Advances in electronic structure theory, Paris, France, April. 27, 2015

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The issue of orthogonality in Frozen-Density Embedding Theory

Alex Zech, Francesco Aquilante, <u>Tomasz A. Wesolowski</u> Department of Physical Chemistry, University of Geneva

- I. Other-than-the-lowest solutions of the Euler-Lagrange Equation in FDET *FDET energy functional, Euler Lagrange Equations,* ρ_A *-dependency of the embedding potential*
- II. Non-orthogonal solutions embedded function (CASCI form), double-SCF, $\langle \Psi_A^{k}|\Psi_A^{m}\rangle$ overlap

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- **III.** Orthogonal solutions from the linearized FDET energy functional Linearized FDET energy functional, ρ_A^{ref}-insensitivity of the excitation energies
- IV. (Lack-of) Homogeneity of the density functional for the interaction energy expectation energy of the FDET embedding potential operator vs. FDET energies

Embedding potentials for variational QC methods

Embedding potential for methods such as HF, MCSF, CI (embedded «interacting wavefunction»)

PHYSICAL REVIEW A 77, 012504 (2008)

Embedding a multideterminantal wave function in an orbital-free environment

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 $\rho_{AB}(\vec{r}) = \rho_B(\vec{r}) + \left\langle \Psi_A^{emb} \left| \Sigma_{i=1}^{N_A} \delta(\vec{r} - \vec{r_i}) \right| \Psi_A^{emb} \right\rangle$

 $E^{FDET}[\rho_B] = \min_{\substack{\forall \vec{r} \ \rho_{AB}(\vec{r}) \ge \rho_B(\vec{r}) \\ \int \rho(\vec{r})d\vec{r} = N_{AB}}} E^{HK}_{v_{AB}}[\rho] = E^{HK}_{v_{AB}}[\rho^{opt}_{AB}]$

 $E_{ ext{emb}}[
ho_B] = \min_{\substack{
ho(\mathbf{r}) \ge
ho_B(\mathbf{r}) \ge 0 \ \int
ho(\mathbf{r}) \mathrm{d}\mathbf{r} = N_{AB}}} E_
u^{ ext{HK}}[
ho]$

$$\frac{\delta E^{EWF}_{AB}[\Psi^{emb}_{A},\rho_{B}]}{\delta \Psi^{emb}_{A}} - \lambda \Psi^{emb}_{A} = 0,$$

$$\left(\hat{H}_A + \hat{v}_{emb}\right)\Psi_A^{emb} = \epsilon \Psi_A^{emb}$$

 v_{emb} (r)= v_{emb} [ρ_A , ρ_B , v_B] (r)

Note that we take a particular perspective on the relation between the wave-function-based methods and densityfunctional theory. A multideterminantal wave function is considered in this work as an auxiliary quantity used to obtain the approximate solution of Eq. (1) and the corresponding electron density by means of variational calculations, whereas the relevant density functionals are considered to be

exact in the derivation of the basic relation.

FDET in capsule: variational method to obtain embedded wavefunction Ψ_A



$$\begin{split} \left\langle \Psi^{A} | \hat{v}_{emb} | \Psi^{A} \right\rangle &= \int \rho_{A}(\vec{r}) v_{emb}[\rho_{A}, \rho_{B}; \vec{r}] d\vec{r} \\ \neq T_{s}^{nad}[\rho_{A}, \rho_{B}] &+ E_{xc}^{nad}[\rho_{A}, \rho_{B}] + \int \rho_{A}(\vec{r}) v_{B}(\vec{r}) d\vec{r} + \int \int \frac{\rho_{A}(\vec{r}) \rho_{B}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} \end{split}$$

I.A. Wesolowski, A. Warshel, J. Phys. Chem. 1993, 97, 8050
T.A. Wesolowski, One-electron equations for embedded orbitals
In: Computational Chemistry: Reviews of current trends, J. Leszczynski Ed. Vol 10 (2006) 1-83
T.A. Wesolowski, Phys. Rev. A, 2008,77, 012504
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FDET: case of $\rho_o(r) \ge \rho_B(r)$ (for all r)



Target:

the grey density (ρ_{total} - ρ_B) as a ground-state of a N_A electron system obtained by adding a local potential to a N_A-electron Hamiltonian

Results:

$$\rho_{\text{o}} = \rho_{\text{total}} = \rho_{\text{B}} + \rho_{\text{A}}^{\text{opt}} \text{ and } \text{E}_{\text{emb}}[\rho_{\text{B}}] = \text{E}_{\text{o}}$$

FDET: case of $\rho_o(r) < \rho_B(r)$ (in some domain of \mathbb{R}^3)



$$\rho_{o} \neq \rho_{total} = \rho_{B} + \rho_{A}^{opt}$$
$$E_{emb}[\rho_{B}] \ge E_{o}$$

FDET: What we gain?

- 1) The theory underlying any QM/MM method using local embedding potentials. Instead of empirical parameters coupling QM with MM systems, FDET uses one descriptor $\rho_{\rm B}$
- Fully self-consistent expressions for:
 i) optimal energy (E_{emb}[ρ_B]), ii) embedded wavefunction, iii) embedded density.
- 3) Possibility to combine QM descriptors (Ψ_A) with any physical theory yielding electron density (nano- and macroscale)

FDET: What is the price?

- 1) Assured is only that $(E_{emb}[\rho_B] \ge E_o)$
- 2) The embedding potential depends on ρ_A (state)
- 3) Pandora's box of challenges concerning approximations for the functional $E_{xc}^{nad}[\rho_A,\rho_B]$ and the functionals :

$$\Delta F^{SC(WFT)}[\rho_A] = \min_{\Psi_A \longrightarrow \rho_A} \left\langle \Psi_A \left| \hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee} \right| \Psi_A \right\rangle$$

$$- \min_{\Psi_A^{WF} \longrightarrow \rho_A} \left\langle \Psi_A^{WF} \left| \hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee} \right| \Psi_A^{WF} \right\rangle$$

$$- \min_{\Psi_s \longrightarrow \rho_A} \left\langle \Psi_A^{WF} \left| \hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee} \right| \Psi_A^{WF} \right\rangle$$

$$- \min_{\Psi_s \longrightarrow \rho_A} \left\langle \Psi_s^{WF} \left| \hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee} \right| \Psi_A^{WF} \right\rangle$$

$$- \min_{\Psi_s \longrightarrow \rho_A} \left\langle \Psi_s^{WF} \left| \hat{T}_{2N_A} + \hat{V}_{2N_A}^{ee} \right| \Psi_A^{WF} \right\rangle$$

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Split-SCF FDET calculations (embedded non-interacting reference system)



FIGURE 1. (a) The *splitSCF* scheme: In the inner loop (i-index), the embedding potential $v_{emb}[\rho_A, \rho_B]$ is evaluated for ρ_A taken from the previous iteration in the outer loop (j-index) and remains constant, whereas the $v_{\text{KS}}[\rho_A]$ component is recalculated as ρ_A changes. (b) The conventional SCF scheme: Both $v_{\text{KS}}[\rho_A]$ and $v_{emb}[\rho_A, \rho_B]$ are recalculated as ρ_A changes.



FIGURE 2. The convergence of the outer-loop of the *splitSCF* procedure for various properties of the H_2O molecule in the H_2O-H_2O complex. The results of conventional self-consistent calculations are indicated by dashed lines.

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Split-SCF FDET calculations for each electronic state

(self-consistent potential and embedded wavefunction but non-orthogonal embedded wavefunctions for different states)



Embedded uracil (embedded CASCI reference system)



$\mathrm{S}_0 \rightarrow$	Charact	er of exc	citation
S_1	$n_1(O)$	\rightarrow	$\pi_1^*(CO)$
S_2	$ mostly \\ \pi_2(N) $	\rightarrow	π^*_{ring}
S_3	$n_2(O)$	\rightarrow	$\pi_2^*(CO)$
S_4	$ \begin{array}{c} \text{mostly} \\ \pi_1(N) \end{array} $	\rightarrow	π^*_{ring}

 Table 3: Wavefunction overlap matrix elements of self-consistent states.

	Ψ_0^{sc}	Ψ_1^{sc}	Ψ_2^{sc}	Ψ_3^{sc}	Ψ_4^{sc}
Ψ_0^{sc}	1			∠ πr kh	tt m>
Ψ_1^{sc}	1.00E-08	1		$<\Psi_A$	
Ψ_2^{sc}	5.19E-06	-2.00E-08	1		
Ψ_3^{sc}	1.25E-06	9.02 E- 05	-3.41E-05	1	
Ψ_4^{sc}	7.10E-07	-4.00E-08	-2.47E-05	7.09E-05	1



Table 16: Wavefunction overlap matrix elements of self-consistent states.

	Ψ_0^{sc}	Ψ_1^{sc}	Ψ_2^{sc}	Ψ_3^{sc}	Ψ_4^{sc}	Ψ_5^{sc}	Ψ_6^{sc}
Ψ_0^{sc}	1						
Ψ_1^{sc}	3.50E-07	1					
Ψ_2^{sc}	1.90E-07	-1.60E-05	1			<Ψ^ ^k	Ψ_{n}
Ψ_3^{sc}	-5.20E-07	2.10E-07	-1.71E-04	1		A - A	- A
Ψ_4^{sc}	2.45 E-06	3.80E-07	-3.03E-06	4.44E-05	1		
Ψ_5^{sc}	5.00E-08	-4.68E-06	-3.42E-05	9.50E-07	1.57 E-05	1	
Ψ_6^{sc}	-4.27E-06	-1.45E-06	-2.51E-05	1.17E-05	2.58E-06	1.03E-04	1

Embedded bromine (embedded CASCI reference system)



Figure 12: Br₂-H₂O complex.

$S_0 \rightarrow$	Charac	ter of excit	tation
S_1	π_x	\rightarrow	σ_z^*
S_2	π_y	\rightarrow	σ_z^*
S_3	π_x	\rightarrow	σ_z^*
S_4	π_y	\rightarrow	σ_z^*
S_5	π_{xy}	\rightarrow	σ_z^*

		vaverunction ov	eriap matrix e	lements of sen	-consistent state	S
	Ψ_0^{sc}	Ψ_1^{sc}	Ψ_2^{sc}	Ψ_3^{sc}	Ψ_4^{sc}	Ψ_5^{sc}
Ψ_0^{sc}	1					
Ψ_1^{sc}	1.09E-06	1			~ Ψ. k Ψ. r	n 、
Ψ_2^{sc}	-7.00E-08	6.60E-07	1			
Ψ_3^{sc}	6.00 E-08	2.31E-05	0.00E + 00	1		
Ψ_4^{sc}	6.00 E-08	0.00E + 00	2.66 E-05	2.90E-07	1	
Ψ_5^{sc}	1.10E-06	-2.82E-06	2.60E-07	-6.85E-06	4.00E-07	1

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Partial conclusions (1):

As a result of the ρ_A -dependence of the embedding potential, the other than lowest energy solutions of the Euler-Lagrange equation in FDET are not orthogonal to the lowest-energy solution.

Is it important?

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$$\begin{split} \frac{\delta E_{AB}^{EWF}[\Psi_{A}^{emb},\rho_{B}]}{\delta \Psi_{A}^{emb}} = 0, \qquad \left(\hat{H}_{A} + \hat{v}_{emb}\right) \Psi_{A}^{emb} = \epsilon \Psi_{A}^{emb}, \\ \hline \mathbf{FDET} \qquad [Wesolowski, Phys. Rev.A. 77 (2008) 012504] \\ \mathbf{E}_{AB}^{EWF}[\Psi^{A},\rho_{B}] = < \Psi^{A} |\hat{H}_{A}|\Psi^{A} > + \int \rho_{A}(\vec{r}) v_{B}(\vec{r}) d\vec{r} + \int \int \frac{\rho_{A}(\vec{r}) \rho_{B}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} \\ + E_{xet}^{mad}[\rho_{A},\rho_{B}] + E_{v_{B}}^{HK}[\rho_{B}] + \int \rho_{B}(\vec{r}) v_{A}(\vec{r}) d\vec{r}, \\ \hline \mathbf{E}_{xet}^{ind}[\rho_{A},\rho_{B}] = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{mad}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \qquad \langle \Psi_{A}^{k} |\Psi_{A}^{m} \rangle \neq \delta_{km} \\ \hline \mathbf{E}_{xet}^{ind}[\rho_{A},\rho_{B}] \approx \tilde{E}_{xet}^{ind}[\rho_{A},\rho_{B}] \approx \tilde{E}_{xet}^{mad}[in] [\rho_{A},\rho_{B}] = \tilde{E}_{xeet}^{ind}[\rho_{A}',\rho_{B}] + \int (\rho_{A} - \rho_{A}^{ref}) \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} - \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{emb}[\rho_{A}^{ref},\rho_{B},v_{B}]\vec{r} = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} + \int (\rho_{A} - \rho_{A}^{ref}) \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} - \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{emb}[\rho_{A}^{ref},\rho_{B},v_{B}]\vec{r} = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} = \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{emb}[\rho_{A}^{ref},\rho_{B},v_{B}]\vec{r} = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} = \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{emb}[\rho_{A}^{ref},\rho_{B},v_{B}]\vec{r} = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} = \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{emb}[\rho_{A}^{ref},\rho_{B},v_{B}]\vec{r} = v_{B}(\vec{r}) + \int \frac{\rho_{B}(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' + \frac{\delta \tilde{E}_{xeet}^{ind}[\rho_{A},\rho_{B}]}{\delta \rho_{A}(\vec{r})} \Big|_{\rho_{A} = \rho_{A}^{ref}} d\vec{r}' \\ \hline \tilde{v}_{A}^{k}[\Psi_{A}^{k}]\Psi_{A}^{k} = \delta_{km} \\ \hline \tilde{v$$

Embedded uracil (Linearized FDET excitation energies)

Differences between FDET and linearized FDET excitation energies (in eV) for different reference densities

(FDET excitation energies are given on the diagonal)

	E_0	E_1	E_2	E_3	E_4
$ ho_{A,0}$	0.00	-2.74E-06	-2.39E-06	-2.50E-06	2.72E-09
$ ho_{A,1}$	2.52E-06	5.13	-8.16E-09	1.52 E-07	2.56E-06
$ ho_{A,2}$	2.40E-06	-1.17E-07	6.44	3.27 E-08	2.46E-06
$ ho_{A,3}$	2.54 E-06	-2.23E-07	1.63E-07	6.77	2.59E-06
$ ho_{A,4}$	-1.69E-07	-2.90E-06	-2.56E-06	-2.42E-06	7.14



Other Uracil-water complexes



Embedded dipeptide (embedded CASCI reference system)

Differences between FDET and linearized FDET excitation energies (in eV) for different reference densities (FDET excitation energies are given on the diagonal)

	E_0	E_1	E_2	E_3	E_4	E_5	E_6
$\rho_{A,0}$	0.00	-9.01E-07	2.93E-06	2.99E-06	-5.88E-07	3.04E-06	3.21E-06
$ ho_{A,1}$	6.23E-07	6.00	3.82E-06	3.56E-06	1.28E-07	3.84E-06	3.80E-06
$ ho_{A,2}$	-2.90E-06	-3.58E-06	6.51	-1.17E-07	-3.54E-06	1.36E-08	2.04E-07
$\rho_{A,3}$	-2.88E-06	-3.89E-06	1.31E-07	8.60	-3.58E-06	-2.99E-08	3.81E-08
$\rho_{A,4}$	4.63 E-07	-2.20E-07	3.52 E-06	3.48E-06	8.82	3.44E-06	3.69E-06
$ ho_{A,5}$	-2.73E-06	-3.72E-06	1.28E-07	1.28E-07	-3.42E-06	9.25	3.48E-07
$ ho_{A,6}$	-3.11E-06	-3.84E-06	1.01E-07	-2.34E-07	-3.66E-06	-5.99E-08	9.38



Embedded bromine (embedded CASCI reference system)

Differences between FDET and linearized FDET excitation energies (in eV) for different reference densities

(FDET excitation energies are given on the diagonal)

	E_0	E_1	E_2	E_3	E_4	E_5
$\rho_{A,0}$	0.00	1.99E-06	5.52E-07	1.93E-06	1.79E-06	-1.09E-07
$ ho_{A,1}$	-1.79E-06	3.23	-1.58E-06	-8.17E-09	-2.50E-07	-1.87E-06
$\rho_{A,2}$	-4.73E-07	1.50E-06	3.24	1.41E-06	1.21E-06	-4.63E-07
$ ho_{A,3}$	-1.73E-06	1.88E-07	-1.43E-06	4.92	-1.93E-07	-1.87E-06
$\rho_{A,4}$	-1.77E-06	1.12E-07	-1.55E-06	1.61E-07	4.93	-1.98E-06
$ ho_{A,5}$	7.67 E-07	2.42E-06	6.99 E- 07	2.11E-06	1.89E-06	6.04



Partial conclusions (2):

1) Linearization (in ρ_A) of the FDET energy as proposed in [Wesolowski, J. Chem. Phys. **140** (2014) 18A530] leads to

- excitation energies remarkably insensitive to the choice of $\rho_A{}^{ref}$
- practically identical energies conventional FDET results (non-linearized)

2) The orthogonality of all embedded wavefunctions is assured by construction without destroying the self-consistency between: energy, embedded density, and embedded wavefunctions (all come from the same Euler-Lagrange equation)

- 3) One embedding calculations for ALL electronic states
- 4) Linearized FDET can be applied for any approximation for $E_{xct}[\rho_A,\rho_B]$

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The meaning of $\langle \Psi_A | \hat{v}_{emb} | \Psi_A
angle$

$$E_{int} = \int \rho_A(\vec{r}) v_B(\vec{r}) d\vec{r} + \int \int \frac{\rho_A(\vec{r}) \rho_B(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r} + E_{xct}^{nad}[\rho_A, \rho_B] \neq \langle \Psi_A | \hat{v}_{emb} | \Psi_A \rangle$$

$$T_{s}[\rho] \neq \int \rho(\vec{r}) \frac{\delta T_{s}[\rho]}{\delta \rho(\vec{r})} d\vec{r},$$

$$E_{x}[\rho] \neq \int \rho(\vec{r}) \frac{\delta E_{x}[\rho]}{\delta \rho(\vec{r})} d\vec{r},$$

$$E_{c}[\rho] \neq \int \rho(\vec{r}) \frac{\delta E_{c}[\rho]}{\delta \rho(\vec{r})} d\vec{r},$$

$$E_{int} = \int \rho_A(\vec{r}) v_B(\vec{r}) d\vec{r} + \int \int \frac{\rho_A(\vec{r}) \rho_B(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r} + E_{xct}^{nad}[\rho_A, \rho_B] \approx \langle \Psi_A | \hat{v}_{emb} | \Psi_A \rangle$$

Uracil-water (conf U1)

State (k)	$\Delta_{\mathbf{k}}$ [Hartree]	$\Delta_{k}\Delta_{o}$ [eV]
0	0.003528983	0.00
1	0.003531545	0.11
2	0.00348885	0.11
3	0.003139088	0.11
4	0.003508729	0.11

Uracil-water (conf U3)

State (k)	Δ_{k} [Hartree]	$\Delta_{k}\Delta_{o}$ [eV]
0	0.003384143	0.00
1	0.003000736	0.11
2	0.003394293	0.10
3	0.003392354	0.10
4	0.003353285	0.10

Uracil-water (conf U4)

State (k)	∆ _k [Hartree]	$\Delta_{k}\Delta_{o}$ [eV]
0	0.001836451	0.0
1	0.001539419	0.10
2	0.001862862	0.10
3	0.001839301	0.10
4	0.001832712	0.10

dipeptide-water

State (k)	∆ _k [Hartree]	$\Delta_{k}\Delta_{o}$ [eV]
0	0.002860501	0.0
1	0.00286837	0.10
2	0.002540398	0.10
3	0.002841887	0.10
4	0.002857505	0.10
5	0.0028504210	0.10
6	0.0028410620	0.10

bromine-water

State (k)	Δ_{k} [Hartree]	$\Delta_{k}\Delta_{o}$ [eV]
0	0.001191772	0.0
1	0.001345661	0.06
2	0.00134587	0.06
3	0.001372212	0.06
4	0.001374507	0.06
5	0.001598166	0.06

Partial Conclusions (3):

$$\int \rho_A(\vec{r}) v_B(\vec{r}) d\vec{r} + \int \int \frac{\rho_A(\vec{r}) \rho_B(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} d\vec{r} + E_{xct}^{nad}[\rho_A, \rho_B] \approx \langle \Psi_A | \hat{v}_{emb} | \Psi_A \rangle$$

A very good approximation for evaluation of excitation energies (total energy differences). Higher than linear (in ρ_A) terms in the energy functional are almost constant (around 0.1 eV).

Conclusions:

1) ρ_A -dependency of the embedding potential is an undesired feature of FDET leading to non-orthogonal embedded wavefunctions associated to different electronics states and the need to one calculation for each state.

- 2) Orthogonality is respected in linearized FDET
 - [Wesolowski, J. Chem. Phys. 140 (2014) 18A530], in which:
- excitation energies remarkably insensitive to the choice of $\rho_A{}^{ref}$
- practically identical energies as the ones obtained using conventional (non-linearized) calculations,
- one calculation for ALL states,
- linearized FDET can be made with ANY approximation to $E_{xct}[\rho_A, \rho_B]$

3) Linearization preserves the structure of FDET

(Euler-Lagrange equations, local embedding potential).

4) The use of expectation value of the embedding potential is a very good approximation in evaluation of excitation energies due to the small variation of the higher-than-linear in ρ_A terms in the FDET energy functional (typical magnitude 0.1 eV).

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¹ Frozen-Density Embedding Strategy for Multilevel Simulations of ² Electronic Structure

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FDET related research topics at University of Geneva

Analytically solvable model systems

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