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Embedding a multideterminantal wave function in an orbital-free environment

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Variational methods to treat a many-electron system embedded in the environment, which is represented by means of only its electron density, are considered. It is shown that the embedding operator is a local potential in the case where the electron-electron repulsion is treated exactly and the trial embedded wave function takes the multideterminantal form with a fixed number of determinants. The local embedding potential is constructed by imposing that it leads to the same electron density as the one which minimizes the Hohenberg-Kohn functional. For the limiting cases of single-determinant and configuration interaction forms of the embedded wave function, the expressions for the local embedding potential using commonly known density functionals are given. The relation between the derived local embedding potential and the effective embedding potential in the case of the embedded Kohn-Sham system [T. A. Wesołowski and A. Warshel, J. Phys. Chem. **97**, 8050 (1993)] is discussed in detail.

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I. INTRODUCTION

Numerical simulations of condensed-matter systems at the quantum-mechanics level face inevitably a dilemma of trading accuracy of the applied approximate method for the possibility of including a large number of atoms in the model. The Hohenberg-Kohn-Sham formulation of density-functional theory [1,2] proved essential in moving the size limits upwards. Indeed, the commonly used approximations to the exchange-correlation ($E_{xc}[\rho]$) energy are sufficiently adequate because the errors due to the fact that they are not exact are acceptable for a large number of problems and systems. Nevertheless, some well-defined systems cannot be described satisfactorily using common simple approximations to $E_{xc}[\rho]$. Such cases include systems for which single-determinantal wave function provides a qualitatively wrong approximation of the exact one [3]. Development of such beyond-Kohn-Sham formalisms, which are based on Hohenberg-Kohn theorems but use other reference systems than the noninteracting electrons, is currently the area of intensive research [3,4] motivated by these flaws. The wave-function-based methods are free from such deficiencies but are applicable only to systems of relatively small size. For a particular type of problems, where the primary interests concern details of the electronic structure which are well-localized in real space, the size limits can be pushed further by means of applying the *embedding strategy*. In this strategy, the wave function or the Kohn-Sham orbitals are constructed for the selected subsystem, whereas the effects of the environment are accounted for by means of a special operator (*embedding operator*). In the simplest case, the embedding operator takes into account only the electrostatic contributions. In more refined approaches, effects of quantum-mechanical origin are also represented using such descriptors of the environment as pseudopotentials or orbitals [5,6].

If the embedded system is described by means of embedded Kohn-Sham orbitals, the *exact* effective potential can be expressed using universal density functionals [7,8]. The part of the whole effective potential taking into account the presence of the environment (*orbital-free effective embedding potential*), does not require any information about the environment besides its electron density and the electrostatic potential generated by other electric charges (nuclei). It is appealing, therefore, to combine the density-functional-theory derived orbital-free effective embedding potential of Ref. [7] with a multideterminantal representation of the embedded subsystem. Such a combination has a potential to overcome two types of limitations of the Kohn-Sham-based methods by pushing the size limit of amenable model systems upwards (when applicable) and the possibility of treating the systems of multideterminantal character. Indeed, these advantages have been recognized by Carter, Wang, and collaborators who applied such an combination in numerical simulations [9,10]. A straightforward application of such a combination leads, however, to the risk of inconsistent treatment of some energy components of the total energy and even conceptual difficulties [11]. In this work, we address these issues by identifying the assumptions and approximations involved. To this end, we derive the relation between the *exact local embedding operator* and the quantities expressed by means of *exact density functionals*.

Finally, we stress that the common element in the present considerations is the requirement that only electron density is used as a descriptor of electrons in the environment. Possible formal frameworks, in which the environment is described using other quantities—pseudopotentials or orbitals for instance [5,6]—lie outside of the scope of this work. The orbital-free representation of the environment is of key importance for applications of the resulting computational approach in the domain of nonempirical multiscale computer simulations [8] because the electron density is a well-defined quantity at both microscopic and macroscopic scales.

II. EMBEDDING A MULTIDETERMINANTAL WAVE FUNCTION IN AN ORBITAL-FREE ENVIRONMENT

A. Construction of the local embedding operator—outline

The strategy applied in this work follows the same general lines as the ones used by others [12–15] to answer the question: "What local correlation potential do you have to add to the Hartree-Fock equation so that the density is exact." In this work, we consider not only the Hartree-Fock method but any method which treats the electron-electron interactions exactly and uses a wave function comprising not only one but any arbitrarily chosen number of determinants. Moreover, the target electron density is not the exact ground-state electron density, but the one which minimizes the Hohenberg-Kohn energy functional keeping one component of the total electron density constant in the present considerations. The potential analyzed in this work is obtained using the following steps:

(i) In all considerations, the environment of an embedded system comprising $2N_A$ electrons is represented by means of a given electron density ($\rho_B(\vec{r})$) and the Coulomb potential generated by nuclei of the environment ($v_{ext}^B(\vec{r})$).

(ii) Two formal frameworks for obtaining the ground-state electron density are considered. In the first one, the embedded electron density is represented by means of embedded Kohn-Sham orbitals, which are obtained from one-electron equations [Eqs. (20) and (21) of Ref. [7]]. In these equations, the total effective potential and its embedding component in particular is expressed by means of explicit density functionals. For the exact effective potential, these equations lead to the density $\rho_{A_o^1}$, which minimizes the Hohenberg-Kohn energy functional for a fixed ρ_B (i.e., at $\delta\rho_B=0$). The second framework uses a multideterminantal wave function to represent the embedded electron density and treats the electron-electron interactions exactly whereas the presence of environment is accounted for by means of the operator $\hat{V}^{emb}$:

$$[\hat{T}_{2N_A} + \hat{V}^{ee}_{2N_A} + \hat{V}^{A}_{ext} + \hat{V}^{emb}]\Psi_A = E_A\Psi_A, \tag{1}$$

where the first three operators define the isolated subsystem.

(iii) The embedding operator is postulated to take the form of a local potential,

$$\hat{V}^{emb} = \sum_i^{2N_A} v^{emb}_{loc}(\vec{r}_i). \tag{2}$$

The electron density ($\rho_{A_o^2}$) obtained as an approximate solution of Eq. (1) by means of variational calculations using trial wave functions of the multideterminantal form with a fixed number of determinants, such as multiconfigurational self consistent-field calculations (MCSCF) for instance, depends on $v^{emb}_{loc}(\vec{r}_i)$. By imposing that

$$\rho_{A_o^1} = \rho_{A_o^2} = \rho_{A_o}, \tag{3}$$

$v^{emb}_{loc}(\vec{r}_i)$ is constructed leading to the principal result of this work—the relation between $v^{emb}_{loc}(\vec{r}_i)$ and universal density functionals.

Note that we take a particular perspective on the relation between the wave-function-based methods and density-functional theory. A multideterminantal wave function is considered in this work as an auxiliary quantity used to obtain the approximate solution of Eq. (1) and the corresponding electron density by means of variational calculations, whereas the relevant density functionals are considered to be exact in the derivation of the basic relation. Approximate functionals are considered only in the discussion part in view of the prospects for practical calculations.

B. Key definitions and notation

The functionals are denoted with capital letters and the quantities, on which they depend explicitly, are given within square brackets (as in $F[y]$). Unless indicated by tildes, the considered functionals are assumed to be exact. The formulas are given in atomic units for spin-compensated electron densities.

For $2N$ electrons in an external potential $v_{ext}(\vec{r})$, the Hohenberg-Kohn energy functional [1] is defined as

$$E^{HK}[\rho] = F^{HK}[\rho] + \int v_{ext}(\vec{r})\, \boldsymbol{\rho}(\vec{r})\, d\vec{r}, \tag{4}$$

where the constrained search definition of $F^{HK}[\rho]$ [18] reads

$$F^{HK}[\rho] = \min_{\Psi\to\rho}\langle\Psi|\hat{T}_{2N} + \hat{V}^{ee}_{2N}|\Psi\rangle. \tag{5}$$

The electron densities considered in the search for the minimum of $E^{HK}[\rho]$ are required to be N *representable* [16]. In finite Coulomb systems, N representability can be easily assured [16,17]. In this work, a stronger condition—the requirement that ρ is *pure-state noninteracting v representable* [17] (v representable in short) is also relevant. For electron densities, which belong to this category (obtained from the Kohn-Sham equations [2] or other one-electron equations with a multiplicative potential, for instance), additional explicit density functionals can be defined using the constrained search procedure [18]

$$T_s[\rho] = \min_{\{\phi_i\}\to\rho}\left(2\sum_i^N \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle\right)$$
$$= 2\sum_i^N \left\langle \phi_i^o \left| -\frac{1}{2}\nabla^2 \right| \phi_i^o \right\rangle, \tag{6}$$

where the search procedure is performed among the orbitals $\{\phi_i\}$ preserving the normalization ($2\Sigma_i^N|\phi_i|^2=\rho$) and orthonormality ($\langle\phi_i|\phi_j\rangle=\delta_{ij}$) conditions.

$E_{xc}[\rho]$ is subsequently defined in the following decomposition of $F^{HK}[\rho]$:

$$F^{HK}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho], \tag{7}$$

where $J[\rho]$ is the Coulomb repulsion integral

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'d\vec{r}. \tag{8}$$

In this work, functionals depending on other quantities than electron density are considered. In the Kohn-Sham framework, which is based on a reference system of noninteracting electrons, the total energy functional (Ξ^{KS}) depends on a set of one-electron functions ($\{\phi_i\}$)—the Kohn-Sham orbitals

$$\Xi^{KS}[\{\phi_i\}] = 2\sum_i^N \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle + J[\rho] + V_{ext}[\rho] + E_{xc}[\rho], \tag{9}$$

where $\rho = 2\Sigma_i^N |\phi_i|^2$.

Obviously,

$$\Xi^{KS}[\{\phi_i\}] \geq \Xi^{KS}[\{\phi_i^o\}] = E^{HK}[\rho], \tag{10}$$

where $\{\phi_i^o\}$ are orbitals associated with ρ via Eq. (6).

Euler-Lagrange minimization of the functional $\Xi^{KS}[\{\phi_i\}]$ taking into account the orthonormality of $\{\phi_i\}$ leads to the celebrated Kohn-Sham equations. For the exact functional $E_{xc}[\rho]$, this procedure is equivalent to minimizing the Hohenberg-Kohn energy functional within the domain of pure-state noninteracting v-representable electron densities.

C. Embedding a Kohn-Sham system in the orbital-free environment

Another total energy functional depending on one-electron functions is used in the orbital-free embedding formalism [7,8] reviewed below. The total electron density (ρ) is represented as a sum of two components,

$$\rho = \rho_A + \rho_B, \tag{11}$$

where the ρ_A part is constructed using one-electron functions similarly as it is made in the Kohn-Sham framework,

$$\rho_A = 2\sum_i^{N^A} |\phi_i^A|^2, \tag{12}$$

whereas the other one (ρ_B) is a given function. In the context of embedding, it is useful to refer to ρ_A as the one of the *embedded subsystem*, which required quantum-mechanical description with the orbital resolution, and to associate its environment with the ρ_B component. The above quantities are used as basic variables in the following functional of the total energy:

$$\Xi^{E}[\{\phi_i^A\},\rho_B] = 2\sum_{i=1}^{N^A} \left\langle \phi_i^A \left| -\frac{1}{2}\nabla^2 \right| \phi_i^A \right\rangle + T_s[\rho_B] + T_s^{nad}[\rho_A,\rho_B] + V_{ext}[\rho] + J[\rho] + E_{xc}[\rho], \tag{13}$$

where ρ and ρ_A are simple functions of ϕ_i^A given in Eqs. (11) and (12), and where $T_s^{nad}[\rho_A,\rho_B]$ denotes the bifunctional of the nonadditive kinetic energy defined as

$$T_s^{nad}[\rho_A,\rho_B] = T_s[\rho_A+\rho_B] - T_s[\rho_A] - T_s[\rho_B]. \tag{14}$$

Splitting the functionals in Eq. (13) into the components representing individual subsystems and the remaining interaction terms,

$$J[\rho] = J[\rho_A] + J[\rho_B] + \int\int \frac{\rho_A(\vec{r})\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'\, d\vec{r}, \tag{15}$$

$$V_{ext}[\rho] = V_{ext}^A[\rho_A] + V_{ext}^A[\rho_B] + V_{ext}^B[\rho_A] + V_{ext}^B[\rho_B], \tag{16}$$

$$E_{xc}[\rho] = E_{xc}[\rho_A] + E_{xc}[\rho_B] + E_{xc}^{nad}[\rho_A,\rho_B], \tag{17}$$

leads to an alternative form of Eq. (13),

$$\begin{aligned}\Xi^{E}[\{\phi_i^A\};\rho_B] = {} & 2\sum_i^{N^A} \left\langle \phi_i^A \left| -\frac{1}{2}\nabla^2 \right| \phi_i^A \right\rangle + E_{xc}[\rho_A] + J[\rho_A] \\ & + V_{ext}^A[\rho_A] + T_s[\rho_B] + J[\rho_B] + E_{xc}[\rho_B] \\ & + V_{ext}^B[\rho_B] + V_{ext}^A[\rho_B] + V_{ext}^B[\rho_A] \\ & + \int\int \frac{\rho_A(\vec{r})\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'\, d\vec{r} + T_s^{nad}[\rho_A,\rho_B] \\ & + E_{xc}^{nad}[\rho_A,\rho_B]. \end{aligned} \tag{18}$$

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

$$2\sum_i^{N^A} |\phi_i^A|^2 = 2\sum_i^{N^A} |\phi_i^{A_o}|^2 = \rho_A, \tag{19}$$

the following inequality holds:

$$\Xi^{E}[\{\phi_i^A\},\rho_B] \geq \Xi^{E}[\{\phi_i^{A_o}\},\rho_B] = E^{HK}[\rho_A+\rho_B], \tag{20}$$

where $\{\phi_i^{A_o}\}$ minimizes $\Xi^{E}[\{\phi_i^A\},\rho_B]$.

Except for the kinetic energy, all other energy components of $\Xi^{E}[\{\phi_i^A\},\rho_B]$ are explicit density functionals. Therefore, $\{\phi_i^{A_o}\}$ also minimize the kinetic energy and can be used to evaluate $T_s[\rho_A]$ [Eq. (6)].

For a given $\rho_B(\vec{r})$, the Euler-Lagrange minimization procedure applied to $\Xi^{E}[\{\phi_i^A\};\rho_B]$ and taking into account the orthonormality of the orbitals $\{\phi_i^A\}$ leads to the following Kohn-Sham-like one-electron equations [7]:

$$\left(-\frac{1}{2}\nabla^2 + v_{KSCED}^{eff}[\rho_A,\rho_B]\right)\phi_i^A = \epsilon_i^A \phi_i^A, \quad i = 1, N^A, \tag{21}$$

where

$$v_{KSCED}^{eff}[\rho_A,\rho_B](\vec{r}) = v_{KS}^{eff}[\rho_A+\rho_B;\vec{r}] + \left.\frac{\delta T_s^{nad}[\rho,\rho_B]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A}. \tag{22}$$

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 ($v_{KSCED}^{eff}[\rho_A,\rho_B] \neq v_{KS}^{eff}[\rho_A;\vec{r}]$ and $v_{KSCED}^{eff}[\rho_A,\rho_B] \neq v_{KS}^{eff}[\rho_A+\rho_B;\vec{r}]$). For the sake of subsequent discussions, v_{KSCED}^{eff} is split into two components: the Kohn-Sham effective potential for the isolated subsystem A (all ρ_B-independent terms) and the remaining part representing the effect of the environment (all ρ_B-dependent terms),

$$v_{KSCED}^{eff}[\rho_A,\rho_B](\vec{r}) = v_{KS}^{eff}[\rho_A;\vec{r}](\vec{r}) + v_{KSCED}^{emb}[\rho_A,\rho_B](\vec{r}), \tag{23}$$

where

$$\begin{aligned} v^{emb}_{KSCED}[\rho_A,\rho_B](\vec{r}) &= v^{B}_{ext}(\vec{r}) + \int \frac{\rho_B(\vec{r}\,')}{|\vec{r}\,'-\vec{r}|}d\vec{r}\,' \\ &+ \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A+\rho_B} - \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A} \\ &+ \left.\frac{\delta T_s^{nad}[\rho,\rho_B]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A} = v^{B}_{ext}(\vec{r}) \\ &+ \int \frac{\rho_B(\vec{r}\,')}{|\vec{r}\,'-\vec{r}|}d\vec{r}\,' + \left.\frac{\delta T_s^{nad}[\rho,\rho_B]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A} \\ &+ \left.\frac{\delta E_{xc}^{nad}[\rho,\rho_B]}{\delta\rho(\vec{r})}\right|_{\rho=\rho_A}. \end{aligned} \tag{24}$$

The first two terms in Eq. (24) are ρ_A independent. They represent the electrostatic potential generated by the environment. Such potential is nonuniform in general. Therefore, they depend explicitly on $\vec{r}$. The remaining terms of v^{emb}_{KSCED} are also position dependent but their $\vec{r}$ dependence is not explicit. It originates from spacial variations of $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$. Application of Eq. (21) in numerical studies of embedded systems hinges on the availability of acceptable approximations for the functional derivatives of the bifunctionals in the nonelectrostatic terms. Recent numerical studies using Eq. (21) for various embedded subsystems [19–26] indicate that, indeed, approximated functionals applicable for certain types of problems already exist.

1. The functional $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$

In the following part, we introduce the functional $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$, which depends explicitely on ρ_B and a trial wave function Ψ_A^{MD}. It is designed to play a similar role as $\Xi^{E}[\{\phi_i^A\},\rho_B]$ in the case of embedding a system of noninteracting electrons discussed previously. In particular, $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$ is constructed to satisfy the condition

$$E^{HK}[\rho_A^{MD}+\rho_B] = \min_{\Psi_A^{MD}\to\rho_A^{MD}} \Xi^{EWF}[\Psi_A^{MD},\rho_B], \tag{25}$$

where $\rho_A^{MD}(\vec{r})=\langle\Psi_A^{MD}|\Sigma_i^{2N_A}\delta(\vec{r}-\vec{r}_i)|\Psi_A^{MD}\rangle$.

Using definitions given in Eqs. (7) and (14)–(17), the Hohenberg-Kohn total energy functional $E^{HK}[\rho_A+\rho_B]$ reads

$$\begin{aligned} E^{HK}[\rho_A+\rho_B] &= T[\rho_A]+V_{ee}[\rho_A]+V^{A}_{ext}[\rho_A]+T_s[\rho_B]+J[\rho_B] \\ &+ E_{xc}[\rho_B]+V^{B}_{ext}[\rho_B]+V^{A}_{ext}[\rho_B]+V^{B}_{ext}[\rho_A] \\ &+ \int\int\frac{\rho_A(\vec{r})\rho_B(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'d\vec{r}+T_s^{nad}[\rho_A,\rho_B] \\ &+ E_{xc}^{nad}[\rho_A,\rho_B]. \end{aligned} \tag{26}$$

In the subsequent steps, the above formula is considered for ρ_A obtained from a multideterminantal wave function with a given number of determinants from just one (MD equals SD) as in the Hartree-Fock method, up to that needed for full configurational interaction type of wave function (MD equals CI): $\rho_A(\vec{r})=\langle\Psi_A^{MD}|\Sigma_i^{2N_A}\delta(\vec{r}-\vec{r}_i)|\Psi_A^{MD}\rangle$. These two cases are considered in detail in this work. For the sake of generality, however, the index MD is used throughout to include any intermediate case where the number of determinants is fixed.

For any Ψ_A^{MD}, the expectation value of the sum of the kinetic-energy and electron-electron repulsion operators ($\langle\Psi_A^{MD}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi_A^{MD}\rangle$) are readily available. Unfortunately, the numerical value of the universal Hohenberg-Kohn functional ($F^{HK}[\rho_A]=T[\rho_A]+V_{ee}[\rho_A]$) is not in general. $F^{HK}[\rho_A]$ is defined using a search procedure among all N-representable wave functions [Eq. (5)], whereas the computational methods to obtain Ψ_A^{MD} considered here take into account only functions of multideterminantal form with a fixed number of determinants. The numerical difference between these two quantities calls for a more careful analysis of the link between the quantities available in practical simulations and universal density functionals. To this end, Eq. (26) is used as a starting point in the subsequent considerations. Adding and subtracting to the right-hand side of Eq. (26) $\langle\Psi_A^{MD}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi_A^{MD}\rangle$ leads to

$$\begin{aligned} E^{HK}[\rho_A+\rho_B] &= \langle\Psi_A^{MD}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi_A^{MD}\rangle + V^{A}_{ext}[\rho_A]+T_s[\rho_B] \\ &+ J[\rho_B]+E_{xc}[\rho_B]+V^{B}_{ext}[\rho_B]+V^{A}_{ext}[\rho_B] \\ &+ V^{B}_{ext}[\rho_A]+\int\int\frac{\rho_A(\vec{r})\rho_B(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'d\vec{r} \\ &+ T_s^{nad}[\rho_A,\rho_B]+E_{xc}^{nad}[\rho_A,\rho_B]+T[\rho_A] \\ &+ V_{ee}[\rho_A]-\langle\Psi_A^{MD}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi_A^{MD}\rangle. \end{aligned} \tag{27}$$

The right-hand side of the above equation is not, however, the desired functional because it does not depend on Ψ_A^{MD} at all. Obviously, the added and subtracted Ψ_A^{MD}-dependent terms cancel each other. We note that the right-hand side of the above equation becomes a true functional of Ψ_A^{MD} and ρ_B after neglecting the last three terms. Such a functional does not satisfy Eq. (25) unless the neglected terms are exactly equal to zero. The conditions, at which the sum of these terms disappears, will be discussed later. Here, we take an alternative approach. We do not introduce any approximations at this stage, but use Eq. (27) as the basis to construct the desired functional $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$, which satisfies Eq. (25) by construction.

Applying the constrained search procedure only to the last term in Eq. (27) leads to the following new density functional:

$$F^{MD}[\rho_A] = \min_{\Psi_A^{MD}\to\rho_A} \langle\Psi_A^{MD}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi_A^{MD}\rangle. \tag{28}$$

The above definition has a particularly simple practical application if ρ_A is obtained from MCSCF calculations. The function minimizing its right-hand side is available in such a case and the numerical value of $F^{MD}[\rho_A]$ can be evaluated. It is important to underline that the universal Hohenberg-Kohn density functional $F^{HK}[\rho]$ is defined for a larger class of electron densities than $F^{MD}[\rho]$. The domain of the functional $F^{MD}[\rho]$ comprises all electron densities ρ_A^{MD} obtained as a result of minimizing the expectation value of the Hamiltonian given in Eq. (1), assuming a given fixed number of determinants used to represent trial functions. Such densities will be subject to the subsequent considerations. They satisfy the Gilbert's conditions of N representability. Therefore, the corresponding $F^{HK}[\rho_A^{MD}]$ exists.

It is worthwhile to underline that such a choice of the search space (form of the trial functions) is rather uncommon in the computational practice. Usually, the number of determinants is not known in advance and the definition of the functional $F^{MD}[\rho]$ seems superficial. There are, however, two limiting cases of great practical relevance: for the single-determinantal form of the trial functions, the functional $F^{MD}[\rho]$ was analyzed formally and numerically already in 1983 by Baroni and Tuncel [12] and is the key component of methods using hybrid functionals with 100% of "exact exchange," whereas $F^{MD}[\rho]$ is nothing else than the universal Hohenberg-Kohn functional $F^{HK}[\rho]$ for the full configurational interaction form of the trial functions.

Since for any ρ_A^{MD} considered in this work either functionals $F^{MD}[\rho_A]$ and $F^{HK}[\rho_A]$ are well defined, the functional

$$\Delta F^{MD}[\rho_A] = F^{HK}[\rho_A] - F^{MD}[\rho_A] \tag{29}$$

also exists.

Applying the constrained search procedure only to the last term in Eq. (27) and using the functional $\Delta F^{MD}[\rho_A]$ given in Eq. (29) defines the following total energy functional:

$$\begin{aligned}\Xi^{EWF}[\Psi_A^{MD},\rho_B] = {} & \langle \Psi_A^{MD}|\hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee}|\Psi_A^{MD}\rangle + T_s[\rho_B] + J[\rho_B] \\ & + E_{xc}[\rho_B] + V_{ext}^{B}[\rho_B] + V_{ext}^{A}[\rho_B] + V_{ext}^{A}[\rho_A] \\ & + V_{ext}^{B}[\rho_A] + \int\int \frac{\rho_A(\vec{r})\rho_B(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'d\vec{r} \\ & + T_s^{nad}[\rho_A,\rho_B] + E_{xc}^{nad}[\rho_A,\rho_B] + \Delta F^{MD}[\rho_A],\end{aligned} \tag{30}$$

where $\rho_A^{MD}(\vec{r}) = \langle \Psi_A^{MD}|\Sigma_i^{2N_A}\delta(\vec{r}-\vec{r}_i)|\Psi_A^{MD}\rangle$.

With the above definition, the condition given in Eq. (25) is automatically satisfied. If $\Psi_{A_o}^{MD}$ denotes the wave function minimizing $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$ and ρ_{A_o} is the corresponding electron density, the definition of $\Xi^{EWF}[\Psi_A^{MD},\rho_B]$ implies that

$$\Xi^{EWF}[\Psi_A^{MD},\rho_B] \geq \Xi^{EWF}[\Psi_{A_o}^{MD},\rho_B] = E^{HK}[\rho_{A_o} + \rho_B] \tag{31}$$

for any Ψ_A^{MD} such that $\langle \Psi_A^{MD}|\Sigma_i^{2N_A}\delta(\vec{r}-\vec{r}_i)|\Psi_A^{MD}\rangle = \rho_{A_o}(\vec{r})$.

In practical calculations, the terms depending explicitly on Ψ_A^{MD} in Eq. (30) are available. The ρ_A-independent terms, which represent the energy of the environment, are not of direct interest to the present work because they are constant in embedding calculations for which $\delta\rho_B = 0$. Other terms are expressed by means of explicit density functionals. The analytic form of the ones corresponding to the electrostatic potential is known. The remaining nonelectrostatic part,

$$G^{MD}[\rho_A,\rho_B] = E_{xc}^{nad}[\rho_A,\rho_B] + T_s^{nad}[\rho_A,\rho_B] + \Delta F^{MD}[\rho_A] \tag{32}$$

must be approximated. Each of its three components is defined in the corresponding constrained search procedure. Approximating each of them represents, however, a different type of challenge. The functional $E_{xc}[\rho]$ is defined in the same way as in the Kohn-Sham formulation of density-functional theory. $E_{xc}^{nad}[\rho_A,\rho_B]$ component of $G^{MD}[\rho_A,\rho_B]$ is just a linear combination of $E_{xc}[\rho]$ calculated at three different densities. Approximating $T_s[\rho]$—the functional also defined in the Kohn-Sham formulation—is not needed in practical calculations because its exact numerical value at the self-consistent electron density ρ is available owing to the knowledge of the corresponding Kohn-Sham orbitals. Approximating $T_s^{nad}[\rho_A,\rho_B]$ is necessary in such beyond Kohn-Sham approaches, which use the orbital-free embedding potential of Eq. (24). Approximating the functional $\Delta F^{MD}[\rho_A] = F^{HK}[\rho_A] - F^{MD}[\rho_A]$ represents, however, an entirely new challenge. $F^{MD}[\rho_A]$ is closely related to the beyond-Kohn-Sham formulation of density functional theory based on multideterminantal reference state (see Ref. [4] for instance). But even in such frameworks, $F^{MD}[\rho]$ is not approximated, only one of its components, which plays the similar role as $E_{xc}[\rho]$ in the Kohn-Sham formalism. Moreover, the label MD is used in this work to specify the class of functions with the given number of determinants, whereas in the beyond-Kohn-Sham approaches based on multideterminantal reference state the number of determinants is determined by the adiabatic connection between the exact- and multideterminantal reference state. Below, we deduce some of the exact properties of $\Delta F^{MD}[\rho_A]$.

Comparing definitions of $F^{MD}[\rho]$ and $F^{HK}[\rho]$ [Eqs. (5) and (29)] shows that these functionals are closely related. In the respective definitions, the constrained search uses the same target electron density (ρ), the same operator ($\hat{T}+\hat{V}_{ee}$), but different search domains. As a consequence

$$\Delta F^{MD}[\rho] \leq 0. \tag{33}$$

Depending on the number of orbitals in Ψ_A^{MD}, the following relation holds:

$$E_c^{SD}[\rho] = \Delta F^{SD}[\rho] \leq \Delta F^{truncated\ CI}[\rho] \leq \Delta F^{CI}[\rho] = 0. \tag{34}$$

The lower bound is a straightforward consequence of the constrained search definition of the functional $E_c^{SD}[\rho]$ (see Ref. [27], for instance),

$$E_c^{SD}[\rho] = \min_{\Psi\to\rho}\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle - \min_{\Psi^{SD}\to\rho}\langle\Psi^{SD}|\hat{T} + \hat{V}_{ee}|\Psi^{SD}\rangle. \tag{35}$$

The upper bound, however, is the result of the fact that the search domains in the definitions of $F^{CI}[\rho]$ and $F^{HK}[\rho]$ are the same.

It is worthwhile to compare Eq. (30) in the single-determinantal case with the total energy functional defined in Eq. (18). These functionals differ although both concern a single-determinantal type of description of the embedded system. Their difference ($E_c^{SD}[\rho_A]$) originates from the fact that the electron-electron repulsion is treated differently in both cases.

2. Euler-Lagrange equation for $\Psi^{MD}_{A_o}$: Density-functional-theory way

Let $\Psi^{MD}_{A_o^1}$ denote the normalized multideterminantal wave function, which minimizes $\Xi^{EWF}[\Psi^{MD}_A,\rho_B]$ for a given $\rho_{A_o^1}$,

$$\min_{\Psi^{MD}_A\to\rho_{A_o^1}} \Xi^{EWF}[\Psi^{MD}_A,\rho_B]=\Xi^{EWF}[\Psi^{MD}_{A_o^1},\rho_B]=E^{HK}[\rho_{A_o^1}+\rho_B]. \tag{36}$$

$\Psi^{MD}_{A_o^1}$ can be obtained from the Euler-Lagrange equation:

$$\frac{\delta\Xi^{EWF}[\Psi^{MD}_{A_o^1},\rho_B]}{\delta\Psi^{MD}_{A_{o^1}}}-\lambda^1\Psi^{MD}_{A_o^1}=0, \tag{37}$$

which using the definition of $\Xi^{EWF}[\Psi^{MD}_A,\rho_B]$ given in Eq. (30) reads

$$\begin{aligned}0={}&\frac{\delta(\langle\Psi^{MD}_{A_o^1}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi^{MD}_{A_o^1}\rangle)}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta V^A_{ext}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta V^B_{ext}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}\\&+\frac{\delta\int\int\frac{\rho_{A_o^1}(\vec{r})\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'d\vec{r}}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta T^{nad}_s[\rho_{A_o^1},\rho_B]}{\delta\Psi^{MD}_{A_o^1}}\\&+\frac{\delta E^{nad}_{xc}[\rho_{A_o^1},\rho_B]}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta\Delta F^{MD}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}-\lambda^1\Psi^{MD}_{A_o^1},\end{aligned} \tag{38}$$

where $\langle\Psi^{MD}_{A_o^1}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi^{MD}_{A_o^1}\rangle$ is the only term in $\Xi^{EWF}[\Psi^{MD}_A,\rho_B]$ which depend explicitly on Ψ^{MD}_A. All other terms are explicit functionals of $\rho_{A_o^1}$ and are constant in the constrained search. Since $\Psi^{MD}_{A_o^1}$ yields the electron density $\rho_{A_o^1}$ and minimizes $\Xi^{EWF}[\Psi^{MD}_A,\rho_B]$, it can be used to obtain $F^{MD}[\rho_{A_o^1}]$,

$$F^{MD}[\rho_{A_o^1}]=\langle\Psi^{MD}_{A_o^1}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}|\Psi^{MD}_{A_o^1}\rangle. \tag{39}$$

The above relation used in Eq. (38) leads to

$$\begin{aligned}0={}&\frac{\delta F^{MD}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta V^A_{ext}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta V^B_{ext}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}\\&+\frac{\delta\int\int\frac{\rho_{A_o^1}(\vec{r})\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'d\vec{r}}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta T^{nad}_s[\rho_{A_o^1},\rho_B]}{\delta\Psi^{MD}_{A_o^1}}\\&+\frac{\delta E^{nad}_{xc}[\rho_{A_o^1},\rho_B]}{\delta\Psi^{MD}_{A_o^1}}+\frac{\delta\Delta F^{MD}[\rho_{A_o^1}]}{\delta\Psi^{MD}_{A_o^1}}-\lambda^1\Psi^{MD}_{A_o^1}.\end{aligned} \tag{40}$$

Subject to standard transformations [chain rule for calculation of derivatives, multiplication by $(\Psi^{MD}_{A_o^1})^*$ and integration], Eq. (40) becomes

$$\begin{aligned}0={}&\rho_{A_o^1}(\vec{r})\frac{\delta F^{MD}[\rho_{A_o^1}]}{\delta\rho_{A_o^1}(\vec{r})}+\rho_{A_o^1}(\vec{r})v^A_{ext}(\vec{r})+\rho_{A_o^1}(\vec{r})v^B_{ext}(\vec{r})\\&+\rho_{A_o^1}(\vec{r})\int\frac{\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'+\rho_{A_o^1}(\vec{r})\frac{\delta T^{nad}_s[\rho_{A_o^1},\rho_B]}{\delta\rho_{A_o^1}(\vec{r})}\\&+\rho_{A_o^1}(\vec{r})\frac{\delta E^{nad}_{xc}[\rho_{A_o^1},\rho_B]}{\delta\rho_{A_o^1}(\vec{r})}+\rho_{A_o^1}(\vec{r})\frac{\delta\Delta F^{MD}[\rho_{A_o^1}]}{\delta\rho_{A_o^1}(\vec{r})}-\lambda^{1\prime}\rho_{A_o^1}(\vec{r}).\end{aligned} \tag{41}$$

3. Euler-Lagrange equation for $\Psi^{MD}_{A_o}$: Variational calculations with embedding potential

Since $\langle\Psi^{MD}_A|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}+\hat{V}^A_{ext}+\Sigma_i^{2N_A}v^{emb}_{loc}(\vec{r}_i)|\Psi^{MD}_A\rangle$ is also a functional depending on Ψ^{MD}_A, the normalized function $\Psi^{MD}_{A_o^2}$, which minimizes this functional, can be obtained from the following Euler-Lagrange equation:

$$0=\frac{\delta\langle\Psi^{MD}_{A_o^2}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}+\hat{V}_{ext}+\sum_i^{2N_A}v^{emb}_{loc}(\vec{r}_i)|\Psi^{MD}_{A_o^2}\rangle}{\delta\Psi^{MD}_{A_o^2}}-\lambda^2\Psi^{MD}_{A_o^2}. \tag{42}$$

Since $v^{emb}_{loc}(\vec{r}_i)$ is local, subject to similar transformations as the ones leading from Eq. (37) to Eq. (41), Eq. (42) becomes

$$\begin{aligned}0={}&\rho_{A_o^2}(\vec{r})\frac{\delta F^{MD}[\rho_{A_o^2}]}{\delta\rho_{A_o^2}(\vec{r})}+\rho_{A_o^2}(\vec{r})v^A_{ext}(\vec{r})+\rho_{A_o^2}(\vec{r})v^{emb}_{loc}(\vec{r})\\&-\lambda^{2\prime}\rho_{A_o^2}(\vec{r}).\end{aligned} \tag{43}$$

4. Local embedding potential

The electron densities $\rho_{A_o^2}$ and $\rho_{A_o^1}$ are obtained from two different Euler-Lagrange equations. They belong to the same class as far as v representability is concerned because they are constructed using trial wave functions Ψ^{MD}_A of the same general form specified by the label MD indicating the number of determinants. Since $\rho_{A_o^1}$ depends on universal density functionals whereas $\rho_{A_o^2}$ depends on $v^{emb}_{loc}(\vec{r})$, the condition that these densities are equal provides the searched for equation for $v^{emb}_{loc}(\vec{r})$. At $\rho_{A_o^2}=\rho_{A_o^1}=\rho_{A_o}$, subtracting Eq. (43) from Eq. (41) leads to the final expression for $v^{emb}_{loc}(\vec{r})$,

$$\begin{aligned}v^{emb}_{loc}(\vec{r})={}&v^B_{ext}(\vec{r})+\int\frac{\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'+\frac{\delta T^{nad}_s[\rho_{A_o},\rho_B]}{\delta\rho_{A_o}(\vec{r})}\\&+\frac{\delta E^{nad}_{xc}[\rho_{A_o},\rho_B]}{\delta\rho_{A_o}(\vec{r})}+\frac{\delta\Delta F^{MD}[\rho_{A_o}]}{\delta\rho_{A_o}}+\text{const}=v^B_{ext}(\vec{r})\\&+\int\frac{\rho_B(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'+\frac{\delta G^{MD}[\rho_{A_o},\rho_B]}{\delta\rho_{A_o}(\vec{r})}+\text{const}.\end{aligned} \tag{44}$$

The above relation holds everywhere where $\rho_{A_o}\neq 0$.

Equation (44) is our principal results showing formally that local embedding potential exists also in the case of multideterminantal description of the embedded subsystem. Its explicit form is not known because it comprises three components expressed by means of universal density functionals of unknown general analytic form. Any method using such embedding potential hinges on approximations to these functionals.

It is worthwhile to underline that Eq. (1) can be used only to obtain the optimal wave function $\Phi^{MD}_{A^2_o}$. The expectation value $\langle\Phi^{MD}_{A^2_o}|\hat{T}_{2N_A}+\hat{V}^{ee}_{2N_A}+\hat{V}^{A}_{ext}+\Sigma_i^{2N_A}v^{emb}_{loc}(\vec{r}_i)|\Phi^{MD}_{A^2_o}\rangle$ is not directly related to the ground-state energy of the total system. Equation (30) provides the ground-state energy of the total system if it is evaluated at $\Phi^{MD}_{A}=\Phi^{MD}_{A^2_o}$. Equations (1), (30), and (44) define, therefore, a complete formal framework to embed a multideterminantal wave function in an environment represented by means of only its charge density.

Finally, we note the close similarity between the embedding potential $v^{emb}_{loc}(\vec{r})$ [Eq. (44)] and the orbital-free effective embedding potential $v^{emb}_{KSCED}[\rho_A,\rho_B]$ [Eq. (24)]. They are closely related although not the same due to the $\frac{\delta\Delta F^{MD}[\rho_{A_o}]}{\delta\rho_{A_o}}$ term.

III. DISCUSSION: LOCAL EMBEDDING OPERATOR ASSOCIATED WITH AN APPROXIMATE DENSITY FUNCTIONAL $\tilde{G}^{MD}[\rho_A,\rho_B]$

Evaluating $G^{MD}[\rho_A,\rho_B]$ using the constrained search definitions of its components is not practical for obvious reasons. Applying in Eq. (44) an approximation to $\tilde{G}^{MD}[\rho_A,\rho_B]$, taking the form of a bifunctional depending explicitly on ρ_A and ρ_B, and using such an approximated expression in Eq. (1) leads to computational framework of great potential. Applicability of such framework depends however on the availability of adequate approximations. The prospects of such calculations are analyzed in this section. Since the definition of $G^{MD}[\rho_A,\rho_B]$ depends on the number of determinants used to represent ρ_A we consider three cases separately.

(i) For MD equals CI, $\tilde{G}^{CI}[\rho_A,\rho_B]=\tilde{T}^{nad}_s[\rho_A,\rho_B]+\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]$. If the full CI form of the embedded wave function is used to represent the embedded electron density, $G^{CI}[\rho_A,\rho_B]$ becomes just a sum of the two bifunctionals T^{nad}_s and E^{nad}_{xc}. Approximating the $E^{SD}_c[\rho]$ component is not needed at all. In this case, the local embedding operator is identical as the orbital-free effective embedding potential of Ref. [7] given in Eq. (24). All numerical experience concerning strengths and weaknesses of a given approximation to Eq. (24) can be used to decide about the adequacy of this particular approximation applied in the framework given in Eq. (1).

Below, the prospects for practical calculations in this case are reviewed below. Since $E^{nad}_{xc}[\rho_A,\rho_B]$ is defined by means of the same functional as the $E_{xc}[\rho]$ functional in the Kohn-Sham formalism, $\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]$ can be obtained simply as $\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]=\tilde{E}_{xc}[\rho_A,\rho_B]-\tilde{E}_{xc}[\rho_A]-\tilde{E}_{xc}[\rho_B]$, where $\tilde{E}_{xc}[\rho]$ is one of the possible approximations used in practical Kohn-Sham calculations. It is worthwhile to underline, however, that it is not the exchange-correlation energy but its differences, which are needed in Eq. (44). Therefore, the accuracy of a given parent functional $\tilde{E}_{xc}[\rho]$ and the corresponding $\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]$ is not necessarily correlated. As far as $\tilde{T}^{nad}_s$ component is concerned, it is used in the Cortona's formulation of density functional theory [28] and in the orbital-free embedding formalism [7]. Approximations, to this functional developed for such calculations can be used in Eq. (44). In development of approximations to $\tilde{T}^{nad}_s$, a possible strategy is to use its exact properties as guidelines [29]. Testing a given approximation of the kinetic-energy component of the effective potential is straightforward [30]. Approximations to $T^{nad}_s[\rho_A,\rho_B]$ adequate for the case, where the electron densities ρ_A and ρ_B do not overlap significantly were developed following this approach (see, for example, Ref. [31]).

(ii) For MD equals SD, $\tilde{G}^{SD}[\rho_A,\rho_B]=\tilde{T}^{nad}_s[\rho_A,\rho_B]+\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]+\tilde{E}^{SD}_c[\rho_A]$. The single-determinant form of the embedded wave function to construct ρ_A stands on the opposite end to the CI case discussed below. It is the least expensive method among the ones which treat electron-electron repulsion exactly. $G^{SD}[\rho_A,\rho_B]$ comprises not only the two bifunctionals discussed in the CI case but also an additional component $E^{SD}_c[\rho_A]$ which depends only on ρ_A. In the discussion of applicability of a given approximated functional $\tilde{E}^{SD}_c[\rho_A]$, one can profit from the accumulated knowledge concerning the adequacy of approximate exchange-correlation functionals in the Kohn-Sham or related frameworks. The exchange and correlation parts of several common approximations to the exchange-correlation energy are well separated ($\tilde{E}_{xc}[\rho]=\tilde{E}_x[\rho]+\tilde{E}_c[\rho]$). Note, however, that the conventional definition of the correlation energy functional $E_c[\rho]$ differs from that of $E^{SD}_c[\rho]$ given in Eq. (35). The single-determinant used to evaluate $E_c[\rho]$ minimizes not $\langle\hat{T}+\hat{V}_{ee}\rangle$ but $\langle\hat{T}\rangle$. The currently known approximations to the correlation energy functional are probably equally adequate for either $E_c[\rho]$ or $E^{SD}_c[\rho]$. It it worthwhile to recall here that a computational method, in which the exchange component is treated exactly whereas only the correlation part is approximated by means of an explicit density functional, was suggested already in the original work by Kohn and Sham [2]. It was further explored formally and numerically in Ref. [12]. A recent practical hint comes from Ref. [32] showing that the Wilson-Levy correlation functional [33] performs very well as far as describing the variation of correlation energy with changing the geometry in weakly interacting intermolecular complexes is concerned.

(iii) For MD equals truncated CI, $\tilde{G}^{truncated\ CI}[\rho_A,\rho_B]=\tilde{T}^{nad}_s[\rho_A,\rho_B]+\tilde{E}^{nad}_{xc}[\rho_A,\rho_B]+\Delta\tilde{F}^{truncated\ CI}[\rho_A]$. This case requires the introduction of additional approximation concerning the functional $\Delta F^{truncated\ CI}[\rho_A]$. Since approximations to this functional represent an uncharted field, it is probably more reasonable to use the upper (zero) or the lower ($\tilde{E}_c[\rho_A]$) bound on this functional $\Delta F^{truncated\ CI}[\rho_A]$ on a case by case basis.

IV. CONCLUSIONS

This work concerns the formal framework to embed a subsystem described at the quantum-mechanical level in the environment represented by a frozen electron density. We formulate the embedding problem as the partial minimization of the total energy with respect to only one component of the electron density keeping the remaining part frozen. This approach was already applied for the embedded subsystem represented by means of an artificial system of noninteracting electrons and a Kohn-Sham-like multiplicative potential for electron-electron repulsion [7]. The present work uses the same strategy of partial minimization, but an alternative representation of the embedded subsystems—a multideterminantal wave function. This change of the reference system is made for pragmatic reasons. Methods based on the Kohn-Sham formal framework are known to fail qualitatively for some systems and these failures are attributed to the use of the reference system of noninteracting electrons. Equation (44) shows that the embedding operator to be used in association with a multideterminantal description of the embedded subsystem takes the form of a local potential ($v_{loc}^{emb}(\vec{r})$). $v_{loc}^{emb}(\vec{r})$ comprises electrostatic components of known analytic form and another local term—the functional derivative of the bifunctional $G[\rho_A,\rho_B]$ ($\frac{\delta G[\rho_A,\rho_B]}{\delta\rho_A}(\vec{r})$). This bifunctional of the electron density of the investigated system (ρ_A) and that of the environment (ρ_B) is universal (system independent). $G^{MD}[\rho_A,\rho_B]$ comprises three components. Two of them are bifunctionals originating in the nonadditivity of two density functionals defined in the Kohn-Sham framework: the exchange-correlation energy and the kinetic energy of noninteracting electrons. The third component ($\Delta F^{MD}[\rho_A]$) is an ordinary functional, which does not depend on ρ_B at all. It originates from the change of the reference system from noninteracting electrons (single-determinantal form of the wave function) to that described by a multideterminantal wave function of an assumed form. As the consequence of the constrained search definition of $\Delta F^{MD}[\rho_A]$, this functional is nonpositive and bound from below. The correlation energy functional $E_c^{SD}[\rho_A]$ defined in the Levy's constrained search provides the lower bound of $\Delta F^{MD}[\rho_A]$ (in the case of one determinant), whereas the upper bound is zero (in the case of the full CI expansion). This third component of $v_{loc}^{emb}(\vec{r})$ is also the only difference between $v_{loc}^{emb}(\vec{r})$ the orbital-free effective embedding potential in Kohn-Sham-like equations for embedded orbitals [7].

As far as approximating the exchange-correlation component of $G^{MD}[\rho_A,\rho_B]$ is concerned, its use to obtain $v_{loc}^{emb}(\vec{r})$ does not involve any particular new challenges compared to the Kohn-Sham framework. One should mention, however, that not the whole functional but its nonadditive component is needed in $v_{loc}^{emb}(\vec{r})$. Approximating the kinetic-energy component of $G^{MD}[\rho_A,\rho_B]$ represents the same challenge as in the case of orbital-free effective embedding potential $v_{KSCED}^{emb}[\rho_A,\rho_B](\vec{r})$ of Ref. [7] or the effective potential in Cortona's formulation of density functional theory [28]. An universal approximation to $\frac{\delta\Delta F^{MD}[\rho_A]}{\delta\rho_A}$, applicable for various systems and various number of determinants, seems to be a rather difficult objective. At the present stage, we advocate using its bounds to approximate $\Delta F^{MD}[\rho_A]$ (either zero or $E_c^{SD}[\rho_A]$) chosen on a case by case basis.

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