa\cdot\xi)^{3/2}}\sqrt{\tau}\ F_o\left(\tau R_{PQ}^2\right). \tag{19}$$

It is noted that $\chi\to\infty$ restores the untampered ERI.

2.3 An expression for the cut-off χ

In order to obtain an expression for χ, we assume that correlation is the reduction of repulsion at short interelectronic distances. Thus, if an independent fermion wave function is assumed, penalty owing to penetration of one electron into the region of another electron should be damped. We write the$[ss|ss]$ integral in the form

$$\frac{2\chi}{\sqrt{\pi}}\int_0^1\iint\exp\left[-\xi r_{1P}^2-\kappa s^2r_{12}^2\right]\exp\left[-\varepsilon s^2r_{12}^2\right]$$
$$\times\exp\left[-\kappa r_{2Q}^2-\xi s^2r_{12}^2\right]\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}s \tag{20}$$

where we have introduced

$$\chi^2=\xi+\kappa+\varepsilon, \tag{21}$$

without any loss of generality. In order to find an expression for ε, Eq. (20) is replaced in [6] by a related expression

$$\frac{2\chi}{\sqrt{\pi}}\int_0^1\int\int\exp\left[-\xi r_{1P}^2-\kappa s^2r_{1Q}^2\right]\exp\left[-\varepsilon s^2R_{PQ}^2\right]$$
$$\times\exp\left[-\kappa r_{2Q}^2-\xi s^2r_{P2}^2\right]\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}s \tag{22}$$

as asymptotic properties of Eq. (21) are explored in order to determine ε. Equation (22) is obtained if each electron is understood to interact with the other, assuming one to be pinned at its Guassian product centre of gravity, i.e. the point $\mathbf{P}(\mathbf{Q})$ for electron 1 1(2) (2). Thus, Eq. (22) becomes

$$\frac{2\chi}{\sqrt{\pi}}\int_0^1\exp\left[-\frac{\xi\kappa s^2}{\xi+\kappa s^2}R_{PQ}^2\right]\times\left(\frac{\pi}{\xi+\kappa s^2}\right)^{\frac{3}{2}}\times\exp\left[-\varepsilon s^2R_{PQ}^2\right]$$
$$\times\exp\left[-\frac{\xi\kappa s^2}{\xi s^2+\kappa}R_{PQ}^2\right]\times\left(\frac{\pi}{\xi s^2+\kappa}\right)^{\frac{3}{2}}\mathrm{d}s. \tag{23}$$

Taking ξ and κ sufficiently small results in

$$2\left(\frac{\varepsilon}{\pi}\right)^{\frac{1}{2}}\int_0^1\left(\frac{\pi}{\xi+\kappa s^2}\right)^{\frac{3}{2}}\times\exp\left[-\varepsilon s^2R_{PQ}^2\right]\times\left(\frac{\pi}{\xi s^2+\kappa}\right)^{\frac{3}{2}}\mathrm{d}s. \tag{24}$$

Large εR_{PQ}^2 makes the exponential in Eq. (24) a steep function of s. We recognize that only the small s contribute and obtain

$$\frac{2\pi^{5/2}}{(\kappa\cdot\xi)^{3/2}}\sqrt{\varepsilon}F_o(\varepsilon R_{PQ}^2). \tag{25}$$

The requirement that Eq. (19) and Eq. (25) should be asymptotically equal produces

$$\varepsilon=\tau \tag{26}$$

which gives

$$\chi^2=\xi+\kappa+\frac{\xi\cdot\kappa}{\xi+\kappa+\frac{\xi\cdot\kappa}{\chi^2}}=\xi+\kappa+\frac{\xi\cdot\kappa}{\chi^2}, \tag{27}$$

i.e.

$$\varepsilon=\frac{\xi\cdot\kappa}{\chi^2} \tag{28}$$

and

$$\chi^2 = \frac{\xi + \kappa}{2} + \sqrt{\left(\frac{\xi + \kappa}{2}\right)^2 + \xi \cdot \kappa} \tag{29}$$

to be introduced into Eq. (28) and subsequently Eq. (19).

2.4 Interpretation of χ

Consider the truncated electrostatic Green's function Eqs. (3, 4). The Gaussian envelope in Eq. (3) ensures that contributions from large $|\mathbf{K}|$-values are damped out. Furthermore, it is immediately obtained from Eq. (4) that $G = 2\chi/\sqrt{\pi}$ in the limit $r_{12} \to 0$. But if $G(|\mathbf{r}_1 - \mathbf{r}_2|; \chi)$ is assumed to mimic a Coulomb hole, then at r_{12} close to zero we expect

$$G_o(|\mathbf{r}_1 - \mathbf{r}_2|; \chi) \approx \frac{1}{r_{12} + \rho(\chi)}. \tag{30}$$

This implies a χ-dependent effective minimum value of r_{12} given by $\rho(\chi) = \sqrt{\pi}/2\chi$. Furthermore, assuming χ^2 to be a given mean square deviation for an "electron-electron momentum" $\langle \Delta k^2 \rangle$ suggests a qualitative understanding of the above regularization in terms of an indeterminacy principle for relative electron positions and moments

$$\rho^2 \langle \Delta k^2 \rangle \approx \frac{\pi}{4\chi^2} \chi^2 > \frac{3}{4} \tag{31}$$

introduced a priori into the effective Green's function.

2.5 Cusp kinetic energy correction

If a correlated wave function is to be assumed, then an explicit account of the cusp kinetic energy has to be given. This has been done in [6], as here, by employing the virial theorem. We note that the electron repulsion contribution to the effective Hamiltonian is obtained by replacing $\frac{1}{r_{12}}$ according to

$$G(|\mathbf{r}_1 - \mathbf{r}_2|, \chi) = \frac{2}{\sqrt{\pi}} \int_0^\chi \exp\left(-s^2 r_{12}^2\right) \mathrm{d}s + \widehat{T}_{\mathrm{cusp}} \;. \tag{32}$$

From the definition of the virial theorem we have

$$\langle \widehat{T} \rangle = -\tfrac{1}{2} \langle \mathbf{r} \cdot \nabla V \rangle \tag{33}$$

and identify

$$\widehat{T}_{\mathrm{cusp}} = -\frac{\mathbf{r}_{12} \cdot \nabla_1}{2} \frac{2}{\sqrt{\pi}} \int_\chi^\infty \exp\left(-s^2 r_{12}^2\right) \mathrm{d}s \tag{34}$$

or equivalently

$$\widehat{T}_{\mathrm{cusp}} = -\frac{\mathbf{r}_{12} \cdot \nabla_1}{2} \left\{ \frac{1}{r_{12}} - \frac{2}{\sqrt{\pi}} \int_0^\chi \exp(-s^2 r_{12}^2) \, \mathrm{d}s \right\}. \tag{35}$$

We note that $\chi \to \infty$ makes the integral in Eq. (32) equal to r_{12}^{-1} and $\widehat{T}_{\mathrm{cusp}}$ in Eq. (35) vanishes. Writing Eq. (35) in a more useful way produces

$$\widehat{T}_{\mathrm{cusp}} = \frac{1}{2r_{12}} + \frac{1}{\sqrt{\pi}} \mathbf{r}_{12} \cdot \nabla_1 \int_0^\chi \exp\left(-s^2 r_{12}^2\right) \mathrm{d}s. \tag{36}$$

We proceed by estimating the modified electron repulsion interaction, in such a way that repeated use of Eq. (32) and Eq. (36) is made in the r_{12}^{-1} terms that are generated by the cusp kinetic energy operator. Summing up the obtained geometric series, we arrive at the expression for a cusp kinetic energy corrected regularized electron repulsion coupling

$$G(|\mathbf{r}_1 - \mathbf{r}_2|, \chi) = \frac{4}{\sqrt{\pi}} \left\{ \int_0^\chi \exp(-s^2 r_{12}^2) \, \mathrm{d}s + \frac{\mathbf{r}_{12} \cdot \nabla_1}{2} \int_0^\chi \exp(-s^2 r_{12}^2) \, \mathrm{d}s \right\} \tag{37}$$

or equivalently

$$G(|\mathbf{r}_1 - \mathbf{r}_2|, \chi) = \frac{2}{\sqrt{\pi}} \left\{ \int_0^\chi \exp(-s^2 r_{12}^2) \, \mathrm{d}s + \chi \exp(-\chi^2 r_{12}^2) \right\}. \tag{38}$$

If the attractive potential V is approximately harmonic, i.e. we have $T \approx V$, then Eq. (38) can be understood to produce a cusp kinetic energy interpretation of the Coulomb singularity, i.e.

$$\left\langle \chi \exp\left(-\chi^2 r_{12}^2\right) \right\rangle \approx \left\langle \int_\chi^\infty \exp\left(-s^2 r_{12}^2\right) \mathrm{d}s. \right\rangle \tag{39}$$

The degree of validity of the approximation in Eq. (39) is seen in Table 1. Semi-quantitative agreement with HF energies is achieved, and it is repeatedly noted that $\chi \to \infty$ gives back $1/r_{12}$. The behaviour of the Green's function in Eq. (37) in a multiconfigurational treatment is left for future investigations and will be presented elsewhere. Here, a description which neglects part of the cusp kinetic energy, and does not change the computational effort is sought. The obvious choice is

$$G_\eta(|\mathbf{r}_1 - \mathbf{r}_2|; \chi) = \frac{4}{\sqrt{\pi}} \left\{ \int_0^\chi \exp(-\eta^2 s^2 r_{12}^2) \, \mathrm{d}s \right\}, \tag{40}$$

which can be written

$$G_\eta(|\mathbf{r}_1 - \mathbf{r}_2|; \chi) = \frac{4}{\sqrt{\pi}} \left\{ \frac{1}{\eta} \int_0^{\eta \cdot \chi} \exp(-s^2 r_{12}^2) \, \mathrm{d}s \right\}. \tag{41}$$

A theme in the regularization approach is to preserve the Coulomb asymptote. This requirement is fulfilled by putting $\eta = 2$, i.e

$$G(|\mathbf{r}_1 - \mathbf{r}_2|; 2 \cdot \chi) = \frac{2}{\sqrt{\pi}} \int_0^{2 \cdot \chi} \exp(-s^2 r_{12}^2) \, \mathrm{d}s. \tag{42}$$

This formulation is also seen to produce the same limiting value ($4\chi\pi^{-1/2}$ for $r_{12} \to 0$) as Eqs. (37) and (38).

In order to find the electron repulsion integrals expressions for Eq. (42) we write

$$G(|\mathbf{r}_1 - \mathbf{r}_2|; f \cdot \chi) = \frac{2}{\sqrt{\pi}} \int_0^{f \cdot \chi} \exp(-s^2 r_{12}^2) \, \mathrm{d}s. \tag{43}$$

Following the same procedure as above, the sought regularized ERI comes out in the form of Eq. (19), but we have

Table 1. Hartree-Fock (*HF*) results are compared with two different cusp kinetic energy-corrected descriptions of the effective Coulomb interaction

{1/2 1/2 1/2} is $\frac{1}{2r_{12}}+\frac{2}{\sqrt{\pi}}\left\{\frac{1}{2}\int \exp\left[-s^2r_{12}^2\right]\mathrm{d}s+\frac{1}{2}\chi \exp\left[-\chi^2\mathrm{r}_{12}^2\right]\right\}$ and {0 1 1} is Eq. (37). I P are ionization potentials

	HF	IP	{1/2 1/2 1/2}	IP	{0 1 1}	IP
H	−0.500	0.500	−0.500	0.500	−0.500	0.50
He	−2.861627	0.862	−2.865819	0.866	−2.870020	0.870
Li	−7.432417	0.196	−7.439188	0.196	−7.445965	0.196
Be	−14.572373	0.296	−14.583756	0.298	−14.595134	0.300
B	−24.527436	0.296	−24.541082	0.295	−24.554745	0.294
C	−37.688520	0.396	−37.702207	0.393	−37.715917	0.390
N	−54.400774	0.513	−54.411329	0.508	−54.421916	0.503
O	−74.811163	0.439	−74.823449	0.440	−74.835774	0.442
F	−99.410071	0.578	−99.421804	0.577	−99.433570	0.576
Ne	−128.545607	0.727	−128.553389	0.723	−128.561185	0.719

$$\tau=\frac{1}{\frac{1}{\kappa}+\frac{1}{\xi}+\frac{1}{(f\cdot\chi)^2}}. \tag{44}$$

Asymptotic considerations produce

$$\tau=f^2\varepsilon \tag{45}$$

and as expected from Eq. (28) we obtain

$$\varepsilon=\frac{\kappa\cdot\xi}{f^2\cdot\chi^2} \tag{46}$$

or equivalently

$$\varepsilon=-\frac{\kappa+\xi}{2}+\sqrt{\left(\frac{\kappa+\xi}{2}\right)^2+\frac{\kappa\cdot\xi}{f^2}} \tag{47}$$

and

$$\chi^2=\frac{\kappa+\xi}{2}+\sqrt{\left(\frac{\kappa+\xi}{2}\right)^2+\frac{\kappa\cdot\xi}{f^2}}. \tag{48}$$

Setting the value for f to 2, in accordance with Eq. (42), produces the sought expression for τ. Note that if f is chosen to be infinity, ε becomes zero and the original expression for the ERIs is recovered.

The fact that ERIs of higher angular moments can be viewed as generated by vertical recurrence relations in terms of linear combinations of derivatives on $[ss|ss]$ type integrals completes the formal discussion [18]. The implementation is straightforward, i.e. $\kappa+\xi$ is replaced by $\kappa+\xi+\varepsilon$ in the kernel of any electron repulsion integrals code that exploits Gaussian basis sets.

3 Results and discussion

The cusp kinetic energy corrected regularized electron repulsion integrals were implemented in the program package MOLCAS [19]. The complete active space self-consistent field (CASSCF) method [20] is employed to describe the static correlation explicitly in the wave function, while the Coulomb hole is employed to describe effective dynamic correlation.

The calculations in the present study are performed variationally in contrast to those presented in [6]. The atomic natural orbital (ANO) basis sets of Pierloot et al. [21] and Widmark et al. [22] are employed to calculate atomic total energies. Only the Widmark basis set is used to calculate molecular CASSCF geometries and binding energies.

Table 2. Restricted Hartree-Fock (*RHF*) and regularized $(2\cdot\chi)$ reg-RHF total energies (Hartree) are compared to the exact values [34]. The atomic natural orbit (ANO) basis sets are 6*s*4*p* [21] and 7*s*7*p* for (7*s* for Li and He) [22]. Regularized $(2\cdot\chi)$ complete active space self-consistent field (reg-CASSCF) describes the static 2*s*-2*p* correlation explicitly

Atom	RHF	reg-RHF	reg-CASSCF	Exact
He				
[21]	−2.858018	−2.883902	–	
[22]	−2.861627	−2.884368		−2.9037
Li				
[21]	−7.431235	−7.470307	–	
[22]	−7.432710	−7.470596		−7.4781
Be				
[21]	−14.566764	−14.637062		
[22]	−14.572988	−14.637670	−14.675880	−14.6674
B				
[21]	−24.513948	−24.620449		
[22]	−24.529060	−24.622008	−24.651537	−24.6539
C				
[21]	−37.679752	−37.812175		
[22]	−37.688573	−37.815113	−37.831234	−37.8450
N				
[21]	−54.382672	−54.561661	–	
[22]	−54.400791	−54.566449		−54.5893
O				
[21]	−74.780490	−75.035848	–	
[22]	−74.811223	−75.043686		−75.067
F				
[21]	−99.366944	−99.710259	–	
[22]	−99.410189	−99.722247		−99.734
Ne				
[21]	−128.483953	−128.933876	–	
[22]	−128.546579	−128.951027		−128.939

3.1 Atomic energy calculations

Additional feeling for how the regularization of the electrostatic Green's function behaves can be acquired

Table 3. Reg-CASSCF ($f = \sqrt{5}$) total energies for atoms. Thw Widmark et al. [22] ANO-basis set is employed. FCI is full CI. Only explicit angular correlation is allowed. Exact energies are given in Table 2

	$1s$(FCI)	$1s1p$(FCI)	$1s1p1d$(FCI)	$1s4p3d$		
He	−2.879884	−2.896232	−2.897754	−2.899559		
	$2s1p$(FCI)	$2s1p1d$(FCI)	$2s1p1d1f$(FCI)	$2s2p$	$2s2s1d$	$2s2p2d$
Li	−7.482521	−7.482522	–	–	–	–
Be	−14.663362	−14.6636665	−14.663744	−14.664282	−14.664613	−14.664613
B	−24.618400	−24.635878	−24.637023	−24.632587	−24.652867	−24.654647
C	−37.800742	−37.837976	−37.841804	−37.805196	−37.844083	−37.846200
N	−54.527878	−54.582146	−54.589669	−54.531583	−54.587446	−54.588273
O	−74.991167	−75.053831	−75.069105	−75.994800	−75.058735	−75.059629
F	−99.653662	−99.723504	−99.743785	−99.656746	−99.727607	−99.728504
Ne	−128.869528	−128.946163	−128.969303	−128.869875	−128.946670	−128.947108

by studying atomic energies. Table 2 apparently implies a situation where dynamic angular correlation is included effectively into $G(|\mathbf{r}_1 - \mathbf{r}_2|; 2 \cdot \chi)$. The success for neon is countered by the failure in the case of helium. It is understood that detailed description of angular correlation is more important for helium than for the larger atoms owing to the smallness of the $1s$ orbital in conjunction with the small nuclear charge. The need for explicit angular correlation is reduced significantly by going to the $n = 2$ shell, both because atomic sizes increase and because $2p$ orbitals become increasingly occupied. As for Be, B and C, the conventional description of energetic stabilizations including the near-degeneracies of the valence shell is found to hold. It is gratifying to note that the numbers come out in good overall agreement with the exact, and that basis set effects are much reduced if regularized CASSCF (reg-CASSCF) is employed.

Additional support for the above understanding is found from full CI calculations. Table 3 shows results obtained on replacing r_{12}^{-1} by $G(|\mathbf{r}_1 - \mathbf{r}_2|; \sqrt{5} \cdot \chi)$. Angular correlation effects on the atomic energetics in general and that of He in particular are seen. Results for improved valence basis sets *without allowing for radial correlation* are also included in Table 3. The angular correlation and basis set effects can be argued to be additive, and are seen to produce semi-quantitative results.

The tendency to produce too low energies indicates a shortcoming of the assumed Coulomb hole description in the $1s$ core. This effect becomes more accentuated for the third-row atoms. The fact that both the explicit and the effective angular correlation descriptions lead to atomic energies close to experimental data for all second-row atoms, stresses the exclusive status of helium.

3.2 Binding energies and structures of small molecules

Full valence molecular calculations were performed with the Widmark et al. basis set [22], employing $4s3p2d$ ANO spaces for the heavy atoms ($5s$ $4p$ $3d$ for phosphorous) and $3s$ $1p$ for hydrogen. Tables 4 and 5 display atomization energies and optimized molecular structures, respectively. The quality of the CASSCF method to describe proper dissociation in conjunction with lack of dynamic correlations is well-known to produce bond distances which are too long. This effect is demonstrated in Table 4 where the impact of the modified $f = 2$ Green's function is seen to generally produce bond distances which are slightly too short. This indicates that $f = 2$ is a lower boundry, although basis set effects have not been investigated.

Table 4. Atomization energies in eV. The CASSCF ($f = \infty$) and reg-CASSCF ($f = 2$) results for full-valence active spaces. B-LYP and experimental results (Exp.) are taken from Ref. [35]

	CASSCF	reg-CASSCF	B-LYP	Exp.
H_2	4.13	4.45	4.84	4.75
Li_2	1.02	1.09	0.88	1.01
HF	4.94	5.48	6.12	6.13
CO	10.51	11.46	11.32	11.23
N_2	8.73	10.07	10.33	9.91
F_2	0.03	1.19	2.15	1.66
P_2	3.74	5.08	5.19	5.08
CH_4	16.07	17.29	18.32	18.25
CH_2O	14.77	16.11	16.46	16.22
CH	3.10	3.43	4.07	3.64
NH	2.79	3.25	3.91	3.67
OH	3.64	4.16	5.18	4.62
LiH	2.36	2.56	2.51	2.52
BeH	1.68	1.87	2.09	2.16
NH_3	10.79	12.10	13.19	12.93
H_2O	8.29	9.27	10.14	10.09
NO	5.23	6.00	7.15	6.61
O_2	3.66	4.69	5.85	5.21

Energetics are found to be generally improved by applying the reg-CASSCF approach. Binding energies are seen to sometimes undershoot or overshoot in an apparently irregular fashion. This effect is not unexpected given that separation between static correlation and dynamic correlation is not well-defined. This was discussed in some detail in the case of Cr_2 [23]. Reference results of a representative density functional are provided in Tables 4 and 5, by means of the Becke gradient correction [5] to the Slater exchange functional [4] in conjunction with the Lee, Yang and Parr correlation functional (B-LYP) [24]. Hence, the main qualitative achievement of the present undertaking from a DFT perspective is to demonstrate that by keeping a proper exchange interaction there is a need for explicit treatment of static correlation. This is in accord with the understanding of Neumann et al. [25].

Table 5. Molecular structures. CASSCF ($f = \infty$) and corresponding reg-CASSCF ($f = 2$) results are shown B-LYP and experimental results are taken from Ref. [35]. Bond distances are in Ångström and angles in degrees

	Quantity	CASSCF	reg-CASSCF	B-LYP	Exp.
H_2	$r_{H—H}$	0.755	0.744	0.743	0.742
Li_2	$r_{Li—Li}$	2.701	2.670	2.724	2.673
FH	$r_{F—H}$	0.917	0.906	0.933	0.917
CO	$r_{C—O}$	1.136	1.120	1.137	1.128
N_2	$r_{N—N}$	1.105	1.088	1.104	1.098
F_2	$r_{F—F}$	1.475	1.424	1.440	1.412
P_2	$r_{P—P}$	1.930	1.876	1.916	1.893
CH_4	$r_{C—H}$	1.102	1.085	1.094	1.086
CH_2O					
	$r_{C—H}$	1.092	1.079	1.114	1.099
	$r_{C—O}$	1.211	1.194	1.212	1.203
	$<$H—C—O	121.9	121.9	122.1	121.8
CH	$r_{C—H}$	1.132	1.114	1.133	1.120
NH	$r_{N—H}$	1.046	1.030	1.051	1.036
OH	$r_{O—H}$	0.973	0.960	0.985	0.970
LiH	$r_{Li—H}$	1.613	1.591	1.609	1.595
BeH	$r_{Be—H}$	1.349	1.331	1.372	1.343
H_2O					
	$r_{O—H}$	0.962	0.949	0.971	0.957
	$<$H—O—H	103.4	103.3	104.3	104.5
NH_3					
	$r_{N—H}$	1.023	1.009	1.021	1.012
	$<$H—N—H	104.7	104.4	106.4	106.7
NO	$r_{N—O}$	1.157	1.139	1.164	1.151
O_2	$r_{O—O}$	1.220	1.198	1.233	1.207

4 Conclusion

Classical and quantum physical properties have served as sources of inspiration to deduce a cusp kinetic energy corrected regularized ERI expression. The performance of the modified Coulomb-Green's function in calculations that treat the static correlation explicitly by means of the CASSCF wave function were investigated. The potential usefulness of such a regularization approach where effects of dynamic electron correlation are crucial, was advocated in a reg-CASSCF study on the binding in Cr_2 [23], and has been further substantiated here.

Target systems of this Coulomb hole augmented CASSCF approach, are those that need near-degenerate independent particle states for their descriptions. Examples are provided in an on-going effort to understand recent experimental evidence of local near-degenerate electronic states in the high-T_c superconducting cuprates by means of cluster model studies [26–29].

The main objective of the present study has been to demonstrate the ease by which important effects of dynamic correlation can be mimicked. Physical arguments were employed to describe many-body interactions effectively. Earlier, a similar such effort resulted in the Thomas-Fermi method [30, 31]. Two traditions developed subsequently, comprising the physical effective approach which produced DFT, and a mathematical school which sought to solve the Schrödinger equation and provide ab initio quantum chemistry. The domain of systems that is spanned by these approaches *today* is impressive. The next generation of computational instruments will most likely exploit the fusion of classical and quantum dynamics with classical and quantum effective medium theories. It is in this context and in the spirit of the Thomas-Fermi method, that the present work hopes to have made a contribution. The behaviour of the kinetic interpretation of the Coulomb singularity Eq. (37) in a multiconfigurational treatment is left for future investigation.

Acknowledgements. This work is an indirect consequence of a postdoctoral year with Jan Almlöf from 1989 to 1990. Then, a multipole-multipole interaction resolution of the ERIs and fragmentation schemes of large molecular systems were suggested in order to benefit from simple effective asymptotically correct long-range interaction expressions [32, 33]. Here again is the morphology of the Gaussian ERI at focus, but this time we mimic the effect of dynamic electron correlation. We observe the coalescence in time of the early works of Clementi and Kohn on the Coulomb hole and DFT. The present work is an effort towards a realization of the early understanding of the former. Access to the MOLCAS program package [19], into which the integral modifications were introduced, is gratefully acknowledged. This work was supported by the Swedish Natural Science Research Council.

References

1. Dirac PAM (1930) The principles of quantum mechanics. Oxford university, Oxford
2. Kohn W, Sham LJ (1965) Phys Rev A136: A1133
3. Hohenberg P, Kohn W (1964) Phys Rev 136: B864
4. Slater JC (1951) Phys Rev 81: 385
5. Becke AD (1988) Phys Rev A38: 3098
6. Panas I (1995) Chem Phys Lett 245: 171
7. Wigner E (1934) Phys Rev 46: 1002
8. (a) Clementi E (1963) Symposium on molecular structure and spectra. Columbus, Ohio; (b) Clementi E October Harvard-MIT Colloquium in Physical Chemistry; (c) Clementi E (1964) Theoretical Gordon Research Conference; (d) Clementi E (1965) IBM J Res Dev 9: 1; (e) Clementi E (1968) Chem Rev 68: 34; (f) Clementi E (1969) Int J Quantum Chem 3: 179
9. Chakravorty S, Clementi E (1989) Phys Rev A 39: 2290
10. Clementi E, Hofmann DWM METECC-94 In: Clementi E Methods and techniques in computational chemistry
11. Clementi E, Hofmann DWM (1995) J Mol Struct (Theochem) 330: 17
12. Goodgame MM, Goddard WA (1985) Phys Rev Lett 54: 661
13. Andersson K, Malmqvist P-Å, Roos BO, Sadlej AJ, Wolinski K (1990) J Phys Chem 94: 5483
14. Ewald PP (1921) Ann Phys 64: 253
15. Panas I (1992) Chem Phys Lett 194: 239
16. Becke AD (1988) J Chem Phys 88: 2547
17. Saunders VR (1975) In: Diercksen GHF, Sutcliffe B, Veillard A (eds) Computational techniques in quantum chemistry and molecular physics. Reidel, Dordrecht p 347
18. Panas I (1991) Chem Phys Lett 184: 86
19. Andersson K, Fülscher MP, Karlstöm G, Lind R, Malmqvist P-Å, Olsen J, Roos BO, Sadlej AJ, Blomberg MRA, Siegbahn PEM, Kellö V, Noga J, Urban M, Widmark PO (1994) MOLCAS Version 3
20. Roos BO (1987) In: Lawley KP (ed) Ab initio methods in quantum chemistry, Part II. Wiley, Chichester
21. Pierloot K, Dumez B, Widmark P-O, Roos BO (1995) Theor Chim Acta 90: 87
22. Widmark P-O, Malmqvist P-Å, Roos BO (1990) Theor Chim Acta 77: 291
23. Panas I (1996) Mol Phys 89: 239
24. Lee C, Yang W, Parr RG (1988) Phys Rev B37: 785

25. Neumann R, Nobes RH, Handy NC (1996) Mol Phys 87: 1
26. Panas I, Gatt R (1996) Chem Phys Lett 259: 241
27. Panas I, Gatt R (1996) Chem Phys Lett 259: 247
28. Panas I, Gatt R (1997) Chem Phys Lett 266: 410
29. Panas I, Gatt R Chem Phys Lett 270: 178–182
30. Thomas LH (1927) Proc Camb Phil Soc 23: 542
31. Fermi E (1927) Rend Acad Lincei 6: 602
32. Panas I, Almlöf JE, Feyereisen MW (1991) Int J Quantum Chem 40: 797
33. Panas I, Almlöf JE (1992) In J Quantum Chem 42: 1073
34. Davidson ER, Hagstrom SA, Chakravorty SJ, Umar VM, Froese C (1991) Phys Rev A 44: 7071
35. Johnson BG, Gill PMW, Pople JA (1993) J Chem Phys 98: 5612