

## Constrained-pairing mean-field theory. III. Inclusion of density functional exchange and correlation effects via alternative densities

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The recently proposed constrained-pairing mean-field theory (CPMFT) is here extended to include exchange and correlation effects from density functional theory (DFT) via alternative densities. We transform from  $\alpha$  and  $\beta$  spin densities to alternatives based on the total and on-top pair densities. This transformation is needed because CPMFT produces correct spin-symmetry and space-symmetry adapted densities that traditional DFT functionals are not designed to work with. The inclusion of DFT exchange and correlation effects in CPMFT is well founded both on practical and methodological reasons. We present multiple benchmarks showing that in many cases our model accurately reproduces unrestricted hybrid functional energies (both regular and range separated) and does so on the correct space-symmetry and spin-symmetry surface. Our approach affords efficient inclusion of dynamical correlation effects absent in CPMFT. © 2010 American Institute of Physics. [doi:10.1063/1.3292640]

### I. INTRODUCTION

In a recent paper,<sup>1</sup> two of us introduced a novel model for accurately describing strong correlations (also known as static or nondynamical correlations) in electronic structure theory. This new model is named CPMFT. In its simplest form, CPMFT can exactly dissociate electron pairs to degenerate orbitals. For the nondegenerate case, we have introduced the concept of *asymptotic constraints* and showed how this extended model can accurately deal with the dissociation of any polyatomic molecule into restricted open-shell Hartree–Fock (ROHF) fragments or atoms.<sup>2</sup> Among the interesting features of CPMFT are its low mean-field computational cost (similar to HF), a natural definition for static correlation, and more importantly for this paper, its resulting space-symmetry and spin-symmetry adapted orbitals and densities that mimic correct wave function values. Our initial contribution on this topic<sup>1</sup> included a simple dynamical correlation functional added to CPMFT, and proved the point that the method is capable of describing metal-insulator transitions on the correct closed-shell surface in strongly correlated hydrogen networks. Here, we wish to extend these ideas about inclusion of dynamical correlation and exchange functionals from density functional theory (DFT) and take advantage of the large body of work developed in that field during the past several decades. To achieve this goal, we unfortunately face a fundamental obstacle: the vast majority of DFT work assumes that densities are space and spin-symmetry broken (orbitals and densities are spin-polarized in cases where spin polarization should be zero). CPMFT orbitals and densities have the correct space and spin symmetries and if fed into standard DFT exchange-correlation subroutines, they would in general return poor quality results. How-

ever, the traditional dogma of working with symmetry broken densities in DFT is a choice, not necessarily an imposition of the theory. We believe that the preference of working with unrestricted orbitals stems from the need of describing left-right correlations, which are essentially nonlocal in a symmetry-adapted formalism, whereas DFT in its traditional formulation prefers to be local or semilocal (i.e., depending on quantities such as the density and orbitals evaluated at a reference point). The choice of working with spin-polarized orbitals is deeply embedded in the DFT community and likely goes back to Slater's  $X\alpha$  method,<sup>3</sup> which precedes the formal birth of modern DFT.<sup>4</sup> Most practitioners are aware that DFT predictions are much more accurate if carried out using symmetry-broken, unrestricted, spin-polarized orbitals as opposed to symmetry-adapted orbitals, except of course for the trivial case when in the absence of symmetry breaking both are the same. We believe that the blessing of describing nonlocal static correlation with spin-polarized orbitals is also a curse. One of the key elements for developing CPMFT is the desideratum of pushing the theory (both HF and DFT) to a different paradigm where space and spin symmetries are preserved. One should point out that of course the formal solution to this conundrum is simply to express the  $N$ -electron wave function as a linear combination of Slater determinants with overall correct symmetry eigenvalues. The computational cost of methods such as complete active space self-consistent field (CASSCF) is, however, daunting, and blows up exponentially with the number of active electrons and orbitals. If one wishes to remain within a computationally affordable approach, there seems to be no other options than resorting to the standard different orbitals for different spins, spin-polarized, unrestricted formalism. Fortunately, this is not true. We have shown in recent work that it is possible to describe strong left-right correlations

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within a fairly black-box scheme breaking an alternative, up to date mostly unexplored symmetry: electron number conservation. Our proposed CPMFT model introduces electron number fluctuations into the wave function and seamlessly blends HF and Hartree–Fock–Bogoliubov (HFB) theories in a hybrid scheme with an effective two-body interaction that yields nonzero pairing interactions where static correlation is important. A good number of benchmark cases in our previous papers<sup>1,2</sup> have hopefully made this point evident.

Nevertheless, we still face the formidable task of blending symmetry correct densities with the traditional DFT functionals if we want to take advantage of the extensive accomplishments in that field. To achieve this goal, we here build on previous work<sup>5–8</sup> where it has been pointed out that the total density and the on-top density are viable alternatives to the standard  $\alpha$  and  $\beta$  densities used in DFT. The literature on adding DFT correlation functionals to symmetry adapted densities is extensive and it is not our purpose to review it here. The pioneering contributions of Yamaguchi and co-workers<sup>9,10</sup> should be mentioned in this context, as well as work on spin potentials.<sup>11–13</sup>

In this paper, we mix CPMFT with HF and DFT and attempt to take advantage of the best that each model has to offer. We will mix DFT exchange and correlation with CPMFT in regular hybrid and range-separated schemes. We will also add dynamical correlation to CPMFT using DFT functionals via alternative densities. The justification for these approaches is well founded and described in detail below and in the Appendix.

## II. THEORY

### A. Alternative densities in Kohn–Sham (KS) theory

In this section, we briefly discuss the approach of defining alternative densities based on the on-top pair density  $P_2(r)$  and the total (or charge) density,  $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ , as independent variables in KS theory.  $P_2(r)$  is the diagonal part of the pair density, i.e.,  $P_2(r) = P_2(r, r' = r)$ . Using Löwdin's normalization, the pair density is defined as

$$P_2(r, r') = \frac{N(N-1)}{2} \int \Psi^*(r_1, \sigma_1, r_2, \sigma_2, \dots, r_N, \sigma_N) \times \Psi(r'_1, \sigma_1, r'_2, \sigma_2, \dots, r_N, \sigma_N) \times d^3r_3 \cdots d^3r_N d\sigma_1 d\sigma_2 \cdots \sigma_N |_{r_1=r_2=r, r'_1=r'_2=r'}, \quad (1)$$

where  $N$  is the number of electrons,  $\Psi$  is the wave function of the system under consideration, and  $r$  and  $\sigma$  are spatial and spin coordinates. Equation (1) is equivalent to

$$P_2(r, r') = \sum_{pqrs} \Gamma_{pq}^{rs} \varphi_p(r) \varphi_q(r') \varphi_r(r) \varphi_s(r'), \quad (2)$$

where  $\Gamma$  is the two-particle density matrix (2PDM) and  $\varphi_p$  are orthonormal spin orbitals. Throughout this paper, we will use  $p, q, \dots$  indices for denoting spin orbitals, and  $i, j, \dots$  for spin-integrated spatial orbitals. We also limit our discussion to real orbitals.

KS calculations with approximations have shown that higher quality results are obtained when the energy functional is chosen to depend on  $\alpha$  and  $\beta$  electron densities

individually, or equivalently, on the total density,  $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ , and the spin polarization density  $m(r) = \rho_\alpha(r) - \rho_\beta(r)$ . The latter has proven to be particularly useful for dissociating closed-shell molecules. KS calculations traditionally use symmetry breaking, which in many situations ensures size consistency. In such cases, however, the significance of a nonzero  $m$  is not clear as it should be zero when the total spin  $S=0$ .

A way out of the dilemma of having to choose between the right spin and spatial symmetries versus having size consistency is to imagine that the spin polarization appearing in unrestricted DFT calculations in fact stands for another quantity, an alternative spin polarization density  $\chi_m$ . In order to take advantage of existing functionals of  $\rho$  and  $m$ ,  $\chi_m$  can be introduced and generated from the  $\alpha$  and  $\beta$  densities of the KS determinant. In this way, one can convert any functional of  $\rho$  and  $m$  (or  $\rho_\alpha$  and  $\rho_\beta$ ) into a functional of  $\rho$  and  $\chi_m$ . Using this prescription, existing functionals can be used as previously, but now  $\chi_m$  gets a new interpretation, viz., generating an alternative, physically relevant, spin polarization.

In the current CPMFT model,<sup>1,2</sup> only closed-shell situations have been considered up to now, and thus  $m(r)=0$ . When dissociating closed-shell molecules, fragments show up for which (when treated individually)  $m(r) \neq 0$ . For each individual fragment, the CPMFT energy expression becomes that obtained with an ROHF determinant. In this limiting situation, we would like to complement the CPMFT energy with correlation density functionals designed for KS calculations. Since  $m(r)=0$ , we can achieve this by using the alternative spin polarization density  $\chi_m$ .

There are many ways to generate such an alternative spin polarization density. Following the work of Yamaguchi and co-workers,<sup>9,10</sup> one can generate alternative densities from the pair density of spin-unrestricted Slater determinants,

$$P_2(r, r') = \frac{1}{2} [\rho(r)\rho(r') - |\gamma_\alpha(r, r')|^2 - |\gamma_\beta(r, r')|^2], \quad (3)$$

where

$$\gamma_\sigma(r, r') = \sum_{ij} (\gamma_\sigma)_{ij} \varphi_{i\sigma}(r) \varphi_{j\sigma}(r') \quad (4)$$

is the one-particle density matrix (1PDM) and  $\varphi_{i\sigma}(r)$  are spatial orbitals  $\varphi_i(r)$  of  $\sigma$  spin. Here  $\rho_\sigma(r) = \gamma_\sigma(r, r)$ . Equation (3) yields the so-called on-top pair density when  $r' = r$ ,

$$P_2(r) = \rho_\alpha(r)\rho_\beta(r). \quad (5)$$

From these equations, one can easily isolate  $\rho_\alpha$  and  $\rho_\beta$  as a function of  $\rho$  and  $P_2$  and replace them in the definition of  $m$  to yield the alternative expression for the spin polarization density,

$$\chi_m(r) = \sqrt{\rho(r)^2 - 4P_2(r)}. \quad (6)$$

In other words, one can replace  $m$  with  $\chi_m$  in any functional of  $\rho$  and  $m$  and obtain identical results if used in unrestricted KS calculations.<sup>5–8</sup>

## B. Alternative densities in CPMFT

Now we elaborate on the extension of this scheme for CPMFT.<sup>1,2</sup> First, the CPMFT 2PDM in the spin-orbital basis is

$$\Gamma_{pq}^{rs} = \frac{1}{2}(\gamma_{pr}\gamma_{qs} - \gamma_{ps}\gamma_{qr} - \kappa_{pq}\kappa_{rs}), \quad (7)$$

where  $\gamma$  and  $\kappa$  are the 1PDM and pairing matrix in the spin-orbital basis. Note that  $-\kappa^2 = \gamma - \gamma^2$  is positive definite. To avoid any confusion, we should emphasize that  $\gamma$  is not the total (or charge) density matrix  $\gamma_c = \gamma_\alpha + \gamma_\beta$ , but is a block matrix with respect to spin blocks, i.e.,

$$\gamma = \begin{pmatrix} \gamma_\alpha & \mathbf{0} \\ \mathbf{0} & \gamma_\beta \end{pmatrix} \quad (8)$$

and similarly for  $\kappa$ ,

$$\kappa = \begin{pmatrix} \mathbf{0} & \kappa_{\alpha\beta} \\ \kappa_{\beta\alpha} & \mathbf{0} \end{pmatrix}, \quad (9)$$

where  $\kappa_{\alpha\beta} = -(\kappa_{\beta\alpha})^T$  by definition. Therefore,  $\kappa$  is antisymmetric. It should be mentioned that one can always diagonalize  $\gamma_\sigma$  to obtain the natural spin occupation numbers  $n_{i\sigma}$  as its eigenvalues, and the natural spin orbitals (NOs),  $\psi$ , in which the pairing matrix is also diagonal,  $\kappa_{i\sigma\sigma'} = \sqrt{n_{i\sigma} - (n_{i\sigma})^2} = \sqrt{n_{i\sigma'} - (n_{i\sigma'})^2}$  ( $\sigma \neq \sigma'$ ). Note that  $0 \leq n_{i\sigma} \leq 1$ . The absence of strong correlation is characterized by  $\kappa = \mathbf{0}$ , which yields an idempotent 1PDM, i.e., regular restricted HF (RHF).

Substituting Eq. (7) into Eq. (2) and then setting  $r' = r$  yields the on-top pair density of CPMFT,

$$P_2(r) = \rho_\alpha(r)\rho_\beta(r) + \frac{1}{2}[\kappa_{\alpha\beta}(r)^2 + \kappa_{\beta\alpha}(r)^2]. \quad (10)$$

In Eq. (10),  $\kappa_{\sigma\sigma'}(r)$  is the pairing matrix in real space. In analogy with Eq. (4),

$$\kappa_{\sigma\sigma'}(r, r') = \sum_{ij} (\kappa_{\sigma\sigma'})_{ij} \varphi_{i\sigma}(r) \varphi_{j\sigma'}(r') \quad (11)$$

and  $\kappa_{\sigma\sigma'}(r) \equiv \kappa_{\sigma\sigma'}(r, r' = r)$ . In this article, we restrict ourselves to closed-shell systems, but will keep the spin labels  $\alpha$  and  $\beta$  for clarity. Therefore,  $\gamma_\alpha = \gamma_\beta$ ,  $\kappa_{\alpha\beta} = -\kappa_{\beta\alpha}$ ,  $\varphi_i(r) = \varphi_{i\alpha}(r) = \varphi_{i\beta}(r)$ , and thus  $\rho_\alpha(r) = \rho_\beta(r)$  and  $\kappa_{\alpha\beta}(r) = -\kappa_{\beta\alpha}(r)$ . We will discuss our open-shell formalism in a forthcoming publication.

Note that Eq. (10) is normalized to the correct number of electron pairs as well as Eq. (7), which is correctly normalized to  $N(N-1)/2$ . However, the 2PDM of CPMFT is in general not  $N$  representable as  $\Psi$  includes fluctuations, i.e., determinants with electron number different from  $N$ .

Now for practical purposes, we introduce the alternative densities  $\chi_\alpha(r)$  and  $\chi_\beta(r)$  satisfying

$$\rho(r) = \chi_\alpha(r) + \chi_\beta(r) \quad (12)$$

and

$$\chi_m(r) = \chi_\alpha(r) - \chi_\beta(r). \quad (13)$$

We put  $\alpha$  and  $\beta$  indices on  $\chi$  for convenience but they do not represent actual electron densities unless  $\kappa_{\alpha\beta}(r)$  is zero. Our first mapping model for defining  $\chi_\alpha$  and  $\chi_\beta$  is based on

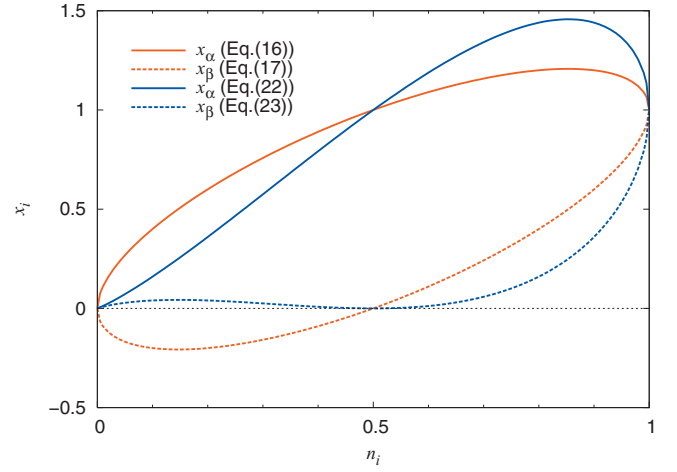


FIG. 1. Plots of  $x_{i\sigma}$  in Eqs. (16) and (17) (in red) and Eqs. (22) and (23) (transformation A, in blue) as functions of  $n_i$ . Note that  $x_{i\beta}$  of Eq. (17) is negative when  $0 < n_i < 0.5$  while that of Eq. (23) is positive everywhere.

Eq. (6). Substituting the CPMFT on-top density Eq. (10) into Eq. (6), one can easily derive

$$\chi_\alpha(r) = \rho_\alpha(r) + \kappa_{\alpha\beta}(r), \quad (14)$$

$$\chi_\beta(r) = \rho_\alpha(r) - \kappa_{\alpha\beta}(r), \quad (15)$$

where we have used  $\rho_\alpha(r) = \rho_\beta(r)$  and  $\kappa_{\alpha\beta}(r) = -\kappa_{\beta\alpha}(r)$ . In a practical sense, we just replace  $\rho_\sigma(r)$  by  $\chi_\sigma(r)$  in a DFT exchange-correlation functional  $E_{xc}$ . Therefore, for the exchange-correlation energy (but not its derivatives), the implementation of this scheme is simple and straightforward: one substitutes  $\chi_\sigma(r)$  into existing DFT subroutines. It should be mentioned that in cases where  $E_{xc}$  depends on density gradients and/or kinetic energy densities, one needs to use the corresponding quantities in terms of  $\chi_\sigma(r)$ . For example, for a generalized gradient approximation such as Perdew–Burke–Ernzerhof (PBE),<sup>14</sup>  $E_{xc}^{GGA}[\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta]$  should be replaced by  $E_{xc}^{GGA}[\chi_\alpha, \chi_\beta, \nabla\chi_\alpha, \nabla\chi_\beta]$ .

One should note, however, the possibility of  $\chi_\beta(r)$  in the above definition Eq. (15) to become negative. The natural occupations,  $x_{i\sigma}$ , of  $\chi_\sigma(r)$  are

$$x_{i\alpha} = n_i + \sqrt{n_i - n_i^2}, \quad (16)$$

$$x_{i\beta} = n_i - \sqrt{n_i - n_i^2}, \quad (17)$$

where we have used  $n_i = n_{i\alpha} = n_{i\beta}$ . As can be clearly seen in Fig. 1,  $x_{i\beta}$  is negative when  $0 < n_i < 0.5$  and therefore so can  $\chi_\beta(r)$ . This result is not surprising, as our CPMFT 2PDM ansatz in Eq. (7) is not  $N$  representable. While the existence of a transformation to alternative densities  $\chi_\sigma(r)$  is well founded, a negative  $\chi_\beta(r)$  would be quite problematic for all present exchange-correlation functionals.

Fortunately, there are many ways of choosing alternative densities  $\chi_\sigma(r)$  for  $E_{xc}$ . When fed in exchange-correlation functionals, we want  $\chi_\sigma(r)$  to behave as if they were *real* densities. In other words, they have to be positive, continuous, and differentiable. We will also require that

- (1)  $x_{i\alpha} = x_{i\beta} = 0$  if  $n_i = 0$ ,
- (2)  $x_{i\alpha} = x_{i\beta} = 1$  if  $n_i = 1$ ,

- (3)  $x_{i\alpha}=1, x_{i\beta}=0$  if  $n_i=0.5$ ,  
 (4)  $x_{i\alpha}+x_{i\beta}=n_{i\alpha}+n_{i\beta}=2n_i$ .

The first and second conditions guarantee that  $E_{xc}[\chi_\alpha(r), \chi_\beta(r)]$  produces exactly  $E_{xc}[\rho_\alpha(r), \rho_\beta(r)]$  when there is no strong correlation (i.e., our model reduces to a standard restricted Kohn–Sham (RKS) solution due to the idempotency of the 1PDM). These conditions also enforce  $\chi_\sigma^{\text{core}}(r) = \rho_\sigma^{\text{core}}(r)$  for the core orbitals because their occupation numbers are always 1 for both  $\alpha$  and  $\beta$  spins. The third condition yields the correct exchange–correlation energy for strongly correlated systems (e.g., dissociation of a molecule). We stress that this only applies to the active orbitals of CPMFT, where  $n_i$  can be fractional. All of the above conditions are satisfied in Eqs. (14) and (15) except for the positivity condition for  $\chi_\beta(r)$ . Based on these requirements, we propose the following alternative densities

$$\chi_\alpha(r) = \rho_\alpha(r) + \int [\rho_\alpha(r, r') \kappa_{\alpha\beta}(r', r) + \kappa_{\alpha\beta}(r, r') \rho_\alpha(r', r)] d^3 r', \quad (18)$$

$$\chi_\beta(r) = \rho_\alpha(r) - \int [\rho_\alpha(r, r') \kappa_{\alpha\beta}(r', r) + \kappa_{\alpha\beta}(r, r') \rho_\alpha(r', r)] d^3 r', \quad (19)$$

which are simple extensions of Eqs. (14) and (15). We will refer to this transformation as *transformation A*. In matrix form, they are

$$\chi_\alpha = \gamma_\alpha + (\gamma_\alpha \kappa_{\alpha\beta} + \kappa_{\alpha\beta} \gamma_\alpha), \quad (20)$$

$$\chi_\beta = \gamma_\alpha - (\gamma_\alpha \kappa_{\alpha\beta} + \kappa_{\alpha\beta} \gamma_\alpha). \quad (21)$$

The eigenvalues of the above  $\chi_\sigma$  are

$$x_{i\alpha} = n_i + 2n_i \sqrt{n_i - n_i^2}, \quad (22)$$

$$x_{i\beta} = n_i - 2n_i \sqrt{n_i - n_i^2}, \quad (23)$$

which are also shown in Fig. 1. This transformation A guarantees that  $\chi_\beta(r)$  is always positive. This is the model used in our previous publication<sup>1</sup> with the Tao–Perdew–Staroverov–Scuseria (TPSS) correlation functional<sup>15</sup> for hydrogen networks and rationalized in detail here.

Following the requirements above, a family of plausible candidates for  $\chi_\sigma$  in matrix form is

$$\chi_\alpha = \frac{1}{2}(\gamma_\alpha + 2^{2q} \kappa_{\alpha\beta}^q \gamma_\alpha \kappa_{\alpha\beta}^q), \quad (24)$$

$$\chi_\beta = \frac{1}{2}(\gamma_\alpha - 2^{2q} \kappa_{\alpha\beta}^q \gamma_\alpha \kappa_{\alpha\beta}^q), \quad (25)$$

where  $q$  is a positive number. We will refer to this family as transformation B. Although these  $\chi_\sigma$  do not have explicit analytical expressions in  $\rho(r)$  and  $P_2(r)$ , one could expand them in terms of these two variables in real space. Figure 2 shows the behavior of natural occupations for this family for different  $q$ . Note that these alternative densities also satisfy all the conditions imposed above. Compared to transformation A, they substantially differ in the way they approach the RKS densities when occupations are close to 1 or 0, espe-

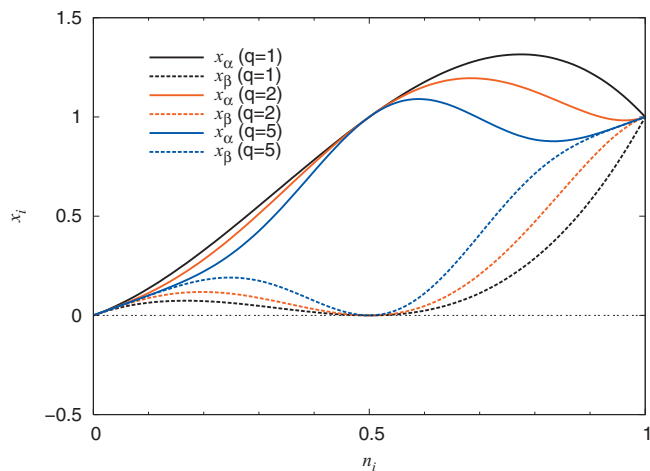


FIG. 2. Plots of  $x_{i\sigma}$  with transformation B for several  $q$  as a function of  $n_i$ .

cially when  $q$  is large. Note that when  $q=1/2$ , transformation B is equivalent to transformation A because  $\gamma_\alpha$  and  $\kappa_{\alpha\beta}$  commute.

### C. CP generalized KS (CPGKS)

As discussed previously,<sup>1,2</sup> the 2PDM of CPMFT is postulated to include only static correlation. Thus, the addition of standard DFT correlation functionals to CPMFT seems like a viable way of adding dynamical correlation effects to our model. In other words, we assume that the pairing energy in CPMFT handles static correlation while regular DFT correlation functionals take care of dynamical correlations. However, one should note that a combination of 100% HF-exchange  $E_x^{\text{HF}}$  plus 100% pairing  $E_p$  (defined below) plus 100% DFT correlation  $E_c^{\text{DFT}}$  would not be fully satisfactory since in many molecules near equilibrium (where the 1PDM turns out to be idempotent), this combination reduces to RHF+ $E_c^{\text{DFT}}$ , which is known to be a less than ideal approximation in terms of accuracy. Therefore, the inclusion of a portion of DFT exchange ( $E_x^{\text{DFT}}$ ) along with  $E_c^{\text{DFT}}$  seems an interesting alternative worth exploring.

It is normally assumed that, as opposed to  $E_c^{\text{DFT}}$ ,  $E_x^{\text{DFT}}$  introduces a portion of static correlation via its localization (and approximation) of the exchange hole, and in doing so, self-interaction error is also introduced. In order to avoid double counting of static correlation effects from the CPMFT pairing energy  $E_p$  and  $E_x^{\text{DFT}}$ , we will consider alternative components for which density functional approximations should be applied.

Here we propose a novel scheme to blend CPMFT with regular DFT. Global hybrid functionals<sup>16</sup> are also referred to as GKS schemes because they contain a portion of nonlocal HF-type exchange potential,

$$E_{xc}^{\text{hyb}} = aE_x^{\text{HF}} + (1-a)E_x^{\text{DFT}} + E_c^{\text{DFT}}, \quad (26)$$

where  $a$  is a mixing parameter and

$$E_x^{\text{HF}} = - \sum_{ijkl} (\gamma_\alpha)_{il} (\gamma_\alpha)_{jk} (ij, kl), \quad (27)$$

where  $(ij, kl)$  is a two-electron integral in Mulliken notation. Here we add to Eq. (26) the pairing energy  $E_p$  defined as

$$E_p = - \sum_{ijkl} (\kappa_{\alpha\beta})_{ij} (\kappa_{\alpha\beta})_{kl} (ik, jl). \quad (28)$$

Our exchange-correlation-pairing (xcp) energy is then given by

$$E_{xcp}^{\text{CPGKS}} = a(E_x^{\text{HF}}[\gamma_\alpha] + E_p[\kappa_{\alpha\beta}]) + (1-a)E_x^{\text{DFT}}[\chi_\alpha, \chi_\beta] + E_c^{\text{DFT}}[\chi_\alpha, \chi_\beta]. \quad (29)$$

We call this scheme CPGKS. Note that  $E_p \leq 0$  always. The coefficient of  $E_p$  must be the same as that of  $E_x^{\text{HF}}$  to get correct energies at dissociation. A simple rationalization of the CPGKS energy expression arises from considering a mixture of the HF, HFB, and DFT energy expressions with electron-electron interactions given by  $2a/r_{12}$ ,  $-a/r_{12}$ , and  $1-a/r_{12}$ , respectively. If all three are added, the CPGKS energy expression is obtained. Note that HF with  $2a/r_{12}$  has excess exchange energy which is compensated with exchange energy from HFB with  $-a/r_{12}$  (recall that HFB itself has a HF-type exchange term). Most importantly, note that  $E_x^{\text{DFT}}$  and  $E_c^{\text{DFT}}$  in Eq. (29) are now explicit functions of  $\chi_\alpha(r)$  and  $\chi_\beta(r)$  introduced in the last section, whereas  $E_x^{\text{HF}}$  and  $E_p$  are dependent on the 1PDM and pairing matrix, respectively. In other words, CPGKS can be considered a *hybrid* scheme where HF, HFB, and semilocal DFT are blended. We emphasize that for this mixture to yield meaningful results, the mixing coefficients and densities (regular versus alternative) need to be chosen as described here.

The above argument can be extended to a range-separated hybrid scheme,<sup>17–22</sup> e.g., with the electron-electron interaction split into

$$\frac{1}{r_{12}} = \frac{2\text{erf}(\omega r_{12})}{r_{12}} - \frac{\text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erfc}(\omega r_{12})}{r_{12}}, \quad (30)$$

where  $\omega$  is a parameter determining the range separation, and the first term is used for HF, the second term for HFB (both exchange and pairing), and the third one for DFT exchange. Again,  $E_x^{\text{HF}}$  with an interaction of  $2\text{erf}(\omega r_{12})/r_{12}$  from HF part partially cancels out with the  $-\text{erf}(\omega r_{12})/r_{12}$  interaction of HFB, yielding  $\text{erf}(\omega r_{12})/r_{12}$  as the total HF-type exchange interaction. The resulting energy expression is

$$E_{xcp} = E_x^{\text{lr-HF}} + E_x^{\text{sr-DFT}} + E_c^{\text{DFT}} + E_p^{\text{lr}}, \quad (31)$$

where superscripts *lr* and *sr* stand for long-range and short-range interactions, respectively. The first term uses a long-range interaction  $\text{erf}(\omega r_{12})/r_{12}$ , the second one a short-range  $\text{erfc}(\omega r_{12})/r_{12}$ , the third one full  $1/r_{12}$ , and the last term a long-range *attractive*  $-\text{erf}(\omega r_{12})/r_{12}$  potential. If one chooses  $\omega=0.4$  bohr<sup>-1</sup> and PBE as the DFT functional, then Eq. (31) is exactly the same functional as LC- $\omega$ PBE (Ref. 21) when the last term is zero. In other words, in the absence of strong correlation, Eq. (31) yields the LC- $\omega$ PBE result. We will here refer to this functional as Constrained-Pairing LC- $\omega$ PBE (CPLC- $\omega$ PBE).

## D. XC potentials in CPGKS

In order to achieve self-consistency in a CPGKS calculation, we need the derivatives of the exchange-correlation energy with respect to alternative densities  $\chi_\sigma(r)$ . Using the chain rule, the potentials are

$$v_\sigma^\rho(r) = \sum_{\sigma'} \int \frac{\partial E_{xc}}{\partial \chi_{\sigma'}(r')} \frac{\partial \chi_{\sigma'}(r')}{\partial \rho_\sigma(r)} d^3 r', \quad (32)$$

$$v_{\alpha\beta}^\kappa(r) = \sum_{\sigma'} \int \frac{\partial E_{xc}}{\partial \chi_{\sigma'}(r')} \frac{\partial \chi_{\sigma'}(r')}{\partial \kappa_{\alpha\beta}(r)} d^3 r'. \quad (33)$$

Note that  $v^\rho$  and  $v^\kappa$  yield contributions to the Fock Hamiltonian [ $\mathbf{F}_\alpha = (1/2)(\partial E / \partial \gamma_\alpha)$ ] and pairing field [ $\Delta_{\alpha\beta} = (1/2) \times (\partial E / \partial \kappa_{\alpha\beta})$ ], respectively. In this section, we derive the explicit forms of these contributions for transformation A. After some simple algebra, we find that the exchange-correlation potential matrices are

$$\mathbf{V}_\alpha^\rho = \frac{1}{2} \frac{\partial E_{xc}}{\partial \gamma_\alpha} = \frac{1}{2} (\mathbf{W} + \tilde{\mathbf{W}} \kappa_{\alpha\beta} + \kappa_{\alpha\beta} \tilde{\mathbf{W}}) = \mathbf{V}_\beta^\rho, \quad (34)$$

$$\mathbf{V}_{\alpha\beta}^\kappa = \frac{1}{2} \frac{\partial E_{xc}}{\partial \kappa_{\alpha\beta}} = \frac{1}{2} (\tilde{\mathbf{W}} \gamma_\alpha + \gamma_\alpha \tilde{\mathbf{W}}), \quad (35)$$

where

$$\mathbf{W} = \left( \frac{\partial}{\partial \chi_\alpha} + \frac{\partial}{\partial \chi_\beta} \right) E_{xc}, \quad (36)$$

$$\tilde{\mathbf{W}} = \left( \frac{\partial}{\partial \chi_\alpha} - \frac{\partial}{\partial \chi_\beta} \right) E_{xc}. \quad (37)$$

Note that  $\mathbf{V}_{\alpha\beta}^\kappa = -\mathbf{V}_{\beta\alpha}^\kappa$  in the same way that  $\Delta_{\alpha\beta} = -\Delta_{\beta\alpha}$ , i.e., they are antisymmetric.

Similarly, it is straightforward to obtain the corresponding potentials for transformation B. Also, as explained in previous papers,<sup>1,2</sup> we separate the NOs between core, active, and virtual spaces introducing different chemical potentials for each space. Therefore, once the desired  $\chi_\sigma$  are obtained, Eqs. (34) and (35) are not restricted to any particular orbital space: they are used for constructing the entire Fock Hamiltonian and pairing field.

## III. RESULTS

We begin this section presenting benchmark calculations for the dissociation curves of N<sub>2</sub> and F<sub>2</sub> with the 6-311++G\*\* basis set using the constrained-pairing scheme for the PBEh functional<sup>23–26</sup> (CPPBEh), which uses PBE exchange and correlation functionals<sup>14</sup> with the global mixing constant  $a=0.25$  in Eq. (29). The value of this mixing parameter is nonempirical and was derived from theoretical arguments. In these calculations, we have used transformation A for  $\chi_\sigma(r)$ . We have chosen six electrons in six active orbitals, (6,6), for N<sub>2</sub>, and two electrons in two active orbitals, (2,2), for F<sub>2</sub>. For N<sub>2</sub>, our calculations are carried out in  $D_{2h}$  symmetry, but in the correct  $D_{\infty h}$  symmetry, the sum of occupation numbers in  $\sigma_g$ - $\sigma_u$ ,  $\pi_{x,u}$ - $\pi_{x,g}$ , and  $\pi_{y,u}$ - $\pi_{y,g}$  active orbital pairs are all fixed to two each (one for each spin).

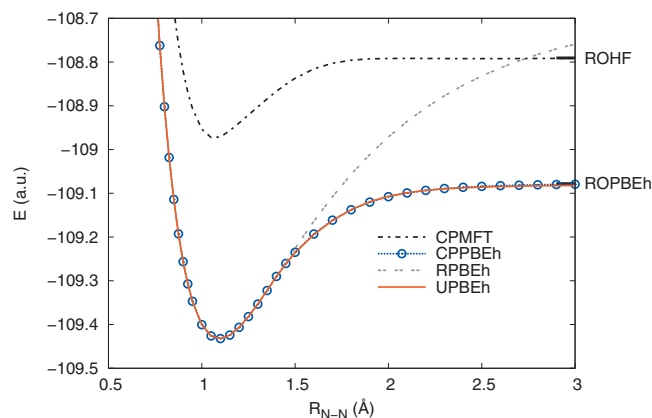


FIG. 3. Potential energy curves of the  $N_2$  molecule with a 6-311++G\*\* basis set. Both CPMFT and CPPBEh dissociate the molecule to the corresponding open-shell fragments.

This can be easily done by using different chemical potentials (as a Lagrange multiplier) that control the occupation numbers of each pair. In Fig. 3, we compare the CPPBEh dissociation curve with that of unrestricted PBEh (UPBEh) for the  $N_2$  molecule, but interestingly we find little difference in energies: both energies are almost identical to each other. In Table I, we list the total energies for the  $N_2$  molecule at several  $R_{N-N}$ . The good agreement between CPPBEh and UPBEh indicates that our formulae for alternative densities (transformation A) are quite reasonable.

Transformation B presented in Eqs. (24) and (25) behaves differently. For  $q \geq 1$ , the critical bond length ( $R_c$ ) where the CPPBEh solution appears is longer compared to UPBEh and CPPBEh with transformation A. For example, in Fig. 3, while  $R_c$  for the latter of two methods are both 1.4 Å, its value for transformation B with  $q=1$  is around 1.6 Å (not shown in Fig. 3). This happens because transformation B approaches the restricted PBE solution much faster when the occupation numbers of the active orbitals are close to zero or one. In the rest of this paper, we report CPGKS results only with transformation A.

Also, we emphasize that in these examples while UPBEh breaks the spin and spatial symmetries as it approaches dissociation, CPPBEh correctly preserves both of them. It also significantly improves over CPMFT and

TABLE I. Total energy of the  $N_2$  molecules calculated with several functionals (in hartree). The basis set used is the same as in Fig. 3.

$R_{N-N}$ (Å)	RPBEh	UPBEh	CPPBEh <sup>a</sup>
0.8	-108.902 12	-108.902 12	-108.902 12
1.2	-109.406 38	-109.406 38	-109.406 38
1.6	-109.164 22	-109.194 61	-109.193 06
2.0	-108.971 29	-109.106 95	-109.107 90
2.4	-108.853 10	-109.087 58	-109.086 26
2.8	-108.782 66	-109.083 10	-109.080 64
3.2	-108.740 75	-109.081 70	-109.078 85
3.6	-108.715 51	-109.081 07	-109.078 24
4.0	-108.699 89	-109.080 86	-109.078 01

<sup>a</sup>Transformation A is used. The sum of the restricted open-shell PBEh energies of two isolated N atoms is -109.077 81 hartree.

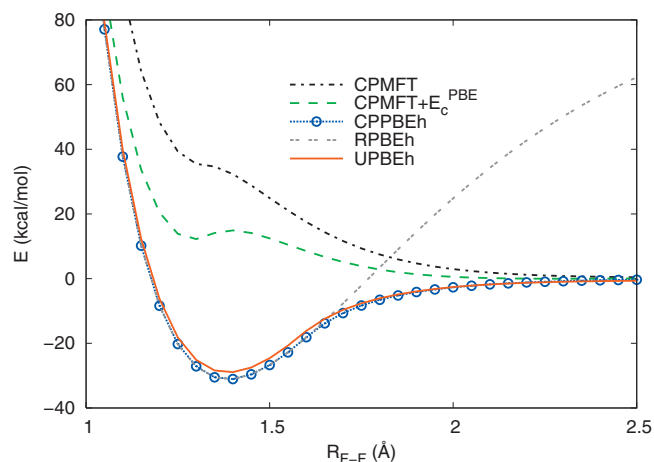


FIG. 4. Potential energy curves of the  $F_2$  molecule.

RPBEh because it has both dynamical and static correlation, and yields a much more accurate dissociation energy  $D_0$  of 218.9 kcal/mol compared to the CPMFT result of 111.2 kcal/mol (the experimental value is 225.1 kcal/mol) (Ref. 27).

$F_2$  is a dramatic example where a balance between  $E_x^{\text{DFT}}$  and  $E_c^{\text{DFT}}$  is needed in order for the molecule to be bound (Fig. 4). Pure CPMFT, which includes no dynamical correlation, predicts a repulsive  $F_2$  potential energy curve, meaning that substantial dynamical correlation is missing near equilibrium. Simply adding  $E_c^{\text{PBE}}$  does not fix this problem as can be seen in the CPMFT+ $E_c^{\text{PBE}}$  curve: it yields a (local) minimum around 1.297 Å, which is too short compared to the experimental bond length of  $R_e=1.412$  Å.<sup>28</sup> On the other hand, CPPBEh gives a bound curve with  $R_e=1.387$  Å, similar to the good performance of PBEh for this system. Again, UPBEh gives a reasonable curve but does so by breaking spin and spatial symmetries.

Figure 5 shows the  $H_2$  dissociation curve of CPLC- $\omega$ PBE along with ULC- $\omega$ PBE, CPPBEh, and Full configuration interaction (CI). The basis set used is 6-311++G\*\*, and the active space is set to (2,2). Both CPLC- $\omega$ PBE and ULC- $\omega$ PBE go below the Full CI curve because the PBE correlation functional is not self-interaction free. Considering

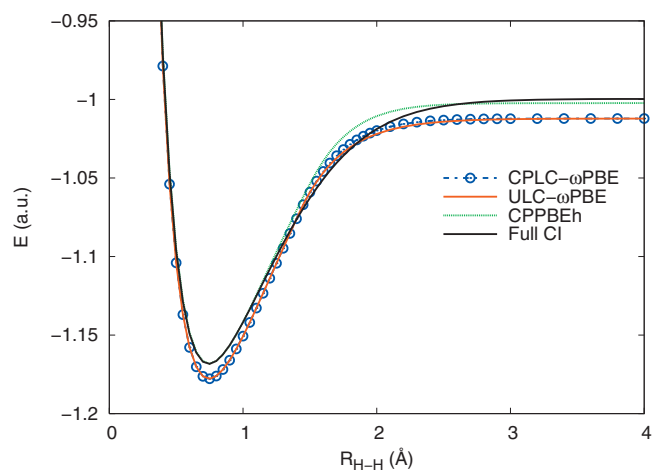


FIG. 5. Potential energy curves of the  $H_2$  molecule with range-separated hybrid functionals.

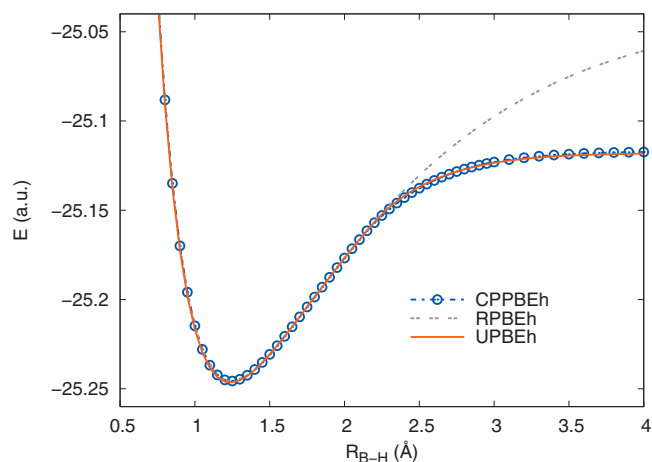


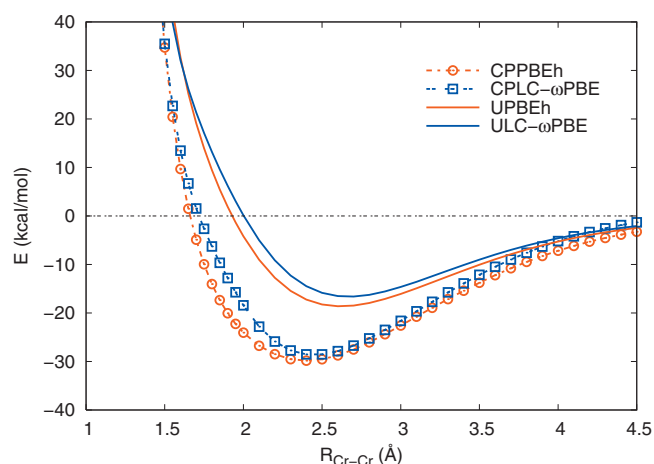
FIG. 6. Potential energy curves of the BH molecule.

that ULC- $\omega$ PBE is very accurate for this system, the mixture of CPMFT and DFT with a range-separated interaction proves also successful.

Our approach is by no means limited to homonuclear systems and can be used for heteronuclear systems with the previously discussed CPMFT+ $\phi$  scheme.<sup>2</sup> In CPMFT+ $\phi$ , we equilibrate the energies of nondegenerate (active) orbitals of dissociated fragments using a Lagrangian matrix  $\Lambda$  that plays the role of an orbital chemical potential shift and fixes the occupation numbers of dissociated orbitals to the correct 1/2 value. Then, along a dissociation curve, one uses  $\Lambda$  in combination with a polynomial of the 1PDM that imposes constraints on both the dissociation and weak (RHF) correlation limits. This has the effect of making our CPMFT model yield dissociation energies identical to CASSCF. For more details, the reader is referred to Ref. 2. It is remarkable that for the BH molecule using CPMFT+ $\phi(2,2)$  and alternative densities (see Fig. 6) with the 6-311++G\*\* basis set, CPPBEh gives very accurate dissociation curves compared to UPBEh.

Although all the hybrid examples presented so far show significant improvement over both CPMFT and restricted GKS, our CPGKS approach yields negligible differences in dissociation curves compared to unrestricted GKS (UGKS). Of course, this might be expected because UPBEh and ULC- $\omega$ PBE essentially give very good results for these systems. Therefore, the fact that CPGKS produces dissociation curves of the same quality as UGKS indicates that our transformation Eqs. (18) and (19) is a good starting point for further developing better functionals that are more suitable to CPGKS.

In order to test whether CPGKS yields significant differences compared to UGKS, we now discuss a more challenging example for hybrid UGKS, one where static correlation is ubiquitous: the chromium dimer Cr<sub>2</sub>. The ground state of Cr<sub>2</sub> is  $^1\Sigma_g^+$ , and dissociates to two septet Cr atoms. The twelve valence electrons have a strong multiconfigurational electronic structure at equilibrium, which makes calculations extremely difficult. It has been reported that unrestricted hybrid functionals predict the bond length to be too long and the dissociation energy  $D_0$  to be too small.<sup>29</sup> Edgecombe and

FIG. 7. Potential energy curves of the Cr<sub>2</sub> molecule.

Becke<sup>30</sup> have shown that hybrid functionals yield very interesting results after a simple spin-projection scheme.

In this paper, we have carried out CPPBEh(12,12) and CPLC- $\omega$ PBE(12,12) calculations of Cr<sub>2</sub> using the CPMFT +  $\phi$  scheme. The Cr 4s and 3d orbitals are not degenerate at dissociation, thus a small chemical potential is needed to equilibrate them.<sup>2</sup> In these calculations, we also constrain the number of electrons in each irreducible representation of the point group symmetry as we did in the N<sub>2</sub> calculations: the sum of occupation numbers in  $\sigma_g$ - $\sigma_u$ ,  $\pi_g$ - $\pi_u$ , and  $\delta_g$ - $\delta_u$  active orbitals are all fixed to four each. The basis set used in the Cr<sub>2</sub> calculations is the contracted 14s 11p 6d 2f/10s 8p 3d 2f Gaussian set of Scuseria and Schaefer.<sup>31</sup>

In Fig. 7, we have plotted the potential energy curves of the Cr<sub>2</sub> molecule obtained with different methods. None of these approaches predict the shoulder at long  $R_e$  obtained with other multi-reference wave function methods.<sup>32</sup> CPPBEh and CPLC- $\omega$ PBE predict a too long  $R_e$  of 2.400 and 2.448 Å, respectively, whereas the experimental value is 1.679 Å.<sup>33</sup> However, they both yield shorter  $R_e$  compared to their parent functional (Table II). The dissociation energy of Cr<sub>2</sub>( $D_e$ ) obtained with CPPBEh and CPLC- $\omega$ PBE (Table II) is much more reasonable than those of hybrid UGKS.

#### IV. CONCLUSIONS

We have developed an approach that uses alternative densities to incorporate semilocal and hybrid exchange and correlation functional effects into CPMFT. The use of alternative densities is required because regular density functionals are trained to deal with unrestricted broken symmetry descriptions whereas CPMFT yields orbitals and densities

TABLE II. Bond length (Å) and dissociation energy (kcal/mol) for Cr<sub>2</sub>.

	CPPBEh	CPLC- $\omega$ PBE	UPBEh	ULC- $\omega$ PBE	Exptl.
$R_e$	2.400	2.448	2.617	2.670	1.679 <sup>a</sup>
$D_e$	29.8	28.6	18.6	16.6	34.0 <sup>b</sup>

<sup>a</sup>Reference 33.

<sup>b</sup>Estimated from the experimental vibrational frequency of 480.6 cm<sup>-1</sup> (Ref. 34) and  $D_0$  of 33.3 kcal/mol (Ref. 35).

that are space adapted and spin adapted. CPMFT is a mean-field theory that breaks a different symmetry: electron number conservation. However, it has on average both the correct number of electrons and correlated electron pairs, as discussed in previous papers of this series.<sup>1,2</sup> The approach presented in this paper can also be applied to functionals that include range separation, as shown above.

One important aim of this work is to demonstrate that in many circumstances CPGKS can accurately mimic unrestricted results. Our approach lets us efficiently incorporate into CPMFT dynamic correlations in semilocal  $E_c^{\text{DFT}}$  functionals and static correlations stemming from the localized nature of the exchange hole in  $E_x^{\text{DFT}}$ . These effects are not intrinsically included in the CPMFT model per se, at least not in its current form. Here we have introduced alternative densities  $\chi_\sigma$  that play a key role for incorporating dynamical correlations accurately. It turns out that for systems such as  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{F}_2$ , and BH, our definition of  $\chi_\sigma$  gives energies almost identical to UGKS. On the other hand, our approach yields results very different to UGKS for systems such as the  $\text{Cr}_2$  molecule, where static correlation is predominant.

The main purpose of this paper is to demonstrate the useful role that alternative densities can play in CPMFT. Detailed comparison to other methodologies and experiment over large benchmark sets will be deferred until other aspects of CPMFT get settled, most importantly how to deal with open-shell systems and how to treat intruder orbitals (i.e., orbitals that are not entangled at dissociation yet play an important static role near equilibrium).

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## APPENDIX: RATIONALIZATION OF CPMFT

We offer here a rationalization for the CPMFT model based on Legendre transforms.<sup>36</sup> Alternatively, one could use the Levy constrained-search formalism.<sup>37</sup> The universal density functional is

$$F[\rho] = \sup_v \left( E(v) - \int v(r)\rho(r)d^3r \right), \quad (\text{A1})$$

where

$$E(v) = \inf_\Psi \langle \Psi | T + V_{\text{ee}} + \sum_{i=1}^N v(r_i) | \Psi \rangle. \quad (\text{A2})$$

$F[\rho]$  is split into a functional that is defined and thus known ( $F_0[\rho]$ ) and a complement that needs to be approximated ( $\bar{F}_0[\rho]$ ),

$$F[\rho] = F_0[\rho] + \bar{F}_0[\rho]. \quad (\text{A3})$$

A common choice for  $F_0$  is obtained by restricting  $E$  to a Hartree form,<sup>4</sup>

$$F_0[\rho] \rightarrow \sup_v \left( E_H(v, \rho) - \int v(r)\rho(r)d^3r \right) = T_s[\rho] + U[\rho], \quad (\text{A4})$$

where

$$E_H(v, \rho) = \inf_\Psi \langle \Psi | T + \sum_{i=1}^N v(r_i) | \Psi \rangle + U[\rho] \quad (\text{A5})$$

and

$$U[\rho] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2. \quad (\text{A6})$$

In this case,  $\bar{F}_0[\rho] \rightarrow E_{\text{xc}}[\rho]$ . Another choice for  $F_0[\rho]$  is obtained by restricting  $E$  to a HF form,<sup>4</sup>

$$F_0[\rho] \rightarrow \sup_v \left( E_{\text{HF}}(v) - \int v(r)\rho(r)d^3r \right), \quad (\text{A7})$$

where

$$E_{\text{HF}}(v) = \inf_\Phi \langle \Phi | T + V_{\text{ee}} + \sum_{i=1}^N v(r_i) | \Phi \rangle. \quad (\text{A8})$$

$\Phi$  is restricted to Slater determinants. In this case,  $\bar{F}_0[\rho] \rightarrow E_c[\rho]$ . In the same spirit, we can choose for  $F_0$  a HFB form

$$F_0[\rho] \rightarrow \sup_v \left( E_{\text{1HFB}}(v) - \int v(r)\rho(r)d^3r \right), \quad (\text{A9})$$

where  $E_{\text{1HFB}}(v)$  is the HFB energy of a system in the external potential  $v(r)$  with a pairing interaction of  $-1/|r-r'|$ .<sup>2</sup> In this case, a new functional is obtained,  $\bar{F}_0[\rho] \rightarrow E_{c,\text{1HFB}}[\rho]$ . CPMFT is a mixture of HF and 1HFB. In all the cases above, there remains a density functional to be approximated ( $E_{\text{xc}}, E_c, E_{c,\text{HFB}}, E_{c,\text{CPMFT}}$ ). The basic approximation for them could be a local density approximation to be discussed in future publications or such as this paper, the use of alternative densities with existing exchange and correlation functionals.

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