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# Molecular properties via a subsystem density functional theory formulation: A common framework for electronic embedding

Sebastian Höfener,<sup>1,a)</sup> André Severo Pereira Gomes,<sup>2,b)</sup> and Lucas Visscher<sup>1,c)</sup>

<sup>1</sup>*Amsterdam Center for Multiscale Modeling (ACMM), VU University Amsterdam, Theoretical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

<sup>2</sup>*Laboratoire PhLAM, CNRS UMR 8523, Université de Lille 1, Bât P5, F-59655 Villeneuve d'Ascq Cedex, France*

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In this article, we present a consistent derivation of a density functional theory (DFT) based embedding method which encompasses wave-function theory-in-DFT (WFT-in-DFT) and the DFT-based subsystem formulation of response theory (DFT-in-DFT) by Neugebauer [J. Neugebauer, J. Chem. Phys. **131**, 084104 (2009)] as special cases. This formulation, which is based on the time-averaged quasi-energy formalism, makes use of the variation Lagrangian techniques to allow the use of non-variational (in particular: coupled cluster) wave-function-based methods. We show how, in the time-independent limit, we naturally obtain expressions for the ground-state DFT-in-DFT and WFT-in-DFT embedding via a local potential. We furthermore provide working equations for the special case in which coupled cluster theory is used to obtain the density and excitation energies of the active subsystem. A sample application is given to demonstrate the method. © 2012 American Institute of Physics. [doi:10.1063/1.3675845]

## I. INTRODUCTION

Non-empirical electronic structure methods, and their implementations in sophisticated computer programs, have become viable tools to study the molecular basis of natural phenomena. By carrying out calculations on quantum chemical models of varying size and complexity, one may, e.g., investigate in detail how interactions between the constituents of a biochemical system determine its function. An attractive feature of this modelling is that one is not restricted to reproduce experimental observations but may also carry out numerical experiments to make predictions about the effect of modifications in a system. These experiments may then be used to aid in tuning the behaviour of artificial or biochemically modified natural systems.

In order to be useful, a given method should be able to provide reliable numerical data with a reasonable computational effort. Methods that have proven to work well in applications on small, isolated, molecules may be difficult to scale up for models of condensed phase systems. This is due to the steep computational scaling with the number of atoms in the system that most methods exhibit. Methods are typically based on density functional theory (DFT) or on post-Hartree-Fock (HF) wave-function (WFT) approaches that have cubic or worse scaling of computational costs with system size. For conventional algorithms, this leads to a limitation in system size of  $\simeq$ tens of atoms (or  $\simeq$ hundreds of atoms in the case of HF or DFT) that is only slowly increased by advances in computer technology.

One way to push the limit of applicability of these methods forward is to utilize techniques in which long-range interactions are treated in a simplified and, therefore, more efficient manner. This is facilitated by the density fitting or resolution-of-identity approach and allows for accurate calculations of medium-sized molecules by coupled cluster (CC) techniques.<sup>1-3</sup> While such linear scaling implementations are essential for benchmark and highly accurate studies, they are still too demanding for standard applications. Another complication of such global descriptions is the interpretation of results in terms of qualitative models. This typically requires an additional analysis step in which the wave-function and molecular properties are decomposed into local contributions.

An alternative is to employ a subsystem approach, in which the total system is *a priori* divided into small, chemically meaningful, units that are considered separately. One may thereby easily approximate less important parts of the system by a computationally efficient approximate method such as molecular mechanics (MM). The most popular realization of such a scheme is the two-level QM/MM method,<sup>4-7</sup> but more general methods in which an arbitrary number of computational methods are combined are also in use.<sup>8,9</sup> The flexibility to combine the most suitable methods (including, e.g., specialized implementations) for the different tasks has led to a multitude of implementations of multilevel approaches. One may thereby distinguish between the so-called embedding approaches, in which the accurate description is intended only for one part of the system, and the true subsystem approaches that build a global property of the system from local properties. In the embedding schemes, one may furthermore distinguish between methods that treat the environment as an unstructured continuum and methods that allow for atomistic detail and include specific interactions with environment. Techniques to calculate molecular

<sup>a)</sup>Electronic mail: s.hoefener@vu.nl.

<sup>b)</sup>Electronic mail: andre.gomes@univ-lille1.fr.

<sup>c)</sup>Author to whom correspondence should be addressed. Electronic mail: l.visscher@vu.nl.

properties by DFT, HF, and CC methods have been successfully combined with both specific (polarizable force-field) and non-specific (dielectric continua) models of the environment by Christiansen, Mikkelsen, Kongsted, and co-workers.<sup>10–14</sup>

While these approaches are very attractive in terms of computational efficiency, they do rely on the chosen parameterization of the environment—which is a drawback, if there is only a limited amount of experimental data available to parameterize the force fields or the continuum description, or when simple parametrizations are difficult due to the nature of the interactions. An alternative is then to resort to *ab initio* methods in which also the environment is modelled as consisting of a collection of interacting units that are each calculated using an appropriate quantum-mechanical method. Such discrete quantum-mechanical (QM/QM) methods are, however, considerably more expensive than QM/MM approaches and require efficient approximations in the less interesting “environmental” region of the system. A promising method is the so-called frozen-density embedding (FDE) scheme by Wesolowski and Warshel,<sup>15</sup> following an approach originally proposed by Senatore and Subbaswamy<sup>16</sup> and later Cortona<sup>17</sup> for solid-state calculations. In FDE all subsystems and their interactions are described by DFT, with computational savings resulting from the fact that typically only one system of interest is fully optimized. The other subsystems are described using a suitably chosen *frozen* electron density. The method is formally exact if a number of boundary conditions on the initial subsystem densities are fulfilled.<sup>18,19</sup> In practice, the quality of results depends on the employed non-additive parts of the kinetic and exchange-correlation energy functionals and derivatives thereof<sup>20–22</sup> to describe the interaction between the chosen subsystems. With the currently available functionals, one may describe primarily electrostatic and hydrogen bonded interactions rather well,<sup>23–25</sup> whereas coordination or covalent bond still present a major problem.<sup>26,27</sup> While the FDE ansatz has been mostly applied in the embedding regime (one small active system surrounded by a large frozen environment), one may also formulate this model as a special case of a more general subsystem DFT approach.<sup>28,29</sup> One then writes the total density as a sum of subsystem densities

$$\rho_{\text{tot}} = \sum_i \rho_i, \quad (1)$$

that are each optimized separately with the density of the other fragments fixed.

The formulation of response theory within the FDE framework was first proposed by Casida and Wesolowski,<sup>30</sup> but only reached its full potential when Neugebauer<sup>31,32</sup> extended the formalism to a general subsystem DFT response approach and provided an efficient implementation in the ADF program package.<sup>33</sup> His formulation does not only recover important environment contributions<sup>34</sup> on polarizabilities and excitation energies in dimers, but also allows for the coupling of local excitations in a complete model.<sup>35</sup> A growing number of applications shows the promise of subsystem DFT in both the (frozen-density) embedding mode<sup>36–40</sup> as well as in the (fully self-consistent) subsystem mode<sup>41</sup> to describe molecular properties.

Notwithstanding the success of the applications mentioned, DFT-in-DFT embedding approaches will always be constrained by the limitations of the DFT itself. One may encounter cases in which present-day functionals fail to provide a quantitatively correct description of one or more of the subsystems. In such cases, we would like to employ WFT approaches, and progress through one of its well-defined hierarchy of methods<sup>42</sup> to improve and check the reliability of the calculated results.

A very useful feature of the FDE is the fact that the embedding potential that is used to obtain the density of the embedded system is local. This absence of nonlocal projection operators facilitates the integration of DFT- and WFT-based methods in one overall model. In order to include WFT in FDE, we need to consider a subsystem  $j$  for which the energy is obtained by optimizing the parameters of a many-electron wave function  $\Psi_j$ . This system should then interact with the other subsystems only via its density

$$\Psi_j^* \Psi_j \rightarrow \rho_j, \quad (2)$$

as in the DFT-in-DFT case. Such a WFT-in-DFT embedding scheme has been pursued by Carter and co-workers,<sup>43–47</sup> who combined DFT and variational methods such as Hartree-Fock, complete active space self-consistent field (CASSCF), or (multireference) CI. Their approach has so far mainly been used to describe localized excitations in solids or surfaces, e.g., for the calculation of excitation energies of CO adsorbed on a platinum surface.<sup>48,49</sup> Some of us<sup>50</sup> implemented furthermore an approximate scheme to employ non-variational WFT methods (based on coupled cluster theory) for the calculation of the low-lying spectra of solvated acetone and the  $f$ - $f$  spectra of the Neptunyl ion embedded in a  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  crystal.

None of these approaches has so far gone beyond the use of an embedding potential constructed for the ground state in the determination of the excited state energies or response properties such as polarizabilities. For such applications, one needs to consider the change in interaction energy caused by changes in the active system as well as by responses of the environment. A straightforward way of taking those changes into account is to choose a state-specific determination of the embedding potential, as recently proposed by Khait and co-workers.<sup>51</sup> This has a drawback, however, that multiple calculations are required if one is interested in more than one excited states. Problematic is also the inclusion of non-variational methods such as (multireference) coupled cluster in which the wave function and the corresponding density are not explicitly calculated. For such methods, it is convenient to formulate the environment contribution to molecular properties and electronic excitations in terms of response theory, as this provides a natural connection to the techniques used in non-variational WFT methods.

Our goal in this paper is to work out a novel and rigorous FDE response theory framework with which it is possible to calculate molecular properties within a general subsystem formulation—capable of handling both DFT-in-DFT and WFT-in-DFT embedding. We will make use of the time-averaged quasi-energy formalism<sup>52,53</sup> which provides a natural way to treat variational and non-variational electronic structure methods in the same fashion. After providing the

necessary background on the FDE energy expressions, we will start by discussing response theory in a subsystem formulation and show how this reduces to the standard formulation in the case of non-interacting subsystems. Next, we will recast the DFT-in-DFT formalism of Neugebauer<sup>31,32</sup> into the time-averaged quasi-energy formalism and define key quantities for the WFT-in-DFT approach. This case is first considered for Hartree-Fock, and then for the case of non-variational coupled cluster methods. We will briefly discuss possible approximations, related to the extent one wishes to consider the coupling of the different subsystems in the time-dependent treatment. With the working equations available, we finish by addressing the similarities and differences between the formalism discussed here and the QM/MM response theory schemes proposed by Christiansen, Mikkelsen, Kongsted, and co-workers.<sup>10-14</sup>

## II. SUBSYSTEM DFT

For the optimization of a particular density  $\rho_I$ , it is convenient to sum the other densities to a frozen environment density  $\rho_{II}$  and rewrite the density partitioning of Eq. (1) as

$$\rho_{\text{tot}} = \rho_I + \sum_{i \neq I} \rho_i = \rho_I + \rho_{II}. \quad (3)$$

The total energy of the system,  $E_{\text{tot}}[\rho_{\text{tot}}]$ , can then be written as

$$E_{\text{tot}}[\rho_I + \rho_{II}] = E_I[\rho_I] + E_{II}[\rho_{II}] + E_{\text{int}}[\rho_I, \rho_{II}], \quad (4)$$

with the internal energy of each of the subsystems  $i$  given as

$$E_i[\rho_i] = \int \rho_i(\mathbf{r}) v_{\text{nuc}}^i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho_i(\mathbf{r}) \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho_i] + T_s[\rho_i] + E_{\text{nuc}}^i, \quad (5)$$

with  $v_{\text{nuc}}^i$  the nuclear potential due to the set of atoms associated with subsystem  $i$  and  $E_{\text{nuc}}^i$  the nuclear repulsion energy. The interaction energy is similarly given by the expression

$$E_{\text{int}}[\rho_I, \rho_{II}] = \int \rho_I(\mathbf{r}) v_{\text{nuc}}^{II}(\mathbf{r}) d\mathbf{r} + \int \rho_{II}(\mathbf{r}) v_{\text{nuc}}^I(\mathbf{r}) d\mathbf{r} + E_{\text{nuc}}^{I,II} + \iint \frac{\rho_I(\mathbf{r}) \rho_{II}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}] + T_s^{\text{nadd}}[\rho_I, \rho_{II}], \quad (6)$$

where non-additive contributions are defined as (see, e.g., Ref. 29)

$$X^{\text{nadd}}[\rho_I, \rho_{II}] = X[\rho_I + \rho_{II}] - X[\rho_I] - X[\rho_{II}]. \quad (7)$$

All interaction energies are defined solely in terms of the subsystem densities that are either determined by a Kohn-Sham (KS) approach or by optimization of the wave function for an interacting system (WFT approach).<sup>50,54</sup> We note that orbitals of different subsystems always belong to independent subsets that are therefore, in general, non-orthogonal.

Equation (4) is the starting point for the response formulation in which we will first consider different parameterizations of the subsystem densities. We note that the internal energy of the environment does not depend on the active density

$\rho_I$  so that minimizing the *total* energy of the system with respect to  $\rho_I$  yields the Euler-Lagrange equation

$$\frac{\delta E_I[\rho_I]}{\delta \rho_I} + \frac{\delta E_{\text{int}}[\rho_I, \rho_{II}]}{\delta \rho_I} = \mu, \quad (8)$$

with the Lagrange multiplier  $\mu$  introduced to keep the number of electrons in system I constant. While this constraint can be avoided in the context of DFT-in-DFT embedding as shown recently by Elliot *et al.*,<sup>55,56</sup> in WFT-in-DFT embedding it can only be relaxed in the DFT subsystems,<sup>57</sup> because wave-function-based methods can only provide accurate densities for systems with an integer number of electrons. In our general formulation, the fixed electron number approximation is applied to all subsystems, offering also the possibility of treating all subsystems with WFT. The derivative of the interaction energy functional that carries the inter-system dependence is the embedding potential, that can be decomposed into the Coulomb interactions with the environment (nuclei and frozen electron density) plus derivatives of the non-additive parts of the exchange-correlation and kinetic energy

$$v_{\text{emb}}^I(\mathbf{r}) = \frac{\delta E_{\text{int}}[\rho]}{\delta \rho_I(\mathbf{r})} = v_{\text{nuc}}^{II}(\mathbf{r}) + \int \frac{\rho_{II}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}^{\text{nadd}}[\rho_I, \rho_{II}] + \left. \frac{\delta T_s^{\text{nadd}}[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho_I}. \quad (9)$$

Regardless of the chosen density parameterization, and methods for evaluating the subsystem energy,  $E_{\text{xc}}^{\text{nadd}}$  and  $T_s^{\text{nadd}}$  are always calculated using a density functional. In this article, we will not discuss details of these density functionals (and their derivatives); benchmarks of various kinetic energy functionals for use in FDE are well available.<sup>23-25,58</sup> We note that improved functionals can nowadays be easily implemented via automatic differentiation techniques.<sup>59</sup>

The conventional way to obtain the density of a subsystem  $i$  is to construct a non-interacting reference system and employ the Kohn-Sham equation for a constrained electron density (KSCED).<sup>15</sup> In this equation,

$$F^{\text{KS}} \phi_{p_i}(\mathbf{r}) = \left[ -\frac{1}{2} \Delta + v_{\text{nuc}}^i(\mathbf{r}) + \int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho_i](\mathbf{r}) + v_{\text{emb}}^i(\mathbf{r}) \right] \phi_{p_i}(\mathbf{r}) = \varepsilon_{p_i}^{\text{KS}} \phi_{p_i}(\mathbf{r}), \quad (10)$$

the local embedding potential of Eq. (9) is seen to represent the environment. The subsystem energy is then calculated according to Eq. (5) if desired.

The alternative way to obtain the density is to employ WFT and consider a constrained minimization of the total energy of the system as a function of the free parameters in the wave function used to model the electrons contained in system  $i$ . In this minimization, the contribution from the derivative of the interaction energy is identical to the DFT expression given above in Eq. (9), but the terms coming from the subsystem energy itself depend on the chosen wave-function model and parameterization thereof. If we take the simplest wave-function model, the single-determinant (SD) Hartree-Fock wave

function, we find the Hartree-Fock analog of the KSCED equation,

$$F^{\text{HF}} \phi_{p_i}(\mathbf{r}) = \left[ -\frac{1}{2} \Delta + v_{\text{nuc}}^i(\mathbf{r}) + \int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{emb}}^i(\mathbf{r}) \right] \times \phi_{p_i}(\mathbf{r}) - \int \frac{\gamma_i(\mathbf{r}', \mathbf{r}) \phi_{p_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \varepsilon_{p_i}^{\text{HF}} \phi_{p_i}(\mathbf{r}). \quad (11)$$

The resulting orbitals may be used to evaluate the subsystem Hartree-Fock energy. Note that this energy should not contain the interaction energy contribution, even though for both Hartree-Fock and Kohn-Sham, the definition of canonical orbitals includes the embedding potential,

$$F_{p_i q_i} \rightarrow F_{p_i q_i} + \langle p_i | v_{\text{emb}}^i | q_i \rangle = \delta_{p_i q_i} \varepsilon_{p_i}. \quad (12)$$

The density-only expression of Eq. (6) is applicable for all methods and the total energy is given according to Eq. (4), independent of the precise method used to determine  $E_i$  and  $\rho_i$ . Since one cannot straightforwardly calculate the interaction energy contribution as an expectation value of the embedding potential (due to the partially nonlinear dependence of the energy on the density<sup>53,60,61</sup>), the subsystem DFT scheme differs from most other embedding approaches (see Sec. VI). Another point that should be mentioned at this stage is that we always assume that the wave-function method is capable of providing the exact subsystem density and energy. This is only rigorously true for a full configuration interaction method in a complete basis, but compensating for missing electron correlation contributions in WFT by adding a correlation functional<sup>62,63</sup> is a notoriously difficult problem that we will not attempt to solve in this work.

### III. QUASI-ENERGY RESPONSE THEORY

In our derivation of subsystem response theory, we follow the work on frequency-dependent response functions of Christiansen *et al.*<sup>52</sup> which is restricted in its time-averaged formulation to time-periodic perturbations. For the sake of completeness and to introduce the notation, we repeat the most important definitions and equations. For a general discussion concerning the applicability of the quasi-energy formalism and DFT, see, e.g., Ref. 53. Let  $\hat{H}^t$  be a general, time-dependent Hamiltonian,

$$\hat{H}^t = \hat{H} + \hat{V}^t, \quad (13)$$

where  $\hat{V}^t$  is the time-dependent perturbation operator which is given as

$$\hat{V}^t = \sum_{k=-N}^N \exp(-i\omega_k t) \sum_x \epsilon_x(\omega_k) \hat{X} \quad (14)$$

with  $\epsilon_x(\omega_k)$  parameters that denote the strength of the perturbing fields. The linear response function is defined via the time evolution of the expectation value of an operator  $\hat{X}$ ,

$$\langle X \rangle(t) = \langle X \rangle_0 + \sum_{k_1} \exp(-i\omega_{k_1} t) \sum_y \langle \langle X; Y \rangle \rangle_{\omega_{k_1}} \epsilon_y(\omega_{k_1}) + \dots \quad (15)$$

The quasi-energy  $Q(t)$  and its time-average  $\{Q(t)\}_T$  are defined as

$$Q(t) = \langle \tilde{O} | \left( \hat{H}^t - i \frac{\partial}{\partial t} \right) | \tilde{O} \rangle, \quad (16)$$

$$\{Q(t)\}_T = \frac{1}{T} \int_{-T/2}^{T/2} Q(t) dt, \quad (17)$$

respectively, where  $T$  is the period of the perturbation in Eq. (14) and the tilde denotes the phase-isolated form of the wave function. For variational methods, such as Hartree-Fock or DFT, the calculation of the linear response function proceeds directly from the quasi-energy itself. In this treatment, the linear response function is obtained as the second derivative of the time-averaged quasi-energy. For non-variational wave functions, first a Lagrangian,

$$L(\lambda, \dot{\lambda}, \bar{\lambda}) = Q(\lambda, \dot{\lambda}) + \bar{\lambda} e(\lambda, \dot{\lambda}), \quad (18)$$

with appropriate constraints  $e(\lambda, \dot{\lambda})$  and Lagrange multipliers  $\bar{\lambda}$  needs to be introduced before proceeding to derive the response functions.

Lagrangian-based formulations can be extended to incorporate environment effects,<sup>64</sup> and will be central to our development. For the subsystem treatment, we define a total quasi-energy Lagrangian consisting of the quasi-energy expressions of the subsystems as well as their interaction,

$$L_{\text{tot}}(t) = \sum_i L_i(t) + Q_{\text{int}}(t). \quad (19)$$

While Eq. (19) allows an arbitrary number of subsystems, it is more convenient to again restrict the derivation to the case of two subsystems. Thus, in the following, subsystem I represents the “active” subsystem of interest, whereas subsystem II consists of the sum of all other subsystems and represents the “environment.” The total quasi-energy expression in Eq. (19) then reduces to

$$L_{\text{tot}}(\lambda, \dot{\lambda}, \bar{\lambda}; \lambda_{\text{II}}, \dot{\lambda}_{\text{II}}, \bar{\lambda}_{\text{II}}) = [Q(\lambda, \dot{\lambda}) + \bar{\lambda} e(\lambda, \dot{\lambda}) + Q_{\text{int}}(\lambda, \dot{\lambda}, \bar{\lambda}; \lambda_{\text{II}}, \dot{\lambda}_{\text{II}}, \bar{\lambda}_{\text{II}}) + [Q_{\text{II}}(\lambda_{\text{II}}, \dot{\lambda}_{\text{II}}) + \bar{\lambda}_{\text{II}} e_{\text{II}}(\lambda_{\text{II}}, \dot{\lambda}_{\text{II}})], \quad (20)$$

where we make the dependence of  $L_{\text{tot}}(t)$  on the wave-function parameters and constraints explicit. Note that all inter-system dependencies are contained in the interaction energy. In the following, we will assume that the environment is optimized with DFT, which is variational, so that we can omit the multipliers  $\bar{\lambda}_{\text{II}}$ .

The time-dependent Lagrangian can then be expanded in orders of the perturbation,

$$L(t) = L^{(0)} + L^{(1)}(t) + L^{(2)}(t) + \dots, \quad (21)$$

TABLE I. Vectors and matrices for general response functions (see Ref. 52).

Quantity	Derivative expr.	Quantity	Derivative expr.	Quantity	Derivative expr.
$\eta^Y$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X) \partial \epsilon_Y(\omega_Y)}$			${}^{\text{II}}\eta^Y$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda_{\text{II}}^{(1)}(\omega_X) \partial \epsilon_Y(\omega_Y)}$
$\xi^Y$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_X) \partial \epsilon_Y(\omega_Y)}$				
$\mathbf{J}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_X) \partial \bar{\lambda}^{(1)}(\omega_Y)}$				
$\mathbf{A}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X) \partial \bar{\lambda}^{(1)}(\omega_Y)}$	${}^{\text{I,II}}\mathbf{A}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \bar{\lambda}^{(1)}(\omega_X) \partial \lambda_{\text{II}}^{(1)}(\omega_Y)}$		
$\mathbf{F}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X) \partial \lambda^{(1)}(\omega_Y)}$	${}^{\text{I,II}}\mathbf{F}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda^{(1)}(\omega_X) \partial \lambda_{\text{II}}^{(1)}(\omega_Y)}$	${}^{\text{II,II}}\mathbf{F}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \lambda_{\text{II}}^{(1)}(\omega_X) \partial \lambda_{\text{II}}^{(1)}(\omega_Y)}$
$\eta$	$\frac{\partial \{Q^{(0)}\}_T}{\partial \lambda^{(0)}}$			${}^{\text{II}}\eta$	$\frac{\partial \{Q_{\text{II}}^{(0)}\}_T}{\partial \lambda^{(0)}}$

and Fourier transformed to the frequency domain. We may similarly expand the parameters in terms of the perturbation strength, obtaining, e.g., the first-order expression,

$$\lambda^{(1)}(\omega_{k_1}) = \sum_x \epsilon_x(\omega_{k_1}) \lambda^X(\omega_{k_1}). \quad (22)$$

Response functions are obtained as derivatives of the time-averaged quasi-energy Lagrangian of  $n$ th order  $\{L^{(n)}\}_T$  with respect to the field-strength variables, e.g., for second order,

$$\langle \langle X; Y \rangle \rangle_{\omega_{k_1}} = \frac{d^2 \{L^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})}, \quad \text{where } \omega_{k_1} = -\omega_0. \quad (23)$$

Using the abbreviations given in Table I and the fact that the contributions from second-order parameters, such as  $\lambda^{(2)}(t)$ ,  $\bar{\lambda}^{(2)}(t)$ , and  $\lambda_{\text{II}}^{(2)}(t)$ , are zero due to the  $2n + 1$  rule, the second derivative becomes

$$\begin{aligned} \frac{d^2 \{L_{\text{tot}}^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} &= \frac{d^2 \{L_1^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} + \frac{d^2 \{Q_{\text{II}}^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} \\ &+ \frac{d^2 \{Q_{\text{int}}^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})}, \end{aligned} \quad (24)$$

where the first two terms are obtained similar to Eq. (3.28) of Ref. 52,

$$\begin{aligned} \frac{d^2 \{L_1^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} &= P(X(\omega_0), Y(\omega_{k_1})) \\ &\times \left\{ \left[ \eta^X + \frac{1}{2} \mathbf{F} \lambda^X(\omega_0) \right] \lambda^Y(\omega_{k_1}) \right. \\ &+ \bar{\lambda}^X(\omega_0) \left[ \frac{1}{2} \mathbf{J} \bar{\lambda}^Y(\omega_{k_1}) + \xi^Y \right. \\ &\left. \left. + \mathbf{A} \lambda^Y(\omega_{k_1}) \right] \right\}, \end{aligned} \quad (25)$$

$$\begin{aligned} \frac{d^2 \{Q_{\text{II}}^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} &= P(X(\omega_0), Y(\omega_{k_1})) \\ &\times \left\{ \left[ {}^{\text{II}}\eta^X + \frac{1}{2} {}^{\text{II,II}}\mathbf{F} \lambda_{\text{II}}^X(\omega_0) \right] \lambda_{\text{II}}^Y(\omega_{k_1}) \right\}, \end{aligned} \quad (26)$$

while the interaction term reads

$$\begin{aligned} \frac{d^2 \{Q_{\text{int}}^{(2)}\}_T}{d\epsilon_x(\omega_0) d\epsilon_y(\omega_{k_1})} &= P(X(\omega_0), Y(\omega_{k_1})) \\ &\times \left\{ \bar{\lambda}^X(\omega_0) \mathbf{A}^{\text{int}} \lambda^Y(\omega_{k_1}) \right. \\ &+ \frac{1}{2} \left[ \mathbf{F}^{\text{int}} \lambda^X(\omega_0) \lambda^Y(\omega_{k_1}) \right. \\ &+ \mathbf{J}^{\text{int}} \bar{\lambda}^X(\omega_0) \bar{\lambda}^Y(\omega_{k_1}) \\ &+ {}^{\text{I,II}}\mathbf{F}^{\text{int}} \lambda^X(\omega_0) \lambda_{\text{II}}^Y(\omega_{k_1}) \\ &\left. \left. + \bar{\lambda}^X(\omega_0) {}^{\text{I,II}}\mathbf{A}^{\text{int}} \lambda_{\text{II}}^Y(\omega_{k_1}) \right] \right\}. \end{aligned} \quad (27)$$

$P(X(\omega_0), Y(\omega_{k_1}))$  ensures symmetry with respect to the interchange of  $X$  and  $Y$  and associated frequencies  $\omega_0$  and  $\omega_{k_1}$ . Throughout the paper, we use supermatrix notation where vectors and matrices are multiplied in order—a notation useful especially for higher order response properties.

For the present purpose, we need only the first-order perturbed quantities. These are obtained by requiring stationarity of the Lagrangian with respect to variations in first-order multipliers  $\bar{\lambda}^X$ , first-order amplitudes  $\lambda^X$ , and first-order parameters of the environment  $\lambda_{\text{II}}^X$ , yielding a set of coupled linear response equations for frequency  $\omega_y$ ,

$$\begin{aligned} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} &= \begin{pmatrix} \xi^Y \\ \eta^Y \\ {}^{\text{II}}\eta^Y \end{pmatrix} + \begin{pmatrix} \mathbf{A}(\omega_y) \mathbf{J} & | & {}^{\text{I,II}}\mathbf{A} \\ \mathbf{F} & | & \mathbf{A}(-\omega_y) \quad {}^{\text{I,II}}\mathbf{F} \\ {}^{\text{I,II}}\mathbf{F} & | & {}^{\text{I,II}}\mathbf{A} \quad {}^{\text{II,II}}\mathbf{F}(\omega_y) \end{pmatrix} \\ &\times \begin{pmatrix} \lambda^Y(\omega_y) \\ \bar{\lambda}^Y(\omega_y) \\ \lambda_{\text{II}}^Y(\omega_y) \end{pmatrix}. \end{aligned} \quad (28)$$

It is convenient to separate contributions from the subsystems Lagrangian and their interaction explicitly by decomposing

the matrix above as

$$\begin{pmatrix} \mathbf{A}(\omega_y) & 0 & 0 \\ \mathbf{F} & \mathbf{A}(-\omega_y) & 0 \\ 0 & 0 & \text{II,II} \mathbf{F}(\omega_y) \end{pmatrix} + \begin{pmatrix} \mathbf{A}_{\text{int}} & \mathbf{J}_{\text{int}} & \text{I,II} \mathbf{A}_{\text{int}} \\ \mathbf{F}_{\text{int}} & \mathbf{A}_{\text{int}} & \text{I,II} \mathbf{F}_{\text{int}} \\ \text{I,II} \mathbf{F}_{\text{int}} & \text{I,II} \mathbf{A}_{\text{int}} & \text{II,II} \mathbf{F}_{\text{int}} \end{pmatrix}. \quad (29)$$

The  $\mathbf{J}$ -term drops out when the  $2n + 2$  rule based on decoupled response equations for  $\lambda^X$  and  $\bar{\lambda}^X$  can be applied<sup>10,52</sup> but contains a non-zero contribution due to the interaction. The response equations (Eq. (28)) allow to write the expression for the total response function as

$$\begin{aligned} \langle\langle X; Y \rangle\rangle_{\omega_y} &= \frac{1}{2} C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \times \left\{ \frac{1}{2} \mathbf{J} \bar{\lambda}^X(\omega_x) \bar{\lambda}^Y(\omega_y) \right. \\ &+ \left[ \left( \frac{\boldsymbol{\eta}^X}{\text{II} \boldsymbol{\eta}^X} \right)^T + \frac{1}{2} \left( \frac{\boldsymbol{\lambda}^X(\omega_x)}{\boldsymbol{\lambda}_{\text{II}}^X(\omega_x)} \right)^T \right. \\ &\left. \left. \times \left( \frac{\mathbf{F}(\omega_y)}{\text{I,II} \mathbf{F}(\omega_y)} \middle| \text{I,II} \mathbf{F}(\omega_y) \right) \right] \left( \frac{\boldsymbol{\lambda}^Y(\omega_y)}{\boldsymbol{\lambda}_{\text{II}}^Y(\omega_y)} \right) \right\}. \quad (30) \end{aligned}$$

The operator  $C^{\pm\omega}$  enforces symmetrization with respect to simultaneous complex conjugation and inversion of the sign of the frequencies.<sup>52</sup> Alternatively, we can rewrite Eq. (30) in terms of the individual (“uncoupled”) subsystems as well as the coupling contribution,

$$\langle\langle X; Y \rangle\rangle_{\omega_y} = \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{unc,I}} + \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{unc,II}} + \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{I,II}}. \quad (31)$$

The individual subsystem contributions can be extracted from Eq. (30) and are given as<sup>52,53,65</sup>

$$\begin{aligned} \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{unc,I}} &= \frac{1}{2} C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \\ &\times \left\{ \frac{1}{2} \mathbf{J} \bar{\lambda}^X(\omega_x) \bar{\lambda}^Y(\omega_y) \right. \\ &\left. + \left[ \boldsymbol{\eta}^X + \frac{1}{2} \mathbf{F} \boldsymbol{\lambda}^X(\omega_x) \right] \boldsymbol{\lambda}^Y(\omega_y) \right\}, \quad (32) \end{aligned}$$

$$\begin{aligned} \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{unc,II}} &= \frac{1}{2} C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \\ &\times \left[ \text{II} \boldsymbol{\eta}^X + \frac{1}{2} \text{II,II} \mathbf{F} \boldsymbol{\lambda}_{\text{II}}^X(\omega_x) \right] \boldsymbol{\lambda}_{\text{II}}^Y(\omega_y). \quad (33) \end{aligned}$$

If only these are included, the result will be denoted “uncoupled”—implying that the response of the interaction energy is included in the “intra-subsystem” blocks in Eq. (28) but that the “inter-subsystem” blocks are neglected. The full, i.e., coupled, result includes also the inter-subsystem response

function

$$\langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{I,II}} = C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \{ \text{I,II} \mathbf{F}_{\text{int}} \boldsymbol{\lambda}^X(\omega_x) \boldsymbol{\lambda}_{\text{II}}^Y(\omega_y) \}. \quad (34)$$

In the limit of non-interacting subsystems, all interaction contributions vanish and the total response function reduces to the sum of the isolated subsystems.

For variational wave functions, we can remove contributions of Lagrangian multipliers and the environment in Eq. (28), and the linear response function then takes the form<sup>52</sup>

$$\langle\langle X; Y \rangle\rangle_{\omega_y} = -\boldsymbol{\eta}^X (\mathbf{F}(\omega_y))^{-1} \boldsymbol{\eta}^Y. \quad (35)$$

The excitation energies are finally calculated from the poles of Eq. (35), whereas properties are obtained from the evaluation of the linear response function at a given frequency  $\omega_y$ . Due to the computational cost, however, instead of calculating the inverse in Eq. (35), typically the linear set of equations,

$$\mathbf{F}(\omega_y) \boldsymbol{\lambda}^Y(\omega_y) = -\boldsymbol{\eta}^Y, \quad (36)$$

is solved,<sup>53,66</sup> from which the linear response function and thus properties such as, frequency-dependent dipole-dipole polarizabilities, are calculated as

$$\langle\langle X; Y \rangle\rangle_{\omega_y} = \boldsymbol{\eta}^X \cdot \boldsymbol{\lambda}^Y(\omega_y). \quad (37)$$

With separate coupling contributions, it is possible to devise computational strategies adapted to the properties of interest.<sup>35</sup> For instance, in cases where the coupling is important, such as excitation energies or polarizabilities, these can be approximated, and in the cases where these are less important, such as local excitations or NMR chemical shifts, these can be dropped. Furthermore, it offers the possibility to operate mostly with the quantities for the isolated subsystems, thus avoiding the formation and handling of matrices and vectors with the dimension of the supermolecular basis.<sup>31,32</sup> In Secs. IV and V, we will derive explicit working expressions for the components of the quasi-energy Lagrangian, as well as the different matrices and vectors needed.

#### IV. REVISITING DFT-IN-DFT RESPONSE THEORY

In this section, we discuss the DFT-in-DFT FDE response theory using the quasi-energy formalism. In order to reformulate the subsystem Kohn-Sham theory in the formalism of second quantization, we follow closely the notation used by Saue and Helgaker.<sup>67</sup> We start by introducing the parameterization of a closed-shell Kohn-Sham determinant of one subsystem in terms of an unitary exponential orbital-rotation operator,

$$|0_i\rangle = \exp(\hat{\kappa}_i) |\tilde{0}_i\rangle \quad \text{with } \hat{\kappa}_i = \sum_{p_i > q_i} (\kappa_{p_i q_i} E_{p_i q_i} - \kappa_{p_i q_i}^* E_{q_i p_i}). \quad (38)$$

In the framework of FDE, the subsystem orbitals are to be considered as two independent sets of auxiliary quantities that serve to provide the exact density and its responses. This implies that admixture of orbitals from a subsystem  $i$  into the orbitals of a different subsystem  $j$  is to be excluded, and the



orbital rotations fulfil the condition

$$\kappa_{p_i q_j} = \delta_{ij} \kappa_{p_i q_i}. \quad (39)$$

The density of a given subsystem can be written as

$$\begin{aligned} \rho_i(\mathbf{r}, \boldsymbol{\kappa}_i) &= \langle 0_i | \exp(-\hat{\kappa}_i) \hat{\rho}_i(\mathbf{r}) \exp(\hat{\kappa}_i) | 0_i \rangle \\ &= \sum_{p_i q_i} \rho_{p_i q_i}(\mathbf{r}) D_{p_i q_i}(\boldsymbol{\kappa}_i), \end{aligned} \quad (40)$$

where  $\hat{\rho}_i(\mathbf{r})$  is the density operator, given in second quantization as

$$\hat{\rho}_i(\mathbf{r}) = \sum_{p_i q_i} \rho_{p_i q_i}(\mathbf{r}) E_{p_i q_i}, \quad (41)$$

$$\rho_{p_i q_i}(\mathbf{r}) = \phi_{p_i}^*(\mathbf{r}) \phi_{q_i}(\mathbf{r}). \quad (42)$$

In order to calculate the density response, the density matrix  $\mathbf{D}(\boldsymbol{\kappa}_i)$  is expanded in orders of orbital rotation parameters using the Baker-Campbell-Hausdorff (BCH) formula,

$$\begin{aligned} D_{p_i q_i}(\boldsymbol{\kappa}_i) &= \langle 0_i | E_{p_i q_i} | 0_i \rangle + \langle 0_i | [\hat{\kappa}_i, E_{p_i q_i}] | 0_i \rangle \\ &+ \frac{1}{2!} \langle 0_i | [[\hat{\kappa}_i, [\hat{\kappa}_i, E_{p_i q_i}]] | 0_i \rangle + \mathcal{O}(\boldsymbol{\kappa}_i^3). \end{aligned} \quad (43)$$

For convenience, we also introduce the (response) density matrices  $\boldsymbol{\Gamma}$  for a single-determinant exponential parameterization,

$$\boldsymbol{\Gamma}_{x_i y_i; p_i q_i}^{\text{SD}} = \left( \frac{\partial D_{x_i y_i}^{\text{SD}(1)}}{\partial \kappa_{p_i q_i}^{(1)}} \right) = \langle 0_i | [E_{p_i q_i}, E_{x_i y_i}] | 0_i \rangle, \quad (44)$$

$$\boldsymbol{\Gamma}_{x_i y_i; p_i q_i, r_i s_i}^{\text{SD}} = \left( \frac{\partial^2 D_{x_i y_i}^{\text{SD}(2)}}{\partial \kappa_{p_i q_i}^{(1)} \partial \kappa_{r_i s_i}^{(1)}} \right) = \frac{1}{2} \langle 0_i | [E_{p_i q_i}, [E_{r_i s_i}, E_{x_i y_i}]] | 0_i \rangle. \quad (45)$$

Note that the number of indices indicates the order of the derivatives.

### A. DFT response theory for isolated subsystems

We first consider the DFT response theory using the quasi-energy formalism and second quantization<sup>53,65</sup> for a single isolated subsystem. Starting point is the DFT quasi-energy expression,

$$\begin{aligned} Q[\rho](t, \epsilon) &= T_s[\rho] + V^I[\rho] + V_{\text{nuc}}[\rho] + J[\rho] \\ &+ E_{\text{xc}}[\rho(\mathbf{r}, t)] - \left\{ \langle \tilde{0} | i \frac{\partial}{\partial t} | \tilde{0} \rangle \right\}_T, \end{aligned} \quad (46)$$

where  $J[\rho]$  denotes the Coulomb contribution. The energy expression is obtained as the (time-independent) zeroth-order quasi-energy,

$$Q^{(0)}[\rho^{(0)}] = T_s[\rho^{(0)}] + V_{\text{nuc}}[\rho^{(0)}] + J[\rho^{(0)}] + E_{\text{xc}}[\rho^{(0)}]. \quad (47)$$

In order to calculate the linear response, we adopt the adiabatic approximation, assuming that the time dependence of the exchange-correlation potential may be fully described

through the time evolution of the density. For a single subsystem, only expressions for  $\mathbf{F}$  and  $\boldsymbol{\eta}^Y$  in terms of the single-determinant Kohn-Sham ansatz are needed,<sup>52,53,68</sup>

$$F_{pq,rs}(\omega_y) = \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \kappa_{pq}^{(1)}(\omega_x) \partial \kappa_{rs}^{(1)}(\omega_y)} = E_{\text{DFT};pq,rs}^{[2]} - \omega_y S_{pq,rs}^{[2]}, \quad (48)$$

$$\eta_{pq}^Y = \frac{\partial^2 \{Q^{(2)}\}_T}{\partial \kappa_{pq}^{(1)}(\omega_x) \partial \epsilon_Y(\omega_y)} = \langle 0 | [\hat{Y}, E_{pq}] | 0 \rangle, \quad (49)$$

and the Hessian  $\mathbf{E}_{\text{DFT}}^{[2]}$  for the closed-shell case reads

$$\mathbf{E}_{\text{DFT}}^{[2]} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}, \quad (50)$$

$$A_{ia,jb} = \delta_{ij} \delta_{ab} (\epsilon_a^{\text{KS}} - \epsilon_i^{\text{KS}}) + 2(ia|bj) + (ia|w_{\text{xc}}|bj), \quad (51)$$

$$B_{ia,jb} = 2(ia|jb) + (ia|w_{\text{xc}}|jb). \quad (52)$$

Throughout the article, round brackets denote charge-cloud notation for two-electron integrals.

### B. DFT-in-DFT response theory

To the contributions from the isolated subsystems considered above, we may next add the contributions from the interaction term  $Q_{\text{int}}$ . Starting point is the expansion

$$\begin{aligned} Q_{\text{int}} &= E_{\text{int}}^{[0]} + \mathbf{E}_{\text{int};I}^{[1]} \boldsymbol{\kappa}_I + \mathbf{E}_{\text{int};II}^{[1]} \boldsymbol{\kappa}_{II} \\ &+ \frac{1}{2!} (\mathbf{E}_{\text{int};I,I}^{[2]} \boldsymbol{\kappa}_I \boldsymbol{\kappa}_I + \mathbf{E}_{\text{int};II,II}^{[2]} \boldsymbol{\kappa}_{II} \boldsymbol{\kappa}_{II} + \mathbf{E}_{\text{int};II,I}^{[2]} \boldsymbol{\kappa}_{II} \boldsymbol{\kappa}_I \\ &+ \mathbf{E}_{\text{int};I,II}^{[2]} \boldsymbol{\kappa}_I \boldsymbol{\kappa}_{II}) + \mathcal{O}(\boldsymbol{\kappa}^3). \end{aligned} \quad (53)$$

In order to evaluate the derivatives of a functional  $E[\rho(\boldsymbol{\kappa})]$ , the functional chain rule,<sup>60</sup>

$$\left( \frac{\partial E[\rho(\mathbf{r}, \boldsymbol{\kappa})]}{\partial \kappa_{pq}} \right) = \int \left( \frac{\delta E[\rho]}{\delta \rho(\mathbf{r}')} \right) \left( \frac{\partial \rho(\mathbf{r}', \boldsymbol{\kappa})}{\partial \kappa_{pq}} \right) d\mathbf{r}', \quad (54)$$

is employed. We furthermore use the short-hand notation for the first [Eq. (9)] and second functional derivative, respectively,

$$v_{\text{emb}}^i(\mathbf{r}') = \frac{\delta E_{\text{int}}[\rho]}{\delta \rho_i(\mathbf{r}')}, \quad w_{\text{emb}}^{ij}(\mathbf{r}', \mathbf{r}'') = \frac{\delta^2 E_{\text{int}}[\rho]}{\delta \rho_i(\mathbf{r}') \delta \rho_j(\mathbf{r}'')}. \quad (55)$$

As this interaction between system I and the sum of the other systems can be considered an embedding of system I, we will denote the potential and the kernel arising from the interaction term as the ‘‘embedding potential’’ and ‘‘embedding kernel,’’ respectively. The first-order contribution of the interaction term can be formulated as

$$\sum_{r_i s_i} E_{\text{int};r_i s_i}^{[1]} \kappa_{r_i s_i} = \sum_{r_i s_i} \sum_{x_i y_i} \boldsymbol{\Gamma}_{x_i y_i; r_i s_i}^{\text{SD}} \langle x_i | v_{\text{emb}}^i | y_i \rangle \kappa_{r_i s_i}. \quad (56)$$

Utilizing the definition of the density matrix in Eq. (44), the non-zero elements for subsystem I are simply

$$E_{\text{int};i a_i}^{[1]} = \langle i | v_{\text{emb}}^I | a_i \rangle. \quad (57)$$

For the diagonal ( $i = j$ ) second-order term

$$E_{\text{int};p_i,q_i,r_i,s_i}^{[2]} = \iint \left( \frac{\delta^2 E_{\text{int}}}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \right) \left( \frac{\partial \rho^{(1)}(\mathbf{r}')}{\partial \kappa_{p_i,q_i}^{(1)}} \right) \times \left( \frac{\partial \rho^{(1)}(\mathbf{r}'')}{\partial \kappa_{r_i,s_i}^{(1)}} \right) d\mathbf{r}' d\mathbf{r}'' + \int \left( \frac{\delta E_{\text{int}}}{\delta \rho(\mathbf{r}')} \right) \left( \frac{\partial^2 \rho^{(2)}(\mathbf{r}')}{\partial \kappa_{p_i,q_i}^{(1)} \partial \kappa_{r_i,s_i}^{(1)}} \right) d\mathbf{r}', \quad (58)$$

the second derivative needs to be evaluated, which yields

$$E_{\text{int};p_i,q_i,r_i,s_i}^{[2]} = \sum_{x_i y_i, t_i u_i} \Gamma_{x_i y_i; p_i q_i}^{\text{SD}} \Gamma_{t_i u_i; r_i s_i}^{\text{SD}} \langle x_i y_i | w_{\text{emb}}^{ii} | t_i u_i \rangle + \sum_{x_i y_i} \Gamma_{x_i y_i; p_i q_i, r_i s_i}^{\text{SD}} \langle x_i | v_{\text{emb}}^i | y_i \rangle. \quad (59)$$

After evaluation of the density matrices, this gives the non-vanishing elements for subsystem I,

$$E_{\text{int};i a_1, b_1 j_1}^{[2]} = (i_1 a_1 | w_{\text{emb}}^{I,1} | b_1 j_1) + \delta_{i_1 j_1} \langle a_1 | v_{\text{emb}}^I | b_1 \rangle - \delta_{a_1 b_1} \langle i_1 | v_{\text{emb}}^I | j_1 \rangle, \quad (60)$$

$$E_{\text{int};i a_1, j_1 b_1}^{[2]} = (i_1 a_1 | w_{\text{emb}}^{I,1} | j_1 b_1). \quad (61)$$

The mixed second derivative leads to a coupling between the sub-blocks of the Hessian for which only the kernel contributions ( $w_{\text{emb}}$ ) survive,

$$E_{\text{int};p_i,q_i,r_j,s_j}^{[2]} = \iint w_{\text{emb}}^{ij}(\mathbf{r}', \mathbf{r}'') \left( \frac{\partial \rho_i^{(1)}(\mathbf{r}')}{\partial \kappa_{p_i,q_i}^{(1)}} \right) \left( \frac{\partial \rho_j^{(1)}(\mathbf{r}'')}{\partial \kappa_{r_j,s_j}^{(1)}} \right) d\mathbf{r}' d\mathbf{r}'' = \sum_{x_i y_i, t_j u_j} \Gamma_{x_i y_i; p_i q_i}^{\text{SD}} \Gamma_{t_j u_j; r_j s_j}^{\text{SD}} \langle x_i y_i | w_{\text{emb}}^{ij} | t_j u_j \rangle. \quad (62)$$

The full embedding kernel contribution can be expressed as

$$w_{\text{emb}}^{ij}(\mathbf{r}', \mathbf{r}'') = w_{\text{xck}}(\mathbf{r}', \mathbf{r}'') - \delta_{ij} \left[ \frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_i} + \frac{\delta^2 E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_i} \right] + (1 - \delta_{ij}) \frac{1}{|\mathbf{r}' - \mathbf{r}''|}, \quad (63)$$

with the delta function indicating that the Coulomb term is only evaluated for the inter-subsystem interaction ( $i \neq j$ ). For convenience, we introduce auxiliary kernel contributions to specify the kinetic energy and exchange-correlation terms in the embedding kernel,

$$w_{\text{xck}}(\mathbf{r}', \mathbf{r}'') = \frac{\delta^2 E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_{\text{tot}}} + \frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_{\text{tot}}}, \quad (64)$$

$$w_{\text{xck}}^i(\mathbf{r}', \mathbf{r}'') = w_{\text{xck}}(\mathbf{r}', \mathbf{r}'') - \left[ \frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_i} + \frac{\delta^2 E_{\text{xc}}}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \Big|_{\rho_i} \right]. \quad (65)$$

## 1. Linear response function

The general response equations in Eq. (28) reduce in the DFT-in-DFT case to

$$\begin{pmatrix} \lambda^X(\omega_y) \\ \lambda_{\Pi}^Y(\omega_y) \end{pmatrix} = - \begin{pmatrix} \mathbf{F}(\omega_y) | \text{I,II} \mathbf{F} \\ \text{I,II} \mathbf{F} | \text{II,II} \mathbf{F}(\omega_y) \end{pmatrix}^{-1} \begin{pmatrix} \eta^Y \\ \Pi \eta^Y \end{pmatrix}. \quad (66)$$

Substituting this result into Eq. (30), we obtain

$$\langle \langle X; Y \rangle \rangle_{\omega_y} = - \begin{pmatrix} \eta^X \\ \Pi \eta^X \end{pmatrix}^T \begin{pmatrix} \mathbf{F}(\omega_y) | \text{I,II} \mathbf{F} \\ \text{I,II} \mathbf{F} | \text{II,II} \mathbf{F}(\omega_y) \end{pmatrix}^{-1} \begin{pmatrix} \eta^Y \\ \Pi \eta^Y \end{pmatrix}. \quad (67)$$

The full matrix  $\mathbf{F}$  collects the different sub-matrices

$$\begin{pmatrix} \mathbf{F}(\omega_y) | \text{II,II} \mathbf{F} \\ \text{I,II} \mathbf{F} | \text{II,II} \mathbf{F}(\omega_y) \end{pmatrix} = \begin{pmatrix} \text{I,I} \mathbf{E}^{[2]} | \text{II,I} \mathbf{E}^{[2]} \\ \text{I,II} \mathbf{E}^{[2]} | \text{II,II} \mathbf{E}^{[2]} \end{pmatrix} - \omega_y \begin{pmatrix} \text{I,I} \mathbf{m} & 0 \\ 0 & \text{II,II} \mathbf{m} \end{pmatrix}, \quad (68)$$

where  $\mathbf{m}$  stands for the metric containing 1 and  $-1$  on the diagonal. With the expressions above, we obtain the Hessian contributions to the matrices  ${}^{i,j} \mathbf{F}^{\text{int}}$  as

$$\mathbf{E}_{\text{int};p_i,q_i,r_j,s_j}^{[2]} = \begin{pmatrix} {}^{i,j} \mathbf{A}^{\text{int}} & {}^{i,j} \mathbf{B}^{\text{int}} \\ {}^{i,j} \mathbf{B}^{\text{int}*} & {}^{i,j} \mathbf{A}^{\text{int}*} \end{pmatrix}, \quad (69)$$

where the diagonal *kernel contributions* to the elements of Eq. (69) are given (for real orbitals) by

$$(i_1 a_1 | w_{\text{emb},1}^{I,1} | j_1 b_1) \rightarrow {}^{I,1} A_{i_1 a_1, j_1 b_1}^{\text{int}}, {}^{I,1} B_{i_1 a_1, j_1 b_1}^{\text{int}}. \quad (70)$$

Adding this contribution to those from Eqs. (48) and (50), we obtain the complete expressions for the supermatrix  $\mathbf{F}$  for each of the subsystems, e.g., for subsystem I,

$${}^{I,1} A_{i_1 a_1, j_1 b_1} = \delta_{i_1 j_1} \delta_{a_1 b_1} (\varepsilon_{a_1}^{\text{KS}} - \varepsilon_{i_1}^{\text{KS}}) + 2(i_1 a_1 | b_1 j_1) + (i_1 a_1 | w_{\text{xc}} | b_1 j_1) + (i_1 a_1 | w_{\text{xck}}^I | b_1 j_1), \quad (71)$$

$${}^{I,1} B_{i_1 a_1, j_1 b_1} = 2(i_1 a_1 | j_1 b_1) + (i_1 a_1 | w_{\text{xc}} | j_1 b_1) + (i_1 a_1 | w_{\text{xck}}^I | j_1 b_1). \quad (72)$$

These diagonal blocks are coupled by the pure interaction block

$${}^{\text{I,II}} A_{i_1 a_1, j_{\text{II}} b_{\text{II}}}^{\text{int}} = {}^{\text{I,II}} B_{i_1 a_1, j_{\text{II}} b_{\text{II}}}^{\text{int}} = 2(i_1 a_1 | j_{\text{II}} b_{\text{II}})_{\text{int}} + (i_1 a_1 | w_{\text{xck}} | j_{\text{II}} b_{\text{II}}). \quad (73)$$

Note that we use the subscript “int” on the right-hand side to emphasize that this Coulomb term arises due to the interaction energy expression in Eq. (63) which goes back to Eq. (6).

Note also that the orbital energies include both the effective and the embedding potential of the subsystem. For DFT-in-DFT, it is therefore convenient to add the non-additive exchange-correlation contribution (contained in the embedding potential) to the subsystem exchange-correlation contribution (which then becomes exchange-correlation potential

for the total density). This gives as final equation the simple expression,

$${}^{I,I}A_{i_1 a_1, j_1 b_1} = \delta_{i_1 j_1} \delta_{a_1 b_1} (\varepsilon_{a_1}^{\text{KS}} - \varepsilon_{i_1}^{\text{KS}}) + 2(i_1 a_1 | b_1 j_1) + (i_1 a_1 | \check{w}_{\text{xcck}}^I | b_1 j_1), \quad (74)$$

$${}^{I,I}B_{i_1 a_1, j_1 b_1} = 2(i_1 a_1 | j_1 b_1) + (i_1 a_1 | \check{w}_{\text{xcck}}^I | j_1 b_1), \quad (75)$$

where the contribution  $\check{w}_{\text{xcck}}^I$  is defined as

$$\check{w}_{\text{xcck}}^I(\mathbf{r}', \mathbf{r}'') = w_{\text{xcck}}(\mathbf{r}', \mathbf{r}'') - \left. \frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r}'')} \right|_{\rho_1}. \quad (76)$$

Up to this point, the subsystem approach enabled the extraction of explicit interaction contributions, but the dimensionality of the problem remains the same compared to a supermolecular treatment. Only in case of uncoupled excitations it is evident that both the response equations and the linear response function become decoupled, leading to smaller dimensions and, thus, significantly reduced computational costs.

As shown by Neugebauer, it is possible to avoid matrices and vectors with supermolecular dimensions in the coupled treatment.<sup>31,32</sup> In a first step, the lowest excitation energies for the different subsystems are calculated. Subsequently, a truncated eigenvalue equation is set up with reduced dimensions for which a reduced number of coupling elements are calculated. Therewith, the frozen-density approach significantly speeds up the calculation of molecular properties, while retaining the accuracy close to a supermolecular calculation.

## V. WFT-IN-DFT RESPONSE THEORY

As discussed in the Introduction, wave-function-based methods present another valid way to obtain the electron density. Following the typical hierarchy in the wave-function ansatz, we start with the variational, single-determinant, Hartree-Fock method. Hartree-Fock should thereby be considered as an approximation and the first step towards coupled-cluster theory.

### A. HF-in-DFT

#### 1. Density parameterization

Analogously to the DFT-in-DFT embedding, we introduce an independent exponential parameterization for each subsystem,

$$\exp(-\hat{\kappa}_I) |0_{\text{HF}}\rangle, \quad (-\hat{\kappa}_{\text{II}}) |0_{\text{DFT}}\rangle, \quad (77)$$

so that the total electron density remains the sum of both subsystems,

$$\rho_{\text{tot}}(\mathbf{r}, t) \stackrel{\text{FDE}}{=} \rho_{\text{WFT}}(\mathbf{r}, \kappa_I, t) + \rho_{\text{DFT}}(\mathbf{r}, \kappa_{\text{II}}, t). \quad (78)$$

With all variational parameters expressed in terms of orbital rotations, the full quasi-energy expression reads

$$Q(t) = \langle 0 | \exp[-\hat{\kappa}(t)] \left( \hat{H} + \hat{V}^t - i \frac{\partial}{\partial t} \right) \exp[\hat{\kappa}(t)] | 0 \rangle + Q_{\text{int}}[\rho_{\text{HF}}(t), \rho_{\text{DFT}}(t)] + Q[\rho_{\text{DFT}}(t)]. \quad (79)$$

## 2. Linear response

The working equations of linear response theory in the HF-in-DFT case are very similar to the DFT-in-DFT case, with differences due to the exact exchange (see, e.g., Ref. 69) appearing only in the diagonal subsystem blocks. Because the treatment of the interaction energy remains identical to DFT, the matrix  $\mathbf{F}_{\text{int}}$  can again be partitioned into  $\mathbf{A}$  and  $\mathbf{B}$  sub-blocks with the expressions for the matrix elements of those sub-blocks being the same as those in Eqs. (70) and (73) (with of course the Hartree-Fock density replacing the DFT density in subsystem I).

The HF-in-DFT derivation thus yields the following one-electron and two-electron contributions for the matrix  $\mathbf{A}^{\text{HF}}$ ,

$$A_{i_1 a_1, j_1 b_1}^{\text{HF}} = \delta_{i_1 j_1} F_{a_1 b_1}^{\text{HF}, I} - \delta_{a_1 b_1} F_{i_1 j_1}^{\text{HF}, I} + [i_1 a_1 | b_1 j_1] + \delta_{i_1 j_1} \langle a_1 | v_{\text{emb}}^I | b_1 \rangle - \delta_{a_1 b_1} \langle i_1 | v_{\text{emb}}^I | j_1 \rangle + (i_1 a_1 | w_{\text{emb}}^{I, I} | b_1 j_1), \quad (80)$$

where square brackets are defined as anti-symmetrized spin-free two-electron integrals,

$$[pq || rs] = 2(pq | rs) - (ps | rq). \quad (81)$$

Collecting all contributions that belong to the Fock matrix, the expressions simplify to

$$A_{i_1 a_1, j_1 b_1}^{\text{HF}} = \delta_{i_1 j_1} \delta_{a_1 b_1} (\varepsilon_{a_1}^{\text{HF}} - \varepsilon_{i_1}^{\text{HF}}) + [i_1 a_1 | b_1 j_1] + (i_1 a_1 | w_{\text{xcck}}^I | b_1 j_1), \quad (82)$$

$$B_{i_1 a_1, j_1 b_1}^{\text{HF}} = [i_1 a_1 | j_1 b_1] + (i_1 a_1 | w_{\text{xcck}}^I | j_1 b_1), \quad (83)$$

where we have used the diagonal form of the Fock matrix (including the embedding potential) and the short-hand notation adapted from Eq. (65). Note that  $\check{w}_{\text{xcck}}^I$  used in Eq. (74) and  $w_{\text{xcck}}^I$  used in Eq. (82) differ by the presence of the second term in Eq. (65), which is based on the fact that the Hartree-Fock part has no exchange-correlation contribution it could cancel with.

A simple approximation in this WFT-in-DFT approach would be to remove the matrix  $\mathbf{B}$  from the environment and coupling blocks. Introducing the 3-component acronym subsystemI-coupling-subsystemII to specify a particular approximation in the coupling block, the TDHF-TDA-TDA model results in the following form of the supermatrix  $\mathbf{F}$ :

$$\left( \begin{array}{c|c} \mathbf{F}(\omega_y) & \mathbf{F} \\ \hline \mathbf{F} & \mathbf{F}(\omega_y) \end{array} \right) = \left( \begin{array}{cc|cc} {}^{I,I} \mathbf{A}^{\text{HF}} & {}^{I,I} \mathbf{B}^{\text{HF}} & {}^{II,I} \mathbf{A} & 0 \\ {}^{I,I} \mathbf{B}^{\text{HF}} & {}^{I,I} \mathbf{A}^{\text{HF}} & 0 & {}^{II,I} \mathbf{A} \\ \hline {}^{II,I} \mathbf{A} & 0 & {}^{II,II} \mathbf{A}^{\text{KS}} & 0 \\ 0 & {}^{I,II} \mathbf{A} & 0 & {}^{II,II} \mathbf{A}^{\text{KS}} \end{array} \right) - \omega_y \left( \begin{array}{c|c} \mathbf{m} & 0 \\ \hline 0 & \mathbf{m} \end{array} \right), \quad (84)$$

where we have used superscripts HF and KS to denote the way in which the density is generated. Neglecting also the  ${}^{I,I} \mathbf{B}^{\text{HF}}$  blocks takes us to a CIS-TDA-TDA model. Such simplifications may be interesting when large environments are to be considered.

## B. Coupled-cluster quasi-energy response theory for an isolated system

We now derive the equations for CC-in-DFT frozen-density embedding, as an example, in which we need Lagrangian multipliers to treat a nonvariational wave function. We start by briefly summarizing conventional coupled-cluster response theory to introduce the Lagrangian technique. For a more detailed discussion, see, e.g., Refs. 52, 65, and 70. In the conventional formalism, orbital rotations are not treated explicitly but enter implicitly via the single-excitation amplitudes.<sup>52,70,71</sup>

We note that  $t$  denotes the time, whereas  $\mathbf{t}$  denote the coupled-cluster amplitudes, which are included in the cluster operator  $\hat{T}$ , and  $\bar{\mathbf{t}}$  Lagrangian multipliers. Since the coupled-cluster energy is not variationally optimized, the time-dependent coupled cluster quasi-energy,

$$Q(\mathbf{t}; t) = \langle \text{HF} | \hat{H}^t \exp(\hat{T}(t)) | \text{HF} \rangle, \quad (85)$$

is combined with the time-dependent cluster amplitude equations

$$0 = \langle \nu | \exp(-\hat{T}(t)) \left( \hat{H}^t - i \frac{\partial}{\partial t} \right) \exp(\hat{T}(t)) | \text{HF} \rangle = \Omega_\nu(\mathbf{t}; t) \quad (86)$$

to give a quasi-energy Lagrangian,

$$L_{\text{CC}}(\mathbf{t}, \bar{\mathbf{t}}; t) = Q(\mathbf{t}; t) + \sum_\nu \bar{t}_\nu \Omega_\nu(\mathbf{t}; t). \quad (87)$$

In the following, the projection manifold is often not specified to keep the derivation general.

In the presence of a (quasi-) periodic perturbation, the time evolution of the system is completely determined by the condition that the time average of the quasi-energy Lagrangian is stationary with respect to variations of the cluster amplitudes and the Lagrangian multipliers. Requiring stationarity of the Lagrangian with respect to the coupled-cluster amplitudes, equations for the zeroth-order Lagrangian multipliers  $\bar{\mathbf{t}}^{(0)}$  are obtained (see also Ref. 12). Including both singles and doubles excitations in the cluster operator yields the CCSD model. Computationally cheaper is the approximated coupled-cluster singles and doubles model, denoted as CC2.<sup>42,72</sup> The CC2 energy and amplitude equations read in the similarity-transformed formulation using the specific projection manifold,<sup>73</sup>

$$E_{\Delta\text{CC}} = \sum_{ia,jb} (t_i^a t_j^b + t_{ij}^{ab}) [ia||jb], \quad (88)$$

$$\begin{aligned} \Omega_{ai} &= \tilde{F}_{ai} + \sum_{kc} (2t_{ik}^{ac} - t_{ki}^{ac}) \tilde{F}_{kc} + \sum_{cdk} (2t_{ik}^{cd} - t_{ki}^{cd}) (kd|\tilde{a}c) \\ &\quad - \sum_{dkl} (2t_{kl}^{ad} - t_{lk}^{ad}) (ld|k\tilde{i}), \end{aligned} \quad (89)$$

$$\begin{aligned} \Omega_{ai,jb} &= \sum_c (t_{ij}^{cb} F_{ac} + t_{ij}^{ac} F_{bc}) \\ &\quad - \sum_k (t_{kj}^{ab} F_{ik} + t_{ik}^{ab} F_{kj}) + (\tilde{i}\tilde{a}|\tilde{j}\tilde{b}). \end{aligned} \quad (90)$$

The tilde indicates quantities calculated from  $T_1$ -transformed molecular orbitals. The CC2 equations are useful to provide an example of CC-in-DFT embedding and can be further approximated to provide a CCS treatment. Note that in order to do this, we do not assume canonical orbitals, because we will in the following consider cases in which the embedding potential is updated relative to the one used in the Hartree-Fock stage of the calculation (in order to be consistent with the coupled cluster density rather than with an input HF or DFT density).

### 1. Linear response

As for the DFT, we refer to the original references for the details of the unembedded CC2 derivation.<sup>52</sup> Adapting Eq. (32) to the coupled-cluster case and applying the  $2n + 2$  rule, the linear response function becomes

$$\begin{aligned} \langle \langle X; Y \rangle \rangle_{\omega_y}^{\text{CC}} &= \frac{1}{2} C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \\ &\quad \times \left[ \eta^X + \frac{1}{2} \mathbf{F} \mathbf{t}^X(\omega_x) \right] \mathbf{t}^Y(\omega_y), \end{aligned} \quad (91)$$

and the solution of the linear response equations yields

$$\mathbf{t}^Y(\omega_y) = -{}^t\tilde{\mathbf{A}}(\omega_y)^{-1} \boldsymbol{\xi}^Y, \quad (92)$$

$$\bar{\mathbf{t}}^Y(\omega_y) = -{}^t\tilde{\mathbf{A}}(-\omega_y)^{-1} (\eta^Y - {}^t\tilde{\mathbf{F}} \mathbf{t}^Y(\omega_y)). \quad (93)$$

Moreover, since  $\mathbf{t}^X(\omega_x) = \mathbf{t}^X(-\omega_x) = -{}^t\tilde{\mathbf{A}}(-\omega_x)^{-1} \boldsymbol{\xi}^X$ , it can be seen that the response function has poles at frequencies corresponding to the eigenvalues of the coupled cluster Jacobian  ${}^t\tilde{\mathbf{A}}$  (see Table II),

$${}^t\tilde{\mathbf{A}} \mathbf{R}^f = \omega_f \mathbf{R}^f. \quad (94)$$

## C. CC-in-DFT

In order to derive working equations for the CC-in-DFT, the expansion of the interaction term has to be carried out in orders of both the coupled-cluster amplitudes and Lagrangian multipliers,

$$\begin{aligned} Q_{\text{int}} &= E_{\text{int}}^{[0]} [\rho_{\text{CC}}(\mathbf{t}, \bar{\mathbf{t}}), \rho_{\text{DFT}}(\kappa_{\text{II}})] + \mathbf{E}_{\text{int};t}^{[1]} \mathbf{t} \\ &\quad + \mathbf{E}_{\text{int};\bar{t}}^{[1]} \bar{\mathbf{t}} + \mathbf{E}_{\text{int};\kappa_{\text{II}}}^{[1]} \kappa_{\text{II}} + \dots \end{aligned} \quad (95)$$

Similar to the SD cases, the amplitudes and multipliers have not yet been expanded in the different orders of the perturbation.

### 1. The coupled-cluster electron density

The coupled-cluster electron density  $\rho_{\text{CC}}(\mathbf{t}, \bar{\mathbf{t}})$  is now needed, which can be calculated as an expectation value. One then uses

$$\langle \Lambda(t) | = \langle \text{HF} | + \sum_\nu \bar{t}_\nu(t) \langle \nu | \exp(-\hat{T}(t)) \quad (96)$$

as the bra state and the normal coupled-cluster wave function as the ket state, so that the norm of such a bra-ket is conserved during time evolution,<sup>74</sup>

$$1 = \langle \Lambda(t) | \text{CC}(t) \rangle. \quad (97)$$

TABLE II. Coupled-cluster response quantities.

Quantity		Vacuum contr.	Uncoup. emb. contr. <sup>a</sup>	cf. Ref.
$\mathbf{t}^{(0)}$	$0 \stackrel{!}{=} \frac{\partial \{L^{(0)}\}_T}{\partial \tilde{\mathbf{t}}_v^{(0)}}$	$0 = \Omega_v$	$+E_{\text{int,WFT};\tilde{v}}^{[1]}$	11, 12
$\tilde{\mathbf{t}}^{(0)}$	$0 \stackrel{!}{=} \frac{\partial \{L^{(0)}\}_T}{\partial \tilde{\mathbf{t}}_\mu^{(0)}}$	$0 = \sum_v \tilde{t}_v^{(0)} \frac{\partial \Omega_v}{\partial \tilde{\mathbf{t}}_\mu^{(0)}} + {}^t \eta_\mu$	$+E_{\text{int,WFT};t;\mu}^{[1]}$	11, 12
${}^t \eta$	$\frac{\partial E_{\text{CC}}}{\partial \tilde{\mathbf{t}}_\mu^{(0)}}$	$\langle \text{HF}   \exp(-\hat{T}^{(0)}) [\hat{H}, \tau_\mu] \exp(\hat{T}^{(0)})   \text{HF} \rangle$		52
$\eta_\mu^Y$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \epsilon_Y(\omega_Y) \partial \tilde{t}_\mu^{(1)}(\omega_Y)}$	$\langle \Lambda   [\hat{Y}, \tau_\mu]   \text{CC} \rangle$		11, 13, 52
$\mathbf{t}^Y(\omega_Y)$	$0 \stackrel{!}{=} \frac{\partial \{L^{(0)}\}_T}{\partial \tilde{\mathbf{t}}_v^{(1)}}$	$0 = ({}^t \mathbf{A} - \omega_Y \mathbf{1}) \mathbf{t}^Y(\omega_Y) + \langle v   \hat{Y}   \text{CC} \rangle$	$+ \tilde{\mathbf{t}}_{\text{int,WFT};\tilde{v}}^{[2]}$	11, 13 <sup>b</sup>
$\tilde{\mathbf{t}}^Y(\omega_Y)$		$0 = \tilde{\mathbf{t}}^Y(\omega_Y) ({}^t \mathbf{A} + \omega_Y \mathbf{1}) + \eta^Y + {}^u \mathbf{F} \mathbf{t}^Y(\omega_Y)$		11, 13 <sup>b</sup>
${}^u F_{\mu\nu}$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \tilde{t}_\mu^{(1)}(\omega_X) \partial \tilde{t}_\nu^{(1)}(\omega_Y)}$	$\langle \Lambda   [[\hat{H}, \tau_\mu], \tau_\nu]   \text{CC} \rangle$	$+E_{\text{int,WFT};t;\mu\nu}^{[2]}$	11, 13
${}^t \tilde{A}_{\mu\nu}(\omega_Y)$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \tilde{t}_\mu^{(1)}(\omega_X) \partial \tilde{t}_\nu^{(1)}(\omega_Y)}$	$\langle v   [\hat{H}, \tau_\mu]   \text{CC} \rangle$	$+E_{\text{int,WFT};\tilde{t};\mu\nu}^{[2]}$	11, 13
$\tilde{\tilde{t}} J_{\mu\nu}$	$\frac{\partial^2 \{L^{(2)}\}_T}{\partial \tilde{t}_\mu^{(1)}(\omega_X) \partial \tilde{t}_\nu^{(1)}(\omega_Y)}$		$E_{\text{int,WFT};\tilde{t};\mu\nu}^{[2]}$	11, 13

<sup>a</sup>Embedding contribution without coupling.<sup>b</sup>Note the embedding contribution in  ${}^t \mathbf{A}$  and  ${}^u \mathbf{F}$ .

The (time-dependent) coupled-cluster electron density can thus be calculated as the expectation value of the electron density operator,

$$\rho(\mathbf{r}; t) = \langle \Lambda(t) | \hat{\rho}(\mathbf{r}) | \text{CC}(t) \rangle = \sum_{pq} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}) D_{pq}^\Lambda(t), \quad (98)$$

where  $\mathbf{D}^\Lambda$  is the one-electron coupled-cluster density matrix.<sup>75</sup> The expansion of  $\rho(\mathbf{r}; t)$  in orders of perturbation is then carried out by expressing  $D_{pq}^\Lambda(t)$  in orders of perturbation,

$$D_{pq}^{\Lambda(0)}(0) = \langle \Lambda | E_{pq} | \text{CC} \rangle, \quad (99)$$

$$D_{pq}^{\Lambda(1)}(t) = \langle \Lambda | [E_{pq}, \hat{T}^{(1)}(t)] | \text{CC} \rangle + \sum_v \tilde{t}_v^{(1)}(t) \langle v | \exp(-\hat{T}^{(0)}) E_{pq} | \text{CC} \rangle, \quad (100)$$

$$D_{pq}^{\Lambda(2)}(t) = \langle \Lambda | [E_{pq}, \hat{T}^{(2)}(t)] + \frac{1}{2} [[E_{pq}, \hat{T}^{(1)}(t)], \hat{T}^{(1)}(t)] | \text{CC} \rangle + \sum_v [\tilde{t}_v^{(1)}(t) \langle v | \exp(-\hat{T}^{(0)}) [E_{pq}, \hat{T}^{(1)}(t)] | \text{CC} \rangle + \tilde{t}_v^{(2)}(t) \langle v | \exp(-\hat{T}^{(0)}) E_{pq} | \text{CC} \rangle], \quad (101)$$

and so on. Explicit expressions for  $\mathbf{D}^{\Lambda(0)}$  can be found in Ref. 73, for example.

## 2. Energy expression

As an example, we list the CC2-in-DFT ground state contributions. The total energy of the CC-in-DFT approach is calculated from the zeroth-order Lagrangian,

$$L^{(0)} = L_{\text{CC}}^{(0)} + Q_{\text{int}}^{(0)} + Q_{\text{DFT}}^{(0)}, \quad (102)$$

which reads explicitly

$$L^{(0)} = \langle 0_{\text{HF}} | \hat{H}_I | 0_{\text{HF}} \rangle + E_{\Delta\text{CC}}^{[0]} + E_{\text{int}}^{[0]} + E_{\text{DFT}}^{[0]}. \quad (103)$$

Similar to HF-in-DFT, the Hartree-Fock energy contribution denotes the expectation value of the Hartree-Fock wave function over the Hamiltonian of subsystem I *without* any explicit embedding contributions, but with orbitals obtained using the embedding potential in the Hartree-Fock equations. The contributions to the amplitude equations are obtained as derivatives of the Lagrangian with respect to the multipliers,

$$0 = \frac{\partial L^{(0)}}{\partial \tilde{t}_v^{(0)}} = \Omega_v + \frac{\partial Q_{\text{int}}^{(0)}}{\partial \tilde{t}_v^{(0)}} = \Omega_v + E_{\text{int};\tilde{v}}^{[1]}, \quad (104)$$

compare also Table II. This yields additional embedding contributions to the normal quantities (see also the discussion in Ref. 76),

$$\Omega_{ia} \leftarrow \langle \tilde{a} | v_{\text{emb}}^I | \tilde{i} \rangle + \sum_{kc} (2t_{ik}^{ac} - t_{ki}^{ac}) \langle k | v_{\text{emb}}^I | c \rangle, \quad (105)$$

$$\Omega_{ia,jb} \leftarrow \sum_c (t_{ij}^{cb} \langle a | v_{\text{emb}}^I | c \rangle + t_{ij}^{ac} \langle b | v_{\text{emb}}^I | c \rangle) - \sum_k (t_{kj}^{ab} \langle i | v_{\text{emb}}^I | k \rangle + t_{ik}^{ab} \langle k | v_{\text{emb}}^I | j \rangle). \quad (106)$$

Note that  $v_{\text{emb}}^I$  itself is not calculated from  $\hat{T}_1$ -transformed orbitals and there is no tilde on the second contribution to the singles amplitude equations. This is in agreement with the conventional coupled cluster in which effectively only the two-electron contribution of the latter term is  $\hat{T}_1$ -transformed. Equations (103)–(106) correspond to the treatment in Ref. 50 in which the embedding potential was included in the Fock matrix elements and no update of the density and the embedding potential was carried out.

There are different strategies possible to achieve full self-consistency for amplitudes and multipliers in case of CC-in-DFT. The simplest is to start from a converged DFT guess for both subsystem densities,<sup>50</sup> and correct for differences between the calculated CC density and the DFT density (note that this difference only arises in approximate theory, in exact theory both densities would be identical) by carrying out the following procedure:

1. Determine the HF and CC parameters and the Lagrange multipliers for the WFT subsystem with a fixed embedding potential.
2. Calculate the coupled-cluster density and correct the embedding potential for difference between the actual and input active density.
3. If not converged, go back to step 1 and update all parameters using the updated potential.

Due to the high computational costs, such a fully converged procedure is probably not worthwhile to pursue, but it may be desirable to correct in case large differences are found between the input (DFT) density and the calculated WFT density. This may both be due to differences in the formalism as well as differences in the basis set that is applied in both calculations (in case the DFT density is obtained using a different program).

### 3. Linear response

In order to calculate the response contributions arising from the interaction energy,  $Q_{\text{int}}$  in Eq. (95), we need to expand and sort with respect to orders of the perturbation. Relevant for determining  $\{^{2n+1}Q_{\text{int}}^{(2)}\}_T$  is, e.g., the second derivative with respect to amplitudes and multipliers,

$$E_{\text{int};t\bar{t};\mu,\nu}^{[2]} = \iint w_{\text{emb}}^{\text{I,I}}(\mathbf{r}', \mathbf{r}'') \left( \frac{\partial \rho^{(1)}(\mathbf{r}')}{\partial t_{\mu}^{(1)}} \right) \left( \frac{\partial \rho^{(1)}(\mathbf{r}'')}{\partial \bar{t}_{\nu}^{(1)}} \right) d\mathbf{r}' d\mathbf{r}'' + \int v_{\text{emb}}^{\text{I}}(\mathbf{r}') \left( \frac{\partial^2 \rho^{(2)}(\mathbf{r}')}{\partial t_{\mu}^{(1)} \partial \bar{t}_{\nu}^{(1)}} \right) d\mathbf{r}' \quad (107)$$

$$= \sum_{x_1 y_1, s_1 u_1} {}^t \Gamma_{x_1 y_1; \mu}^{\text{CC}} \bar{t} \Gamma_{s_1 u_1; \nu}^{\text{CC}} (x_1 y_1 | w_{\text{emb}}^{\text{I,I}} | s_1 u_1) + \sum_{x_1 y_1} {}^{t\bar{t}} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} \langle x_1 | v_{\text{emb}}^{\text{I}} | y_1 \rangle. \quad (108)$$

Using the expansion of the electron density, expressions for the intermediate densities are obtained,

$${}^t \Gamma_{x_1 y_1; \mu}^{\text{CC}} = \left( \frac{\partial D_{x_1 y_1}^{\Lambda(1)}}{\partial t_{\mu}^{(1)}} \right) = \langle \Lambda | [E_{x_1 y_1}, \tau_{\mu}] | \text{CC} \rangle, \quad (109)$$

$$\bar{t} \Gamma_{x_1 y_1; \nu}^{\text{CC}} = \left( \frac{\partial D_{x_1 y_1}^{\Lambda(1)}}{\partial \bar{t}_{\nu}^{(1)}} \right) = \langle \nu | \exp(-T) E_{x_1 y_1} | \text{CC} \rangle, \quad (110)$$

$${}^{t\bar{t}} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} = \left( \frac{\partial^2 D_{x_1 y_1}^{\Lambda(2)}}{\partial t_{\mu}^{(1)} \partial \bar{t}_{\nu}^{(1)}} \right) = \langle \nu | \exp(-T) [E_{x_1 y_1}, \tau_{\mu}] | \text{CC} \rangle, \quad (111)$$

where the expressions for  $D_{x_1 y_1}^{\Lambda(n)}$  arise from Eqs. (98)–(101). Furthermore, the following densities are needed:

$${}^{tt} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} = \left( \frac{\partial^2 D_{x_1 y_1}^{\Lambda(2)}}{\partial t_{\mu}^{(1)} \partial t_{\nu}^{(1)}} \right) = \langle \Lambda | [[E_{x_1 y_1}, \tau_{\mu}], \tau_{\nu}] | \text{CC} \rangle, \quad (112)$$

$$\bar{\bar{t}} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} = \left( \frac{\partial^2 D_{x_1 y_1}^{\Lambda(2)}}{\partial \bar{t}_{\mu}^{(1)} \partial \bar{t}_{\nu}^{(1)}} \right) = 0, \quad (113)$$

to express

$${}^{t\bar{t}} A_{\mu,\nu}^{\text{int}} = \sum_{x_1 y_1, s_1 u_1} {}^t \Gamma_{x_1 y_1; \mu}^{\text{CC}} \bar{t} \Gamma_{s_1 u_1; \nu}^{\text{CC}} (x_1 y_1 | w_{\text{emb}}^{\text{I,I}} | s_1 u_1) + \sum_{x_1 y_1} {}^{t\bar{t}} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} \langle x_1 | v_{\text{emb}}^{\text{I}} | y_1 \rangle, \quad (114)$$

$${}^{tt} F_{\mu,\nu}^{\text{int}} = \sum_{x_1 y_1, s_1 u_1} {}^t \Gamma_{x_1 y_1; \mu}^{\text{CC}} {}^t \Gamma_{s_1 u_1; \nu}^{\text{CC}} (x_1 y_1 | w_{\text{emb}}^{\text{I,I}} | s_1 u_1) + \sum_{x_1 y_1} {}^{tt} \Gamma_{x_1 y_1; \mu\nu}^{\text{CC}} \langle x_1 | v_{\text{emb}}^{\text{I}} | y_1 \rangle, \quad (115)$$

$$\bar{\bar{t}} J_{\mu,\nu}^{\text{int}} = \sum_{x_1 y_1, s_1 u_1} \bar{t} \Gamma_{x_1 y_1; \mu}^{\text{CC}} \bar{t} \Gamma_{s_1 u_1; \nu}^{\text{CC}} (x_1 y_1 | w_{\text{emb}}^{\text{I,I}} | s_1 u_1). \quad (116)$$

In order to calculate the contributions to the total linear response function, the interaction energy has to be expanded not only in orders of the amplitudes and multipliers, but also in orders of the orbital rotation parameters of the subsystem II. Therefore, for the elements of the coupling matrix, expressions analogous to Eq. (62) are obtained, but now with the appropriate auxiliary coupled-cluster densities  $\Gamma^{\text{CC}}$  replacing  $\Gamma^{\text{SD}}$  for subsystem I,

$${}^{\text{II}} A_{\mu, r_{\text{II}} s_{\text{II}}} = \sum_{x_1 y_1, t_{\text{II}} u_{\text{II}}} \bar{t} \Gamma_{x_1 y_1; \mu}^{\text{CC}} \Gamma_{t_{\text{II}} u_{\text{II}}; r_{\text{II}} s_{\text{II}}}^{\text{KS}} (x_1 y_1 | w_{\text{emb}}^{\text{I,II}} | t_{\text{II}} u_{\text{II}}), \quad (117)$$

$${}^{\text{II}} F_{\mu, r_{\text{II}} s_{\text{II}}} = \sum_{x_1 y_1, t_{\text{II}} u_{\text{II}}} {}^t \Gamma_{x_1 y_1; \mu}^{\text{CC}} \Gamma_{t_{\text{II}} u_{\text{II}}; r_{\text{II}} s_{\text{II}}}^{\text{KS}} (x_1 y_1 | w_{\text{emb}}^{\text{I,II}} | t_{\text{II}} u_{\text{II}}). \quad (118)$$

The superscripts of the embedding kernel indicate that the Coulomb contribution is present for the inter-subsystem contributions.

The approximate uncoupled linear response function is obtained from Eqs. (28) and (30),

$$\langle \langle X; Y \rangle \rangle_{\omega_y} = \frac{1}{2} C^{\pm\omega} P(X(\omega_x), Y(\omega_y)) \times \left\{ \frac{1}{2} \bar{t} \mathbf{J} \bar{\mathbf{t}}^X(\omega_x) \bar{\mathbf{t}}^Y(\omega_y) + \left[ \left( \frac{\eta^X}{\Pi \eta^X} \right)^T + \frac{1}{2} \left( \frac{\mathbf{t}^X(\omega_x)}{\kappa_{\text{II}}^X(\omega_x)} \right)^T \left( \frac{{}^{tt} \mathbf{F} \quad 0}{0 \quad \Pi, \text{II} \mathbf{F}(\omega_y)} \right) \right] \times \left( \frac{\mathbf{t}^Y(\omega_y)}{\kappa_{\text{II}}^Y(\omega_y)} \right) \right\}, \quad (119)$$

and the perturbed parameters are calculated from the decoupled set of linear response equations (cf. Sec. VI),

$$\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \xi^Y \\ \eta^Y \\ \Pi \eta^Y \end{pmatrix} + \begin{pmatrix} \bar{t}^I \mathbf{A} - \omega_y \mathbf{1} & \bar{t}^I \mathbf{J} & 0 \\ \bar{t}^I \mathbf{F} & \bar{t}^I \mathbf{A} + \omega_y \mathbf{1} & 0 \\ 0 & 0 & \Pi, \Pi \mathbf{F}(\omega_y) \end{pmatrix} \cdot \begin{pmatrix} \mathbf{t}^Y(\omega_y) \\ \bar{\mathbf{t}}^Y(\omega_y) \\ \kappa_{\Pi}^Y(\omega_y) \end{pmatrix}. \quad (120)$$

Therefore, the linear response function can trivially be expressed as the sum of the two subsystem contributions.

For coupled response properties, the full response function in Eq. (31) becomes

$$\langle\langle X; Y \rangle\rangle_{\omega_y} = \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{CC}} + {}^{\text{I,II}}\mathbf{F} \mathbf{t}^X(\omega_x) \kappa_{\Pi}^Y(\omega_y) + \langle\langle X; Y \rangle\rangle_{\omega_y}^{\text{DFT}} \quad (121)$$

and can be calculated after solving for the perturbed amplitudes and multipliers according to Eq. (28),

$$\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \xi^Y \\ \eta^Y \\ \Pi \eta^Y \end{pmatrix} + \begin{pmatrix} \bar{t}^I \mathbf{A} - \omega_y \mathbf{1} & \bar{t}^I \mathbf{J} & {}^{\text{I,II}}\mathbf{A} \\ \bar{t}^I \mathbf{F} & \bar{t}^I \mathbf{A} + \omega_y \mathbf{1} & {}^{\text{I,II}}\mathbf{F} \\ {}^{\text{I,II}}\mathbf{F} & {}^{\text{I,II}}\mathbf{A} & \Pi, \Pi \mathbf{F}(\omega_y) \end{pmatrix} \cdot \begin{pmatrix} \mathbf{t}^Y(\omega_y) \\ \bar{\mathbf{t}}^Y(\omega_y) \\ \kappa_{\Pi}^Y(\omega_y) \end{pmatrix}. \quad (122)$$

In this case, all three parameter responses ( $\mathbf{t}^X$ ,  $\bar{\mathbf{t}}^X$ , and  $\kappa^X$ ) are coupled. Again, as already discussed for DFT-in-DFT, the computational cost becomes a key issue. Since the coupled-cluster Jacobian is typically already very large, a further increase of the dimension should be avoided. Here, one may first transform to a smaller basis of solutions before considering the coupling between the systems, similar to the strategy employed for the DFT-in-DFT.<sup>31</sup> Additional savings can be obtained by considering approximations in the coupling blocks, e.g., using the interactions' locality.

#### 4. Exemplary working equations

The expressions above are valid for a general truncation level, and it is instructive to consider a few cases for which the actual expressions for the densities  $\Gamma^{\text{CC}}$  are rather simple. For CCS, a fair amount of simplifications apply to Eqs. (114)–(118). The ground-state density that is to be used to evaluate the kernel integrals becomes then exactly that of the Hartree-Fock. The auxiliaries are, however, different,

$${}^t\Gamma_{x_1 y_1; i_1 a_1}^{\text{CCS}} = \left( \frac{\partial D_{x_1 y_1}^{\Lambda(1)}}{\partial t_{i_1}^{a_1(1)}} \right) = \langle \Lambda | [E_{x_1 y_1}, E_{a_1 i_1}] | \text{CC} \rangle = \delta_{j_1 x_1} \delta_{a_1 y_1}, \quad (123)$$

$$\begin{aligned} \bar{t}^I \Gamma_{x_1 y_1; j_1 b_1}^{\text{CCS}} &= \left( \frac{\partial D_{x_1 y_1}^{\Lambda(1)}}{\partial \bar{t}_{j_1}^{b_1(1)}} \right) \\ &= \langle \bar{b}_1 | \exp(-T) E_{x_1 y_1} | \text{CC} \rangle = \delta_{j_1 x_1} \delta_{b_1 y_1}, \end{aligned} \quad (124)$$

$$\begin{aligned} \bar{t}^I \Gamma_{x_1 y_1; i_1 a_1, j_1 b_1}^{\text{CCS}} &= \left( \frac{\partial^2 D_{x_1 y_1}^{\Lambda(2)}}{\partial t_{i_1}^{a_1(1)} \partial \bar{t}_{j_1}^{b_1(1)}} \right) \\ &= \langle \bar{b}_1 | \exp(-T) [E_{x_1 y_1}, E_{a_1 i_1}] | \text{CC} \rangle \\ &= \delta_{i_1 j_1} \delta_{x_1 a_1} \delta_{y_1 b_1} - \delta_{a_1 b_1} \delta_{x_1 i_1} \delta_{y_1 j_1}. \end{aligned} \quad (125)$$

This leads to the potential and kernel contribution to the coupled-cluster Jacobian,

$$\begin{aligned} {}^{\bar{t}^I} A_{i_1 a_1, j_1 b_1}^{\text{CCS, int}} &= \sum_{x_1 y_1, s_1 u_1} {}^t \Gamma_{x_1 y_1; j_1 b_1}^{\text{CCS}} \bar{t}^I \Gamma_{s_1 u_1; i_1 a_1}^{\text{CCS}} (x_1 y_1 | w_{\text{emb}}^{\text{I,I}} | s_1 u_1) \\ &\quad + \sum_{x_1 y_1} \bar{t}^I \Gamma_{x_1 y_1; i_1 a_1, j_1 b_1}^{\text{CCS}} \langle x_1 | v_{\text{emb}}^{\text{I}} | y_1 \rangle \\ &= \delta_{i_1 j_1} \langle a_1 | v_{\text{emb}}^{\text{I}} | b_1 \rangle - \delta_{ab} \langle i_1 | v_{\text{emb}}^{\text{I}} | j_1 \rangle + (i_1 a_1 | w_{\text{ck}}^{\text{I}} | b_1 j_1) \end{aligned} \quad (126)$$

that are equivalent to the elements of the Hessian in the case of CIS-in-DFT, compare Eq. (82) and, if neglecting the  ${}^{\text{I,I}}\mathbf{B}^{\text{HF}}$  blocks, Eq. (84). Coupling elements are obtained similarly,

$${}^{\text{I,II}} A_{i_1 a_1, j_1 b_1} = \sum_{x_1 y_1, t_1 u_1} \bar{t}^I \Gamma_{x_1 y_1; i_1 a_1}^{\text{CC}} \Gamma_{t_1 u_1; j_1 b_1}^{\text{KS}} (x_1 y_1 | w_{\text{emb}}^{\text{I,II}} | t_1 u_1) \quad (127)$$

$$= 2(i_1 a_1 | b_1 j_1)_{\text{int}} + (i_1 a_1 | w_{\text{ck}} | b_1 j_1). \quad (128)$$

This example is of course only presented to illustrate the general theory, typically WFT descriptions will be aimed at improving upon a DFT description by using a method of at least CC2 quality.

## VI. RELATION TO QM/MM METHODS

The discussion above has mostly been concerned with the formalism and the connection to prior work within the context of DFT-in-DFT or WFT-in-DFT frozen-density embedding. Nevertheless, for the “embedding” mode of the formalism it is illustrative also to make a connection to other related approaches such as the SD/molecular mechanics (SD/MM) (Ref. 77) and coupled-cluster/molecular mechanics (CC/MM) (Refs. 10–13) methods, and the more recent polarizable embedding (PE) approaches, PE-SD (Ref. 78) and PE-CC,<sup>14</sup> proposed by Christiansen, Mikkelsen, Kongsted, and co-workers.

Conceptually similar is the treatment of Coulombic interactions. The major difference lies in the continuous electron density in case of FDE, whereas MM and PE use a discrete multipole expansion. In both cases, the quadratic density dependence in the energy transfers to a linear dependence in the embedding potential. The differences come from the exchange-correlation and kinetic energy contributions

that provide the Pauli repulsion that is lacking in the classical approaches. These also lead to a nonlinear dependency on changes in the (partitioned) density due to the perturbing field.

Despite these differences in the physical content in the FDE and CC/MM approaches, the working equations exhibit a number of similarities. An important example is, for instance, the matrix  $\mathbf{J}$  which is absent for the vacuum case. For both FDE and CC/MM or PE-CC,  $\mathbf{J}$  is responsible for coupling the response equations determining the perturbed coupled-cluster amplitudes and Lagrangian multipliers.<sup>11,14</sup> In our formalism,  $\mathbf{J}$  describes changes in the response of the coupled-cluster system due to the environment that are caused by changes in the (intra-subsystem) non-additive exchange-correlation and kinetic energy contributions, while explicit “inter-subsystem” coupling effects are accounted for by the off-diagonal blocks of the matrices  $\mathbf{A}$  and  $\mathbf{F}$ . In the CC/MM or PE-CC, the “inter-subsystem” contributions are also present in  $\mathbf{J}$ , since the interactions with the environment (including its response) are expressed as “effective” contributions to the QM part.

There is also a relation with respect to pole and residue analysis of the response function that is discussed in the context of classical embedding.<sup>10–12</sup> The specific coupling of the amplitudes and multipliers leads to poles of higher order compared to exact theory in vacuum. For CC/MM, it has been proposed to ignore the coupling of the  $\mathbf{t}$  and  $\bar{\mathbf{t}}$  responses so that the same formal expressions for transition properties are obtained compared to the vacuum case, with the difference that they include the embedding contributions. A similar approach could be followed here.

## VII. NUMERICAL EXAMPLE

Although the present article is mainly concerned with the theoretical aspects of FDE response formalism, a pilot application is presented to assess the importance of the various environment contributions. The model system is a solvated water molecule as investigated by Jacob *et al.* in the context of evaluating the performance of FDE for ground-state and response properties vs. the discrete reaction field method.<sup>34</sup>

The formalism presented is implemented in a library currently interfaced to a development version of the DIRAC program package,<sup>79</sup> following up on previous work,<sup>50</sup> and restricting the discussion to HF-in-DFT response. The details of the implementation and its use in connection to electron correlation methodologies will be addressed in subsequent publications. In our calculations we employ the PyADF scripting framework<sup>80</sup> in order to perform FDE calculations with the ADF code<sup>33,81</sup> (using the PBE functional for  $E_{xc}$  and  $E_{xc}^{nadd}$ , and PW91k for  $T_s^{nadd}$ , and a TZ2P basis set augmented with diffuse functions). Following one of the strategies discussed in Ref. 34, the frozen density is constructed as a superposition of fragment densities obtained for an isolated molecule. The DIRAC calculations are performed employing the aug-cc-pVTZ basis in combination with the Levy-Leblond (non-relativistic) Hamiltonian.

Our results for the three lowest singlet excitation energies are shown in Table III. We observe that our calculations and those reported in Ref. 34 yield similar trends, although

TABLE III. TDHF excitation energies (in eV) for the first three singlet states of a water molecule, isolated ( $E_{iso}$ ) and solvated ( $E_{sol}$ ) by 127 water molecules employing FDE. The FDE corrections are further subdivided into “diagonal” and “response,” i.e., arising from the potential and the kernel contributions, see Eqs. (80) and (83), denoted by  $\Delta E_{env}^{diag}$  and  $\Delta E_{env}^{resp}$ , respectively.

State	$E_{iso}$ (eV)	$E_{sol}$ (eV)	$\Delta E_{env}^{diag}$ (eV)	$\Delta E_{env}^{resp}$ (eV)
1	8.65	9.24	0.53	0.06
2	10.33	10.85	0.47	0.05
3	10.94	11.47	0.47	0.06

quantitative differences occur. For instance, in both cases the shifts in the energies due to solvation are positive and show little variation, but the HF-in-DFT values are roughly two-thirds of those obtained by Jacob *et al.* As for the response (kernel) contributions, we can see that for the lowest singlet state both calculations yield similar results, namely, 0.06 eV for HF-in-DFT and 0.07 eV for DFT-in-DFT.

Similar behavior is seen for the dipole moments. Using HF-in-DFT, we obtain a shift of +0.57 D from the value for the isolated molecule (1.98 D), whereas the DFT calculations in Ref. 34 show a shift of +0.65 D from the value of the isolated molecule (1.80 D).

## VIII. CONCLUSIONS

We have presented a formalism suitable for calculating the time-dependent molecular properties within a subsystem embedding framework, the key aspects of which are: First, the definition of a time-dependent Lagrangian expression that connects the energies of the isolated subsystems and their interaction energy. Second, the use of the time-averaged quasi-energy formalism in order to identify the molecular properties with the (time-averaged) derivatives of the Lagrangian with respect to the perturbing fields’ strengths.<sup>52</sup> As usual, the time-independent properties are also accessible, as a special (zero-frequency) case.

The crucial ansatz in our formalism is the expression of the interaction contribution to the Lagrangian in a purely DFT fashion, that is, as a functional of the (time-dependent) electron density for the total system. In addition, we consider the number of particles in each subsystem as fixed, although for subsystems treated by DFT it may be possible to relax this constraint, see, e.g., Refs. 47, 55, and 56. However, these features provide several advantages: there is no double counting of electron correlation; the total density can be expressed as the sum of overlapping subsystem densities, and variational and non-variational WFT methods can be treated on the same footing. Furthermore, it offers the pathway to an efficient description with a large number of subsystems.<sup>82</sup> The calculation of the interaction contributions is straightforward, being limited primarily by the accuracy of the approximate exchange-correlation and kinetic energy functionals used to calculate the non-additive kinetic and exchange-correlation contributions.



While we have restricted the discussion to coupled-cluster as an example of non-variational wave functions and to Hartree-Fock as a simple example of variational methods, we note that the methodology presented can be applied to other non-variational methods such as MP2 as well as to variational methods such as MCSCF. Since the interaction contribution to the quasi-energy Lagrangian is a functional of the (total) electron density, we only require a formulation of the time-dependent electron density using the method of choice. We believe that for time-independent properties, the simplest WFT-in-DFT model in practice should be MP2-in-DFT as simpler models will not improve upon the DFT description. For time-dependent properties, we propose the CC2-in-DFT—although the pole structure is more complicated to the vacuum case, approximations offer the possibility to correct this deficiency, whereas MP2 itself exhibits inherently a wrong pole structure.

In the preceding discussion, we have hinted at some strategies to take advantage of the subsystem formulation in the calculation of the response parameters and (coupled) excitation energies. In the future work, we plan to investigate this further and implement efficient approximate embedding treatments.

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