

# Orbital-Free Effective Embedding Potential: Density-Matrix Functional Theory Case

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**ABSTRACT:** Minimization of the Hohenberg–Kohn total energy functional  $E^{\text{HK}}[\rho]$  in the presence of the constraint  $\rho - \rho_B \geq 0$ , where  $\rho_B$  is some arbitrarily chosen electron density comprising integer number of electrons is considered. To access better numerical accuracy of approximations to  $E^{\text{HK}}[\rho]$  in practice, the search for optimal  $\rho - \rho_B$  is performed using auxiliary quantities such as orbitals of a reference system of non-interacting electrons [Wesolowski and Warshel, J Phys Chem 1993, 97, 8050] or a wavefunction-like object corresponding to interacting electrons [Wesolowski, Phys Rev A 2008, 77, 012504]. In both cases, the condition  $\rho - \rho_B \geq 0$  leads to a local potential (*orbital-free effective embedding potential*) of the same general form if expressed by means of universal density functionals. In this work, it is shown that the same local potential is obtained if the search for optimal  $\rho - \rho_B$  is performed among one-particle reduced density matrices. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2520–2525, 2009

**Key words:** density functional theory; density matrix functional theory; embedding potential

## Introduction

We consider a system comprising  $2N$  electrons in an external potential  $v_{\text{ext}}(\vec{r})$  and the minimisation of the total energy functional  $E^{\text{HK}}[\rho]$  of Hohenberg–Kohn [1] in the presence of an additional constraint:

$$\rho - \rho_B \geq 0, \quad (1)$$

where  $\rho_B$  is some arbitrarily chosen non-negative function such that  $\int \rho_B d\vec{r} = 2N_B$ . For simplicity, spin-compensated systems are considered throughout the present work. Following Hohenberg–Kohn theorems:

$$E^{\text{emb}} = \min_{\rho \rightarrow 2N, \rho \geq \rho_B} E^{\text{HK}}[\rho]$$

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$$\begin{aligned}
 &= \min_{\rho_A \rightarrow 2N-2N_B} E^{\text{HK}}[\rho_A + \rho_B] \\
 &= E^{\text{HK}}[\rho_A^{\text{opt}} + \rho_B] \geq E_0,
 \end{aligned} \quad (2)$$

where  $E_0$  denotes the ground-state energy of the whole system. The domain of electron densities considered in the above search includes  $N$ -representable densities for which the  $E^{\text{HK}}[\rho]$  is defined. For more complete discussion of the relation between  $E^{\text{emb}}$  and  $E_0$  for various choices of  $\rho_B$ , see Ref. [2].

The search of Eq. (2) encompasses a growing body of numerical simulation methods in which different levels of descriptions are used for different parts of the investigated system referred to sometimes as *embedding methods*, *QM/MM*, *QM/QM'*, or *multilevel numerical simulations* (see Ref. [3] for a representative sample). In such methods, electron density of a selected part is represented by means of auxiliary quantities such as Kohn–Sham orbitals, or wavefunctions of the Hartree–Fock-, MPn-, Coupled Cluster-, CI, etc. form, allowing for adequate treatment of electron–electron repulsion whereas the electron density of the other parts is treated in a simplified manner. In view of this, the complementary component of the total electron density can be identified with  $\rho_B$  in Eq. (2). Following this interpretation, the notion of *environment* is used throughout this work for this component.

Various practical strategies to perform the minimization of Eq. (2) are possible. The direct strategy, where  $E^{\text{HK}}[\rho]$  is approximated by means of some explicit functional of electron density is not practical in view of the absence of universally applicable approximations [4]. The use of auxiliary quantities to represent  $\rho - \rho_B$  making it possible to approach better  $E^{\text{HK}}[\rho]$  seems, at present, indispensable. In our original work, the reference system of noninteracting electrons was considered for this purpose [5].

Instead of performing the search for  $\rho_A^{\text{opt}}$  directly, orbitals of a reference system of noninteracting electrons ( $\phi_i^A$ ) are used to construct  $\rho - \rho_B$  and perform the search. To distinguish them from Kohn–Sham orbitals defined for the whole system, such orbitals will be referred to as *embedded orbitals*. The set of optimal embedded orbitals is obtained from Kohn–Sham-like one-electron equations [Eqs. (20–21) in Ref. [5]]:

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}^{\text{KSCED}}[\rho_A, \rho_B] \right] \phi_i^A = \epsilon_i^A \phi_i^A \quad i = 1, N_A, \quad (3)$$

where:

$$\begin{aligned}
 v_{\text{eff}}^{\text{KSCED}}[\rho_A, \rho_B](\vec{r}) &= v_{\text{eff}}^{\text{KS}}[\rho_A + \rho_B; \vec{r}] \\
 &+ \frac{\delta T_s[\rho]}{\delta \rho} \Big|_{\rho=\rho_A+\rho_B} - \frac{\delta T_s[\rho]}{\delta \rho} \Big|_{\rho=\rho_A},
 \end{aligned} \quad (4)$$

where  $v_{\text{eff}}^{\text{KS}}[\rho_A + \rho_B; \vec{r}]$  is the Kohn–Sham effective potential for the whole system evaluated at density  $\rho = \rho_A + \rho_B$  and  $T_s[\rho]$  is the kinetic energy of noninteracting reference system defined in the Levy’s constrained search procedure [6]. 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 ( $v_{\text{eff}}^{\text{KSCED}}[\rho_A, \rho_B] \neq v_{\text{eff}}^{\text{KS}}[\rho_A; \vec{r}]$  and  $v_{\text{eff}}^{\text{KSCED}}[\rho_A, \rho_B] \neq v_{\text{eff}}^{\text{KS}}[\rho_A + \rho_B; \vec{r}]$ ). The difference between  $v_{\text{eff}}^{\text{KSCED}}[\rho_A, \rho_B](\vec{r})$  and  $v_{\text{eff}}^{\text{KS}}[\rho_A; \vec{r}]$  is also a local potential and reads

$$\begin{aligned}
 v_{\text{emb}}^{\text{KSCED}}[\rho_A, \rho_B; \vec{r}] &= v_{\text{ext}}^B(\vec{r}) + \int \frac{\rho_B(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \\
 &+ \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \Big|_{\rho=\rho_A+\rho_B} - \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \Big|_{\rho=\rho_A} \\
 &+ \frac{\delta T_s[\rho]}{\delta \rho} \Big|_{\rho=\rho_A+\rho_B} - \frac{\delta T_s[\rho]}{\delta \rho} \Big|_{\rho=\rho_A},
 \end{aligned} \quad (5)$$

where  $E_{\text{xc}}[\rho]$  is the conventional exchange–correlation functional defined in the Kohn–Sham formalism [7].

The potential  $v_{\text{emb}}^{\text{KSCED}}[\rho_A, \rho_B](\vec{r})$  given in Eq. (5) will be referred to in this work as *orbital-free effective embedding potential* for obvious reasons: it disappears in the absence of the subsystem  $B$  and is expressed by means of explicit functionals of the electron density.

Equation (3) can lead only to electron densities  $\rho_A$  which are pure-state noninteracting  $v$ -representable whereas the density  $\rho_A^{\text{opt}}$  defined in Eq. (2) does not have to fall into this category. Although the optimal  $\rho_A$  derived from Eq. (3) might be sufficiently similar to  $\rho_A^{\text{opt}}$ , the above restriction is undesirable. We underline here that these considerations concern the exact functional case. In practical applications of Eq. (3), the obtained  $\rho_A$  differs from  $\rho_A^{\text{opt}}$  also due to the use for approximants to the exchange–correlation- and kinetic-energy dependent components of the orbital-free effective embedding potential. Owing to the constrained search definitions of the functionals  $E_{\text{xc}}[\rho]$  and  $T_s[\rho]$ , the potential given in Eq. (5),  $v_{\text{emb}}^{\text{KSCED}}[\rho_A, \rho_B](\vec{r})$ , is also well-defined for a larger than

pure-state noninteracting  $v$ -representable class of densities  $\rho_A$ . It is worthwhile, therefore, to consider other quantities than the orbitals of noninteracting system in performing the search given in Eq. (2). Indeed, using a multideterminant form of the wavefunction representing  $\rho - \rho_B$  in the search procedure and exact treatment of the electron–electron repulsion operator leads to a local embedding potential which is closely related to that given in Eq. (5) and is even the same at some well-defined conditions as shown recently [8].

Using a reference system of noninteracting electrons to represent  $\rho - \rho_B$  implies also very practical inconveniences. The commonly used approximants to the exchange–correlation potential in Kohn–Sham equations are known to fail qualitatively in some cases (biradicals for instance). For such systems, therefore, the prospects of using Eq. (3) are rather bleak not due to the embedding component of the total effective potential but due to lack of adequate approximants for  $v_{xc}[\rho_A]$ . Exact treatment of the electron–electron interactions for the density  $\rho - \rho_B$  as in the formal framework given in Ref. [8] overcomes these difficulties. It comes, however, at the price of high computational costs.

In the present work, we consider representing  $\rho - \rho_B$  by means of yet another quantity, i.e., one-particle reduced density matrix. Density-matrix functional theory (DMFT) is currently the area of intensive research. Various research groups are engaged in developments of approximants to the relevant functionals of this quantity (for recent example see [9]). Arguably, DMFT is seen as a potential successor of Kohn–Sham DFT which is substantiated by increasing body of numerical evidence (for a recent comprehensive overview, see [10]). Some of the known difficulties encountered if the Kohn–Sham strategy can be overcome by DMFT (for example, the recently proposed density matrix functional properly describes the static correlation effects in molecules [11, 12]). In the context of embedding, DMFT formal framework offers also an advantage. Compared with the noninteracting reference system, using one-matrix as a search quantity allows one to find the optimal density among a larger class of densities. All  $N$ -representable densities are accessible—not only pure-state noninteracting  $v$ -representable ones. It can be expected, therefore, that such change of the search quantity from noninteracting reference system to that described by a complete one-particle reduced density matrix can lead to a computational methods benefiting from both these advantages. It is worthwhile to notice that DMFT methods are less

demanding computationally than methods in which electron–electron repulsion is treated exactly.

This work is organized as follows: (i) We start with the key definitions in DMFT, (ii) In the subsequent section, we formulate the problem of optimizing the Hohenberg–Kohn functional in the presence of a constraint  $\rho \geq \rho_B$  in which *embedded one-matrix* ( $\Gamma_A$ ) is used to perform the search. (iii) In the final section, we demonstrate that the constraint  $\rho \geq \rho_B$  leads to a term in the effective potential which is multiplicative and is exactly the same as the effective embedding potential in the case of using noninteracting reference system to perform such a search—the case considered in our original work [5].

## One-Electron Reduced Density Matrix Functional

Consider a system comprising  $2N$  electrons, described in terms of the one-electron reduced density matrix defined as (for simplicity assume a closed-shell case and skip spin variable)

$$\Gamma(\vec{r}, \vec{r}') \equiv 2N \int \Psi^*(\vec{r}', \dots, \vec{r}_N) \Psi(\vec{r}, \dots, \vec{r}_N) d\vec{r}_2 \dots \vec{r}_N, \quad (6)$$

$$\rho(\vec{r}) = \Gamma(\vec{r}, \vec{r}).$$

The energy functional of the one-matrix reads

$$E[\Gamma] = T[\Gamma] + \int \Gamma(\vec{r}, \vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} + E_{\text{ee}}[\Gamma], \quad (7)$$

where  $v_{\text{ext}}(\vec{r})$  denotes an external potential, the kinetic energy functional reads

$$T[\Gamma] = -\frac{1}{2} \int \int \delta(\vec{r} - \vec{r}') \nabla_{\vec{r}}^2 \Gamma(\vec{r}, \vec{r}') d\vec{r} d\vec{r}', \quad (8)$$

and the electron–electron interaction energy functional is defined through the constrained-search procedure of Levy as

$$E_{\text{ee}}[\Gamma] = \min_{\Psi \rightarrow \Gamma} \langle \Psi | \hat{V}_{\text{ee}} | \Psi \rangle. \quad (9)$$

Note that the domain of this functional (and therefore of the functional  $E[\Gamma]$ ) is limited to the ensemble  $N$ -representable one-matrices ( $N$ -rep  $\Gamma$ ). The ground-state energy results from the minimization of the energy functional, namely

$$E_0 = \min_{N\text{-rep } \Gamma} E[\Gamma]. \quad (10)$$

The constraint minimisation of the density matrix functional amounts to solving a variational equation

$$\frac{\delta\{E[\Gamma] - \mu(Tr[\Gamma] - 2N)\}}{\delta\Gamma(\vec{r}, \vec{r}')} = 0, \quad (11)$$

(the Lagrange multiplier  $\mu$  is such that the normalization condition  $Tr[\Gamma] = 2N$  is satisfied) that takes form of the operator equation

$$\delta(\vec{r} - \vec{r}') \left[ -\frac{1}{2} \nabla_{\vec{r}}^2 + v_{\text{ext}}(\vec{r}) \right] + v_{\text{ee}}(\vec{r}, \vec{r}') = \mu \delta(\vec{r} - \vec{r}'), \quad (12)$$

where the electron–electron interaction kernel  $v_{\text{ee}}(\vec{r}, \vec{r}')$  is formally defined as (see a discussion in Refs. [13] and [14])

$$v_{\text{ee}}(\vec{r}, \vec{r}') = \frac{\delta E_{\text{ee}}[\Gamma]}{\delta\Gamma(\vec{r}, \vec{r}')} \quad (13)$$

In other words, the functional derivative  $\frac{\delta E[\Gamma]}{\delta\Gamma(\vec{r}, \vec{r}')}$  computed for the optimal one-electron reduced density matrix acts like a delta Dirac function multiplied by a constant. If one uses the spectral representation of the one-matrix

$$\Gamma(\vec{r}, \vec{r}') = \sum_i n_i \varphi_i(\vec{r}')^* \varphi_i(\vec{r}) \quad (14)$$

the one-matrix functional can be viewed as a functional of the natural occupation numbers  $\{n_i\}$  and the natural orbitals  $\{\varphi_i(\vec{r})\}$ , i.e.,  $E[\Gamma] = E[\{\varphi_i\}, \{n_i\}]$ . In fact, all of the functionals proposed so far are defined by means of the natural occupation numbers and the natural orbitals and are only implicit functionals of  $\Gamma$  [15]. The equivalent formulation of the variational equation Eq. (12) reads in this case

$$\begin{aligned} \forall_i \quad \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}} \right| \varphi_i \right\rangle + \frac{\partial E_{\text{ee}}[\{n_j\}, \{\varphi_j\}]}{\partial n_i} &= \mu, \\ \forall_{i \neq j} \quad \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}} + v_{\text{ee}} \right| \varphi_j \right\rangle &= 0. \end{aligned} \quad (15)$$

It is easy to connect the Hohenberg-Kohn density functional  $F^{\text{HK}}[\rho]$  with the one-matrix functional  $T[\Gamma] + E_{\text{ee}}[\Gamma]$  defined in Eqs. (8) and (9), namely,

$$F^{\text{HK}}[\rho] = \min_{\Gamma \rightarrow \rho} \{T[\Gamma] + E_{\text{ee}}[\Gamma]\}, \quad (16)$$

where  $\Gamma$  is  $N$ -rep.

The above relation provides a link between DFT and DMFT which holds for any  $\rho$ . It can be interpreted as a search procedure for the optimal  $\Gamma$  for a given  $\rho$ . In practical DMFT calculations, the search is performed directly among one-matrices and only after finding the optimal  $\Gamma$  the corresponding  $\rho$  is obtained. As Eq. (16) holds for any  $\rho$  it holds also for the optimal one. So Eq. (16) does not involve any additional constraint on the search. Note the full analogy with Kohn-Sham calculations, in which optimal orbitals are obtained and they are used to evaluate the corresponding  $T_s[\rho]$  although  $\rho$  is unknown a priori. In this work, we will use the relation of Eq. (16) to construct a particular local potential of our interest. This relation is applied for  $\Gamma$  obtained from the unconstrained search and the corresponding  $\rho$ .

Note that Eqs. (16) and (7) imply the following relation

$$\forall_{\Gamma \rightarrow \rho} \quad E^{\text{HK}}[\rho] \leq E[\Gamma], \quad (17)$$

where

$$E^{\text{HK}}[\rho] = F^{\text{HK}}[\rho] + \int \rho(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r}. \quad (18)$$

Concerning practical computational strategies based on DMFT, it is worthwhile to notice that the functional  $E_{\text{ee}}[\Gamma]$  comprises the Coulomb component of known analytic form and the remaining part which needs to be represented by some analytic expression. Usually, the expressions used in practice do not depend explicitly on  $\Gamma$  but on orbitals and orbital occupancies used as auxiliary quantities to express  $\Gamma$  ( $E_{\text{ee}}[\Gamma] = E_{\text{ee}}[\{\varphi_i\}, \{n_i\}]$ ). Such computational frameworks, in the current stage of their development, lead to results of the overall quality which compares favorably with that of methods based on Kohn-Sham formulation of DFT (for a recent overview see Ref. [10] and the references therein). In the present work, we will make no distinction between approximants to  $E_{\text{ee}}[\Gamma]$  which depend on  $\Gamma$  directly or not because the the considerations concern either cases.

## Embedding One-Matrix in the Orbital-Free Environment

Consider two subsystems  $A$  and  $B$  and assume the electron density of the total system as  $\rho = \rho_A + \rho_B$ . We want to describe a subsystem  $A$  in terms of the one-matrix  $\Gamma_A$ . The goal is to construct a functional

$\Xi^\Gamma$  of  $N$ -rep  $\Gamma_A$  and  $\rho_B$  such that the following condition holds

$$\min_{\Gamma_A \rightarrow \rho_A} \Xi^\Gamma[\Gamma_A, \rho_B] = E^{\text{HK}}[\rho_A + \rho_B]. \quad (19)$$

Let us write a Hohenberg–Kohn functional in the following form

$$\begin{aligned} E^{\text{HK}}[\rho_A + \rho_B] &= T_s[\rho_A] + E_{\text{xc}}[\rho_A] + J[\rho_A, \rho_A] + \int \rho_A(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} \\ &+ T_s[\rho_B] + E_{\text{xc}}[\rho_B] + J[\rho_B, \rho_B] + \int \rho_B(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} \\ &+ 2J[\rho_A, \rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] + E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B] \\ &= E^{\text{HK}}[\rho_A] + \int \rho_A(\vec{r}) v_{\text{ext}}^B(\vec{r}) d\vec{r} \\ &+ 2J[\rho_A, \rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] + E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B] \\ &+ E^{\text{HK}}[\rho_B] + \int \rho_B(\vec{r}) v_{\text{ext}}^A(\vec{r}) d\vec{r}, \end{aligned} \quad (20)$$

where

$$v_{\text{ext}} = v_{\text{ext}}^A + v_{\text{ext}}^B, \quad (21)$$

the Coulomb integral  $J$  reads

$$J[f, g] = \frac{1}{2} \int \int f(\vec{r}) g(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r} d\vec{r}', \quad (22)$$

and the nonadditive kinetic and exchange–correlation functionals are defined as

$$T_s^{\text{nad}}[\rho_A, \rho_B] = T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B] \quad (23)$$

and

$$E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B] = E_{\text{xc}}[\rho_A + \rho_B] - E_{\text{xc}}[\rho_A] - E_{\text{xc}}[\rho_B], \quad (24)$$

respectively. Define now a bifunctional of  $N$ -rep one-matrix  $\Gamma_A$  and  $\rho_B$  as

$$\begin{aligned} \Xi^\Gamma[\Gamma_A, \rho_B] &= E[\Gamma_A] + \int \rho_A(\vec{r}) v_{\text{ext}}^B(\vec{r}) d\vec{r} \\ &+ 2J[\rho_A, \rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] + E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B] \\ &+ E^{\text{HK}}[\rho_B] + \int \rho_B(\vec{r}) v_{\text{ext}}^A(\vec{r}) d\vec{r}, \end{aligned} \quad (25)$$

where the definition given in Eq. (7) has been used. Comparing Eq. (25) with (20) one immediately sees

that due to the relation (17) the functional  $\Xi^\Gamma[\Gamma_A, \rho_B]$  possesses a desired property (19).

As a result, the total energy  $E^{\text{emb}}$  from Eq. (2) may be written as

$$E^{\text{emb}} = \min_{\Gamma_A \rightarrow 2N-2N_B} \Xi^\Gamma[\Gamma_A, \rho_B] \quad (26)$$

where  $\Gamma_A$  is  $N$ -rep.

## Variational Equation for $\Gamma_A$ With a Local Embedding Potential

To find an optimal one-matrix  $\Gamma_A$  for a frozen density  $\rho_B$  the functional  $\Xi^\Gamma[\Gamma_A, \rho_B]$  defined in Eq. (25) undergoes a constrained optimization that results in the variational equation

$$\frac{\delta \Xi^\Gamma[\Gamma_A, \rho_B]}{\delta \Gamma_A(\vec{r}, \vec{r}')} = \frac{\delta E[\Gamma_A]}{\delta \Gamma_A(\vec{r}, \vec{r}')} + \delta(\vec{r} - \vec{r}') v_{\text{loc}}^{\text{emb}}(\vec{r}) = \mu \delta(\vec{r} - \vec{r}'), \quad (27)$$

where the *local* embedding potential  $v_{\text{loc}}^{\text{emb}}(\vec{r})$  is defined as

$$\begin{aligned} v_{\text{loc}}^{\text{emb}}(\vec{r}) &= v_{\text{ext}}^B(\vec{r}) + \int \rho_B(\vec{r}') |\vec{r} - \vec{r}'|^{-1} d\vec{r}' + \frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \\ &+ \frac{\delta E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}. \end{aligned} \quad (28)$$

As all known approximations to the one-matrix functional are given in terms of the occupation numbers and the orbitals, the variational equation can be written in an equivalent form [cf. Eq. (15)]

$$\begin{aligned} \forall_i \quad &\left\langle \varphi_i^A \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}^A + v_{\text{loc}}^{\text{emb}} \right| \varphi_i^A \right\rangle \\ &+ \frac{\partial E_{\text{ee}}[\{n_j^A\}, \{\varphi_j^A\}]}{\partial n_i^A} = \mu, \\ \forall_{i \neq j} \quad &\left\langle \varphi_i^A \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}^A + v_{\text{ee}}^A + v_{\text{loc}}^{\text{emb}} \right| \varphi_j^A \right\rangle = 0, \end{aligned} \quad (29)$$

that can be used in practical calculations. Note that the occupancies  $\{n_i^A\}$  and the orbitals  $\{\varphi_i^A\}$  correspond to the one-matrix of the subsystem  $A$ ,  $\mu$  is the Lagrange multiplier related to the normalization condition  $\text{Tr}[\Gamma_A] = 2N - 2N_B$ , and the kernel of the operator  $v_{\text{ee}}^A$  is defined as  $v_{\text{ee}}^A(\vec{r}, \vec{r}') = \frac{\delta E_{\text{ee}}[\Gamma_A]}{\delta \Gamma_A(\vec{r}, \vec{r}')}$ . Thus, finding the optimal one-matrix  $\Gamma_A$  for a system  $A$  embedded in the subsystem  $B$  with the frozen density  $\rho_B$ , amounts to optimizing the functional  $E[\Gamma_A] +$

$\int \Gamma_A(\vec{r}, \vec{r}) v_{\text{loc}}^{\text{emb}}(\vec{r}) d\vec{r}$  under the only constraint that  $\Gamma_A$  is  $N$ -representable. This is the main result of this work. Moreover, comparing the right-hand-sides of Eqs. (5) and (28) shows that the local potentials  $v_{\text{loc}}^{\text{emb}}(\vec{r})$  and  $v_{\text{emb}}^{\text{KSCEd}}[\rho_A, \rho_B; \vec{r}]$  are the same. After the optimal one-matrix  $\Gamma_A$  is found for a given density  $\rho_B$ , the energy of the total system comprising the subsystems  $A$  and  $B$  obtains as a value of the bifunctional  $\Xi^\Gamma$  defined in (25).

The variational calculations following Eq. (27) represent indeed a generalization of Eq. (3). If  $\rho_A^{\text{opt}}$  is pure-state non-interacting  $v$ -representable, it can be obtained from either Eqs. (27) or (3). Obviously, using a pure-state noninteracting  $v$ -representable density as  $\rho_A^{\text{opt}}$  in either  $v_{\text{loc}}^{\text{emb}}(\vec{r})$  or  $v_{\text{emb}}^{\text{KSCEd}}[\rho_A, \rho_B; \vec{r}]$  leads to exactly the same local potential because the right-hand-sides of Eqs. (5) and (28) are the same. This potential is well-defined regardless whether the density  $\rho_A$  is pure-state noninteracting  $v$ -representable or not. If  $\rho_A^{\text{opt}}$  is not pure-state noninteracting  $v$ -representable, however, only Eq. (27) has  $\rho_A^{\text{opt}}$  as a solution. It is important to note, in this context, that in deriving Eq. (28) we started directly from Hohenberg–Kohn variational principle without using the assumption of pure-state noninteraction  $v$ -representability of  $\rho_A^{\text{opt}}$ .

## Conclusions

It was shown that the local potential given in Eq. (5) is the exact embedding potential if the embedded system is represented by means of the one-matrix and its environment by some electron density  $\rho_B$ . As a consequence of the main result of this work, i.e., the equality of the right-hand-sides in Eq. (5) and Eq. (28), the domain of applicability of Eq. (5) was, therefore, extended from the two previously considered cases as far as the embedded objects are concerned: (i) a reference system of non-interacting electrons [5], and (ii) an interacting system at some well-defined conditions [8], to another one. In all three cases, applying the embedding potential in variational calculations leads to the minimum of the Hohenberg–Kohn energy functional in the presence of the constraint  $\rho \geq \rho_B$ . The case of embedded one-matrix considered in this work is of great possible practical utility. Compared with the embedding non-interacting system [5], the search space for  $\rho - \rho_B$  is more complete because it is not restricted to pure-state noninteracting  $v$ -representable densities. Moreover, density-matrix-functional theory level of

description of the embedded system itself offers practical advantages over that of Kohn and Sham. On the other hand, embedding an interacting system [8], especially at conditions at which the embedding potential given in Eq. (5) is exact, involves significantly more computational effort than in the case of one-matrix.

Turning back to the issue of universality of the DFT form of the embedding potential given in Eq. (5) we should underline that the consideration of the present work as well as the previous ones concern construction of a *local potential* to be used as addition to the external potential in the isolated subsystem described by means of the considered three different types of objects: reference system of noninteracting electrons [5], wave-function [8] or one-matrix (this work), to optimize the total electron density. The relation of local potential constructed in the proposed way to a pseudopotential [16] expressed by means of projection operators is not straightforward. The latter is a *nonlocal operator* and it is not equivalent to the optimal effective embedding potential discussed in this work except of some particular cases [Savin and Wesolowski, in preparation].

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