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Embedding potentials for excited states of embedded species

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Frozen-Density-Embedding Theory (FDET) is a formalism to obtain the upper bound of the ground-state energy of the total system and the corresponding embedded wavefunction by means of Euler-Lagrange equations [T. A. Wesolowski, *Phys. Rev. A* **77**(1), 012504 (2008)]. FDET provides the expression for the embedding potential as a functional of the electron density of the embedded species, electron density of the environment, and the field generated by other charges in the environment. Under certain conditions, FDET leads to the exact ground-state energy and density of the whole system. Following Perdew-Levy theorem on stationary states of the ground-state energy functional, the other-than-ground-state stationary states of the FDET energy functional correspond to excited states. In the present work, we analyze such use of other-than-ground-state embedded wavefunctions obtained in practical calculations, i.e., when the FDET embedding potential is approximated. Three computational approaches based on FDET, that assure self-consistent excitation energy and embedded wavefunction dealing with the issue of orthogonality of embedded wavefunctions for different states in a different manner, are proposed and discussed. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4870014>]

I. INTRODUCTION

Frozen-Density Embedding Theory (FDET) provides the formal foundations for computational methods to study ground-states of embedded species, which are described by quantum-mechanical descriptors such as: (a) reference system of non-interacting electrons,^{1,2} (b) interacting wavefunction,³ and (c) one-particle reduced density matrix,⁴ in the presence of an environment which is described by means of the charge densities: frozen electron density (ρ_B) and the potential generated by the nuclei ($v_B(\vec{r})$). FDET is not an alternative to Density Functional Theory (DFT) formulation of many electron problem. It is rather a formal basis of multi-level computer simulations using quantum mechanical descriptors only for a selected subsystem. Although for some choices for ρ_B the ground state energy can be obtained, FDET assures only reaching the upper limit of the ground-state energy for the total system for arbitrarily chosen density ρ_B and obtaining the corresponding quantum mechanical descriptor for the embedded species self-consistently from Euler-Lagrange equations. Formal frameworks and computational methods closely related to FDET targeting the exact ground-state energy were proposed in the literature, in which ρ_B is not an input quantity but the result of calculations. They include partition methods such as subsystem formulation of DFT⁵ introduced originally for studies of ionic solids which found its principal domain of applicability for studies of intermolecular complexes,⁶ the partition DFT⁷ which is also a DFT formulation and the recently introduced partition method using embedded wavefunctions for different subsystems.⁸ All these frameworks share the same feature with FDET—some local potential coupling the subsystems. Concerning extending FDET to the excited states, the Linear-Response Time-Dependent Density Functional Theory (LR-TDDFT) formal

framework⁹ does not involve construction of excited state wavefunction. Such extension of FDET was proposed and tested for local excitations.¹⁰ It has been shown to be a powerful tool in modeling the effect of environment on local excitations in embedded chromophores.^{10–12} References 13 and 14 provide comprehensive recent reviews. The FDET/LR-TDDFT framework can be seen as introduction of an additional approximation, namely, Neglect of the Dynamic Response of the Environment in the LR-TDDFT generalization of the ground-state subsystem DFT formulation⁵ to excited states.¹⁵ For review of generalization of subsystem DFT to excited state, see Ref. 13 and the references therein.

Embedding methods using the charge-densities as the only descriptors for the environment, in which the wavefunction is explicitly constructed,¹⁶ attract increasing attentions as an alternative for excited states.^{17–19} They were pioneered by Carter and co-workers¹⁷ as an *ad hoc* combination²⁰ of the embedding potential derived for embedding a non-interacting electrons reference system in a frozen density environment¹ with the wave-function based methods of quantum chemistry. Reference 3 provides the formal justification of such combination and identification of additional approximations made if used for ground-state. Perdew-Levy theorem on the meaning of stationary states of the ground-state energy functional as excited states²¹ provides the justification for interpreting the other-than-ground-state stationary solutions as excited states. The use of explicit wavefunction for the excited state, in contrast to the methods based on the LR-TDDFT framework, has an obvious advantage. Besides the possibility to overcome the known flaws of approximate LR-TDDFT methods (disappointing results for charge-transfer or double excitations and excitations from open-shell ground-state, for instance), it is possible to obtain excitation energies as differences of expectation values of conventional quantum mechanical operators.

For an isolated species comprising N_A electrons in an external potential ($v_A(\vec{r})$), the excitation energy can be evaluated as the difference of expectation values of the corresponding Hamiltonian (\hat{H}_A) (not to mention the possibility to evaluate expectation values of two-particle operators):

$$E_I - E_J = \langle \Psi_I^{A_0} | \hat{H}_A | \Psi_I^{A_0} \rangle - \langle \Psi_J^{A_0} | \hat{H}_A | \Psi_J^{A_0} \rangle, \quad (1)$$

where $\Psi_I^{A_0}$ is the wavefunction for the I th state obtained from an adequately chosen quantum chemistry method in the absence of any environment.

If the same species is embedded and the approximate embedding potential used to represent the environment ($\hat{v}_{emb}^0(\vec{r})$) is ρ_A -independent (for example, if \hat{v}_{emb}^0 is the Coulomb potential generated by the charges in the environment), the above formula can be trivially generalized and the excitation energies can be also obtained as differences of expectation values of two different wavefunctions,

$$E_I^{emb} - E_J^{emb} = \langle \Psi_I^A | \hat{H}_A + \hat{v}_{emb}^0 | \Psi_I^A \rangle - \langle \Psi_J^A | \hat{H}_A + \hat{v}_{emb}^0 | \Psi_J^A \rangle. \quad (2)$$

Unfortunately, the exact embedding potential given in Eq. (5) and derived in Refs. 3 and 23 depends on the embedded wavefunction. The simple formula given in Eq. (2) is, therefore, not applicable. The FDET embedding potential assures that the optimization of the total energy functional in Euler-Lagrange equations for the embedded wavefunction yields the total electron density which minimizes the total energy functional subject to the additional constraint: the total electron density is larger or equal to the arbitrarily chosen electron density associated with the environment of the embedded species (ρ_B). As noticed in Ref. 22, Perdew-Levy theorem,²¹ that associates stationary points of the density functional for the total energy with electronic states, other-than-ground-state solutions of the Euler-Lagrange equations for the embedded wavefunction correspond to excited states. In the present work, we analyze how this observation might be implemented in practice. The present work is the sequel to Ref. 3, where the Frozen-Density Embedding Theory embedding potential was derived for the case of an arbitrary choice for ρ_B to assure obtaining the upper bound of the ground state energy of the whole system. The provided equations concerned the case of the exact functionals, and arbitrarily chosen ρ_B , and embedded wavefunction of the form corresponding to some variational principle based method of quantum chemistry. The practical implementation of the formalism introduced in Ref. 3 for ground-state calculations is straightforward even if approximate functionals are used. The situation is different in the case of excited states. The use of approximations might affect different states differently. Three computational strategies to deal with this issue are proposed.

II. FROZEN-DENSITY EMBEDDING THEORY

A. Euler-Lagrange equations for the embedded wavefunction: Ground state

For embedded wavefunction of any form, the FDET expression for the total energy functional depending on the em-

bedded wavefunction (Ψ^A) and electron density of the environment (ρ_B) reads

$$\begin{aligned} E_{AB}^{EWF}[\Psi^A, \rho_B] &= \langle \Psi^A | \hat{H}_A | \Psi^A \rangle + \Delta F^{MD}[\rho_A] \\ &+ \int \rho_A(\vec{r}) v_B(\vec{r}) d\vec{r} + \iint \frac{\rho_A(\vec{r}) \rho_B(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \\ &+ T_s^{nad}[\rho_A, \rho_B] + E_{xc}^{nad}[\rho_A, \rho_B] \\ &+ E_{v_B}^{HK}[\rho_B] + \int \rho_B(\vec{r}) v_A(\vec{r}) d\vec{r}, \end{aligned} \quad (3)$$

where (a) ρ_A denotes the electron density corresponding to Ψ^A , (b) $X^{nad}[\rho_A, \rho_B]$ denotes the bifunctional $X^{nad}[\rho_A, \rho_B] = X[\rho_A + \rho_B] - X[\rho_A] - X[\rho_B]$ (with $X[\rho] = T_s[\rho]$ or $E_{xc}[\rho]$ —density functionals for the non-interacting reference kinetic energy and exchange-correlation energy, respectively, defined in the constrained search procedure^{24,25}), (c) the functional $\Delta F^{MD}[\rho_A]$ represents the part of the correlation energy functional which is not taken into account by a wavefunction based method (see Ref. 3 for details), and (d) $E_{v_B}^{HK}[\rho_B]$ denotes the Hohenberg-Kohn energy functional²⁶ corresponding to $v_B(\vec{r})$.

In FDET, the minimization of $E_{AB}^{EWF}[\Psi^A, \rho_B]$ with respect to Ψ^A is performed by means of Euler-Lagrange equations:

$$\frac{\partial E_{AB}^{EWF}[\Psi_{opt}^A, \rho_B]}{\partial \Psi_{opt}^A} - \lambda \Psi_{opt}^A = 0. \quad (4)$$

This assures full self-consistency of the minimizer Ψ_{opt}^A , the embedding potential given in Eq. (5), and the energy $E_{AB}^{EWF}[\Psi_{opt}^A, \rho_B]$. The energy $E_{AB}^{EWF}[\Psi_{opt}^A, \rho_B]$ is the upper bound of the ground-state energy of the total system. For some choices for ρ_B , Euler-Lagrange equations might even lead to the *exact* ground-state energy and density for the total system.³

Equation (4) corresponds to the one of many variational-principle based methods of quantum chemistry (Hartree-Fock, MCSCF, truncated or full CI). The working equations for each of these methods are different and will not be given here. The present work deals with the common issues related to the embedding potential. For such methods, the multiplicative part of the derivative $\frac{\partial E_{AB}^{EWF}[\Psi_{opt}^A, \rho_B]}{\partial \Psi_{opt}^A}$ (effective potential) differs from the external potential in the absence of the environment ($v_A(\vec{r})$) by the following additional term:

$$\begin{aligned} v_{emb}[\rho_A, \rho_B; \vec{r}] &= v_B(\vec{r}) + \int \frac{\rho_B(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \\ &+ \frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} + \frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} + \frac{\delta \Delta F^{MD}[\rho_A]}{\delta \rho_A(\vec{r})}. \end{aligned} \quad (5)$$

The non-electrostatic terms in the embedding potential: $\frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$, $\frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$, and $\frac{\delta \Delta F^{MD}[\rho_A]}{\delta \rho_A(\vec{r})}$ depend on ρ_A . This

originates from the fact that the functionals $T_s^{nad}[\rho_A, \rho_B]$, $E_{xc}^{nad}[\rho_A, \rho_B]$, and $\Delta F^{MD}[\rho_A]$ are not order-one homogeneous in ρ_A . The case uniform electron gas, for which the exact functionals $T_s[\rho]$ and $E_x[\rho]$ are known, provides an obvious example the inhomogeneity of such functionals. The inhomogeneity lies at the origin of the fact that excitation energy cannot be obtained as the difference of two expectation values of the Hamiltonian as in Eq. (2), which is applicable only for ρ_A -independent embedding potentials.

B. Euler-Lagrange equations for the embedded wavefunction: Excited state

On the virtue of Perdew-Levy theorem on the stationary states of the ground-state energy functional,²¹ other than ground-state solutions of the FDET version of the Euler-Lagrange equations (Eq. (4)) correspond to excited states.

We underline that, all subsequent considerations concerning the excited states apply strictly only if the density ρ_B is such that $\rho_B < \rho_{total}^o$ and $\rho_B < \rho_{total}^I$, where ρ_{total}^o and ρ_{total}^I denote the exact ground state and excited state of the whole system, respectively. Only for such densities FDET leads to exact solutions (energy and density). If the density ρ_B does not satisfy these conditions, FDET leads to the upper bound of the ground-state energy of the whole system. For excited states, however, interpreting the stationary solutions of the Euler-Lagrange equations of FDET as an approximation for excited states, remains an unproven Ansatz.

Since the functionals $T_s^{nad}[\rho_A, \rho_B]$, $E_{xc}^{nad}[\rho_A, \rho_B]$, and $\Delta F^{MD}[\rho_A]$ are not order-one homogeneous in ρ_A , the embedding potential depends on the state. We underline that the functional for the FDET embedding potential, which is given in Eq. (5), is the same regardless the state but the embedding potential is different because the functional is evaluated for ρ_A which is different for each state. As a result, the embedded wavefunctions for different states are not orthogonal. This reflects the main feature of FDET which considers the embedded wavefunction merely as an auxiliary quantity used to perform constrained optimization of the total electron density. Such interpretation of the embedded wavefunction is correct from the formal point of view but calls for more detailed analysis. Any FDET based method used in practice uses some approximations for the functionals for the potentials (or directly approximating the potentials) $\frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$, $\frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$, and $\frac{\delta \Delta F^{MD}[\rho_A]}{\delta \rho_A(\vec{r})}$. (The last of these potentials is usually set to zero in practical calculations.) There is no reason to assume that the errors in such approximated potentials evaluated with different ρ_A are the same. Since the quality of the embedding potential affects directly the quality of the embedded wavefunction, the overlap between the embedded wavefunctions for different states might reflect not the real effect but the differences in the errors in the used approximations made to evaluate the FDET embedding potential for different states. We notice also that accurate calculations of excitation energies, even for isolated species of medium size, are usually quite a challenge for quantum chemistry methods. Any studies of embedded species should use a carefully chosen type of

the wavefunction describing adequately the excited states of the isolated species. Usually, the environment provides a minor correction to the excitation energy and it is very likely that allowing for non-orthogonality of embedded wavefunctions might affect the performance of the chosen wavefunction-based method in an uncontrollable manner. Enforcing orthogonality might be, therefore, a “brute force” method to safeguard that the errors depend less on the state which might, however, over-correct these errors.

The notion of state-specificity of the embedding potential is also known in methods (not necessarily based on FDET), which take into account differential polarization of the environment for different electronic states of the embedded species. In terms of FDET, this contribution to state-specificity arises from the ρ_B -dependence of the potential given in Eq. (5). To our knowledge, the first comprehensive study of significance of differential polarization of the environment in a FDET based method is reported in Ref. 27. The contribution to the excitation energies due to the ρ_A -dependence was also estimated in Ref. 27. It was found to be at least one order of magnitude smaller than the contribution due to the ρ_B -dependence. The relative importance of the two effects might be quite different for other systems and excitations. Moreover, the procedure applied in Ref. 27 most likely overestimates the importance of the ρ_B -dependence. According to the analysis provided in Ref. 28, simultaneous optimization of ρ_A and ρ_B reflects both the physical effect of electronic polarization and the artificial effect - minimization of the error in the approximation to the non-additive kinetic energy functional.

III. FDET AND BEYOND-FDET APPROXIMATE METHODS FOR EXCITED STATES

Solving Eq. (4) cannot be made without further approximations. The ρ_A -dependence of the FDET embedding potential does not cause any significant problems for practical calculations in which these functionals are approximated for the ground-state besides the necessity to update the embedding potential during the self-consistent procedure for solving Euler-Lagrange equations. Equations (3)–(5) remain the same. The only difference between the exact and approximate case is that these functionals are replaced by their approximate counterparts (denoted with tildes throughout the present work). The situation is different for excited states because the errors in these approximate functionals might also depend on the state.

We note that $\Delta F^{MD}[\rho_A]$ does not depend on any quantity associated with the environment. It is a matter of semantics to count this term as part of the embedding potential or be considered as correction for the correlation energy in the variational method used to obtain the embedded wavefunction. This term disappears if the form of the embedded wavefunction allows for taking into account the correlation energy fully. In other cases, omitting this term completely (in the energy functional and in the embedding potential) does not invalidate the key feature of FDET: the energy evaluated with this potential will still be the upper bound of the ground-state energy of the total system. Numerical examples show

that neglecting this term in the total potential leads to a minor error in energy²⁹ even if the simplest form (single determinant) of the embedded wavefunction. Until now, we kept the $\Delta F^{MD}[\rho_A]$ term in all equations for the sake of completeness and generality—to include methods which do not take into account the correlation effects within the embedded subsystem completely. In the subsequent part dealing with approximate methods, this term will be neglected in all equations and discussions.

We assume that the considered computational method uses some approximations for the non-electrostatic components of the FDET embedding potential for each state (denoted with I):

$$\left. \frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A=\rho_A^I} \approx \tilde{v}_{tnad}^I(\vec{r}), \quad (6)$$

$$\left. \frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A=\rho_A^I} \approx \tilde{v}_{xcnad}^I(\vec{r}) \quad (7)$$

are used instead of its exact counterparts.

The above approximations make possible to implement excited state generalization of FDET in practice following various practical schemes dealing with the issue of orthogonality of embedded wavefunctions in a different manner. In Secs. III A–III C three such schemes are introduced and discussed.

A. Straightforward application of FDET

In such a case, using the approximations to the relevant functionals does not affect the equations for energy and embedding potential. The relevant formulas are the same as the ones given in (Eq. (3) for energy and Eq. (5) for the embedding potential). The exact functionals $T_s^{nad}[\rho_A, \rho_B]$, $E_{xc}^{nad}[\rho_A, \rho_B]$ are just replaced by $\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$ and the functional $\Delta F^{MD}[\rho_A]$ is neglected.

A practical procedure to obtain fully self-consistent energies and the embedded wavefunction for each state can proceed in an iterative manner. At the first step, the ground-state embedded wavefunction is obtained and the corresponding ground-state embedded density (ρ_A^0) is generated. At this step, all quantities in the Euler-Lagrange equations: embedded ground-state wavefunction, the corresponding ρ_A^0 , the embedding potential, and the upper-bound of the total energy are self-consistent. The excited state embedded wavefunction obtained with this potential is, however, not self-consistent because the embedded density corresponding to the excited state differs from ρ_A^0 . In the next step, the embedded density corresponding to the excited state obtained in the previous step is used to generate a new embedding potential. The procedure of updating the embedding potential to the actual embedded excited state density can be repeated until self-consistency is reached. It cannot be expected that such procedure preserves the orthogonality of the embedded wavefunction for the considered excited state and that for the ground state. If the same self-consistent procedure is applied to another excited state, the orthogonality between the embedded wave-

functions for different excited states is also expected to be lost. Although, even the exact FDET formal framework allows for non-orthogonality of the embedded wavefunctions for different states, the use of approximations might introduce to state-specific errors in the approximated embedding potential. As the result of different errors in embedding potentials for different states, the overlap between embedded wavefunctions for different states might artificially increase. Below, the key advantages and disadvantages of such computational procedure are summarized:

- + The procedure is a straightforward practical implementation of FDET leading to self-consistent energy and excited state wavefunction for each analyzed state without introducing any additional approximations beside the use of approximate density functionals.
- + This strategy is suited, for studies of photochemical processes, where a particular excited-state potential energy surface is the target.
- + If the targets are energy differences for different excited states, for which the corresponding electron distributions differ significantly (charge-transfer excitations, for instance) this strategy might be also the method of choice.
- The procedure has to be applied for each state. The time of calculations is proportional to the number of analyzed states.
- The procedure is based on Perdew-Levy theorem,²¹ which does not guarantee that each excited state can be found.
- The order of states might be interchanged during the iterative calculations leading to convergence problems.
- The quality of the excited state energy might be different for different states because of the fact that the errors in approximations to the potentials $\frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ and $\frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ might be different for different states.

B. Linearization of the functionals $\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$

Compared to the direct strategy discussed in Sec. III A, this approach uses as an additional quantity—some reference electron density (ρ_A^{ref}) which does not differ significantly from the densities corresponding to the considered excited states. Linearization of $\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$ ³⁰ leads to the following approximation for the exact quantities:

$$\begin{aligned} T_s^{nad}[\rho_A, \rho_B] &\approx \tilde{T}_s^{nad}[\rho_A^{ref}, \rho_B] \\ &+ \int (\rho_A - \rho_A^{ref}) \left. \frac{\delta \tilde{T}_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A=\rho_A^{ref}} d\vec{r}, \end{aligned} \quad (8)$$

$$\begin{aligned} E_{xc}^{nad}[\rho_A, \rho_B] &\approx \tilde{E}_{xc}^{nad}[\rho_A^{ref}, \rho_B] \\ &+ \int (\rho_A - \rho_A^{ref}) \left. \frac{\delta \tilde{E}_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A=\rho_A^{ref}} d\vec{r}. \end{aligned} \quad (9)$$

The corresponding embedding potential is ρ_A -independent and reads

$$\begin{aligned} \tilde{v}_{emb}[\rho_A^{ref}, \rho_B; \vec{r}] &= v_A(\vec{r}) + \int \frac{\rho_B(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \\ &+ \frac{\delta \tilde{T}_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \Big|_{\rho_A=\rho_A^{ref}} + \frac{\delta \tilde{E}_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \Big|_{\rho_A=\rho_A^{ref}}. \end{aligned} \quad (10)$$

We underline that, compared to the strategy discussed in Sec. III A (straightforward application of the FDET equations) where these energy components are evaluated just as

$$T_s^{nad}[\rho_A, \rho_B] \approx \tilde{T}_s^{nad}[\rho_A, \rho_B], \quad (11)$$

$$E_{xc}^{nad}[\rho_A, \rho_B] \approx \tilde{E}_{xc}^{nad}[\rho_A, \rho_B], \quad (12)$$

the energy expressions for the linearized functionals are different. Only using Eqs. (8) and (9) in Eq. (3) assures self-consistency between the embedded wavefunctions, energy, and the linearized FDET embedding potential. Besides this modification of the FDET working equation there is also another qualitative difference between the two strategies—linearization of the non-electrostatic components of the functional for the embedding potential assures orthogonality of the embedded wavefunctions. The embedding potential is the same for each state.

The embedding potential depends on the choice of the reference density ρ_A^{ref} . The obvious choice for ρ_A^{ref} is the optimal ground-state density. Another possibility is to use as ρ_A^{ref} the density which is the average of several states. This might be a good strategy for studies of spectra where it is important that the quality of the embedding potential is similar for each analyzed state. Below, the key advantages and disadvantages of such a computational procedure are summarized:

- + The calculations assure orthogonality of embedded wavefunctions for each state.
- + Linearization strategy is most likely suited for such cases where the electrostatic interactions between the environment and the embedded species dominate. The electrostatic component of the FDET embedding potential is ρ_A -independent!
- + Equations (8)–(10) lead to self-consistent energy and the embedded wavefunction.
 - The procedure is based on Perdew-Levy theorem.²¹ It does not guarantee that each excited state is found.
 - Previous knowledge of the nature of the investigated state is needed to choose the reference density. The electron distributions in the reference state and in the investigated state must be similar.

C. Enforcing orthogonality by means of projection operators

This can be achieved by addition to the FDET embedding potential (Eq. (5)) a non-local operator projecting out from the

embedded wavefunction of interest the contributions from all embedded wavefunctions for all lower-lying states,

$$\begin{aligned} \hat{v}_{emb}^{nonlocal} &= \sum_i^{N_A} \hat{v}_{emb}[\rho_A, \rho_B; \vec{r}] \delta(\vec{r} - \vec{r}_i) \\ &- \sum_J^{N_{states}} |\Psi_J^{emb}\rangle \langle \Psi_J^{emb}|, \end{aligned} \quad (13)$$

where $J = 1, \dots, N_{states}$ the embedded wavefunctions for which the orthogonality condition is strictly enforced. Below, the key advantages and disadvantages of such a computational procedure are summarized:

- + Owing to replacing the FDET embedding potential by a non-local operator, excited states that are not stationary states of the ground-state energy functional, for which Perdew-Levy theorem does not apply, might be found.
- + The artificial increase of the overlap between embedded wavefunctions for different states arising from state-specific errors in the potentials $\frac{\delta \tilde{T}_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ and $\frac{\delta \tilde{E}_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ or make the errors less state-dependent.
- + Self-consistency between the embedded wavefunction and energy is assured for each state.
- Such method is an *ad hoc* modification of the FDET equations. The embedding operator is no longer a potential (multiplicative operator). The condition of orthogonality of embedded wavefunctions is not needed in the case of exact functionals in FDET. As a result, the errors in the energy of each state due to approximations for $\frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ and $\frac{\delta E_{xc}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$ might be “over-corrected.”

IV. DISCUSSION AND CONCLUSIONS

The considerations presented in this work are based on Perdew-Levy theorem, which states that other than ground-state extrema of the ground-state density functional for energy yield density and energy of excited states. This theorem is relatively little known (Web of Science Index lists just 69 citations, Ref. 21). In the recent overview of DFT methods,³¹ Perdew and co-workers refer to this theorem as a formal results rather than as a basis for successful numerical applications. In fact, attempts to use Perdew-Levy theorem in practice were not encouraging. The discussion on this issue made in a comprehensive review by Singh and Deb³² ends with the following summary: ... *there is little practical utility in the viewpoint which says that, since the ground-state density determines the Hamiltonian, it also determines the ground state and all excited states of the system.* The skepticism concerning practical usefulness of this theorem originates probably from the following reasons. First of all, the reverse is not true. Not all excited states are extrema of the ground-state density functional for energy. Even with the exact density functional for energy, Perdew-Levy theorem would, therefore, not yield the complete information about the system. Moreover, for densities which are not pure-state v -representable, Perdew-Levy theorem yields only the lower bound of the excitation

energy. Arguably, this can be treated as a warning against the use of Perdew-Levy theorem in order to obtain the excited states. But this argument holds only if one wishes to obtain the *exact* density of a given excited state. The analytically solvable model systems³³ provide examples of series of potentials v , which yield a series of the corresponding densities ρ approaching arbitrarily closely a target density which is not v -representable. The second reason is more related to the computational practice. The domain of excited-state densities is larger than the domain of ground-state densities. It includes densities which are not v -representable. The approximate density functionals are usually constructed/parametrized for ground-state properties of representative molecules or taking into account exact properties of model systems in ground state. The errors of the energy evaluated for densities belonging to a larger domain might be, therefore, uncontrollable. The known difficulties in obtaining the “divine functional” for ground-state energy indicates that perspectives to develop a universal approximation for the density functional, which would yield the ground- and excited- (all of them) energies with a comparable accuracy seem, therefore, bleak. The above skepticism concerns the use of Perdew-Levy theorem in DFT calculations for the whole system, i.e., when both the embedded species and the environment are treated as one quantum system. Concerning the first from the above two reasons, the FDET does not differ from DFT. Concerning the second one, however, the situation is rather different in FDET and in DFT. The availability of the embedded wavefunction makes it possible to evaluate one part of the total energy exactly, i.e., as the expectation value of the environment-free Hamiltonian (the first term in the right-hand-side of Eq. (3)). In typical applications of FDET, this part dominates and the remaining one provides a small correction. Moreover, the electrostatic component of this correction is known exactly. It can be expected, therefore, that FDET based methods using a properly chosen form of the embedded wavefunction might yield energies of different states with comparable accuracy.

Turning back to practical, i.e., using approximations, calculations based on FDET for excited states, the embedded wavefunction is considered as an auxiliary quantity and the non-orthogonality of embedded wavefunctions for different states do not violate any exact condition. The lack of strict orthogonality of embedded wavefunctions might be seen, however, as an undesired feature. We analyzed this issue in more detail. Three computational strategies are proposed to deal with the state-specificity of the embedding potential and the orthogonality issue in practical calculations where the FDET embedding potential is not exact because of replacing the functionals $T_s^{nad}[\rho_A, \rho_B]$ and $E_{xc}^{nad}[\rho_A, \rho_B]$ in ρ_A (and/or their functional derivatives) by their approximate counterparts ($\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$).

(i) *The straightforward strategy which used the same equations for energy and potential as the formal framework of FDET*

This strategy would lead to the exact solution if exact functionals were used. It assures self-consistency of energy and embedded wavefunction but leads to non-orthogonality of embedded wavefunctions for different states. It is probably best suited for studies of the potential energy surface

for a particular state for which the electron distribution at ground- and excited states differ significantly. This strategy involves performing independent self-consistent solutions of the Euler-Lagrange equations for each state. It is also possible that the error in the embedding potentials for the ground state and excited state which is the same will accumulate during the self-consistent procedure leading to artificial increase of the overlap between embedded wavefunctions for different states. In this strategy, Eqs. (3) and (5) retain the same form as in FDET. The use of approximations is reflected just by tildes in $\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$ and neglecting the $\Delta F^{MD}[\rho_A]$ term.

(ii) *Linearization of the approximated functionals $\tilde{T}_s^{nad}[\rho_A, \rho_B]$ and $\tilde{E}_{xc}^{nad}[\rho_A, \rho_B]$ in ρ_A*

This strategy retains the FDET formal framework. The embedded wavefunctions for different states remain orthogonal. The expressions for the FDET energy functional and the embedding potential must be, however, modified to retain self-consistency about the quantities obtained from the Euler-Lagrange equations: energy, embedded wavefunction, and embedding potential. Linearization hinges, however, on an arbitrary choice for the reference density ρ_A^{ref} used to evaluate the common embedding potential for all investigated states. This strategy is probably most adapted for studies of several excitations where the electron densities of each state do not differ significantly.

(iii) *Beyond-FDET framework with non-local embedding potential*

In this strategy, the FDET expression for the total energy is retained but the embedding potential is replaced by a non-local operator. The projection operator added to the FDET embedding potential is used to assure the orthogonality of embedded wavefunctions for different states. Such addition is an *ad hoc* “beyond-FDET” approach to deal with state-specific errors due to approximations in the FDET embedding potential. This approach leads to self-consistent energy and embedded wavefunctions for different states and assures their orthogonality. It might also yield such excited states which are not stationary states of the ground-state energy functional. On the other hand, it might “over-correct” the energies if sufficiently accurate approximate functionals are used in Eq. (5).

Although the present considerations lead to identification of the domain of applicability of each of the three strategies, the adequacy of each of them depends on a particular case (type of excitations of type of interactions between embedded species and its environment) which must be put to scrutiny by numerical simulations.

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