A density-based basis set correction for wave function theory

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We report a universal density-based basis set incompleteness correction that can be applied to any wave function theory method.

I. INTRODUCTION

Contemporary quantum chemistry has developed in two directions — wave function theory (WFT)[1] and density-functional theory (DFT).[2] Although both spring from the same Schrödinger equation, each of these philosophies has its own advantages and shortcomings.

WFT is attractive as it exists a well-defined path for systematic improvement. For example, the coupled cluster (CC) family of methods offers a powerful WFT approach for the description of weakly correlated systems and is well regarded as the gold standard of quantum chemistry. By increasing the excitation degree of the CC expansion, one can systematically converge, for a given basis set, to the exact, full configuration interaction (FCI) limit, although the computational cost associated with such improvement is usually pricey. One of the most fundamental drawback of conventional WFT methods is the slow convergence of energies and properties with respect to the size of the one-electron basis set. This undesirable feature was put into light by Kutzelnigg more than thirty years ago,[3] who proposed, to palliate this, to introduce explicitly the interelectronic distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ as a basis function.[3–8] The resulting F12 methods yields a prominent improvement of the energy convergence, and achieve chemical accuracy for small organic molecules with relatively small Gaussian basis sets.[9–12] For example, at the CCSD(T) level, it is advertised that one can obtain quintuple-zeta quality correlation energies with a triple-zeta basis,[13] although computational overheads are introduced by the large auxiliary basis used to resolve three- and four-electron integrals.

Present-day DFT calculations are almost exclusively done within the so-called Kohn-Sham (KS) formalism, which corresponds to an exact dressed one-electron theory.[14] DFT's attractivity originates from its very favorable cost/efficient ratio as it can provide accurate energies and properties at a relatively low computational cost. Thanks to this, KS-DFT[14,15] has become the workhorse of electronic structure calculations for atoms, molecules and solids.[16] To obtain accurate results within DFT, one only requires an exchange and correlation functionals, which can be classified in various families depending on their physical input quantities.[17] Although there is no clear way on how to systematically improve density-functional approximations (DFAs), climbing the Jacob's ladder of DFT is potentially the most satisfactory way forward (or upward in that case).[18,19] In the present context, one of the

interesting feature of density-based methods is their much faster convergence with respect to the size of the basis set.[20]

Progress toward unifying these two approaches are ongoing. Using accurate and rigorous WFT methods, some of us have developed radical generalisations of DFT that are free of the well-known limitations of conventional DFT. In that respect range-separated DFT (RS-DFT) is particularly promising as it allows to perform multi-configurational DFT calculations within a rigorous mathematical framework. Range-separated hybrids, i.e. single-determinant approximations of RS-DFT, correct for the wrong long-range behavior of the usual hybrid approximations thanks to the inclusion of the long-range part of the Hartree-Fock (HF) exchange.

The present manuscript is organised as follows. Unless otherwise stated, atomic used are used.

II. THEORY

The basis-set correction investigated here proposes to use the RSDFT formalism to capture a part of the short-range correlation effects missing from the description of the WFT in a finite basis set. Here, we briefly explain the working equations and notations needed for this work, and the interested reader can find the detailed formal derivation of the theory in [21].

A. Correcting the basis set error of a general WFT model

Consider a $N-$electron physical system described in an incomplete basis-set $\mathcal{B}$ and for which we assume to have both the FCI density $n_{\Psi_{\text{FCI}}^{\mathcal{B}}}$ and energy $E_{\text{FCI}}^{\mathcal{B}}$. Assuming that $n_{\Psi_{\text{FCI}}^{\mathcal{B}}}$ is a good approximation of the *exact* ground state density, according to equation (15) of [21], one can approximate the exact ground state energy E_0 as

$$E_0 \approx E_{\text{FCI}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[n_{\Psi_{\text{FCI}}^{\mathcal{B}}}] \tag{1}$$

where $\bar{E}^{\mathcal{B}}[n]$ is the complementary density functional defined in equation (8) of [21]

$$\begin{aligned} \bar{E}^{\mathcal{B}}[n] = &\min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle \\ &- \min_{\Psi^{\mathcal{B}} \to n} \left\langle \Psi^{\mathcal{B}} \middle| \hat{T} + \hat{W}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle, \end{aligned} \tag{2}$$

$\Psi^{\mathcal{B}}$ is a wave function obtained from the $N-$electron Hilbert space spanned by $\mathcal{B}$, Ψ is a general $N-$electron wave function being obtained in a complete basis, and both wave functions $\Psi^{\mathcal{B}}$ and Ψ yield the same target density n.

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Provided that the functional $\bar{E}^{\mathcal{B}}[n]$ is known exactly, the only approximation performed in (1) is that the FCI density $n_{\Psi^{\mathcal{B}}_{\text{FCI}}}$ coincides with the exact ground state density, which in general is a reasonable approximation as the density converges rapidly with the basis set.

An important aspect of such a theory is that, in the limit of a complete basis set $\mathcal{B}$ (which we refer as $\mathcal{B} \to \infty$), the functional $\bar{E}^{\mathcal{B}}[n]$ tends to zero

$$\lim_{\mathcal{B}\to\infty} \bar{E}^{\mathcal{B}}[n] = 0 \qquad \forall\ n\ , \tag{3}$$

which implies that the exact ground state energy coincides with the FCI energy in complete basis set (which we refer as E^{∞}_{FCI})

$$\lim_{\mathcal{B}\to\infty} E^{\mathcal{B}}_{\text{FCI}} + \bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}] = E^{\infty}_{\text{FCI}} \ . \tag{4}$$

Here we propose to generalize such approach to a general WFT model, referred here as $\mathcal{Y}$, projected in a basis set $\mathcal{B}$ which must provides a density $n^{\mathcal{B}}_{\mathcal{Y}}$ and an energy $E^{\mathcal{B}}_{\mathcal{Y}}$. As any wave function model is necessary an approximation to the FCI model, one can write

$$E^{\mathcal{B}}_{\text{FCI}} \approx E^{\mathcal{B}}_{\mathcal{Y}} \tag{5}$$

and

$$n_{\Psi^{\mathcal{B}}_{\text{FCI}}} \approx n^{\mathcal{B}}_{\mathcal{Y}} \tag{6}$$

and by defining the energy provided by the model $\mathcal{Y}$ in the complete basis set

$$E^{\infty}_{\mathcal{Y}} = \lim_{\mathcal{B}\to\infty} E^{\mathcal{B}}_{\mathcal{Y}} \ , \tag{7}$$

we can then write

$$E^{\infty}_{\mathcal{Y}} \approx E^{\mathcal{B}}_{\mathcal{Y}} + \bar{E}^{\mathcal{B}}[n^{\mathcal{B}}_{\mathcal{Y}}] \tag{8}$$

which verifies the correct limit since

$$\lim_{\mathcal{B}\to\infty} \bar{E}^{\mathcal{B}}[n^{\mathcal{B}}_{\mathcal{Y}}] = 0 \ . \tag{9}$$

B. Basis set correction for the CIPSI algorithm and the CCSD(T) ansatz

In this work we propose to apply the basis set correction to a selected CI algorithm, namely the CIPSI algorithm, and to the CCSD(T) ansatz in order to speed-up the basis set convergence of these models.

1. Basis set correction for the CCSD(T) energy

The CCSD(T) method is a very popular WFT approach which is known to provide very good estimation of the correlation energies for weakly correlated systems, whose wave function are dominated by the HF Slater determinant. Defining $E^{\mathcal{B}}_{\text{CCSD(T)}}$ as the CCSD(T) energy obtained in $\mathcal{B}$, in the present notations we have

$$E^{\mathcal{B}}_{\mathcal{Y}} = E^{\mathcal{B}}_{\text{CCSD(T)}} \ . \tag{10}$$

In the context of the basis set correction, one needs to choose a density as the density of the model $n^{\mathcal{B}}_{\mathcal{Y}}$, and we chose here the HF density

$$n^{\mathcal{B}}_{\mathcal{Y}} = n^{\mathcal{B}}_{\text{HF}} \ . \tag{11}$$

Such a choice can be motivated by the fact that the correction to the HF density brought by the excited Slater determinants are at least of second-order in perturbation theory. Therefore, we approximate the complete basis set CCSD(T) energy $E^{\infty}_{\text{CCSD(T)}}$ by

$$E^{\infty}_{\text{CCSD(T)}} \approx E^{\mathcal{B}}_{\text{CCSD(T)}} + \bar{E}^{\mathcal{B}}[n^{\mathcal{B}}_{\text{HF}}] \ . \tag{12}$$

2. Correction of the CIPSI algorithm

The CIPSI algorithm approximates the FCI wave function through an iterative selected CI procedure, and the FCI energy through a second-order multi-reference perturbation theory. The CIPSI algorithm belongs to the general class of methods build upon selected CI[22–28] which have been successfully used to converge to FCI correlation energies, one-body properties, and nodal surfaces.[26,29–40] The CIPSI algorithm used in this work uses iteratively enlarged selected CI spaces and Epstein–Nesbet[41,42] multi-reference perturbation theory. Within a basis set $\mathcal{B}$, the CIPSI energy is

$$E^{\mathcal{B}}_{\text{CIPSI}} = E_{\text{v}} + E^{(2)} \ , \tag{13}$$

where E_{v} is the variational energy

$$E_{\text{v}} = \min_{\{c_{\text{I}}\}} \frac{\left\langle \Psi^{(0)} \middle| \hat{H} \middle| \Psi^{(0)} \right\rangle}{\left\langle \Psi^{(0)} \middle| \Psi^{(0)} \right\rangle} \ , \tag{14}$$

where the reference wave function $\left| \Psi^{(0)} \right\rangle = \sum_{\text{I}\in\mathcal{R}} c_{\text{I}} \left| \text{I} \right\rangle$ is expanded in Slater determinants I within the CI reference space $\mathcal{R}$, and $E^{(2)}$ is the second-order energy correction

$$E^{(2)} = \sum_{\kappa} \frac{|\left\langle \Psi^{(0)} \middle| \hat{H} \middle| \kappa \right\rangle|^2}{E_{\text{v}} - \left\langle \kappa \middle| H \middle| \kappa \right\rangle} = \sum_{\kappa} e^{(2)}_{\kappa} \ , \tag{15}$$

where κ denotes a determinant outside $\mathcal{R}$. To reduce the cost of the evaluation of the second-order energy correction, the semi-stochastic multi-reference approach of Garniron *et al.*[43] was used, adopting the technical specifications recommended in that work. The CIPSI energy is systematically refined by doubling the size of the CI reference space at each iteration, selecting the determinants κ with the largest $|e^{(2)}_{\kappa}|$. In order to reach a faster convergence of the estimation of the FCI

energy, we use the extrapolated FCI energy (exFCI) proposed by Holmes *et al*[44] which we refer here as $E_{\text{exFCI}}^{\mathcal{B}}$.

In the context of the basis set correction, we use the following conventions

$$E_{\mathcal{Y}}^{\mathcal{B}} = E_{\text{exFCI}}^{\mathcal{B}} \tag{16}$$

$$n_{\mathcal{Y}}^{\mathcal{B}}(\mathbf{r}) = n_{\text{CIPSI}}^{\mathcal{B}}(\mathbf{r}) \tag{17}$$

where the density $n_{\text{CIPSI}}^{\mathcal{B}}(\mathbf{r})$ is defined as

$$n_{\text{CIPSI}}^{\mathcal{B}} = \sum_{ij \in \mathcal{B}} \left\langle \Psi^{(0)} \middle| \hat{a}_i^\dagger \hat{a}_j \middle| \Psi^{(0)} \right\rangle \phi_i(\mathbf{r})\phi_j(\mathbf{r}) , \tag{18}$$

and $\phi_i(\mathbf{r})$ are the spin orbitals in the MO basis evaluated at $\mathbf{r}$. As it was shown in [21] that the CIPSI density converges rapidly with the size of $\Psi^{(0)}$ for weakly correlated systems, $n_{\text{CIPSI}}^{\mathcal{B}}(\mathbf{r})$ can be thought as a reasonable approximation of the FCI density $n_{\Psi_{\text{FCI}}^{\mathcal{B}}}$.

Finally, we approximate complete basis set exFCI energy $E_{\text{exFCI}}^{\infty}$ as

$$E_{\text{exFCI}}^{\infty} \approx E_{\text{exFCI}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[n_{\text{CIPSI}}^{\mathcal{B}}] \tag{19}$$

C. General scheme for the approximation of the unknown complementary functional $\bar{E}^{\mathcal{B}}[n]$

The functional $\bar{E}^{\mathcal{B}}[n]$ is not universal as it depends on the basis set $\mathcal{B}$ used and a simple analytical form for such a functional is of course not known. Following the work of [21], we approximate $\bar{E}^{\mathcal{B}}[n]$ in two-steps which grantee the correct behaviour in the limit of a complete basis set (see (4)). First, we define a real-space representation of the coulomb interaction projected in $\mathcal{B}$, which is then fitted with a long-range interaction thanks to a range-separation parameter $\mu(r)$ varying in space (see II D). Then, we choose a specific class of short-range density functionals, namely the short-range correlation functionals with multi-determinantal reference (ECMD) introduced by Toulouse *et al*[45], that we evaluate at the density $n_{\mathcal{Y}}^{\mathcal{B}}$ provided by the model (see II E 1) and with the range-separation parameter $\mu(r)$ varying in space.

D. Definition of a real-space representation of the coulomb operator truncated in a basis-set $\mathcal{B}$

One of the consequences of the use of an incomplete basis-set $\mathcal{B}$ is that the wave function does not present a cusp near the electron coalescence point, which means that all derivatives of the wave function are continuous. As the exact electronic cusp originates from the divergence of the coulomb interaction at the electron coalescence point, a cusp-free wave function could also originate from an Hamiltonian with a non-divergent electron-electron interaction. Therefore, the impact of the incompleteness of a finite basis-set $\mathcal{B}$ can be thought as a cutting of the divergence of the coulomb interaction at the electron coalescence point.

The present paragraph briefly describes how to obtain an effective interaction $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ which:

- is non-divergent at the electron coalescence point as long as an incomplete basis set $\mathcal{B}$ is used,

- tends to the regular $1/r_{12}$ interaction in the limit of a complete basis set $\mathcal{B}$.

1. General definition of an effective interaction for the basis set $\mathcal{B}$

Consider the coulomb operator projected in the basis-set $\mathcal{B}$

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \frac{1}{2} \sum_{ijkl \,\in\, \mathcal{B}} V_{ij}^{kl} \; \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i, \tag{20}$$

where the indices run over all orthonormal spin-orbitals in $\mathcal{B}$ and V_{ij}^{kl} are the usual coulomb two-electron integrals. Consider now the expectation value of $\hat{W}_{\text{ee}}^{\mathcal{B}}$ over a general wave function $\Psi^{\mathcal{B}}$ belonging to the $N-$electron Hilbert space spanned by the basis set $\mathcal{B}$. After a few mathematical work (see appendix A of [21] for a detailed derivation), such an expectation value can be rewritten as an integral over the two-electron spin and space coordinates:

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}_{\text{ee}}^{\mathcal{B}} \middle| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint d\mathbf{X}_1 \, d\mathbf{X}_2 \; f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) , \tag{21}$$

where the function $f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ is

$$f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{ijklmn \,\in\, \mathcal{B}} V_{ij}^{kl} \; \Gamma_{kl}^{mn}[\Psi^{\mathcal{B}}]$$
$$\phi_n(\mathbf{X}_2)\phi_m(\mathbf{X}_1)\phi_i(\mathbf{X}_1)\phi_j(\mathbf{X}_2) , \tag{22}$$

$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}]$ is the two-body density tensor of $\Psi^{\mathcal{B}}$

$$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] = \left\langle \Psi^{\mathcal{B}} \middle| \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_n \hat{a}_m \middle| \Psi^{\mathcal{B}} \right\rangle , \tag{23}$$

and $\mathbf{X}$ collects the space and spin variables,

$$\mathbf{X} = (\mathbf{r}, \sigma) \qquad \mathbf{r} \in \mathbb{R}^3, \; \sigma = \pm\frac{1}{2}$$
$$\int d\mathbf{X} = \sum_{\sigma=\pm\frac{1}{2}} \int_{\mathbb{R}^3} d\mathbf{r} . \tag{24}$$

Then, consider the expectation value of the exact coulomb operator over $\Psi^{\mathcal{B}}$

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint d\mathbf{X}_1 \, d\mathbf{X}_2 \; \frac{1}{r_{12}} n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2) \tag{25}$$

where $n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2)$ is the two-body density associated to $\Psi^{\mathcal{B}}$. Because $\Psi^{\mathcal{B}}$ belongs to $\mathcal{B}$, such an expectation value coincides with the expectation value of $\hat{W}_{\text{ee}}^{\mathcal{B}}$

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}_{\text{ee}}^{\mathcal{B}} \middle| \Psi^{\mathcal{B}} \right\rangle = \left\langle \Psi^{\mathcal{B}} \middle| \hat{W}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle, \tag{26}$$

which can be rewritten as:

$$\iint d\mathbf{X}_1 \, d\mathbf{X}_2 \; W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \; n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$$
$$= \iint d\mathbf{X}_1 \, d\mathbf{X}_2 \; \frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \; n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2). \quad (27)$$

where we introduced $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$

$$W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \frac{f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}{n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}, \quad (28)$$

which is the effective interaction in the basis set $\mathcal{B}$.

As already discussed in 21, such an effective interaction is symmetric, *a priori* non translational nor rotational invariant if the basis set $\mathcal{B}$ does not have such symmetries and is necessary *finite* at the electron coalescence point for an incomplete basis set $\mathcal{B}$. Also, as demonstrated in the appendix B of 21, $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ tends to the regular coulomb interaction $1/r_{12}$ for all points $(\mathbf{X}_1, \mathbf{X}_2)$ and any choice of $\Psi^{\mathcal{B}}$ in the limit of a complete basis set $\mathcal{B}$.

2. Definition of a valence effective interaction

As most of the WFT calculations are done using a frozen core approximation, it is important to define an effective interaction within a general subset of molecular orbitals that we refer as $\mathcal{B}_{\text{val}}$.

According to (32) and (21), the effective interaction is defined by the expectation value of the coulomb operator over a wave function $\Psi^{\mathcal{B}}$. Therefore, to define an effective interaction accounting only for the valence electrons, one needs to define a function $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ satisfying

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint d\mathbf{X}_1 \, d\mathbf{X}_2 \; f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2), \quad (29)$$

where $\hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}}$ is the valence coulomb operator defined as

$$\hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}} = \frac{1}{2} \sum_{ijkl \, \in \, \mathcal{B}_{\text{val}}} V^{kl}_{ij} \, \hat{a}^\dagger_k \hat{a}^\dagger_l \hat{a}_j \hat{a}_i \;, \quad (30)$$

and $\mathcal{B}_{\text{val}}$ is the subset of molecular orbitals for which we want to define the expectation value, which will be typically the all MOs except those frozen. Following the spirit of (22), the function $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ can be defined as

$$f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{ij \, \in \, \mathcal{B}} \sum_{klmn \, \in \, \mathcal{B}_{\text{val}}} V^{kl}_{ij} \, \Gamma^{mn}_{kl}[\Psi^{\mathcal{B}}]$$
$$\phi_n(\mathbf{X}_2)\phi_m(\mathbf{X}_1)\phi_i(\mathbf{X}_1)\phi_j(\mathbf{X}_2). \quad (31)$$

Then, the effective interaction associated to the valence $W^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ is simply defines as

$$W^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \frac{f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}{n^{(2)}_{\Psi^{\mathcal{B}}, \text{val}}(\mathbf{X}_1, \mathbf{X}_2)}, \quad (32)$$

where $n^{(2)}_{\Psi^{\mathcal{B}}, \text{val}}(\mathbf{X}_1, \mathbf{X}_2)$ is the two body density associated to the valence electrons:

$$n^{(2)}_{\Psi^{\mathcal{B}}, \text{val}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{klmn \, \in \, \mathcal{B}_{\text{val}}} \Gamma^{kl}_{mn}[\Psi^{\mathcal{B}}] \, \phi_m(\mathbf{X}_1)\phi_n(\mathbf{X}_2)\phi_k(\mathbf{X}_1)\phi_l(\mathbf{X}_2). \quad (33)$$

It is important to notice in (31) the difference between the set of orbitals for the indices (i, j), which span the full set of MOs within $\mathcal{B}$, and the (k, l, m, n), which span only the valence space $\mathcal{B}_{\text{val}}$. Only with such a definition, one can show (see annex) that $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ fulfills (29) and tends to the exact interaction $1/r_{12}$ in the limit of a complete basis set $\mathcal{B}$, whatever the choice of subset $\mathcal{B}_{\text{val}}$.

3. Definition of a range-separation parameter varying in space

To be able to approximate the complementary functional $\bar{E}^{\mathcal{B}}[n]$ thanks to functionals developed in the field of RSDFT, we fit the effective interaction with a long-range interaction having a range-separation parameter *varying in space*. More precisely, if we define the value of the interaction at coalescence as

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}) = W_{\Psi^{\mathcal{B}}}(\mathbf{X}, \bar{\mathbf{X}}). \quad (34)$$

where $(\mathbf{X}, \bar{\mathbf{X}})$ means a couple of anti-parallel spins at the same point in $\mathbf{r}$, we propose a fit for each point in $\mathbb{R}^3$ of $W_{\Psi^{\mathcal{B}}}(\mathbf{r})$ with a long-range-like interaction:

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}) = w^{\text{lr}, \mu(\mathbf{r}; \Psi^{\mathcal{B}})}(\mathbf{r}, \mathbf{r}) \quad (35)$$

where the long-range-like interaction is defined as:

$$w^{\text{lr}, \mu(\mathbf{r})}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left(\frac{\text{erf}(\mu(\mathbf{r}_1) \, r_{12})}{r_{12}} + \frac{\text{erf}(\mu(\mathbf{r}_2) \, r_{12})}{r_{12}} \right). \quad (36)$$

The equation (34) is equivalent to the following condition for $\mu(\mathbf{r}; \Psi^{\mathcal{B}})$:

$$\mu(\mathbf{r}; \Psi^{\mathcal{B}}) = \frac{\sqrt{\pi}}{2} W_{\Psi^{\mathcal{B}}}(\mathbf{r}). \quad (37)$$

As we defined an effective interaction for the valence electrons, we also introduce a valence range-separation parameter as

$$\mu_{\text{val}}(\mathbf{r}; \Psi^{\mathcal{B}}) = \frac{\sqrt{\pi}}{2} W^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{r}). \quad (38)$$

An important point to notice is that, in the limit of a complete basis set $\mathcal{B}$, as

$$\lim_{\mathcal{B} \to \infty} W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = 1/r_{12} \quad \forall \; (\mathbf{X}_1, \mathbf{X}_2)$$
$$\lim_{\mathcal{B} \to \infty} W^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = 1/r_{12} \quad \forall \; (\mathbf{X}_1, \mathbf{X}_2) \;, \quad (39)$$

one has

$$\lim_{\mathcal{B} \to \infty} W_{\Psi^{\mathcal{B}}}(\mathbf{r}) = +\infty \;,$$
$$\lim_{\mathcal{B} \to \infty} W^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{r}) = +\infty \;, \quad (40)$$

and therefore

$$\lim_{\mathcal{B}\to\infty} \mu(\mathbf{r}; \Psi^{\mathcal{B}}) = +\infty$$
$$\lim_{\mathcal{B}\to\infty} \mu_{\text{val}}(\mathbf{r}; \Psi^{\mathcal{B}}) = +\infty \ . \tag{41}$$

E. Approximations for the complementary functional $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$

1. General scheme

In [21] the authors have proposed to approximate the complementary functional $\bar{E}^{\mathcal{B}}[n]$ by using a specific class of SRDFT energy functionals, namely the ECMD whose general definition is[45]:

$$\bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu] = \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle \\ - \langle \Psi^{\mu}[n(\mathbf{r})]| \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mu}[n(\mathbf{r})]\rangle, \tag{42}$$

where the wave function $\Psi^{\mu}[n(\mathbf{r})]$ is defined by the constrained minimization

$$\Psi^{\mu}[n(\mathbf{r})] = \arg \min_{\Psi \to n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \Psi \rangle, \tag{43}$$

where $\hat{W}_{\text{ee}}^{\text{lr},\mu}$ is the long-range electron-electron interaction operator

$$\hat{W}_{\text{ee}}^{\text{lr},\mu} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \ w^{\text{lr},\mu}(|\mathbf{r}_1 - \mathbf{r}_2|)\hat{n}^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \tag{44}$$

with

$$w^{\text{lr},\mu}(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{\text{erf}(\mu|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{45}$$

and the pair-density operator $\hat{n}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) - \delta(\mathbf{r}_1 - \mathbf{r}_2)\hat{n}(\mathbf{r}_1)$. The ECMD functionals admit two limits as function of μ

$$\lim_{\mu\to\infty} \bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu] = 0 \quad \forall \ n(\mathbf{r}) \tag{46}$$

$$\lim_{\mu\to 0} \bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu] = E_{\text{c}}[n(\mathbf{r})] \quad \forall \ n(\mathbf{r}) \tag{47}$$

where $E_{\text{c}}[n(\mathbf{r})]$ is the usual universal correlation functional defined in the Kohn-Sham DFT. These functionals differ from the standard RSDFT correlation functional by the fact that the reference is not the Kohn-Sham Slater determinant but a multi determinant wave function, which makes them much more adapted in the present context where one aims at correcting the general multi-determinant WFT model.

The general scheme for estimating $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$ is the following. Consider a given approximated ECMD functional $\bar{E}_{\text{c,md-}\mathcal{X}}^{\text{sr}}[n; \mu]$ labelled by ECMD-$\mathcal{X}$. Such a functional of the density $n(\mathbf{r})$ (and potentially its derivatives $\nabla n(\mathbf{r})$) is defined

for any value of the range-separation parameter μ. A general scheme to approximate $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$ is to use $\bar{E}_{\text{c,md-}\mathcal{X}}^{\text{sr}}[n; \mu]$ with the $\mu(\mathbf{r})$ defined in (32) and to evaluate it at the density defined by the model $n_{\mathcal{Y}}^{\mathcal{B}}$

$$\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}] \approx \bar{E}_{\text{c,md-}\mathcal{X}}^{\text{sr}}[n_{\mathcal{Y}}^{\mathcal{B}}; \mu(\mathbf{r})] \tag{48}$$

Therefore, any approximated ECMD can be used to estimate $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$. It is important to notice that in the limit of a complete basis set, according to equations (41) and (46) one has

$$\lim_{\mathcal{B}\to\infty} \bar{E}_{\text{c,md-}\mathcal{X}}^{\text{sr}}[n_{\mathcal{Y}}^{\mathcal{B}}; \mu(\mathbf{r})] = 0 \quad , \tag{49}$$

for whatever choice of density $n_{\mathcal{Y}}^{\mathcal{B}}$, wave function $\Psi^{\mathcal{B}}$ used to define the interaction, and ECMD functional used to approximate the exact ECMD.

2. LDA approximation for the complementary functional

As done in Ref. [21], one can define an LDA-like approximation for $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$ as

$$\bar{E}_{\text{LDA}}^{\mathcal{B},\Psi^{\mathcal{B}}}[n_{\mathcal{Y}}^{\mathcal{B}}] = \int d\mathbf{r} \ n_{\mathcal{Y}}^{\mathcal{B}}(\mathbf{r}) \ \bar{\varepsilon}_{\text{c,md}}^{\text{sr,unif}}\left(n_{\mathcal{Y}}^{\mathcal{B}}(\mathbf{r}); \mu(\mathbf{r}; \Psi^{\mathcal{B}})\right) , \tag{50}$$

where $\bar{\varepsilon}_{\text{c,md}}^{\text{sr,unif}}(n, \mu)$ is the multi-determinant short-range correlation energy per particle of the uniform electron gas for which a parametrization can be found in Ref. [46]. In practice, for open-shell systems, we use the spin-polarized version of this functional (i.e., depending on the spin densities) but for simplicity we will continue to use only the notation of the spin-unpolarized case.

3. New PBE interpolated ECMD functional

The LDA-like functional defined in (61) relies only on the transferability of the physics of UEG which is certainly valid for large values of μ but which is known to over correlate for small values of μ. In order to correct such a defect, we propose here a new ECMD functional inspired by the recently proposed functional of some of the present authors[47] which interpolates between the usual PBE correlation functional when $\mu \to 0$ and the exact behaviour which is known when $\mu \to \infty$.

Thanks to the study of the behaviour in the large μ limit of the various quantities appearing in the ECMD[48–50], one can have an analytical expression of $\bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu]$ in that regime

$$\bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu] = \frac{2\sqrt{\pi}\left(1 - \sqrt{2}\right)}{3 \mu^3} \int d\mathbf{r} \ n^{(2)}(r) \tag{51}$$

where $n^{(2)}(\mathbf{r})$ is the *exact* on-top pair density for the ground state of the system. As the exact ground state on-top pair

density $n^{(2)}(r)$ is not known, we propose here to approximate it by that of the UEG at the density of the system:

$$n^{(2)}(r) \approx n_{\text{UEG}}^{(2)}(n_\uparrow(r), n_\downarrow(r)) \tag{52}$$

where $n_\uparrow(r)$ and $n_\downarrow(r)$ are, respectively, the up and down spin densities of the physical system at r, $n_{\text{UEG}}^{(2)}(n_\uparrow, n_\downarrow)$ is the UEG on-top pair density

$$n_{\text{UEG}}^{(2)}(n_\uparrow, n_\downarrow) = 4\, n_\uparrow\, n_\downarrow\, g_0(n_\uparrow, n_\downarrow) \tag{53}$$

and $g_0(n_\uparrow, n_\downarrow)$ is the correlation factor of the UEG whose parametrization can be found in[?] .

As the form in (54) diverges for small values of μ as $1/\mu^3$, we follow the work proposed in[47] and interpolate between the large-μ limit and the $\mu = 0$ limit where the $\bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu]$ reduces to the Kohn-Sham correlation functional (see equation (47)), for which we take the PBE approximation as in[47]. More precisely, we propose the following expression for the

$$\bar{E}_{\text{c,md}}^{\text{sr}}[n(\mathbf{r}); \mu] = \int d\mathbf{r}\, \bar{e}_{\text{c,md}}^{\text{PBE}}(n(r), \nabla n(r); \mu) \tag{54}$$

with

$$\bar{e}_{\text{c,md}}^{\text{PBE}}(n, \nabla n; \mu) = \frac{e_c^{PBE}(n, \nabla n)}{1 + \beta_{\text{c,md PBE}}(n, \nabla n; \mu)\mu^3} \tag{55}$$

$$\beta(n, \nabla n; \mu) = \frac{3 e_c^{PBE}(n, \nabla n)}{2\sqrt{\pi}\left(1 - \sqrt{2}\right) n_{\text{UEG}}^{(2)}(n_\uparrow, n_\downarrow)}. \tag{56}$$

Therefore, we propose this approximation for the complementary functional $\bar{E}^{\mathcal{B}}[n_{\mathcal{Y}}^{\mathcal{B}}]$:

$$\bar{E}_{\text{PBE}}^{\mathcal{B},\Psi^{\mathcal{B}}}[n] = \int d\mathbf{r}\, \bar{e}_{\text{c,md}}^{\text{PBE}}(n(\mathbf{r}), \nabla n(\mathbf{r}); \mu(\mathbf{r})) \tag{57}$$

F. Valence-only approximation for the complementary functional

We now introduce a valence-only approximation for the complementary functional which is needed to correct for frozen core WFT models. Defining the valence one-body spin density matrix as

$$\rho_{ij,\sigma}^{\text{val}}[\Psi^{\mathcal{B}}] = \left\langle \Psi^{\mathcal{B}} \left| a_{i,\sigma}^\dagger a_{j,\sigma} \right| \Psi^{\mathcal{B}} \right\rangle \quad \text{if } (i,j) \in \mathcal{B}_{\text{val}}$$
$$= 0 \quad \text{in other cases} \tag{58}$$

then one can define the valence density as:

$$n_\sigma^{\text{val}}(\mathbf{r}) = \sum_{i,j} \rho_{ij,\sigma}^{\text{val}}[\Psi^{\mathcal{B}}] \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \tag{59}$$

Therefore, we propose the following valence-only approximations for the complementary functional

$$\bar{E}_{\text{LDA, val}}^{\mathcal{B},\Psi^{\mathcal{B}}}[n] = \int d\mathbf{r}\, n^{\text{val}}(\mathbf{r})\, \bar{\varepsilon}_{\text{c,md}}^{\text{sr,unif}}\left(n^{\text{val}}(\mathbf{r}); \mu_{\text{val}}(\mathbf{r}); \Psi^{\mathcal{B}})\right), \tag{60}$$

$$\bar{E}_{\text{PBE, val}}^{\mathcal{B},\Psi^{\mathcal{B}}}[n] = \int d\mathbf{r}\, \bar{e}_{\text{c,md}}^{\text{PBE}}(n^{\text{val}}(\mathbf{r}), \nabla n^{\text{val}}(\mathbf{r}); \mu_{\text{val}}(\mathbf{r})) \tag{61}$$

III. RESULTS

A. Comparison between the CIPSI and CCSD(T) models in the case of C_2, N_2, O_2, F_2

We begin the investigation of the behavior of the basis-set correction by the study of the atomization energies of the C_2, N_2, O_2, F_2 homo-nuclear diatomic molecules in the Dunning cc-pVXZ and cc-pCVXZ (X=D,T,Q,5) using both the CIPSI algorithm and the CCSD(T). All through this work, we follow the frozen core (FC) convention of Klopper *et. al*[51] which consists in all-electron calculations for Li-Be, a He core for B-Na atoms and a Ne core for the Al-Cl series. In the context of the DFT correction for the basis-set, this implies that, for a given system in a given basis set $\mathcal{B}$, the set of valence orbitals $\mathcal{B}_{\text{val}}$ involved in the definition of the valence interaction $W_{\Psi^{\mathcal{B}}}^{\text{val}}(\mathbf{X}_1, \mathbf{X}_2)$ and density $\rho_{ij,\sigma}^{\text{val}}$ refers to all MOs except the core.

1. CIPSI calculations and the basis-set correction

All CIPSI calculations were performed in two steps. First, a CIPSI calculation was performed until the zeroth-order wave function reaches 10^6 Slater determinants, from which we extracted the natural orbitals. From this set of natural orbitals, we performed CIPSI calculations until the $E_{\text{exFCI}}^{\mathcal{B}}$ reaches about 0.1 mH convergence for each systems. Such convergence criterion is more than sufficient for the CIPSI densities $n_{\text{CIPSI}}^{\mathcal{B}}$. Regarding the wave function $\Psi^{\mathcal{B}}$ chosen to define the local range-separation parameter $\mu(\mathbf{r})$, we take a single Slater determinant built with the natural orbitals of the first CIPSI calculation.

2. CCSD(T) calculations and the basis-set correction

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TABLE I. Dissociation energy (D_e) in kcal/mol of the C_2, O_2, N_2 and F_2 molecules computed with various methods and basis sets.

Molecule	Method	Dunning's basis set				
		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	E^∞_{QZ5Z}
C_2	(FC)FCIQMC	130.0(1)	139.9(3)	143.3(2)		144.9
	(FC)FCIQMC+F12	142.3	145.3			
	ex (FC)FCI	132.0	140.3	143.6	144.3	
	ex (FC)FCI+LDA-val	143.0	145.4	146.4	146.0	
	ex (FC)FCI+PBE-val	147.4	146.1	146.4	145.9	
	exFCI+PBE-on-top-val	143.3	144.7	145.7	145.6	
		cc-pCVDZ	cc-pCVTZ	cc-pCVQZ	cc-pCV5Z	E^∞_{CQZC5Z}
	ex FCI	131.0	141.5	145.1	146.1	147.1
	ex FCI+LDA	141.4	146.7	147.8	147.6	
	ex FCI+PBE	145.1	147.0	147.7	147.5	

Molecule	Method	Dunning's basis set				
		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	E^∞_{QZ5Z}
N_2	ex (FC)FCI	201.1	217.1	223.5	225.7	227.8
	ex (FC)FCI+LDA-val	217.9	225.9	228.0	228.6	
	ex (FC)FCI+PBE-val	227.7	227.8	228.3	228.5	
	exFCI+PBE-on-top-val	224.8	226.7	228.3	228.3	
	(FC)CCSD(T)	199.9	216.3	222.8	225.0	227.2
	ex (FC)CCSD(T)+LDA-val	216.3	224.8	227.2	227.8	
	ex (FC)CCSD(T)+PBE-val	225.9	226.7	227.5	227.8	
		cc-pCVDZ	cc-pCVTZ	cc-pCVQZ	cc-pCV5Z	E^∞_{QZ5Z}
	ex FCI	202.2	218.5	224.4	226.6	228.8
	ex FCI+LDA	218.0	226.8	229.1	229.4	
	ex FCI+PBE	226.4	228.2	229.1	229.2	

[a] Results from Ref. 52.

[b] Results from Ref. 53.

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TABLE II. Dissociation energy (D_e) in kcal/mol of the C_2, O_2, N_2 and F_2 molecules computed with various methods and basis sets.

Molecule	Method	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	E^∞_{QZ5Z}
O_2	exFCI	105.2	114.5	118.0	119.1	120.0
	exFCI+LDA-val	112.4	118.4	120.2	120.4	
	exFCI+PBE-val	117.2	119.4	120.3	120.4	
	(FC)CCSD(T)	103.9	113.6	117.1	118.6	120.0
	ex (FC)CCSD(T)+LDA-val	110.6	117.2	119.2	119.8	
	ex (FC)CCSD(T)+PBE-val	115.1	118.0	119.3	119.8	
Molecule	Method	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	E^∞_{QZ5Z}
F_2	exFCI	26.7	35.1	37.1	38.0	39.0
	exFCI+LDA-val	30.4	37.2	38.4	38.9	
	exFCI+PBE -val	33.1	37.9	38.5	38.9	
	(FC)CCSD(T)	25.7	34.4	36.5	37.4	38.2
	ex (FC)CCSD(T)+LDA-val	29.2	36.5	37.2	38.2	
	ex (FC)CCSD(T)+PBE-val	31.5	37.1	37.8	38.2	

[a] Results from Ref. 52.

[b] Results from Ref. 53.

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