Synergy between pair coupled cluster doubles and pair density functional theory

Alejandro J. Garza and Ireneusz W. Bulik

Department of Chemistry, Rice University, Houston, Texas, 77251-1892, USA

Thomas M. Henderson

*Department of Chemistry and Department of Physics and Astronomy,
Rice University, Houston, Texas, 77251-1892, USA*

Gustavo E. Scuseria

*Department of Chemistry and Department of Physics and Astronomy,
Rice University, Houston, Texas, 77251-1892, USA; Chemistry Department,
Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia*

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Pair coupled cluster doubles (pCCD) has been recently studied as a method capable of accounting for static correlation with low polynomial cost. We present three combinations of pCCD with Kohn–Sham functionals of the density and on-top pair density (the probability of finding two electrons on top of each other) to add dynamic correlation to pCCD without double counting. With a negligible increase in computational cost, these pCCD+DFT blends greatly improve upon pCCD in the description of typical problems where static and dynamic correlation are both important. We argue that—as a black-box method with low scaling, size-extensivity, size-consistency, and a simple quasidiagonal two-particle density matrix—pCCD is an excellent match for pair density functionals in this type of fusion of multireference wavefunctions with DFT.

I. INTRODUCTION

The combination of multireference (MR) wavefunctions with density functional theory (DFT) is motivated by the promise of computationally affordable methods that offer a simultaneous description of static and dynamic correlation. The premise for this is that MR methods are suitable for capturing static correlation but inefficient for the dynamic one, while the opposite is true for many approximations in DFT. One may thus expect a good approximation to the exact energy to be

$$E \approx E^{\text{MR}} + E_c^{\text{DFT}}[n], \quad (1)$$

where E^{MR} is the MR energy and E_c^{DFT} is a dynamic correlation functional of the density n . However, for an appropriate description of correlation, MR+DFT mixtures such as the one above must address two problems: symmetry inconsistencies and double counting. The first problem refers to the breaking of symmetry by commonly used (*e.g.*, Kohn–Sham) density functionals, particularly in strongly correlated systems—MR methods provide symmetry-adapted densities that are thus unsuitable for DFT in these cases. The second problem is a consequence of the fact that, in general, E^{MR} contains some dynamic correlation, resulting in double counting when adding E_c^{DFT} to it.

About 40 years ago, Lie and Clementi [1, 2] reported what to the best of our knowledge is the first MR+DFT combination in the literature. Since then, a substantial amount of effort has been devoted to develop better MR+DFT schemes that avoid the aforementioned problems [3–26]. Perdew *et al.* [27] have provided a rigorous way around the symmetry dilemma within Kohn–Sham (KS) DFT. The idea is based on formulating KS-DFT in

terms of the total density $n(r)$ and the on-top pair density $P_2(r)$ (the probability of finding two electrons at r), rather than $n(r)$ and the spin density $m_z(r)$. Noting that $n(r) = n_\uparrow(r) + n_\downarrow(r)$, $m_z(r) = n_\uparrow(r) - n_\downarrow(r)$, and—for a Slater determinant [28, 29] using Löwdin’s normalization [30] for the pair density— $P_2(r) = n_\uparrow(r)n_\downarrow(r)$, one arrives at the following alternative definition for the spin density [5]

$$m(r) = \sqrt{n(r)^2 - 4P_2(r)}, \quad (2)$$

so that KS-DFT functionals can be redefined in terms of $n(r)$ and $P_2(r)$. For MR wavefunctions, $m_z(r) \neq m(r)$ and one obtains spin polarized densities fit for KS-DFT correlation functionals. Nevertheless, in practice, this solution is not perfect because $m(r)$ in Eq. 2 can become imaginary for certain strongly correlated systems [31]. Also, since $P_2(r)$ is generally computed as

$$P_2(r) = \sum_{pqrs} \Gamma_{pq}^{rs} \varphi_p^*(r) \varphi_q^*(r) \varphi_r(r) \varphi_s(r), \quad (3)$$

storage of the two-particle density matrix Γ_{pq}^{rs} is required, which limits the size of the calculation due to computer hardware restrictions. Still, $m(r)$ has been used in a number of MR+DFT studies with satisfactory results [5, 12, 15].

A number of approaches have also been devised to tackle the second problem, double counting. The simplest is to use small active spaces and reparametrized functionals [1–3], but this is not always satisfactory. Alternatively, the (interelectron) Coulomb operator may be divided into complementary MR and DFT parts to create MR+DFT hybrids without double counting [9–12], at the cost of introducing inexact DFT exchange (which

is associated with self-interaction error [32–34]). A different strategy that avoids the use of DFT exchange is to use a local scaling factor $f(r)$ of the correlation energy density [15–17]. In this case, however, $f(r)$ does not eliminate the double counting exactly; $f(r)$ is approximated at the LDA level. Again, despite these imperfections, these approaches have been used before and the outcomes have been encouraging [11, 12, 17].

There is also a third, rarely acknowledged, problem for most of the MR+DFT methods reported in the literature. This problem is actually the most likely reason for which MR+DFT schemes have not found widespread use. It is the fact that typical MR methods of quantum chemistry are not really computationally affordable for medium to large systems. Most MR methods have a poor scaling (typically combinatorial), which ultimately hinders their applicability, and further suffer from size-extensivity and size-consistency problems. This motivated us to develop combinations of DFT with a mean-field projected Hartree–Fock [35, 36] (PHF) methodology in place of a traditional MR wavefunction [25, 26]. Our PHF+DFT schemes were relatively successful; however, they are also limited by the lack of size-extensivity and size-consistency of PHF, and the fact that PHF does not always capture all of the static correlation.

Here, we explore the possibility of combining DFT with another low scaling MR technique: pair coupled cluster doubles [37–42] (pCCD). Although pCCD is a simplification of CCD, it has been shown to be able to describe multireference problems while having low polynomial scaling [42] (N^3 , neglecting the basis transformation of the two-body interaction). In fact, pCCD is exact for any electron pair and its wavefunction closely reproduces that of seniority zero full CI [42]. Contrary to PHF and traditional MR methods, pCCD is size-extensive and size-consistent. Furthermore, the pCCD wavefunction has a Γ_{pq}^{rs} with only $2N^2$ nonzero elements in the natural orbital basis [42], which greatly reduces the cost of computing $P_2(r)$ for large systems. All of this makes pCCD a good candidate for being combined with KS-DFT functionals in the $P_2(r)$ formulation of DFT. Below, we present three pCCD+DFT schemes that avoid double counting and, as a proof of concept, test the performance of these methods for describing molecular dissociations and the Beryllium isoelectronic series. Our aim is to convince the reader that pCCD+DFT is a sound approach for post-SCF incorporation of dynamic correlation in pCCD and, consequently, for improving the description of problems in which both types of correlation are important.

II. THEORY AND METHODS

A. pCCD

We begin by giving a minimal description of pCCD. Let i and a be indices for occupied and virtual orbitals,

respectively. The pCCD *ansatz* is [42]

$$|\Psi\rangle = e^{\hat{T}}|0\rangle, \quad (4)$$

where $|0\rangle$ is a closed-shell reference determinant and

$$\hat{T} = \sum_{ia} t_i^a c_{a\uparrow}^\dagger c_{a\downarrow}^\dagger c_{i\downarrow} c_{i\uparrow}. \quad (5)$$

A number of features make pCCD very suitable for combinations with pair DFT (*i.e.*, the $P_2(r)$ formulation of KS-DFT). In contrast with traditional MR methods of quantum chemistry, pCCD is black-box. Because the $\hat{T}$ operator is restricted to include only pair excitations, the equations for the t_i^a amplitudes can be solved in $\mathcal{O}(N^3)$ time. The exponential *ansatz* of Eq. 4 guarantees size-extensivity. Size-consistency is achieved by optimizing the orbitals that define the pair operators $c_{p\uparrow}c_{p\downarrow}$. This optimization can be done efficiently with low mean-field cost [42]. We note, however, that the size consistency applies strictly only for systems composed of closed shell fragments; Eq. 4 does not apply to open shells since $|0\rangle$ is closed-shell. Lastly, Γ_{pq}^{rs} has only $2N^2$ ($2N^2 - N$, to be precise) nonzero elements in the natural orbital basis, and the number of unique elements is even smaller due to symmetry. The formulas for the one- and two-particle density matrices, along with a detailed description of pCCD, can be found in a recent paper [42].

B. Evading the symmetry dilemma

We now discuss the alternative densities that we use to circumvent the symmetry dilemma in pCCD+DFT. The $P_2(r)$ formulation (Eq. 2) of KS-DFT [27] is employed. To avoid the appearance of imaginary $m(r)$ in Eq. 2, we follow the prescription suggested in Refs. [12, 15]

$$m(r) = \begin{cases} \sqrt{n(r)^2 - 4P_2(r)} & \text{if } n(r)^2 \geq 4P_2(r) \\ 0 & \text{if } n(r)^2 < 4P_2(r). \end{cases} \quad (6)$$

So, an exchange-correlation functional of $n(r)$ and $m_z(r) = n_\uparrow(r) - n_\downarrow(r)$, $E_{xc}[n, m_z]$, becomes $E_{xc}[n, m]$. For generalized gradient approximations (GGAs), an alternative gradient spin density is also required. We define $n'(r) = |\nabla n(r)|$ and use the translation procedure of Ref. [12]

$$m'(r) = \begin{cases} n'(r) \sqrt{1 - \frac{4P_2(r)}{n(r)^2}} & \text{if } n(r)^2 \geq 4P_2(r) \\ 0 & \text{if } n(r)^2 < 4P_2(r), \end{cases} \quad (7)$$

which has been shown to produce reasonable results [12]. Hence, the standard GGA $E_{xc}[n, m_z, n', m'_z]$ becomes $E_{xc}[n, m, n', m']$.

C. Suppressing the double count

Next, we describe the techniques used here to suppress double counting. As suggested in Ref. [12], a simple way

FIG. 1: Types of excitations taken into account by $\epsilon_c^{\text{hom}}(n, \infty)$ and $\epsilon_c^{\text{hom}}(n, \eta_{\text{ref}})$. The latter suppresses contributions to the correlation from excitations that go to levels higher in energy than those with occupations $n_k \neq 0$.

to avoid double counting is to evaluate all of the two-electron energy at the DFT level. The expression for the electronic energy is thus

$$E = \langle \Psi | \hat{\mathcal{H}}_{\text{core}} | \Psi \rangle + E_{\text{Hx}}^{\text{DFT}} + E_c^{\text{DFT}}, \quad (8)$$

where $|\Psi\rangle$ is the pCCD wavefunction, $\hat{\mathcal{H}}_{\text{core}}$ the one-electron core Hamiltonian, and $E_{\text{Hx}}^{\text{DFT}}$ the DFT Hartree-exchange energy. Following Sharkas *et al.* [11], we can extend the above equation to a hybrid scheme

$$E = \langle \Psi | \hat{\mathcal{H}}_{\text{core}} + \lambda r_{12}^{-1} | \Psi \rangle + (1 - \lambda) E_{\text{Hx}}^{\text{DFT}} + (1 - \lambda^2) E_c^{\text{DFT}} \quad (9)$$

where $\lambda \in [0, 1]$ is the hybrid parameter. We remark that, for $\lambda = 0$, Eq. 9 is analogous to the multiconfiguration pair DFT scheme of Li Manni *et al.* [12]; however, for $0 \leq \lambda < 1$, our application of Eq. 9 is not equivalent to that by Sharkas *et al.* [11] since we are employing the $P_2(r)$ formulation of KS-DFT—alternative densities are not used in Ref [11].

The energy formulas in Eqs. 8 and (neglecting density scaling [11]) 9 eliminate the double counting between pCCD and DFT *exactly*. However, they pay a price for it: $E_{\text{Hx}}^{\text{DFT}}$ needs to be included, which introduces self-interaction error [32–34]. One may, however, choose to pay with a different coin: to exclude $E_{\text{Hx}}^{\text{DFT}}$ in exchange for an *approximate* elimination of double counting. In this approach, the electronic energy expression takes the form

$$E = \langle \Psi | \hat{\mathcal{H}}_{\text{core}} + r_{12}^{-1} | \Psi \rangle + \int d^3r n(r) f(r) \epsilon_c^{\text{DFT}}(n, P_2), \quad (10)$$

where is $f(r)$ a local scaling factor and ϵ_c^{DFT} the DFT correlation energy density. The $f(r)$ used here is an adaptation for pCCD from the one developed for CAS-DFT by Miehlich *et al.* [15], analogous to the adaptation for PHF in our PHF+ f DFT method [26]. To compute $f(r)$, we first construct a *reference* density

$$\varrho_{\text{ref}}(r) = \sum_k^{n_k \neq 0} 2 |\psi_k(r)|^2, \quad (11)$$

FIG. 2: Dissociation energy profiles for the hydrogen molecule. The pCCD curve is exact for this system. Hybrid methods use $\lambda = 3/4$.

where $\psi_k(r)$ are the natural orbitals and the sum runs over all $\psi_k(r)$ with nonzero occupation numbers n_k . A local measure of the size of the active space can then be defined as

$$\eta_{\text{ref}}(r) = \left(\frac{\varrho_{\text{ref}}(r)}{n(r)} \right)^{1/3}, \quad (12)$$

and the scaling factor is

$$f(n, \eta_{\text{ref}}) = 1 - \frac{\epsilon_c^{\text{hom}}(n, \eta_{\text{ref}})}{\epsilon_c^{\text{hom}}(n, \infty)}, \quad (13)$$

where $\epsilon_c^{\text{hom}}(n, \infty)$ is the correlation energy density in jellium, while $\epsilon_c^{\text{hom}}(n, \eta_{\text{ref}})$ represents the same term but when excitations are restricted to the highest energy level of ϱ_{ref} , ϵ_{ref} [17, 43]. The types of excitations taken into account by $\epsilon_c^{\text{hom}}(n, \infty)$ and $\epsilon_c^{\text{hom}}(n, \eta_{\text{ref}})$ are illustrated in Fig. 1. Thus, the scaling factor is calculated at the LDA level. In practice, we evaluate $f(n, \eta_{\text{ref}})$ using the parametrization provided in Ref. [15].

It is convenient now to *introduce notation* to refer to the pCCD+DFT schemes described so far. We denote methods using Eq. 9 with $\lambda \neq 0$ as pCCD- λ DFT; when $\lambda = 0$ (*i.e.*, the case of Eq. 8) the nomenclature is pCCD-0DFT. When Eq 10 is employed (*i.e.*, the scaling factor approach), the method is referred to as pCCD+ f DFT. Lastly, the direct addition of DFT correlation to the pCCD energy without any scaling—that is, Eq. 10 with $f(r) = 1$ for all r —is denoted as pCCD+1DFT. We refer to methods combining pCCD and DFT in general as pCCD+DFT.

D. Computational details

In-house programs are used for the pCCD part of the pCCD+DFT calculations; the DFT part is carried out in a modified version of *Gaussian* [44]. For all the

FIG. 3: Symmetric dissociations of H_4 , H_6 (both linear chains), and H_2O [$\angle(HOH) = 104.474^\circ$]. Hybrid methods use $\lambda = 3/4$. The FCI data are from Ref. [52] and use spherical basis functions and $\angle(HOH) = 110.6^\circ$ (see text). Relative energies are with respect to the molecule at the dissociation limit.

pCCD+DFT combinations presented here, the pCCD wavefunction is determined self-consistently; the DFT energy is evaluated afterward in a single point calculation using the $n(r)$ and $P_2(r)$ from pCCD. Unless otherwise indicated, all hybrid pCCD- λ DFT schemes use $\lambda = 3/4$, since this value provides reasonable results for a number of systems (*vide infra*). The threshold on n_k for an orbital to contribute to ϱ_{ref} in Eq. 11 is set to $n_k \leq 1 \times 10^{-12}$; no appreciable differences in the results given here are observed when using $n_k \leq 1 \times 10^{-8}$.

The LDA functional that we employ uses VWN5 correlation [45] and 2/3 of Slater [46] exchange—this scaling has been used before in MR+DFT [12] and we observed that it helps to reduce the typical overbinding of LDA. For combinations of pCCD with GGAs, we use both PBE exchange and correlation [47]. All calculations use cartesian basis functions unless noted otherwise.

FIG. 4: Dissociations of the CO bond in formaldehyde [$r(\text{HC}) = 1.110 \text{ \AA}$, $\angle(\text{HCO}) = 122.33^\circ$] and the nitrogen molecule. Hybrid methods use $\lambda = 3/4$. The FCI data are from [53] and use spherical basis functions and a $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ frozen core. Relative energies are with respect to the molecule at the dissociation limit.

III. RESULTS AND DISCUSSION

The dissociation energy curves for the H_2 molecule calculated by different pCCD+DFT methods are shown in Fig. 2. Since pCCD is exact for two-electron systems, H_2 provides a suitable testing ground for the schemes that suppress double counting. Except for pCCD+1PBE (which does not exclude double counting) and pCCD-0LDA, all of the pCCD+DFT methods provide excellent agreement with experiment [48–50] and the exact pCCD curve. In the case of pCCD-0LDA, the problem is remedied in pCCD-λLDA by including a fraction ($\lambda = 3/4$) of the pCCD two-electron energy. For pCCD+1PBE, the problem is clearly double counting and the scaling factor in pCCD+fPBE heals this issue. We do not employ the pCCD+fLDA variant because LDA provides correlation energies that are too large in magnitude; this problem is not so severe in hybrid schemes due to error cancellation with the LDA exchange. This is a well-known feature of LDA functionals, which are not recommendable for MR+DFT combinations with 100% MR exchange [15, 26].

Figure 3 shows the energy profiles for the symmetric dissociation of an H_4 chain, an H_6 chain (both linear),

and the water molecule [$\angle(\text{HOH}) = 104.474^\circ$]. Of course, pCCD is no longer exact for these systems so we provide reference data from unrestricted coupled cluster singles, doubles and perturbative triples [51] [UCCSD(T)] calculations, and (when available) full configuration interaction [52, 53] (FCI) and experimental data from the literature [48–50]. We stress, however, that the FCI data for water [52] are not directly comparable to our results here because they use a spherical basis and a different HOH angle (110.6°); they should be taken only as a complementary guide. Likewise, experimental data do not include zero-point corrections so it should also be regarded only as a reference. In the total energy plots, pCCD-λLDA and pCCD-0LDA data are not shown because the energies for these methods are too high as a result of the LDA exchange. However, pCCD-λLDA provides satisfactory relative energies and bond lengths; it is significantly better than pCCD-0LDA, which systematically overestimates bond lengths. The improvement of pCCD-λPBE and pCCD+fPBE over pCCD is clear from Figure 3. The two schemes are in good agreement with UCCSD(T), and available FCI and experimental data, in terms of both total and relative energies. It is also notable that the hybrid and scaling factor approaches ap-

FIG. 5: Dependence of dissociation energy on the hybrid parameter λ for pCCD- λ PBE.

FIG. 6: Correlation energies (with respect to RHF) for the Be isoelectronic series. The accurate data are from Ref. [55]. The SUHF+ f TPSS data are from Ref. [26] and use a spherical cc-pVTZ basis; all other calculations use a cc-pVTZ(-f) basis.

pear to be largely effective for suppressing double counting. Indeed, excluding these corrections (pCCD+1PBE curves) results in significant overbinding and total energies that are well below those of UCCSD(T) and FCI.

The breaking of the multiple bonds in formaldehyde and N_2 is studied in Fig. 4. Analogous trends to those appearing in Fig. 3 are observed. Again, the raw addition of DFT dynamical correlation to pCCD (pCCD+1PBE) leads to substantial overcorrelation due to double counting. The schemes to avoid the double count improve significantly upon both pCCD and pCCD+1PBE. One important difference though is that, at the dissociation limit, the pCCD wavefunction seems to be less suited for describing the strong correlations than in the previous cases of Fig. 3. This results in too-high energies at large bond lengths for all pCCD-based methods, specially in the case of N_2 . Indeed, for N_2 at large bond lengths the pCCD energy is higher than that of unrestricted Hartree-

FIG. 7: Types of excitations taken into account by different methods. The scaling factor eliminates the double counting but may also suppress dynamic correlation missing in pCCD, resulting in underestimation of the correlation energy.

Fock (UHF limit). The most likely reason for this problem is the restricted determinant underlying the pCCD wavefunction. It is possible that this issue can be alleviated via unrestricted pCCD formalisms, which are currently under investigation.

Throughout the calculations discussed so far, we have employed $\lambda = 3/4$ in the pCCD- λ DFT methods. We note, however, that results can depend significantly on the value of λ , albeit the above choice appears to consistently produce reasonable data. The dependence of the dissociation energy (D_e) on λ for the molecules that we have studied is analyzed in Fig. 5. While for H_2 this dependence is rather small, this does not hold true for stronger bonds such as the triple bond in N_2 . The degree of dependence of D_e on λ seems to be somewhat correlated with the overall magnitude of D_e . Still, with $\lambda = 3/4$, pCCD- λ PBE yields results that are comparable to pCCD+ f PBE and benchmark data. Furthermore, the λ value used here corresponds to a rather conservative approach because most of the energy is evaluated at the pCCD level; only 25% E_{Hx}^{DFT} and $\sim 44\%$ E_c^{DFT} are included. Hence, it is reasonable to expect good behavior from pCCD- λ DFT with $\lambda = 3/4$, at least in cases when pCCD is qualitatively correct.

We discuss now a different type of benchmark for pCCD+DFT: the Beryllium isoelectronic series (*i.e.*, $X^{(Z-4)+}$ ions). The strong correlation in a $X^{(Z-4)+}$ ion is different from the “left-right” correlation in molecular dissociations; it is angular $s^2 \rightarrow p^2$ correlation and increases linearly with the nuclear charge Z . The description of $X^{(Z-4)+}$ ions has proven to be challenging for other MR+DFT methods, such as our combination [26] of spin-projected Hartree-Fock [36] (SUHF) with the functional by Tao *et al.* [54] (TPSS). Fig. 6 compares the pCCD+DFT correlation energies with accurate data from Ref. [55] and results from the SUHF+ f TPSS method of Ref. [26]. SUHF+ f TPSS has a similar problem to that of CAS(2,2)+DFT [15] methods; the magnitude of the correlation increases as $\ln Z$, rather than linearly. In contrast, pCCD displays the correct qual-

itative trend of the correlation and pCCD+*f*PBE and pCCD- λ PBE maintain this behavior while also providing an improvement of the energy. As could be expected from what we have seen so far, pCCD+1PBE significantly overshoots the correlation energy. We also remind the reader that pCCD is exact for any electron pair and hence it is exact for the Helium isoelectronic series, a related benchmark set often contrasted with the Be series.

Something that can also be noted from the results presented here is a slight tendency of pCCD+*f*PBE to underestimate the correlation energy. This can be understood as a feature of the scaling factor: if the MR wavefunction does not fully correlate the orbitals with $n_k \neq 0$ and which hence contribute to $\varrho_{\text{ref}}(r)$ in Eq. 11, then the missing correlations should ideally be incorporated from DFT but are suppressed by the scaling factor. This situation is illustrated in Fig. 7. The problem affects pCCD+*f*DFT because pCCD excludes correlations of the active orbitals that break electron pairs [42]. This issue of the scaling factor holds for other MR+*f*DFT methods (albeit for different reasons), such as CAS+*f*DFT and PHF+*f*DFT, where it typically is related to core orbitals with $n_k \approx 2$ [17, 26]. In pCCD+*f*DFT, orbitals with small n_k may also be affected given that it is unlikely to get occupations numbers that are exactly zero due to the structure of the pCCD density matrix (although exact zeros by symmetry are possible). To see this, we note that the occupation numbers in pCCD are

$$n_i = 2 - 2 \sum_a t_i^a z_a^i \quad (14)$$

for occupied orbitals, and

$$n_a = 2 \sum_i t_i^a z_a^i \quad (15)$$

for virtual ones, where the z amplitudes come from the left-hand eigenvector of the transformed Hamiltonian $e^{-\hat{T}} \hat{H} e^{\hat{T}}$, $\langle 0 | (1 + \hat{Z})$, and $\hat{Z}$ is defined analogously to $\hat{T}$ in Eq. 5 [42]. In most of our calculations, we observed a large number of, rather small, nonzero occupations with magnitudes of about 1×10^{-3} to 1×10^{-6} . Thus, most orbitals contribute to $\varrho_{\text{ref}}(r)$ which can be expected to lead to exaggeration of the scaling and hence underestimation of the DFT correlation. It is likely that, for calculations employing very large basis sets, higher thresholds on n_k than the ones used here be required to avoid a too-large artificial scaling of E_c^{DFT} . Nevertheless, we note that despite this issue our results for pCCD+*f*PBE are quite satisfactory, suggesting that the effect of this problem is

not too dramatic. In addition, as noted above, this problem can be alleviated by simply relaxing the threshold on n_k for orbitals to contribute to $\varrho_{\text{ref}}(r)$, or by the various improvements of the scaling factor that have been proposed in the literature [16, 17, 26]. For example, increasing the threshold on n_k to 1×10^{-5} for the Be series leads to *ca.* 5 mHartree more of DFT correlation, resulting in better agreement with the accurate data. We also note that the pCCD- λ DFT hybrids also provide good results here and eliminate double counting exactly (disregarding uniform density scaling, which is not considered in usual hybrid approximations [11]). Ultimately, however, functionals designed to work specifically with the pCCD pair density are needed to avoid double counting in the best possible manner and develop the full potential of pCCD+DFT.

IV. CONCLUSIONS

The pCCD+*f*DFT and pCCD- λ DFT schemes are economical and robust tools for incorporating dynamical correlation in pCCD, improving the description of the energy. Our results demonstrate the importance of suppressing double counting in pCCD+DFT, and also provide further evidence of the soundness of using the $P_2(r)$ formulation of KS-DFT for combining MR wavefunctions with DFT. For the pCCD+DFT combinations studied here, using a GGA functional is nearly always preferable over the use of LDA. Likewise, pCCD- λ DFT with $\lambda = 3/4$ is recommendable over pCCD-0DFT. Consistently good results are provided by pCCD+*f*PBE and pCCD- λ PBE. It should also be noted that pCCD has a number of qualities which make it more suitable for combinations with DFT than other MR methods: pCCD is black-box, has low scaling, is size-consistent, is size-extensive, and its two-particle density matrix is sparse. We hope that these qualities and the good results obtained here can stimulate the further development of pCCD+DFT methods.

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