Self-consistency in frozen-density embedding theory based calculations

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The bi-functional for the non-electrostatic part of the exact embedding potential of frozen-density embedding theory (FDET) depends on whether the embedded part is described by means of a real interacting many-electron system or the reference system of non-interacting electrons (see [Wesolowski, Phys. Rev. A. 77, 11444 (2008)]). The difference \( \frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})} \), where \( F_{MD}[\rho_A] \) is the functional bound from below by the correlation functional \( E_C[\rho_A] \) and from above by zero. Taking into account \( F_{MD}[\rho_A] \) in both the embedding potential and in energy is indispensable for assuring that all calculated quantities are self-consistent and that FDET leads to the exact energy and density in the limit of exact functionals. Since not much is known about good approximations for \( F_{MD}[\rho_A] \), we examine numerically the adequacy of neglecting \( F_{MD}[\rho_A] \) entirely. To this end, we analyze the significance of \( \frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})} \) in the case where the magnitude of \( F_{MD}[\rho_A] \) is the largest, i.e., for Hartree-Fock wavefunction. In hydrogen bonded model systems, neglecting \( \frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})} \) in the embedding potential marginally affects the total energy (less than 5% change in the interaction energy) but results in qualitative changes in the calculated hydrogen-bonding induced shifts of the orbital energies. Based on this estimation, we conclude that neglecting \( \frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})} \) may represent a good approximation for multi-reference variational methods using adequate choice for the active space. Doing the same for single-reference perturbative methods is not recommended. Not only it leads to violation of self-consistency but might result in large effect on orbital energies. It is shown also that the errors in total energy due to neglecting \( \frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})} \) do not cancel but rather add up to the errors due to approximation for the bi-functional of the non-additive kinetic potential.


I. INTRODUCTION

Density functional theory (DFT) in its various flavours such as most commonly used Kohn-Sham formulation1 – but also other formulations such as Hartree-Fock-correlation,2 Orbital-Free DFT,3 subsystem DFT,4, 5 etc. – leads to the exact ground-state energy and density in the limit of the exact functionals provided that the target ground-state density satisfies specific representability conditions for a given formulation (pure-state non-interacting v-representability in the Kohn-Sham case for instance). The same cannot be said about variational methods used in conventional wave-function based schemes, which – except for the full configuration interaction (FCI) in the limit of complete basis set – lead to energies approaching the exact one from above whereas perturbational methods do not provide such bound. In frozen-density embedding theory (FDET),6–9 the exact solution is not the ground-state energy and density but the minimum of the Hohenberg-Kohn energy functional \( (E_{HK}[\rho])^{10} \) in the presence of an additional constraint \( \rho \geq \rho_B \), where \( \rho_B \) is some given electron density characterizing the environment of the embedded system, and the corresponding minimizer \( \rho_{\min} \). The minimizer \( \rho_{\min} \) might be different from the ground-state density. Throughout this work, the difference \( \rho_{\min} - \rho_B \) is denoted with \( \rho_A \). Similarly as in the Kohn-Sham DFT, the approximate solutions are obtained in practice due to the use of approximations for the relevant density functionals: exchange-correlation functional \( (E_C[\rho]) \) in the case of Kohn-Sham and both \( E_{\xi}[\rho] \) and the bi-functional for the non-additive kinetic energy \( (T_{\xi}^{\text{adj}}[\rho_A, \rho_B]) \) in the case of the most popular variant of FDET introduced in Ref. 6 based on one-electron equations for embedded orbitals (Eq. (20) and (21) of Ref. 6 and Eq. (15) below). For most recent practical applications see Refs. 11–15 and 17–20. The analyses presented in Ref. 8 show that an approach, in which the bi-functional for non-electrostatic component of the embedding potential introduced for the case of embedded reference system of non-interacting electrons given in Eq. (3) in Ref. 21 and Eq. (18) below, is used for embedding an interacting system which does not satisfy the condition of the exact-functionals limit unless the embedded system is described by means of a wavefunction of the FCI form. As the exact functional limit, we understand the condition that using the exact functionals in all equations of a given computational method leads to the exact value of \( E_{\text{emb}} \) as defined in Eq. (3) below. To reach the exact solution, an additional term \( (\Delta F_{MD}[\rho_A]) \) is needed in the expression for the total energy. \( F_{MD}[\rho_A] \) is the functional of the density \( \rho_A \). Its functional derivative \( (\frac{\delta F_{MD}[\rho_A]}{\delta \rho_B(\vec{r})}) \) enters as an additional component in the embedding potential. The functional \( F_{MD}[\rho_A] \) is defined as:

\[
\Delta F_{MD}[\rho_A] = F_{HK}[\rho_A] - F_{MD}[\rho_A].
\]
where $F^{HK}[\rho_A]$ is the universal Hohenberg-Kohn functional\(^{10}\) and
\[
F^{MD}[\rho_A] = \min_{\Psi_A^{\text{HF}} \rightarrow \rho_A} \langle \Psi_A^{MD} | \hat{T}_{2N_A} + \hat{V}_{ee}^{\text{rep}} | \Psi_A^{MD} \rangle
\]
and where $\Psi_A^{MD}$ denotes a function of the multideterminantal form comprising MD determinants, $2N_A$ denotes the total number of electrons in the embedded subsystem (all subsequent equations are written in the close-shell version and in atomic units). Whereas $F^{HK}[\rho]$ is the well-known universal Hohenberg-Kohn functional, $F^{MD}[\rho]$ attracts less attention. It has, however, a simple interpretation. If $\rho$ is the ground-state density obtained in any variational method taking electron-electron interaction explicitly into account (Hartree-Fock, truncated- or full CI, for instance), the expectation value of the sum of the kinetic- and electron-electron repulsion operators evaluated with the optimized wavefunction is just $F^{MD}[\rho]$. As a consequence, $E_\text{c}[\rho] \leq \Delta F^{MD}[\rho] \leq 0$, where $E_\text{c}[\rho]$ is the density functional of the correlation energy defined in the Levy constrained search.\(^{22}\)

Turning back to embedding methods based on a reference system of non-interacting electrons, they “inherit” all the known flaws of methods based on the Kohn-Sham formulation\(^{1}\) of DFT. For that reason, we advocate using the methods based on Eqs. (20) and (21) of Ref. 6 target environment induced shifts of properties related directly to the electronic structures rather to obtain the absolute values of such quantities (see, for instance, the recent benchmark studies on the environment induced shifts of excitation energies\(^{19}\)). The quality of the shifts is determined mainly by the adequacy of the approximations in the embedding potential of which the dominant component in the case of non-covalently bound environment is provided by the Coulombic part which does not involve any approximated density functional. This limitation was recognized by Carter and collaborators,\(^{23}\) who proposed an ad hoc combination of the Wesolowski-Warshel embedding potential given also in Eq. (18) below, with the wave-function based level of description of the embedded part in which the electron-electron interaction is taken explicitly into account. Such combination – appealing for practical reasons and followed also by others\(^{24,25}\) – lacks, however, a formal justification\(^{26}\) and as shown in Ref. 8 requires taking into account the $\Delta F^{MD}[\rho_A]$ term in the energy and in the embedding potential to lead to the exact solution at the limit of exact functionals. The energies of embedded interacting system obtained with neglecting $\Delta F^{MD}[\rho_A]$ can be, in principle, corrected by some method to account for electron correlation such as the Møller-Plesset based perturbation theory. Taking into account $\Delta F^{MD}[\rho_A]$ is less straightforward because it involves functional derivative. Assuring self-consistency between the energy and the embedded wavefunction would involve construction of a local potential corresponding to the perturbative corrections to the energy in a similar way as in the construction of the optimized effective potential.\(^{27}\) This way of assuring self-consistency is not practical and has not been done so far to our knowledge for embedded systems. As self-consistency condition, we understand requirement that the embedded wavefunction is the solution of the Euler-Lagrange equation with the total energy expressed as the functional of the wavefunction.

In the present work, we analyze numerically the importance of the $\Delta F^{MD}[\rho_A]$ component of the embedding potential. Such analyses cannot be made directly because the analytic form of none of the (bi)functionals for non-electrostatic terms in the embedding potential is known. Therefore, the following closely related issues are analyzed numerically:

(i) The magnitude of the numerical effect on energy and on orbital energies following neglecting $\Delta F^{MD}[\rho_A]$ in the case where a good approximation for the functional $\Delta F^{MD}[\rho_A]$ is known and the magnitude of $\Delta F^{MD}[\rho_A]$ is the largest (embedded Hartree-Fock case).

(ii) The relation between two errors in the total energy: the one due to neglect of $\Delta F^{MD}[\rho_A]$ and the ones due to the used approximations for other terms of the embedding potential in the considered embedded Hartree-Fock case.

Although the practical interests in FDET concern multi-level simulations,\(^2\) where the embedded system is small and the environment is much larger, the analyses reported here concern model systems where only one molecule represents the environment ($\rho_B$). Six hydrogen-bonded dimers are considered for this purpose. The choice of hydrogen-bonded complexes is, on the other hand, motivated by the fact that the case of non-covalently bound environments appears to be the main domain of applicability of FDET based multi-level computational methods (see the validations concerning the potential energy surface energy\(^{28-30}\) and increasing number of applications for various electronic properties\(^{11,19,20,31}\)).

The present work is organized as follows: the elements of the frozen-density embedding theory used in the present work together with the embedded Hartree-Fock version of the relevant equations introduced in Ref. 8 are overviewed in Sec. II, details of the numerical procedures are given in Sec. III. The numerical results are discussed in Sec. IV.

II. FROZEN-DENSITY EMBEDDING THEORY

A. Basic variables

In FDET, the total investigated system is characterized by two quantities: the density $\rho_A(\vec{r})$ and the density $\rho_B(\vec{r})$. Only $\rho_A$ is subject to optimization whereas $\rho_B$ is frozen. In all working equations of FDET, $\rho_B$ occurs as a parameter. Any FDET based simulation method involves the procedure to generate $\rho_B$. In practice, various strategies can be applied to obtain $\rho_B$ depending on the physical and chemical properties of the investigated system. For multi-level type of numerical simulations, the fact that electron density is a well-defined quantity at any scale is crucial. The functional relation between $\rho_B$ and any observables obtained from FDET makes it possible to obtain the orbital-free embedding potential for $\rho_B$ obtained without even solving approximately the Schrödinger equation for the environment. An example of such construction of $\rho_B$ for FDET-based
multi-level modelling was introduced recently.\textsuperscript{17,20} The solvent surrounding a solvated chromophore was represented by its average electron density ($\rho_B$), which was used as a parameter in all FDET equations which led to very accurate solvatochromatic shifts. ($\rho_B$) was obtained by means of dressing up the nuclear site-probabilities obtained from the classical theory of liquids with spherically symmetric atomic densities. It is worthwhile to note that such ($\rho_B$) does not correspond to the ground-state electron density obtained within Born-Oppenheimer approximation for any real system. In principle, experimental $\rho_B$ can be used in all FDET equations.

Concerning $\rho_A$, various auxiliary quantities can be used to optimize this component of the total density. The embedding potentials were derived for embedding the following auxiliary quantities: occupied orbitals of non-interacting reference system,\textsuperscript{6,7} interacting wave-function,\textsuperscript{8} or one-particle density matrix.\textsuperscript{9} The working equations for evaluation of the electronic excitations in a system embedded in a frozen density were also formulated and implemented numerically.\textsuperscript{32} They are based on the general framework of the linear-response time-dependent DFT.\textsuperscript{33} A general formulation for electronic excitations going below the description of the environment by a frozen $\rho_B$ but taking into account its dynamic response was introduced\textsuperscript{34} and numerical implementations involving additional approximations for the dynamic response of $\rho_B$ are also available.\textsuperscript{35}

**B. Search for the optimal $\rho_A$ in the presence of environment-induced constraint ($\rho \geq \rho_B$)**

The optimal electron density $\rho_A(\vec{r})$ is defined as the result of the following search:

$$
E_{emb}[\rho_B] = \min_{\rho_A \geq \rho_B} E^{HK}[\rho_A + \rho_B] \text{ for } \int \rho_A(\vec{r})d\vec{r} = N_A
$$

$$
= \min_{\rho_A \geq \rho_B \geq 0} E^{HK}[\rho] = E^{HK}[\rho_{\text{min}}],
$$

(3)

where $\rho_B$ is a given electron density such that $\int \rho_B(\vec{r})d\vec{r} = N_B$.

As a consequence of the Hohenberg-Kohn theorem,\textsuperscript{10} the following inequality holds:

$$
E_{emb}[\rho_B] \geq E_o,
$$

(4)

which becomes an equality only for particular class of pairs of electron densities $\rho_A$ and $\rho_B$ such that the difference between the ground-state electron density of the whole system ($\rho_A$) and the assumed $\rho_B$ is the ground-state electron density of some system. In the case of the embedded non-interacting reference system,\textsuperscript{6} this condition means that $E_{emb}[\rho_B] = E_o$ only if the density $\rho_B$ is such that the difference $\rho_A - \rho_B$ is pure-state non-interacting v-representable.\textsuperscript{7} Such condition cannot be verified a priori. The distinction between $E_{emb}[\rho_B]$ and $E_o$ should be made, therefore, in the context of FDET based methods.

**C. Performing the constrained search by modifying the external potential**

The search for the optimal $\rho_A$ defined in Eq. (3) is conducted in practice by the following equation:

$$
(\hat{H}_o + \hat{v}_{emb})\Psi_A = E_{emb}\Psi_A
$$

(5)

in which $\hat{H}_o$ is the environment-free Hamiltonian $\hat{H}_o$ and the $\hat{v}_{emb}(\vec{r})$ has the form of a local potential ($v_{emb}^{\text{eff}}(\vec{r})$), which is determined by the pair of densities $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$, hence the orbital-free embedding potential. $\Psi_A$ is considered to be an auxiliary quantity used to perform the search.

**D. Orbital-free embedding potential**

According to basic formal results obtained in FDET reported in Refs. 6–9, the embedding potential $v^{\text{eff}}_{emb}(\vec{r})$ comprises the classical (electrostatic) components and a term which is uniquely determined by the pair of electron densities $\rho_A$ and $\rho_B$:

$$
v^{\text{eff}}_{emb}[\rho_A, \rho_B; \vec{r}] = v^{\text{non-electrostatic}}_{emb}[\rho_A, \rho_B; \vec{r}] + \int \rho_B(\vec{r'})d\vec{r'}
$$

(6)

$v^{\text{non-electrostatic}}_{emb}[\rho_A, \rho_B; \vec{r}]$ is thus a bi-functional of $\rho_A$ and $\rho_B$. This bi-functional depends on the quantity used to perform the search given in Eq. (3) (for the detailed discussion see Ref. 8).

The present work concerns the case of $\hat{H}_o$ being the exact, i.e., interacting, Hamiltonian and $\Psi_A$ being a single determinant. Such case will be referred to as embedded Hartree-Fock for obvious reasons. The bi-functional $v^{\text{non-electrostatic}}_{emb}[\rho_A, \rho_B; \vec{r}]$ is different for different number of determinants in the embedded wavefunction.\textsuperscript{8}

**E. Two particular cases: Embedding Kohn-Sham and Hartree-Fock systems**

Equation (5) encapsulates many possible formalisms. In the one based on non-interacting reference system,\textsuperscript{6} in which the electron-electron repulsion interaction is treated implicitly in $\hat{H}_o$, the embedding potential is given in Eq. (18). If electron-electron repulsion is included explicitly in $\hat{H}_o$, the functional for the non-electrostatic part of the embedding potential in Eq. (5) differs from Eq. (18).\textsuperscript{8} Moreover, the functional for this potential changes if the number of determinants in the embedded wavefunction changes. It is instructive to analyze such embedding potentials for various forms of the wavefunction from the perspective of the Levy constrained search.\textsuperscript{22} In the limit of exact functionals, any variant of FDET should lead to the same $\rho_A$ provided that this density corresponds to the ground-state of some system and it can be represented by means of the used auxiliary quantities (Kohn-Sham orbitals of non-interacting reference system,\textsuperscript{6} the wavefunction of truncated CI form,\textsuperscript{8} for instance). Such condition seems to be very restrictive but is probably not very important in practice. Baerends and collaborators (see Ref. 37, for instance) constructed non-interacting systems for molecules, for which the ground state is traditionally represented by a multi-determinantal wavefunction (CH2.
or stretched H₂ for instance). Reproducing such interacting densities by non-interacting ones involves, however, a specific Kohn-Sham potential which is quite different from the potentials obtained using conventional approximations for the exchange-correlation functional. Nevertheless, the target density could be represented by means of a single-determinant. It was also shown recently for an analytically solvable system that a density which is not pure-state non-interacting v-representable can be approached arbitrarily closely by a ground-state density of non-interacting system with a smooth effective potential. In view of this, we see that in approaching the exact \( E_{emb}[\rho_B] \) and the exact \( \rho_A = \rho_{min} - \rho_B \) defined in Eq. (3) the critical factor is the use of approximations for the non-electrostatic component of the embedding potential than the representability related issues. We have chosen the embedded Hartree-Fock case for studying the importance of \( \Delta F^{MD}[\rho_A] \). For embedded wavefunctions of the single-determinant form, \( \Delta F^{MD}[\rho_A] \) has a simple interpretation as the correlation functional defined in the Levy constrained search formulation of DFT. The working equations for the exact functionals and bi-functionals as defined in the Levy’s constrained search procedure. Similar equations for the embedded Kohn-Sham case introduced already elsewhere, where the embedded system is also represented by means of single determinant, are also given for the sake of completeness.

1. Embedded Kohn-Sham system

The search given in Eq. (3) is performed by means of optimizing the orbitals of the reference system of non-interacting electrons (\( \{ \phi_i^A \} \)). For a given \( \rho_B \), the optimal set of \( \{ \phi_i^A \} \) is obtained through minimization of the functional \( \Xi^{KS}[\{ \phi_i^A \}, \rho_B] \) defined below and taking into account the orthonormality constraints for \( \{ \phi_i^A \} \)

\[
\Xi^{KS}[\{ \phi_i^A \}, \rho_B] = 2 \sum_{i=1}^{N^A} |\phi_i^A|^2 - \frac{1}{2} \nabla^2 |\phi_i^A|^2 + T_s[\rho_B]
+ T_s^{nad}[\rho_A, \rho_B] + V_{ext}[\rho] + J[\rho] + E_{xc}[\rho],
\]

(7)

where \( \rho_A(\vec{r}) = \sum_{i=1}^{2N_A} |\phi_i^A|^2 \) and \( \rho = \rho_A + \rho_B, T_s[\rho] \) and \( E_{xc}[\rho] \) are density functionals defined in Levy constrained search. \( J[\rho] \) is the density functional for the classical electron-electron repulsion, and \( V_{ext}[\rho] \) is the density functional for the energy of interaction with the external potential. The bi-functional \( T_s^{nad}[\rho_A, \rho_B] \) is defined as:

\[
T_s^{nad}[\rho_A, \rho_B] = T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B].
\]

(8)

For a trial set of embedded orbitals \( \{ \phi_i^A \} \) such that

\[
2 \sum_{i=1}^{N^A} |\phi_i^A|^2 = 2 \sum_{i=1}^{N^A} |\phi_i^A|^2 = \rho_A.
\]

(9)

the following inequality holds:

\[
\Xi^{KS}[\{ \phi_i^A \}, \rho_B] \geq \Xi^{KS}[\{ \phi_i^A \}, \rho_B] = E^{HK}[(\rho_A + \rho_B),
\]

(10)

where \( \{ \phi_i^A \} \) minimizes \( \Xi^{KS}[\{ \phi_i^A \}, \rho_B] \).

Except for the kinetic energy, all other energy components of \( \Xi^{KS}[\{ \phi_i^A \}, \rho_B] \) are explicit density functionals. Therefore, the optimal orbitals \( \{ \phi_i^A \} \) minimize also the kinetic energy for a fixed \( \rho_A \) and can be used to evaluate numerically \( T_s[\rho_A] \) without actually knowing the analytical form of \( T_s[\rho] \) as explicit density functional.

Splitting the functionals in Eq. (7) into the components representing individual subsystems and the remaining interaction terms:

\[
J[\rho] = J[\rho_A] + J[\rho_B] + \int \frac{\rho_A(r)\rho_B(r')}{|r-r'|} d\vec{r} d\vec{r}'
\]

(11)

\[
V_{ext}[\rho] = V_{ext}^A[\rho_A] + V_{ext}^B[\rho_B] + V_{ext}^B[\rho_A] + V_{ext}^B[\rho_B]
\]

(12)

\[
E_{xc}[\rho] = E_{xc}[\rho_A] + E_{xc}[\rho_B] + E_{xc}^{nad}[\rho_A, \rho_B]
\]

(13)

leads to an alternative form of Eq. (7):

\[
\Xi^{KS}[\{ \phi_i^A \}; \rho_B] = 2 \sum_{i=1}^{N^A} |\phi_i^A| - \frac{1}{2} \nabla^2 |\phi_i^A|
+ E_{xc}[\rho_A] + J[\rho_A] + V_{ext}^A[\rho_A]
+ T_s[\rho_B] + J[\rho_B] + E_{xc}[\rho_B] + V_{ext}^B[\rho_B]
+ V_{ext}^A[\rho_B] V_{ext}^B[\rho_A] + \int \frac{\rho_A(r)\rho_B(r')}{|r-r'|} d\vec{r} d\vec{r}'
+ T_s^{nad}[\rho_A, \rho_B] + E_{xc}^{nad}[\rho_A, \rho_B].
\]

(14)

For a given \( \rho_B(\vec{r}) \), the Euler-Lagrange minimization procedure applied to \( \Xi^{KS}[\{ \phi_i^A \}; \rho_B] \) and taking into account the orthonormality of the orbitals \( \{ \phi_i^A \} \) leads to the following Kohn-Sham-like one-electron equations (Eqs. (20) and (21) in Ref. 6):

\[
-\frac{1}{2} \nabla^2 + v_{KSCED}^{eff}[\rho_A, \rho_B; \vec{r}] \phi_i^A = \epsilon_i^A \phi_i^A \quad i = 1, N^A,
\]

(15)

where

\[
v_{KSCED}^{eff}[\rho_A, \rho_B; \vec{r}] = v_{KS}^{eff}[\rho_A+\rho_B; \vec{r}] + \frac{\delta T_s^{nad}[\rho, \rho_B]}{\delta \rho(\vec{r})}_{\rho=\rho_A}.
\]

(16)

The label KSCED (Kohn-Sham equations with constrained electron density) is used here to indicate that the multiplicative potential and the obtained one-electron functions differ from the corresponding quantities in the Kohn-Sham framework (\( v_{KSCED}^{eff}[\rho_A, \rho_B; \vec{r}] \neq v_{KS}^{eff}[\rho_A; \vec{r}] \) and \( v_{KSCED}^{eff}[\rho_A, \rho_B; \vec{r}] \neq v_{KS}^{eff}[\rho_A + \rho_B; \vec{r}] \)). For the sake of
subsequent discussions, $v_{\text{KS}}^{\text{SCED}}$ is split into two components: the Kohn-Sham expression for the total effective potential in the isolated subsystem $A$ (all $\rho_B$-independent terms) and the remaining part representing the effect of the environment (all $\rho_B$-dependent terms):

$$v_{\text{KS}}^{\text{SCED}}[\rho_A, \rho_B; \vec{r}] = v_{\text{KS}}[\rho_A; \vec{r}] + v_{\text{SCED}}^{\text{emb}}[\rho_A, \rho_B; \vec{r}],$$

(17)

where

$$v_{\text{SCED}}^{\text{emb}}[\rho_A, \rho_B; \vec{r}] = v_{\text{ext}}^{B}[\vec{r}] + \int \frac{\rho_B(\vec{r})}{|\vec{p} - \vec{r}|} d\vec{p} + \frac{\delta E_{\text{xc}}(\rho)}{\delta \rho(\vec{r})}_{\rho = \rho_A + \rho_B}$$

$$- \delta E_{\text{xc}}(\rho) \frac{\delta}{\delta \rho(\vec{r})}_{\rho = \rho_A} + \frac{\delta T_{\text{nad}}^{A}(\rho, \rho_B)}{\delta \rho(\vec{r})}_{\rho = \rho_A} + \frac{\delta E_{\text{xc}}(\rho, \rho_B)}{\delta \rho(\vec{r})}_{\rho = \rho_A}$$

$$= v_{\text{ext}}^{B}[\vec{r}] + \int \frac{\rho_B(\vec{r})}{|\vec{p} - \vec{r}|} d\vec{p}$$

$$+ \frac{\delta T_{\text{nad}}^{A}(\rho, \rho_B)}{\delta \rho(\vec{r})}_{\rho = \rho_A} + \frac{\delta E_{\text{xc}}(\rho, \rho_B)}{\delta \rho(\vec{r})}_{\rho = \rho_A}.$$

(18)

Note that the notation used for the potential in the above equations, such as $v[\rho_A, \rho_B; \vec{r}]$ instead of $v[\rho_A; \vec{r}]$, reflects the fact that the potential in question is not the bi-functional of $\rho_A$ and $\rho_B$. The distinction between a potential $v(\vec{r})$ determined by the pair $\rho_A$ and $\rho_B$ and some other quantities, which are $\rho_A$ and $\rho_B$-independent (for instance, $v_{\text{ext}}^{B}(\vec{r})$ in Eq. (18)), and the bi-functional for these quantities which is uniquely determined by the pair $\rho_A$ and $\rho_B$ is frequently overlooked as it has only marginal consequences in practical simulations. It is of key importance, however, in studies of exact relations between exact density functionals in FDETs.

2. Embedded Hartree-Fock system

Similarly to the Kohn-Sham case, if a Hartree-Fock system is embedded, the search given in Eq. (3) is performed among the orbitals $\{\phi_i^A\}$. However, due to different treatment of electron-electron repulsion (explicit evaluation of exchange energy), the total energy is expressed by a different functional depending on $\rho_B$ and $\{\phi_i^A\}$. If $\Psi_A$ denotes the Slater determinant constructed with $\{\phi_i^A\}$ the relevant energy functional reads

$$\Sigma_{HF}[\Psi_A^{SD}, \rho_B]$$

$$= \langle \Psi_A^{SD} | \hat{\tilde{T}}_{2N_A} + \hat{V}_{\text{ee}}^{cc} | \Psi_A^{SD} \rangle + V_{\text{ext}}^{A}[\rho_B]$$

$$+ T_{s}[\rho_B] + J[\rho_B] + E_{xc}[\rho_B] + V_{\text{ext}}^{B}[\rho_B]$$

$$+ V_{\text{ext}}^{A}[\rho_B] + V_{\text{ext}}^{B}[\rho_B] + \int \frac{\rho_A(\vec{r}) \rho_B(\vec{r})}{|\vec{p} - \vec{r}|} d\vec{p} d\vec{r}$$

$$+ T_{\text{nad}}^{A}[\rho_A, \rho_B] + E_{\text{nad}}^{A}[\rho_A, \rho_B] + E_{L}[\rho_A],$$

(19)

where $\rho_{HF}^{A}(\vec{r}) = \langle \Psi_A^{SD} | \sum_{\nu,\nu'}^{2N_A} \delta(\vec{r} - \vec{r}_\nu) \Psi_A^{SD} \rangle = \sum_{\nu,\nu'}^{2N_A} |\phi_{\nu}^{A}|^2$ and $E_{L}[\rho_A]$ is the density functional of the correlation energy. We underline that $E_{xc}[\rho]$ and all other density functionals considered in the present work $V_{\text{ee}}[\rho], E_{xc}[\rho],$ and $T_{s}[\rho]$ are defined in the constrained search procedure.\(^{22}\)

Equation (19) can be used to illustrate the fact that $\Delta F_{MD}[\rho_A]$ must depend on the number of determinants in the trial-wavefunction. Performing the search among wavefunctions $\Psi_A^{MD}$ comprising more than one determinant can only lower the value of $\langle \Psi_A^{MD} | \hat{\tilde{T}}_{2N_A} + \hat{V}_{\text{ee}}^{cc} | \Psi_A^{MD} \rangle$ if the wavefunctions $\Psi_A^{MD}$ and $\Psi_A^{SD}$ are constrained to yield the same density $\rho_A$, $\Delta F_{MD}[\rho_A]$ is equal to this lowering. It ranges from zero, if $\Psi_A^{MD}$ is the wavefunctions of WCI form, to $E_{L}[\rho_A]$ if $\Psi_A^{MD}$ is just single determinant.\(^{36}\) As a consequence, the corresponding term in the embedding potential ($\frac{\delta E_{\text{emb}}[\rho_A]}{\delta \rho(\vec{r})}$) changes if the number of determinants changes.

In the Hartree-Fock case, the optimal orbitals $\{\phi_i^A\}$ are obtained from the Euler-Lagrange equations for $\Sigma_{HF}[\Psi_A^{SD}, \rho_B]$ taking into account the orthonormality conditions for $\{\phi_i^A\}$

$$\begin{align*}
\left[-\frac{1}{2} \nabla^2 + \hat{\rho}_{HF} + \hat{v}_{HFCD}[\rho_A, \rho_B; \vec{r}] \right] \phi_i^A &= \epsilon_i^A \phi_i^A \quad i = 1, N^A, \\
\end{align*}$$

(20)

where $\hat{\rho}_{HF}$ is the Fock operator in the Hartree-Fock theory, whereas the potential $v_{HFCD}[\rho_A, \rho_B; \vec{r}]$ reads

$$v_{HFCD}^{\text{emb}}[\rho_A, \rho_B; \vec{r}]$$

$$= v_{\text{ext}}^{B}[\vec{r}] + \int \frac{\rho_B(\vec{r})}{|\vec{p} - \vec{r}|} d\vec{p}$$

$$+ \frac{\delta T_{s}^{A}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} + \frac{\delta E_{xc}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} + \frac{\delta E_{L}[\rho_A]}{\delta \rho_A}.$$

(21)

The label HFCED stands for Hartree-Fock equations with constrained electron density. Similarly to $v_{\text{KS}}^{\text{emb}}[\rho_A, \rho_B; \vec{r}]$, $v_{HFCD}^{\text{emb}}[\rho_A, \rho_B; \vec{r}]$ has a form of a multiplicative operator. Note that these two potentials differ only by the $\frac{\delta E_{\text{emb}}}[\rho_A]}{\delta \rho_A}$ term.

If $\rho_B$ is kept frozen, the terms $T_s[\rho_B], J[\rho_B], E_{xc}[\rho_B],$ and $V_{\text{ext}}^{B}[\rho_B]$ are constant. Their sum is the Hohenberg-Kohn energy functional $\langle \Psi_A^{SD} | \hat{E}_{HF}[\rho_B] \rangle$ corresponding to the external potential $v_{HFCD}^{B}[\vec{r}]$. Their numerical values are not needed for evaluation of the energy differences which accompany changes in $\rho_A$ only. If the total energy is needed, or energies corresponding to different $\rho_B$ are investigated, the numerical evaluation of the $T_s[\rho_B]$ and $E_{xc}[\rho_B]$ is required. In such a case, the energy given in Eq. (19) can be expressed by means of the functional $\Omega_{HF}[\Psi_A^{SD}, \Psi_B^{SD}]$ which depends explicitly on two single determinant wavefunctions $\Psi_A^{SD}$ and $\Psi_B^{SD}$

$$\Omega_{HF}[\Psi_A^{SD}, \Psi_B^{SD}]$$

$$= \{\Psi_A^{SD} | \hat{\tilde{T}}_{2N_A} + \hat{V}_{\text{ee}}^{cc} | \Psi_A^{SD} \} + V_{\text{ext}}^{A}[\rho_A]$$

$$+ \{\Psi_B^{SD} | \hat{\tilde{T}}_{2N_B} + \hat{V}_{\text{ee}}^{cc} | \Psi_B^{SD} \} + V_{\text{ext}}^{B}[\rho_B]$$

$$+ V_{\text{ext}}^{A}[\rho_B] + V_{\text{ext}}^{B}[\rho_A] + \int \frac{\rho_A(\vec{r}) \rho_B(\vec{r})}{|\vec{p} - \vec{r}|} d\vec{p} d\vec{r}$$

$$+ T_{s}^{A}[\rho_A, \rho_B] + E_{s}^{A}[\rho_A, \rho_B] + E_{L}[\rho_A + \rho_B].$$

(22)
where $\rho_B(r) = \langle \Psi^{SD}_B | \sum_{2N_b} \delta(r - r_i) | \Psi^{SD}_B \rangle = \sum_{2N_b} | \phi_B^i |^2$ and $E^{\text{na}}_x[\rho_A, \rho_B]$ is the bi-functional for the non-additive exchange energy.

Different symbols are used for the two energy functionals $\Sigma^{HF}$ and $\Omega^{HF}$ to indicate that they depend on other quantities.

If $\Psi^{SD}_B[\rho_B]$ denotes the determinant minimizing the expectation value of the kinetic energy subject to the condition $\Psi^{SD}_B \rightarrow \rho_B$, the functional $\Sigma^{HF}[\Psi^{SD}_A, \rho_B]$ can be expressed by means of $\Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B]$: 

$$\Sigma^{HF}[\Psi^{SD}_A, \rho_B] = \Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B(\rho_B)].$$ (23)

The functional $\Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B]$ has the following property:

$$\min_{\Psi^{SD}_A \rightarrow \rho_A, \rho_B \rightarrow \rho_B} \Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B] = E^{HK}(\rho_A + \rho_B).$$ (24)

which holds for any electron density $\rho_A + \rho_B$ such that each component, $\rho_A$ and $\rho_B$ can be obtained from some single determinant.

**III. COMPUTATIONAL DETAILS**

For a given approximations for the functional $E_c[\rho]$ and the bi-functionals $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{xc}}_c[\rho_A, \rho_B]$, the numerical analysis of the relative importance of the $\delta E^{\text{add}}[\rho_A]$ term in the orbital-free embedding potential, which equals to $\frac{\delta E^{\text{add}}[\rho_A]}{\delta \rho_A}$ in the embedded Hartree-Fock case, can be performed in a straightforward manner by comparing the solutions of Eq. (20) obtained with and without this term in the embedding potential. The following approximations are used in all calculations: the PBE functional for the correlation energy (and potential), the Thomas-Fermi functional for the non-additive kinetic energy (and potential), and the bi-functional for the non-additive exchange-correlation energy (and potential) from the PBE exchange-correlation functional. To avoid redundancy, we use the labels to exact equations given in the previous sections also when referring to their approximated counterparts used in the reported calculations. The approximate versions can be obtained by means of substituting $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$, and $E_c[\rho]$ by $T^{\text{na}}_x[\rho_A, \rho_B]$, $E^{\text{na}}_x[\rho_A, \rho_B]$, and $E_c[\rho]$ where tilde indicates an approximated object.

The effect of neglecting $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$ is investigated in either partially (embedding) or fully variational calculations. In the former case, the electron density of one of the molecules ($B$ in the $A-B$ dimer) plays the role of $\rho_B$. Estimation of errors due to neglecting $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$, in such case, relates to FDET based multi-scale simulations in which $\rho_B$ is not subject to the same optimization procedure as $\rho_A$. Since the embedded Hartree-Fock case is considered in this work, the obtained numerical values can be used as estimates of the upper bounds for the magnitude of the effect of neglecting $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$ on energy in methods treating electron-electron repulsion explicitly in $\hat{H}_e$ and using more than one determinant for the embedded wavefunction.

In order to compare the magnitudes of errors due to neglecting $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$ with the errors due to the approximations for $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$, a similar procedure to the one introduced in Ref. 21 for analysis of the approximations to $T^{\text{na}}_x[\rho_A, \rho_B]$ was applied. The procedure is based on comparisons between the energy of a dimer obtained in fully variational calculations, i.e., embedding calculations in which both $\rho_A$ and $\rho_B$ are optimized, with the energy considered as the limit at the exact bi-functional $T^{\text{na}}_x[\rho_A, \rho_B]$. Compared to the analyses reported in Ref. 21, where the embedded Kohn-Sham case was considered, the exact functionals limit corresponds to exact bi-functionals $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$ in the embedded Hartree-Fock case. The target value of the total energy at the exact bi-functionals $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$ cannot be obtained in direct calculations based on Eq. (20) because these quantities do not have known analytic form. Instead, we used the fact that, subject to some conditions of technical nature (equality of grids, the same set of basis functions, the same approximation for the correlation functional, and other numerical procedure related details) and representatively related ones (the target density must be representable by means of a sum of two components each being a ground-state density of some system — see Sec. II), the total energy of the dimer corresponding to the limit of exact $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$ is the energy obtained in Hartree-Fock+correlation calculations (labeled here with Hartree-Fock+$E_\omega[\rho]$). If $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$ is neglected in fully variational embedding calculations, the deviation from the target values changes. The sign and magnitude of such changes are discussed subsequently. Optimizing both $\rho_A$ and $\rho_B$ was performed by means of the freeze-and-thaw procedure. Note that at infinite separations, the fully variational Eq. (20) based calculations and Hartree-Fock+$E_\omega[\rho]$ lead to the same solution by construction even if approximations are used for the bi-functionals for $T^{\text{na}}_x[\rho_A, \rho_B]$ and $E^{\text{na}}_x[\rho_A, \rho_B]$. We will discuss the interaction energies rather than total energies in the Results section for the sake of convenience. We underline that Hartree-Fock+$E_\omega[\rho]$ calculations are performed neither to propose an alternative scheme for evaluation of interaction nor to advocate a particular choice for the correlation functional in the Hartree-Fock+$E_\omega[\rho]$ framework (PBE in our case) but to provide the targets for the analysis of the investigated approximations.

The geometries of the considered hydrogen bonded complexes were taken from Ref. 40 and correspond to the minima and interaction energy of the benchmark quality as far as wave-function methods are concerned. In all calculations, the cc-pVQZ atomic basis set was used for each atomic center (in all reported embedding calculations a full set of atomic centers including both subsystems were used – super-molecular expansion of the monomer densities). The calculations were performed using the Molcas quantum chemistry software, with the Hartree-Fock module modified for the purpose of the present work, i.e., for solving Eq. (5) with single-determinantal wavefunction and potential given in

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**Notes:**
- A. Aquilante and T. A. Wesołowski
- Enad
- $084120-6$
- $F. A. Aquilante and T. A. Wesołowski$
- $\Omega^{HF}$
- $\Sigma^{HF}$
- $\Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B]$
- $\min_{\Psi^{SD}_A \rightarrow \rho_A, \rho_B \rightarrow \rho_B} \Omega^{HF}[\Psi^{SD}_A, \Psi^{SD}_B]$
- $E^{HK}(\rho_A + \rho_B)$
- $E^{\text{add}}[\rho_A]$
- $\frac{\delta E^{\text{add}}[\rho_A]}{\delta \rho_A}$
- $T^{\text{na}}_x[\rho_A, \rho_B]$
- $E^{\text{na}}_x[\rho_A, \rho_B]$
- $E_c[\rho]$
- $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$
- $\frac{\delta E^{\text{MD}}[\rho_A]}{\delta \rho_A}$
- $T^{\text{na}}_x[\rho_A, \rho_B]$
- $E^{\text{na}}_x[\rho_A, \rho_B]$
- $E_c[\rho]$
- $\hat{H}_e$
- $\rho_B$
- $\rho_A$
- $\rho_B$
- $\rho_A$
- $\rho_B$
- $\rho_A$
- $\rho_B$
- $\rho_A$
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- $\rho_A$
- $\rho_B$
Eq. (21) (self-consistent case) or Eq. (18) (not self-consistent case). The implementation uses Cholesky-based \textit{ab initio} density fitting representation for the two-electron integrals: the required auxiliary basis set is not pre-optimized through data-fitting but it is generated through Cholesky decomposition of each atomic sub-block of the integral matrix.\cite{45} Besides the computational advantage compared to conventional integral calculations, this type of density fitting guarantees, to a large extent, a complete control of error in energy\cite{42} and in energy derivatives\cite{46} approximations. The threshold for the atomic Cholesky decompositions was set to $10^{-4}$, and the LK screening\cite{47} based on Cholesky orbitals\cite{48} was used for fast evaluation of the Hartree-Fock exchange matrix. The threshold of $10^{-4}$ was also used for convergence criterion in \textit{freeze-and-thaw}, which was usually reached in 6 to 8 iterations.

IV. RESULTS AND DISCUSSIONS

A. Embedding calculations

Throughout this section, the labels A and B refer to the first and the second molecule in the A-B complex, respectively. For each complex, $\rho_B$ was chosen to be the electron density of the isolated molecule B obtained in Hartree-Fock+$\tilde{E}_r[\rho]$ calculations. Such choice for $\rho_B$ neglects the hydrogen-bonding induced changes in $\rho_B$. The obtained total energies are, therefore, smaller than their fully variational counterparts discussed in the subsequent sections in which also $\rho_B$ is optimized. In evaluation of the interaction energies and shifts in orbital energies, the quantities corresponding to the isolated molecule A were obtained also from the Hartree-Fock+$\tilde{E}_r[\rho]$ calculations.

1. Energies

For each complex, two solutions of Eq. (20) were obtained: one with the full embedding potential given in Eq. (21) (self-consistent) or with truncated embedding potential given in Eq. (18) (violating self-consistency) and the same frozen $\rho_B$ (non-relaxed). The two embedded wavefunctions $\Psi^SD_A$ were used to evaluate the total energy by means of Eq. (23).

The self-consistent energies are lower by a non-negligible amount (from 0.15 to 0.63 Hartree) which reflects the variational character of the method (see Table I). The effect of violating self-consistency condition is also small compared to the interaction energies in these systems (Table IV). It is roughly proportional (about 5\% in each case) to the interaction energy. Such small relative errors seem acceptable from the practical point of view. The small effect on energy of violating self-consistency might be the result of compensation of errors in energy due to used approximation for $E_r[\rho]$ (determining the energy directly) and the corresponding functional derivative (determining the density).

To analyze this issue in more detail, the effect of self-consistency orbital energies – the quantities directly affected by the potential – is analyzed in the subsequent section.

2. Orbital energy shifts

Any change in the total effective potential in Eq. (20) affects directly the eigenvectors and eigenvalues (orbital energies). For the sake of simplicity of the analysis, we report the energies of the highest occupied embedded orbitals obtained with and without the $\frac{\Delta E_{\text{HF}}}{\delta \rho_A}$ term instead of showing the corresponding graphs of the effective potentials. The absolute values of the orbital energies of an embedded system do not have, however, direct physical interpretation. The link between the ionization potential and the highest occupied eigenvalue determined by the asymptotic behavior of the total electron density does not apply for embedded orbitals. As shown in model studies on analytically solvable systems,\cite{38} a given ground-state electron density can be partitioned in infinite numbers of pairs $\rho_A$ and $\rho_B$. Each such partitioning leads to different sets of energies of embedded orbitals. The environment-induced shifts of energies of embedded orbitals have, however, large interpretation and practical value. They lead to accurate ligand-field splitting of f-levels of embedded rare-earth cations, determine the environment induced shifts of the vertical excitation energies in Linear-Response Time-Dependent\cite{19} calculations applied for embedded systems,\cite{19} for instance. Therefore, we focus the analysis of the numerical results on hydrogen-bonding induced shifts of the highest occupied embedded orbital (HOEO) collected in Table II.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Self-consistent</th>
<th>Not self-consistent</th>
<th>$\Delta E_{\text{HOEO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O–H\textsubscript{2}O</td>
<td>−0.0107</td>
<td>+0.0286</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}–H\textsubscript{2}O</td>
<td>(−0.0404)</td>
<td>(−0.4647)</td>
<td></td>
</tr>
<tr>
<td>HCOOH–HCOOH</td>
<td>−0.0609</td>
<td>−0.0249</td>
<td></td>
</tr>
<tr>
<td>HCONH\textsubscript{2}–HCONH\textsubscript{2}</td>
<td>−0.4833</td>
<td>(−0.4473)</td>
<td></td>
</tr>
<tr>
<td>HF–HF</td>
<td>−0.0562</td>
<td>−0.0166</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}–NH\textsubscript{3}</td>
<td>(−0.5191)</td>
<td>(−0.4795)</td>
<td></td>
</tr>
</tbody>
</table>

TABLE I. The total energy (in Hartree) evaluated as $\Xi_{\text{HF}}[\Psi^SD_A, \rho_B]$ with $\Psi^SD_A$ (Eq. (19)) obtained with either the self-consistent (Eq. (21)) or not self-consistent (Eq. (18)) embedding potential. $B$ refers to the second molecule in the A–B complex. The difference between these two energies ($\Delta$) is given in kcal/mol.

TABLE II. The hydrogen-bonding induced shifts of the energy of the highest occupied embedded orbital ($\Delta E_{\text{HOEO}}$ in Hartree) in the embedded orbital evaluated either with- or without $\frac{\Delta E_{\text{HF}}}{\delta \rho_A}$ in the orbital-free embedding potential. The orbital energies from the corresponding environment-free values are given in brackets.
TABLE IV. Interaction energies ($E_{\text{int}}$ in kcal/mol) obtained in fully variational calculations with either self-consistent and not self-consistent embedding potential. The corresponding supermolecular target value ($E_{\text{target}}$) and the reference benchmark interaction energy ($E_{\text{ref}}$) taken from Ref. 40 are given for reference.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Self-consistent</th>
<th>Not self-consistent</th>
<th>$E_{\text{target}}$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O–H$_2$O</td>
<td>4.25</td>
<td>3.75</td>
<td>5.71</td>
<td>4.97</td>
</tr>
<tr>
<td>NH$_3$–H$_2$O</td>
<td>5.53</td>
<td>4.87</td>
<td>7.18</td>
<td>6.41</td>
</tr>
<tr>
<td>HCOOH–HCOOH</td>
<td>15.10</td>
<td>14.12</td>
<td>20.95</td>
<td>16.15</td>
</tr>
<tr>
<td>HCONH$_2$–HCONH$_2$</td>
<td>13.53</td>
<td>12.29</td>
<td>17.17</td>
<td>14.94</td>
</tr>
<tr>
<td>HF–HF</td>
<td>4.07</td>
<td>3.8</td>
<td>5.40</td>
<td>4.57</td>
</tr>
<tr>
<td>NH$_3$–NH$_3$</td>
<td>2.38</td>
<td>1.57</td>
<td>3.24</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Compared to the interaction energies, the relative effect of neglecting $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$ on the orbital energies is more significant. In the (H$_2$O)$_2$ and (HCONH)$_2$ dimers, even the sign of the hydrogen-bonding induced shift in the energy of the highest occupied orbital changes upon switching-off $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$. The self-consistency seems to be, therefore, of crucial significance in studies targeting such properties of the embedded species which are directly related to the electronic structure.

B. Fully variational calculations

In this section, we compare the errors in energy resulting from neglecting $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$ with the errors due to the use of approximations for $T^{\text{nad}}_s(\rho A, \rho B)$ and $E^{\text{nad}}_{\text{xc}} (\rho A, \rho B)$. Tables III and IV collect the energies and interaction energies obtained with either the self-consistent or not self-consistent embedding potentials together with the corresponding target values. The magnitude of the errors due to the use of approximations for $T^{\text{nad}}_s(\rho A, \rho B)$ and $E^{\text{nad}}_{\text{xc}} (\rho A, \rho B)$ is significantly larger than that of the errors due to neglect of self-consistency. For instance, the target interacting energy in the HCOOH dimer equals 20.95 kcal/mol whereas the fully variational value is 15.10 kcal/mol. The difference can be attributed to errors in approximations to the bi-functional $T^{\text{nad}}_s(\rho A, \rho B)$ and $E^{\text{nad}}_{\text{xc}} (\rho A, \rho B)$. The approximation to the functional $E_{\text{xc}}(\rho)$ does not contribute to the difference because the same functional (PBE) is used to obtain the target value. The difference is thus 5.76 kcal/mol, which amounts to about 30% of the target interaction energy. Neglecting $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$ increases this difference further by additional 0.96 kcal/mol. A similar ratio of errors due to these two factors occurs for other dimers. Interestingly, the error due to neglecting self-consistency adds to the one due to the approximations for $T^{\text{nad}}_s(\rho A, \rho B)$ and $E^{\text{nad}}_{\text{xc}} (\rho A, \rho B)$ in each case. The compensation of errors occurs in none among the studied systems. The self-consistent energies are always closer to the target values than the non-self-consistent ones. The effect of neglecting $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$ on energy is about two times larger in fully variational calculations than in embedding calculations reported in Sec. IV A 1 (compare the values of $\Delta$ reported in Tables I and III). This reflects the fact that the considered dimers comprise molecules of the same size. Finally, we notice that the results obtained from fully variational and self-consistent calculations reproduce quite reasonably the reference interaction energies obtained from high-quality wave-function based calculations reported in Ref. 40. These rather good numerical results together with similar ones obtained using the fully variational embedded Kohn-Sham calculations indicate, rather, the great potential of the subsystem-based strategies in describing intermolecular interactions.

V. CONCLUSIONS

The effect of neglecting $\delta E_{\text{MD}}^{\rho A \rho B} (\vec{r})$ in the embedding potential was investigated in the embedded Hartree-Fock
case, for which the expected effect on the results is the largest because for the lower bound for the functional $\Delta F^{MD}[\rho_A]$ occurs for embedded single determinant. The numerical values of the changes in the calculated quantities can be considered, therefore, as the upper bounds for errors introduced by neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$. The errors are only marginally affected. Even in fully variational calculations in which the errors in energies of both subsystems accumulate, neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ leads to the increase of energy by $0.25–1.35 \text{ kcal/mol}$, which represents only a small fraction (not exceeding 8%) of the best estimate for the binding energies in any case. The effect on orbital energies is, however, more significant. The hydrogen-bonding induced shift of the highest occupied embedded orbital even change sign in some cases upon neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$. The latter observation indicates that, in embedding calculations aimed at properties related directly to the electronic structure, the inclusion of the $\Delta F^{MD}[\rho_A]$ should be object of considerations. In targeting the potential energy surface, however, neglecting $\Delta F^{MD}[\rho_A]$ in both the energy and in the embedding potential seems to be a reasonable approximation. This confirms the usefulness of the ad hoc approach introduced originally by Carter and collaborators,23 combining the wave-function description of the embedded system and the orbital-free expression for the embedding potential derived by Wesolowski and Warshel for embedding a non-interacting reference system. Moreover, the present results were obtained for the worst scenario, i.e., embedded Hartree-Fock case. This scenario is the least interesting in practice as the advantage of replacing reference system of non-interacting electrons by the interacting one lies in the possibility of better estimation of the correlation energy in the embedded subsystem and not in the possibility to evaluate exactly the exchange energy. Neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ in calculations, in which the embedded wavefunction is represented by more than one determinant, is expected to lead to even smaller effects because the magnitude of $\Delta F^{MD}[\rho_A]$ decreases with increasing number of determinants.8 Therefore, neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ can be recommended as a useful approximation for "embedding" any post-Hartree-Fock variational method of quantum chemistry in a frozen density $\rho_B$ especially if the energy is the target of the simulations. At this point, one has to make a distinction between variational and non-variational methods of quantum chemistry. In any variational principle based method, neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ in the embedding potential and neglecting the $\Delta F^{MD}[\rho_A]$ contribution to the total energy does not violate self-consistency condition (it does not satisfy the condition of the exact-functionalists limit though). In methods based on perturbation theory, however, using the original Wesolowski-Warshel embedding potential (Eq. (18) here) means that the $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ term is neglected in the embedding potential entirely, whereas the contribution of $\Delta F^{MD}[\rho_A]$ to the total energy is taken into account partially as a perturbation to the energy. This leads to violation of the self-consistency. The wavefunction is not the minimizer of the total energy functional obtained from the Euler-Lagrange equations. If the second-order Møller-Plessett calculations are combined with embedding potential given in Eq. (18), the error is introduced in the orbital energies of the magnitude of the errors discussed in the present work. We rather think that prospects for development of good approximations for the functional $\Delta F^{MD}[\rho_A]$ are rather bleak because this functional is different for different number of determinants. Benefiting from the fact that the magnitude of $\Delta F^{MD}[\rho_A]$ is bound from above by $[E_i[\rho_A]]$, we rather recommend neglecting $\Delta F^{MD}[\rho_A]$ entirely in calculations using a suitably chosen set of several determinants to represent the embedded wavefunction. In view of the numerical results of this work, the ad hoc combination of the embedding potential given in Eq. (15) with single-reference perturbation methods of quantum chemistry should be avoided as prone to the largest violation of self-consistency, whereas in multi-reference methods with properly chosen active space neglecting $\Delta F^{MD}[\rho_A]$ in both energy and the corresponding component in the embedding potential seems to be a good working approximation.

Concerning the possible accumulation/compensation of errors due to approximation to the functional $\Delta F^{MD}[\rho_A]$ and to the bi-functional $T^{ad}[\rho_A, \rho_B]$, the numerical data indicate clearly that the errors rather accumulate. Neglecting the $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ worsens the whole embedding potential. The magnitude of errors due to neglecting $\frac{\delta F^{MD}[\rho_A]}{\delta \rho_A(r)}$ is, however, smaller than the ones resulting from approximations for $T^{ad}[\rho_A, \rho_B]$. Improvement of the latter quantity and the associated functional derivatives remains, therefore, the principal object of concern for methods based on frozen-density embedding theory.

ACKNOWLEDGMENTS

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