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

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

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Embedding potentials for variational QC methods

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

Embedding a multideterminantal wave function in an orbital-free environment

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

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

Note that we take a particular perspective on the relation between the wave-function-based methods and density-functional 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.

$$E_{\mathrm{emb}}[\rho_B] = \min_{\substack{\rho(\mathbf{r}) \geq \rho_B(\mathbf{r}) \geq 0 \\ \int \rho(\mathbf{r})d\mathbf{r} = N_{AB}}} E_v^{\mathrm{HK}}[\rho]$$

$$\frac{\delta E_{AB}^{EWF}[\Psi_A^{emb}, \rho_B]}{\delta \Psi_A^{emb}} - \lambda \Psi_A^{emb} = 0,$$

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

$$v_{\mathrm{emb}}(r) = v_{\mathrm{emb}}[\rho_A, \rho_B, v_B](r)$$

FDET in capsule: variational method to obtain embedded wavefunction Ψ_A

1) Constraint for the total density (ρ_B – is arbitrary)

$$E_{\mathrm{emb}}[\rho_B] = \min_{\substack{\rho(\mathbf{r}) \geq \rho_B(\mathbf{r}) \geq 0 \\ \int \rho(\mathbf{r})\mathrm{d}\mathbf{r} = N_{AB}}} E_v^{\mathrm{HK}}[\rho]$$

2) Energy as the functional of ρ_B and Ψ_A

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

3) Euler-Lagrange equation

$$\frac{\delta E_{AB}^{EWF}[\Psi_A^{emb}, \rho_B]}{\delta \Psi_A^{emb}} - \lambda \Psi_A^{emb} = 0,$$

4) Functional for the local embedding potential

$$v_{emb}[\rho_A, \rho_B, v_B](\vec{r}) = v_B(\vec{r}) + \int \frac{\rho_B(\vec{r'})}{|\vec{r'}-\vec{r}|}d\vec{r'} + \frac{\delta E_{xct}^{nad}[\rho_A,\rho_B]}{\delta\rho_A(\vec{r})}$$

Attention:
inhomogeneity of the "interaction energy functional"

$$\left\langle \Psi^A|\hat{v}_{emb}|\Psi^A\right\rangle = \int \rho_A(\vec{r})v_{emb}[\rho_A,\rho_B;\vec{r}]d\vec{r}$$

$$\neq T_s^{nad}[\rho_A,\rho_B] + E_{xc}^{nad}[\rho_A,\rho_B] + \int \rho_A(\vec{r})v_B(\vec{r})d\vec{r} + \int\int \frac{\rho_A(\vec{r})\rho_B(\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r'}d\vec{r}$$

T.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
K. Pernal and T.A. Wesolowski, *Intl.J. Quant. Chem.* **2009,** *109,* 2520

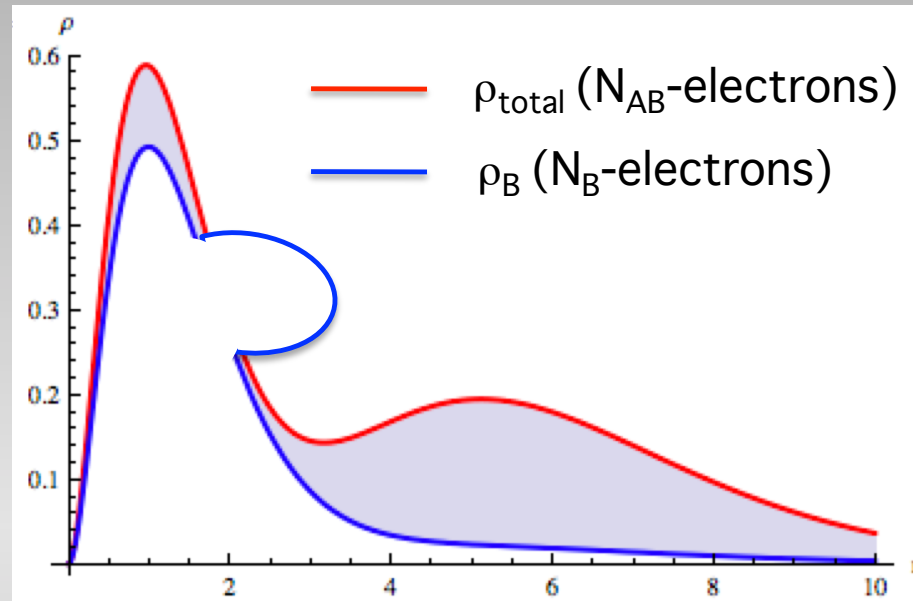# FDET: case of $\rho_o(r) \geq \rho_B(r)$ (for all r)
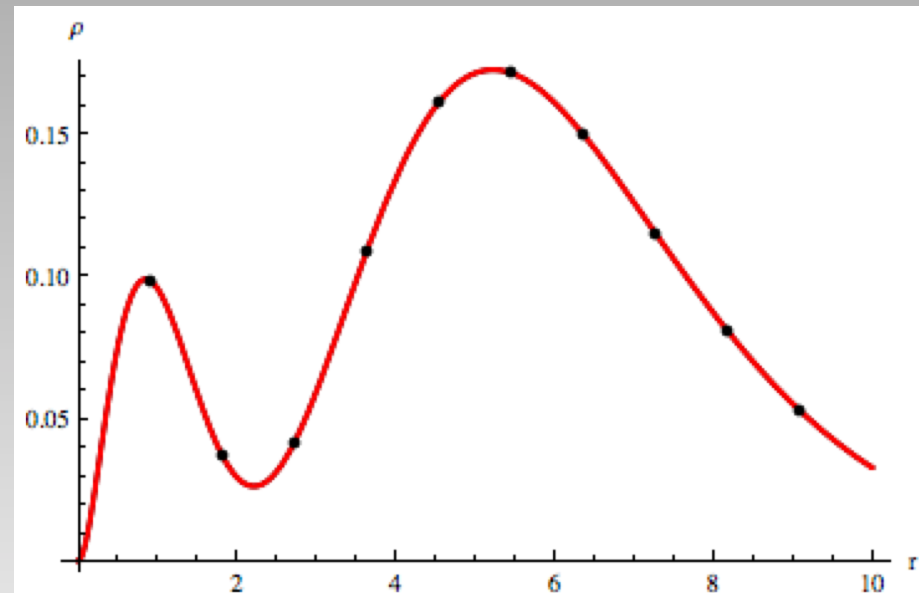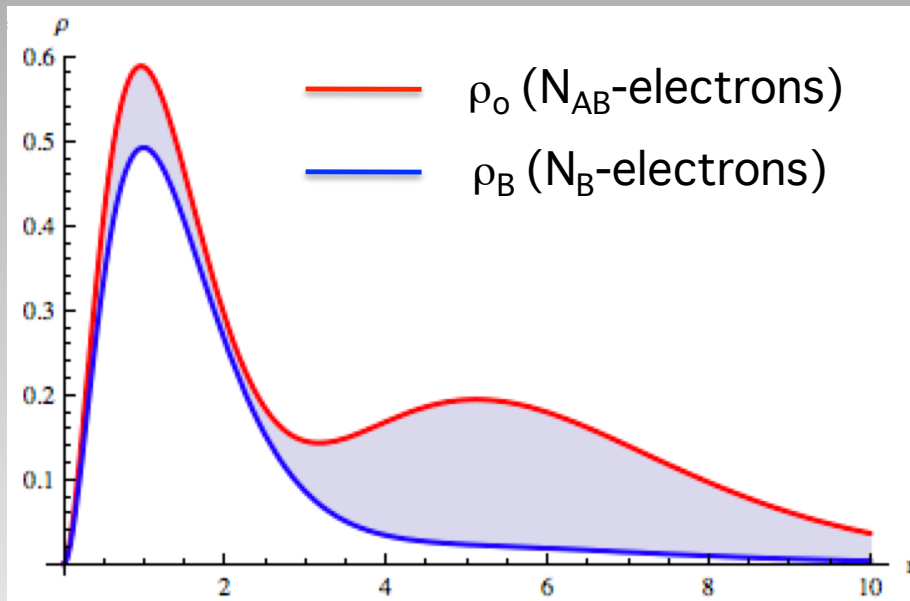
Target:

the grey density $(\rho_{total} - \rho_B)$ as a ground-state of a N_A electron system obtained by adding **a local potential** to a N_A-electron Hamiltonian

Results:

$$\rho_o = \rho_{total} = \rho_B + \rho_A{}^{opt} \quad \text{and} \quad E_{emb}[\rho_B] = E_o$$

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

$$\rho_o \neq \rho_{total} = \rho_B + \rho_A^{opt}$$

$$E_{emb}[\rho_B] \geq E_o$$

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 ρ_B

2) Fully self-consistent expressions for:
   i) optimal energy ($E_{emb}[\rho_B]$), *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 ($E_{emb}[\rho_B] \geq E_o$)

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 :

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

$$T_s^{nad}[\rho_A, \rho_B] = \min_{\Psi_s \to \rho_A + \rho_B} \langle \Psi_s | \hat{T} | \Psi_s \rangle - \min_{\Psi_s \to \rho_A} \langle \Psi_s | \hat{T} | \Psi_s \rangle - \min_{\Psi_s \to \rho_B} \langle \Psi_s | \hat{T} | \Psi_s \rangle$$

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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 $v_{KS}[\rho_A]$ component is recalculated as ρ_A changes. (b) The conventional SCF scheme: Both $v_{KS}[\rho_A]$ and $v_{emb}[\rho_A, \rho_B]$ are recalculated as ρ_A changes.
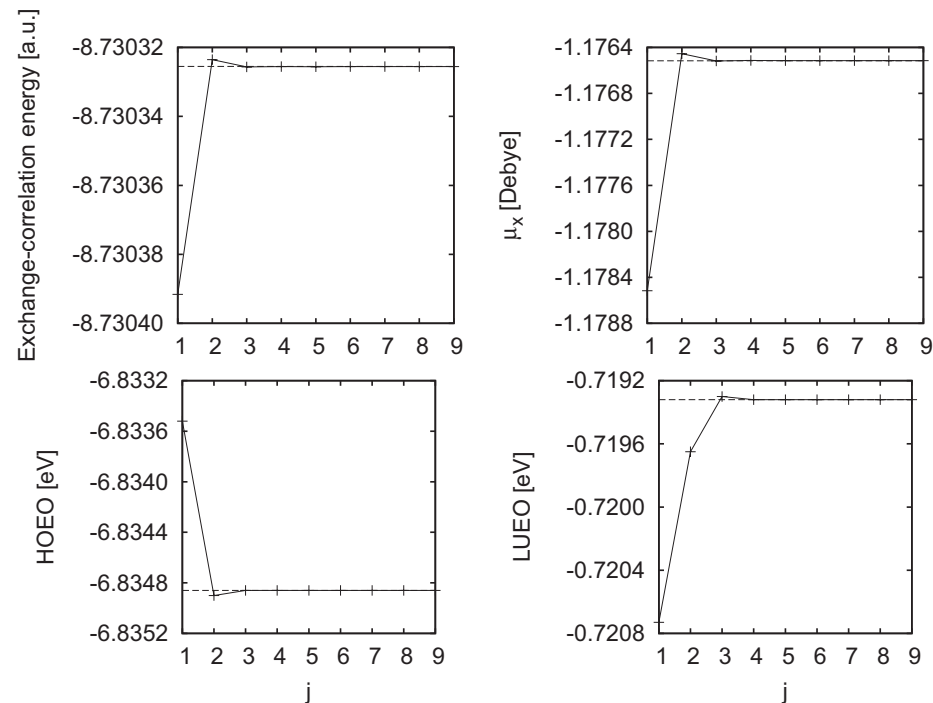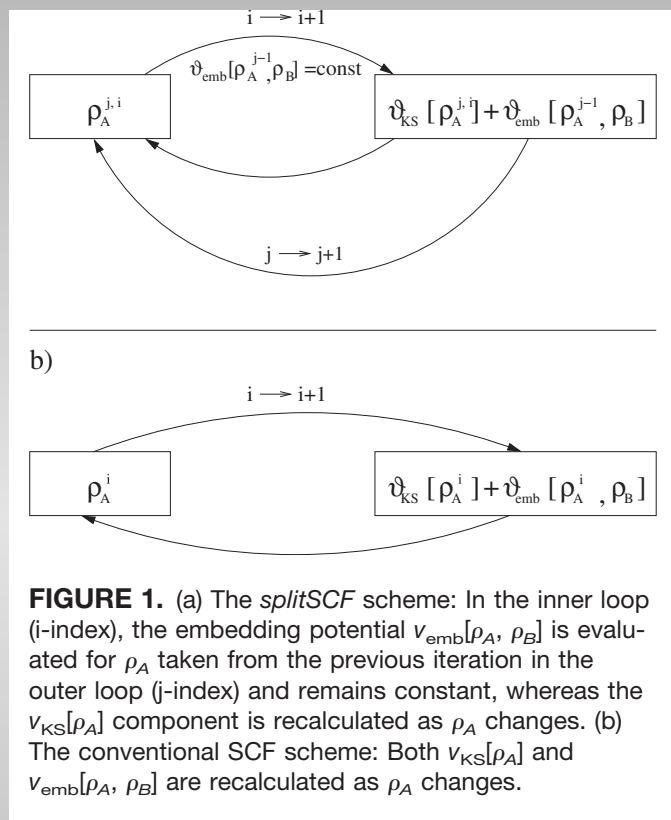
FIGURE 2. The convergence of the outer-loop of the *splitSCF* procedure for various properties of the H_2O molecule in the H_2O-H_2O complex. The results of conventional self-consistent calculations are indicated by dashed lines.

Split-SCF FDET calculations for each electronic state
(self-consistent potential and embedded wavefunction but non-orthogonal embedded wavefunctions for different states)
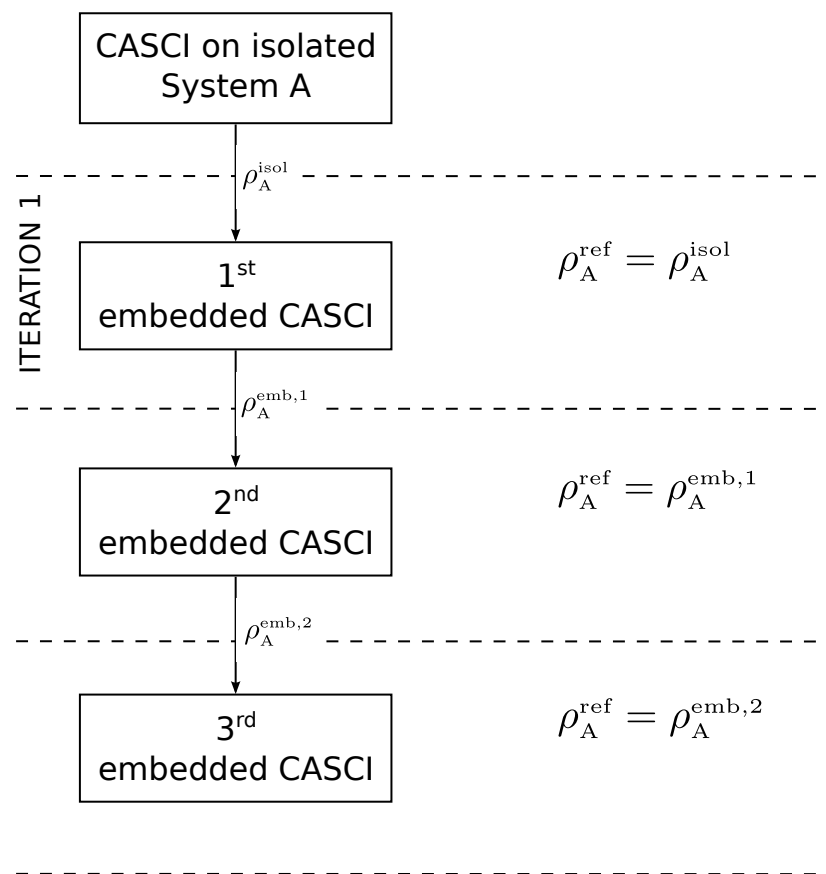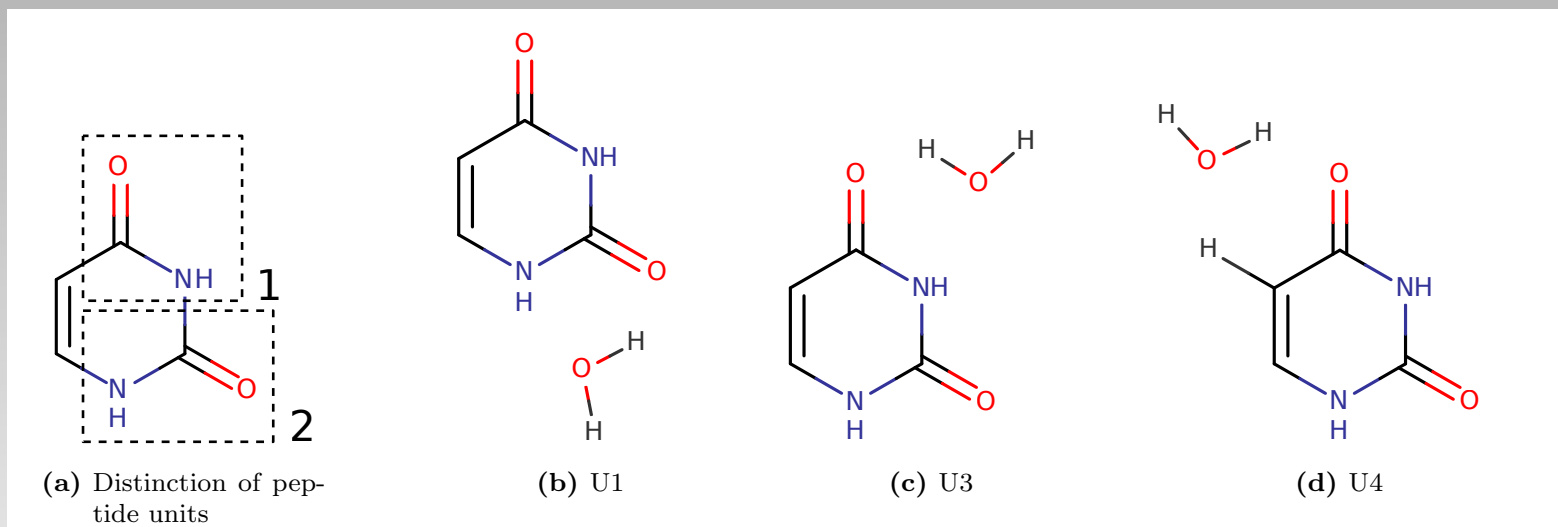

Figure 1: CASCI iteration cycles with regard to ρ_A updates.

(a) Distinction of peptide units

(b) U1

(c) U3

(d) U4

$S_0 \rightarrow$	Character of excitation		
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	mostly $\pi_1(N)$	$\rightarrow$	π_{ring}^*

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

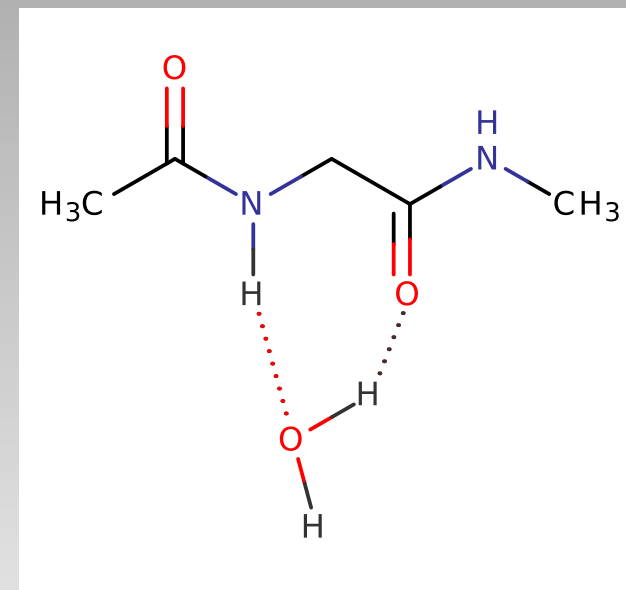|	Ψ_0^{sc}	Ψ_1^{sc}	Ψ_2^{sc}	Ψ_3^{sc}	Ψ_4^{sc}
Ψ_0^{sc}	1				
Ψ_1^{sc}	1.00E-08	1			
Ψ_2^{sc}	5.19E-06	-2.00E-08	1		
Ψ_3^{sc}	1.25E-06	9.02E-05	-3.41E-05	1	
Ψ_4^{sc}	7.10E-07	-4.00E-08	-2.47E-05	7.09E-05	1

$$\langle \Psi_A^k | \Psi_A^m \rangle$$

Embedded dipeptide
(embedded CASCI reference system)

$S_0 \rightarrow$	Character of excitation		
S_1	$n_1(O)$	$\rightarrow$	$\pi_1^*(CO)$
S_2	$n_2(O)$	$\rightarrow$	$\pi_2^*(CO)$
S_3	$\pi_1(CO)$ $\pi_1(N)$	$\rightarrow$	$\pi_2^*(CO)$ $\pi_1^*(N)$
S_4	$\pi_2(N)$	$\rightarrow$	$\pi_2^*(CO)$
S_5	$n_1(O)$ $\pi_1(N)$	$\rightarrow$	$\pi_2^*(CO)$ $\pi_2^*(N)$
S_6	$\pi_1(N)$	$\rightarrow$	$\pi_1^*(CO)$
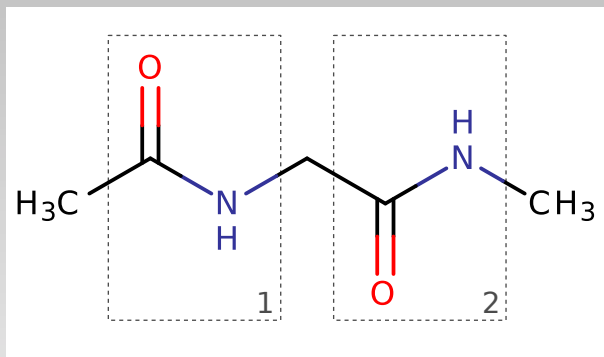
(a) Distinction of peptide units

(b) Dipeptide-H_2O complex

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_3^{sc}	-5.20E-07	2.10E-07	-1.71E-04	1			
Ψ_4^{sc}	2.45E-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	1.57E-05	1	
Ψ_6^{sc}	-4.27E-06	-1.45E-06	-2.51E-05	1.17E-05	2.58E-06	1.03E-04	1

$\langle \Psi_A^k | \Psi_A^m \rangle$
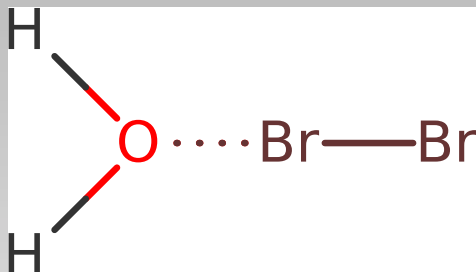
Embedded bromine
(embedded CASCI reference system)

Figure 12: Br_2-H_2O complex.

$S_0 \rightarrow$	Character of excitation		
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^*

Table 21: 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_0^{sc}	1					
Ψ_1^{sc}	1.09E-06	1				
Ψ_2^{sc}	-7.00E-08	6.60E-07	1			
Ψ_3^{sc}	6.00E-08	2.31E-05	0.00E+00	1		
Ψ_4^{sc}	6.00E-08	0.00E+00	2.66E-05	2.90E-07	1	
Ψ_5^{sc}	1.10E-06	-2.82E-06	2.60E-07	-6.85E-06	4.00E-07	1

$<\Psi_A{}^k|\Psi_A{}^m>$

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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$$\frac{\delta E_{AB}^{EWF}[\Psi_A^{emb}, \rho_B]}{\delta \Psi_A^{emb}} - \lambda \Psi_A^{emb} = 0,$$

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

FDET

[Wesolowski, Phys. Rev.A. **77** (2008) 012504]

$$E_{AB}^{EWF}[\Psi^A, \rho_B] = <\Psi^A|\hat{H}_A|\Psi^A> + \int \rho_A(\vec{r})v_B(\vec{r})d\vec{r} + \int\int \frac{\rho_A(\vec{r})\rho_B(\vec{r'})}{|\vec{r}-\vec{r'}|}d\vec{r'}d\vec{r}$$

$$+ \quad E_{xct}^{nad}[\rho_A, \rho_B] + E_{v_B}^{HK}[\rho_B] + \int \rho_B(\vec{r})v_A(\vec{r})d\vec{r},$$

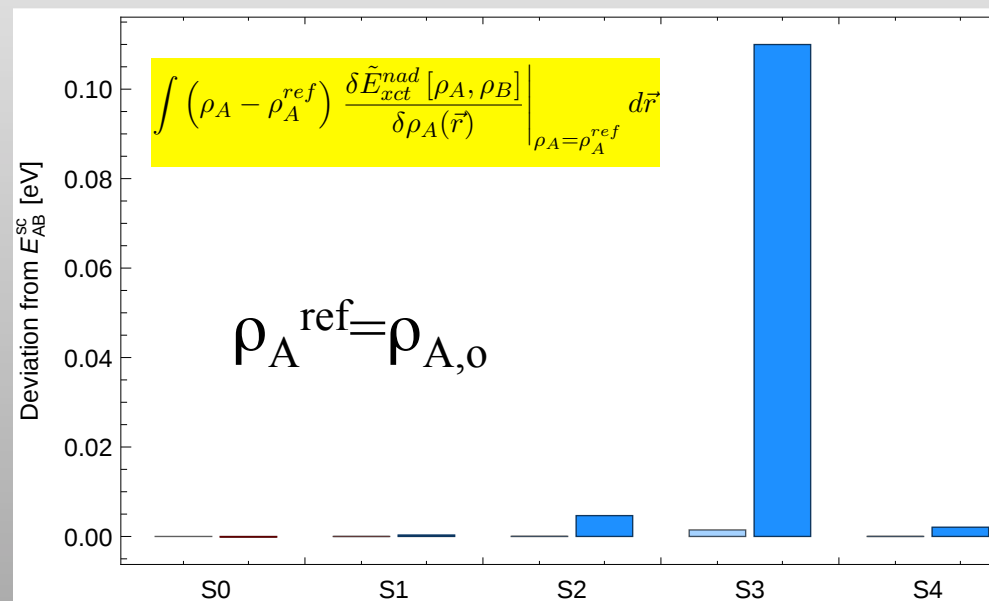$$E_{xct}^{nad}[\rho_A, \rho_B] = E_{xc}^{nad}[\rho_A, \rho_B] + T_s^{nad}[\rho_A, \rho_B] + \Delta F^{SC}[\rho_A]$$

$$\tilde{v}_{emb}[\rho_A^{ref}, \rho_B, v_B]\vec{r} = v_B(\vec{r}) + \int \frac{\rho_B(\vec{r'})}{|\vec{r'}-\vec{r}|}d\vec{r'} + \frac{\delta \tilde{E}_{xct}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}$$

$$<\Psi_A{}^k|\Psi_A{}^m> \neq \delta_{km}$$

Linearized FDET

[Wesolowski, J. Chem. Phys. **140** (2014) 18A530]

$$E_{xct}^{nad}[\rho_A, \rho_B] \approx \tilde{E}_{xct}^{nad}[\rho_A, \rho_B] \approx \tilde{E}_{xct}^{nad(lin)}[\rho_A, \rho_B] = \tilde{E}_{xct}^{nad}\left[\rho_A^{ref}, \rho_B\right] + \int \left(\rho_A - \rho_A^{ref}\right) \frac{\delta \tilde{E}_{xct}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}\bigg|_{\rho_A=\rho_A^{ref}} d\vec{r}$$

$$\tilde{v}_{emb}[\rho_A^{ref}, \rho_B, v_B]\vec{r} = v_B(\vec{r}) + \int \frac{\rho_B(\vec{r'})}{|\vec{r'}-\vec{r}|}d\vec{r'} + \frac{\delta \tilde{E}_{xct}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})}\bigg|_{\rho_A=\rho_A^{ref}}$$

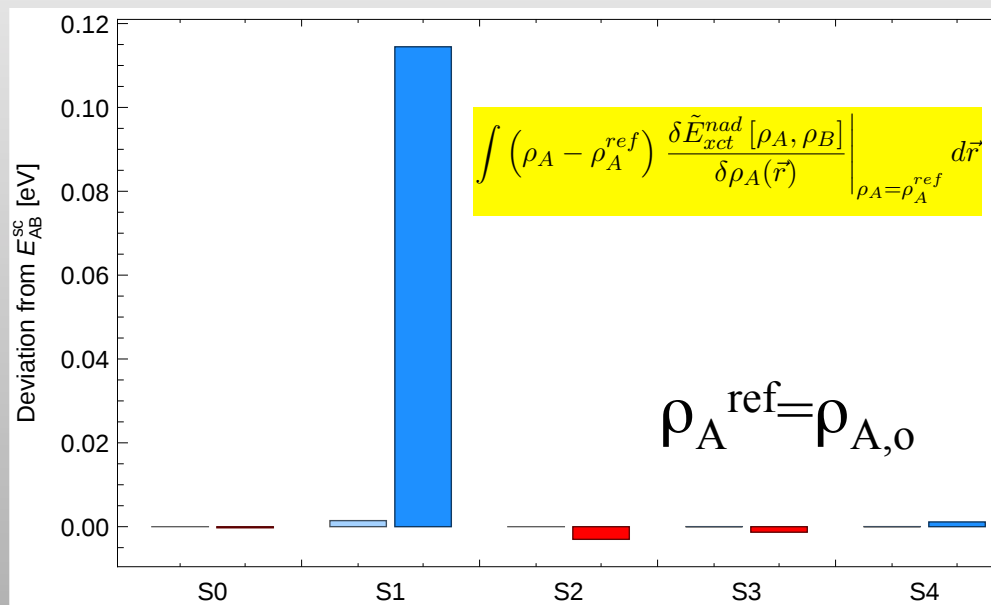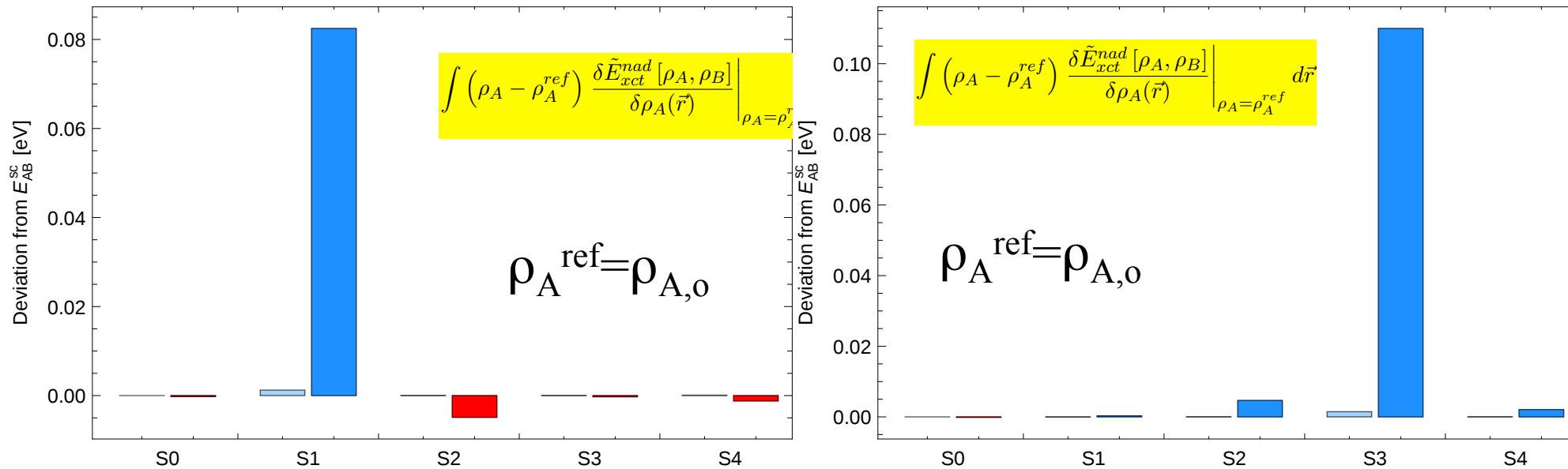$$<\Psi_A{}^k|\Psi_A{}^m> = \delta_{km}$$

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

$$\int \left(\rho_A - \rho_A^{ref} \right) \left. \frac{\delta \tilde{E}_{xct}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A = \rho_A^{ref}} d\vec{r}$$

$\rho_A^{ref} = \rho_{A,o}$

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
$\rho_{A,1}$	6.23E-07	**6.00**	3.82E-06	3.56E-06	1.28E-07	3.84E-06	3.80E-06
$\rho_{A,2}$	-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
$\rho_{A,4}$	4.63E-07	-2.20E-07	3.52E-06	3.48E-06	**8.82**	3.44E-06	3.69E-06
$\rho_{A,5}$	-2.73E-06	-3.72E-06	1.28E-07	1.28E-07	-3.42E-06	**9.25**	3.48E-07
$\rho_{A,6}$	-3.11E-06	-3.84E-06	1.01E-07	-2.34E-07	-3.66E-06	-5.99E-08	**9.38**
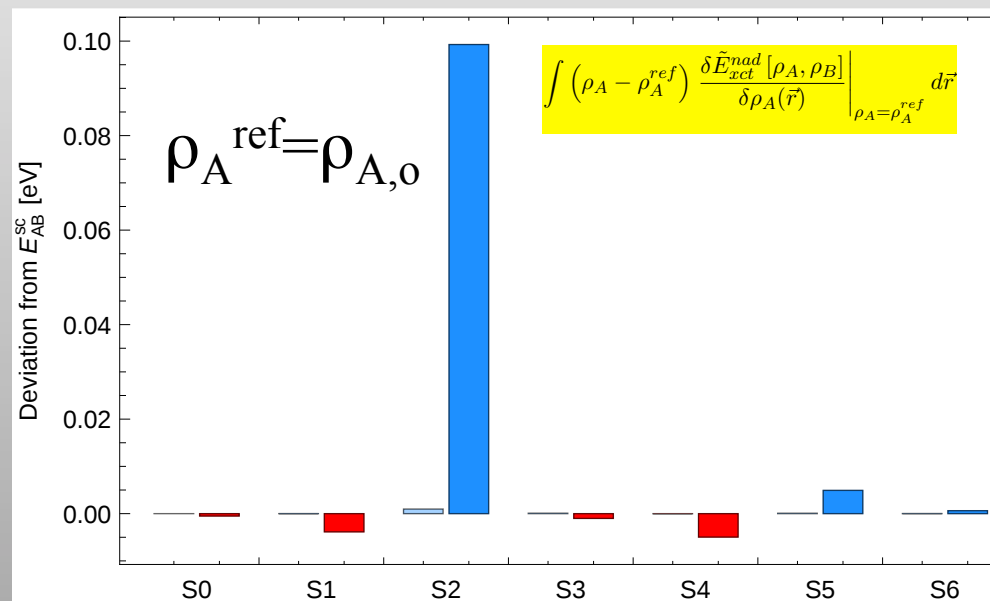
$$\int \left(\rho_A - \rho_A^{ref} \right) \left. \frac{\delta \tilde{E}_{xct}^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \right|_{\rho_A = \rho_A^{ref}} d\vec{r}$$

$\rho_A{}^{ref} = \rho_{A,o}$

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
$\rho_{A,1}$	-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
$\rho_{A,3}$	-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
$\rho_{A,5}$	7.67E-07	2.42E-06	6.99E-07	2.11E-06	1.89E-06	**6.04**

$$\int \left(\rho_A - \rho_A^{ref} \right) \frac{\delta \tilde{E}_{xct}^{nad} [\rho_A, \rho_B]}{\delta \rho_A(\vec{r})} \Bigg|_{\rho_A = \rho_A^{ref}} d\vec{r}$$

$$\rho_A^{ref} = \rho_{A,o}$$
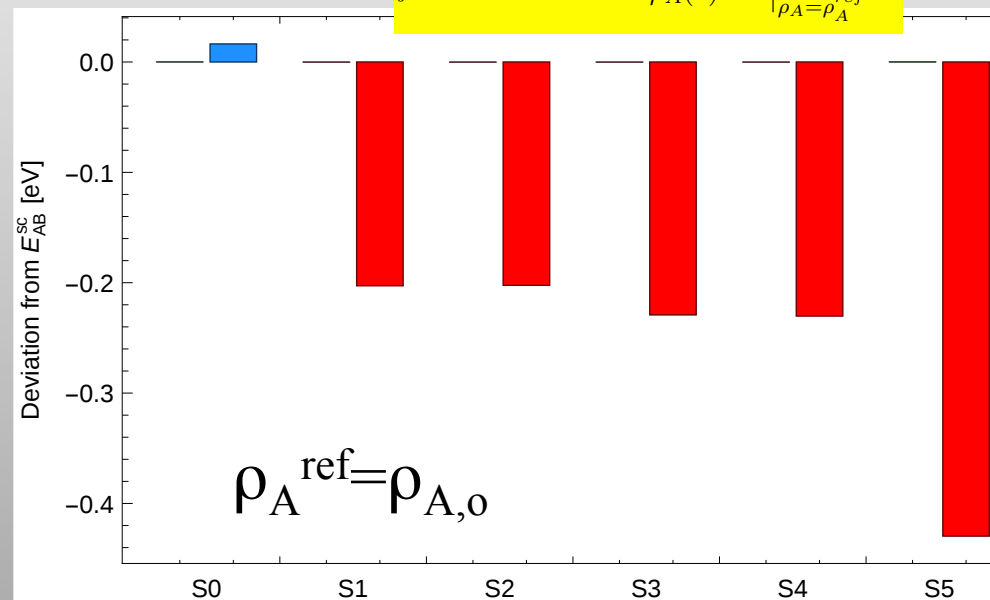
Partial conclusions (2):

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 ρ_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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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

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

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

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

$$
\begin{aligned}
T_s[\rho] &\neq \int \rho(\vec{r}) \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} d\vec{r}, \\
E_x[\rho] &\neq \int \rho(\vec{r}) \frac{\delta E_x[\rho]}{\delta \rho(\vec{r})} d\vec{r}, \\
E_c[\rho] &\neq \int \rho(\vec{r}) \frac{\delta E_c[\rho]}{\delta \rho(\vec{r})} d\vec{r},
\end{aligned}
$$

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

Uracil-water (conf U1)

$$\Delta_k = E_{int}[\rho_k] - \langle\Psi_k|v_{emb}[\rho_{A,k}]|\Psi_k\rangle$$

State (k)	Δ_k [Hartree]	Δ_k-Δ_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)

$$\Delta_k = E_{int}[\rho_k] - \langle\Psi_k|v_{emb}[\rho_{A,k}]|\Psi_k\rangle$$

State (k)	Δ_k [Hartree]	$\Delta_k - \Delta_0$ [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)

$$\Delta_k = E_{int}[\rho_k] - \langle \Psi_k | v_{emb}[\rho_{A,k}] | \Psi_k \rangle$$

State (k)	Δ_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

$$\Delta_k = E_{int}[\rho_k] - \langle \Psi_k | v_{emb}[\rho_{A,k}] | \Psi_k \rangle$$

State (k)	Δ_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

$$\Delta_k = E_{int} [\rho_k] - \langle\Psi_k|v_{emb}[\rho_{A,k}]|\Psi_k\rangle$$

State (k)	Δ_k [Hartree]	Δ_k-Δ_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 ρ_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).

CHEMICAL REVIEWS

Frozen-Density Embedding Strategy for Multilevel Simulations of Electronic Structure

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FDET related research topics at University of Geneva

Approximations for $T_s^{nad}[\rho_A, \rho_B]$
Wesolowski, *J. Chem. Phys.* **106**, 1997, 8516;
Garcia Lastra et al., *J. Chem. Phys.* **129** (2008) 074107;
Bernard et al. *J. Phys. A.* **41** (2008) 055302;
Savin & Wesolowski, in "Recent Progress in OF-DFT", WORLD SCIENTIFIC 2013

Analytically solvable model systems
Savin & Wesolowski *Prog. Theor. Chem.& Phys.* **19** (2009) 327;
De Silva & Wesolowski, *J. Chem. Phys.* **137** (2012) 094110

Multi-level FDET based continnum solvent model
Kaminski et al., *J. Phys. Chem A*, **114** (2010) 6082;
Zhou et al., *Phys.Chem.Chem.Phys.*, **13** (2011) 10565

ρ_A dependency of $V_{emb}{}^{FDET}[\rho_A,\rho_B;r]$
linearization
Dulak et al., *Intl. J. Quant. Chem.*, **109** (2009) 1883
state-dependency for excited states
Wesolowski, *J. Chem. Phys* , **140**, (2014) 18A530

$$\frac{\delta E_{AB}^{EWF}[\Psi_A^{emb}, \rho_B]}{\delta \Psi_A^{emb}} - \lambda \Psi_A^{emb} = 0,$$

FDET based mullti-level models of molecular environments
UV/Vis, ESR, NMR
clusters:
Fradelos et al., *J. Phys. Chem. A* **113** (2009) 9766
porous solids:
Zhou et al., *Phys. Chem. Chem. Phys*, **15**, (2013) 159
proteins:
Zhou et al., *J. Am. Chem. Soc.*, **136**, (2014) 2723

Algorithms and code developments
eveluation of particular properties, ρ_B- generation,
deMon, deMon2K, ADF, MOLCAS

Approximations for $\Delta F^{MD}[\rho_A]$
Aquilante & Wesolowski, *J. Chem. Phys.*, **135** (2011) 084120

Extracting chemical information from electron density
(single exponential decay detector, SEDD)
de Silva et al, *ChemPhysChem*, **13**,(2012) 3462;
J. Chem. Phys., **140**, (2014) 164301