

# Extended Hartree-Fock method based on pair density functional theory

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A practical electronic structure method in which a two-body functional is the fundamental variable is constructed. The basic formalism of our method is equivalent to Hartree-Fock density matrix functional theory [M. Levy, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987)]. The implementation of the method consists of solving Hartree-Fock equations and using the resulting orbitals to calculate two-body corrections to account for correlation. The correction terms are constructed so that the energy of the system in the absence of external potentials can be made to correspond to approximate expressions for the energy of the homogeneous electron gas. In this work, the approximate expressions we use are based on the high-density limit of the homogeneous electron gas. Self-interaction is excluded from the two-body functional itself. It is shown that our pair density based functional does not suffer from the divergence present in many density functionals when homogeneous scaling is applied. Calculations based on our pair density functional lead to quantitative results for the correlation energies of atomic test cases.

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## I. INTRODUCTION

The most commonly used methods in electronic structure for atoms and molecules are density functional theory<sup>1-4</sup> (DFT) and Hartree-Fock<sup>5,6</sup> (HF) theory. The former is based on the Hohenberg-Kohn theorems, which state that all ground state observables, in particular, the energy, can be written as a functional of the one-body density.<sup>1</sup> Since the functional itself is unknown, in actual implementations the system of interacting electrons is mapped onto an auxiliary system of noninteracting electrons, resulting in the Kohn-Sham single-particle equations.<sup>2</sup> This ansatz implicitly assumes that all densities originating from antisymmetric many-body wave functions can be represented by a noninteracting wave function. The Kohn-Sham energy functional includes a correction term, which is known as the exchange-correlation energy, which accounts for effects of exchange and correlation, and is usually approximated using the theory of the homogeneous electron gas<sup>4,7-13</sup> (HEG). This correction term usually depends on the one-body density, although orbital-dependent variations also exist.<sup>14</sup>

The HF approximation<sup>5,6</sup> is based on the use of a Slater determinant for the many-body wave function; hence, the work-horse equations are also single-particle equations (as in DFT), but exchange is incorporated in this case. Correlation effects are neglected. There are a variety of methods which incorporate correlation effects into HF, such as use of a linear combination of Slater determinants,<sup>6</sup> perturbation theory,<sup>5,6</sup> or a combination thereof, but all at the cost of greatly increasing computational demand<sup>15</sup> (both methods involve the use of virtual orbitals, increasing the size of the Hilbert space, in which the wave function is calculated). The connections between HF and DFT have also been investigated<sup>16,17</sup> and it has been shown that the Hohenberg-Kohn theorems apply within the Hilbert space of Slater determinants; hence, it is in principle possible to construct a DFT that corresponds to HF.

There has also been active interest in extending DFT by using the pair density<sup>18-33</sup> [pair density functional theory (PDFT)] or the density matrix<sup>34-38</sup> as the fundamental variable. Most PDFT studies have dealt with formal issues, an example of an exception being the work of Gonis *et al.*,<sup>30</sup> where an implementation is developed in the context of strongly correlated systems. The development of a practical electronic structure method based on PDFT, and applicable to atomic and molecular systems in general appears to be lacking.

PDFT is an extension of the standard DFT in that the Hohenberg-Kohn theorems<sup>1</sup> are generalized to the two-body (or  $N$ -body) density.<sup>18-21,23,25,26,29,30</sup> Application of the Kohn-Sham ansatz<sup>2</sup> is not straightforward in the case of PDFT since a noninteracting pair density, such as that obtained from a Slater determinant can not represent all possible pair densities arising from an arbitrary antisymmetric wave function. The lack of correlation between electrons with antiparallel spin presents an obstacle to representing an arbitrary antisymmetric many-body wave function via Slater determinants.

An approach that is related to PDFT based on reduced density matrices (RDMs) is also under considerable investigation.<sup>34-38</sup> Levy<sup>35</sup> demonstrated that a correction term due to correlation is a unique functional of the Hartree-Fock density matrix. Levy<sup>35</sup> also suggested possible starting points for the construction of such correlation corrections.

In this work, we construct a PDFT-based method that is robust and simple, and it can be implemented in an HF context. We argue that an *exact* energy functional can, in principle, be constructed based on the HF pair density. Since the HF pair density and one-particle RDM are related one to one, our formalism is equivalent to that derived by Levy.<sup>35</sup> A pair density based correction to HF was also recently suggested by Higuchi and Higuchi.<sup>33</sup>

We also construct approximations to the exact correlation functional via generalizing known scaling relations,<sup>19</sup> which allow the construction of pair density dependent correlation

functionals based on the theory of the HEG.<sup>4,7-13</sup> The method suggested by Higuchi and Higuchi<sup>33</sup> uses the standard scaling relations derived by Levy and Ziesche.<sup>19</sup> In particular, in this work, we construct correlation functionals which correspond to expressions valid for the HEG in the high-density limit<sup>9-13</sup> (expected to be a good approximation for the atomic test cases presented herein). Our procedure can, in principle, be extended to other functional forms (power series in the density, such as the low-density form) for the correlation energy as well. Since our method amounts to implementing a correction term to an HF calculation (to account for correlation), and it does not require the use of virtual orbitals, the scaling with system size is that of HF itself. We apply our method to calculate atomic energies and obtain quantitative agreement with known correlation energies.

We also investigate the properties of our constructed functionals under homogeneous coordinate scaling. DFT correlation energy functionals with logarithmic terms<sup>9-13</sup> are known to be divergent when the scaling parameter is made infinite.<sup>39,40</sup> This behavior contradicts the known<sup>40-42</sup> scaling behavior of the actual correlation energy which is bounded below. It is shown that our correlation functionals do not exhibit this deficiency.

This paper is organized as follows. In Sec. II, the formal development is presented. We describe a procedure to construct correlation functionals based on known scaling relations in PDFT and comment on the properties of the kinetic energy functional. The explicit construction of energy functionals is explained in Sec. III. In Sec. IV, we discuss the details of our calculations. Section V consists of our results and analysis. We conclude our work in Sec. VI.

## II. FORMAL DEVELOPMENT

### A. Two-body density functionals

The ground state energy of a many-body fermionic system has been shown to be a unique functional of the single-particle many-body density matrix.<sup>4,34</sup> In Ref. 35, it was shown that there exists an additive correction to the HF energy functional that depends on the HF one-body RDM. The proof is based on investigating the correspondence between the HF one-body RDM and the one-body potential of a given system. In particular, an exact formula is provided by which one can determine the external potential as a function of the HF orbitals.

In standard DFT, an applicable method is constructed via the Kohn-Sham ansatz.<sup>2</sup> This ansatz involves a mapping between the interacting system of electrons to an auxiliary non-interacting one, enabling the use of single-particle equations. The solutions of the single-particle equations are single-particle orbitals, and one must choose a way of writing the density in terms of these single particle orbitals. The most often used choice is the one that satisfies the Pauli principle,

$$\rho(\mathbf{r}) = \sum_{i,\sigma} f_{i,\sigma} |\phi_{i,\sigma}(\mathbf{r})|^2, \quad (1)$$

where  $\rho(\mathbf{r})$  denotes the density  $f_{i,\sigma}$  denotes an occupation number and  $\phi_{i,\sigma}(\mathbf{r})$  denotes a particular spin orbital. Usually

$f_{i,\sigma}=1$  which corresponds to the unrestricted HF density. To our knowledge, it is not proved that the noninteracting form for the density based on a single determinant can represent all interacting densities corresponding to antisymmetric many-body wave functions.

While standard DFT was made into an applicable electronic structure method by the Kohn-Sham ansatz, the generalization of the ansatz to the case of two-body functionals such as the pair density is not straightforward due to representability issues.<sup>26-29,32</sup> Writing a *noninteracting* energy functional requires the definition of the pair density  $n(\mathbf{r}, \mathbf{r}')$  in terms of the orbitals of the noninteracting system. An obvious initial choice is

$$n_{HF}(\mathbf{r}, \mathbf{r}') = \sum_{i,j,\sigma,\sigma'} \{ |\phi_{i,\sigma}(\mathbf{r})|^2 |\phi_{j,\sigma'}(\mathbf{r}')|^2 - \phi_{i,\sigma}(\mathbf{r}) \phi_{i,\sigma}(\mathbf{r}') \phi_{j,\sigma'}(\mathbf{r}) \phi_{j,\sigma'}(\mathbf{r}') \}, \quad (2)$$

which is obtained from a Slater determinant (also known as the Hartree-Fock pair density). When this definition for the pair density is used, it can be shown that the motion of electrons with antiparallel spins is uncorrelated.<sup>5</sup> Since this is not so for the antisymmetric many-body wave function, exact representation of an interacting system by a noninteracting one does not appear to be possible. In the theory of correlated wave functions, this effect is usually implemented via the cusp condition for correlation factors.<sup>8</sup>

On the other hand, using the result of Levy,<sup>35</sup> one can easily argue that the energy is a unique functional of the Hartree-Fock pair density since the density matrix and the Hartree-Fock pair density are in a one-to-one relation. Hence, the correlation energy may be written, as

$$E_c[n_{HF}] = \tilde{E}[n_{HF}] - E_{HF}[n_{HF}], \quad (3)$$

i.e., as a unique functional of the HF two-body density [in Eq. (3),  $\tilde{E}[n_{HF}](E_{HF}[n_{HF}])$  denote the exact energy (Hartree-Fock energy) as a functional of the Hartree-Fock pair density  $n_{HF}$ ]. Below, we construct approximations for  $E_c[n_{HF}]$ .

Here, as in the case of DFT, arguments based on mappings establish one-to-one relations between observables (ground state energy) and coordinate-dependent functionals (density); however, the exact functional relations are not given by the formalism. While in the Kohn-Sham DFT method a mapping between noninteracting and interacting systems is invoked, where the two are constrained to have the same density, in the formalism developed above one does not have the two-body density readily available. Although, in principle, a perturbative approach carried out to infinite order gives an exact solution, in practice one has to content oneself with an approximate solution to this problem. Higuchi and Higuchi<sup>33</sup> suggested minimizing the energy of an augmented Hartree-Fock equation, but this method can only be approximate due to lack of opposite-spin correlation. Possible alternative approaches are perturbation theory,<sup>10,11,43</sup> two-body generalization of plane-wave perturbation theory,<sup>11</sup> or variational approaches such as the Fermi hypernetted-chain<sup>44,45</sup> method. A two-body density can also be obtained from an HF solution via constructing a Jastrow-Slater wave function

to generally account for correlation, and the relevant observables could be evaluated by quantum Monte Carlo methods.<sup>46</sup> In all of these methods, the HF wave function serves as input, and the output consists of the many-body properties.

Unfortunately, our formalism does not provide an inversion formula that can be used to determine the two-body potential from the two-body density in the HF case. This is due to the fact that, although the HF two-body density is a two-body object, it is composed of single-particle orbitals. If a particular two-body potential is assumed (Coulomb repulsion between electrons), then the inversion formula presented by Levy<sup>35</sup> can be used to obtain the one-body potential.

The method constructed from the above reasoning requires an HF calculation, supplemented by a correction term due to correlation. The correction term is a functional of the HF pair density. Knowledge of the HF wave function gives exact information about the ground state energy (and by extension all ground state observables) in principle, and it is not necessary to calculate the exact wave-function, if one is interested only in ground state expectation values. This cannot be done exactly due to the lack of the exact functional form, and approximation schemes need to be conceived for the particular set of observables in mind. In this study, we develop such a scheme for the ground state energy, or more specifically, the correlation energy.

### B. Generalized scaling relations and sum rules

To construct correlation functionals  $E_c[n_{HF}]$ , we write the scaling relations due to Levy and Ziesche.<sup>19</sup> In Ref. 19, it was shown that possible terms that contribute to an expansion of the kinetic energy functional (per particle) of the form

$$t[n] = \frac{1}{N} \sum_b A_b \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}, \mathbf{r}')^a |\mathbf{r} - \mathbf{r}'|^b, \quad (4)$$

must be such that the relation  $6a - b = 8$  is satisfied. To derive the HF kinetic energy functional for the *homogeneous* case, we substitute the relation

$$n_{HF}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|) \quad (5)$$

into Eq. (4). In Eq. (5),  $\rho$  denotes the one-body density and  $g(r)$  denotes the radial distribution function. Using the dimensionless distance scaled by the Fermi wave-vector  $x = k_F r$ , where  $k_F = (3\pi^2 \rho)^{1/3}$ , elementary manipulations lead to the kinetic energy expression

$$t[n_{HF}] = \rho^{2/3} \sum_b \tilde{A}_b \int_0^\infty dx x^{b+2} g(x)^a, \quad (6)$$

where<sup>4,9</sup>

$$g(x) = \left\{ 1 - \frac{9}{2x^6} [\sin(x) - x \cos(x)]^2 \right\}. \quad (7)$$

The “ $\sim$ ” on  $\tilde{A}_b$  indicates that some constants have been absorbed into  $\tilde{A}_b$ . It is well known<sup>3,4,9</sup> that the kinetic energy in the HF approximation can be written as

$$t[n_{HF}] = \frac{3}{10} (3\pi^2)^{2/3} \rho^{2/3}, \quad (8)$$

thus, from Eqs. (6) and (8), a sum rule is established on the coefficients  $\tilde{A}_b$  for the homogeneous noninteracting case, which we write as

$$\sum_b \tilde{A}_b \int_0^\infty dx x^{b+2} g(x)^a = \frac{3}{10} (3\pi^2)^{2/3}. \quad (9)$$

Regarding an homogeneous interacting system, we can also conclude from the above analysis that if the kinetic energy exhibits scaling other than  $\rho^{2/3}$ , then the scaled radial distribution function  $g(x)$  also depends on the density.

It is possible and useful to generalize the scaling relations of Levy and Ziesche<sup>19</sup> so that a particular functional can reproduce a given density dependence when a homogeneous noninteracting system is invoked. A general functional of the pair density  $n$  may be written

$$f(\Gamma)[n] = \frac{1}{N} \sum_a C_a \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}, \mathbf{r}')^a |\mathbf{r} - \mathbf{r}'|^b, \quad (10)$$

where the condition  $6a - b = 6 + \Gamma$  has to be satisfied. For the homogeneous noninteracting case [i.e., when Eq. (5) is substituted for  $n_{HF}$ ],  $f(\Gamma)[n]$  will exhibit a density scaling

$$f(\Gamma)[n_{HF}] = \Omega_\Gamma \rho^\Gamma, \quad (11)$$

resulting in the generalized sum rule

$$\Omega_\Gamma = \sum_a \tilde{C}_a \int_0^\infty dx x^{b+2} g(x)^a, \quad (12)$$

which is valid for the auxiliary non-interacting system. The  $\sim$  on  $\tilde{C}_a$  indicates that some constants have been absorbed into  $\tilde{C}_a$ . By using Eq. (11), one can construct pair density analogs for correlation functionals that are given in terms of power series in the density  $\rho$  (examples are the low- and high-density approximations). It is also possible to obtain sum rules of the form Eq. (12) valid for the correlation energy.

### C. Properties of the kinetic energy functional

The properties of the integral in Eq. (6) can now be studied since the functional form of the radial distribution function is known [Eq. (7)]. The behavior of  $g(x)$  at zero and infinity place bounds on the exponent  $a$  (and hence  $b$ ). At large distances,  $g(x)^a$  approaches 1; hence,

$$b + 2 < -1. \quad (13)$$

Close to zero, however,  $g(x)$  for the unpolarized case approaches a constant ( $\frac{1}{2}$ ), which leads to the relation

$$b + 2 > -1, \quad (14)$$

which is inconsistent with Eq. (13). Hence, for the spin-unpolarized case, the integral is divergent. This divergence is due to the radial distribution function being finite at the origin in the case of the *ideal* Fermi gas.

The divergence can be eliminated in several ways. One is to assume that the kinetic energy is a sum of terms, one for

each electron spin component. The radial distribution function corresponding to one spin component only is zero at the origin; therefore, the divergence does not arise. In HF, this procedure is implicit. Corrections to the energy functional can also be constructed in terms of the exchange hole, as is done below.

### III. CONSTRUCTION OF ENERGY FUNCTIONALS

Since the HF method is now well established, our principal aim is to construct energy functionals that are tractable by equivalent numerical methods. To achieve this aim, we construct approximations for the correlation energy  $E_c$  in terms of the Hartree-Fock pair density. Since in the HF theory of the HEG the quantity that appears is the so called exchange-correlation hole defined as

$$n_{xc}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}'), \quad (15)$$

we find it more convenient to use  $n_{xc}$  as our fundamental quantity (input function). Below, we derive approximations from the theory of the HEG, and in HEG, the energy would diverge without the constant positive background. The second term in Eq. (15) corresponds to the positive background; hence, the divergence is canceled. The scaling relations derived in the previous section are valid for  $n_{xc}$  as well since both terms on the right-hand side of Eq. (15) exhibit the same coordinate scaling. When the HF approximation is invoked, the exchange correlation hole becomes the exchange hole

$$n_x(\mathbf{r}, \mathbf{r}') = - \sum_{i,j,\sigma} \phi_{i,\sigma}(\mathbf{r})\phi_{i,\sigma}(\mathbf{r}')\phi_{j,\sigma}(\mathbf{r})\phi_{j,\sigma}(\mathbf{r}'). \quad (16)$$

Equation (16) reintroduces self-interaction, which can be excluded here by restricting the summation to  $i \neq j$ ,

$$\tilde{n}_x(\mathbf{r}, \mathbf{r}') = - \sum_{i \neq j, \sigma} \phi_{i,\sigma}(\mathbf{r})\phi_{i,\sigma}(\mathbf{r}')\phi_{j,\sigma}(\mathbf{r})\phi_{j,\sigma}(\mathbf{r}'), \quad (17)$$

where the prime indicates the self-interaction corrected (SIC) sum. In the two-body density functional theory presented here, self-interaction is thus excluded from the density functional itself. In DFT, SIC is usually achieved by subtracting energies (LSD energy functionals for Hartree, exchange, and correlation) corresponding to single-particle densities.<sup>14</sup> Recently, Lundin and Eriksson<sup>47</sup> proposed a SIC procedure where the self-interaction is addressed by subtracting single-particle densities from the total density.

It has been pointed out based on scaling arguments in the case of the exchange energy that self-interaction terms disappear in the thermodynamic limit.<sup>48,49</sup> The reason for the disappearance of the self-interaction terms is that self-interaction terms have to scale as  $N$  with the number of particles, whereas the overall number of interactions between different particles scales as  $N(N-1)/2$ . An underlying assumption of the argument which is valid for the exchange energy is a single-particle picture, in which one can decompose the interactions between different pairs of particles. Since the correlation energy in the high-density limit which serves as the basis for our approximations here is also a

TABLE I. Table of constants for different correlation energy functionals (Har) [functional forms are given in Eqs. (20) and (22)].

	Gell-Mann and Brueckner	Nozières and Pines	RPA
$A_c$	-0.048	-0.058	-0.071
$B_c$	+0.0311	+0.016	+0.0311
$A$	-0.0619	-0.0649	-0.0859
$B$	-0.0104	-0.00517	-0.0104
$\tilde{A}$	-0.0598	-0.0639	-0.0838
$\tilde{B}$	-0.0622	-0.031	-0.0622

single-particle based expression (the diagrammatic summation gives an operator whose expectation value has to be evaluated over a Slater determinant<sup>9,12,13</sup>) and it is also valid in the thermodynamic limit, the arguments in Refs. 48 and 49 are valid for the correlation functionals used here [below Eq. (18)] as well. Thus, the expressions used below for the correlation energy [Eq. (18)], which are valid in the thermodynamic limit, do not exhibit self-interaction. It can also be expected that use of the SIC exchange hole to reproduce the functionals such as Eq. (18) is thus, advantageous since it lacks self-interaction by construction.

In addition to power series forms, it is also possible to represent logarithmic terms in a pair density context. A simple functional form for the correlation energy per particle common to the approximations of Gell-Mann and Brueckner<sup>12</sup> (GB), Nozières and Pines,<sup>13</sup> (NP), and the random-phase approximation<sup>9</sup> (RPA) may be written as

$$e_c(r_s) = A_c + B_c \ln r_s, \quad (18)$$

or taking advantage of the definition of  $r_s$ ,

$$\frac{4\pi r_s^3}{3} = \frac{1}{\rho}, \quad (19)$$

$$e_c(\rho) = A + B \ln \rho. \quad (20)$$

The first term (constant  $A$ ) converts analogously to Eqs. (4) and (6). In the local-density approximation for DFT without SIC, the constant term would correspond to  $AN$ , where  $N$  denotes the number of particles. The second term, however, can be written in a PDFT form as

$$B \ln \rho = C + \frac{D}{2N} \int d\mathbf{r} d\mathbf{r}' \tilde{n}_x(\mathbf{r}, \mathbf{r}') \ln |\mathbf{r} - \mathbf{r}'|, \quad (21)$$

and hence one can arrive at a PDFT analog of the form

$$e_c[\tilde{n}_x] = \tilde{A} + \frac{\tilde{B}}{2N} \int d\mathbf{r} d\mathbf{r}' \tilde{n}_x(\mathbf{r}, \mathbf{r}') \ln |\mathbf{r} - \mathbf{r}'|. \quad (22)$$

The derivation of the constants analogously proceeds to the derivation in Eqs. (4) and (6) (one uses the HF pair-density and the definition of the Fermi wave vector). The values of the constants for GB and NP for both cases (DFT and PDFT) are given in Table I. The values of the constant  $\tilde{A}$  and  $\tilde{B}$  are fixed by requiring that the correlation energies be equal to the known values for the homogeneous case [i.e.,

Eq. (22) reproduces Eq. (20)]. The derivation of the relation between the constants is given in the appendix.

The use of the SIC exchange-correlation hole in Eq. (22) has two important consequences. It has been pointed out<sup>39,40</sup> that under homogeneous coordinate scaling the logarithmic term in the approximate correlation energy functionals, such as GB, NP, and RPA, diverges as the scaling parameter  $\lambda$  is made infinite. This divergence is avoided in Eq. (22) due to the use of the exchange hole. Indeed, coordinate scaling shifts the functional in Eq. (22) by an amount proportional to  $\int d\mathbf{r}d\mathbf{r}'\tilde{n}_x(\mathbf{r},\mathbf{r}')\ln\lambda$ , which integrates to zero in the case of an orthonormal basis set. This is advantageous since it has also been shown that the actual correlation functional scales to a bounded constant.<sup>40-42</sup> For two-electron atoms, the constant has been calculated:  $-0.0467$  Har.<sup>50,51</sup> In our case, this constant is zero for one class of our constructed functionals [Eq. (23)] and it corresponds to the constant  $\tilde{A}$  shown in Table I for the other [Eq. (24)]. The divergence would arise had we not applied the SIC to the exchange hole.

Another consequence is that self-interaction is avoided by construction. The first term in Eq. (22) is therefore zero, and the constant term  $\tilde{A}$  does not contribute. This can be shown by considering Eqs. (10) and (11). When the exponent  $\Gamma$  in Eq. (11) is taken to be zero, and the exponent  $a$  in Eq. (10) is taken to be one it follows that  $b=0$ . In this case, a constant term in the correlation functional again corresponds to an integration over the exchange hole [Eq. (16)] giving a contribution of zero. The disappearance of the constant term is also present in the SIC of Lundin and Eriksson.<sup>47</sup> In the standard DFT version of the correlation functional, the constant term also does not contribute if the SIC procedure of Perdew and Zunger<sup>14</sup> is applied to the functional *within the local density approximation* (for an example of an application of the SIC in an LDA context see Ref. 52) since the constant term in the correlation energy of the electron gas (which is defined as energy per particle) corresponds to a term consisting of an integral over the density to the first power. Applying the SIC to such an integral leads to cancel-

lation. The problem does not arise when the SIC is formulated in the local spin density (LSD) approximation since the constant is scaled<sup>53</sup> in the SIC term which is subtracted from the uncorrected functional. Below, we also compare using the two different versions of SIC for the constant term.

It should be emphasized that in both cases the cancellation of the constant term is an artifact of the self-interaction procedure used, which in this case estimates the self-interaction component to be as large as the exchange constant itself. The constant in Eq. (18),  $A_c$ , arises from direct and exchange interactions,<sup>12</sup> and it would be a severe approximation to discard it. One possible way around this problem in our formalism, in principle, is to relax the condition  $a=1$ . Such a procedure would, however, significantly worsen the scaling of the method since explicit evaluation of the two-body density would be necessitated. Instead, we apply the standard LSD-based SIC procedure of Perdew and Zunger<sup>14</sup> to  $\tilde{A}$  in the correlation functionals, which amounts to an additive term of  $\tilde{A}N/2$ . Applying an LSD based SIC procedure to the constant term is not inconsistent with the SIC procedure we use since our SIC corrected exchange hole  $\tilde{n}_x$  is a sum over different spin components.

Another point to emphasize is that although the exchange hole includes correlations between electrons with parallel spins only, the energy functionals constructed according to our procedure account, at least in principle, for all interactions that are included in the approximate high-density correlation energy functionals (RPA, GB, and NP). The interactions accounted for are determined by the functionals to which our PDFT based functionals are made to correspond. By analogous logic, in DFT the correlation energy functional depends on the density only, a one-body object without correlations, yet it accounts for correlation by virtue of being required to reproduce the energetics of approximations to correlation in the HEG.

Our correlation energy functional (total as opposed to per particle) thus looks like

TABLE II. Correlation energies (Har) from DFT calculations using various correlation functionals and their self-interaction corrected versions for closed-shell atoms.

$E_c$	He	Be	Ne	Mg	Ar
RPA	0.130	0.251	0.884	1.17	1.69
GB	0.0821	0.154	0.644	0.782	1.26
NP	0.109	0.213	0.662	0.935	1.24
RPA-SIC-LDA	0.014	0.033	0.198	0.222	0.398
GB-SIC-LDA	0.014	0.033	0.198	0.222	0.398
NP-SIC-LDA	0.0072	0.016	0.0987	0.111	0.198
RPA-SIC-LSD	0.082	0.161	0.589	0.689	1.13
GB-SIC-LSD	0.058	0.113	0.469	0.545	0.912
NP-SIC-LSD	0.063	0.124	0.404	0.476	0.761
VMC <sup>a</sup>		0.073	0.346	0.372	0.576
Clementi and Hoffmann <sup>b</sup>	0.045	0.094	0.3870	0.438	0.722

<sup>a</sup>Reference 57.

<sup>b</sup>Reference 56.

TABLE III. Correlation energies (Har) from DFT calculations using various correlation functionals and their self-interaction corrected versions for closed-shell atoms.

$E_c$	Ca	Zn	Kr	Xe
RPA	1.85	3.15	3.88	6.12
GB	1.37	2.43	3.01	4.83
NP	1.36	2.23	2.73	4.24
RPA-SIC-LDA	0.429	0.822	1.01	1.66
GB-SIC-LDA	0.429	0.822	1.01	1.66
NP-SIC-LDA	0.214	0.410	0.505	0.83
RPA-SIC-LSD	1.23	2.13	2.62	4.15
GB-SIC-LSD	0.994	1.77	2.18	3.50
NP-SIC-LSD	0.836	1.39	1.70	2.67
VMC <sup>a</sup>	0.619	1.27	1.43	2.03
Clementi and Hoffmann <sup>b</sup>	0.842	1.74	2.26	4.04

<sup>a</sup>Reference 57.

<sup>b</sup>Reference 56.

$$E_c^I[\tilde{n}_x] = + \frac{\tilde{B}}{2} \int d\mathbf{r}d\mathbf{r}' \tilde{n}_x(\mathbf{r}, \mathbf{r}') \ln|\mathbf{r} - \mathbf{r}'|. \quad (23)$$

When the constant term  $\tilde{A}$  is subject to LSD based SIC treatment, the correlation energy functional becomes

$$E_c^II[\tilde{n}_x] = \frac{\tilde{A}N}{2} + \frac{\tilde{B}}{2} \int d\mathbf{r}d\mathbf{r}' \tilde{n}_x(\mathbf{r}, \mathbf{r}') \ln|\mathbf{r} - \mathbf{r}'|. \quad (24)$$

#### IV. CALCULATION DETAILS

While the above formalism amounts to a modified HF, here we perform a normal HF calculation and calculate the correlation energies using the HF orbitals. Thus, our calculations amount to a perturbative treatment. This treatment was also suggested by Levy.<sup>35</sup> Given that for our test cases (closed subshell atoms) the correlation energies are  $\sim 1\%$  of

the total energy, the perturbative approach can be expected to be a good approximation.

We have performed atomic HF calculations using the most recent version<sup>54</sup> of the atomic program written by Fischer.<sup>55</sup> Subsequently, we have used the orbitals obtained from the atomic program to calculate the correlation energy contributions given by the PDFPT analogs that we constructed. For comparison, we have also calculated the correlation energies from the DFT analogs of GB and NP. The GB<sup>12</sup> and NP<sup>13</sup> correlation functionals are based on a diagrammatic perturbation summation for the HEG. While the GB is an expansion valid in the limit of high density, the NP functional is an interpolation formula approximately valid for all density ranges.<sup>4,9</sup>

For reference purposes, we have calculated the correlation energies within DFT. In Tables II and III, we present the correlation energies for a sequence of closed-shell and closed sub-shell atoms calculated by using the GB, NP, and RPA forms. The results of Clementi and Hoffmann<sup>56</sup> and the variational Monte Carlo results of Buendía *et al.*<sup>57</sup> are also shown. As expected, the correlation energies are overestimated due to the absence of SIC. Application of SIC based on LDA leads to an underestimation of the correlation energy, whereas the LSD based SIC leads to an improvement over both previous methods. When improved correlation energy functionals are used the correlation energy is quantitatively recovered.<sup>14</sup>

#### V. RESULTS AND ANALYSIS

In Table IV, the correlation energies based on the PDFPT analogs of the RPA, GB, and NP correlation functionals are presented for a sequence of closed subshell atoms He, Be, Ne, Mg, and Ar [I refers to the functional given in Eq. (23)]. The calculated correlation energies capture the qualitative trend for all three functionals. An apparent deficiency is the fact that the correlation energy for the helium atom is zero. This deficiency stems from the use of the SIC exchange-correlation hole as the functional to construct the correlation energy functional. The SIC exchange correlation hole [Eq. (15)] for a noninteracting system consists of interactions be-

TABLE IV. Correlation energies (Har) from PDFPT calculations using various exchange correlation functionals. For the meaning of the different functionals (I and II), see the text.

$E_c$	He	Be	Ne	Mg	Ar
RPA-I	0.0	0.00133	0.0704	0.0755	0.156
GB-I	0.0	0.00133	0.0704	0.0755	0.156
NP-I	0.0	0.000661	0.0351	0.0376	0.0776
RPA-II	0.0838	0.169	0.489	0.578	0.910
GB-II	0.0598	0.121	0.369	0.434	0.694
NP-II	0.0639	0.128	0.354	0.421	0.652
VMC <sup>a</sup>		0.073	0.346	0.372	0.576
Clementi and Hoffmann <sup>b</sup>	0.045	0.094	0.3870	0.438	0.722

<sup>a</sup>Reference 57.

<sup>b</sup>Reference 56.

TABLE V. Correlation energies (Har) from PDFT calculations using various exchange correlation functionals. For the meaning of the different functionals (I and II), see the text.

$E_c$	Ca	Zn	Kr	Xe
RPA-I	0.166	0.362	0.340	0.829
GB-I	0.166	0.362	0.340	0.829
NP-I	0.0830	0.181	0.170	0.368
RPA-II	0.99	1.62	1.84	3.09
GB-II	0.763	1.26	1.42	2.44
NP-II	0.722	1.14	1.32	2.13
VMC <sup>a</sup>	0.619	1.27	1.43	2.03
Clementi and Hoffmann <sup>b</sup>	0.842	1.74	2.26	4.04

<sup>a</sup>Reference 57.

<sup>b</sup>Reference 56.

tween electrons with parallel spins. Since the two electrons in a helium atom (ground state) are an antiparallel pair it, can be expected that a correlation energy functional of the exchange correlation hole give zero as a result.

We note that there is a qualitative similarity and at the same time a quantitative difference between this shortcoming of functional I [Eq. (23)] and the spurious self-interaction in the case of the original LDA density functionals. In LDA it is a property of the *input function* (the one-body density) that gives rise to the spurious contribution. Since the one-body density is some finite positive-definite function even for a single electron, a functional that depends on it gives a finite contribution in general. The similar artifact of the SIC exchange hole as an input function is that it lacks terms with antiparallel interactions; therefore, it is not expected to give contributions when a system with one single interaction between electrons of antiparallel spins is considered, such as helium.

In Table IV results for the approximately corrected version [Eq. (24)] of the PDFT correlation energy are also presented (RPA-II, GB-II, and NP-II). All three functionals are considerably improved compared to their values without the SIC Table IV and quantitative (near exact) agreement is observed for the GB-II and NP-II functionals when compared to the results of Clementi and Hoffmann.<sup>56</sup>

The pair density ansatz GB-II appears to give the best results for the sequence of atoms when compared to the results of Clementi and Hoffmann.<sup>56</sup> The results for GB-II are also consistently better than the corresponding DFT results in Table II (GB-SIC-LSD).

The recent results of Buendía *et al.*<sup>57</sup> are also presented for comparison. This study is based on a variational Monte Carlo calculation using a correlated basis function. Our results compare well with the known results, and overall the agreement appears to be as good as the VMC calculation of Buendía *et al.*<sup>57</sup> The fact that in our case the agreement worsens for small atom systems can be attributed to the fact that the correlation functional is approximated from the HEG, a system in the thermodynamic limit.

In Table V results for a heavier sequence of closed subshell atoms Ca, Zn, Kr, and Xe are also presented. The cor-

relation energies of Clementi and Hoffmann<sup>56</sup> are also shown for comparison. While our results are no longer in as good agreement for the correlation energy as for the lighter atoms in Table IV, they appear to be close to the results of the VMC calculation of Buendía *et al.*<sup>57</sup> The results of Clementi and Hoffmann<sup>56</sup> appear to be better reproduced by DFT in this case (Table III). A potential source of error in our case is the fact that we are using functionals based on the high-density limit of the HEG,<sup>9,12,13</sup> which may not be a good approximation for electrons farther from the nucleus.

## VI. CONCLUSION

We developed an electronic structure method based on pair density functional theory that is simple to implement. We have shown that exact energy functionals can in principle be constructed in terms of the Hartree-Fock pair density, and that the representability question can be circumvented. Our formalism is closely related to the work of Levy on Hartree-Fock density matrix functional theory.<sup>35</sup> In applications, approximations have to be developed to account for correlation. In our method, correlation is accounted for by auxiliary pair-potentials between electrons in a Hartree-Fock setting; thus, the method scales also as Hartree-Fock. The correlation approximations tested give good agreement for atomic test cases with other methods. In DFT, there are many possible options for correlation functionals which have been developed over the past few decades, often with specific chemical or physical situations in mind. The close agreement for the two simple PDFT correlation functionals developed and tested in this work indicates that there is potential in developing correlation functionals for PDFT as well. Since the pair density is a quantity depending on the coordinates of two particles it can be expected to give a better overall, more robust description of correlation than the ones used in one-body DFT.

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## APPENDIX

In this appendix, we show how to determine the relation between the constants for a correlation energy for the HEG of the form<sup>9,12,13</sup>

$$e_c(\rho) = A + B \ln \rho. \quad (\text{A1})$$

The two-body functional form we assume for the correlation functional can be written as

$$e_c(\tilde{n}_x) = \tilde{A} + \frac{\tilde{B}}{2N} \int d\mathbf{r}\mathbf{r}' \tilde{n}_x(\mathbf{r}, \mathbf{r}') \ln |\mathbf{r} - \mathbf{r}'|. \quad (\text{A2})$$

Using the fact that

$$\tilde{n}_x(|\mathbf{r} - \mathbf{r}'|) = \rho^2 [g(|\mathbf{r} - \mathbf{r}'|) - 1], \quad (\text{A3})$$

we can rewrite Eq. (26) as

$$\epsilon(\tilde{n}_x) = \tilde{A} + 2\pi\tilde{B}\rho \int r^2 dr [g(r) - 1] \ln|r|. \quad (\text{A4})$$

Scaling the coordinate  $r$  as

$$\begin{aligned} x &= k_f r, \\ k_f &= (3\pi^2\rho)^{1/3} \end{aligned} \quad (\text{A5})$$

results in

$$e_c(\tilde{n}_x) = \tilde{A} + \frac{2\tilde{B}}{3\pi} \int x^2 dx [g(x) - 1] \ln|x| + \frac{\tilde{B}}{6} \ln 3\pi^2\rho. \quad (\text{A6})$$

Using the form of  $g(x)$ ,<sup>9</sup> the relation between the constants can then be shown to be

$$\begin{aligned} \tilde{A} &= A - \frac{4B}{\pi} \int x^2 dx [g(x) - 1] \ln|x| - B \ln 3\pi^2 \\ \tilde{B} &= 6B. \end{aligned} \quad (\text{A7})$$

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