

Towards a practical pair density-functional theory for many-electron systems

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In pair density-functional theory, the only unknown piece of the energy is the kinetic energy T as a functional of the pair density $P(x_1, x_2)$. Although $T[P]$ has a simpler structure than the Hohenberg-Kohn functional of conventional density-functional theory, computational requirements are still moderate. In the present work, a particularly convenient model system to represent many-electron pair densities is introduced. This “boson pair model” (BPM) approximately treats electron pairs as noninteracting bosons. The resulting explicit model for the kinetic energy $T_2[P]$ is shown to be exact for two-electron systems and a lower bound to $T[P]$ for more than two electrons. The one- and two-particle density matrices obtained from the BPM yield upper bounds for the corresponding many-electron quantities. This suggests a partitioning $T[P] = T_2[P] + T_{\text{eff}}[P]$, where only the remainder $T_{\text{eff}}[P] \geq 0$ needs to be approximated. If the BPM is constrained to yield the exact ground-state pair density, a two-electron Schrödinger equation with an effective local two-particle potential results; the latter is identified as a sum of the bare Coulomb interaction and the functional derivative of $T_{\text{eff}}[P]$. This self-consistent scheme to minimize the energy with respect to P is more efficient than previous procedures. Further information on the functional derivative of $T_{\text{eff}}[P]$ is derived from a contracted Schrödinger equation. Since $T_{\text{eff}}[P]$ is explicitly known in the two-electron and noninteracting (Hartree-Fock) limits, the present method provides an alternative to density-matrix functional theories, which can be exact in the same limits and are similar in computational cost.

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I. INTRODUCTION

In past years, Kohn-Sham (KS) density-functional methods [1] have successfully been applied to a variety of problems in solid-state physics and quantum chemistry. These methods use the one-particle density $\rho(x)$ as the basic variable, which is the probability amplitude of finding an electron at the position $x = (\mathbf{r}, \sigma)$. According to the Hohenberg-Kohn (HK) theorem [2], the ground-state energy is fully determined by ρ ; however, its exchange-correlation part is a complicated functional of the density and difficult to approximate in practice.

An obvious way to tackle this problem is to use a basic variable that contains more information than ρ , so that a smaller portion of the total energy needs to be approximated. The pair density $P(x_1, x_2)$ is a fundamental indicator of correlation effects in many-electron systems. For an N -electron system ($N \geq 2$) in a stationary state Ψ , P is defined by

$$P(x_1, x_2) = N(N-1) \int dx_3 \cdots dx_N |\Psi(x_1, \dots, x_N)|^2. \quad (1)$$

$P(x_1, x_2)$ corresponds to the probability amplitude of finding an electron at the position x_1 and another electron at the position x_2 . Consequently, the one-particle density ρ can be obtained from P by integrating over the position of one electron,

$$\rho(x_1) = \frac{1}{N-1} \int dx_2 P(x_1, x_2). \quad (2)$$

Effective many-particle theories based on the pair distribution function, which is closely related to P , have a long tradition for uniform systems [3–6]. Even in the nonuniform case, the potential energy is fully determined by the pair density, because the nonrelativistic Hamiltonian contains local pair interactions only; the “difficult” term left is just the kinetic energy T as a functional of P . This has motivated HK-type theorems for the ground-state energy and a constrained-search definition of $T[P]$ [7,8] for general systems, which constitutes the foundation of pair density-functional theory (PDFDT).

For the next step towards a working theory of electronic structure, more insight into the structure of $T[P]$ is necessary. Levy and Ziesche [9] have pointed out that $T[P]$ satisfies simple uniform scaling relations, which suggests that it might be easier to approximate than the exchange-correlation functional of density-functional theory. The present work provides an explicit lower bound on $T[P]$ (Sec. V A). Bounds such as, e.g., the Lieb-Oxford bound [10], have been important guidelines in the construction of nonempirical density functionals [11,12]. The bounds presented here are physically motivated by a two-electron-like model for the two-particle density matrix,

$$\Gamma(x_1, x'_1, x_2, x'_2) = N(N-1) \int dx_3 \cdots dx_N \Psi(x_1, x_2, x_3, \dots, x_N) \times \Psi^*(x'_1, x'_2, x_3, \dots, x_N) \quad (3)$$

in terms of the pair density. In this “boson pair” model (BPM), all electron pairs are treated as bosons condensed in

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the same two-electron state $\psi(x_1, x_2)$, as explained in Sec. II B. From the model two-particle density matrix, other quantities related to the kinetic energy such as the one-particle density matrix

$$\gamma(x_1, x'_1) = N \int dx_2 \cdots dx_N \Psi(x_1, x_2, \dots, x_N) \Psi^*(x'_1, x_2, \dots, x_N), \quad (4)$$

the two-electron kinetic energy density

$$\begin{aligned} \Sigma(x_1, x_2) &= N(N-1) \int dx_3 \cdots dx_N |\nabla_1 \Psi(x_1, \dots, x_N)|^2 \\ &= \nabla_1 \nabla'_1 \Gamma(x_1, x'_1, x_2, x_2) \Big|_{x'_1=x_1}, \end{aligned} \quad (5)$$

and the kinetic energy density

$$\tau(x_1) = \frac{N}{2} \int dx_2 \cdots dx_N |\nabla_1 \Psi(x_1, x_2, \dots, x_N)|^2 \quad (6)$$

can be derived. These models are all shown to be bounds to the corresponding exact quantities in Sec. III.

In Sec. IV it is shown that a ψ yielding the exact pair density of any N -electron state satisfies a two-electron Schrödinger equation with an effective local two-particle potential. This motivates a KS-type variational procedure (Sec. V B) which can in turn be used to obtain the exact ground-state pair density and energy from a BPM system. If the BPM provides a reasonable model for the physical system, the remaining unknown piece of the kinetic energy $T_{\text{eff}}[P]$ is small. Important constraints on approximations to $T_{\text{eff}}[P]$ are summarized in Sec. V C, and the prospects of PDFDT compared to other effective many-electron theories are discussed.

II. MOTIVATION

A. Two-electron systems

For two-electron systems, Eq. (1) reduces to

$$P(x_1, x_2) = 2|\Psi(x_1, x_2)|^2. \quad (7)$$

This representation of the pair density by the absolute square of a two-electron wave function is the basic idea that motivates the developments for many-electron systems in the subsequent sections. We shall assume throughout the paper that $P(x_1, x_2)$ does not vanish on a set of nonzero measure and that Ψ is real, i.e., external magnetic fields are absent.

For two-electron systems, the pair density fully determines not only the potential part of the energy but also the kinetic part. As Ψ is real, it follows from Eq. (7) that

$$|\nabla_1 P(x_1, x_2)|^2 = 8P(x_1, x_2) |\nabla_1 \Psi(x_1, x_2)|^2. \quad (8)$$

Therefore,

$$\Sigma(x_1, x_2) = 2|\nabla_1 \Psi(x_1, x_2)|^2 = |\nabla_1 \sqrt{P(x_1, x_2)}|^2, \quad (9)$$

where the second equality holds only for $P(x_1, x_2) \neq 0$. This is “almost everywhere” and sufficient to determine the kinetic energy. (Compare also the discussion in Appendix A.) As a consequence, the kinetic energy density of a two-

electron system is an explicit functional of the pair density,

$$\tau(x_1) = \frac{1}{2} \int dx_2 |\nabla_1 \sqrt{P(x_1, x_2)}|^2. \quad (10)$$

Likewise, the kinetic energy is given by

$$T = \frac{1}{2} \int dx_1 dx_2 |\nabla_1 \sqrt{P(x_1, x_2)}|^2. \quad (11)$$

Since the potential energy is an explicit functional of P as well, it follows that the total energy of two-electron systems (not necessarily in the ground state) is fully determined by the pair density as long as no external magnetic fields are present.

B. The boson pair model

According to Eq. (7), the pair density is simply two times the absolute square of the wave function in the two-electron case. For more than two electrons, we represent the pair density by a two-electron wave function or geminal ψ which satisfies

$$P(x_1, x_2) = N(N-1) |\psi(x_1, x_2)|^2. \quad (12)$$

For a given pair density $P(x_1, x_2)$, Eq. (12) defines the modulus of ψ ,

$$\psi(x_1, x_2) = \sqrt{\frac{P(x_1, x_2)}{N(N-1)}} e^{i\pi k(x_1, x_2)}. \quad (13)$$

ψ is obviously square integrable and normalized to unity. We choose ψ to be real, which implies that the function $k(x_1, x_2)$ can take on integer values. (We will continue to use the complex conjugate of ψ for notational clarity.) In addition, we require ψ to be antisymmetric, which guarantees that $P(x_1, x_1) = 0$. This means that the difference $k(x_1, x_2) - k(x_2, x_1)$ must be an odd number for all x_1, x_2 . $k(x_1, x_2)$ is arbitrary otherwise. This nonuniqueness of ψ is not a flaw of the theory, because the results presented below do not depend on the actual form of $k(x_1, x_2)$ (except on a set of zero measure). The main reason to introduce ψ is to provide an intuitive representation of the pair density, thus keeping the analogy to the two-electron case. As shown in Appendix A, the freedom to choose $k(x_1, x_2)$ may be used to make ψ as well-behaved as possible; the resulting ψ corresponds best to the intuitive notion of a two-electron wave function.

Drawing the analogy to the two-electron case once more, we use ψ to define the model two-particle density matrix,

$$\Gamma_2(x_1, x'_1, x_2, x'_2) = N(N-1) \psi(x_1, x_2) \psi^*(x'_1, x'_2). \quad (14)$$

Γ_2 corresponds to a system of $N(N-1)$ bosonlike electron pairs that are all “condensed” in the same state, ψ . The use of Γ_2 for fermions will therefore be referred to as the “boson pair model” (BPM) in the following. Γ_2 is properly antisymmetric; it also has correct normalization, because it reduces to $P(x_1, x_2)$ for $x'_1 = x_1, x'_2 = x_2$, as does the exact two-particle density matrix. For $N \geq 2$, Γ_2 can never be exact for electrons, however, as the following argument shows. The exact two-particle density matrix has a spectral representation in

terms of natural geminals g_p and geminal occupation numbers ξ_p ,

$$\Gamma(x_1, x'_1, x_2, x'_2) = \sum_p \xi_p g_p(x_1, x_2) g_p^*(x'_1, x'_2). \quad (15)$$

The occupation numbers are bounded by $0 \leq \xi_p \leq N$ for fermions [13]. On the other hand, there is only one geminal with an occupation of number of $N(N-1)$ in the BPM. The BPM is therefore N -representable only for $N=2$, i.e., Γ_2 can be derived from a fermion wave function only for $N=2$. Physically speaking, electron pairs do not behave like non-interacting bosons. This invalidates a straightforward application of the BPM to many-electron systems. Nevertheless, the BPM has important bound properties for many-electron systems, as shown below. In addition, the error that is introduced by the BPM can be corrected in the framework of PDFT, very much in the spirit of the KS method.

The BPM should not be confused with the antisymmetrized geminal power (APG) model where the N -electron wave function is given by an antisymmetrized product of a single geminal [14,15]. The AGP model leads to upper bounds for the total energy; the relation between the geminal generating the wave function and the pair density is complicated, however, which impairs its use in PDFT.

III. BOUNDS FOR MANY-ELECTRON SYSTEMS

A. Reduced two- and one-particle density matrices

While Γ_2 reduces to P as Γ for $x'_1=x_1, x'_2=x_2$, the off-diagonal part of the exact two-particle density matrix is always screened compared to Γ_2 , as stated by the following theorem.

Theorem III.1.

$$|\Gamma(x_1, x'_1, x_2, x'_2)| \leq |\Gamma_2(x_1, x'_1, x_2, x'_2)|. \quad (16)$$

Proof. We start from the definition of the two-particle density matrix (3) and apply the Cauchy-Schwarz inequality to electrons $3, \dots, N$,

$$\begin{aligned} & |\Gamma(x_1, x'_1, x_2, x'_2)|^2 \\ &= \left| N(N-1) \int dx_3 \cdots dx_N \Psi(x_1, x_2, x_3, \dots, x_N) \right. \\ & \quad \left. \times \Psi^*(x'_1, x'_2, x_3, \dots, x_N) \right|^2 \\ &\leq \left[N(N-1) \int dx_3 \cdots dx_N |\Psi(x_1, x_2, x_3, \dots, x_N)|^2 \right] \\ & \quad \times \left[N(N-1) \int dx_3 \cdots dx_N |\Psi(x'_1, x'_2, x_3, \dots, x_N)|^2 \right]. \end{aligned} \quad (17)$$

Using Eq. (12), we arrive at

$$\begin{aligned} |\Gamma(x_1, x'_1, x_2, x'_2)|^2 &\leq N(N-1) |\psi(x_1, x_2)| |\psi(x'_1, x'_2)| \\ &= |\Gamma_2(x_1, x'_1, x_2, x'_2)|. \end{aligned} \quad (18)$$

Next, consider the one-particle density matrix derived from Γ_2 ,

$$\gamma_2(x_1, x'_1) = N \int dx_2 \psi(x_1, x_2) \psi^*(x'_1, x_2). \quad (19)$$

While Γ_2 and hence γ_2 depend on the pair density, the von Weizsäcker model for the one-particle density matrix

$$\gamma_w(x_1, x'_1) = N \chi(x_1) \chi^*(x'_1), \quad (20)$$

where χ satisfies $|\chi(x_1)|^2 = \rho(x_1)/N$, depends on the one-particle density ρ only.

Theorem III.2.

$$|\gamma(x_1, x'_1)| \leq |\gamma_2(x_1, x'_1)| \leq |\gamma_w(x_1, x'_1)|. \quad (21)$$

Proof. The first part of the inequality follows from

$$\begin{aligned} |\gamma(x_1, x'_1)| &= N \left| \int dx_2 \cdots dx_N \Psi(x_1, x_2, \dots, x_N) \right. \\ & \quad \left. \times \Psi^*(x'_1, x_2, \dots, x_N) \right| \\ &\leq N \int dx_2 \left| \int dx_3 \cdots dx_N \Psi(x_1, x_2, \dots, x_N) \right. \\ & \quad \left. \times \Psi^*(x'_1, x_2, \dots, x_N) \right| \end{aligned} \quad (22)$$

by application of the Cauchy-Schwarz inequality to electrons $3, \dots, N$. The second part is obtained by applying the Cauchy-Schwarz inequality with respect to electron 2 to the definition of γ_2 (19). ■

The eigenvalues n_p of the true one-particle density matrix γ , also known as natural orbital occupation numbers, satisfy $0 \leq n_p \leq 1$ for fermion systems [13]. γ_w has only one eigenvalue equal to N ; it therefore corresponds to a fictitious system of N noninteracting bosons in the state χ . As suggested by Theorem III.2, γ_2 compromises between these two cases. Since ψ is an antisymmetric two-electron wave function, the eigenvalues η_p of γ_2 occur in degenerate pairs [13] and satisfy $0 \leq \eta_p \leq N/2$; this follows directly from Eq. (19).

We finally note that the spectral representation of γ_2 ,

$$\gamma_2(x_1, x'_1) = \sum_p \eta_p \phi_p(x_1) \phi_p^*(x'_1), \quad (23)$$

can be used to expand ψ (and hence P) in a particularly convenient way [16,17]. Assuming that the η_p are in descending order, we have

$$\psi(x_1, x_2) = \frac{1}{\sqrt{N}} \sum_p \sqrt{\eta_{2p}} \sigma_{2p}(x_1, x_2), \quad (24)$$

where

$$\sigma_p(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_p(x_1) & \phi_{p-1}(x_1) \\ \phi_p(x_2) & \phi_{p-1}(x_2) \end{vmatrix} \quad (25)$$

■ is a two-particle determinant.

B. Kinetic energy densities

As shown in the previous section, the models Γ_2 and γ_2 provide bounds to the true two- and one-particle density matrices of many-electron systems. In the context of PDFT, the properties of the kinetic energy parts

$$\Sigma_2(x_1, x_2) = N(N-1) |\nabla_1 \psi(x_1, x_2)|^2 \quad (26)$$

and

$$\tau_2(x_1) = \frac{N}{2} \int dx_2 |\nabla_1 \psi(x_1, x_2)|^2 \quad (27)$$

derived from the BPM are of primary interest, because the kinetic energy is the unknown piece of the total energy here. While $|\Gamma_2|$ gives an *upper* bound to the exact two-particle density matrix, the following theorem reveals that Σ_2 is a *lower* bound to the exact two-particle kinetic energy density Σ .

Theorem III.3. For an N -electron system with $N \geq 2$,

$$\Sigma(x_1, x_2) \geq \Sigma_2(x_1, x_2), \quad (28)$$

where $N=2$ is sufficient for the equality to hold.

Proof. We exploit a strategy first used by Hoffmann-Ostenhof and Hoffmann-Ostenhof to derive a lower bound to the kinetic energy density (see below) [18]. From Eq. (1),

$$|\nabla_1 P(x_1, x_2)| = 2N(N-1) \left| \int dx_3 \cdots dx_N \Psi^*(x_1, \dots, x_N) \times \nabla_1 \Psi(x_1, \dots, x_N) \right|, \quad (29)$$

where it has been used that Ψ is real. Since Ψ and $\nabla_1 \Psi$ are square-integrable, the Cauchy-Schwarz inequality holds certainly for electrons 3 to N , yielding

$$|\nabla_1 P(x_1, x_2)|^2 \leq 4 \left[N(N-1) \int dx_3 \cdots dx_N |\Psi(x_1, \dots, x_N)|^2 \right] \times \left[N(N-1) \int dx_3 \cdots dx_N |\nabla_1 \Psi(x_1, \dots, x_N)|^2 \right] = 4P(x_1, x_2) \Sigma(x_1, x_2). \quad (30)$$

On the other hand, Eq. (12) implies that

$$|\nabla_1 P(x_1, x_2)|^2 = 4P(x_1, x_2) \Sigma_2(x_1, x_2). \quad (31)$$

In the two-electron case, equality holds according to Eq. (9). ■

By integration over x_2 in Eq. (28), one obtains another inequality for the many-electron case,

$$\tau(x_1) \geq \tau_2(x_1). \quad (32)$$

The question arises how this is related to the well-known von Weizsäcker bound [18,19] for the kinetic energy density,

$$\tau(x_1) \geq \tau_W(x_1), \quad (33)$$

where the von Weizsäcker kinetic energy

$$\tau_W(x_1) = \frac{N}{2} |\nabla_1 \chi(x_1)|^2 \quad (34)$$

is exact for one-electron systems. τ_2 and τ_W can be formally derived from the upper bound model one-particle density matrices γ_2 and γ_W , respectively. The following theorem shows that the lower bound provided by Eq. (32) is tighter than the von Weizsäcker bound.

Theorem III.4. For $N \geq 2$, we have the combined inequality

$$\tau(x_1) \geq \tau_2(x_1) \geq \tau_W(x_1). \quad (35)$$

Proof. Using the fact that $\gamma_2(x_1, x'_1)$ reduces to $\rho(x_1)$ for $x'_1 = x_1$, we obtain

$$|\nabla_1 \rho(x_1)| = 2N \left| \int dx_2 \psi(x_1, x_2) \nabla_1 \psi(x_1, x_2) \right|. \quad (36)$$

The finiteness of ρ and τ implies that $\psi(x_1, x_2)$ and $\nabla_1 \psi(x_1, x_2)$ are square-integrable, respectively. Thus, the Cauchy-Schwarz inequality can be invoked once more,

$$|\nabla_1 \rho(x_1)|^2 \leq 4N^2 \int dx_2 |\psi(x_1, x_2)|^2 \int dx_2 |\nabla_1 \psi(x_1, x_2)|^2 = 4N\rho(x_1) \int dx_2 |\nabla_1 \psi(x_1, x_2)|^2, \quad (37)$$

or, using $\chi(x_1) = \sqrt{\rho(x_1)/N}$,

$$|\nabla_1 \chi(x_1)|^2 \leq \int dx_2 |\nabla_1 \psi(x_1, x_2)|^2. \quad (38)$$

Inserting the definitions of τ_2 (27) and τ_W (34) yields the second part of Eq. (35), while the first part is given by Eq. (32). ■

A consequence of the last theorem is a combined inequality for the exact kinetic energy T , the two-electron-like kinetic energy

$$T_2 = \frac{N}{2} \int dx_1 dx_2 |\nabla_1 \psi(x_1, x_2)|^2, \quad (39)$$

and the one-electron-like von Weizsäcker kinetic energy

$$T_W = \frac{N}{2} \int dx_1 |\nabla_1 \chi(x_1)|^2. \quad (40)$$

Corollary III.1. For $N \geq 2$,

$$T \geq T_2 \geq T_W. \quad (41)$$

Proof. Integration over x_1 in Eq. (35). ■

We note in passing that the last inequality can be extended in a straightforward manner by using the square root of the n -particle density for $n > 2$.

IV. EFFECTIVE TWO-PARTICLE SCHRÖDINGER EQUATION

For two electrons, ψ can be chosen identical to the wave function which satisfies the two-electron Schrödinger equa-

tion. Again, a generalization to the many-electron case is possible, as stated by the following theorem.

Theorem IV. 1. Consider an N -electron system, $N > 2$, in a stationary state Ψ with energy E . Then ψ satisfies the effective two-electron Schrödinger equation,

$$\left[-\frac{1}{2}(\Delta_1 + \Delta_2) + v(x_1) + v(x_2) + (N-1)\left(\frac{1}{r_{12}} + v_{\text{eff}}(x_1, x_2)\right) \right] \psi(x_1, x_2) = \mu \psi(x_1, x_2), \quad (42)$$

where $\mu = E - E_0(N-2)$, and $E_0(N-2)$ is the ground-state energy of the $(N-2)$ -electron system.

The effective two-particle potential v_{eff} is given by

$$v_{\text{eff}}(x_1, x_2) = v_{\text{scr}}(x_1, x_2) + v_{\text{kin}}(x_1, x_2) + v_{N-2}(x_1, x_2), \quad (43)$$

where

$$v_{\text{scr}}(x_1, x_2) = \frac{1}{N-1} \sum_{i=3}^N \int dx_3 \cdots dx_N \left(\frac{1}{r_{1i}} + \frac{1}{r_{2i}} - \frac{1}{r_{12}} \right) \times |\Phi(x_1, \dots, x_N)|^2, \quad (44a)$$

$$v_{\text{scr}}(x_1, x_2) = \frac{1}{2(N-1)} \int dx_3 \cdots dx_N (|\nabla_1 \Phi(x_1, \dots, x_N)|^2 + |\nabla_2 \Phi(x_1, \dots, x_N)|^2), \quad (44b)$$

$$v_{N-2}(x_1, x_2) = \int dx_3 \cdots dx_N \Phi^*(x_1, \dots, x_N) \times [H_{N-2} - E_0(N-2)] \Phi(x_1, \dots, x_N). \quad (44c)$$

H_{N-2} is the Hamiltonian of the $(N-2)$ -electron system, and

$$\Phi(x_1, \dots, x_N) = \frac{\Psi(x_1, \dots, x_N)}{\psi(x_1, x_2)}. \quad (45)$$

Proof. We start from the Schrödinger equation for the N -particle system,

$$H_N \Psi(x_1, \dots, x_N) = E \Psi(x_1, \dots, x_N). \quad (46)$$

Multiplication by Ψ^* from the left and integration over x_3, \dots, x_N yields, after some rearrangement,

$$\begin{aligned} & -\frac{1}{2} \int dx_3 \cdots dx_N \Psi^*(x_1, \dots, x_N) (\Delta_1 + \Delta_2) \Psi(x_1, \dots, x_N) \\ & + \left(v(x_1) + v(x_2) + \frac{N-1}{r_{12}} \right) |\psi(x_1, x_2)|^2 \\ & + \sum_{i=3}^N \int dx_3 \cdots dx_N \left(\frac{1}{r_{1i}} + \frac{1}{r_{2i}} - \frac{1}{r_{12}} \right) |\Psi(x_1, \dots, x_N)|^2 \\ & + \int dx_3 \cdots dx_N \Psi^*(x_1, \dots, x_N) [H_{N-2} - E_0(N-2)] \\ & \times \Psi(x_1, \dots, x_N) = E |\psi(x_1, x_2)|^2. \end{aligned} \quad (47)$$

After taking the real part of both sides of the equation, the fact can be used that

$$\begin{aligned} \Delta_1 |\psi(x_1, x_2)|^2 &= 2[\psi(x_1, x_2) \Delta_1 \psi(x_1, x_2) + |\nabla_1 \psi(x_1, x_2)|^2] \\ &= \int dx_3 \cdots dx_N [\Psi^*(x_1, \dots, x_N) \Delta_1 \Psi(x_1, \dots, x_N) \\ & \quad + \text{c.c.} + 2|\nabla_1 \Psi(x_1, \dots, x_N)|^2]. \end{aligned} \quad (48)$$

Moreover, since

$$\int dx_3 \cdots dx_N |\Phi(x_1, \dots, x_N)|^2 = 1, \quad (49)$$

we have

$$\begin{aligned} & \int dx_3 \cdots dx_N |\nabla_1 \Phi(x_1, \dots, x_N)|^2 \\ &= \int dx_3 \cdots dx_N \frac{|\nabla_1 \Psi(x_1, \dots, x_N)|^2 - |\nabla_1 \psi(x_1, x_2)|^2}{|\psi(x_1, x_2)|^2}; \end{aligned} \quad (50)$$

analogous relations hold with respect to the second electron coordinate. We thus arrive at

$$\begin{aligned} & -\frac{1}{2} \psi(x_1, x_2) (\Delta_1 + \Delta_2) \psi(x_1, x_2) + \left[v(x_1) + v(x_2) + (N-1) \left(\frac{1}{r_{12}} \right. \right. \\ & \quad \left. \left. + v_{\text{eff}}(x_1, x_2) \right) \right] |\psi(x_1, x_2)|^2 = \mu |\psi(x_1, x_2)|^2, \end{aligned} \quad (51)$$

which leads to Eq. (42). \blacksquare

The factor $(N-1)$ multiplying the interaction potential in Eq. (42) reflects the fact that the number of pair interactions increases quadratically with the number of electrons. The many-electron effects are accounted for by the effective local two-particle potential $v_{\text{eff}}(x_1, x_2)$. Explicit computation of $v_{\text{eff}}(x_1, x_2)$ according to Eqs. (44) requires up to four-particle density matrices. In fact, Eq. (42) may be considered a special case of the contracted Schrödinger equation [20,21], whose approximate solution has been the subject of revived interest [22,23]. However, some statements on the nature of v_{eff} can be derived by elementary means.

Corollary IV.1.

$$v_{\text{eff}}(x_1, x_2) \geq -\frac{N-2}{N-1} \frac{1}{r_{12}}. \quad (52)$$

Proof. Since

$$\frac{1}{r_{1i}} + \frac{1}{r_{2i}} \geq 0 \quad (53)$$

and Φ is normalized according to Eq. (49),

$$v_{\text{scr}}(x_1, x_2) \geq \frac{N-2}{N-1} \frac{1}{r_{12}}. \quad (54)$$

Further, $v_{\text{kin}}(x_1, x_2) \geq 0$ due to Theorem III.3, and $v_{N-2}(x_1, x_2) \geq 0$ due to the variational principle for the $(N-2)$ -electron system. \blacksquare

This result is largely equivalent to the so-called Schrödinger inequality for the square root of the pair density [18]. The bound (52) also implies that the total two-electron potential in Eq. (42) satisfies

$$(N-1)\left(\frac{1}{r_{12}} + v_{\text{eff}}(x_1, x_2)\right) \geq \frac{1}{r_{12}}, \quad (55)$$

which means that the total effective interaction is always more repulsive than in the two-electron case.

V. IMPLICATIONS FOR A PAIR DENSITY-FUNCTIONAL THEORY

A. Lower bound for the kinetic energy functional

The constrained-search [24] definition of the kinetic energy as a functional of the pair density is [7,8]

$$T[P] = \inf_{\Psi \rightarrow P} \langle \Psi | T | \Psi \rangle, \quad (56)$$

where $\Psi \rightarrow P$ means that the infimum is taken over all N -electron states Ψ that yield a given pair density P . An unresolved problem is that the domain D of $T[P]$ is not known. The obvious choice

$$D = \left\{ P | P \text{ symmetric, positive, } \int dx_1 dx_2 P(x_1, x_2) = N(N-1) \right\} \quad (57)$$

might still include pair densities that are not N -representable [25], i.e., there might be P in D that cannot be obtained from any N -electron state.

For N -representable P , Corollary III.1 yields lower bounds on $T[P]$,

$$T[P] \geq T_2[P] \geq T_w[P]. \quad (58)$$

This motivates a restriction of admissible P to

$$E = \{P | P \in D, T_2[P] < \infty\}. \quad (59)$$

The last condition excludes certain pair densities contained in D that lead to an infinite kinetic energy. Whether this is sufficient for the N -representability of P remains an open question.

B. Variational principle for an effective two-electron system

The total energy as a functional of the pair density is

$$E[P] = T[P] + V[P], \quad (60)$$

where the potential energy $V[P]$ is an explicit functional of P ,

$$V[P] = \frac{1}{2} \int dx_1 dx_2 \left(\frac{2}{N-1} v(x_1) + \frac{1}{r_{12}} \right) P(x_1, x_2). \quad (61)$$

The HK-type theorem derived by Ziesche [7] states that the ground-state energy and pair density of an N -electron system can be determined by minimizing $E[P]$ with respect to P . On

the other hand, the results of Sec. III suggest to introduce a new functional

$$T_{\text{eff}}[P] = T[P] - T_2[P] \geq 0 \quad (62)$$

accounting for effects beyond the BPM. The total energy can thus be rewritten

$$E[P] = T_2[P] + V[P] + T_{\text{eff}}[P], \quad (63)$$

where $T_2[P]$ and $V[P]$ are known explicitly. To carry out the actual variation, the effective two-electron wave function ψ is very convenient. We define the Lagrangian

$$\begin{aligned} L[\psi, \epsilon] = & \frac{N}{4} \int dx_1 dx_2 [|\nabla_1 \psi(x_1, x_2)|^2 + |\nabla_2 \psi(x_1, x_2)|^2] \\ & + \frac{N}{2} \int dx_1 dx_2 \left(v(x_1) + v(x_2) + \frac{N-1}{r_{12}} \right) |\psi(x_1, x_2)|^2 \\ & + T_{\text{eff}}[P] - \frac{N}{2} \epsilon \left(\int dx_1 dx_2 |\psi(x_1, x_2)|^2 - 1 \right), \end{aligned} \quad (64)$$

where the real Lagrange multiplier ϵ enforces proper normalization of ψ . P is implicitly related to ψ via Eq. (12). Variation of L with respect to ψ and ϵ leads to the self-consistent scheme

$$\begin{aligned} & \left[-\frac{1}{2}(\Delta_1 + \Delta_2) + v(x_1) + v(x_2) \right. \\ & \left. + (N-1) \left(\frac{1}{r_{12}} + 2 \frac{\delta T_{\text{eff}}[P]}{\delta P(x_1, x_2)} \right) \right] \psi(x_1, x_2) = \epsilon \psi(x_1, x_2), \end{aligned} \quad (65a)$$

$$\int dx_1 dx_2 |\psi(x_1, x_2)|^2 = 1, \quad (65b)$$

which can be solved iteratively for a given (approximate) $T_{\text{eff}}[P]$. A basis-set approach to Eqs. (65) is outlined in Appendix B.

A different but no less useful interpretation of the self-consistent scheme derived above starts from a BPM system instead of a two-electron system. The BPM Lagrangian L_{BPM} satisfies

$$L_{\text{BPM}}[\psi, \epsilon] + T_{\text{eff}}[P] = L[\psi, \epsilon], \quad (66)$$

because $T_{\text{eff}}[P]=0$ for the BPM by definition. Since any pair density contained in E can be represented by the BPM, we may constrain the BPM system to yield the *physical* ground-state pair density P_0 by introducing an additional Lagrange multiplier $w(x_1, x_2)$. The new Lagrangian

$$\begin{aligned} K[\psi, \epsilon, w] = & L_{\text{BPM}}[\psi, \epsilon] + \frac{1}{2} \int dx_1 dx_2 w(x_1, x_2) \\ & \times [N(N-1) |\psi(x_1, x_2)|^2 - P_0(x_1, x_2)] \end{aligned} \quad (67)$$

is required to be stationary with respect to ψ , ϵ , and w ,

$$\left[-\frac{1}{2}(\Delta_1 + \Delta_2) + v(x_1) + v(x_2) + (N-1)\left(\frac{1}{r_{12}} + w(x_1, x_2)\right) \right] \psi(x_1, x_2) = \epsilon \psi(x_1, x_2), \quad (68a)$$

$$\int dx_1 dx_2 |\psi(x_1, x_2)|^2 = 1, \quad (68b)$$

$$N(N-1)|\psi(x_1, x_2)|^2 = P_0(x_1, x_2). \quad (68c)$$

$w(x_1, x_2)$ thus corresponds to a local effective two-particle potential forcing the BPM to yield the exact pair density P_0 . Both Lagrangians, L and K , are stationary at the exact ψ ,

$$\frac{\delta L[\psi, \epsilon]}{\delta \psi(x_1, x_2)} = \frac{\delta K[\psi, \epsilon, w]}{\delta \psi(x_1, x_2)} = 0. \quad (69)$$

Therefore, w is given (up to a constant) by

$$w(x_1, x_2) = 2 \frac{\delta T_{\text{eff}}[P_0]}{\delta P(x_1, x_2)}, \quad (70)$$

which leads back to Eq. (65a).

If P equals a ground-state pair density P_0 , Eqs. (42) and (65a) can be compared as well. Bearing in mind that the functional derivative $\delta T_{\text{eff}}/\delta P(x_1, x_2)$ is only determined up to a constant, we choose

$$\epsilon = \mu, \quad (71)$$

so that

$$2 \frac{\delta T_{\text{eff}}[P_0]}{\delta P(x_1, x_2)} = v_{\text{eff}}(x_1, x_2). \quad (72)$$

This provides an explicit expression for the functional derivative of $T[P]$ via Eq. (43).

C. Discussion and outlook

The practical value of the pair density-functional theory outlined in this work will depend on the availability of approximations to the functional $T_{\text{eff}}[P]$ that are accurate and computationally efficient. Such approximations should satisfy the following properties.

(i) As it follows from Theorem III.3,

$$T_{\text{eff}}[P] \geq 0, \quad (73)$$

where $T_{\text{eff}}[P]=0$ is the exact two-electron limit.

(ii) For noninteracting pair densities P^{det} , $T[P]$ reduces to

$$T[P^{\text{det}}] = \frac{1}{8} \int dx_1 [|\nabla_1 \rho(x_1)|^2 - 2\nabla_1 \nabla_2 P^{\text{det}}(x_1, x_2)|_{x_2=x_1}] / \rho(x_1). \quad (74)$$

This follows from the fact that, for noninteracting systems,

$$|\gamma(x_1, x_2)|^2 = \rho(x_1)\rho(x_2) - P^{\text{det}}(x_1, x_2) \quad (75)$$

is the square of the one-particle density matrix. For electrons with a scaled Coulomb interaction α/r_{12} , the interaction

strength α is accessible from the corresponding pair density P_α via the cusp condition [26,27]. Denoting the average of P_α with respect to all coordinates except r_{12} by $\bar{P}_\alpha(r_{12})$, we have

$$\alpha = \frac{d\bar{P}_\alpha/dr_{12}|_{r_{12}=0}}{\bar{P}_\alpha(0)}. \quad (76)$$

(iii) $T_{\text{eff}}[P]$ has the simple scaling property [9]

$$T_{\text{eff}}[P_\lambda] = \lambda^2 T_{\text{eff}}[P], \quad (77)$$

where $P_\lambda(x_1, x_2) = \lambda^6 P(\lambda \mathbf{r}_1, \sigma_1, \lambda \mathbf{r}_2, \sigma_2)$, and λ is a uniform scaling parameter.

The variational procedure presented in Sec. V B requires a *single* geminal ψ only to determine the ground-state energy and pair density; the computational effort is similar to that of the Hartree-Fock method, as discussed in Appendix B. The present method is therefore considerably more efficient than the independent pair type variational procedure proposed by Ziesche [7], which requires $N(N-1)$ geminals. The price for this improved efficiency is that the portion of the kinetic energy functional that has to be approximated is larger. Whether or not approximations obeying the above list of constraints are accurate enough to rival conventional electronic-structure methods with similar cost needs to be tested in future work.

In view of the very similar computational demands, it is obvious to ask how the present PDFT compares to density-matrix functional theory (DMFT) [28–30] and recent variants such as natural orbital functional theory [31] and the geminal functional theory proposed by Mazziotti [32], which is based on the AGP model. In these methods, the one-particle density matrix is the basic variable but the pair density is unknown, while in the present approach the exact pair density is obtained, but the BPM one-particle density matrix γ_2 is fictitious. The important two-electron and noninteracting (HF) limits are known explicitly in both theories. However, the kinetic energy functional takes on a somewhat simpler form for two-electron systems, while the electron repulsion energy, which is the unknown in DMFT, is simpler in the noninteracting limit. One might say that the two-electron case is the natural limit in PDFT, while the noninteracting (HF) case is the natural limit in DMFT. Significant differences between the two methods arise in the presence of magnetic fields: While the pair density is no longer sufficient to determine the ground state, the total energy is still a unique functional of the one-particle density matrix. A formal advantage of DMFT is the apparent absence of an N -representability problem. On the other hand, PDFT may have some practical advantages, e.g., it greatly facilitates an explicit treatment of short-range correlation effects resulting from the electron coalescence cusp. Both theories are thus complementary to some extent, and it might be worthwhile to investigate if their good sides can be combined.

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APPENDIX A: EXPLICIT CONSTRUCTION OF A WELL-BEHAVED EFFECTIVE TWO-ELECTRON WAVE FUNCTION ψ FROM THE PAIR DENSITY

We seek functions $k(x_1, x_2) \in \mathbf{Z}$ to make the effective two-electron wave function ψ given by Eq. (13) as well-behaved as possible. First, consider regions of configuration space with $P(x_1, x_2) \neq 0$. It is natural to choose

$$\Delta k(x_1, x_2) = 0, \quad P(x_1, x_2) \neq 0, \quad (\text{A1})$$

i.e., k is constant over these regions. Apart from a constant corresponding to a global sign factor of ψ , this fixes k almost everywhere. The relative phase of different regions with non-zero P remains to be determined. This fixes the change of k on nodal hyperplanes of P . We consider a point (z_1, z_2) on a nodal hyperplane. The spatial coordinate perpendicular to the node will be designated by ξ . In a vicinity of (z_1, z_2) , the wave function has the expansion

$$\Psi(z_1, z_2, \xi, x_3, \dots, x_N) = \xi^n \frac{\partial^n \Psi(z_1, z_2, \xi, x_3, \dots, x_N)}{\partial \xi^n} \Big|_{\xi=0} + O(\xi^{n+1}), \quad (\text{A2})$$

$n \in \mathbf{N}$. This leads to

$$\begin{aligned} \psi(z_1, z_2, \xi) &= |\xi^n| \left\{ \int dx_3 \cdots dx_N \left| \frac{\partial^n \Psi(z_1, z_2, \xi, x_3, \dots, x_N)}{\partial \xi^n} \Big|_{\xi=0} \right|^2 \right\}^{1/2} \\ &\quad \times e^{i\pi \Delta k(z_1, z_2) + O(\xi^{n+1})}. \end{aligned} \quad (\text{A3})$$

ψ is continuously differentiable if we choose

$$\Delta k(z_1, z_2) = \begin{cases} 1, & n \text{ odd} \\ 0, & n \text{ even.} \end{cases} \quad (\text{A4})$$

Thus, $\nabla_1 \psi(x_1, x_2)$ exists always, while $\nabla_1 \sqrt{P(x_1, x_2)}$ exists only for even n . The choice (A4) ensures that the phase change is constant over the whole nodal hyperplane, because any change in n from odd to even or vice versa would create an additional node. As a byproduct, the ψ constructed in this way satisfies the Pauli principle, because n is odd for nodes containing electron coalescence points $x_1 = x_2$.

APPENDIX B: BASIS-SET APPROACH TO THE SELF-CONSISTENT SCHEME (65)

1. Separation of the spin degrees of freedom

To eliminate the spin from Eqs. (65), we require conservation of the z component of the total spin. This is a common approximation underlying, e.g., spin-unrestricted HF or KS methods. We denote the spin-constrained quantities by subscripted spin variables, e.g., $\psi_{\sigma, \sigma'}(\mathbf{r}_1, \mathbf{r}_2)$. As a result of the spin constraint, the numbers of α (up) and β (down) spins N_α and N_β are conserved separately, which translates into separa-

rate normalization conditions for same and opposite spin pairs,

$$\int d^3 r_1 d^3 r_2 P_{\sigma \sigma'}(\mathbf{r}_1, \mathbf{r}_2) = N_\sigma (N_{\sigma'} - \delta_{\sigma \sigma'}). \quad (\text{B1})$$

This includes the original normalization condition (65) and thus represents an additional constraint in the variation of L .

2. Introduction of a one-particle basis

The spin-constrained effective two-particle wave function $\psi_{\sigma \sigma'}(\mathbf{r}_1, \mathbf{r}_2)$ may be expanded in a basis of orthonormal one-particle states φ_p ,

$$\psi_{\sigma \sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\frac{N_\sigma (N_{\sigma'} - 1)}{N(N-1)}} \sum_{\substack{pq \\ p < q}} C_{pq}^{\sigma \sigma'} \sigma_{pq}(\mathbf{r}_1, \mathbf{r}_2), \quad (\text{B2a})$$

$$\psi_{\alpha \beta}(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\frac{N_\alpha N_\beta}{N(N-1)}} \sum_{pq} C_{pq}^{\alpha \beta} \varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2). \quad (\text{B2b})$$

$\sigma_{pq}(\mathbf{r}_1, \mathbf{r}_2)$ is a two-electron Slater determinant,

$$\sigma_{pq}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_p(\mathbf{r}_1) & \varphi_q(\mathbf{r}_1) \\ \varphi_p(\mathbf{r}_2) & \varphi_q(\mathbf{r}_2) \end{vmatrix}. \quad (\text{B3})$$

Condition (B1) implies that the expansion coefficients $C_{pq}^{\sigma \sigma'}$ are normalized to unity. $\psi_{\beta \alpha}$ can be eliminated using the Pauli principle,

$$\psi_{\beta \alpha}(\mathbf{r}_1, \mathbf{r}_2) = -\psi_{\alpha \beta}(\mathbf{r}_2, \mathbf{r}_1). \quad (\text{B4})$$

We do not impose any further constraints on the orbitals φ_p here. They may be generated, e.g., by diagonalization of the one-particle part of the Hamiltonian, or by a conventional KS or HF calculation. An alternative emphasizing the analogy to DMFT is the natural orbitals ϕ_p . This special basis reduces $C_{pq}^{\sigma \sigma'}$ to a diagonal matrix of square roots of natural orbital occupation numbers, as explained in Sec. III A. The computational effort remains the same, however, because the natural orbitals now need to be determined together with their occupations numbers. The resulting procedure is analogous to the direct determination of natural orbitals for two-electron systems [33,34].

3. Self-consistent scheme

The spin-constrained Lagrangian as a functional of the coefficient vector C takes the form

$$\begin{aligned}
L[C, \epsilon] = & \frac{1}{2} \sum_{\sigma} \frac{N_{\sigma}(N_{\sigma}-1)}{N-1} \sum_{p < q, r < s} C_{pq}^{\sigma\sigma} [h_{pr} \delta_{qs} + h_{qs} \delta_{pr} - h_{ps} \delta_{qr} - h_{qr} \delta_{ps} + (N-1)(\langle pq|rs\rangle - \langle pq|sr\rangle)] C_{rs}^{\sigma\sigma} + \frac{N_{\alpha} N_{\beta}}{N-1} \sum_{pqrs} C_{pq}^{\alpha\beta} [h_{pr} \delta_{qs} \\
& + h_{qs} \delta_{pr} + (N-1)\langle pq|rs\rangle] C_{rs}^{\alpha\beta} + T_{\text{eff}}[P] - \frac{1}{2} \sum_{\sigma} \frac{N_{\sigma}(N_{\sigma}-1)}{N-1} \epsilon_{\sigma\sigma} \left(\sum_{pq} |C_{pq}^{\sigma\sigma}|^2 - 1 \right) - \frac{N_{\alpha} N_{\beta}}{N-1} \epsilon_{\alpha\beta} \left(\sum_{pq} |C_{pq}^{\alpha\beta}|^2 - 1 \right). \quad (\text{B5})
\end{aligned}$$

Here, matrix elements of the one-particle operators have been gathered into

$$h_{pq} = \int d^3r \left(\frac{1}{2} \nabla \varphi_p(\mathbf{r}) \nabla \varphi_q(\mathbf{r}) + \varphi_p(\mathbf{r}) v(\mathbf{r}) \varphi_q(\mathbf{r}) \right), \quad (\text{B6})$$

and the usual (Dirac) notation for two-electron repulsion integrals is used,

$$\langle pq|rs\rangle = \int d^3r_1 d^3r_2 \frac{\varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2) \varphi_r(\mathbf{r}_1) \varphi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (\text{B7})$$

For simplicity, we have assumed that the external potential v is spin-independent.

We require L to be stationary with respect to C and ϵ . This leads to a set of three nonlinear eigenvalue problems (EVPs) for same and opposite spin pairs,

$$\mathbf{H}^{\sigma\sigma} C^{\sigma\sigma} = \epsilon_{\sigma\sigma} C^{\sigma\sigma}, \quad (\text{B8a})$$

$$C^{\sigma\sigma} T C^{\sigma\sigma} = 1,$$

$$\mathbf{H}^{\alpha\beta} C^{\alpha\beta} = \epsilon_{\alpha\beta} C^{\alpha\beta}, \quad (\text{B8b})$$

$$C^{\alpha\beta} T C^{\alpha\beta} = 1,$$

which constitute the matrix equivalent of the scheme (65). The matrix elements of the effective two-particle Hamiltonians $\mathbf{H}^{\sigma\sigma'}$ are

$$\begin{aligned}
H_{pqrs}^{\sigma\sigma} = & h_{pr} \delta_{qs} + h_{qs} \delta_{pr} - h_{ps} \delta_{qr} - h_{qr} \delta_{ps} + (N-1)(\langle pq|rs\rangle \\
& - \langle pq|sr\rangle) + \langle pq|V_{\text{eff}}^{\sigma\sigma}|rs\rangle - \langle pq|V_{\text{eff}}^{\sigma\sigma}|sr\rangle, \quad (\text{B9a})
\end{aligned}$$

$$\begin{aligned}
H_{pqrs}^{\alpha\beta} = & h_{pr} \delta_{qs} + h_{qs} \delta_{pr} + (N-1)(\langle pq|rs\rangle + \langle pq|V_{\text{eff}}^{\alpha\beta}|rs\rangle), \\
& \quad (\text{B9b})
\end{aligned}$$

where

$$\begin{aligned}
\langle pq|V_{\text{eff}}^{\sigma\sigma'}|rs\rangle = & 2 \int d^3r_1 d^3r_2 \varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2) \\
& \times \frac{\delta T_{\text{eff}}[P]}{\delta P_{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)} \varphi_r(\mathbf{r}_1) \varphi_s(\mathbf{r}_2) \quad (\text{B10})
\end{aligned}$$

contains the functional derivative of T_{eff} and depends on P . P itself is given by

$$P_{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) = N_{\sigma}(N_{\sigma}-1) \sum_{pqrs} C_{pq}^{\sigma\sigma'} C_{rs}^{\sigma\sigma'} \sigma_{pq}(\mathbf{r}_1, \mathbf{r}_2) \sigma_{rs}(\mathbf{r}_1, \mathbf{r}_2), \quad (\text{B11a})$$

$$P_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = P_{\beta\alpha}(\mathbf{r}_2, \mathbf{r}_1)$$

$$\begin{aligned}
= & N_{\alpha} N_{\beta} \sum_{pqrs} C_{pq}^{\alpha\beta} C_{rs}^{\alpha\beta} \varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2) \varphi_r(\mathbf{r}_1) \varphi_s(\mathbf{r}_2). \\
& \quad (\text{B11b})
\end{aligned}$$

In a finite one-particle basis, Eqs. (B8) reduce to a set of finite-dimensional matrix EVPs. Due to the dependence of $\mathbf{H}^{\sigma\sigma'}$ on P , these EVPs are nonlinear, which is the main difference from a standard two-electron configuration-interaction (CI) problem. Starting from an initial guess for P , Eqs. (B8) first need to be solved for the coefficient vector C . After that, a new P is calculated from Eq. (B11); this is repeated until self-consistency is reached. (Efficient implementations will take advantage of approximate second-order methods familiar from HF theory.) For fixed P , the EVPs are efficiently treated by iterative methods [35], because only the lowest eigenvectors are required. The time-determining step is the computation of one matrix-vector product $\mathbf{H}^{\sigma\sigma'} C^{\sigma\sigma'}$ per iteration. Using direct CI techniques [36], the contribution arising from the two-electron integrals $\langle pq|rs\rangle$ becomes almost identical to a Fock matrix construction, which is the time-determining step in direct HF algorithms. Depending on the form of T_{eff} , the additional term $\langle pq|V_{\text{eff}}^{\sigma\sigma'}|rs\rangle$ may require numerical quadrature, but it has the same scaling of cost with N as the two-electron repulsion integrals $\langle pq|rs\rangle$, as long as T_{eff} depends only locally on P and its derivatives. As a result, the cost for solving Eqs. (B8) scales with the same power of N as the cost for a HF calculation, i.e., $O(N^4)$, which may be reduced to $O(N^2)$ by prescreening. The prefactor will be somewhat higher than that of a HF calculation, however.

$\psi_{\alpha\beta}$ is generally a mixture of singlet and triplet wave functions, because the effective Hamiltonian $\mathbf{H}^{\alpha\beta}$ does not commute with the total spin operator. For closed-shell singlet N -electron states, however, $P_{\alpha\beta}$ becomes symmetric, and the solutions of Eqs. (B8b) are either symmetric or antisymmetric. This can be used to reduce the dimensionality of Eqs. (B8b) by a factor of 2. In addition, the same spin contributions to the pair density are identical in the closed-shell singlet case.

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