Comparison of Two-Electron Densities Reconstructed from One-Electron Density Matrices

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ABSTRACT: We consider approximate reconstruction of spinless and spin-resolved two-electron charge densities, intracule densities, and extracule densities utilizing only the one-electron reduced density matrix. Using large basis set, configuration interaction density matrices for the ground state of Be, we compare the two-electron densities obtained using several proposed reconstruction functionals ("natural orbital functionals") for the two-electron density and density matrix. We also analyze the intracule and extracule densities obtained from these reconstructions. Several of the proposed natural orbital functionals are found to produce unphysical negative values for the pair density when two parallel-spin electrons approach one another. Ancillary results from this study include new, simplified formulas for the intracule and extracule densities, and a mathematical justification for an approximate relation between atomic intracule and extracule densities that has previously been reported on the basis of extensive Hartree–Fock calculations. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 90: 355–369, 2002

Key words: density matrix functional theory; natural orbitals; reduced density matrices; intracule density; pair density

Introduction

Recently there has been significant interest in electronic structure methods based upon the one-electron reduced density matrix (1-RDM or 1-matrix) [1–14]. Since the one-electron charge density (1-CD) $\rho(\mathbf{r})$ is the diagonal part of the spinless 1-matrix, the theorems of Hohenberg and Kohn [15] imply that the electronic energy of a nondegenerate ground state may be written as a functional of either $\rho(\mathbf{r})$ or the full 1-RDM $\gamma(\mathbf{x};\mathbf{x}')$. [Here $\mathbf{x} = (\mathbf{r}, \xi)$ is a composite space-spin coordinate for a single electron.] The exact kinetic energy is readily calculated if the full 1-matrix is known, so in 1-RDM functional theories approximation enters only in construction of $V_{\mathrm{ee}}[\gamma(\mathbf{x};\mathbf{x}')]$, the functional for the electron–electron repulsion energy. In contrast, the

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exact kinetic energy density functional is unknown. A further advantage of 1-matrix functional methods is that the existence of an exact, ground state energy functional $E[\gamma(\mathbf{x};\mathbf{x}')]$ is assured even for nonlocal potentials [16], for which the Hohenberg–Kohn theorems are not valid.

For the usual spin-independent, Born–Oppenheimer electronic Hamiltonian $\hat{H}_{\mathrm{BO}}$, the exact electronic energy is a *known* functional of the two-electron reduced density matrix (2-RDM or 2-matrix) $\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')$, namely $E_{\mathrm{BO}}[\Gamma] = \mathrm{tr}\,(\hat{H}_{\mathrm{BO}}\Gamma)$. (For brevity we henceforth suppress the electronic coordinates in our functional notation.) However, the energy can also be given explicitly in terms of the spinless 1-matrix and the two-electron charge density (2-CD). The former is defined as

$$\gamma_0(\mathbf{r};\mathbf{r}') \equiv \int d\xi\, \gamma(\mathbf{r},\xi;\mathbf{r}',\xi), \tag{1}$$

while the 2-CD is given by

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) \equiv \int d\xi_1\, d\xi_2\, \Gamma(\mathbf{r}_1,\xi_1,\mathbf{r}_2,\xi_2;\mathbf{r}_1,\xi_1,\mathbf{r}_2,\xi_2). \tag{2}$$

The energy functional in terms of these quantities is

$$\begin{aligned} E_{\mathrm{BO}}[\gamma_0,\rho_2] = -\int d\mathbf{r}\Bigg(\sum_{\mu}\frac{Z_\mu\rho(\mathbf{r})}{|\mathbf{r}_1-\mathbf{r}_\mu|} \\ + \frac{1}{2}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}')\hat{\nabla}_r^2\gamma_0(\mathbf{r};\mathbf{r}')\Bigg) \\ + \int d\mathbf{r}_1\int d\mathbf{r}_2\frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}, \end{aligned} \tag{3}$$

in which Z_μ is the atomic number of the nucleus located at $\mathbf{r}_\mu$ and $\rho(\mathbf{r}) = \gamma_0(\mathbf{r};\mathbf{r})$. We need γ_0 rather than simply ρ in order to obtain the kinetic energy, since the operator $\hat{\nabla}_r^2$ acts only on the unprimed coordinates (the ket space); only *after* this operation has been carried out do we set $\mathbf{r} = \mathbf{r}'$. We are able to integrate over the spin variables because $\hat{H}_{\mathrm{BO}}$ is spin-free, and we may use ρ_2 in lieu of Γ for the two-electron contribution to E_{BO} because the two-electron part of $\hat{H}_{\mathrm{BO}}$ is strictly multiplicative.

The energy functional in Eq. (3) depends on both $\gamma_0(\mathbf{r};\mathbf{r}')$ and $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$, and this suggests an alternative viewpoint regarding 1-matrix functional theories. Rather than attempting to develop approximate energy functionals $E_{\mathrm{BO}}[\gamma]$ of the 1-RDM, one could employ the exact functional in Eq. (3) but with an approximate two-electron charge density that is built from γ using a *reconstruction functional* $\rho_2[\gamma]$. Several such reconstructions have been proposed [3, 6, 9–12] and are known in the literature as *natural orbital functionals* because they are based upon the spectral expansion of γ. Alternatively, Valdemoro [17] has proposed an approximate reconstruction of the full 2-matrix in terms of γ, which provides another reconstruction functional for ρ_2.

In this article we compare these proposed reconstructions of the 2-CD starting from a very accurate configuration interaction 1-matrix [18] for Be atom in its ground state. Since ρ_2 is a six-dimensional density, an immediate concern is how one may best summarize this information to affect the comparison. We reduce the dimensionality in two ways. We first fix $\mathbf{r}_1$, which allows us to examine the conditional probability distribution $\rho_2(\mathbf{r}_1|r_2,\theta_2)$ for the second electron. (Because the system is spherically symmetric this distribution is independent of the azimuthal angle ϕ_2.) Second, we derive from ρ_2 the extracule (center of mass) and intracule (relative coordinate) densities [19, 20] for the electron pair, which again reduces the problem to a comparison of two-dimensional densities (but which still contain correlated, two-electron information).

Although the proposed reconstructions generally produce qualitatively (and, in some cases, quantitatively) correct pair densities for electrons of opposite spin, only Valdemoro's reconstruction yields physically reasonable results for electrons with parallel spins. The remaining reconstructions lead to negative values of various same-spin pair densities not only at small values of the electron-electron distance, but in some cases all the way out to a separation of about 1.0 a.u., by which point the density has decayed nearly to zero. This unphysical behavior is ultimately related to the fact that only Valdemoro's reconstruction corresponds to an antisymmetric 2-RDM, and suggests that future development of 1-RDM functional theories should be couched in terms of explicitly antisymmetric reconstructions of the 2-RDM.

This paper is arranged as follows. The Pair Density section provides some formal definitions for the densities and density matrices of interest here. In the Intracule Density: Analytic Formulas section we derive new analytic formulas to evaluate atomic intracule densities using a reconstructed 2-RDM (for which one does not necessarily possess a wavefunction). A similar analysis for the extracule density is carried out in the Extracule Density and Its Relation to $I(\mathbf{u})$ section, where we also provide a mathematical justification for an approximate relationship between atomic intracule and extracule densities that has been reported by Koga [21, 22]. In the Reconstruction Functionals for the Pair Density section we introduce the reconstruction functionals to be analyzed, and in the Numerical Comparison and Discussion section we present Be pair densities obtained from these reconstructions, along with a discussion. The Conclusion section summarizes our results.

The Pair Density

It is convenient to expand the exact RDMs in a basis $\{\varphi_1, \ldots, \varphi_{2\nu}\}$ of orthonormal spin orbitals,

$$\gamma(\mathbf{x}; \mathbf{x}') = \sum_{j,k=1}^{2\nu} \boldsymbol{\gamma}^j_k \varphi^*_j(\mathbf{x}')\varphi_k(\mathbf{x}), \tag{4a}$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \sum_{j_1,j_2=1}^{2\nu} \sum_{k_1,k_2=1}^{2\nu} \boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2} \varphi^*_{j_1}(\mathbf{x}'_1) \times \varphi^*_{j_2}(\mathbf{x}'_2)\varphi_{k_1}(\mathbf{x}_1)\varphi_{k_2}(\mathbf{x}_2). \tag{4b}$$

The tensor $\boldsymbol{\Gamma}$ of expansion coefficients is self-adjoint, $\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2} = (\boldsymbol{\Gamma}^{k_1 k_2}_{j_1 j_2})^*$, and antisymmetric,

$$\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2} = -\boldsymbol{\Gamma}^{j_2 j_1}_{k_1 k_2} = -\boldsymbol{\Gamma}^{j_1 j_2}_{k_2 k_1} = \boldsymbol{\Gamma}^{j_2 j_1}_{k_2 k_1}. \tag{5}$$

The coefficients $\boldsymbol{\gamma}^j_k$ are obtained from the expansion of Γ by contraction,

$$\boldsymbol{\gamma}^j_k = \frac{2}{N-1} \sum_{n=1}^{2\nu} \boldsymbol{\Gamma}^{jn}_{kn}, \tag{6}$$

where N is the number of electrons. This relationship will be denoted $\gamma = {}^2_1\!\downarrow \Gamma$, where ${}^2_1\!\downarrow$ is a linear map consisting of the above partial trace and factor of $2/(N-1)$. The RDMs are normalized such that

$$\operatorname{tr}\Gamma = \sum_{j,k=1}^{2\nu} \boldsymbol{\Gamma}^{jk}_{jk} = \tfrac{1}{2}N(N-1) \tag{7}$$

and

$$\operatorname{tr}\gamma = \sum_{k=1}^{2\nu} \boldsymbol{\gamma}^k_k = N. \tag{8}$$

We wish to integrate over the spin variables, so let us introduce an orthonormal orbital basis $\{\chi_1, \ldots, \chi_\nu\}$ and use this basis to construct the orthonormal spin orbitals $\{\varphi_1, \ldots, \varphi_{2\nu}\}$. We confine our discussion to $\hat{S}_z$ eigenstates and assume, without loss of generality, that the spin orbitals are of pure spin type. Order them such that $\varphi_\kappa(\mathbf{r}, \xi) = \chi_\kappa(\mathbf{r})\alpha(\xi)$ if $\kappa \le \nu$ and $\varphi_\kappa(\mathbf{r}, \xi) = \chi_{\kappa-\nu}(\mathbf{r})\beta(\xi)$ for $\kappa > \nu$. Following integration over ξ_1 and ξ_2 we obtain

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j_1,j_2=1}^{2\nu} \sum_{k_1,k_2=1}^{2\nu} (\boldsymbol{\rho}_2)^{j_1 j_2}_{k_1 k_2} \chi^*_{j_1}(\mathbf{r}_1) \times \chi^*_{j_2}(\mathbf{r}_2)\chi_{k_1}(\mathbf{r}_1)\chi_{k_2}(\mathbf{r}_2) \tag{9}$$

with expansion coefficients

$$(\boldsymbol{\rho}_2)^{j_1,j_2}_{k_1,k_2} = \boldsymbol{\Gamma}^{j_1,j_2}_{k_1,k_2} + \boldsymbol{\Gamma}^{j_1,j_2+\nu}_{k_1,k_2+\nu} + \boldsymbol{\Gamma}^{j_1+\nu,j_2}_{k_1+\nu,k_2} + \boldsymbol{\Gamma}^{j_1+\nu,j_2+\nu}_{k_1+\nu,k_2+\nu} \tag{10}$$

for $j_1, j_2, k_1, k_2 \le \nu$. The tensor $\boldsymbol{\rho}_2$ is self-adjoint but not antisymmetric.

We will also consider spin-resolved two-electron densities. These are obtained by decomposing ρ_2 into spin components,

$$\rho_2 = \rho_2^{\alpha\alpha} + \rho_2^{\alpha\beta} + \rho_2^{\beta\alpha} + \rho_2^{\beta\beta}, \tag{11}$$

where $\rho_2^{\alpha\beta}$, for example, has matrix elements $(\boldsymbol{\rho}_2^{\alpha\beta})^{j_1 j_2}_{k_1 k_2} = \boldsymbol{\Gamma}^{j_1,j_2+\nu}_{k_1,k_2+\nu}$. In developing the formalism that follows, we assume a *spin-compensated* state, defined as one for which the one-electron α- and β-spin densities are identical. In this case $\rho_2^{\alpha\alpha} = \rho_2^{\beta\beta}$ and $\rho_2^{\alpha\beta} = \rho_2^{\beta\alpha}$. $\rho_2^{\alpha\alpha} + \rho_2^{\beta\beta}$ is the pair density of same-spin electrons, while $\rho_2^{\alpha\beta} + \rho_2^{\beta\alpha}$ is the pair density for two electrons with opposite spins.

Intracule Density: Analytic Formulas

In terms of the N-electron wavefunction Ψ, the intracule density $I(\mathbf{u})$ is defined as [19, 20]

$$I(\mathbf{u}) \equiv \sum_{j<k}^{N} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \, \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \times \delta(\mathbf{u} - \mathbf{r}_{jk}) \tag{12}$$

with $\mathbf{r}_{jk} \equiv \mathbf{r}_j - \mathbf{r}_k$. $I(\mathbf{u})$ is thus the expectation value of a local, spin-free, symmetric N-electron operator $\hat{I}$,

$$\hat{I}(\mathbf{u}) \equiv \sum_{j<k}^{N} \delta(\mathbf{u} - \mathbf{r}_{jk}). \tag{13}$$

Consequently [23] its expectation value may be computed using only ρ_2:

$$I(\mathbf{u}) = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \delta(\mathbf{u} - \mathbf{r}_{12})\rho_2(\mathbf{r}_1, \mathbf{r}_2). \tag{14}$$

Starting from the definition of $I(\mathbf{u})$ in Eq. (12) for single- [24] and multi-determinant [25] atomic wavefunctions, Koga and Matsuyama have discussed analytic evaluation of the angular integrals in Eq. (12) for a Slater-type orbital basis. Here we present the analogous derivation starting from the density-matrix formulation of the intracule density, Eq. (14). This allows us to evaluate the intracule and extracule densities associated with reconstructed 2-RDMs. For the radial integrals we furthermore provide analytic formulas that do not appear in the work of Koga and Matsuyama.

Employing the orbital expansion of ρ_2 in Eq. (9) along with the identity

$$\delta(\mathbf{r}) = \frac{1}{8\pi^3}\int d\mathbf{s}\, e^{i\mathbf{r}\cdot\mathbf{s}}, \tag{15}$$

the intracule density may be recast as

$$I(\mathbf{u}) = \frac{1}{8\pi^3}\sum_{j_1 j_2 k_1 k_2} (\boldsymbol{\rho}_2)^{j_1 j_2}_{k_1 k_2} \int d\mathbf{s}\, e^{i\mathbf{u}\cdot\mathbf{s}} F^*_{k_1,j_1}(\mathbf{s}) F_{j_2,k_2}(\mathbf{s}), \tag{16}$$

where

$$F_{j,k}(\mathbf{s}) = \int d\mathbf{r}\, e^{i\mathbf{r}\cdot\mathbf{s}} \chi_j^*(\mathbf{r})\chi_k(\mathbf{r}). \tag{17}$$

To simplify F_{jk} we assume that the orbital basis functions have the form

$$\chi_k(\mathbf{r}) = R_k(r) \mathrm{Y}_{\ell_k, m_k}(\Omega_r), \tag{18}$$

with the notation $\mathbf{r} = (r, \Omega_r) = (r, \theta_r, \phi_r)$. This form of orbital is common in atomic calculations. For molecules, Cartesian Gaussians are more common; evaluation of the intracule density in such a basis has been discussed by Ugalde et al. [26].

In what follows we will make frequent use of the expansion of a plane wave in terms of spherical waves [27],

$$e^{\pm i\mathbf{s}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} (\pm i)^\ell j_\ell(sr) \mathrm{Y}^*_{\ell m}(\Omega_s)\mathrm{Y}_{\ell m}(\Omega_r), \tag{19}$$

where j_ℓ denotes a spherical Bessel function,

$$j_\ell(x) \equiv \left(\frac{\pi}{2x}\right)^{1/2} J_{\ell+1/2}(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}. \tag{20}$$

The angular integrals in $I(\mathbf{u})$ will be evaluated in terms of Gaunt coefficients [28],

$$\begin{aligned} &c^{(\ell)}(\ell_1, m_1; \ell_2, m_2) \\ &\quad\equiv \left[4\pi/(2\ell+1)\right]^{1/2} \\ &\qquad\times \int d\Omega\, \mathrm{Y}_{\ell, m_1-m_2}(\Omega)\mathrm{Y}^*_{\ell_1 m_1}(\Omega)\mathrm{Y}_{\ell_2 m_2}(\Omega) \\ &\quad= \left(\frac{2}{2\ell+1}\right)^{1/2} \\ &\qquad\times \int_0^\pi d\theta \sin\theta\, \Theta_{\ell, m_1-m_2}(\theta)\Theta_{\ell_1 m_1}(\theta)\Theta_{\ell_2 m_2}(\theta), \end{aligned} \tag{21}$$

with $\mathrm{Y}_{\ell m}(\theta,\phi) = (2\pi)^{-1/2}\Theta_{\ell m}(\theta)e^{im\phi}$. The constant factor in the above definition is included to match the integrals tabulated by Condon and Shortley [29]. These can be evaluated analytically in the general case [28], and the result can be written in terms of $3j$-symbols [30]. From the general formula it follows that $c^{(\ell)}(\ell_1, m_1; \ell_2, m_2) = 0$ unless $\ell + \ell_1 + \ell_2$ is even (the parity condition) and $|\ell_1 - \ell_2| \le \ell \le \ell_1 + \ell_2$ (the triangle rule).

Using the expansion (19), we may evaluate the angular integrals in $F_{jk}(\mathbf{s})$ analytically in terms of the Gaunt coefficients,

$$\begin{aligned} F_{j,k}(\mathbf{s}) = \sqrt{4\pi} \sum_{\ell=|\ell_j-\ell_k|}^{\ell_j+\ell_k} & i^\ell \sqrt{2\ell+1}\, c^{(\ell)}(\ell_j, m_j; \ell_k, m_k) \\ & \times \mathrm{Y}^*_{\ell, m_j-m_k}(\Omega_s)\mathcal{H}_\ell\left[R_j^* R_k\right](s). \end{aligned} \tag{22}$$

Here $\mathcal{H}_\ell$ denotes the spherical Bessel transform of order ℓ, an integral transform defined by

$$\mathcal{H}_\ell[f](s) \equiv \int_0^\infty dr\, r^2 j_\ell(sr) f(r). \tag{23}$$

Next substitute Eq. (22) into Eq. (16) and expand $\exp(i\mathbf{u}\cdot\mathbf{s})$ using Eq. (19) once again. To simplify the resulting expression, observe that $(\boldsymbol{\rho}_2)^{j_1 j_2}_{k_1 k_2} = 0$ unless $m_{j_1} + m_{k_1} = m_{j_2} + m_{k_2}$, since the bra- and ket-sides of the density operator must have the same M_L quantum number (we assume that M_L is a good quantum number). Performing the integration over Ω_s, one finds that only the $m = 0$ spherical harmonics survive in the expansion of $\exp(i\mathbf{u}\cdot\mathbf{s})$. We write these as $\mathrm{Y}_{\ell,0}(\theta,\phi) = (2\pi)^{-1/2}\Theta_{\ell,0}(\theta)$, where $\Theta_{\ell,0}(\theta) \propto P_\ell(\cos\theta)$, the ℓth Legendre polynomial, normalized according to

$$\int_0^\pi d\theta\, \sin\theta\, \Theta^2_{\ell,0}(\theta) = 1. \tag{24}$$

The final expression for the intracule density is then

$$\begin{aligned} I(u,\theta) = \frac{1}{\pi^2\sqrt{2}} \sum_{j_1,j_2,k_1,k_2=1}^{\nu} & (\boldsymbol{\rho}_2)^{j_1 j_2}_{k_1 k_2} \delta_{m_{j_1}+m_{k_1}, m_{j_2}+m_{k_2}} \\ & \times \sum_\ell \sum_{\ell_1} \sum_{\ell_2} i^{\ell+\ell_1+\ell_2}(-1)^{\ell_1+m_{j_2}-m_{k_2}} \\ & \times \sqrt{(2\ell+1)(2\ell_1+1)(2\ell_2+1)} \\ & \times c^{(\ell)}(\ell_1, m_{j_1}-m_{k_1}; \ell_2, m_{k_2}-m_{j_2}) \\ & \times c^{(\ell_1)}(\ell_{j_1}, m_{j_1}; \ell_{k_1}, m_{k_1}) c^{(\ell_2)}(\ell_{j_2}, m_{j_2}; \ell_{k_2}, m_{k_2}) \\ & \times \mathcal{H}_\ell\left\{\mathcal{H}_{\ell_1}\left[R^*_{j_1}R_{k_1}\right]\mathcal{H}_{\ell_2}\left[R^*_{j_2}R_{k_2}\right]\right\}(u) \\ & \times P_\ell(\cos\theta). \end{aligned} \tag{25}$$

Some remarks concerning this expression are in order. First, the sums over ℓ, ℓ_1, and ℓ_2 extend formally over all non-negative integers but are truncated in practice by the triangle rule so that, for example, $|\ell_{j_1} - \ell_{j_2}| \le \ell_1 \le \ell_{j_1} + \ell_{j_2}$. Furthermore, $c^{(\ell)}(\ell_1, m_{j_1} - m_{k_1}; \ell_2, m_{k_2} - m_{j_2}) = 0$ except when $\ell + \ell_1 + \ell_2$ is even so $i^{\ell+\ell_1+\ell_2} = \pm 1$. Finally, the fact that $I(\mathbf{u})$ for an atom does not depend upon the azimuthal angle ϕ is easily understood using a coordinate system in which one electron is placed at the origin and the nucleus lies along the z axis. $I(\mathbf{u})$, the conditional probability distribution for a second electron, must then possess cylindrical symmetry about the z axis. $I(\mathbf{u})$ cannot, however, be independent of θ, as this would imply that the presence of the nucleus does not affect the electron distribution.

When the radial functions $R_k(r)$ are Gaussian- or Slater-type functions, the integral transforms $\mathcal{H}_{\ell_1}[R^*_{j_1} R_{k_1}](s)$ and $\mathcal{H}_{\ell_2}[R^*_{j_2} R_{k_2}](s)$ in Eq. (25) may be evaluated analytically. Here we work with Slater-type basis functions and put

$$R_k(r) = \sum_j C_{kj} r^{n_j + \ell_k} e^{-a_j r}, \tag{26}$$

with ℓ_k the orbital angular momentum quantum number for orbital χ_k and $a_j > 0$ for each j. The coefficients $\{C_{kj}\}$ are constrained so that the $R_k(r)$ are orthonormal. To evaluate the integral transforms, let us first write down the spherical Bessel functions explicitly. For even orders they are

$$j_{2n}(x) = \sum_{k=0}^{n} b^{(2n)}_{2k+1} \frac{\sin x}{x^{2k+1}} + \sum_{k=1}^{n} b^{(2n)}_{2k} \frac{\cos x}{x^{2k}}, \tag{27a}$$

where $n = 0, 1, 2, \ldots$. The odd-order functions are given by

$$j_{2n+1}(x) = \sum_{k=0}^{n} b^{(2n+1)}_{2k+1} \frac{\cos x}{x^{2k+1}} + \sum_{k=1}^{n+1} b^{(2n+1)}_{2k} \frac{\sin x}{x^{2k}}. \tag{27b}$$

The constants $\{b^{(j)}_k\}$ are readily obtained from the definition, Eq. (20). Since the product of two Slater-type functions is also a Slater-type function, we content ourselves to evaluate the transform of a generic Slater function $r^n \exp(-ar)$ with $a > 0$.

From Eq. (25) and the triangle rule, it follows that we must calculate $\mathcal{H}_{\ell_1}[R_{j_1} R_{k_1}](s)$ only for $\ell_1 \le \ell_{j_1} + \ell_{k_1}$. The kernel of this transform, $j_{\ell_1}(sr)$, contains powers of r in the denominator up to r^{ℓ_1+1}. However, each term in the function $r^2 R_{j_1} R_{k_1}$ contains an equal or larger power of r, so we need only to evaluate the generic transform $\mathcal{H}_\ell[r^n \exp(-ar)](s)$ for $n \ge 0$. A similar analysis applied to $\mathcal{H}_{\ell_2}[R_{j_2} R_{k_2}](s)$ leads to the same conclusion. The transform is evaluated using standard integrals [31]. For even ℓ (put $\ell = 2p$) we obtain

$$\begin{aligned} \mathcal{H}_{2p}&\left[r^n e^{-ar}\right](s) \\ &= \sum_{k=0}^{p} b^{(2p)}_{2k+1} \frac{(n+1-2k)!\,a^{n+2-2k}}{s^{2k+1}(a^2+s^2)^{n+2-2k}} \\ &\quad \times \sum_{j=0}^{\lfloor (n+1-2k)/2 \rfloor} (-1)^j \binom{n+2-2k}{2j+1} \left(\frac{s}{a}\right)^{2j+1} \\ &\quad + \sum_{k=1}^{p} b^{(2p)}_{2k} \frac{(n+2-2k)!\,a^{n+3-2k}}{s^{2k}(a^2+s^2)^{n+3-2k}} \\ &\quad \times \sum_{j=0}^{\lfloor (n+3-2k)/2 \rfloor} (-1)^j \binom{n+3-2k}{2j} \left(\frac{s}{a}\right)^{2j}, \end{aligned} \tag{28}$$

with $\lfloor q \rfloor$ the greatest integer less than or equal to q. For $\ell = 2p + 1$ the result is

$$\begin{aligned} \mathcal{H}_{2p+1}&\left[r^n e^{-ar}\right](s) \\ &= \sum_{k=0}^{p} b^{(2p+1)}_{2k+1} \frac{(n+1-2k)!\,a^{n+2-2k}}{s^{2k+1}(a^2+s^2)^{n+2-2k}} \\ &\quad \times \sum_{j=0}^{\lfloor (n+2-2k)/2 \rfloor} (-1)^j \binom{n+2-2k}{2j} \left(\frac{s}{a}\right)^{2j} \\ &\quad + \sum_{k=1}^{p+1} b^{(2p+1)}_{2k} \frac{(n+2-2k)!\,a^{n+3-2k}}{s^{2k}(a^2+s^2)^{n+3-2k}} \\ &\quad \times \sum_{j=0}^{\lfloor (n+2-2k)/2 \rfloor} (-1)^j \binom{n+3-2k}{2j+1} \left(\frac{s}{a}\right)^{2j+1}. \end{aligned} \tag{29}$$

That the transform $\mathcal{H}_\ell$ of a Slater-type function may be evaluated analytically does not seem to have been recognized by Koga, Matsuyama, and co-workers in their extensive studies of Hartree–Fock atomic intracule densities [24, 32–34]. Wang and Smith [35], however, have given alternative formulas to our Eqs. (28) and (29) in terms of some recurrence relations. To our knowledge, the outermost transform $\mathcal{H}_\ell$ in Eq. (25) must be evaluated numerically, and for this we use Talman's algorithm [36].

The Extracule Density and Its Relation to $I(\mathbf{u})$

Starting from the 2-CD ρ_2, the extracule density $X(\mathbf{R})$ is defined as [cf. Eq. (14)]

$$X(\mathbf{R}) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \delta\!\left(\mathbf{R} - \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)\right) \rho_2(\mathbf{r}_1, \mathbf{r}_2). \tag{30}$$

The preceding simplifications for $I(\mathbf{u})$ may be applied equally well to $X(\mathbf{R})$. At the risk of seeming repetitive we present the final, simplified form of $X(\mathbf{R})$ so that we may compare it to $I(\mathbf{u})$ in Eq. (25):

$$\begin{aligned}
X(R,\theta) \\
&= \frac{8}{\pi^2\sqrt{2}} \sum_{j_1,j_2,k_1,k_2=1}^{\nu} (\boldsymbol{\rho}_2)_{k_1k_2}^{j_1j_2} \delta_{m_{j_1}+m_{k_1},m_{j_2}+m_{k_2}} \\
&\quad \times \sum_{\ell}\sum_{\ell_1}\sum_{\ell_2} i^{\ell+\ell_1+\ell_2}(-1)^{\ell_1+\ell_2+m_{j_2}-m_{k_2}} \\
&\quad \times \sqrt{(2\ell+1)(2\ell_1+1)(2\ell_2+1)} \\
&\quad \times c^{(\ell)}(\ell_1, m_{j_1}-m_{k_1}; \ell_2, m_{k_2}-m_{j_2}) \\
&\quad \times c^{(\ell_1)}(\ell_{j_1}, m_{j_1}; \ell_{k_1}, m_{k_1}) c^{(\ell_2)}(\ell_{j_2}, m_{j_2}; \ell_{k_2}, m_{k_2}) \\
&\quad \times \mathcal{H}_\ell\big\{\mathcal{H}_{\ell_1}\big[(R_{j_1}^* R_{k_1}) \circ 2\big]\mathcal{H}_{\ell_2}\big[(R_{j_2}^* R_{k_2}) \circ 2\big]\big\}(R) \\
&\quad \times P_\ell(\cos\theta). \qquad (31)
\end{aligned}$$

The notation $f\circ\omega$, where $f = f(x)$ and ω is a constant, denotes the convolution of f with the function ωx, $(f\circ\omega)(x) \equiv f(\omega x)$. This convolution arises in Eq. (31) due to the factor of $1/2$ in the δ-function integrand of Eq. (30).

By changing integration variables one may easily show that for $\omega \neq 0$,

$$\omega^3 \mathcal{H}_\ell[f](\omega s) = \mathcal{H}_\ell\left[f \circ \frac{1}{\omega}\right](s), \qquad (32)$$

or in function notation $\omega^3(\mathcal{H}_\ell[f]\circ\omega) = \mathcal{H}_\ell[f \circ \frac{1}{\omega}]$. Consequently

$$\begin{aligned}
&\mathcal{H}\{\mathcal{H}_{\ell_1}[R_{j_1}^* R_{k_1}]\mathcal{H}_{\ell_2}[R_{j_2}^* R_{k_2}]\}(2R) \\
&\quad = 8\mathcal{H}_\ell\big\{\mathcal{H}_{\ell_1}\big[(R_{j_1}^* R_{k_1}) \circ 2\big]\mathcal{H}_{\ell_2}\big[(R_{j_2}^* R_{k_2}) \circ 2\big]\big\}(R) \qquad (33)
\end{aligned}$$

is an exact symmetry. The reader will recognize that the expression on the right appears in $X(\mathbf{R})$, while the expression on the left appears in $I(2\mathbf{R})$. In light of this, the expressions for $X(\mathbf{R})$ and $I(2\mathbf{R})$ differ only by the factor of $(-1)^{\ell_2}$ that is present in the former. Of course ℓ_2 is a summation index (it runs from $|\ell_{j_2} - \ell_{k_2}|$ to $\ell_{j_2} + \ell_{k_2}$) but this suggests that if ℓ_2 were always even or always odd then we would have $X(\mathbf{R}) \propto I(2\mathbf{R})$. In reality this proportionality is only approximate, as we now show.

Consider the radial (spherically-averaged) intracule and extracule densities, defined as

$$I(u) \equiv \frac{1}{4\pi}\int d\Omega\, I(\mathbf{u}) = \frac{1}{2}\int_0^\pi d\theta\, \sin\theta I(u,\theta) \qquad (34)$$

and

$$X(R) \equiv \frac{1}{4\pi}\int d\Omega\, X(\mathbf{R}) = \frac{1}{2}\int_0^\pi d\theta\, \sin\theta X(R,\theta). \qquad (35)$$

(Other author′ definitions sometimes include a volume factor of $4\pi u^2$ or $4\pi R^2$.) Since

$$\int_0^\pi d\theta\, \sin\theta\,\Theta_{\ell,0}(\theta) = \delta_{\ell,0}\sqrt{2}, \qquad (36)$$

integration over θ introduces a constant and also eliminates the sum over ℓ in $I(\mathbf{u})$ and $X(\mathbf{R})$.

Now consider the expansion coefficients $(\boldsymbol{\rho}_2)_{k_1k_2}^{j_1j_2}$. Even for a correlated, multi-determinant treatment, the expansion coefficients largest in magnitude will be those for which $j_1 = k_1$, $j_2 = k_2$, and the orbitals χ_{j_1} and χ_{j_2} are occupied in the Hartree–Fock determinant. If $j_2 = k_2$ then $\ell_{j_2} = \ell_{k_2}$, which implies that $c^{(\ell_2)}(\ell_{j_2}, m_{j_2}; \ell_{k_2}, m_{k_2}) = 0$ unless ℓ_2 is even. ℓ_2 being even is precisely what we need to establish a proportionality between the intracule and extracule densities. If we neglect all matrix elements of ρ_2 except for the aforementioned largest-magnitude ones, then using the identity in Eq. (33) we obtain the approximate relationship

$$I(2R) \approx X(R). \qquad (37)$$

This provides a sound, mathematical justification for the approximate relation that Koga [21, 22] was able to surmise by examining spherically-averaged Hartree–Fock intracule and extracule densities for each atom from He to Xe [24, 32–34].

In fact, we may arrive at Eq. (37) by retaining all diagonal matrix elements $(\boldsymbol{\rho}_2)_{j_1j_2}^{j_1j_2}$, regardless of whether χ_{j_1} or χ_{j_2} is occupied at the Hartree–Fock level. The argument used to establish the intracule–extracule proportionality is therefore valid beyond the Hartree–Fock approximation, although the approximate proportionality undoubtedly breaks down at correlated levels of theory, where off-diagonal elements of the 2-RDM are more significant. Neglect of the off-diagonal elements of $\boldsymbol{\rho}_2$ could be used in similar fashion to establish a proportionality between $I(2\mathbf{R})$ and $X(\mathbf{R})$, but since these quantities contain an additional sum (over ℓ) relative to their radial counterparts $I(u)$ and $X(R)$, the necessary approximation neglects even more terms. One therefore expects $I(2\mathbf{R}) \approx X(\mathbf{R})$ to be a worse approximation than $I(2R) \approx X(R)$.

Reconstruction Functionals for the Pair Density

A reconstruction functional $\rho_2[\gamma]$ consists of an expression for the elements $(\boldsymbol{\rho}_2)_{k_1k_2}^{j_1j_2}$ in terms of the $\{\boldsymbol{\gamma}_k^j\}$. When γ is the 1-RDM corresponding to a single-determinant (SD) wavefunction, γ is idempotent and the 2-RDM is given by [23]

$$\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2} \overset{\mathrm{SD}}{=} \tfrac{1}{2}\big(\boldsymbol{\gamma}^{j_1}_{k_1}\boldsymbol{\gamma}^{j_2}_{k_2} - \boldsymbol{\gamma}^{j_1}_{k_2}\boldsymbol{\gamma}^{j_2}_{k_1}\big). \tag{38}$$

We denote this relationship for a SD 2-matrix with the shorthand $\Gamma \overset{\mathrm{SD}}{=} \gamma \wedge \gamma$, where "$\wedge$" indicates the above antisymmetrization. For arbitrary (multi-determinant) γ, Eq. (38) is not correct but has been suggested [17, 37] as an approximation in the case of correlated density matrices. This form for Γ may be derived from the fermion anticommutation relations under the approximation that the particle and hole RDMs separate, in the sense described in Refs. [17, 38]. This approximation has also been discussed in relation to cumulant expansions of RDMs [39–41].

$\gamma \wedge \gamma$ is self-adjoint, antisymmetric, and positive semidefinite (positivity is proved in the Appendix; the other two properties are obvious). For nonidempotent γ, however, $\gamma \wedge \gamma$ does not satisfy the contraction and normalization requirements in Eqs. (6) and (8). The two-electron matrix $\gamma \wedge \gamma$ contracts to a one-electron matrix given by

$${}^{2}_{1}{\downarrow}(\gamma \wedge \gamma) = \big(N\gamma - \gamma^2\big)/(N-1) \tag{39}$$

and its normalization is

$$\mathrm{tr}\,(\gamma \wedge \gamma) = \tfrac{1}{2}N(N-\eta), \tag{40}$$

where $\eta = \mathrm{tr}\,\gamma^2/N$.

Recently, several reconstruction functionals unrelated to $\gamma \wedge \gamma$ have been proposed [6, 9–12]. These are known as in the literature as "natural orbital functionals" because they consist of expressions for the matrix elements of $\boldsymbol{\Gamma}$ or $\boldsymbol{\rho}_2$ in terms of the natural occupation numbers (eigenvalues) $\{\lambda_k\}$ of γ,

$$\gamma(\mathbf{x};\mathbf{x}') = \sum_{k=1}^{2\nu} \lambda_k \varphi_k^*(\mathbf{x}')\varphi_k(\mathbf{x}). \tag{41}$$

Henceforth we assume that the φ_k are the natural spin orbitals (NSOs) of γ. We limit our discussion to $\hat{S}_z$ eigenstates and thus assume, without loss of generality, that the φ_k have pure spin type. The proposed natural orbital functionals express $\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2}$ (the expansion coefficient of Γ in the NSO basis) as a function of λ_{j_1}, λ_{j_2}, λ_{k_1}, and λ_{k_2}. Using an example of two noninteracting subsystems, Goedecker and Umrigar [12] have reasoned that $\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2}$ cannot depend on the eigenvalues of γ apart from these four. $\boldsymbol{\Gamma}^{j_1 j_2}_{k_1 k_2}$ could, however, depend explicitly on the form of the NSOs themselves, but this dependence in neglected in approximations proposed to date.

We can subsume many of the proposed reconstruction functionals for Γ into a single formula with one fixed parameter ζ. Thus we define

$$\begin{aligned}\Gamma_\zeta[\gamma](\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &\equiv \frac{1}{2}\sum_{j\neq k}^{2\nu}\big[\lambda_j\lambda_k\varphi_j^*(\mathbf{x}_1')\varphi_k^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2) \\ &\quad - \delta_{s_j,s_k}(\lambda_j\lambda_k)^{\zeta/2}\varphi_k^*(\mathbf{x}_1')\varphi_j^*(\mathbf{x}_2')\varphi_j(\mathbf{x}_1)\varphi_k(\mathbf{x}_2)\big],\end{aligned} \tag{42}$$

where $s_k = \pm 1/2$ is the m_s quantum number for φ_k. (In our indexing scheme, $s_k = +1/2$ if $k \leq \nu$ and $s_k = -1/2$ for $k > \nu$.) The $j = k$ terms excluded above constitute the so-called self-interaction term $\Gamma^{\mathrm{SI}}_\zeta$ Ref. [9],

$$\begin{aligned}\Gamma^{\mathrm{SI}}_\zeta[\gamma](\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') &\equiv \frac{1}{2}\sum_{k=1}^{2\nu}\big(\lambda_k^2 - \lambda_k^\zeta\big) \\ &\quad \times \varphi_k^*(\mathbf{x}_1')\varphi_k^*(\mathbf{x}_2')\,\varphi_k(\mathbf{x}_1)\varphi_k(\mathbf{x}_2).\end{aligned} \tag{43}$$

We define two classes of reconstruction functionals based upon the above ansatz. Because Cioslowski and Pernal [8, 11] have studied the reconstruction functionals Γ_ζ without the self-interaction terms, we refer to the reconstruction $\Gamma_\zeta[\gamma]$ as CP(ζ). (The functional CP(1) is equivalent to an earlier, independent proposal advanced by Goedecker and Umrigar (GU) [6, 12], and CP(2) is equivalent to $\gamma \wedge \gamma$.) When the self-interaction terms are included, so that the approximate 2-RDM is $\Gamma_\zeta + \Gamma^{\mathrm{SI}}_\zeta$, we call the reconstruction SICP(ζ). In the NSO representation, the reconstructed 2-matrix elements are

$$\big(\widetilde{\boldsymbol{\Gamma}}[\gamma]\big)^{j_1 j_2}_{k_1 k_2} = \begin{cases} \tfrac{1}{2}\lambda_{j_1}\lambda_{j_2} & \text{if } j_1 = k_1, j_2 = k_2, \\ & \quad \text{and } j_1 \neq j_2; \\ \tfrac{1}{2}g^{\zeta}_{j_1,j_2}\delta_{s_{j_1},s_{j_2}} & \text{if } j_1 = k_2, j_2 = k_1, \\ & \quad \text{and } j_1 \neq j_2; \\ f_{j_1} & \text{if } j_1 = j_2 = k_1 = k_2; \\ 0 & \text{otherwise,} \end{cases} \tag{44}$$

where $f_j = (\lambda_j^2 - \lambda_j^\zeta)/2$ for the SICP(ζ) functionals and $f_j = 0$ for the CP(ζ) functionals; the function $g^{\zeta}_{j,k} = -(\lambda_j\lambda_k)^{\zeta/2}$ for both functionals. The tilde in $\widetilde{\boldsymbol{\Gamma}}$ is meant to indicate that the reconstruction is approximate.

A few properties of these reconstructions are immediately obvious. Both the CP(ζ) and SICP(ζ) 2-RDMs are self-adjoint but neither is antisymmetric (except when $\zeta = 2$). In either case, $\widetilde{\Gamma}[\gamma](\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \widetilde{\Gamma}[\gamma](\mathbf{x}_2,\mathbf{x}_1;\mathbf{x}_2',\mathbf{x}_1')$ for each ζ. In the next section we demonstrate, by numerical example, that both CP(ζ) and SICP(ζ) can fail to be positive for certain ζ. The SICP(ζ) functionals satisfy the contraction and normalization requirements, Eqs. (6) and (8), but the CP(ζ) functionals do not. Specifically, CP(ζ) contracts to a one-particle matrix whose elements are [cf. Eq. (39)]

$$\left({}^{2}_{1}\!\downarrow \Gamma_{\zeta}[\gamma]\right)^{j}_{k} = \delta_{jk}\frac{\lambda_k(N-\lambda_k)}{N-1}, \tag{45}$$

independent of ζ. The normalization for the CP(ζ) 2-matrix, given previously in Eq. (40), is equal to $N(N-1)/2$ if and only if γ corresponds to a SD. To see this, note that $\eta = 1$ when γ represents a SD, in which case $\operatorname{tr}\Gamma_\zeta = N(N-1)/2$. Conversely, if $\eta = 1$ then $\sum_k \lambda_k^2 = N = \sum_k \lambda_k$. Since $0 \le \lambda_k \le 1$ for each k [42], this implies that each $\lambda_k = 0$ or 1; that is, γ is a SD 1-RDM.

Other properties of these functionals are not so obvious. By examining the homogeneous, spin-compensated electron gas, Cioslowski and Pernal [8, 11] concluded that only when $\frac{4}{5} < \zeta < \frac{4}{3}$ is the reconstruction CP(ζ) consistent with the mutual requirements of homogeneous scaling, N-representability, and stability of the energy functional with respect to perturbations in the 1-matrix. However, these authors later concluded [13] that CP(ζ) cannot furnish an entirely satisfactory description of the homogeneous electron gas for any ζ.

Integration over the spin coordinates in Eqs. (42) and (43) provides an expression for the approximate, reconstructed 2-CD $\widetilde{\rho}_2[\gamma]$. For a spin-compensated state this density has the following matrix elements in the NSO basis:

$$\left(\widetilde{\boldsymbol{\rho}}_2[\gamma]\right)^{j_1 j_2}_{k_1 k_2} = \begin{cases} 2\lambda_{j_1}\lambda_{j_2} & \text{if } j_1 = k_1,\, j_2 = k_2, \\ & \quad\text{and } j_1 \neq j_2; \\ g^{\zeta}_{j_1,j_2} & \text{if } j_1 = k_2,\, j_2 = k_1, \\ & \quad\text{and } j_1 \neq j_2; \\ \lambda^2_{j_1} + h^{\zeta}_{j_1} & \text{if } j_1 = j_2 = k_1 = k_2; \\ 0 & \text{otherwise.} \end{cases} \tag{46}$$

Here $h^{\zeta}_j = \lambda^2_j - \lambda^{\zeta}_j$ for SICP(ζ) and $h^{\zeta}_j = 0$ for CP(ζ). Note that j_1, j_2, k_1, and k_2 above are orbital indices; each is less than or equal to ν within the indexing scheme introduced previously. In contrast, the indices in Eq. (44) are spin-orbital indices and range from 1 to 2ν.

In addition to the CP(ζ) and SICP(ζ) functionals, we will consider the natural orbital functional proposed by Csányi and Arias (CA) [10]. This reconstruction has matrix elements $(\boldsymbol{\rho}_2)^{j_1 j_2}_{k_1 k_2}$ in the natural orbital basis that are given by Eq. (46) with $g^{\zeta}_{j_1,j_2} = -\lambda_{j_1}\lambda_{j_2} - \sqrt{\lambda_{j_1}\lambda_{j_2}(1-\lambda_{j_1})(1-\lambda_{j_2})}$ and $h^{\zeta}_j = \lambda^2_j\lambda_j - 1$. (There is no ζ parameter in CA.) Like the SICP(ζ) functionals, the CA reconstruction satisfies the contraction and normalization constraints of Eqs. (6) and (8) but is not antisymmetric.

To calculate spin-resolved two-electron densities we require the spin components [43, 44] of the reconstructed 2-RDMs, expressed in the orbital basis $\{\chi_1, \ldots, \chi_\nu\}$. The spin component $\Gamma^{\alpha\beta}_{\alpha\beta}$ is identical in each reconstruction considered here and is given (for a spin-compensated state) by

$$\left(\widetilde{\boldsymbol{\Gamma}}[\gamma]^{\alpha\beta}_{\alpha\beta}\right)^{j_1 j_2}_{k_1 k_2} = \tfrac{1}{2}\lambda_{j_1}\lambda_{j_2}\delta_{j_1,k_1}\delta_{j_2,k_2}, \tag{47}$$

where $j_1, j_2, k_1, k_2 \le \nu$ are orbital indices. Since all of the reconstructions considered here satisfy the exact symmetry relation $\Gamma^{\alpha\beta}_{\alpha\beta} = \Gamma^{\beta\alpha}_{\beta\alpha}$ [44], there is no need to consider the $\Gamma^{\beta\alpha}_{\beta\alpha}$ component. The other relevant spin component is

$$\left(\widetilde{\boldsymbol{\Gamma}}[\gamma]^{\alpha\alpha}_{\alpha\alpha}\right)^{j_1 j_2}_{k_1 k_2} = \begin{cases} \frac{1}{2}\lambda_{j_1}\lambda_{j_2} & \text{if } j_1 = k_1,\, j_2 = k_2, \\ & \quad\text{and } j_1 \neq j_2; \\ \frac{1}{2}g^{\zeta}_{j_1,j_2} & \text{if } j_1 = k_2,\, j_2 = k_1, \\ & \quad\text{and } j_1 \neq j_2; \\ \frac{1}{2}h^{\zeta}_{j_1} & \text{if } j_1 = j_2 = k_1 = k_2; \\ 0 & \text{otherwise.} \end{cases} \tag{48}$$

In particular for CP(2) ($\gamma \wedge \gamma$), this works out to be

$$\left[(\boldsymbol{\gamma} \wedge \boldsymbol{\gamma})^{\alpha\alpha}_{\alpha\alpha}\right]^{j_1 j_2}_{k_1 k_2} = \tfrac{1}{2}\lambda_{j_1}\lambda_{j_2}(\delta_{j_1,k_1}\delta_{j_2,k_2} - \delta_{j_1,k_2}\delta_{j_2,k_1}). \tag{49}$$

All of the reconstructions considered herein satisfy the requirement $\Gamma^{\alpha\alpha}_{\alpha\alpha} = \Gamma^{\beta\beta}_{\beta\beta}$ (for spin-compensated states).

Numerical Comparison and Discussion

In this section we compare the approximate reconstructions introduced in the previous section, using accurate configuration interaction (CI) 1- and 2-RDMs for the ground state of Be. For the CP(ζ) and SICP(ζ) reconstructions, we have chosen the representative values $\zeta = 4/5$, 1, and $4/3$. The values $4/5$ and $4/3$ are the endpoints of the range of acceptable ζ values as determined by Cioslowski and Pernal [8, 11], while $\zeta = 1$ corresponds to the GU functional [6, 12]. Since CP(ζ) and $\gamma \wedge \gamma$ do not correctly reproduce the trace of the 2-matrix, densities obtained using these reconstructions have been scaled so that all densities share a common normalization [prior to this renormalization, $\operatorname{tr}(\Gamma_{\mathrm{CI}})/\operatorname{tr}(\gamma \wedge \gamma) \approx 0.972412$].

Reduced density matrices were obtained from Bunge's CI wavefunction [18], which consists of

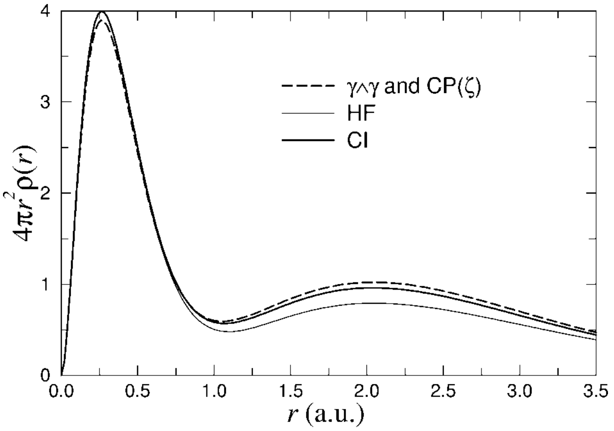

FIGURE 1. One-electron charge densities, $4\pi r^2\rho(r)$, for the Be ground state. The renormalized approximations $\gamma \wedge \gamma$ and CP(ζ) contract to the same one-electron density. On this scale the HF density is indistinguishable from the CI result within the first electron shell.

180 configurations represented in a Hartree–Fock (HF) optimized basis [45] consisting of 96 *s*, *p*, and *d* Slater-type spin orbitals. The resulting energy bound $E_{\mathrm{CI}} = -14.664193$ a.u. recovers 96.7% of the estimated (nonrelativistic) correlation energy of the Be ground state. The total nonrelativistic energy estimated from experiment is -14.667328 ± 25 a.u. [46, 47].

In Figure 1 we plot $4\pi r^2\rho(r)$ for the approximations and the CI calculation. The CA and SICP(ζ) reconstructions satisfy the exact contraction relation, Eq. (6), and therefore yield the same 1-CD as the input CI 1-RDM. The CP(ζ) and $\gamma \wedge \gamma$ densities are identical to one another but deviate somewhat from the CI density. These reconstructions are, however, superior to HF in the second electron shell.

To compare 2-CDs we fix one electron at a distance r_1 from the nucleus and use this electron to define the z axis ($\theta_1 = 0 = \phi_1$). We then examine ρ_2 as a function of r_2 and θ_2. We find that the 2-CD from CP(4/5) becomes negative as the two electrons approach one another, as shown in Figure 2 for $r_1 = 0.1$ a.u. This negativity is most severe when r_1 and θ_2 are small (the case shown in Fig. 2), but for $\theta_2 \approx 0$ persists all the way out to $r_1 \approx 1.0$ a.u. In addition, when $\theta_2 \gtrsim 108°$, the CP(4/5) 2-CD for fixed θ_2 exhibits a local maximum away from $r_2 = 0$. This maximum is not present in the CI 2-CD, which increases monotonically as $r_2 \to 0$ for each fixed value of θ_2.

Also plotted in Figure 2 for the CP(4/5) approximation is the function ρ_2 integrated over the angular variables of the second electron (again with $\mathbf{r}_1$ fixed). Notably, this spherical averaging—which is common in studies of electron pair densities—disguises the negativity of the density as well as its unrealistic deviations from monotonicity.

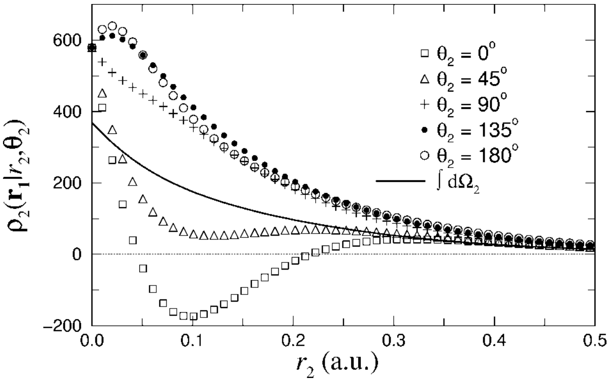

FIGURE 2. Two-electron charge density for the CP(4/5) functional with $r_1 = 0.1$ a.u. and $\theta_1 = 0 = \phi_1$. The solid line represents the spherical average obtained by integrating over the angular variables Ω_2 for the second electron.

Based upon a thorough numerical examination at many fixed values of r_1, we conclude that the remaining reconstruction functionals considered here produce positive 2-CDs that display the correct monotone behavior as $r_2 \to 0$. However, analysis of the spin-resolved pair densities $\rho_2^{\alpha\alpha} + \rho_2^{\beta\beta}$ and $\rho_2^{\alpha\beta} + \rho_2^{\beta\alpha}$ [see Eq. (11)] shows that this is somewhat misleading. In Figure 3 we plot the same-spin pair densities $\rho_2^{\alpha\alpha} + \rho_2^{\beta\beta}$, integrated over θ_2, with $\theta_1 = 0 = \phi_1$ and $r_1 = 0.2655$ a.u. This value of r_1 represents the most probable location for a single electron

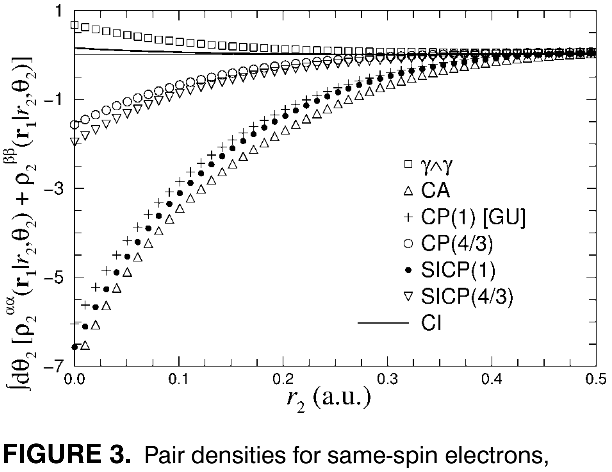

FIGURE 3. Pair densities for same-spin electrons, integrated over θ_2, with $\theta_1 = 0 = \phi_1$ and $r_1 = 0.2655$ a.u.

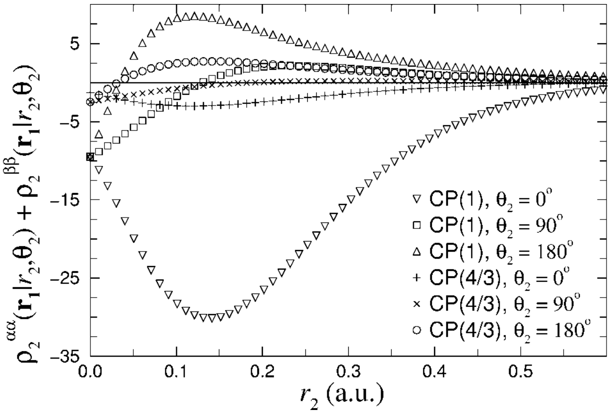

FIGURE 4. Pair densities for same-spin electrons, with $\theta_1 = 0 = \phi_1$ and $r_1 = 0.2655$ a.u. The corresponding CI plots (Fig. 5) increase monotonically as $r_2 \to 0$, reaching a maximum value of 0.246 at $r_2 = 0$.

(see Fig. 1). Of the approximations, only $\gamma \wedge \gamma$ produces a positive same-spin pair density. The lack of positivity in the remaining reconstructions is most pronounced when θ_2 is small, but even for the maximum value $\theta_2 = 180°$, the same-spin pair densities are qualitatively incorrect, as illustrated in Figure 4 for two of the reconstruction functionals.

In contrast, the same-spin pair density from $\gamma \wedge \gamma$ is at least qualitatively correct, although for small r_2 this density is too large (Fig. 3) and for large θ_2 it does not correctly locate the local minimum (Fig. 5). Because $\gamma \wedge \gamma$ is antisymmetric, the exchange hole centered at $r_2 = 0.2655$ a.u. and $\theta_2 = 0$ is recovered.

With the exception of $\gamma \wedge \gamma$, the reconstructed same-spin pair densities are fundamentally incorrect; however, for antiparallel-spin electrons the reconstructed pair densities are good approximations to the CI result, qualitatively as well as quantitatively. Because the opposite-spin density is so much larger than the same-spin density, the total, reconstructed 2-CDs are quite close to the CI result, in spite of the unphysical nature of the same-spin distribution. In order to distinguish between the reconstructed 2-CDs we must subtract out the HF 2-CD, which defines the correlation hole. In Figure 6 we plot the spherically averaged correlation holes for each approximation. As before we have fixed $\theta_1 = 0 = \phi_1$ and $r_1 = 0.2655$ a.u.

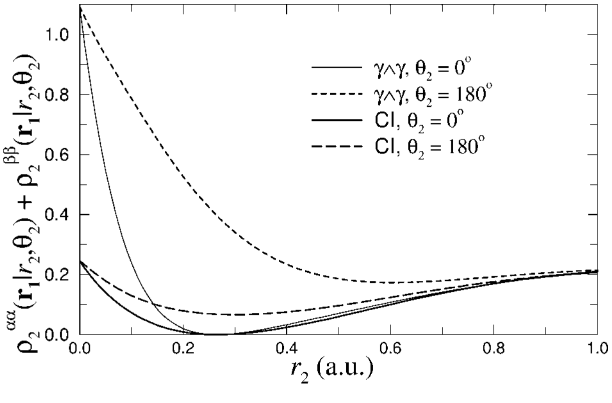

FIGURE 5. Pair densities for same-spin electrons, with $\theta_1 = 0 = \phi_1$ and $r_1 = 0.2655$ a.u.

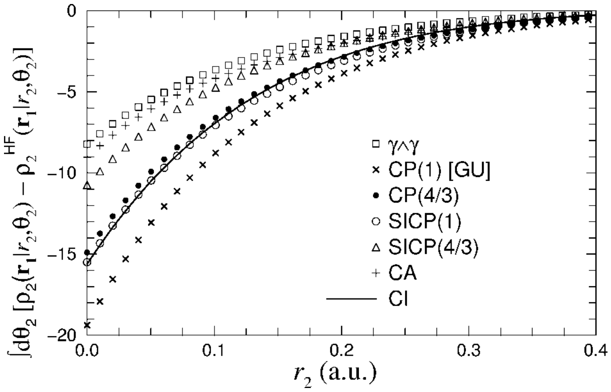

FIGURE 6. Two-electron correlation holes for Be, integrated over θ_2, with $r_1 = 0.2655$ a.u. and $\theta_1 = 0 = \phi_1$.

Figure 6 illustrates several trends that are present at each value of r_1. The $\gamma \wedge \gamma$, CP(4/3), and CA reconstructions each produce a correlation hole that is too shallow. In fact, considering that $\gamma \wedge \gamma$ equals CP(2), we see that the depth of the correlation hole increases as ζ increases. Inclusion of the self-interaction contribution renders the hole more shallow for each ζ, and because the CP(1) correlation hole is too deep, this translates into a very good 2-CD produced with SICP(1). On the other hand, for $\zeta = 4/3$ the approximation is degraded by the inclusion of self-interaction. As $r_1 \to 0$, the absolute deviation from the CI result increases but these trends remain, whereas when $r_1 \to \infty$ all of the reconstructions approach the CI result.

INTRACULE DENSITIES

The radial intracule density $I(u)$ is defined in Eq. (34); in Figure 7 we plot a portion of the function $4\pi u^2 I(u)$. (The complete plot from a CI calculation can be found in Ref. [48], but the approximations considered here are accurate outside the region plotted in Fig. 7.) Shown are the HF and CI results

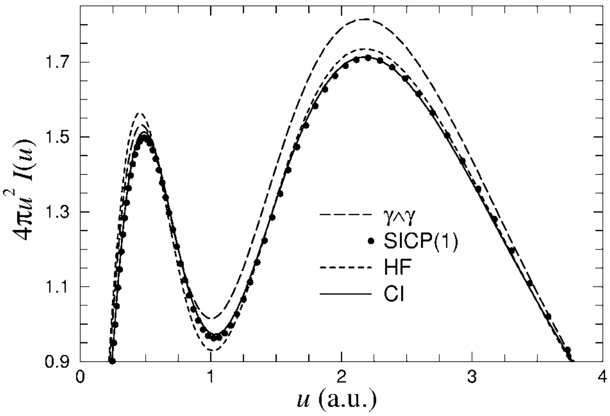

FIGURE 7. Selected region of the radial (spherically averaged) intracule density for Be.

along with two of the approximate reconstructions: SICP(1), which is an extremely close match to $I(u)$ over the entire range of u, and $\gamma \wedge \gamma$, which of all the reconstructions gives the least accurate values for the local minimum and local maxima of $I(u)$. The other reconstructions each lie between the $\gamma \wedge \gamma$ and CI values at these extrema.

To better compare the reconstructions, we plot the correlation hole $4\pi u^2[I(u) - I_{\mathrm{HF}}(u)]$ in Figures 8–10. The $\zeta = 1$ functionals (Fig. 9) reproduce the shape of the hole quite well, meaning that the exact and the approximate densities $I(u)$ have their extrema at the same locations. As we saw with ρ_2, the CP(1) correlation hole is too deep, but when shifted upward by the self-interaction gives good agreement with the CI result. The remaining reconstructions (Figs. 8 and 10) do not locate the extrema in $I(u)$ as accurately and this leads to correlation holes that deviate significantly from the CI result for $u > 1$ a.u. of the second maximum ($u \approx 2.2$ a.u.).

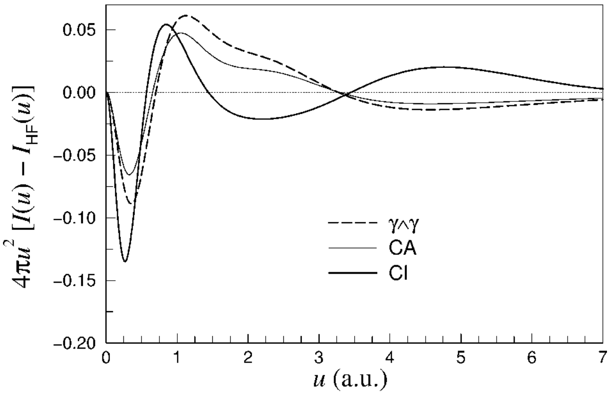

FIGURE 8. Radial intracule correlation holes for Be.

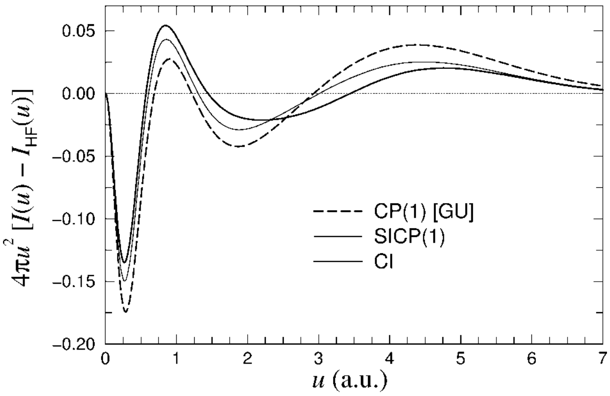

FIGURE 9. Radial intracule correlation holes for Be.

We next decompose the intracule density into spin components using the decomposition of ρ_2 in Eq. (11). The radial intracule density of same-spin electrons is $I_{\alpha\alpha}(u) + I_{\beta\beta}(u)$ where, for example, $I_{\alpha\alpha}(u)$ is obtained by replacing ρ_2 in Eq. (14) with $\rho_2^{\alpha\alpha}$. For a spin-compensated system $I_{\alpha\alpha}(u) = I_{\beta\beta}(u)$, and each of the approximations considered here exactly satisfies this symmetry relation. In Figure 11 we plot $I_{\alpha\alpha}(u) + I_{\beta\beta}(u)$. With the exception of $\gamma \wedge \gamma$, each functional produces an approximate same-spin intracule density that is nonzero (in fact, negative) at $u = 0$, an unphysical behavior that stems directly from the lack of antisymmetry in these reconstructions. The $\gamma \wedge \gamma$ result, on the other hand, is indistinguishable from the CI calculation on the scale in Figure 11. For larger values of ζ the violation of the Pauli Principle is less severe [recall that CP(2) is equivalent to $\gamma \wedge \gamma$], but the presence or absence of the self-interaction makes little difference.

The reconstructed $\Gamma_{\alpha\beta}^{\alpha\beta}$ is the same for each functional considered here and, as shown in Figure 12,

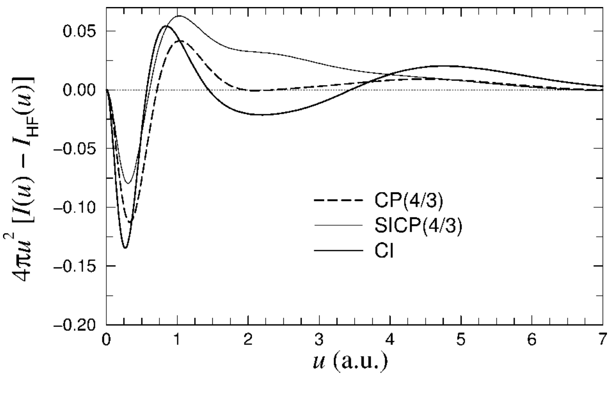

FIGURE 10. Radial intracule correlation holes for Be.

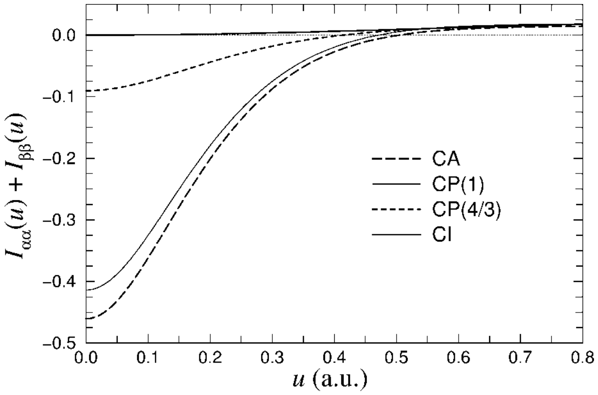

FIGURE 11. Radial intracule densities for parallel-spin electrons. The CP(ζ) results do not differ appreciably from their self-interacting counterparts so the latter are not shown. The $\gamma \wedge \gamma$ density is not shown because it is indistinguishable from the CI result (which is small but nonzero) on this scale.

gives rise to an opposite-spin intracule density that approximates the CI result rather well. Quantitatively, this density is essentially the same as HF (which, for clarity, is not shown in the figure) when $u \lesssim 3$ a.u. For $u > 3$ a.u. the HF density lies between the reconstruction and the CI result.

Finally, in Table I we list the Be ground state energies obtained from each of the approximate 2-RDMs. For a spin-compensated state this calculation requires only the spin components $\Gamma^{\alpha\alpha}_{\alpha\alpha}$ and $\Gamma^{\alpha\beta}_{\alpha\beta}$, which explains why existing 2-RDM reconstructions do not concern themselves with spin components such as $\Gamma^{\alpha\beta}_{\beta\alpha}$, even though this component is related by permutational symmetry to $\Gamma^{\alpha\beta}_{\alpha\beta}$ [44]. Recall that only the CA and SICP(ζ) reconstructions provide a properly normalized 2-matrix, so for the other functionals we also calculate the energy following a uniform scaling of the reconstructed 2-RDM to trace $\binom{N}{2} = 6$.

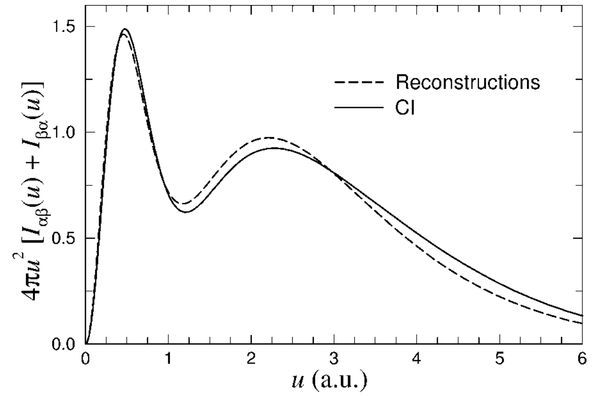

FIGURE 12. Radial intracule densities for two electrons of opposite spin. The $\Gamma^{\alpha\beta}_{\alpha\beta}$ spin component is the same for all approximations considered here [Eq. (47)], hence the opposite-spin intracule densities are the same.

TABLE I

Calculated energies for the Be ground state using reconstructed 2-RDMs. Values in parentheses are the energies prior to renormalization of the 2-RDM. The nonrelativistic energy estimated from experiment is −14.667328 ± 25 a.u. [46, 47].

2-RDM	E/a.u.
$\gamma \wedge \gamma$	−14.20128
	(−14.60418)
CA	−14.54141
CP(4/5)	−14.56732
	(−14.98061)
SICP(4/5)	−14.87729
CP(1) [GU]	−14.37621
	(−14.78407)
SICP(1)	−14.68075
CP(4/3)	−14.25890
	(−14.66343)
SICP(4/3)	−14.60963
HF	−14.57299
CI	−14.66419

Prior to renormalization, the functionals CA, SICP(1), CP(4/3), and $\gamma \wedge \gamma$ produce energies that are closer to the CI energy than is HF. We note that the CP(1) energies in Table I differ from the CI value and from experiment by 0.1 a.u. (0.3 a.u. prior to renormalization), while Goedecker and Umrigar [6] report an essentially correct energy of −14.667 a.u. obtained by minimizing the CP(1) energy functional with respect to variations in the 1-matrix. This indicates that the optimum-energy orbitals obtained by this minimization procedure must differ substantially from the CI NOs.

EXTRACULE DENSITIES

We now focus on the radial center-of-mass distribution $X(R)$ and immediately turn our attention to its same-spin and opposite-spin components. For the former it is found that all approximate reconstructions produce qualitatively incorrect forms for

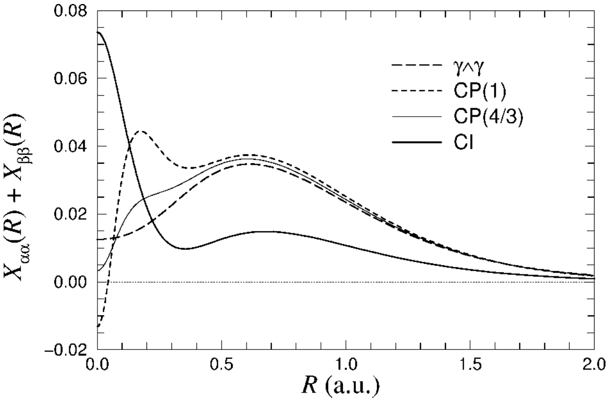

FIGURE 13. Radial (spherically averaged) extracule densities for two electrons of the same spin.

$X_{\alpha\alpha}(R) + X_{\beta\beta}(R)$, as shown in Figure 13. To avoid clutter the SICP(ζ) plots are not included in this figure since the self-interaction terms do not change the extracule density significantly. The same-spin extracule density from CA is almost identical to that of the CP(4/3) functional and is also excluded from Figure 13. It is worth pointing out that a plot of the function $4\pi R^2[X_{\alpha\alpha}(R)+X_{\beta\beta}(R)]$ washes out all of the small-R features that distinguish the reconstructions in Figure 13.

Conclusion

We have compared electron-pair densities reconstructed from the one-electron reduced density matrix γ using the antisymmetrized product $\gamma \wedge \gamma$ suggested by Valdemoro [17] as well as the natural orbital functionals proposed by Goedecker and Umrigar [6, 12], Cioslowski and Pernal [8, 11], and Csányi and Arias [10]. Each of these reconstructions represents a formula for the 2-RDM in terms of the 1-RDM, and each has failings that are general and readily demonstrable. All fail to satisfy the contraction and normalization sum rules, Eqs. (6) and (8), and none save $\gamma \wedge \gamma$ is antisymmetric. For the natural orbital functionals, the former problem may be corrected by adding a self-interaction term that was not included in the work cited above.

Using an accurate 1-RDM for the ground state of Be we have examined the reconstructions numerically. With or without the self-interaction, we find that each natural orbital functional violates the positivity requirement to some degree. (In contrast, $\gamma \wedge \gamma$ is always positive when γ is N-representable, as shown in the Appendix.) The functional CP(4/5) defined previously exhibits large deviations from positivity whenever two electrons approach one another. For the remaining functionals examined here, the reconstructed electron-pair densities for opposite-spin electrons are rather good (quantitatively as well as qualitatively). For electrons of the same spin, $\gamma \wedge \gamma$ correctly describes the shape of the pair density as well as the exchange hole, but the approximate density is too large. The natural orbital functionals, in contrast, produce same-spin pair densities that are negative throughout much of their domains and are qualitatively unreasonable even where they are positive.

Finally, we have examined intracule and extracule densities and their reconstruction from γ. Several of the natural orbital functionals—especially CP(1) and its self-interacting analog, SICP(1)—are able to reproduce the shape (and in some cases, the magnitude) of the intracule and extracule densities quite well. Once again, however, we find that for parallel-spin electrons, the densities obtained from the natural orbital functionals exhibit wild deviations from positivity. In contrast, $\gamma \wedge \gamma$ provides a reasonable description of the same-spin intracule density. $\gamma \wedge \gamma$ also successfully reproduces the opposite-spin extracule density but does not provide a correct description of the same-spin extracule density, a fault shared by each of the natural orbital functionals.

With the exception of the same-spin extracule density, $\gamma \wedge \gamma$ provides a qualitatively correct description of each of the various pair densities examined herein for Be. This is to be contrasted with the nonantisymmetric CA, CP(ζ), and SICP(ζ) functionals, which produce fundamentally incorrect descriptions of the correlated behavior of parallel-spin electrons. For electrons with opposite spins, some of the natural orbital functionals are quite good approximations, although $\gamma \wedge \gamma$ is only slightly worse. Furthermore, the CP(ζ) and $\gamma \wedge \gamma$ reconstructions each violate the contraction and normalization sum rules, Eqs. (6) and (8), by exactly the same amount, and this violation disappears (only) in the single-determinant limit.

On the basis of all these considerations, $\gamma \wedge \gamma$ appears to be the superior reconstruction. This suggests that future efforts to develop 1-RDM functional theories should take antisymmetry to be a paramount constraint for reconstruction of the 2-RDM.

Note Added in Proof

Recently, an alternative form for the CP(ζ) reconstruction has been privately communicated to us by Cyrus Umrigar. This new proposal [cf. Eq. (42)],

$$\begin{aligned}
&\Gamma_\zeta[\gamma](\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') \\
&\quad \equiv \frac{1}{2} \sum_{j \neq k}^{2\nu} \big[\lambda_j \lambda_k \varphi_j^*(\mathbf{x}_1') \varphi_k^*(\mathbf{x}_2') \varphi_j(\mathbf{x}_1) \varphi_k(\mathbf{x}_2) \\
&\qquad\qquad - \lambda_j \lambda_k \delta_{s_j, s_k} \varphi_k^*(\mathbf{x}_1') \varphi_j^*(\mathbf{x}_2') \varphi_j(\mathbf{x}_1) \varphi_k(\mathbf{x}_2) \\
&\qquad\qquad + (1 - \delta_{s_j, s_k}) \big[\lambda_j \lambda_k - (\lambda_j \lambda_k)^{\zeta/2}\big] \\
&\qquad\qquad\quad \times \varphi_k^*(\mathbf{x}_1') \varphi_j^*(\mathbf{x}_2') \varphi_j(\mathbf{x}_1) \varphi_k(\mathbf{x}_2)\big],
\end{aligned}$$

can be shown to yield exactly the same energy as CP(ζ). However, the form above forces the same-spin intracule density to go to zero at the origin. In light of the analysis herein, the above form should be utilized in all future calculations. We thank Cyrus Umrigar for his comments.

Appendix: Positivity of $\gamma \wedge \gamma$

Let

$$\gamma(\mathbf{x}; \mathbf{x}') = \sum_k \lambda_k \varphi_k^*(\mathbf{x}') \varphi_k(\mathbf{x}) \tag{A.1}$$

be an N-representable [42] 1-RDM; that is, $0 \leq \lambda_k \leq 1$ for each k. Define orthonormal spin geminals

$$\Phi_{jk}(\mathbf{x}_1, \mathbf{x}_2) \equiv \frac{1}{\sqrt{2}} \big[\varphi_j(\mathbf{x}_1) \varphi_k(\mathbf{x}_2) - \varphi_k(\mathbf{x}_1) \varphi_j(\mathbf{x}_2)\big]. \tag{A.2}$$

It follows immediately that

$$\begin{aligned}
&\big[\gamma \wedge \gamma\big](\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') \\
&\quad = \frac{1}{2} \big[\gamma(\mathbf{x}_1; \mathbf{x}_1') \gamma(\mathbf{x}_2; \mathbf{x}_2') - \gamma(\mathbf{x}_1; \mathbf{x}_2') \gamma(\mathbf{x}_2; \mathbf{x}_1')\big] \\
&\quad = \sum_{j<k} \lambda_j \lambda_k \Phi_{jk}^*(\mathbf{x}_1', \mathbf{x}_2') \Phi_{jk}(\mathbf{x}_1, \mathbf{x}_2).
\end{aligned} \tag{A.3}$$

Hence $\gamma \wedge \gamma$ has eigenvalues $\lambda_j \lambda_k$ and is therefore positive semidefinite.

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