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Density-orbital embedding theory

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In the article density-orbital embedding (DOE) theory is proposed. DOE is based on the concept of density orbital (DO), which is a generalization of the square root of the density for real functions and fractional electron numbers. The basic feature of DOE is the representation of the total supermolecular density ρ_s as the square of the sum of the DO φ_a , which represents the active subsystem A and the square root of the frozen density ρ_f of the environment F . The correct ρ_s is obtained with φ_a being negative in the regions in which ρ_f might exceed ρ_s . This makes it possible to obtain the correct ρ_s with a broad range of the input frozen densities ρ_f so that DOE resolves the problem of the frozen-density admissibility of the current frozen-density embedding theory. The DOE Euler equation for the DO φ_a is derived with the characteristic embedding potential representing the effect of the environment. The DO square φ_a^2 is determined from the orbitals of the effective Kohn-Sham (KS) system. Self-consistent solution of the corresponding one-electron KS equations yields not only φ_a^2 , but also the DO φ_a itself.

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I. INTRODUCTION

In order to efficiently treat complex molecular systems and aggregates within density-functional theory (DFT), the frozen-density embedding (FDE) approach has been developed in the literature [1–9]. In FDE a total supermolecular system S of the density ρ_s is partitioned to an active system A of the density ρ_a embedded in an environment F with the predetermined density ρ_f , which serves as an input of FDE. The total density ρ_s is represented in FDE as the sum

$$\rho_s(\mathbf{r}) = \rho_a(\mathbf{r}) + \rho_f(\mathbf{r}), \quad (1)$$

with the environmental density ρ_f being frozen and the active density ρ_a being determined from the effective one-electron Kohn-Sham (KS) equations for the active system A with the characteristic embedding potential [5]. Then, with the total density ρ_s determined from (1), FDE avoids the full conventional supermolecular calculation of the system S , thus representing, in principle, an efficient computational approach.

Though looking inoffensive and natural, the partitioning (1) presents, in reality, a serious problem for the rigorous foundation of FDE [10]. The point is that, in a customary DFT fashion, all densities in (1) are considered as non-negative functions, which is the necessary condition for their N representability [11]. With this, the partitioning (1) is, in principle, unable to yield the correct density ρ_s in the regions in which the input frozen density ρ_f might happen to be larger than the total exact density, $\rho_f(\mathbf{r}) > \rho_s(\mathbf{r})$. This means that the FDE appears to be well-defined at the exact level only for a severely restricted subset of so-called admissible frozen densities ρ_f , which do not exceed the exact ρ_s everywhere in the space, $\rho_f(\mathbf{r}) \leq \rho_s(\mathbf{r})$. Since the admissibility of a given ρ_f cannot be, in general, verified other than by that same full supermolecular calculation, which FDE is intended to avoid, the partitioning (1) turns FDE into the ill-posed problem [10].

In this article, an alternative density-orbital embedding (DOE) theory is proposed, which is free from the

aforementioned frozen-density admissibility problem of FDE. DOE is based on the concept of density orbital (DO) introduced in Sec. II, which is a generalization of the square root of the density characterized in DFT with the corresponding Euler-Lagrange (EL) equation [12–15]. The DO $\varphi_a(\mathbf{r})$ is a real function, with which the total supermolecular density is determined from the relation

$$\rho_s(\mathbf{r}) = [\varphi_a(\mathbf{r}) + \sqrt{\rho_f(\mathbf{r})}]^2. \quad (2)$$

The Euler equation for the DO φ_a is derived in Sec. III from the EL equation for the square root of the total density ρ_s . Besides the KS potential $v_s[\varphi_a^2]$ and the DO analog $v_\varphi[\varphi_a]$ of the Pauli potential for the active system A , it contains also the embedding potential $v_{\text{emb}}([\varphi_a])$, which represents the effect of the environment. In Sec. IV the noninteracting system A_φ with a fractional number N_φ of electrons is introduced, the density of which is the square of the DO φ_a . One-electron equations for the KS orbitals of this system are derived, which contains the potentials $v_s[\varphi_a^2]$ and $v_{\text{emb}}([\varphi_a])$. A possible computational DOE scheme is considered. In Sec. V the discussion of the proposed DOE theory is given and the conclusions are made. Unlike the current FDE, with the DO being negative in the regions where $\rho_f(\mathbf{r}) > \rho_s(\mathbf{r})$, DOE is able, in principle, to yield the correct ρ_s for a broad range of input frozen densities ρ_f .

II. DENSITY ORBITAL CONCEPT

In this section a concept of the DO is introduced. Just as the previous FDE, the present DOE theory employs the partition of a supermolecule S with N electrons to an environment F with N_f electrons and an active system (N and N_f are both integer numbers). In both FDE and DOE the environment F is represented with the (non-negative) frozen density ρ_f . However, the description of A in DOE differs crucially from that of FDE. As was already mentioned in the Introduction, in FDE the active system A is represented with the non-negative density ρ_a and the total density ρ_s is determined as the sum (1). Because of this, FDE is unable to reproduce the exact ρ_s in the

regions, in which this density is smaller than an inadmissible input frozen density, $\rho_s(\mathbf{r}) < \rho_f(\mathbf{r})$ [10].

To remedy this serious deficiency of FDE, we propose in the present article the concept of the DO to describe the active system within the embedding theory. By its definition, the DO $\varphi_a(\mathbf{r})$ is the real function with which the total density is partitioned according to Eq. (2). In the regions where $\rho_f(\mathbf{r}) > \rho_s(\mathbf{r})$, the DO $\varphi_a(\mathbf{r})$ is negative. Thus, according to (2), the excess of the input ρ_f in a certain region is compensated with the negative value of the DO $\varphi_a(\mathbf{r})$. With this, any reasonable input frozen density ρ_f of embedding theory becomes admissible density for the proposed DOE (see the next section for a condition on ρ_f).

The DO φ_a introduced in this section can be considered as a generalization of the square root of the density, which is characterized in DFT with the EL equation for $\sqrt{\rho}$ [15]. Indeed, by its definition (2), in the absence of the environment, that is, when $\rho_f(\mathbf{r}) = 0$, φ_a turns to $\sqrt{\rho_s}$. In a general case, while the square root of a non-negative N -representable density is also a non-negative function, the DO φ_a might be either positive or negative in a certain region, depending on the relative magnitude of $\rho_s(\mathbf{r})$ and $\rho_f(\mathbf{r})$ in this region.

The DO φ_a is a generalization of the square root of the density in yet another respect. While for an individual system the density (i.e., the square of $\sqrt{\rho}$) integrates to an integer number of electrons N , the square of the DO integrates (in a general case) to a fractional number N_φ ,

$$N_\varphi = \int \varphi_a^2(\mathbf{r}) d\mathbf{r} = N - N_f - N_{fa}, \quad (3)$$

where

$$N_{fa} = 2 \int d\mathbf{r} \varphi_a(\mathbf{r}) \sqrt{\rho_f(\mathbf{r})}. \quad (4)$$

In the following sections equations will be derived, which determine both the form of the DO and its normalization.

III. EULER EQUATION FOR THE DENSITY ORBITAL

In this section the Euler equation for the DO is derived. We consider the EL equation for the total KS system corresponding to the supermolecular density ρ_s :

$$\frac{\delta T_s[\rho_s]}{\delta \rho_s(\mathbf{r})} + v_s\{[\rho_s(\mathbf{r})]; \mathbf{r}\} = \epsilon_H. \quad (5)$$

Equation (5) is obtained from minimization of the total energy E_s of the noninteracting KS system,

$$E_s[\rho_s] = T_s[\rho_s] + \int \rho_s(\mathbf{r}) v_s\{[\rho_s(\mathbf{r})]; \mathbf{r}\} d\mathbf{r}, \quad (6)$$

with respect to ρ_s , which preserves the normalization of ρ_s to N electrons. In (5) and (6) T_s is the functional of the KS kinetic energy and v_s is the canonical KS potential,

$$v_s([\rho_s]; \mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho_s]}{\delta \rho_s(\mathbf{r})}, \quad (7)$$

where v_{ext} is the external potential and E_{xc} is the exchange-correlation (xc) energy.

Equation (5) can be rewritten as the EL equation for the square root of ρ_s [12–15]:

$$\left\{ -\frac{1}{2} \nabla^2 + v_s([\rho_s]; \mathbf{r}) + v_\theta([\rho_s]; \mathbf{r}) \right\} \sqrt{\rho_s(\mathbf{r})} = \epsilon_H \sqrt{\rho_s(\mathbf{r})}. \quad (8)$$

In Eq. (8) v_θ is the Pauli potential, the functional derivative with respect to ρ_s ,

$$v_\theta([\rho_s]; \mathbf{r}) = \frac{\delta T_\theta[\rho_s]}{\delta \rho_s(\mathbf{r})}, \quad (9)$$

of the kinetic functional,

$$T_\theta[\rho_s] = T_s[\rho_s] - \int d\mathbf{r} \sqrt{\rho_s(\mathbf{r})} \left(-\frac{1}{2} \nabla^2 \right) \sqrt{\rho_s(\mathbf{r})}. \quad (10)$$

In the present DOE the master equation (5) is rewritten as an equation for the DO φ_a analogous to Eq. (8) for the square root of the total density. To accomplish this, we insert in Eq. (5) the density partitioning (2). Then we add to and subtract from Eq. (5) the derivative of the KS kinetic functional $\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} |_{\rho=\varphi_a^2}$ evaluated at the density φ_a^2 as well as the kinetic term $-\varphi_a^{-1}(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_a(\mathbf{r})$ with the DO φ_a . Both sides of the resultant equation are multiplied by $\varphi_a(\mathbf{r})$, thus giving the Euler equation for the DO:

$$\left\{ -\frac{1}{2} \nabla^2 + v_s([\varphi_a^2]; \mathbf{r}) + v_\varphi([\varphi_a]; \mathbf{r}) + v_{\text{emb}}([\varphi_a]; \mathbf{r}) \right\} \varphi_a(\mathbf{r}) = \epsilon_H \varphi_a(\mathbf{r}). \quad (11)$$

In (11), $v_s([\varphi_a^2]; \mathbf{r})$ is the following KS potential:

$$v_s([\varphi_a^2]; \mathbf{r}) = v_{\text{ext}}^a(\mathbf{r}) + \int d\mathbf{r}' \frac{\varphi_a^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\varphi_a^2}. \quad (12)$$

It includes the external potential v_{ext}^a of the active subsystem A and it depends on the density, the square of the DO φ_a . Another potential in (11) depending solely on φ_a is v_φ , which is an analog of the Pauli potential of Eq. (9):

$$v_\varphi([\varphi_a]; \mathbf{r}) = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\varphi_a^2} - \varphi_a^{-1}(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \varphi_a(\mathbf{r}). \quad (13)$$

The environment is represented in (11) with the embedding potential v_{emb} , which assumes the following form:

$$v_{\text{emb}}([\varphi_a]; \mathbf{r}) = v_s([\varphi_a^2 + 2\varphi_a \sqrt{\rho_f} + \rho_f]; \mathbf{r}) - v_s([\varphi_a^2]; \mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\varphi_a^2 + 2\varphi_a \sqrt{\rho_f} + \rho_f} - \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\varphi_a^2}. \quad (14)$$

In (12)–(14) the generalization of the functionals $E_{\text{xc}}[\rho]$ and $T_s[\rho]$ and their density derivatives for the densities with a fractional number of electrons is considered, which was introduced in Ref. [16]. To employ this generalization, the density φ_a^2 is to be represented with an ensemble of the N_φ^i - and $(N_\varphi^i + 1)$ -electron systems, where N_φ^i is the closest integer from below to the number of electrons N_φ of Eq. (3). The

ensemble was defined in Ref. [16] as an open system, which is in equilibrium with its environment. Due to this, DOE is defined on a set of the input frozen densities ρ_f , for which their counterparts, the DOs φ_a , are ensemble-representable densities in the aforementioned sense. This condition appears to be not a very restrictive one, so that the proposed DOE could, in principle, accommodate a broad range of input densities ρ_f .

IV. NONINTERACTING KS SYSTEM WITH THE DO SQUARE AS ITS DENSITY

In this section the DO is characterized within the KS approach. In order to accomplish this, we introduce the noninteracting system A_φ , which has the square φ_a^2 of the DO as its density. This system is described with the EL equation of the type of Eq. (5),

$$\left. \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\varphi_a^2} + v_s^{\text{eff}}([\varphi_a]; \mathbf{r}) = \epsilon_\mu, \quad (15)$$

with the effective KS potential v_s^{eff} . The Lagrange multiplier ϵ_μ in (15) represents the condition of normalization of φ_a^2 to N_φ , with the latter parameter being well defined at the solution point.

The combination of (13) and (15) yields the equation for φ_a ,

$$\left\{ -\frac{1}{2}\nabla^2 + v_s^{\text{eff}}([\varphi_a]; \mathbf{r}) + v_\varphi([\varphi_a]; \mathbf{r}) \right\} \varphi_a(\mathbf{r}) = \epsilon_\mu \varphi_a(\mathbf{r}), \quad (16)$$

which includes v_s^{eff} . Then from the comparison of (16) with (11) we obtain the following expression for v_s^{eff} (up to the uniform shift $\epsilon_\mu - \epsilon_H$, which can be neglected):

$$v_s^{\text{eff}}([\varphi_a]; \mathbf{r}) = v_s([\varphi_a^2]; \mathbf{r}) + v_{\text{emb}}([\varphi_a]; \mathbf{r}). \quad (17)$$

This potential determines the KS spin orbitals ψ_i^a from the one-electron KS equations:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s^{\text{eff}}([\varphi_a]; \mathbf{r}) \right\} \psi_i^a(\mathbf{r}) = \epsilon_i \psi_i^a(\mathbf{r}). \quad (18)$$

In its turn, the KS spin orbitals yield the density φ_a^2 ,

$$\varphi_a^2(\mathbf{r}) = \sum_i^{N_\varphi} |\psi_i^a(\mathbf{r})|^2 + (N_\varphi - N_\varphi^i) |\psi_{(N_\varphi^i+1)}^a(\mathbf{r})|^2. \quad (19)$$

A possible computational approach to determining the DO φ_a from the KS equations (18) can be formulated as the minimization of the following integral:

$$\int |\varphi_{ap}^2(\{c_{kp}\}, N_{\varphi p}; \mathbf{r}) - \varphi_{ao}^2(\{c_{kp}\}, N_{\varphi p}; \mathbf{r})| d\mathbf{r} = \min. \quad (20)$$

In Eq. (20) φ_{ap} is the ‘‘potential’’ DO, which is used to calculate the effective KS potential (17) and which is expanded with a set of auxiliary functions f_k :

$$\varphi_{ap}(\mathbf{r}) = \sum_k c_{kp} f_k(\mathbf{r}). \quad (21)$$

The parameter $N_{\varphi p}$ in (20) is the normalization of φ_{ap} ,

$$N_{\varphi p} = \int \varphi_{ap}^2(\mathbf{r}) d\mathbf{r} \quad (22)$$

$$= N - N_f - 2 \int d\mathbf{r} \varphi_{ap}(\mathbf{r}) \sqrt{\rho_f(\mathbf{r})}, \quad (23)$$

while the function φ_{ao}^2 in (20) is the DO square of Eq. (19), which is obtained from the KS orbitals calculated with the potential $v_s^{\text{eff}}([\varphi_{ap}]; \mathbf{r})$. At the point of the solution of the KS equations (18), $\varphi_{ap}^2(\mathbf{r}) = \varphi_{ao}^2(\mathbf{r})$. A numerical approach to this point could be achieved with a direct nonlinear optimization of the coefficients c_{kp} of (21) and of the parameter $N_{\varphi p}$ of (22) in order to satisfy the requirement (20).

V. CONCLUSIONS

In this article the DOE theory is proposed. Formally, a more symmetric (than in Sec. II) description of this theory can be given, with both active system A and its environment F being represented in DOE with the DOs φ_a and φ_f , respectively, with $\varphi_f \equiv \sqrt{\rho_f}$. This description shows clearly that, conceptually, the DO is, indeed, the generalization of the square root of the density for the case of real functions and fractional number of electrons.

The basic feature of the proposed DOE is the partition of the total supermolecular density through the DOs,

$$\rho_s(\mathbf{r}) = [\varphi_a(\mathbf{r}) + \varphi_f(\mathbf{r})]^2 = \varphi_a^2(\mathbf{r}) + 2\varphi_a(\mathbf{r})\varphi_f(\mathbf{r}) + \varphi_f^2(\mathbf{r}), \quad (24)$$

which makes it possible to obtain the correct ρ_s with a broad range of the input frozen densities ρ_f . A given ρ_f is accommodated in the partition (24) through the quantum interference of the DOs φ_a and φ_f represented with the second term in the last line of Eq. (24). Specifically, the excess of the input $\rho_f(\mathbf{r})$ in a certain region (its inadmissibility in the current FDE) is compensated with the negative values of the aforementioned interference term in this region.

The DO φ_a satisfies the Euler equation (11) analogous to that for the square root of the density. The characteristic DOE feature of this equation is its embedding potential (14), which describes the effect of the environment.

The DO square φ_a^2 is obtained via Eq. (19) from the orbitals of the effective KS system. In order to yield the correct ρ_s through (19) and (24), all KS orbitals must have nodes at all points where the input frozen density is equal to the correct supermolecular density, $\rho_f(\mathbf{r}) = \rho_s(\mathbf{r})$. At these points, the effective KS potential (17) might well have singularities. One can anticipate, however, that for a typical input density ρ_f , such points would constitute only a set of the zero measure. Then the KS theory can, in principle, afford the construction of a local effective potential, which is singular on a zero-measure set.

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