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On the correlation potential in Frozen-Density Embedding Theory

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Abstract

The correlation functional $E_c[\rho]$ known in Levy's constrained search formulation of density functional theory is also one of the components of the energy functional in Frozen-Density Embedding Theory (FDET) [Wesolowski, *Phys. Rev. A*, **77** (2008) 012504] if the embedded wavefunction has the single determinant form. The relation between the FDET energy and quantities available from an auxiliary system is derived. In the auxiliary system, $E_c[\rho]$ and its functional derivative (correlation potential) are entirely neglected. The relation is exact up to the quadratic terms density changes caused by electron-electron correlation. It is discussed in view of its practical applications in modelling electronic structure of embedded species.

Introduction

The total energy functional in the density embedding formalism introduced in Ref.[1] comprises the componenent that depends on the number of determinants used to represent the embedded wavefunction. If the embedded wavefunction is a single determinant (SD), this component is just correlation functional ($E_c[\rho]$) well known in Density Functional Theory.

Its constrained search definition is given by Levy.[2] Approximating $E_c[\rho]$ by means of an explicit density functional $\tilde{E}_c[\rho]$ accurately enough to be applied in generalised Kohn-Sham frameworks such as the one proposed by Baroni and Tuncel[3] remains still an unachieved objective. A good approximation $\tilde{E}_c[\rho] \approx E_c[\rho]$ should not only yield accurate correlation energy for a given $\rho(\mathbf{r})$ but also a good functional derivative $\tilde{v}_c[\rho](\mathbf{r}) = \frac{\delta \tilde{E}_c[\rho]}{\delta \rho(\mathbf{r})}$ (correlation potential). The latter determines the accuracy of the optimal density, which is equal to the exact ground-state density for the exact correlation potential. The Baroni-Tuncel way of generalizing the Kohn-Sham[4] formulation of density functional theory seems not to be pursued nowadays and is replaced rather by the strategy based on the adiabatic connection[5] leading to the hybrid representation of the exchange-correlation energy.[6,7] In the language of hybrid functionals, the Baroni-Tuncel framework is equivalent to a method with 100% of "exact exchange". The Baroni-Tuncel formal framework can be also seen as a way of interpreting the conventional post-Hartree-Fock results. The Hartree-Fock energy and density differ from the exact counterparts. The exact post-Hartree-Fock calculations correct them and bring both energy and density to the exact values without the need of any approximation for either $E_c[\rho]$ or $v_c[\rho](\mathbf{r})$.

In the formalism introduced in Ref.,[1] which will be referred to as FDET (Frozen-Density Embedding Theory), approximating $E_c[\rho]$ involves an additional issue. The FDET embedding potential comprises besides $v_c[\rho](\mathbf{r})$ also another component that depends on the optimized single determinant. Any error in the used $\tilde{v}_c[\rho](\mathbf{r})$ (in particular if it is completely neglected) results in the error in the embedding potential. As a consequence, it leads indirectly to the error in the total electronic energy. The present work concerns taking into account this effect in the extreme case where $E_c[\rho]$ and $v_c[\rho](\mathbf{r})$ are entirely neglected. The formula for the correction to the total electronic energy due to neglecting the correlation energy functional in FDET is derived. The formula comprises the expected correlation energy term but alse the contribution specific for FDET. All contributions to the electronic energy, that are linear in correlation-caused changes of electron density, are taken into account exactly.

Definitions and notation

Implicit density functionals from constrained search

For N electrons in a given external potential, $v(\mathbf{r})$, $E_v^{HK}[\rho]$ denotes the universal Hohenberg-Kohn functional,[8] $\rho_v^o(\mathbf{r})$ - the ground-state density, $E_v^{HK}[\rho_v^o] = E_v^o$ - the ground-state energy, and Ψ_v^o - the ground state wavefunction.

The following universal, i.e. system-independent density functionals (i.e. independent on $v(\mathbf{r})$), are defined in the Levy's constrained search:[2,3]

$$\begin{aligned} F^{HK}[\rho] &= \min_{\Psi\longrightarrow\rho} \left\langle \Psi|\hat{T}+\hat{V}^{ee}|\Psi\right\rangle = \left\langle \Psi^o[\rho]|\hat{T}+\hat{V}^{ee}|\Psi^o[\rho]\right\rangle \\ &= \left\langle \Psi^o[\rho]|\hat{T}|\Psi^o[\rho]\right\rangle + \left\langle \Psi^o[\rho]|\hat{V}^{ee}|\Psi^o[\rho]\right\rangle = T[\rho] + V_{ee}[\rho] \end{aligned} \tag{1}$$

$$T_s[\rho] = \min_{\Phi\longrightarrow\rho} \left\langle \Phi|\hat{T}|\Phi\right\rangle = \left\langle \Phi^o[\rho]|\hat{T}|\Phi^o[\rho]\right\rangle \tag{2}$$

$$\begin{aligned} E_{xc}[\rho] &= \min_{\Psi\longrightarrow\rho} \left\langle \Psi|\hat{T}+\hat{V}^{ee}|\Psi\right\rangle - T_s[\rho] - J[\rho] \\ &= \left\langle \Psi^o[\rho]|\hat{T}+\hat{V}^{ee}|\Psi^o[\rho]\right\rangle - T_s[\rho] - J[\rho] \end{aligned} \tag{3}$$

$$\begin{aligned} E_c[\rho] &= \min_{\Psi\longrightarrow\rho} \left\langle \Psi|\hat{T}+\hat{V}^{ee}|\Psi\right\rangle - \min_{\Phi\longrightarrow\rho} \left\langle \Phi|\hat{T}+\hat{V}^{ee}|\Phi\right\rangle \\ &= \left\langle \Psi^o[\rho]|\hat{T}+\hat{V}^{ee}|\Psi^o[\rho]\right\rangle - \left\langle \Phi^o[\rho]|\hat{T}+\hat{V}^{ee}|\Phi^o[\rho]\right\rangle, \end{aligned} \tag{4}$$

where $\hat{v}_{ee}$ is the electron-electron repulsion operator and $J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}|}\mathrm{d}\mathbf{r}'\mathrm{d}\mathbf{r}$. Throughout the present work, $E_{xct}^{nad}[\rho_A,\rho_B]$ denotes the functional depending on two electron densities

$\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$:

$$\begin{aligned} E^{nad}_{xct}[\rho_A,\rho_B] &\equiv E_{xc}[\rho_A+\rho_B]-E_{xc}[\rho_A]-E_{xc}[\rho_B] \\ &+ T_s[\rho_A+\rho_B]-T_s[\rho_A]-T_s[\rho_B] \end{aligned} \tag{5}$$

which is used throughout this work. The corresponding functional derivatives are denoted with:

$$v^{nad}_{xct}[\rho_A,\rho_B](\mathbf{r}) = \frac{\delta E^{nad}_{xct}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})} \tag{6}$$

$$f^{nad}_{xct}[\rho_A,\rho_B](\mathbf{r},\mathbf{r}') = \frac{\delta^2 E^{nad}_{xct}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})\delta\rho_A(\mathbf{r}')} \tag{7}$$

Through this work, the following convention will be used for the arguments for ALL considered functionals. A superscript indicates a specific function (ground state electron density $\rho^o(\mathbf{r})$ in $E^{HK}_v[\rho^o]$ for instance) whereas the absence of any superscript denotes any admissible function (as in $E^{HK}_v[\rho]$).

Notation for the functionals in FDET

The embedding formalism introduced in Ref.,[1] which is referred to in the present work as FDET (Frozen-Density Embedding Theory concerns the system of N_{AB} electrons in the external potential $v_{AB}(\mathbf{r})$. (The notation used in the present work differs slightly from that in the original publication to facilitate the considerations in the present work.) In contrast to Hohenberg-Kohn formulation of the N_{AB}-electron problem,[8] an additional constraint on the N_{AB}-electron density ($\rho_{AB}(\mathbf{r})$) is introduced:

$$\forall_{\mathbf{r}}\rho_{AB}(\mathbf{r}) \geq \rho_B(\mathbf{r}), \tag{8}$$

where $\rho_B(\mathbf{r})$ is some non-negative function such that:

$$\int \rho_B(\mathbf{r})d\mathbf{r} = N_B < N_{AB} \tag{9}$$

and N_B is an integer.

The optimal density $\rho_{AB}^{o(FDET)}$ satisfying the above constraint, is not necessarily equal to the exact ground-state density ($\rho^o_{v_{AB}}(\mathbf{r})$) of the system of N_{AB} electrons in the external potential $v_{AB}(\mathbf{r})$. Following the second Hohenberg-Kohn theorem,

$$E^{HK}_{v_{AB}}[\rho_{AB}^{o(FDET)}] \geq E_{v_{AB}}[\rho^o_{v_{AB}}] \equiv E^o_{v_{AB}}. \tag{10}$$

For a given $\rho_B(\mathbf{r})$ and $v_{AB}(\mathbf{r})$, the equality is reached only if $\forall_{\mathbf{r}} \rho_B(\mathbf{r}) \leq \rho^o_{v_{AB}}(\mathbf{r})$.

The density $\rho^o_A(\mathbf{r})$ defined as

$$\rho^o_A(\mathbf{r}) \equiv \rho_{AB}^{o(FDET)}(\mathbf{r}) - \rho_B(\mathbf{r}) \tag{11}$$

is non-negative and integrates to $N_A = N_{AB} - N_B$ by construction. In FDET, it is not $\rho_A(\mathbf{r})$ that is directly optimised but rather the embedded wavefunction of a given form. (The equivalence of these two ways to optimize $\rho_A(\mathbf{r})$ is subject to the condition of representability of $\rho^o_A(\mathbf{r})$ by a wavefunction of the chosen form.) The total electronic energy of this system is represented by means of the functional depending on two quantities, the N_A-electron wavefunction and $\rho_B(\mathbf{r})$. The constrained search definitions given in Eqs. 4 and 5 are used to define the FDET energy functional for each form of the embedded wavefunction. It will be denoted with $E^{FDET(SD)}_{v_{AB}}[\Phi_A, \rho_B; v_B]$ if the embedded wavefunctions are single determinants (SD) and $E^{FDET(FS)}_{v_{AB}}[\Psi_A, \rho_B; v_B]$ if this restriction is lifted. These two cases represent two extreme possibilities as far as the search space among the embedded N_A-electron functions is concerned. The total electronic energy functionals for the two cases are given below:

$$\begin{aligned}
E_{v_{AB}}^{FDET(SD)}[\Phi_A,\rho_B;v_B] &= \langle\Phi_A|\hat{H}_A+\hat{v}_{emb}^{FDET(SD)}[\rho_A,\rho_B;v_B]|\Phi_A\rangle \\
&+ E_{xct}^{nad}[\rho_A,\rho_B]+E_c[\rho_A] \\
&- \int\left(v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})+v_c[\rho_A](\mathbf{r})\right)\rho_A(\mathbf{r})d\mathbf{r} \\
&+ E_{v_B}^{HK}[\rho_B]+V_A[\rho_B], \\
\text{where}\qquad \rho_A(\mathbf{r}) &= \langle\Phi_A|\sum_{i=1}^{N_A}\delta(\mathbf{r}_i-\mathbf{r})|\Phi_A\rangle, \\
v_{emb}^{FDET(SD)}[\rho_A,\rho_B;v_B](\mathbf{r}) &= v_B(\mathbf{r})+\int\frac{\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})+v_c[\rho_A](\mathbf{r}),
\end{aligned}\tag{12}$$

and

$$\begin{aligned}
E_{v_{AB}}^{FDET(FS)}[\Psi_A,\rho_B;v_B] &= \langle\Psi_A|\hat{H}_A+\hat{v}_{emb}^{FDET(FS)}[\rho_A,\rho_B;v_B]|\Psi_A\rangle+E_{xct}^{nad}[\rho_A,\rho_B] \\
&- \int v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})\rho_A(\mathbf{r})d\mathbf{r} \\
&+ E_{v_B}^{HK}[\rho_B]+V_A[\rho_B], \\
\text{where}\qquad \rho_A(\mathbf{r}) &= \langle\Psi_A|\sum_{i=1}^{N_A}\delta(\mathbf{r}_i-\mathbf{r})|\Psi_A\rangle \\
v_{emb}^{FDET(FS)}[\rho_A,\rho_B;v_B](\mathbf{r}) &= v_B(\mathbf{r})+\int\frac{\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r}).
\end{aligned}\tag{13}$$

In either energy functionals, the potential $v_A(\mathbf{r}) = v_{AB}(\mathbf{r}) - v_B(\mathbf{r})$, is used to define the environment-free N_A-electron Hamiltonian $\hat{H}_A$ and $V_A[\rho_A] = \int \rho_A(\mathbf{r})v_A(\mathbf{r})d\mathbf{r}$. This splitting of the total external potential $v_{AB}(\mathbf{r})$ is made for the sake of simplicity in the interpretation of the discussed equations and their numerical implementation. The total energy does not depend on the way $v_{AB}(\mathbf{r})$ is split into $v_A(\mathbf{r})$ and $v_B(\mathbf{r})$.

Note that that the functional $E_{v_{AB}}^{FDET(FS)}[\Psi_A,\rho_B;v_B]$ does not depend on $v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})$ at all. $v_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})$ occurs in two places with opposite sign: in the mean value and in the integral. The same observation concerns appearance of $v_{xct}^{nad}[\rho_A,\rho_B] + v_c[\rho_A](\mathbf{r})$ in

$E^{FDET(SD)}_{v_{AB}}[\Phi_A, \rho_B; v_B]$. Such form of the expression for the total energy functional is used here to facilitate the interpretation of the discussed relations.

In either cases, the optimal wavefunction ($\Phi_A^{o(SD)}$ or $\Psi_A^{o(FS)}$) minimising the corresponding energy functional is obtained from the Euler-Lagrange equation which proceeds by iterative solution of the corresponding eigenvalue problem:

$$\begin{aligned}
\left(\hat{H}_A + \hat{v}_{emb}^{FDET(SD)}[\rho_A^{o(SD)}, \rho_B; v_B]\right) \Phi_A^{o(SD)} &= \lambda^{SD} \Phi_A^{o(SD)}, \\
&\downarrow \\
\rho_A^{o(SD)}(\mathbf{r}) &= \langle \Phi_A^{o(SD)} | \sum_{i=1}^{N_A} \delta(\mathbf{r}_i - \mathbf{r}) | \Phi_A^{o(SD)} \rangle \\
&\downarrow \\
v_{emb}^{FDET(SD)}[\rho_A^{o(SD)}, \rho_B; v_B](\mathbf{r}) = v_B(\mathbf{r}) &+ \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xct}^{nad}[\rho_A^{o(SD)}, \rho_B](\mathbf{r}) + v_c[\rho_A^{o(SD)}](\mathbf{r}),
\end{aligned} \tag{14}$$

and

$$\begin{aligned}
\left(\hat{H}_A + \hat{v}_{emb}^{FDET(FS)}[\rho_A^{o(FS)}, \rho_B; v_B]\right) \Psi_A^{o(FS)} &= \lambda^{FS} \Psi_A^{o(FS)} \\
&\downarrow \\
\rho_A^{o(FS)}(\mathbf{r}) &= \langle \Psi_A^{o(FS)} | \sum_{i=1}^{N_A} \delta(\mathbf{r}_i - \mathbf{r}) | \Psi_A^{o(FS)} \rangle \\
&\downarrow \\
v_{emb}^{FDET(FS)}[\rho_A^{o(FS)}, \rho_B; v_B](\mathbf{r}) = v_B(\mathbf{r}) &+ \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xct}^{nad}[\rho_A^{o(FS)}, \rho_B](\mathbf{r}).
\end{aligned} \tag{15}$$

The constrained search definition of the functional $E_c[\rho]$ given in Eq. 4 guarantees that the self-consistent solutions of Eqs. (14-15), yield the same optimal density which is equal to $\rho_A^o(\mathbf{r})$:

$$\rho_A^{o(SD)}(\mathbf{r}) = \langle \Phi_A^{o(SD)} | \sum_{i=1}^{N_A} \delta(\mathbf{r}_i - \mathbf{r}) = | \Phi_A^{o(SD)} \rangle = \rho_A^o(\mathbf{r}) \tag{16}$$

$$\rho_A^{o(FS)}(\mathbf{r}) = \langle \Psi_A^{o(FS)} | \sum_{i=1}^{N_A} \delta(\mathbf{r}_i - \mathbf{r}) = | \Psi_A^{o(FS)} \rangle = \rho_A^o(\mathbf{r}), \tag{17}$$

and the same total electronic energy equal to $E^{HK}_{v_{AB}}[\rho^o_A + \rho_B]$:

$$E^{FDET(SD)}_{v_{AB}}[\Phi^{o(SD)}_A, \rho_B] \;=\; E^{HK}_{v_{AB}}[\rho^o_A + \rho_B] \geq E^o_{v_{AB}}, \tag{18}$$

$$E^{FDET(FS)}_{v_{AB}}[\Psi^{o(FS)}_A, \rho_B] \;=\; E^{HK}_{v_{AB}}[\rho^o_A + \rho_B] \geq E^o_{v_{AB}}. \tag{19}$$

The theorem on the increase of the total energy if $v_c[\rho_A](\mathbf{r})$ is neglected and the embedded wavefunction is single determinant

Construction of such approximated density functional $v_c[\rho_A](\mathbf{r})$ that would lead to the density satisfying the equality given in Eq. 16 represents a formidable task in practice and concerns not only FDET.[3] In this section, the effect on energy due to neglecting this functional entirely is analysed in detail, instead of approximating $E_c[\rho_A]$ (and $v_c[\rho_A](\mathbf{r})$). Throughout this work, $\Phi^{'}_A$ denotes the *optimal and self-consistently obtained* single determinant in such a case. The corresponding density is denoted with $\rho^{'}_A(\mathbf{r})$. Unless the exact $v_c[\rho_A](\mathbf{r})$ is constant, $\rho^{'}_A(\mathbf{r})$ differs from $\rho^{o(SD)}_A(\mathbf{r})$

$$\rho^{'}_A(\mathbf{r}) \neq \rho^{o(SD)}_A(\mathbf{r}) = \rho^{o(FS)}_A(\mathbf{r}) = \rho^o_A(\mathbf{r}). \tag{20}$$

Since $\Phi^{o(SD)}_A$ is the determinant minimising $E^{FDET(SD)}_{v_{AB}}[\Phi_A, \rho_B]$,

$$E^{FDET(SD)}_{v_{AB}}[\Phi^{'}_A, \rho_B] \;\geq\; E^{FDET(SD)}_{v_{AB}}[\Phi^{o(SD)}_A, \rho_B] = E^{HK}_{v_{AB}}[\rho^o_A + \rho_B]. \tag{21}$$

The functional $E^{FDET(FS)}_{v_{AB}}[\Psi_A, \rho_B]$ admits all N_A-electron functions. Since $\Psi^{o(FS)}_A$ is the one minimising $E^{FDET(FS)}_{v_{AB}}[\Psi_A, \rho_B]$,

$$E^{FDET(FS)}_{v_{AB}}[\Phi^{'}_A, \rho_B] \;\geq\; E^{FDET(FS)}_{v_{AB}}[\Psi^{o(FS)}_A, \rho_B] = E^{HK}_{v_{AB}}[\rho^o_A + \rho_B]. \tag{22}$$

The difference between the left- and right-hand sides of the above inequality, represents the increase of the total energy which is to be determined. It will be denoted with Δ^{novc}.

$$\begin{aligned}
\Delta^{novc} &\equiv E_{v_{AB}}^{FDET(FS)}[\Phi_A^{'}, \rho_B] - E_{v_{AB}}^{HK}[\rho_A^o + \rho_B], \\
&\equiv E_{v_{AB}}^{FDET(FS)}[\Phi_A^{'}, \rho_B] - E_{v_{AB}}^{FDET(FS)}[\Psi_A^{o(FS)}, \rho_B], \\
&\equiv E_{v_{AB}}^{FDET(FS)}[\Phi_A^{'}, \rho_B] - E_{v_{AB}}^{FDET(SD)}[\Phi_A^{o(SD)}, \rho_B] \\
&\equiv E_{v_{AB}}^{FDET(FS)}[\Phi_A^{'}, \rho_B] - E_{v_{AB}}^{FDET(FS)}[\Phi_A^{o(FS)}, \rho_B] - E_c[\rho_A^o].
\end{aligned} \tag{23}$$

It is expressed above in different equivalent ways for the sake of the subsequent discussions. The total potential potential $v'(\mathbf{r})$ obtained self-consistently but with $v_c[\rho_A](\mathbf{r}) = 0$ will be denoted with:

$$\begin{aligned}
v'(\mathbf{r}) &= v_A(\mathbf{r}) + v_{emb}^{FDET(FS)}[\rho_A^{'}, \rho_B; v_B](\mathbf{r}) \\
&= v_A(\mathbf{r}) + v_B(\mathbf{r}) + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xct}^{nad}[\rho_A^{'}, \rho_B](\mathbf{r}).
\end{aligned} \tag{24}$$

$v'(\mathbf{r})$ defines an auxiliary N_A-electron Hamiltonian:

$$\hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{v}'. \tag{25}$$

The corresponding ground-state wavefunction, density, and energy, are denoted with $\Psi_{v'}(\mathbf{r})$, $E_{v'}$, $\rho_{v'}(\mathbf{r})$. For the sake of the proof of the theorem given below the energy and density are decomposed further in their Hartree-Fock and correlation components: $E_{v'}^c \equiv E_{v'} - E_{v'}^{HF}$ and $\Delta\rho_{v'}^c(\mathbf{r}) \equiv \rho_{v'}(\mathbf{r}) - \rho_{v'}^{HF}(\mathbf{r})$. We note that $\Phi_A^{'}$ is the Hartree-Fock wavefunction for the Hamiltonian $\hat{H}'$: $\Phi_{v'}^{HF} \equiv \Phi_A^{'}$ and $\rho_{v'}^{HF}(\mathbf{r}) \equiv \rho_A^{'}(\mathbf{r})$.

Theorem

Neglecting $E_c[\rho_A]$ in FDET using single-determinant form of the embedded wavefunction leads to the increase of the total electronic energy Δ^{novc} given by:

$$\Delta^{novc} = -\Delta^{novc(lin)} + O(\Delta^2\rho),$$

where

$$\Delta^{novc(lin)} = E^c_{v'} - \int \Delta\rho^c_{v'}(\mathbf{r}) \int \rho^{'}_A(\mathbf{r}') f^{nad}_{xct}[\rho^{'}_A, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' d\mathbf{r}, \tag{26}$$

and where $E^c_{v'}$ (correlation energy) and $\Delta\rho^c_{v'}$ (correlation correction to the Hartree-Fock density $\rho^{'}_A(\mathbf{r})$) are obtained from the exact solution of $\hat{H}'\Psi_{v'} = E_{v'}\Psi_{v'}$ with $\hat{H}'$ given in Eq. 25. $O(\Delta^2\rho)$ collects the contributions of the quadratic order in the correlation-caused density perturbations.

Proof

The proof of Eq. 26 uses two auxiliary N_A-electron Hamiltonians defined by different external potentials: $v(\mathbf{r})$ - the exact embedding potential, and $v'(\mathbf{r})$ given in Eq. 24.

Step 1: splitting Δ^{novc} into Δ^{TS} and Δ^{PT+TS}

Taking into account equalities given in Eq. 23, Δ^{novc} reads:

$$\begin{aligned}
\Delta^{novc} &= E^{FDET(FS)}_{v_{AB}}[\Psi^{o(FS)}_A, \rho_B] - E^{FDET(FS)}_{v_{AB}}[\Phi^{'}_A, \rho_B] \\
&= \langle\Psi^{o(FS)}_A|\hat{H}_A + \hat{v}^{FDET(FS)}_{emb}[\rho^{o(FS)}_A, \rho_B; v_B]|\Psi^{o(FS)}_A\rangle \\
&- \langle\Phi^{'}_A|\hat{H}_A + \hat{v}^{FDET(FS)}_{emb}[\rho^{'}_A, \rho_B; v_B]|\Phi^{'}_A\rangle \\
&+ E^{nad}_{xct}[\rho^{o(FS)}_A, \rho_B] - E^{nad}_{xct}[\rho^{'}_A, \rho_B] \\
&- \int v^{nad}_{xct}[\rho^{o(FS)}_A, \rho_B](\mathbf{r})\rho^{o(FS)}_A(\mathbf{r})d\mathbf{r} + \int v^{nad}_{xct}[\rho^{'}_A, \rho_B](\mathbf{r})\rho^{'}_A(\mathbf{r})d\mathbf{r}.
\end{aligned} \tag{27}$$

Δ^{novc} is split into two contributions ($\Delta^{novc} = \Delta^{TS} + \Delta^{PT+TS}$), that will be treated in a different manner.

Step 2a: Taylor-series expansion for Δ^{TS}

Δ^{TS} is given by the system-independent functional depending only on $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$:

$$\begin{aligned}\Delta^{TS} &= E_{xct}^{nad}[\rho_A^{o(FS)}, \rho_B] - E_{xct}^{nad}[\rho_A^{'}, \rho_B] \\ &- \int v_{xct}^{nad}[\rho_A^{o(FS)}, \rho_B](\mathbf{r})\rho_A^{o(FS)}(\mathbf{r})d\mathbf{r} + \int v_{xct}^{nad}[\rho_A^{'}, \rho_B](\mathbf{r})\rho_A^{'}(\mathbf{r})d\mathbf{r}.\end{aligned}$$

Taylor series in $\Delta\rho^{v_c=0}(\mathbf{r}) = \rho^{o(FS)}(\mathbf{r}) - \rho_A^{'}(\mathbf{r})$ yields:

$$\begin{aligned}\Delta^{TS} &= E_{xct}^{nad}[\rho_A^{o(FS)}, \rho_B] - E_{xct}^{nad}[\rho_A^{'}, \rho_B] \\ &- \int v_{xct}^{nad}[\rho_A^{o(FS)}, \rho_B](\mathbf{r})\rho_A^{o(FS)}(\mathbf{r})d\mathbf{r} + \int v_{xct}^{nad}[\rho_A^{'}, \rho_B](\mathbf{r})\rho_A^{'}(\mathbf{r})d\mathbf{r} \\ &= -\int \rho_A^{'}(\mathbf{r}')\left(\int \left(\rho^{o(FS)}(\mathbf{r}) - \rho_A^{'}(\mathbf{r})\right) f_{xct}^{nad}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}')d\mathbf{r}'\right) d\mathbf{r} + O(\Delta^2\rho^{v_c=0}).\end{aligned} \tag{28}$$

Step 2b: Perturbation theory and Taylor-series expansion for Δ^{PT+TS}

Δ^{PT+TS} is given as the difference between two expectation values for two different Hamiltonians:

$$\begin{aligned}\Delta^{PT+TS} &= \langle\Psi_A^{o(FS)}|\hat{H}_A + \hat{v}_{emb}^{FDET(FS)}[\rho_A^{o(FS)}, \rho_B; v_B]|\Psi_A^{o(FS)}\rangle \\ &- \langle\Phi_A^{'}|\hat{H}_A + \hat{v}_{emb}^{FDET(FS)}[\rho_A^{'}, \rho_B; v_B]|\Phi_A^{'}\rangle.\end{aligned} \tag{29}$$

In the first term, $\Psi_A^{o(FS)}$ is the eigenfunction of the corresponding Hamiltonian whereas $\Phi_A^{'}$ in the second term is not. In the next step, two N_A-electron Hamiltonians are considered: $\hat{H}_{v'}$ given in Eq. 25 and $\hat{H}_v$ defined by the potential:

$$v(\mathbf{r}) = v_A(\mathbf{r}) + v_{emb}^{FDET(FS)}[\rho_A^{o(FS)}, \rho_B; v_B](\mathbf{r}). \tag{30}$$

To simplify the notation used in this step, $\Psi_A^{o(FS)}$, which is the eigenfunction of $\hat{H}_v$, will be denoted with $\Psi_A^{o(FS)} \equiv \Psi_v$. Δ^{PT+TS} is given by:

$$\Delta^{PT+TS} = \langle \Psi_v | \hat{H}_v | \Psi_v \rangle - \langle \Phi_A^{'} | \hat{H}_{v'} | \Phi_A^{'} \rangle. \tag{31}$$

Addition of $\langle \Psi_{v'} | \hat{H}_{v'} | \Psi_{v'} \rangle$ to both sides of Eq. 31 yields

$$\begin{aligned} \Delta^{PT+TS} &= \langle \Psi_v | \hat{H}_v | \Psi_v \rangle - \langle \Psi_{v'} | \hat{H}_{v'} | \Psi_{v'} \rangle \\ &+ \langle \Psi_{v'} | \hat{H}_{v'} | \Psi_{v'} \rangle - \langle \Phi_A^{'} | \hat{H}_{v'} | \Phi_A^{'} \rangle \\ &= E_v - E_{v'} + E_{v'}^c, \end{aligned} \tag{32}$$

where $E_{v'}^c = \langle \Psi_{v'} | \hat{H}_{v'} | \Psi_{v'} \rangle - \langle \Phi_A^{'} | \hat{H}_{v'} | \Phi_A^{'} \rangle$ is the correlation energy in the N_A-electron system defined by the Hamiltonian $\hat{H}_{v'}$.

In the subsequent part, $E_v - E_{v'}$ is evaluated from the perturbation theory treating $v(\mathbf{r}) - v'(\mathbf{r})$ as the perturbation given by

$$\begin{aligned} v(\mathbf{r}) - v'(\mathbf{r}) &= v_{emb}^{FDET(FS)}[\rho_v, \rho_B; v_B](\mathbf{r}) - v_{emb}^{FDET(FS)}[\rho_{v'}, \rho_B; v_B](\mathbf{r}) \\ &= v_{xct}^{nad}[\rho_v, \rho_B](\mathbf{r}) - v_{xct}^{nad}[\rho_{v'}, \rho_B](\mathbf{r}) \\ &= \int \Delta\rho_{vv'}(\mathbf{r'}) f_{xct}^{nad}[\rho_{v'}, \rho_B](\mathbf{r}, \mathbf{r'}) d\mathbf{r'} + O(\Delta^2 \rho_{vv'}), \end{aligned} \tag{33}$$

where $\Delta\rho_{vv'}(\mathbf{r}) = \rho_v(\mathbf{r}) - \rho_{v'}(\mathbf{r})$.

The first-order correction due to $\int \Delta\rho_{vv'}(\mathbf{r'}) f_{xct}^{nad}[\rho_{v'}, \rho_B](\mathbf{r}, \mathbf{r'}) d\mathbf{r'}$ is

$$E_v^{PT1} - E_{v'}^{PT1} = \int \rho_{v'}(\mathbf{r'}) \left(\int \left(\rho_v(\mathbf{r}) - \rho_{v'}(\mathbf{r}) \right) f_{xct}^{nad}[\rho_{v'}, \rho_B](\mathbf{r}, \mathbf{r'}) d\mathbf{r'} \right) d\mathbf{r}, \tag{34}$$

whereas that due to $O(\Delta^2 \rho_{vv'})$ in Eq. 33 is also of the order of $O(\Delta^2 \rho_{vv'})$. The same concerns the higher orders in perturbation theory, which are also collected in $O(\Delta^2 \rho_{vv'})$, leading thus to:

$$E_v - E_{v'} = \int \rho_{v'}(\mathbf{r}') \left(\int \left(\rho_v(\mathbf{r}) - \rho_{v'}(\mathbf{r})\right) f^{nad}_{xct}[\rho_{v'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} + O(\Delta^2 \rho_{vv'}). \quad (35)$$

Step 3: Common expansion point for the Taylor-series expansion

Before combining expressions for Δ^{TS} and Δ^{PT+TS}, we notice that the Taylor-series expansion of $v^{nad}_{xct}[\rho_A, \rho_B](\mathbf{r})$ in Eqs. 28 and Eq. 35 is made at different points. In Eq. 28, it is $\rho_A^{'}(\mathbf{r}) = \rho^{HF}_{v'}(\mathbf{r})$, whereas in Eq. 35 it is $\rho_{v'}(\mathbf{r}) = \rho^{HF}_{v'}(\mathbf{r}) + \Delta^c_{v'}(\mathbf{r})$. Shifting the expansion point in Eq. 35 by $\Delta\rho^c_{v'}(\mathbf{r})$ and recalling that: $\rho_A^{'}(\mathbf{r}) \equiv \rho^{HF}_{v'}(\mathbf{r})$ and $\rho_A^{o(FS)}(\mathbf{r}) \equiv \rho_v(\mathbf{r})$ leads to:

$$\begin{aligned} E_v - E_{v'} &= \int \rho_A^{'}(\mathbf{r}) \left(\int \left(\rho_A^{o(FS)}(\mathbf{r}') - \rho_A^{'}(\mathbf{r}')\right) f^{nad}_{xct}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &- \int \rho_A^{'}(\mathbf{r}) \left(\int \Delta\rho^c_{v'}(\mathbf{r}') f^{nad}_{xct}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &+ O(\Delta^2 \rho_{vv'}) + O(\Delta\rho^c_{v'} \Delta\rho_{vv'}) + O(\Delta^2 \rho^c_{v'}). \end{aligned} \quad (36)$$

Step 4: The final results

Collecting the partial results given in Eqs. 28, 32, and 36, yields:

$$\begin{aligned} \Delta^{novc} &= E^c_{v'} + \int \rho_A^{'}(\mathbf{r}) \left(\int \left(\rho_A^{o(FS)}(\mathbf{r}') - \rho_A^{'}(\mathbf{r}')\right) f^{nad}_{xct}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &- \int \rho_A^{'}(\mathbf{r}) \left(\int \Delta\rho^c_{v'}(\mathbf{r}') f^{nad}_{xct}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &- \int \rho_A^{'}(\mathbf{r}') \left(\int \left(\rho^{o(FS)}(\mathbf{r}) - \rho_A^{'}(\mathbf{r})\right) f^{nad}_{xct}[\rho_A^{'}, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &+ O(\Delta^2 \rho_{vv'}) + O(\Delta\rho^c_{v'} \Delta\rho_{vv'}) + O(\Delta^2 \rho^c_{v'}). \end{aligned}$$

The contributions to Δ^{novc} due to $\rho_A^{o(FS)}(\mathbf{r}') - \rho_A^{'}(\mathbf{r}')$ cancel completely in the first order. As a result, the first order correction to the energy obtained self-consistently but with neglected $E_c[\rho_A]$, contains only the contributions available from the auxiliary Hamiltonian $\hat{H}'$ defined in Eq. 25. The final expression for Δ^{novc} reads:

$$\begin{aligned}\Delta^{novc} &= E^c_{v'} - \int \rho^{'}_A(\mathbf{r}) \left(\int \Delta\rho^c_{v'}(\mathbf{r}') f^{nad}_{xct}[\rho^{'}_A, \rho_B](\mathbf{r},\mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} \\ &+ O(\Delta^2 \rho_{vv'}) + O(\Delta\rho^c_{v'} \Delta\rho_{vv'}) + O(\Delta^2 \rho^c_{v'}). \qquad (37)\end{aligned}$$

End of the proof

The derived expression for Δ^{novc} holds only if the single determinant yielding $\rho^{'}_A(\mathbf{r})$ is obtained variationally AND with the self-consistent embedding potential whereas the correlation anergy $E^c_{v'}$ and the correlation-caused density change $\Delta\rho^c_{v'}(\mathbf{r})$ are the exact quantities for the potential $v'(\mathbf{r})$.

Discussion and Conclusions

The origin of the $f^{nad}_{xct}[\rho^{'}_A, \rho_B]$-dependent term

In the absence of the environment, FDET(SD) is equivalent to the Baroni-Tuncel formulation of DFT.[3] In this case, Eq. 26 represents, the trivial observation that the exact solution of the N_A-electron problem given as the sum of the Hartree-Fock plus correlation energy, can be obtained using the auxiliary single determinant and the exact correlation potential (provided the exact ground-state density is single-determinant representable). In FDET, the additional contribution to the total energy given by the kernel dependent term in the right-hand-side of Eq. 26 arises from the fact that the FDET embedding potential comprises another ρ_A-dependent term $v^{nad}_{xct}[\rho_A, \rho_B](\mathrm{r})$ besides $v_c[\rho_A](\mathbf{r})$. As a result, the correlation energy obtained for the system defined by the potential $v'(\mathbf{r})$ (Eq. 24), is not the same as the correlation energy in the system defined by the exact potential given in Eq. 30. Finally, we notice that the $\int \rho^{'}_A(\mathbf{r}) \left(\int \Delta\rho^c_{v'}(\mathbf{r}') f^{nad}_{xct}[\rho^{'}_A, \rho_B](\mathbf{r},\mathbf{r}') d\mathbf{r}' \right) d\mathbf{r}$ term, has the form of a system-independent universal functional depending only on electron densities.

The basic FDET equality for the total energy

Correcting the inexact FDET energy obtained for the embedded single determinant but with incorrect total energy functional (with neglected correlation functional) by addition of the two terms given in the right-hand side of Eq. 26, restores the basic FDET equality for energy which is given in Eq. 18. Using the quantities defined in the previous section, this equality reads:

$$\begin{aligned} E^{HK}_{v_{AB}}[\rho^o_A+\rho_B] &= E^{FDET(FS)}_{v_{AB}}[\Phi^{'}_A,\rho_B]+E^c_{v'}-\int\rho^{'}_A(\mathbf{r})\left(\int\Delta\rho^c_{v'}(\mathbf{r}')f^{nad}_{xct}[\rho^{'}_A,\rho_B](\mathbf{r},\mathbf{r}')d\mathbf{r}'\right)d\mathbf{r} \\ &+ O(\Delta^2\rho). \end{aligned} \tag{38}$$

where $E^{FDET(FS)}_{v_{AB}}[\Phi^{'}_A,\rho_B]$ is the total energy functional given in Eq. 13.

Besides the $O(\Delta^2\rho)$ term, the right-hand-side of Eq. 38 comprises only contributions available from the solution of an auxiliary N_A-electron problem defined by the fixed external potential $v'(\mathbf{r})$. Neglecting the correlation functionals and potential affects both the optimal density and directly the correlation energy. The fact that owing to the theorem given in Eq. 26 the basic equality of FDET (Eq. 18) is restored up to the quadratic terms, eliminates the possibility of any over- or under-counting of the correlation related contributions to the total energy.

Practical simulations with $E^{nad}_{xct}[\rho_A,\rho_B]\approx\tilde{E}^{nad}_{xct}[\rho_A,\rho_B]$

Evaluation of the total energy according to Eq. 38 in practice follows the steps shown in Figure 1. So far, all considerations were made for the exact functional $E^{nad}_{xct}[\rho_A,\rho_B]$ and the corresponding first and second derivatives with respect to $\rho_A(\mathbf{r})$. The analytical form of the functional $E^{nad}_{xct}[\rho_A,\rho_B]$ is not known and the practical applications of FDET rely on the approximation:

$$E^{nad}_{xct}[\rho_A,\rho_B]\approx\tilde{E}^{nad}_{xct}[\rho_A,\rho_B] \tag{39}$$

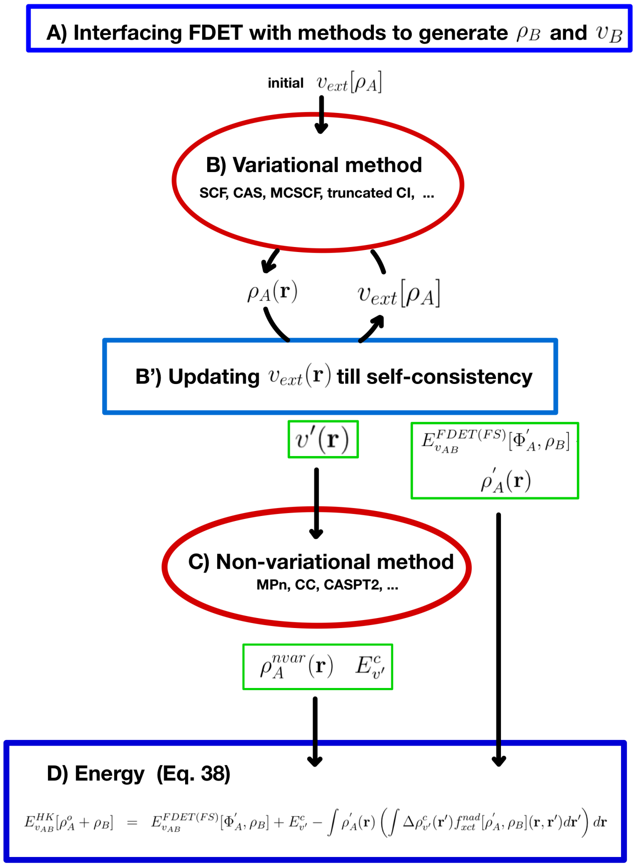

Figure 1: The key steps in the evaluation of the ground-state energy according to Eq. 38 in a multi-level simulation. Red boxes indicate approximated quantum mechanical methods for N_A electrons in a given external potential $v_{ext}(\mathbf{r})$. In step B, variational calculations are performed repetitively with iteratively updated ρ_A-dependent part of the external potential till self-consistency. The non-variational calculations (step C) are performed for the converged external potential ($v'(\mathrm{r})$).

For $\tilde{E}^{nad}_{xct}[\rho_A,\rho_B]$ of explicit analytical form, it is possible to evaluate the corresponding derivatives.

$$\begin{aligned}
\tilde{v}^{nad}_{xct}[\rho_A,\rho_B](\mathbf{r}) &= \frac{\delta \tilde{E}^{nad}_{xct}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})} && (40)\\
\tilde{f}^{nad}_{xct}[\rho_A,\rho_B](\mathbf{r},\mathbf{r}') &= \frac{\delta^2 E^{nad}_{xct}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})\delta\rho_A(\mathbf{r}')} && (41)
\end{aligned}$$

Although the basic FDET equalities (Eqs. 18, 19, and Eq. 42) does not hold if $E^{nad}_{xct}[\rho_A,\rho_B]$ is approximated, the theorem on the increase of the total energy due to neglect of the correlation potential (Eq. 26) remains valid. The right-hand side Eq. 26 comprises the term ($E^c_{v'}$ - correlation energy in the auxiliary system). The presence of the correlation energy in the expression for the energy correction is expected. It is there in the absence of any environment. In principle, $E^c_{v'}$ can be evaluated with arbitrary accuracy. The situation is different for the $\tilde{f}^{nad}_{xct}[\rho_A,\rho_B]$-dependent term in Eq. 26. It cannot be evaluated exactly but it is approximated in practice. The approximation to $E^{nad}_{xct}[\rho_A,\rho_B]$ affect this term in two ways: *i*) an error in $\tilde{v}^{nad}_{xct}[\rho_A,\rho_B](\mathbf{r})$ results in the error of the optimal density at which $\tilde{f}^{nad}_{xct}[\rho_A,\rho_B]$ is evaluated, and *ii*) $\tilde{f}^{nad}_{xct}[\rho_A,\rho_B]$ itself is not exact. This indicates that the numerical significance of the kernel-dependent term can be strongly approximation- and system dependent. We notice that if a semi-local approximation is used for $E^{nad}_{xct}[\rho_A,\rho_B]$, the $\tilde{f}^{nad}_{xct}[\rho_A,\rho_B]$-dependent term includes just one integration of the product of two functions: $\Delta\rho^c_{v'}(\mathbf{r})$ - the correlation caused density change, which is expected to be localised on the embedded species, and the diagonal element of the kernel, which disappears at zero overlap between $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$. These observation calls for dedicated numerical studies on the numerical significance of $\int \Delta\rho^c_{v_{ext}[\rho_A^{var}]}(\mathbf{r}) \int \rho_A^{var}(\mathbf{r}') f^{nad}_{xct}[\rho_A^{var},\rho_B](\mathbf{r},\mathbf{r}')d\mathbf{r}'d\mathbf{r}$. Such studies are currently under way in our research lab [C. Gonzalez-Espinoza *et al.*, to be published]. Preliminary analyses show that this term is small but not negligible if evaluated using local density approximation for the first and the second derivatives of $E^{nad}_{xct}[\rho_A,\rho_B]$. In case of complexes formed by small organic molecules and water: X-H_2O with X=N_2, CO, formamide, and glycine) at their equilibrium geometry, the magnitude of this contribution evaluated using using the cc-pVTZ basis sets localised only at atoms of X (monomer expansion), varies from 0.02 to 0.06 kcal/mol. It can be expected that going beyond local density approximation and/or using more complete basis sets allowing for increase of the overlap between $\rho_B(\mathbf{r})$ and the optimised $\rho_A(\mathbf{r})$ would rather increase these values. $\tilde{v}_{xct}^{nad}[\rho_A,\rho_B](\mathbf{r})$ approximated using local density approximation is most repulsive among semi-local approximations which leads to artificially small overlap between the optimal $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ (see for instance Refs.[9,10]).

Generalisation of the Eq. 26 for the variationally obtained embedded wavefunctions of the multi-determinant form

If more than one determinant is used to represent the variationally obtained embedded wavefunction, the corresponding FDET energy functional comprises the functional $\Delta F^{MD}[\rho]$ instead of $E_c[\rho]$.[1] Similarly as $E_c[\rho]$, its presence in the total energy functional assures that the optimal wavefunction yields the exact density and the total energy. Approximating $\Delta F^{MD}[\rho]$ represents, however, even more challenging tasks than doing it for $E_c[\rho]$. The functional $\Delta F^{MD}[\rho]$ is different for different number of determinants. It is appealing, therefore, to neglect it completely and to evaluate the resulting increase of the total energy in a similar way as it was made in the case of the embedded single determinant (Eq. 26). The generalised theorem applicable for such case (variational embedded wavefunction in the form of several determinants and neglected $\Delta F^{MD}[\rho]$) reads:

$$\begin{aligned} E_{v_{AB}}^{HK}[\rho_A^o+\rho_B] &= E_{v_{AB}}^{FDET}[\Psi_A^{var},\rho_B] + \left\langle \Psi^{nvar} \left| \hat{H}_{v''} \right| \Psi^{nvar} \right\rangle - \left\langle \Psi^{var} \left| \hat{H}_{v''} \right| \Psi^{var} \right\rangle \\ &- \int \Delta\rho^c_{v_{ext}[\rho_A^{var}]}(\mathbf{r}) \int \rho_A^{var}(\mathbf{r}') f_{xct}^{nad}[\rho_A^{var},\rho_B](\mathbf{r},\mathbf{r}') d\mathbf{r}' d\mathbf{r} \end{aligned} \tag{42}$$

The proof follows identical steps as the one given in the present work. It is sufficient to replace $E_c[\rho]$ by $\Delta F^{MD}[\rho]$ and Φ by Ψ^{MD}, where MD indicates the number of determinants in a given method. Note that the auxiliary Hamiltonian $|\hat{H}_{v''}$ in general cases is the Hamiltonian defined by the external potential $v''(\mathbf{r})$ which comprises the ρ_A-dependent component evaluated at self-consistent variationally obtained $\rho_A^{var}(\mathbf{r})$.

In case of embedded single determinant, Eq. 42 is equivalent to Eq. 38 because the difference $\left\langle \Psi^{nvar} \left| \hat{H}_{v'} \right| \Psi^{nvar} \right\rangle - \left\langle \Psi^{var} \left| \hat{H}_{v'} \right| \Psi^{var} \right\rangle$ is equal to the correlation energy ($E^c_{v'}$).

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