

Electron intracule densities with correct electron coalescence cusps from Hiller–Sucher–Feinberg-type identities

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(Received 22 May 1995; accepted 10 July 1995)

Identities for the electron intracule density $I(\mathbf{R})$ in atoms and molecules are derived within the Hiller–Sucher–Feinberg (HSF) formalism. It is proven that, when applied to arbitrary (exact or approximate) electronic wave functions, these identities produce intracule densities that satisfy a modified condition for the electron coalescence cusp. A corollary of this proof provides a new, simplified derivation of the cusp condition for the exact $I(\mathbf{R})$. An expression for the Hartree–Fock approximation to the HSF electron intracule density that contains only two- and three-electron terms is obtained and its properties are analyzed. A simple scaling of the three-electron contributions in this expression assures integrability of the approximate $I(\mathbf{R})$ and improves its overall accuracy. Numerical tests carried out for the H^- , He, Li^+ , Be^{2+} , Li, and Be systems demonstrate that the application of the scaled HSF-type identity to Hartree–Fock wave functions affords dramatic improvements in the short-range behavior of the electron intracule density. © 1995 American Institute of Physics.

I. INTRODUCTION

The understanding of electron correlation in atoms and molecules requires abandoning one-particle quantities in favor of those describing properties of electron pairs. One of these quantities, called the electron intracule density, has been the object of several recent studies. Let $|\Psi\rangle \equiv |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)\rangle$ be an eigenfunction of the electronic Hamiltonian,

$$\hat{H} = -(1/2) \sum_i \hat{\nabla}_i^2 - \sum_I Z_I \sum_i |\mathbf{r}_i - \mathbf{R}_I|^{-1} + (1/2) \sum_{i \neq j} r_{ij}^{-1}. \quad (1)$$

Let

$$\mathbf{s} \equiv \mathbf{r}_1 - \mathbf{r}_2 \quad \text{and} \quad \mathbf{r} \equiv (1/2)(\mathbf{r}_1 + \mathbf{r}_2), \quad (2)$$

be the interparticle-distance (intracular) and the center-of-mass (extracular) coordinates of an electron pair. The expectation value

$$I(\mathbf{R}) = (1/2)N(N-1) \langle \Psi | \hat{\delta}(\mathbf{s} - \mathbf{R}) | \Psi \rangle, \quad (3)$$

is known as the electron intracule density or simply the intracule density.^{1,2} Since

$$dsd\mathbf{r} = d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

one may rewrite Eq. (3) as

$$I(\mathbf{s}) = (1/2)N(N-1) \sum_{\sigma_1 \sigma_2} \int \Psi^* \Psi d\mathbf{r} d\mathbf{x}_3 \cdots d\mathbf{x}_N, \quad (5)$$

where $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ and the summation runs over the spin coordinates σ_1 and σ_2 of the electrons 1 and 2.

The properties of the intracule density are well known. $I(\mathbf{R})$ is an even function of \mathbf{R} ,

$$I(\mathbf{R}) = I(-\mathbf{R}), \quad (6)$$

satisfying the normalization conditions,

$$\int I(\mathbf{R}) d\mathbf{R} = 4\pi \int I(R) R^2 dR = N_{\text{ep}} = (1/2)N(N-1), \quad (7)$$

and

$$\int I(\mathbf{R}) R^{-1} d\mathbf{R} = 4\pi \int I(R) R dR = W, \quad (8)$$

where $R \equiv |\mathbf{R}|$, N_{ep} is the number of electron pairs, W is the electron–electron repulsion energy, and

$$I(\mathbf{R}) \equiv \langle I(\mathbf{R}) \rangle, \quad (9)$$

is the spherically averaged intracule density. Intracule densities computed from approximate Hartree–Fock (HF) or correlated wave functions exhibit maxima at \mathbf{R} coinciding with the internuclear vectors.^{3,4} These maxima are ascribed to “interatomic” electron pairs.

The electron coalescence cusp at $\mathbf{R} = \mathbf{0}$,^{5,6}

$$\langle \nabla I(\mathbf{0}) \rangle = I(\mathbf{0}), \quad (10)$$

where $\langle \nabla I(\mathbf{0}) \rangle$ is the spherically averaged gradient of $I(\mathbf{R})$ at $\mathbf{R} = \mathbf{0}$, is an important property of the intracule density. Unfortunately, approximate intracule densities computed from HF and CI wave functions lack the electron coalescence cusps, as their spherically averaged gradients vanish at the

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origin. In fact, an electronic wave function has to include terms that are explicitly linear in the interelectron distance, $s \equiv |\mathbf{s}|$, in order to produce a cusp at $\mathbf{R}=\mathbf{0}$ in the corresponding approximate intracule density. While such explicitly correlated wave functions are commonly employed in the description of two-electron systems, their use is impractical for most atoms and molecules of chemical interest.

In 1978, Hiller, Sucher, and Feinberg (HSF) derived identities that express the electron density $\rho(\mathbf{R})$ and the intracule density at the origin $I(\mathbf{0})$ in terms of global operators.⁷ For exact wave functions, the HSF formulas yield densities identical with those obtained from conventional definitions involving Dirac's delta operators [compare Eq. (3)]. On the other hand, dramatic improvements in the accuracy of $\rho(\mathbf{R})$ are observed when the HSF identity is used in conjunction with approximate wave functions.⁸ These improvements are due to the fact that the expectation value of the HSF operator for electron density is sensitive to the overall rather than the local accuracy of a wave function.

In this paper, we first generalize the two-electron HSF identity to the general case of $I(\mathbf{R})$ with $\mathbf{R} \neq \mathbf{0}$. Then, we demonstrate that the resulting HSF intracule density satisfies

a modified cusp condition analogous to that recently derived for the HSF electron density.⁹ Next, we derive a new identity which is particularly suitable for wave functions that are eigenfunctions of well-defined approximate Hamiltonians and use it in conjunction with the HF method. By investigating the long-range behavior of the resulting HSF intracule density we obtain corrections that assure its integrability. Finally, we illustrate the usefulness of the newly derived identities with several numerical examples.

II. THEORY

A. The HSF identity for the intracule density

In analogy with the previously published derivation,⁷ let us consider a two-electron operator

$$\hat{Q}_s = |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s, \quad (11)$$

where

$$\nabla_s = (1/2)(\nabla_1 - \nabla_2). \quad (12)$$

The commutator between \hat{Q}_s and the electronic Hamiltonian \hat{H} [Eq. (1)] equals

$$\begin{aligned} [\hat{Q}_s, \hat{H}] &= 2|\mathbf{s}-\mathbf{R}|^{-3}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s + 2|\mathbf{s}-\mathbf{R}|^{-3}[(\mathbf{s}-\mathbf{R}) \times \nabla_s]^2 + |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s \left[- \sum_I Z_I \sum_i |\mathbf{r}_i - \mathbf{R}_I|^{-1} + (1/2) \sum_{i \neq j} r_{ij}^{-1} \right] \\ &= 2|\mathbf{s}-\mathbf{R}|^{-3}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s + 2|\mathbf{s}-\mathbf{R}|^{-3}[(\mathbf{s}-\mathbf{R}) \times \nabla_s]^2 + (1/2)|\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot (\nabla_1 - \nabla_2) \\ &\quad \times \left[- \sum_I Z_I \sum_i |\mathbf{r}_i - \mathbf{R}_I|^{-1} + (1/2) \sum_{i \neq j} r_{ij}^{-1} \right] \\ &= 2|\mathbf{s}-\mathbf{R}|^{-3}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s + 2|\mathbf{s}-\mathbf{R}|^{-3}[(\mathbf{s}-\mathbf{R}) \times \nabla_s]^2 + (1/2)|\mathbf{s}-\mathbf{R}|^{-1} \sum_I Z_I (\mathbf{s}-\mathbf{R}) \\ &\quad \cdot [(\mathbf{r}_1 - \mathbf{R}_I)|\mathbf{r}_1 - \mathbf{R}_I|^{-3} - (\mathbf{r}_2 - \mathbf{R}_I)|\mathbf{r}_2 - \mathbf{R}_I|^{-3}] - (1/2)|\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot \left[\sum_{i \neq 1} (\mathbf{r}_{1i}/r_{1i}^3) - \sum_{i \neq 2} (\mathbf{r}_{2i}/r_{2i}^3) \right] \\ &= 2|\mathbf{s}-\mathbf{R}|^{-3}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s + 2|\mathbf{s}-\mathbf{R}|^{-3}[(\mathbf{s}-\mathbf{R}) \times \nabla_s]^2 + (1/2)|\mathbf{s}-\mathbf{R}|^{-1} \sum_I Z_I (\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_1 - \mathbf{R}_I)|\mathbf{r}_1 - \mathbf{R}_I|^{-3} \\ &\quad - (\mathbf{r}_2 - \mathbf{R}_I)|\mathbf{r}_2 - \mathbf{R}_I|^{-3}] - |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot (s/s^3) - (1/2)|\mathbf{s}-\mathbf{R}|^{-1} \sum_{i > 2} (\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_{1i}/r_{1i}^3) - (\mathbf{r}_{2i}/r_{2i}^3)]. \end{aligned} \quad (13)$$

Taking into account that⁷

$$\langle \Psi | 2|\mathbf{s}-\mathbf{R}|^{-3}(\mathbf{s}-\mathbf{R}) \cdot \nabla_s | \Psi \rangle = -4\pi \langle \Psi | \hat{\delta}(\mathbf{s}-\mathbf{R}) | \Psi \rangle, \quad (14)$$

and

$$\langle \Psi | [\hat{Q}_s, \hat{H}] | \Psi \rangle = 0, \quad (15)$$

one obtains

$$\begin{aligned} \langle \Psi | \hat{\delta}(\mathbf{s}-\mathbf{R}) | \Psi \rangle &= (2\pi)^{-1} \langle \Psi | |\mathbf{s}-\mathbf{R}|^{-3}[(\mathbf{s}\mathbf{R}) \times \nabla_s]^2 | \Psi \rangle \\ &\quad + (8\pi)^{-1} \langle \Psi | \sum_I Z_I |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_1 - \mathbf{R}_I)|\mathbf{r}_1 - \mathbf{R}_I|^{-3} - (\mathbf{r}_2 - \mathbf{R}_I)|\mathbf{r}_2 - \mathbf{R}_I|^{-3}] | \Psi \rangle \\ &\quad - (4\pi)^{-1} \langle \Psi | |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot (s/s^3) | \Psi \rangle - (8\pi)^{-1} \langle \Psi | \sum_{i > 2} |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_{1i}/r_{1i}^3) - (\mathbf{r}_{2i}/r_{2i}^3)] | \Psi \rangle. \end{aligned}$$

Equation (16), which holds for exact electronic wave functions, leads to the desired definition of the HSF intracule density,

$$\begin{aligned} \tilde{I}(\mathbf{R}) = & (16\pi)^{-1}N(N-1) \left\{ 4\langle \Psi | |\mathbf{s}-\mathbf{R}|^{-3} [(\mathbf{s}-\mathbf{R}) \times \nabla_{\mathbf{s}}]^2 | \Psi \rangle \right. \\ & + \langle \Psi | \sum_I Z_I |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_1-\mathbf{R}_I) |\mathbf{r}_1-\mathbf{R}_I|^{-3} - (\mathbf{r}_2-\mathbf{R}_I) |\mathbf{r}_2-\mathbf{R}_I|^{-3}] | \Psi \rangle \\ & \left. - 2\langle \Psi | |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{s}/s^3) | \Psi \rangle - (N-2) \langle \Psi | |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot [(\mathbf{r}_{13}/r_{13}^3) - (\mathbf{r}_{23}/r_{23}^3)] | \Psi \rangle \right\}. \end{aligned} \quad (17)$$

B. The electron coalescence cusp in the HSF intracule density

It is straightforward to show that the aforedefined $\tilde{I}(\mathbf{R})$ satisfies a modified cusp condition analogous to that derived recently for the HSF electron density.⁹ The first, second, and fourth terms in the right-hand side of Eq. (17) possess continuous gradients at the limit of $\mathbf{R} \rightarrow \mathbf{0}$. On the other hand, the contribution of $\tilde{I}(\mathbf{R})$ that stems from the third term

$$\begin{aligned} \tilde{I}^{(3)}(\mathbf{R}) = & -(8\pi)^{-1}N(N-1) \\ & \times \langle \Psi | |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{s}/s^3) | \Psi \rangle, \end{aligned} \quad (18)$$

gives rise to a cusp at $\mathbf{R}=\mathbf{0}$, as one can demonstrate by explicitly evaluating the difference

$$\begin{aligned} \tilde{I}^{(3)}(\mathbf{R}) - \tilde{I}^{(3)}(\mathbf{0}) = & -(8\pi)^{-1}N(N-1) \\ & \times \langle \Psi | s^{-2} [|\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{s}/s) \\ & - 1] | \Psi \rangle. \end{aligned} \quad (19)$$

Since the expression that enters Eq. (19) in square brackets decays rapidly outside the region given by $s \leq |\mathbf{R}|$, one can write

$$\begin{aligned} \tilde{I}^{(3)}(\mathbf{R}) - \tilde{I}^{(3)}(\mathbf{0}) = & -(8\pi)^{-1}N(N-1) \langle \Psi | \delta(\mathbf{s}) | \Psi \rangle \\ & \times \int s^{-2} [|\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{s}/s) - 1] ds, \end{aligned} \quad (20)$$

for vanishingly small values of \mathbf{R} . Taking into account that⁹

$$s^{-2} [|\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{s}/s) - 1] ds = -4\pi |\mathbf{R}|, \quad (21)$$

one obtains

$$\begin{aligned} \tilde{I}^{(3)}(\mathbf{R}) - \tilde{I}^{(3)}(\mathbf{0}) = & (1/2)N(N-1) \langle \Psi | \delta(\mathbf{s}) | \Psi \rangle |\mathbf{R}| \\ = & I(\mathbf{0}) |\mathbf{R}|, \end{aligned} \quad (22)$$

at the limit of $|\mathbf{R}| \rightarrow 0$.

Equation (22) implies that the HSF intracule density possesses a discontinuous gradient at $\mathbf{R}=\mathbf{0}$. The magnitude of this discontinuity can be gauged by considering the spherically averaged gradient $\langle \nabla I(\mathbf{0}) \rangle$. Since all of the continuous contributions to this gradient average to zero, the condition

$$\langle \nabla \tilde{I}(\mathbf{0}) \rangle = I(\mathbf{0}), \quad (23)$$

follows from Eq. (22). Equation (23) constitutes the electron coalescence cusp condition for the HSF intracule density. It is analogous to Eq. (10), to which it reduces at the limit of

exact electronic wave functions [at which $\tilde{I}(\mathbf{0})$ and $I(\mathbf{0})$ are identical]. As in the one-electron case,⁹ there is an important conceptual difference between the cusp conditions for the conventional and the HSF intracule densities, the former following from the properties of the Schrödinger equation^{6,10,11} and the latter being directly built into the definition of $\tilde{I}(\mathbf{R})$ [Eq. (17)].

C. The Hartree–Fock approximation to the HSF intracule density

Since both the exact and the approximate HSF intracule densities possess electron–electron cusps, one expects $\tilde{I}(\mathbf{R})$ calculated with the HF method to partially incorporate electron correlation effects. Direct application of Eq. (17) to a single-determinantal wave function $|\Psi_{\text{HF}}\rangle$ is rather inconvenient because of the complicated matrix elements of the $|\mathbf{s}-\mathbf{R}|^{-3} [(\mathbf{s}-\mathbf{R}) \times \nabla_{\mathbf{s}}]^2$ operator. However, one can readily develop an alternative formalism that makes the calculation of HSF intracule densities feasible at any level of theory.

Let $|\Psi\rangle$ be an eigenfunction of an approximate Hermitian Hamiltonian \hat{H}_0 . The equations

$$\langle \Psi | [\hat{Q}_s, \hat{H}_0] | \Psi \rangle = 0, \quad (24)$$

and [compare Eqs. (13), (14), and (17)]

$$\tilde{I}(\mathbf{R}) = I(\mathbf{R}) + (8\pi)^{-1}N(N-1) \langle \Psi | [\hat{Q}_s, (\hat{H} - \hat{H}_0)] | \Psi \rangle, \quad (25)$$

are obviously satisfied. If \hat{H}_0 is assumed to include the one-electron part of \hat{H} , the core Hamiltonian (the electron kinetic energy and the electron–nuclear attraction) terms are absent in the difference $\hat{H} - \hat{H}_0$. In the particular case of the HF approximation,

$$\hat{H} - \hat{H}_0 = (1/2) \sum_{i \neq j} r_{ij}^{-1} - \sum_i \hat{V}_i^{\text{HF}}, \quad (26)$$

where the HF operator \hat{V}_i^{HF} for the i th electron is defined as¹²

$$\hat{V}_i^{\text{HF}}\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N) = \left[\sum_a \int \phi_a^*(\mathbf{r}') \phi_a(\mathbf{r}') |\mathbf{r}' - \mathbf{r}_i|^{-1} d\mathbf{x}' \right] \Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N) - \left[\sum_a \int \phi_a^*(\mathbf{r}') \Psi(\mathbf{x}_1, \dots, \mathbf{x}', \dots, \mathbf{x}_N) |\mathbf{r}' - \mathbf{r}_i|^{-1} d\mathbf{x}' \right] \phi_a(\mathbf{r}_i). \quad (27)$$

In Eq. (27), the sums run over the set $\{\phi_a\}$ of occupied spin-orbitals from which $|\Psi_{\text{HF}}\rangle$ is constructed. By combining Eqs. (11), (12), and (25)–(27), one arrives at

$$\tilde{I}_{\text{HF}}(\mathbf{R}) = I_{\text{HF}}(\mathbf{R}) + (8\pi)^{-1} N(N-1) \{ -\langle \Psi_{\text{HF}} | |\mathbf{s} - \mathbf{R}|^{-1} (\mathbf{s} - \mathbf{R}) \cdot (\mathbf{s}/s^3) | \Psi_{\text{HF}} \rangle - (1/2)(N-2) \langle \Psi_{\text{HF}} | |\mathbf{s} - \mathbf{R}|^{-1} (\mathbf{s} - \mathbf{R}) \cdot [(\mathbf{r}_{13}/r_{13}^3) - (\mathbf{r}_{23}/r_{23}^3)] | \Psi_{\text{HF}} \rangle - (1/2) \langle \Psi_{\text{HF}} | |\mathbf{s} - \mathbf{R}|^{-1} (\mathbf{s} - \mathbf{R}) \cdot [(\nabla_1 \hat{V}_1^{\text{HF}}) - (\nabla_2 \hat{V}_2^{\text{HF}})] | \Psi_{\text{HF}} \rangle \}, \quad (28)$$

where $I_{\text{HF}}(\mathbf{R})$ is the conventional intracule density computed from the HF wave function $|\Psi_{\text{HF}}\rangle$. One should note that $\tilde{I}(\mathbf{R})$ [Eq. (17)] and $\tilde{I}_{\text{HF}}(\mathbf{R})$ [Eq. (28)] are identical for $|\Psi_{\text{HF}}\rangle$ constructed from exact HF spin-orbitals.

With the help of the Slater–Condon rules,¹² $I_{\text{HF}}(\mathbf{R})$ can be expressed in terms of spin-orbital contributions,

$$I_{\text{HF}}(\mathbf{R}) = (1/2) \sum_{ab} [\langle ab | \hat{\delta}(\mathbf{s} - \mathbf{R}) | ab \rangle - \langle ab | \hat{\delta}(\mathbf{s} - \mathbf{R}) | ba \rangle], \quad (29)$$

where $|ab\rangle$ is a shorthand for $|\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)\rangle$, etc. Similarly,

$$\begin{aligned} \tilde{I}_{\text{HF}}(\mathbf{R}) - I_{\text{HF}}(\mathbf{R}) &= - \sum_{ab} [\langle ab | \hat{C}(\mathbf{R}) | ab \rangle - \langle ab | \hat{C}(\mathbf{R}) | ba \rangle] - \sum_{abc} [\langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | abc \rangle \\ &\quad - \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | acb \rangle + \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | cab \rangle - \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | cba \rangle \\ &\quad + \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | bca \rangle - \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | bac \rangle] + \sum_{abc} [\langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | abc \rangle \\ &\quad - \langle abc | \hat{D}_1(\mathbf{R}) - \hat{D}_2(\mathbf{R}) | bac \rangle - \langle abc | \hat{D}_1(\mathbf{R}) | cba \rangle + \langle abc | \hat{D}_1(\mathbf{R}) | cab \rangle + \langle abc | \hat{D}_2(\mathbf{R}) | acb \rangle \\ &\quad - \langle abc | \hat{D}_2(\mathbf{R}) | bca \rangle], \end{aligned} \quad (30)$$

where

$$\hat{C}(\mathbf{R}) = (8\pi)^{-1} |\mathbf{s} - \mathbf{R}|^{-1} (\mathbf{s} - \mathbf{R}) \cdot (\mathbf{s}/s^3), \quad (31)$$

and

$$\hat{D}_i(\mathbf{R}) = (16\pi)^{-1} |\mathbf{s} - \mathbf{R}|^{-1} (\mathbf{s} - \mathbf{R}) \cdot (\mathbf{r}_{i3}/r_{i3}^3), \quad i = 1, 2. \quad (32)$$

In Eq. (30), the second sum arises from the electron repulsion operator, whereas the third sum originates from the HF Coulombic and exchange terms. Further simplification of Eq. (30) yields

$$\begin{aligned} \tilde{I}_{\text{HF}}(\mathbf{R}) - I_{\text{HF}}(\mathbf{R}) &= - \sum_{ab} [\langle ab | \hat{C}(\mathbf{R}) | ab \rangle - \langle ab | \hat{C}(\mathbf{R}) | ba \rangle] + \sum_{abc} [\langle abc | \hat{D}_1(\mathbf{R}) | acb \rangle - \langle abc | \hat{D}_1(\mathbf{R}) | bca \rangle + \langle abc | \hat{D}_2(\mathbf{R}) | cab \rangle \\ &\quad - \langle abc | \hat{D}_2(\mathbf{R}) | cba \rangle] \\ &= - \sum_{ab} [\langle ab | \hat{C}(\mathbf{R}) | ab \rangle - \langle ab | \hat{C}(\mathbf{R}) | ba \rangle] + \sum_{abc} [\langle abc | \hat{D}_1(\mathbf{R}) + \hat{D}_1(-\mathbf{R}) | acb \rangle - \langle abc | \hat{D}_1(\mathbf{R}) + \hat{D}_1(-\mathbf{R}) | bca \rangle], \end{aligned} \quad (33)$$

where permutational symmetries among the orbital indices have been exploited.

Two observations concerning Eq. (33) are in order. First, the difference $\tilde{I}_{\text{HF}}(\mathbf{R}) - I_{\text{HF}}(\mathbf{R})$, which can be interpreted as a measure of the Coulomb hole,² is an even function of \mathbf{R} , as demanded by Eq. (6). Second, the analogous difference $\tilde{\rho}_{\text{HF}}(\mathbf{R}) - \rho_{\text{HF}}(\mathbf{R})$ between the electron densities equals zero, as the one-electron counterpart of \hat{Q}_s commutes with $\hat{H} - \hat{H}_0$ given by Eq. (26). In other words, the application of the HSF identity is not expected to bring any improvement to the electron density calculated from exact HF spin-orbitals.¹³

D. The spherically averaged HSF intracule density and its long-range asymptotics

Spherical averaging of Eq. (33) results in

$$\begin{aligned} & \tilde{I}_{\text{HF}}(R) - I_{\text{HF}}(R) \\ &= - \sum_{ab} [\langle ab | \hat{C}_{\text{av}}(R) | ab \rangle - \langle ab | \hat{C}_{\text{av}}(R) | ba \rangle] \\ &+ \sum_{abc} [\langle abc | \hat{D}_{\text{av}}(R) | acb \rangle - \langle abc | \hat{D}_{\text{av}}(R) | bca \rangle], \end{aligned} \quad (34)$$

where

$$\begin{aligned} \hat{C}_{\text{av}}(R) &= (8\pi R)^{-1} s^{-1} [\min(1, R/s) \\ &- (1/3)\min(1, R^3/s^3)], \end{aligned} \quad (35)$$

and

$$\begin{aligned} \hat{D}_{\text{av}}(R) &= (8\pi R)^{-1} (\mathbf{s} \cdot \mathbf{r}_{13}) r_{13}^{-3} [\min(1, R/s) \\ &- (1/3)\min(1, R^3/s^3)]. \end{aligned} \quad (36)$$

The difference

$$\Delta I_{\text{HF}}(R) = \tilde{I}_{\text{HF}}(R) - I_{\text{HF}}(R), \quad (37)$$

constitutes an approximation to the Coulomb hole as defined by Coulson and Neilson.^{2,14} The long-range asymptotics of $\Delta I_{\text{HF}}(R)$, in which the leading term is inversely proportional to R ,

$$\begin{aligned} & \lim_{R \rightarrow \infty} R \Delta I_{\text{HF}}(R) \\ &= (12\pi)^{-1} \left[- \sum_{ab} (\langle ab | s^{-1} | ab \rangle - \langle ab | s^{-1} | ba \rangle) \right. \\ &+ \sum_{abc} (\langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | acb \rangle \\ &\left. - \langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | bca \rangle) \right], \end{aligned} \quad (38)$$

and the other terms decay exponentially, is readily obtained from Eqs. (34)–(36). The three-electron terms in Eq. (38) can be substantially simplified by noting that

$$\begin{aligned} & \sum_{abc} \langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | acb \rangle \\ &= \sum_{abc} \langle acb | \mathbf{s} \cdot \mathbf{r}_{13} / s^3 | abc \rangle \\ &= \sum_{abc} (\langle acb | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | abc \rangle - \langle acb | \mathbf{s} \cdot \mathbf{r}_3 / s^3 | abc \rangle) \\ &= \sum_{abc} (\langle ac | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ab \rangle \langle b | c \rangle - \langle ac | \mathbf{s} / s^3 | ab \rangle \cdot \langle b | \mathbf{r} | c \rangle) \\ &= \sum_{ab} \langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ab \rangle - \sum_{abc} \langle ac | \mathbf{s} / s^3 | ab \rangle \cdot \langle b | \mathbf{r} | c \rangle, \end{aligned} \quad (39)$$

$$\begin{aligned} & \sum_{abc} \langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | bca \rangle \\ &= \sum_{abc} \langle acb | \mathbf{s} \cdot \mathbf{r}_{13} / s^3 | bac \rangle \\ &= \sum_{abc} (\langle acb | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | bac \rangle - \langle acb | \mathbf{s} \cdot \mathbf{r}_3 / s^3 | bac \rangle) \\ &= \sum_{abc} (\langle ac | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ba \rangle \langle b | c \rangle - \langle ac | \mathbf{s} / s^3 | ba \rangle \cdot \langle b | \mathbf{r} | c \rangle) \\ &= \sum_{ab} \langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ba \rangle - \sum_{abc} \langle ac | \mathbf{s} / s^3 | ba \rangle \cdot \langle b | \mathbf{r} | c \rangle, \end{aligned} \quad (40)$$

$$\begin{aligned} & 2 \sum_{ab} \langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ab \rangle \\ &= \sum_{ab} (\langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ab \rangle - \langle ba | \mathbf{s} \cdot \mathbf{r}_2 / s^3 | ba \rangle) \\ &= \sum_{ab} \langle ab | s^{-1} | ab \rangle, \end{aligned} \quad (41)$$

$$\begin{aligned} & 2 \sum_{ab} \langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ba \rangle \\ &= \sum_{ab} (\langle ab | \mathbf{s} \cdot \mathbf{r}_1 / s^3 | ab \rangle - \langle ba | \mathbf{s} \cdot \mathbf{r}_2 / s^3 | ab \rangle) \\ &= \sum_{ab} \langle ab | s^{-1} | ba \rangle, \end{aligned} \quad (42)$$

and

$$\begin{aligned} & 2 \sum_{abc} \langle ac | \mathbf{s} / s^3 | ba \rangle \cdot \langle b | \mathbf{r} | c \rangle \\ &= \sum_{abc} (\langle ac | \mathbf{s} / s^3 | ba \rangle \cdot \langle b | \mathbf{r} | c \rangle - \langle ca | \mathbf{s} / s^3 | ab \rangle \cdot \langle b | \mathbf{r} | c \rangle) \\ &= 0, \end{aligned} \quad (43)$$

where the hermiticity of the operators, the real-valuedness of the spin-orbitals, and the permutational symmetries among the three electrons have been invoked. By combining Eqs. (39)–(43) one arrives at

$$\begin{aligned} & \sum_{abc} (\langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | acb \rangle - \langle abc | \mathbf{s} \cdot \mathbf{r}_{13} / r_{13}^3 | bca \rangle) \\ &= (1/2) \sum_{ab} (\langle ab | s^{-1} | ab \rangle - \langle ab | s^{-1} | ba \rangle) \\ &- \sum_{abc} \langle ac | \mathbf{s} / s^3 | ab \rangle \cdot \langle b | \mathbf{r} | c \rangle. \end{aligned} \quad (44)$$

The fact that the three-electron terms cancel out only about half of the two-electron contribution to the long-range asymptotics of $\Delta I_{\text{HF}}(R)$ [Eq. (38)] implies that the HSF intracule density defined by Eq. (33) is nonintegrable. In this

TABLE I. Intracule densities in selected two-electron systems.^a

Property (method)	System			
	H ⁻	He	Li ⁺	Be ²⁺
<i>I</i> (0) HF	0.0163(0.0221)	0.1905(0.1900)	0.7697(0.7684)	1.9891(1.9817)
HF/HSF	0.0000(0.0015)	0.1060(0.1056)	0.5543(0.5533)	1.5826(1.5762)
“exact”	0.0027	0.1063	0.5337	1.5229
<i>R</i> _{max} HF	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)	0.0000(0.0000)
HF/HSF	0.9159(0.8817)	0.1857(0.1867)	0.0802(0.0804)	0.0449(0.0450)
“exact”	0.9272	0.1937	0.0834	0.0465
<i>I</i> _{max} HF	0.0163(0.0221)	0.1905(0.1900)	0.7697(0.7684)	1.9891(1.9817)
HF/HSF	0.0057(0.0096)	0.1224(0.1221)	0.5840(0.5829)	1.6262(1.6197)
“exact”	0.0040	0.1165	0.5558	1.5581
<i>N</i> _{ep} HF	1.0000(1.0000)	1.0000(1.0000)	1.0000(1.0000)	1.0000(1.0000)
HF/HSF	0.7526(0.8006)	0.8745(0.8760)	0.9236(0.9236)	0.9452(0.9452)
“exact”	1.0000	1.0000	1.0000	1.0000
<i>W</i> HF	0.4592(0.5329)	1.0261(1.0269)	1.6510(1.6503)	2.2756(2.2731)
HF/HSF	0.3021(0.3824)	0.8590(0.8606)	1.4860(1.4854)	2.1118(2.1093)
“exact”	0.3110	0.9458	1.5677	2.1909

^aThe 6-311G data followed by the 6-31G data in parentheses.

respect, the application of the HSF identity brings about the same qualitative changes to the intracule density as it does to its one-electron counterpart, namely it furnishes the coalescence cusp at the expense of an incorrect long-range asymptotic behavior.¹⁵ However, unlike in the one-electron case, this deficiency of $\tilde{I}(\mathbf{R})$ can be easily alleviated by multiplying the three-electron terms in Eq. (33) by a corrective factor κ ,

$$\begin{aligned} & \tilde{I}_{\text{HF}}(\mathbf{R}) - I_{\text{HF}}(\mathbf{R}) \\ &= - \sum_{ab} [\langle ab | \hat{C}(\mathbf{R}) | ab \rangle - \langle ab | \hat{C}(\mathbf{R}) | ba \rangle] \\ &+ \kappa \sum_{abc} [\langle abc | \hat{D}_1(\mathbf{R}) + \hat{D}_1(-\mathbf{R}) | acb \rangle \\ &- \langle abc | \hat{D}_1(\mathbf{R}) + \hat{D}_1(-\mathbf{R}) | bca \rangle]. \end{aligned} \quad (45)$$

The factor κ is a solution of the equation [compare Eqs. (38) and (44)]

$$(\kappa - 2)W_{\text{HF}} - 2\kappa \sum_{abc} \langle ac | s | s^3 | ab \rangle \cdot \langle b | \mathbf{r} | c \rangle = 0, \quad (46)$$

where W_{HF} is the HF electron–electron repulsion energy. This simple modification, which does not affect the cusp condition [Eq. (23)], not only assures that $\tilde{I}_{\text{HF}}(\mathbf{R})$ decays exponentially with $R \rightarrow \infty$ but, as demonstrated in the following section of this paper, also markedly improves its accuracy for all values of \mathbf{R} . One should note that for spherically symmetrical systems with only the *s*-type spin–orbitals occupied, $\langle b | \mathbf{r} | c \rangle$ vanishes for all spin–orbital pairs (*b, c*), implying $\kappa=2$.

III. NUMERICAL EXAMPLES

In order to assess the usefulness of the newly derived identities, the HF [Eq. (29)] and HF-HSF [Eq. (45)] intracule

densities were computed for several atoms and ions. Electronic wave functions calculated at the HF/6-31G and HF/6-311G levels of theory with the GAUSSIAN 92 suite of programs¹⁶ were used. The latter basis set is expected to yield electronic properties that do not deviate significantly from those obtained at the HF limit—a supposition that is supported by the agreement between the respective values of 0.1905 (Table I) and 0.1906 (Ref. 19) for $I_{\text{HF}}(\mathbf{0})$ in the helium atom. The computed intracule densities are reported in Tables I and II. All values are listed in atomic units.

The “exact” intracule densities of two-electron systems including H⁻ [Fig. 1(a)], He [Fig. 1(b)], Li⁺ [Fig. 1(c)], and Be²⁺ [Fig. 1(d)] were derived from explicitly correlated

TABLE II. Intracule densities in the lithium and beryllium atoms.^a

Property (method)	System	
	Li	Be
<i>I</i> (0) HF	0.7841(0.7865)	2.0981(2.1155)
HF/HSF	0.5639(0.5657)	1.6593(1.6729)
“exact”	0.5426	1.6069
<i>R</i> _{max} HF	0.0000(0.0000)	0.0000(0.0000)
HF/HSF	0.0801(0.0800)	0.0448(0.0446)
“exact”	0.0842	0.0468
<i>I</i> _{max} HF	0.7841(0.7865)	2.0981(2.1155)
HF/HSF	0.5941(0.5959)	1.7051(1.7189)
“exact”	0.5652	1.6444
<i>N</i> _{ep} HF	3.0000(3.0000)	6.0000(6.0000)
HF/HSF	2.8589(2.8555)	5.5518(5.5641)
“exact”	3.0000	6.0000
<i>W</i> HF	2.2818(2.2968)	4.4895(4.5502)
HF/HSF	2.0825(2.0950)	4.1017(4.1581)
“exact”	2.1895	4.3787

^aThe 6-311G data followed by the 6-31G data in parentheses.

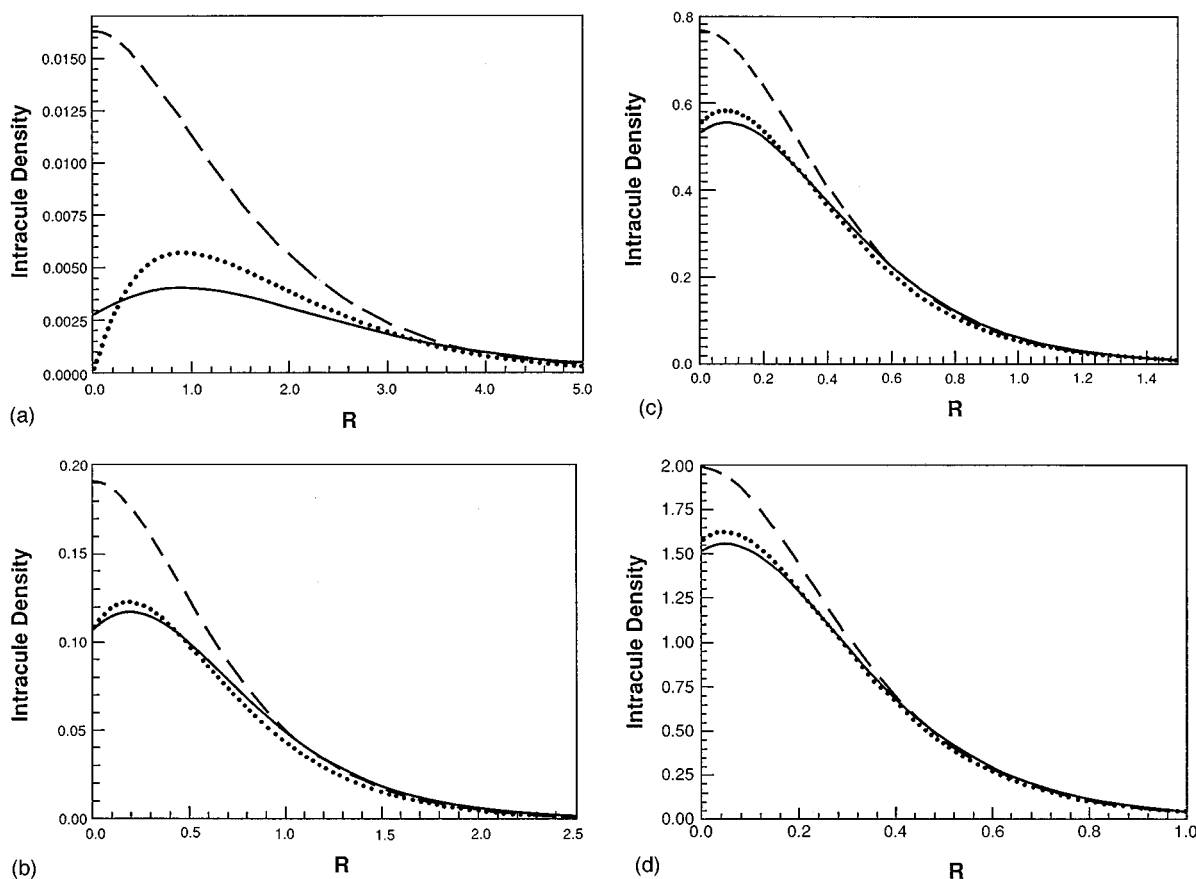


FIG. 1. Intracule densities [solid line, “exact” $I(R)$; broken line, $I_{HF}(R)$, Eq. (29); dotted line, $\tilde{I}_{HF}(R)$, Eq. (45)] in select two-electron systems; (a) H^- , (b) He , (c) Li^+ , and (d) Be^{2+} .

Hylleraas-type wave functions¹⁷ with 491 terms. Details of these calculations, which included terms in the Fock expansion necessary for an accurate description of the three-particle coalescence region, have been published elsewhere.¹⁸ The computed “exact” value of 0.1063 for $I(0)$ in the helium atom (Table I) agrees very well with those of 0.1071 (Ref. 20) and 0.1063 (Ref. 19) obtained previously from 20- and 184-term Hylleraas-type wave functions, respectively. Similarly good agreement is observed between the present (Table I) and the previously reported²⁰ radial positions (R_{max} : 0.1937 vs 0.1905) and magnitudes (I_{max} : 0.1165 vs 0.1165) of the maximum in $I(\mathbf{R})$. The present “exact” estimates of $I(0)$ in H^- , Li^+ , and Be^{2+} also match the literature data¹⁹ very closely.

Comparisons of the HF and HF-HSF intracule densities with their “exact” counterparts (Table I and Fig. 1) reveal dramatic improvements in accuracy brought by the application of Eq. (45). These improvements are of both qualitative and quantitative nature. First of all, the cusps at $\mathbf{R}=0$ that are missing in $I_{HF}(\mathbf{R})$ appear in the respective $\tilde{I}_{HF}(\mathbf{R})$. The intracule densities at $\mathbf{R}=0$ are significantly reduced, bringing them into much closer agreement with those obtained from explicitly correlated wave functions. Moreover, the locations R_{max} and the magnitudes I_{max} of the radial maxima in $I(\mathbf{R})$ precipitated by the presence of the electron coalescence cusps are reproduced with impressive accuracy by the HF-HSF calculations.

The data obtained for the helium atom illustrates the importance of the corrective factor κ present in Eq. (45). As mentioned above, $I_{HF}(0)$ equals 0.1905 for this system, which amounts to an overestimation by as much as 80%. The application of Eq. (45) lowers the intracule density to 0.1060, which is within 0.4% off the “exact” value. On the other hand, the uncorrected identity [Eq. (33)] yields $\tilde{I}_{HF}(0)$ equal to 0.0749, grossly exaggerating the effects of electron correlation on the intracule density. One should mention that the latter value is close to that of 0.0787 reported in the original HSF paper⁷ for $\tilde{I}(0)$ computed from the one-term Hylleraas wave function (which can be regarded as a crude approximation to the HF wave function). In conclusion, the choice of the corrective factor κ that assures integrability of $\tilde{I}_{HF}(\mathbf{R})$ also enhances its accuracy at small interelectron distances. As expected from the considerations presented in the preceding section of this paper, this choice corresponds to setting $\kappa=2$ for all systems studied here.

The improvement brought by the application of Eq. (45) is limited to the short-range portion of the intracule density. This fact is uncovered by numerical integrations of $\tilde{I}_{HF}(\mathbf{R})$ [Eqs. (7) and (8)] which produce values of N_{ep} and W that are markedly lower than their “exact” counterparts (see the last two sections of Table I). In particular, the decrease in the electron–electron repulsion W due to electron correlation, which (except for H^-) amounts to ~ 0.08 in the helium series, is overestimated by about 100%. Similarly, the com-

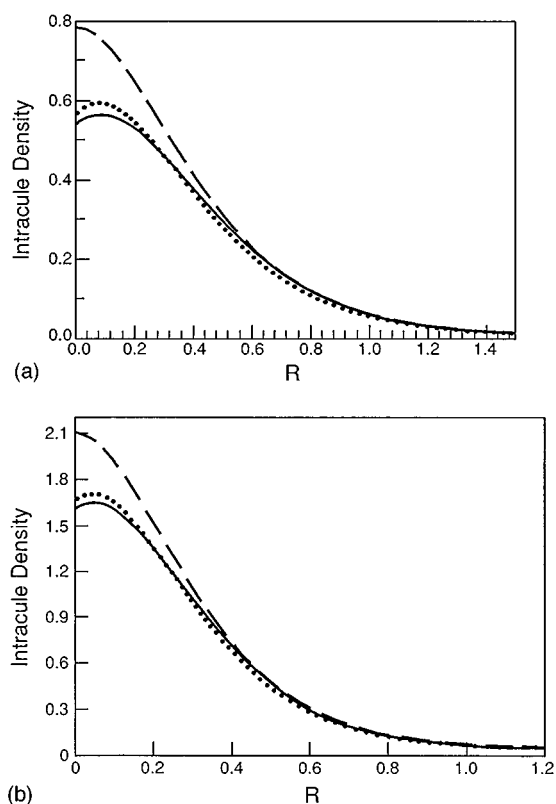


FIG. 2. Intracule densities [solid line, “exact” $I(R)$; broken line, $I_{\text{HF}}(R)$, Eq. (29); dotted line, $\tilde{I}_{\text{HF}}(R)$, Eq. (45)] in (a) Li and (b) Be.

puted numbers of electron pairs N_{ep} are too low by amounts approximately proportional to $(Z - \frac{5}{16})^{-1}$. The failure of $\tilde{I}_{\text{HF}}(\mathbf{R})$ to yield accurate N_{ep} and W is a direct consequence of the fact that $\tilde{I}_{\text{HF}}(\mathbf{R}) < I_{\text{HF}}(\mathbf{R})$ everywhere, implying $\Delta I_{\text{HF}}(R) < 0$ for all values of R (see Fig. 1), whereas the actual Coulomb hole is known to be negative for small R and positive at larger interelectron distances, reflecting a charge-conserving shift in the probability density that reduces the electron–electron repulsion W .^{2,14}

The “exact” intracule densities in the Li and Be atoms were calculated by a variational Monte Carlo method. Accurate electronic wave functions that recover 99.6% and 99.2% of the correlation energy in Li and Be, respectively, were first computed with a variance minimization technique²¹ and then used in accelerated Metropolis Monte Carlo calculations²² of the intracule densities. Comparisons of these densities with the corresponding HF and HF-HSF data show that the improvements in the computed values of $I(0)$, R_{max} , and I_{max} (Table II) obtained upon the application of the corrected HSF identity [Eq. (45)] parallel those observed in the two-electron systems. However, as in the two-electron case, the HSF corrections to $I(\mathbf{R})$, which restore the electron coalescence cusp and improve the overall accuracy for small values of R (Fig. 2), have a negative effect on the global properties such as N_{ep} or W .

IV. CONCLUSIONS

Electron intracule densities that possess the electron coalescence cusp at the origin can be calculated from arbitrary

(exact or approximate) wave functions with the help of identities derived within the Hiller–Sucher–Feinberg (HSF) formalism. Applications of such identities range from a new, simplified derivation of the cusp condition for exact intracule densities to the computation of the Coulomb holes and design of new density and density matrix functionals.

When applied to the Hartree–Fock single-determinantal wave functions, the HSF formalism yields a correction to the HF intracule density that involves only two- and three-electron terms. Although this correction does not lead to integrable $I(\mathbf{R})$, the integrability is readily restored by scaling of the three-electron contributions. The scaled expression for $\tilde{I}_{\text{HF}}(\mathbf{R})$ [Eq. (45)] produces intracule densities that, when compared with their “exact” counterparts, are found to be at least one order of magnitude more accurate than the densities obtained from the conventional definition [Eqs. (3) and (29)]. In addition, the HF-HSF intracule densities not only possess cusps at their origins but also exhibit maxima with radial positions and magnitudes closely paralleling those present in the “exact” $I(\mathbf{R})$.

Although the newly derived identities tend to grossly overestimate the effects of electron correlation on the electron–electron repulsion energy, they constitute the first step in the quest for energy functionals of the HF density matrix that do not involve semiempirical modeling of the Coulomb hole. With the short-range electron–electron interactions accurately accounted for in our approach, the future improvements in the accuracy of $I(\mathbf{R})$ (and thus W) will have to come from a better description of the medium- and long-range correlation effects.

ACKNOWLEDGMENTS

This work was partially supported by the National Science Foundation under Contract No. CHE-9224806, the Florida State University through time granted on its Cray Y-MP digital computer, and the U.S. DOE through its Supercomputer Computations Research Institute. One of the authors (C.J.U.) was supported by ONR Grant No. N00014-92-J-1158. Part of this research was conducted using the resources of the Cornell Theory Center.

APPENDIX

The one-center, two-electron integrals that occur in calculations of the electron intracule densities in the helium-, lithium-, and berylliumlike atoms and ions possess the general form

$$\langle ik | \hat{O} | jl \rangle = \int \int \exp(-\alpha_i r_1^2 - \alpha_k r_2^2) \hat{O}(\mathbf{s}) \times \exp(-\alpha_j r_1^2 - \alpha_l r_2^2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (\text{A1})$$

where the operator \hat{O} is a potential that depends on the variable \mathbf{s} [Eq. (2)] only. Evaluation of these integrals commences with the substitution of $(\mathbf{r}_1, \mathbf{r}_2)$ by (\mathbf{r}, \mathbf{s}) , followed by the integration over \mathbf{r} ,

$$\begin{aligned} \langle ik|\hat{O}|jl\rangle &= \int \int O(\mathbf{s}) \exp[-\alpha_{ij}(\mathbf{r}+\mathbf{s}/2)^2 - \alpha_{kl}(\mathbf{r}-\mathbf{s}/2)^2] d\mathbf{r} d\mathbf{s} & \alpha &= \alpha_{ij}\alpha_{kl}/\alpha_{ijkl}. & (A3) \\ &= \int \int O(\mathbf{s}) \exp[-\alpha_{ijkl}(r^2+s^2/4) - (\alpha_{ij}-\alpha_{kl})(\mathbf{r}\cdot\mathbf{s})] d\mathbf{r} d\mathbf{s} & \text{For the integrals } \langle ik|\hat{\delta}(\mathbf{s}-\mathbf{R})|jl\rangle & \text{ that arise from Eq. (29) one obtains} \\ &= (\pi/\alpha_{ijkl})^{3/2} \int O(\mathbf{s}) \exp(-\alpha s^2) d\mathbf{s}, & \langle ik|\hat{\delta}(\mathbf{s}-\mathbf{R})|jl\rangle &= (\pi/\alpha_{ijkl})^{3/2} \int \hat{\delta}(\mathbf{s}-\mathbf{R}) \exp(-\alpha s^2) d\mathbf{s} \\ & & &= (\pi/\alpha_{ijkl})^{3/2} \exp(-\alpha R^2), & (A4) \end{aligned}$$

where

$$\alpha_{ij} = \alpha_i + \alpha_j, \quad \alpha_{kl} = \alpha_k + \alpha_l, \quad \alpha_{ijkl} = \alpha_{ij} + \alpha_{kl},$$

and

in agreement with the previously published formulas.^{3,23} The integrals

$$C_{ikjl}(\mathbf{R}) \equiv (8\pi)^{-1} \langle ik||\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R})\cdot(\mathbf{s}/s^3)|jl\rangle, \quad (A5)$$

that enter Eqs. (33) and (45), giving rise to the cusp at $\mathbf{R}=\mathbf{0}$ [see Eqs. (18)–(22)], are computed as follows:

$$\begin{aligned} C_{ikjl}(\mathbf{R}) &= (8\pi)^{-1} (\pi/\alpha_{ijkl})^{3/2} \int |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R})\cdot(\mathbf{s}/s^3) \exp(-\alpha s^2) d\mathbf{s} \\ &= \pi^{-2} (\pi/\alpha_{ijkl})^{3/2} \int_0^\infty \int_0^\infty w^2 dudw \int \exp[-u^2(\mathbf{s}-\mathbf{R})^2] \exp(-w^2 s^2) (\mathbf{s}-\mathbf{R})\cdot\mathbf{s} \exp(-\alpha s^2) d\mathbf{s} \\ &= \pi^{-2} (\pi/\alpha_{ijkl})^{3/2} \int_0^\infty \int_0^\infty w^2 dudw \int \exp[-(u^2+w^2+\alpha)s^2 - u^2 R^2 + 2u^2(\mathbf{s}\cdot\mathbf{R})] (\mathbf{s}-\mathbf{R})\cdot\mathbf{s} d\mathbf{s} \\ &= \pi^{-2} (\pi/\alpha_{ijkl})^{3/2} \int_0^\infty \int_0^\infty w^2 \exp[-u^2(w^2+\alpha)(u^2+w^2+\alpha)^{-1} R^2] dudw \int \exp[-(u^2+w^2+\alpha)s'^2] \\ &\quad \times [\mathbf{s}' - (w^2+\alpha)(u^2+w^2+\alpha)^{-1}\mathbf{R}] \cdot [\mathbf{s}' + u^2(u^2+w^2+\alpha)^{-1}\mathbf{R}] d\mathbf{s}', \\ &= \pi^{-1/2} (\pi/\alpha_{ijkl})^{3/2} \int_0^\infty \int_0^\infty w^2 (u^2+w^2+\alpha)^{-5/2} [(3/2) - u^2(w^2+\alpha)(u^2+w^2+\alpha)^{-1} R^2] \\ &\quad \times \exp[-u^2(w^2+\alpha)(u^2+w^2+\alpha)^{-1} R^2] du dw, & (A6) \end{aligned}$$

where the Laplace transforms for $|\mathbf{s}-\mathbf{R}|^{-1}$ and s^{-3} have been used. The next step in the evaluation of $C_{ikjl}(\mathbf{R})$ involves the substitution

$$w = \alpha^{1/2}(t^2-1)^{1/2}, \quad dw = \alpha^{1/2}t(t^2-1)^{-1/2} dt, \quad t \in [1, \infty), \quad (A7)$$

which leads to

$$\begin{aligned} C_{ikjl}(\mathbf{R}) &= \pi^{-1/2} (\pi\alpha/\alpha_{ijkl})^{3/2} \int_0^\infty \int_1^\infty t(t^2-1)^{1/2} (u^2+\alpha t^2)^{-5/2} [(3/2) - \alpha u^2 t^2 (u^2+\alpha t^2)^{-1} R^2] \\ &\quad \times \exp[-\alpha u^2 t^2 (u^2+\alpha t^2)^{-1} R^2] du dt. & (A8) \end{aligned}$$

The second substitution

$$u = \alpha^{1/2}tv(1-v^2)^{-1/2}, \quad du = \alpha^{1/2}t(1-v^2)^{-3/2} dv, \quad v \in [0, 1], \quad (A9)$$

results in

$$\begin{aligned} C_{ikjl}(\mathbf{R}) &= (\pi\alpha)^{-1/2} (\pi/\alpha_{ijkl})^{3/2} \int_0^1 \int_1^\infty t^{-3} (t^2-1)^{1/2} (1-v^2) [(3/2) - \alpha v^2 t^2 R^2] \exp(-\alpha v^2 t^2 R^2) dv dt \\ &= (\pi\alpha)^{-1/2} (\pi/\alpha_{ijkl})^{3/2} \int_1^\infty t^{-3} (t^2-1)^{1/2} \{ (3/2) F_0(\alpha t^2 R^2) - [(3/2) + \alpha t^2 R^2] F_1(\alpha t^2 R^2) + \alpha t^2 R^2 F_2(\alpha t^2 R^2) \} dt \\ &= (\pi\alpha)^{-1/2} (\pi/\alpha_{ijkl})^{3/2} \int_1^\infty t^{-3} (t^2-1)^{1/2} F_0(\alpha t^2 R^2) dt, & (A10) \end{aligned}$$

where the recursion²⁴

$$F_n(x) = (2x)^{-1}[(2n-1)F_{n-1}(x) - \exp(-x)], \quad (\text{A11})$$

for the well-known functions $F_n(x)$,

$$F_n(x) \equiv \int_0^1 y^{2n} \exp(-xy^2) dy, \quad (\text{A12})$$

has been employed. By applying the identity,²⁵

$$\int_1^\infty t^{-3}(t^2-1)^{1/2} F_0(At^2) dt = (\pi/12)(3+2A)[1 - \text{erf}(A^{1/2})] + (1/6)\pi^{1/2}A^{-1/2}[1 - (1+A)\exp(-A)], \quad (\text{A13})$$

one finally arrives at

$$C_{ijkl}(\mathbf{R}) = (1/12)\alpha^{-1/2}(\pi/\alpha_{ijkl})^{3/2}\{\pi^{1/2}(3+2\alpha R^2)[1 - \text{erf}(\alpha^{1/2}R)] + 2(\alpha R^2)^{-1/2}[1 - (1+\alpha R^2)\exp(-\alpha R^2)]\}. \quad (\text{A14})$$

The one-center, three-electron integrals,

$$D_{ikmjln}(\mathbf{R}) \equiv (16\pi)^{-1}\langle ikm || |\mathbf{s}-\mathbf{R}|^{-1}(\mathbf{s}-\mathbf{R}) \cdot (\mathbf{r}_{13}/r_{13}^3) || jln \rangle \quad (\text{A15})$$

that enter Eqs. (33) and (45) are evaluated as follows:

$$\begin{aligned} D_{ikmjln}(\mathbf{R}) &= (16\pi)^{-1} \int \int \int \exp(-\alpha_i r_1^2 - \alpha_k r_2^2 - \alpha_m r_3^2) |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot (\mathbf{r}_{13}/r_{13}^3) \exp(-\alpha_j r_1^2 - \alpha_l r_2^2 - \alpha_n r_3^2) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ &= (1/4)\pi^{-1/2} \int_0^\infty t^2 dt \int \int \int \exp(-\alpha_{ij} r_1^2 - \alpha_{kl} r_2^2 - \alpha_{mn} r_3^2 - t^2 r_{13}^2) |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot \mathbf{r}_{13} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ &= (1/4)\alpha_{mn} \int_0^\infty t^2 (\alpha_{mn} + t^2)^{-5/2} dt \int \int \exp[-\alpha_{ij} r_1^2 - \alpha_{kl} r_2^2 - \alpha_{mn} t^2 (\alpha_{mn} + t^2)^{-1} r_1^2] |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot \mathbf{r}_1 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= (1/4) \int_0^1 w^2 dw \int \int \exp[-(\alpha_{ij} + w^2 \alpha_{mn}) r_1^2 - \alpha_{kl} r_2^2] |\mathbf{s}-\mathbf{R}|^{-1} (\mathbf{s}-\mathbf{R}) \cdot \mathbf{r}_1 d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (\text{A16})$$

where the Laplace transform for $|\mathbf{r}_{13}|^{-1}$ and the substitution

$$t = \alpha_{mn}^{1/2} w (1-w^2)^{-1/2}, \quad dt = \alpha_{mn}^{1/2} (1-w^2)^{-3/2} dw, \quad w \in [0, 1], \quad (\text{A17})$$

have been used. Application of another Laplace transform for $|\mathbf{s}-\mathbf{R}|^{-1}$ leads to

$$\begin{aligned} D_{ikmjln}(\mathbf{R}) &= (1/2)\pi^{-1/2} \int_0^\infty \int_0^1 w^2 du dw \int \int \exp[-(\alpha_{ij} + \alpha_{mn} w^2) r_1^2 - \alpha_{kl} r_2^2 - u^2 (\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R})^2] (\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}) \cdot \mathbf{r}_1 d\mathbf{r}_1 d\mathbf{r}_2 \\ &= (\pi/2)\alpha_{kl} \int_0^\infty \int_0^1 (\alpha_{kl} + u^2)^{-5/2} w^2 \alpha_{kl}^{1/2} du dw \int \exp[-(\alpha_{ij} + \alpha_{mn} w^2) r_1^2 - \alpha_{kl} u^2 (\alpha_{kl} + u^2)^{-1} (\mathbf{r}_1 - \mathbf{R})^2] \\ &\quad \times (\mathbf{r}_1 - \mathbf{R}) \cdot \mathbf{r}_1 d\mathbf{r}_1 \\ &= (\pi/2)\alpha_{kl}^{-1} \int_0^1 \int_0^1 (1-z^2) w^2 dz dw \int \exp[-(\alpha_{ij} + \alpha_{mn} w^2) r_1^2 - \alpha_{kl} z^2 (\mathbf{r}_1 - \mathbf{R})^2] (\mathbf{r}_1 - \mathbf{R}) \cdot \mathbf{r}_1 d\mathbf{r}_1 \\ &= (1/2)\pi^{5/2} \alpha_{kl}^{-1} \int_0^1 \int_0^1 (1-z^2) w^2 (\alpha_{ij} + \alpha_{mn} w^2 + \alpha_{kl} z^2)^{-5/2} [(3/2) - \alpha_{kl} z^2 (\alpha_{ij} + \alpha_{mn} w^2) \\ &\quad \times (\alpha_{ij} + \alpha_{mn} w^2 + \alpha_{kl} z^2)^{-1} R^2] \exp[-\alpha_{kl} z^2 (\alpha_{ij} + \alpha_{mn} w^2) (\alpha_{ij} + \alpha_{mn} w^2 + \alpha_{kl} z^2)^{-1} R^2] dz dw, \end{aligned} \quad (\text{A18})$$

where the substitution

$$u = \alpha_{kl}^{1/2} z (1-z^2)^{-1/2}, \quad du = \alpha_{kl}^{1/2} (1-z^2)^{-3/2} dz, \quad z \in [0, 1], \quad (\text{A19})$$

has been employed. A further simplification of Eq. (A19) is achieved with two subsequent substitutions

$$w = (t^2 - \beta)^{1/2}, \quad dw = t(t^2 - \beta)^{-1/2} dt, \quad t \in [\beta^{1/2}, (1+\beta)^{1/2}], \quad (\text{A20})$$

and

$$z = \alpha_{mn}^{1/2} t v [\alpha_{mn} t^2 + \alpha_{kl} (1-v^2)]^{-1/2}, \quad dz = \alpha_{mn}^{1/2} t (\alpha_{mn} t^2 + \alpha_{kl}) [\alpha_{mn} t^2 + \alpha_{kl} (1-v^2)]^{-3/2} dv, \quad v \in [0, 1], \quad (\text{A21})$$

where

$$\beta = \alpha_{ij} / \alpha_{mn}. \quad (\text{A22})$$

This results in

$$\begin{aligned} D_{ikmjln}(\mathbf{R}) &= (1/2) \pi^{5/2} \alpha_{kl}^{-1} \int_0^1 \int_{\beta^{1/2}}^{(1+\beta)^{1/2}} (1-z^2) t (t^2 - \beta)^{1/2} (\alpha_{mn} t^2 + \alpha_{kl} z^2)^{-5/2} [(3/2) - \alpha_{kl} z^2 \alpha_{mn} t^2 (\alpha_{mn} t^2 + \alpha_{kl} z^2)^{-1} R^2] \\ &\quad \times \exp[-\alpha_{kl} z^2 \alpha_{mn} t^2 (\alpha_{mn} t^2 + \alpha_{kl} z^2)^{-1} R^2] dz dt \\ &= (1/2) \pi^{5/2} \alpha_{mn}^{-2} \alpha_{kl}^{-1} \int_0^1 \int_{\beta^{1/2}}^{(1+\beta)^{1/2}} (1-v^2) t^{-3} (t^2 - \beta)^{1/2} (\alpha_{kl} + \alpha_{mn} t^2)^{-1/2} [(3/2) - \alpha_{kl} \alpha_{mn} (\alpha_{kl} + \alpha_{mn} t^2)^{-1} v^2 t^2 R^2] \\ &\quad \times \exp[-\alpha_{kl} \alpha_{mn} (\alpha_{kl} + \alpha_{mn} t^2)^{-1} v^2 t^2 R^2] dv dt \\ &= (1/2) \pi^{5/2} \alpha_{mn}^{-2} \alpha_{kl}^{-1} \int_{\beta^{1/2}}^{(1+\beta)^{1/2}} t^{-3} (t^2 - \beta)^{1/2} (\alpha_{kl} + \alpha_{mn} t^2)^{-1/2} F_0[\alpha_{kl} \alpha_{mn} (\alpha_{kl} + \alpha_{mn} t^2)^{-1} t^2 R^2] dt. \end{aligned} \quad (\text{A23})$$

The final substitution

$$t = (\alpha \alpha_{kl} / \alpha_{mn})^{1/2} \tau (\alpha_{kl} - \alpha \tau^2)^{-1/2}, \quad dt = (\alpha \alpha_{kl} / \alpha_{mn})^{1/2} \alpha_{kl} (\alpha_{kl} - \alpha \tau^2)^{-3/2} d\tau, \quad \tau \in [1, \gamma], \quad (\text{A24})$$

where

$$\gamma = (1 + \alpha_{kl} / \alpha_{ij})^{1/2} [1 + \alpha_{kl} / (\alpha_{ij} + \alpha_{mn})]^{-1/2}, \quad (\text{A25})$$

yields

$$D_{ikmjln}(\mathbf{R}) = (1/2) \pi^{5/2} \alpha_{mn}^{-3/2} \alpha_{kl}^{-1} \alpha_{ij}^{1/2} \alpha_{kl}^{-3/2} \int_1^\gamma \tau^{-3} (\tau^2 - 1)^{1/2} F_0(\alpha \tau^2 R^2) d\tau. \quad (\text{A26})$$

This integral, which is analogous to that appearing in Eq. (A10), cannot be expressed in a closed form. In the actual calculations reported in this paper an equivalent expression,

$$D_{ikmjln}(\mathbf{R}) = (1/4) \pi^3 \alpha_{ij}^{-1} \alpha_{kl}^{-3/2} \alpha_{mn}^{-3/2} R^{-1} \int_0^{(\beta+1)^{-1/2}} \text{erf}[\alpha_{ij}^{1/2} \alpha_{kl}^{1/2} R (\alpha_{ijkl} - \alpha_{kl} t^2)^{-1/2}] t^2 dt, \quad (\text{A27})$$

is employed for the sake of a superior numerical accuracy. A 40-point scaled Chebyshev–Gauss quadrature produces integrals with absolute errors of less than 10^{-3} and 10^{-5} when used in conjunction with Eqs. (A26) and (A27), respectively.

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