

Constrained minimisation of the Hohenberg-Kohn energy functional: challenge for theory and opportunities for multi-scale simulations

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Lecture on Frozen-Density Embedding Theory (FDET) at QIF23

- 1 Notation, terminology, statement of the problem
 - What we will need for this lecture?
 - What is FDET about?
- 2 Variants of FDET
 - Density functionals defined in constrained search
 - FDET for variational embedded wavefunction and interacting Hamiltonian
 - Ψ_A of a Full Configuration Interaction form
 - Ψ_A of a single determinant form
- 3 Approximations for numerical applications
 - Upper bound of E_{VAB}^0 from FDET
 - Excited states
 - State-independent ρ_B
 - State-specific ρ_B
 - Approximating the $T_s^{nad}[\rho_A, \rho_B]$ component of $E_{xct}^{nad}[\rho_A, \rho_B]$
- 4 Combining physical laws for different scales in FDET



- **Variational principle in QM:**

$$\min_{\Psi \rightarrow N} \langle \Psi | \hat{H}_v | \Psi \rangle = \langle \Psi^0 | \hat{H} | \Psi^0 \rangle = E_v^0$$

- **Perturbation theory (first order):**

For two N-electron Hamiltonians (\hat{H}' and \hat{H}) with Ψ^0 being the ground-state wavefunction for \hat{H} :

$$E'^0 - E^0 = \langle \Psi^0 | \hat{H}' - \hat{H} | \Psi^0 \rangle + \text{higher orders}$$

$$E'^0 - E^0 = \int \rho^0(\mathbf{r}) (v'(\mathbf{r}) - v(\mathbf{r})) d\mathbf{r} + \text{higher orders} \leftarrow \text{if } \hat{H}' - \hat{H} \text{ is a potential}$$

- **Density Functional Theory:**

$$\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H}_v | \Psi \rangle = E_v^{HK}[\rho] \leftarrow \text{The Hohenberg-Kohn density functional}$$

$$\min_{\rho \rightarrow N} E_v^{HK}[\rho] = E_v^{HK}[\rho^0] = E_v^0 \leftarrow \text{The second Hohenberg-Kohn theorem}$$



Functional derivative of a functional $F[\rho]$

$$v_F[\rho](\mathbf{r}) \equiv \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} = \lim_{h \rightarrow 0} \frac{F[\rho + h \cdot g(\mathbf{r})] - F[\rho]}{h}$$

for any admissible function $g(\mathbf{r})$

Attention "false friend"! usually $F[\rho] \neq \int v_F[\rho](\mathbf{r}) \cdot \rho(\mathbf{r}) d\mathbf{r}$



The functional $E_v^{HK}[\rho]$ for $\rho \neq \rho_v^0$

$$\min_{\Psi_{AB} \rightarrow \rho_{AB}} \langle \Psi_{AB} | \hat{H}_{AB} | \Psi_{AB} \rangle = E_{v_{AB}}^{HK}[\rho_{AB}] \geq E_{v_{AB}}^{HK}[\rho_{AB}^0] = E_{v_{AB}}^0$$

Notation: N_{AB} - number of electrons ($N_{AB} = N_A + N_B$), v_{AB} - external potential ($v_{AB} = v_A + v_B$).

Why to consider $E_{v_{AB}}^{HK}[\rho_{AB}]$ for other densities than the ground-state density?

- The $E_{v_{AB}}^{HK}[\rho_{AB}]$ might have other stationary points than ρ_{AB}^0
Perdew-Levy theorem on extrema of $E_v^{HK}[\rho]$
- Behaviour of $E_{v_{AB}}^{HK}[\rho_{AB}]$ at $\rho_{AB} \approx \rho_{AB}^0$
response theory, reactivity indices, numerical algorithms:
- **Minimisation of $E_{v_{AB}}^{HK}[\rho_{AB}]$ with additional constraints imposed on ρ_{AB}**
Case of FDET: the constraint is $\forall_{\mathbf{r}} \rho_{AB}(\mathbf{r}) \geq \rho_B(\mathbf{r})$



Why this constraint: $\forall_{\mathbf{r}} \rho_{AB}(\mathbf{r}) \geq \rho_B(\mathbf{r})$?

Frequently, we know something about the total density and we would like to use this knowledge in setting up a numerical simulation:

$$\rho_{AB} \approx \rho_A^{\text{unknown}} + \rho_B^{\text{known}}$$

- **Core-valence separation:**

ρ_B^{known} - density of core electrons, ρ_A^{unknown} density of valence electrons

- **Multi-level/multi-scale simulations:**

ρ_A^{unknown} obtained from embedded N_A electron wavefunction (Ψ_A with $N_A < N_{AB}$) and ρ_B from experiment or from inexpensive methods.

We cannot assure, however, that there exists such ρ_A that

$$\forall_{\mathbf{r}} \left(\rho_A(\mathbf{r}) + \rho_B^{\text{known}}(\mathbf{r}) = \rho_{vAB}^0(\mathbf{r}) \right)$$

the functional $E_{vAB}^{HK}[\rho_{AB}]$ must be considered for other than ground-state densities.



Frozen-Density Embedding Theory (FDET) concerns the **constrained optimisation of the Hohenberg-Kohn functional**:

$$\text{Energy}^{\text{FDET}} = \min_{\substack{\rho(\mathbf{r}) \rightarrow N_{AB} \\ \forall \mathbf{r} \rho(\mathbf{r}) \geq \rho_B(\mathbf{r})}} E_{v_{AB}}^{\text{HK}}[\rho]$$

Note the difference with the second Hohenberg-Kohn theorem:

$$E_{v_{AB}}^0 = \min_{\rho(\mathbf{r}) \rightarrow N_{AB}} E_{v_{AB}}^{\text{HK}}[\rho]$$

$\text{Energy}^{\text{FDET}}$ is thus the **lowest possible energy** (not necessarily $E_{v_{AB}}^0 = E_{v_{AB}}^{\text{HK}}[\rho_{AB}^0]$) for the total density constructed as $\rho_{AB} = \rho_A + \rho_B^{\text{known}}$.

Since good approximations for the explicit density functional ($E_v^{\text{HK}}[\rho] \approx \tilde{E}_v^{\text{HK}}[\rho]$) do not exist, the constrained optimisation problem must be formulated not for ρ_A but for some auxiliary quantum mechanical descriptors for the embedded N_A electrons.



Examples of relations between quantum mechanical descriptors (X_{AB}) and $E_{vAB}^{HK}[\rho_{AB}]$
for a system of N_{AB} electrons in an external potential $v_{AB}(\mathbf{r})$

- $X_{AB} = \rho_{AB}$ (Orbital-free DFT):

$$\min_{\rho_{AB} \rightarrow N_{AB}} E_{vAB}^{HK}[\rho_{AB}] = E_{vAB}^{HK}[\rho_{AB}^0] = E_{vAB}^0$$

- $X_{AB} = \Phi_{AB}^{KS}$ (Kohn-Sham DFT):

$$\min_{\Phi_{AB}^{KS} \rightarrow N_{AB}} \langle \Phi_{AB}^{KS} | \hat{H}_{AB}^{KS} | \Phi_{AB}^{KS} \rangle = E_{vAB}^{HK}[\rho_{AB}^0] + \int \rho_{AB}^0 v_{xc}[\rho_{AB}^0] d\mathbf{r} - E_{xc}[\rho_{AB}^0] + \frac{1}{2} J[\rho_{AB}^0]$$

- $X_{AB} = \Psi_{AB}$ (Variational methods - interacting Hamiltonians):

$$\min_{\Psi_{AB} \rightarrow N_{AB}} \langle \Psi_{AB} | \hat{H}_{AB} | \Psi_{AB} \rangle = E_{vAB}^{HK}[\rho_{AB}^0]$$

- $X_{AB} = \Phi_{AB}^{HF}, E_{vAB}^{corr}$ (Non-variational methods - interacting Hamiltonians):

$$\min_{\Phi_{AB}^{HF} \rightarrow N_{AB}} \langle \Phi_{AB}^{HF} | \hat{H}_{AB} | \Phi_{AB}^{HF} \rangle = E_{vAB}^{HK}[\rho_{AB}^0] - E_{vAB}^{corr}$$



The basic equality enforced in the construction of the FDET energy functional

$$\text{Energy}^{\text{FDET}}(X_A^{\text{min}}, \rho_B) = E_{\text{vAB}}^{\text{HK}}[\rho = \rho(X_A^{\text{min}}) + \rho_B]$$

- X_A is a quantum mechanical descriptor (or descriptors) for $N_A < N_{AB}$ electrons, which is (are) available in multi-level level simulations (Kohn-Sham orbitals, embedded wavefunction, correlation energy, density matrix, etc.). The subsystem for which X_A is used as a descriptor will be labelled as **quantum system**.
- $\rho_B(\vec{r})$ is a non-negative function such that $\int \rho_B = N_B = N_{AB} - N_A$. The subsystem for which ρ_B is used as a descriptor will be labelled **environment**.
- The total density $\rho(\vec{r})$ is constructed in the **bottom-up** way using the available quantum mechanical descriptor for N_A electrons and a given ρ_B :

$$\rho = \rho_A(X_A) + \rho_B$$



The descriptor X_A , for which the basic energy equality of FDET holds, is obtained in the constrained minimisation of $E_{v_{AB}}^{HK}[\rho]$:

$$\text{Energy}^{FDET}(X_A^{min}, \rho_B) = \overbrace{\min_{X_A \rightarrow N_A} \text{Energy}^{FDET}(X_A, \rho_B)}^{N_A\text{-electron problem}} = \overbrace{\min_{\substack{\rho(r) \rightarrow N_{AB} \\ \forall r \rho(r) \geq \rho_B(r)}} E_{v_{AB}}^{HK}[\rho]}^{N_{AB}\text{-electron problem}}$$

- Nothing is over- or undercounted: the basic FDET equality for energy
- Any theory - classical or quantum - can be used to generate ρ_B
- Optimal X_A from the Euler-Lagrange equation

From now on, we consider some arbitrary splitting of the total external potential ($v_{AB} = v_A + v_B$) defining the Hamiltonian \hat{H}_A and the functional $E_{v_B}^{HK}[\rho_B]$.



The functionals in Kohn-Sham DFT defined implicitly [M. Levy, *Proc. Natl. Acad. Sci. USA*, **76** (1972) 6062]

$$\min_{\tilde{\Psi} \rightarrow \rho} \langle \tilde{\Psi} | \hat{T} + \hat{V}^{ee} | \tilde{\Psi} \rangle = \langle \tilde{\Psi}^o[\rho] | \hat{T} + \hat{V}^{ee} | \tilde{\Psi}^o[\rho] \rangle = T[\rho] + V_{ee}[\rho] \leftarrow \text{variational principle}$$

Ψ is N - representable

$$\min_{\tilde{\Psi}_s \rightarrow \rho} \langle \tilde{\Psi}_s | \hat{T} | \tilde{\Psi}_s \rangle = \langle \tilde{\Psi}_s^o[\rho] | \hat{T} | \tilde{\Psi}_s^o[\rho] \rangle = T_s[\rho] \leftarrow \text{Kohn - Sham DFT (Levy)}$$

Ψ_s is single - determinant : $\Psi_s \equiv \Phi$

$$E_{xc}[\rho] = V_{ee}[\rho] - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + T[\rho] - T_s[\rho]$$

$$E_c[\rho] \equiv T[\rho] + V_{ee}[\rho] - \min_{\tilde{\Phi} \rightarrow \rho} \langle \tilde{\Phi} | \hat{T} + \hat{V}^{ee} | \tilde{\Phi} \rangle$$

For FDET:

$$\text{where } E_{xcT}^{nad}[\rho_A, \rho_B] \equiv T_s^{nad}[\rho_A, \rho_B] + E_{xc}^{nad}[\rho_A, \rho_B]$$

$$E_{xc}^{nad}[\rho_A, \rho_B] \equiv E_{xc}[\rho_A + \rho_B] - E_{xc}[\rho_A] - E_{xc}[\rho_B]$$

$$T_s^{nad}[\rho_A, \rho_B] \equiv T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B]$$

Case of variational embedded wavefunction and interacting Hamiltonian

Embedding a multi-determinantal wavefunction in orbital-free environment

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



The total energy functional (Full CI form of Ψ_A)

$$\begin{aligned}
 E_{VAB}^{\text{FDET}}[\Psi_A, \rho_B] &= \langle \Psi_A | \hat{H}_A + \hat{v}_{\text{emb}}^{\text{FDET}}[\rho_A, \rho_B; v_B] | \Psi_A \rangle + E_{\text{xcT}}^{\text{nad}}[\rho_A, \rho_B] \\
 &- \int (v_{\text{xcT}}^{\text{nad}}[\rho_A, \rho_B](\mathbf{r})) \rho_A(\mathbf{r}) d\mathbf{r} + E_{v_B}^{\text{HK}}[\rho_B] + V_A[\rho_B]
 \end{aligned}$$

 Ψ_A^0 from Euler-Lagrange equation

$$\frac{\delta E_{VAB}^{\text{FDET}}[\Psi_A, \rho_B]}{\delta \Psi_A} - \lambda \Psi_A = 0 \quad \longrightarrow \quad [\hat{T}_{N_A} + \hat{V}_{N_A}^{\text{ee}} + \hat{V}_A + \hat{v}_{\text{emb}}^{\text{FDET}}[\rho_A, \rho_B; v_B]] \Psi_A = \lambda \Psi_A$$

with the multiplicative embedding operator (embedding potential)

$$\begin{aligned}
 \hat{v}_{\text{emb}}^{\text{FDET}} &= v_{\text{emb}}^{\text{FDET}}[\rho_A, \rho_B, v_B](\mathbf{r}) \\
 &= v_B(\mathbf{r}) + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \left. \frac{\delta E_{\text{xcT}}^{\text{nad}}[\rho, \rho_B]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r})=\rho_A(\mathbf{r})=\langle \Psi_A | \hat{n} | \Psi_A \rangle}
 \end{aligned}$$



The total energy functional ($\Psi_s \equiv \Phi_A \leftarrow$ single determinant form)

$$E_{v_{AB}}^{\text{FDET}}[\Phi_A, \rho_B] = \langle \Phi_A | \hat{H}_A + \hat{v}_{emb}^{\text{FDET}}[\rho_A, \rho_B; v_B] | \Phi_A \rangle + E_{xcT}^{\text{nad}}[\rho_A, \rho_B] + E_c[\rho_A] \\ - \int \left(v_{xcT}^{\text{nad}}[\rho_A, \rho_B](\mathbf{r}) + v_c[\rho_A](\mathbf{r}) \right) \rho_A(\mathbf{r}) d\mathbf{r} + E_{v_B}^{\text{HK}}[\rho_B] + V_A[\rho_B]$$

Φ_A^0 from Euler-Lagrange equation

$$\frac{\delta E_{v_{AB}}^{\text{FDET}}[\Phi_A, \rho_B]}{\delta \Phi_A} - \lambda \Phi_A = 0 \quad \rightarrow \quad \left[\hat{T}_{N_A} + \hat{V}_{N_A}^{ee} + \hat{V}_A + \hat{v}_{emb}^{\text{FDET}}[\rho_A, \rho_B; v_B] \right] \Phi_A = \lambda \Phi_A$$

with the multiplicative embedding operator (embedding potential)

$$\hat{v}_{emb}^{\text{FDET}} = v_{emb}^{\text{FDET}}[\rho_A, \rho_B, v_B](\mathbf{r}) \\ = v_B(\mathbf{r}) + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \frac{\delta \left(E_{xcT}^{\text{nad}}[\rho, \rho_B] + E_c[\rho_A] \right)}{\delta \rho(\mathbf{r})} \Bigg|_{\rho(\mathbf{r}) = \rho_A(\mathbf{r}) = \langle \Phi_A | \hat{n} | \Phi_A \rangle}$$



FDET for other descriptors obtained variationally

- FDET for embedded reference non-interacting system: $X_A \equiv \Phi_A^{KS}$
Wesolowski & Warshel *J. Phys. Chem.* **97**, (1993) 8050
- FDET for embedded one-matrix: $X_A \equiv \gamma_A$
Pernal & Wesolowski, *IJQC*, **109** (2009) 2520



Variational methods - Summary

The above variants of FDET provide thus the exact formulation of the embedding problem for multiplicative embedding potentials.

The basic FDET equality:

$$\min_{X_A \rightarrow N_A} E_{vAB}^{FDET(X_A)} [X_A, \rho_B] = E_{vAB}^{FDET(X_A)} [X_A^o, \rho_B] = E_{vAB}^{HK} [\rho_A^o + \rho_B]$$

is satisfied for any of the considered above descriptors **if obtained from variational methods** to solve the corresponding FDET eigenvalue equation.

From the practical points of view:

- ↓ $X_A \equiv \Psi_A^{\text{Full Configuration Interaction}}$ - not practical,
- ↓ $X_A \equiv \Psi_A^{\text{Truncated Configuration Interaction}}$ - not used commonly,
- ↓ $X_A \equiv \Phi_A^{\text{Single Determinant}}$ - requires approximations to $E_c[\rho]$
(not much success so far)
- ↑ $X_A \equiv \Phi_A^{\text{KS}}$ - quite successful used by us and others since introduction in 1993.



Non-variational methods to solve FDET eigenvalue equation

On the correlation potential in frozen-density embedding theory

[Wesolowski, *J. Chem. Theor. & Comput.*, **16** (2020) 6880]



FDET eigenvalue equation:

$$\left[\hat{T}_{N_A} + \hat{V}_{N_A}^{ee} + \hat{V}_A + \hat{v}_{emb}^{FDET}[\rho_A, \rho_B; v_B] \right] \Psi_A = \lambda \Psi_A$$

The basic equality of FDET:

$$\min_{\Psi_A \rightarrow N_A} E_{v_{AB}}^{FDET}[\Psi_A, \rho_B] = E_{v_{AB}}^{FDET}[\Psi_A^0, \rho_B] = E_{v_{AB}}^{HK}[\rho_A^0 + \rho_B]$$

is satisfied only if Ψ_A (or any other descriptor) is obtained **variationally** AND for **self-consistent embedding potential**.

Which ρ_A to use in $v_{emb}^{FDET}[\rho_A, \rho_B; v_B]$ and how to use the obtained λ and $\rho_A(\mathbf{r}) = \langle \Psi_A | \hat{n} | \Psi_A \rangle$ in non-variational calculations to obtain the energy consistent with the Hohenberg-Kohn functional?

Several authors (Carter, Neugebauer, Höffener, and others) developed methods, in which various arbitrary additional approximations are made in the FDET eigenvalue equation and non-variational methods to solve it. The choices were motivated by numerical significance or "intuition".



Theorem (the variant for single reference methods)Wesolowski, *J. Chem. Theor. & Comput.*, **16** (2020) 6880

$$E_{v_{AB}}^{HK}[\rho_A^0 + \rho_B] = E_{v_{AB}}^{FDET}[\tilde{\Phi}_A^0, \rho_B] + \tilde{E}_{v'}^c - \int \tilde{\rho}_A^0(\mathbf{r}) \left(\int \Delta\rho_{v'}^c(\mathbf{r}') f_{xct}^{nad}[\tilde{\rho}_A^0, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} + O(\Delta^2 \rho)$$

where,

$$v'(\mathbf{r}) = v_A(\mathbf{r}) + v_{emb}^{FDET}[\tilde{\rho}_A^0, \rho_B; v_B](\mathbf{r})$$

$$f_{xct}^{nad}[\rho, \rho_B](\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xct}^{nad}[\rho, \rho_B]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}$$

and where $\Delta\rho_{v'}^c(\mathbf{r})$ and $\tilde{E}_{v'}^c$ is the correlation correction to density and to energy in the auxiliary N_A -electron system defined by a fixed external potential $v'(\mathbf{r})$.

The equality holds if the embedded determinant is obtained variationally and at self-consistent embedding potential!



Theorem (the variant for multi-reference methods)Wesolowski, *J. Chem. Theor. & Comput.*, **16** (2020) 6880

$$\begin{aligned}
 E_{v_{AB}}^{HK}[\rho_A^0 + \rho_B] &= E_{v_{AB}}^{FDET}[\tilde{\Psi}_A^{MR^0}, \rho_B] + \tilde{E}_{v'}^{c(dynamic)} \\
 &- \int \tilde{\rho}_A^0(\mathbf{r}) \left(\int \Delta \rho_{v'}^{c(dynamic)}(\mathbf{r}') f_{xct}^{nad}[\tilde{\rho}_A^0, \rho_B](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right) d\mathbf{r} + O(\Delta^2 \rho)
 \end{aligned}$$

where,

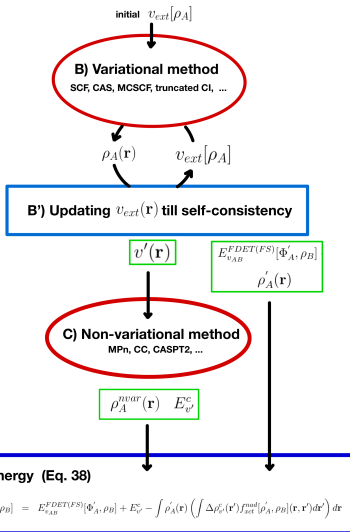
$$\begin{aligned}
 v'(\mathbf{r}) &= v_A(\mathbf{r}) + v_{emb}^{FDET}[\tilde{\rho}_A^0, \rho_B; v_B](\mathbf{r}) \\
 f_{xct}^{nad}[\rho, \rho_B](\mathbf{r}, \mathbf{r}') &= \frac{\delta^2 E_{xct}^{nad}[\rho, \rho_B]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}
 \end{aligned}$$

and where $\Delta \rho_{v'}^{c(dynamic)}(\mathbf{r})$ and $\tilde{E}_{v'}^{c(dynamic)}$ is the "dynamic" correlation correction to density and to energy in the auxiliary N_A -electron system defined by a fixed external potential $v'(\mathbf{r})$.

The equality holds if the embedded multi-reference wavefunction is obtained variationally and at self-consistent embedding potential!



A) Interfacing FDET with methods to generate ρ_B and v_B



Geneva:
 A. Zech
 C. Gonzalez-Espinoza



Heidelberg:
 A. Dreuw
 S. Präger



N-representability of the target density in Frozen-Density Embedding Theory based methods: Numerical significance and its relation to electronic polarisation

Ricardi, Gonzalez-Espinoza, & Wesolowski, *J. Chem. Phys.* **157** (2022) 064108



The basic FDET equality yields only the upper bound of E_{vAB}^0 :

$$\min_{\Psi_{A \rightarrow N_A}} E_{vAB}^{FDET}[\Psi_A, \rho_B] = E_{vAB}^{FDET}[\Psi_A^o, \rho_B] = \overbrace{E_{vAB}^{HK}[\rho_A^o + \rho_B]}^{\text{Error due to the choice of } \rho_B} \geq E_{vAB}^{HK}[\rho_{AB}^o] = E_v^o$$

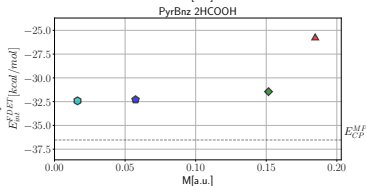
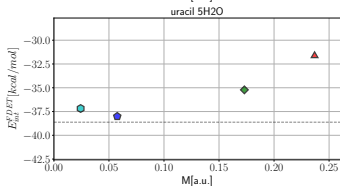
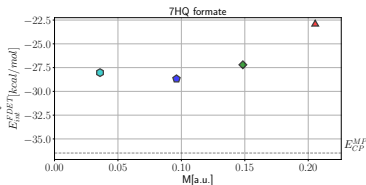
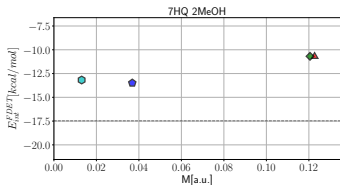
Is $\Delta E = E_{vAB}^{HK}[\rho_A^o + \rho_B] - E_{vAB}^{HK}[\rho_{AB}^o]$ numerically significant if one takes as ρ_B the density of isolated molecule B ?

Numerical examples:

FDET-MP2 variant of FDET and $E_{xct}^{nad}[\rho_A, \rho_B] \approx \tilde{E}_{xct}^{nad(LDA)}[\rho_A, \rho_B]$

Ricardi, Gonzalez-Espinoza, & Wesolowski, *J. Chem. Phys.* **157** (2022) 064108





Ricardi, Gonzalez-Espinoza, & Wesolowski, *J. Chem. Phys.* **157** (2022) 064108

FDET-MP2 Interaction energy E_{int} and the measure of non-negativity violation M for FDET calculations using different ρ_B : $\tilde{\rho}_B^{opt}$ (light blue), $\tilde{\rho}_B^{isol}$ (red) and polarised by electric field $\tilde{\rho}_B^{prepol}$ (dark blue). Horizontal lines are reference MP2 interaction energies.



FDET for excited states

- **Non-interacting Hamiltonian: LR-TDDFT**

T.A. Wesolowski, *J. Am. Chem. Soc.*, **126** (2004) 11444

M.E. Casida, T.A. Wesolowski *Intl. J. Quant. Chem.* 2004, **96**, 577

- **Interacting Hamiltonian: Levy-Perdew theorem on extrema of $E_v^{HK}[\rho]$**

T.A. Wesolowski, *J. Chem. Phys.*, **140** (2014) 18A530

A. Zech, F. Aquilante, T.A. Wesolowski, *J. Chem. Phys.*, **143** (2015) 164106



FDET eigenvalue equation might have more than just one stationary solution $k > 0$

$$\left[\hat{T}_{N_A} + \hat{V}_{N_A}^{ee} + \hat{V}_A + \hat{v}_{emb}^{FDET}(\Psi_A^k) \right] \Psi_A^k = \lambda^k \Psi_A^k$$

$$\begin{aligned} \hat{v}_{emb}^{FDET}(\Psi_A^k) &= v_{emb}^{FDET}[\rho_A^k, \rho_B, v_B](\mathbf{r}) \\ &= v_B(\mathbf{r}) + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \left. \frac{\delta E_{xct}^{nad}[\rho, \rho_B]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r}) = \rho_A^k(\mathbf{r}) = \langle \Psi_A^k | \hat{n} | \Psi_A^k \rangle} \end{aligned}$$

Ψ_A^k for different k are obtained with different embedding potential. They might be non-orthogonal. This undesired feature can be eliminated through the linearisation of $E_{xct}^{nad}[\rho, \rho_B]$:

$$E_{xct}^{nad}[\rho, \rho_B] \approx E_{xct}^{nad(lin)}[\rho, \rho_A^{ref}, \rho_B] = E_{xct}^{nad}[\rho^0, \rho_B] + \int v_{xct}^{nad}[\rho^0, \rho_B](\rho - \rho^0) d\mathbf{r}$$

T.A. Wesolowski, *J. Chem. Phys.*, **140** (2014) 18A530

A. Zech, F. Aquilante T.A. Wesolowski, *J. Chem. Phys.*, **143** (2015) 164106

In ρ_A -linearised FDET: $\langle \Psi_A^I | \Psi_A^J \rangle = \delta_{IJ}$ and $E^J - E^I = \lambda^J - \lambda^I!$



Chromophores

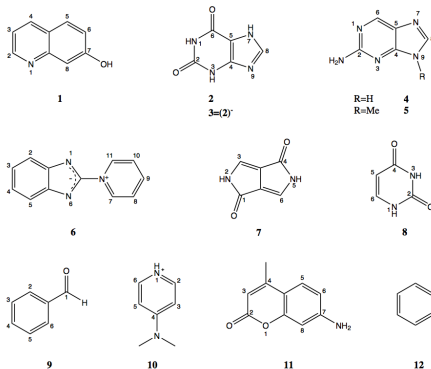


Figure 1: Chromophores considered in this work are (1) 7-hydroxyquinoline, (2) xanthine, (3) xanthinide, (4) 2-aminopurine, (5) 7-methyl-2-aminopurine, (6) pyridiniumyl benzimidazole, (7) diketopyrrolopyrrole, (8) uracil, (9) benzaldehyde, (10) 4-dimethylaminopyridine, (11) 7-Amino-4-methylcoumarin and (12) benzene.

Environments

$(H_2O)_n$, $n=1,10$
 $(NH_3)_n$, $n=1,4$
 mixed (H_2O, NH_3)
 $(HCOOH)_n$, $n=1,2$
 $(MeOH)_n$, $n=1,3$
 formamide, formimidamide, guanidine,
 acetamide, pyridine, $HCOO^-$

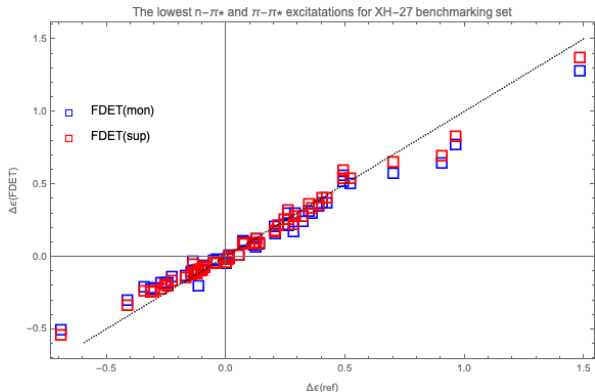
Statistics: 351 electronic excitations

$$\Delta\epsilon = \epsilon_{complex}^{ADC(2)} - \epsilon_{chromophore}^{ADC(2)}$$

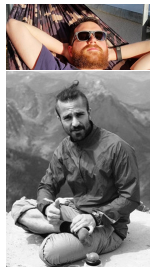
$$\delta\epsilon = \epsilon_{complex}^{FDET/ADC(2)} - \epsilon_{complex}^{ADC(2)}$$

ME=39meV (0.9kcal/mol),
 SD=43meV (1.0kcal/mol)

Benchmarking vertical excitation energies



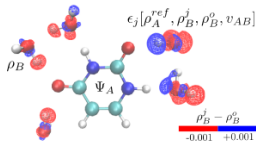
A. Zech, N. Ricardi, S. Prager, A. Dreuw & TAW., *J. Chem. Theor. & Comput.* **14** (2018) 4028



Excitation energies of embedded chromophores from Frozen-Density Embedding Theory using state-specific electron densities of the environment

M. Fu & T.A. Wesolowski, *J. Phys. Chem. A.*, **127** (2023) 535





Levy-PerdewTheorem

ΔE_j

$\underbrace{=}$

$$E_{vAB}^{HK}[\rho_A^j + \rho_B^j] - E_{vAB}^{HK}[\rho_A^o + \rho_B^o]$$

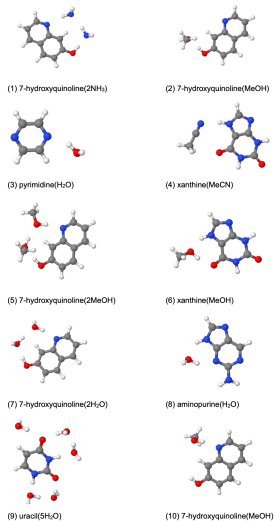
Fu&Wesolowski2022

$\underbrace{=}$

$$\epsilon_j[\rho_A^{ref}, \rho_B^j, \rho_B^o, v_{AB}] + O(\Delta^2 \rho)$$

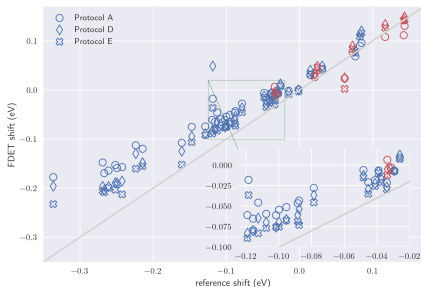
$$\begin{aligned} \epsilon_j &\equiv \overbrace{\lambda_j[\rho_A^{ref}, \rho_B^j] - \lambda_o[\rho_A^{ref}, \rho_B^j]}^{\epsilon_j^A} \\ &+ \overbrace{\left\langle \Phi_A^{o(j)} \left| \hat{H}_A + \hat{v}_{emb}^{FDET}[\rho_A^{ref}, \rho_B^j] \right| \Phi_A^{o(j)} \right\rangle - \left\langle \Phi_A^{o(o)} \left| \hat{H}_A + \hat{v}_{emb}^{FDET}[\rho_A^{ref}, \rho_B^o] \right| \Phi_A^{o(o)} \right\rangle + E_{v'j}^C - E_{v'o}^C}^{\epsilon_j^B} \\ &- \overbrace{\left(\int \rho_A^{ref}(\mathbf{r}) v_{xct}^{nad}[\rho_A^{ref}, \rho_B^j](\mathbf{r}) d\mathbf{r} - \int \rho_A^{ref}(\mathbf{r}) v_{xct}^{nad}[\rho_A^{ref}, \rho_B^o](\mathbf{r}) d\mathbf{r} \right) + E_{xct}^{nad}[\rho_A^{ref}, \rho_B^j] - E_{xct}^{nad}[\rho_A^{ref}, \rho_B^o]}^{\epsilon_j^C} \\ &+ \overbrace{E_{vB}^{HK}[\rho_B^j] - E_{vB}^{HK}[\rho_B^o]}^{\epsilon_j^D} + \overbrace{V_A[\rho_B^j] - V_A[\rho_B^o]}^{\epsilon_j^E} \end{aligned}$$





State specificity	ρ_B -polarising field	excitation energy average error (eV)
No	none	0.0468 ± 0.0414
No	isolated chromophore in ground state	0.0395 ± 0.0322
Yes	isolated chromophore in the corresponding state	0.0384 ± 0.0337
Yes	embedded chromophore in the corresponding state	0.0300 ± 0.0258

In state specific case, Eq. 14 from Fu&Wesolowski, JPCA 2023 was used for ΔE_J . In state-non-specific case $\Delta E_J = \lambda_J - \lambda_0$.



Improving upon local density approximation for $v_t^{nad}[\rho_A, \rho_B]$

- **Problem detected and reported:**

Frozen Density Functional Approach for ab initio Calculations of Solvated Molecules [Wesolowski & Warshel, *J. Phys. Chem.* **97**, (1993) 8050]

- **Attempted solution:**

Orbital-free effective embedding potential at nuclear cusps
[Lastra et al., *J. Chem. Phys.* **129** (2008) 074107]

- **Solution found for $v_t^{nad}[\rho_A, \rho_B]$ but not for $T_s^{nad}[\rho_A, \rho_B]$:**

A non-decomposable approximation on the complete density function space for the non-additive kinetic potential [Polak et al., *J. Chem. Phys.* **156** (2022) 044103]

- **Solution found for $v_t^{nad}[\rho_A, \rho_B]$ and $T_s^{nad}[\rho_A, \rho_B]$:**

Symmetrized non-decomposable approximations of the non-additive kinetic energy functional [Polak et al., *J. Chem. Phys.* **158** (2023) 17410]



Statement of the problem

Let us consider two subsystems comprising N_{AB} -electron system partitioned into N_A and N_B consistently with the number of electrons upon separation of the two subsystems.

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

- $\tilde{v}_{emb}^{FDET}[\rho_A, \rho_B, v_B](\vec{r})$ has a singularity at each nucleus due to v_B .
- What if:
 - A** The used approximation for $v_{xct}^{nad}[\rho_A, \rho_B]$ is such that the singularity due to v_B remains negative and the total embedding potential has a bound state. and
 - B** The energy of this bound state is lower than that of one of the occupied orbitals obtained in the FDET eigenvalue equation.

Case **B** is in contradiction with our assumption that the partitioning $N_{AB} = N_A + N_B$ correspond to the dissociation limit.



Challenge for $\tilde{v}_t^{nad}[\rho_A, \rho_B]$

Case **B** is not hypothetical: both exact $v_{xc}^{nad}[\rho_A, \rho_B]$ and Coulomb component of $v_{emb}^{FDET}[\rho_A, \rho_B, v_B]$ are finite the nuclei. $\tilde{v}_t^{nad(LDA)}[\rho_A, \rho_B]$ is also finite.

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

Challenge for $\tilde{v}_t^{nad}[\rho_A, \rho_B]$:

It is the only component of $v_{xct}^{nad}[\rho_A, \rho_B]$ that can stop such an artificial transfer of electrons from *A* to *B*.

Remark:

In QM/MM practice this problem is usually pragmatically avoided by not using any basis sets centered on atoms in the environment. A proper theory should yield meaningful solutions for a complete basis set!



Exact relation for the functional $v_t^{nad}[\rho_A, \rho_B](\mathbf{r})$

For $\int \rho_B(\mathbf{r}) d\mathbf{r} = 2$ and $\rho_A(\mathbf{r}) \rightarrow 0$

$$v_t^{nad}[\rho_A, \rho_B](\mathbf{r}) \longrightarrow v_t^{nad(limit)}[\rho_B](\mathbf{r}) = -\frac{1}{4} \frac{\nabla^2 \rho_B}{\rho_B(\mathbf{r})} + \frac{1}{8} \frac{|\nabla \rho_B|^2}{\rho_B^2(\mathbf{r})}$$

Lastra et al., *J. Chem. Phys.* **129** (2008) 074107

This property of $v_t^{nad}[\rho_A, \rho_B](\mathbf{r})$ cannot be reproduced by any decomposable approximation based on gradient-expansion approximation! **But it is highly desirable.**

$$v_t^{nad(limit)}[\rho_B^{exp}](\mathbf{r}) = -\frac{1}{4} \frac{\nabla^2 \rho_B}{\rho_B(\mathbf{r})} + \frac{1}{8} \frac{|\nabla \rho_B|^2}{\rho_B^2(\mathbf{r})} = \underbrace{-\frac{\zeta^2}{2}}_{\text{constant}} + \underbrace{\frac{\zeta}{r}}_{\text{repulsive}} \quad \text{if } \rho_B^{exp}(\mathbf{r}) = A \exp(-2\zeta r)$$



Our first attempt: NDSD approximation

$$\tilde{v}_t^{\text{nad(NDSD)}}[\rho_A, \rho_B] = v_t^{\text{nad(LDA)}}[\rho_A, \rho_B] + f^{\text{NDSD}}(\rho_B) v_t^{\text{limit}}[\rho_B]$$

with $v_t^{\text{nad(TF)}}[\rho_A, \rho_B] = \frac{5}{3} C_{TF} \left((\rho_A + \rho_B)^{2/3} - \rho_A^{2/3} \right)$

$$\begin{aligned} v_t^{\text{nad(limit)}}[\rho_B^{\text{exp}}](\mathbf{r}) &= \overbrace{-\frac{1}{4} \frac{\nabla^2 \rho_B}{\rho_B(\mathbf{r})} + \frac{1}{8} \frac{|\nabla \rho_B|^2}{\rho_B^2(\mathbf{r})}}^{\text{differential operator}} \\ &= \underbrace{-\frac{\zeta^2}{2}}_{\text{undesired}} + \underbrace{\frac{\zeta}{r}}_{\text{desired}} \quad \text{if } \rho_B^{\text{exp}}(\mathbf{r}) = A \exp(-2\zeta r) \end{aligned}$$

[Lastra et al., *J. Chem. Phys.* **129** (2008) 074107]



The follow up: Part I

The differential operator

$$D_\gamma[\rho] = |\nabla\rho|^2 - \gamma\rho\nabla^2\rho$$

corresponds to $v_t^{nad(limit)}[\rho_B^{exp}]$ if $\gamma = 2$.

The analysis of spaces solving the homogeneous differential equation $D_{\gamma=2}[\rho] = 0$ involves functions which cannot be electron densities. Only if $\gamma = 1$, the solutions of $D_\gamma[\rho] = 0$ are exponential densities, i.e. the functions covering completely the space of molecular electron densities.



NEW non-decomposable approximation:

does not contain the undesired constant!

$$\tilde{v}_t^{nad(NDCS)}[\rho_A, \rho_B] = v_t^{nad(TF)}[\rho_A, \rho_B] + \overbrace{f^{NDCS}(\rho_B) \cdot D_{\gamma=1}[\rho_B]}$$

Differences between subsystem DFT density and the reference Kohn-Sham density

$$\|(\rho_A + \rho_B - \rho_{ref})^{1/2}\|^2 = \int \left(|(\rho_A + \rho_B - \rho_{ref})^{1/2}|^2 + |\nabla(\rho_A + \rho_B - \rho_{ref})^{1/2}|^2 \right)$$

optimisation of ρ_A and ρ_B with various $\tilde{v}_t^{nad}[\rho_A, \rho_B]$

A	B	TF	GEA2	NDSD	NDCS	$\ (\rho_A^{isol} + \rho_B^{isol} - \rho_{ref})^{1/2}\ ^2$
Li ⁺	H ₂ O	0.0620	0.1227	0.0508	0.0447	0.3675
Be ²⁺	H ₂ O	0.5149	0.7295	0.3951	0.2422	1.0457
Na ⁺	H ₂ O	0.0200	0.0711	0.0174	0.0168	0.2879
Mg ²⁺	H ₂ O	0.0942	0.2487	0.0695	0.0489	0.7177
K ⁺	H ₂ O	0.0678	–	–	0.0322	0.2418
Rb ⁺	H ₂ O	0.4949	0.5185	0.5461	0.4906	0.6546
Li ⁺	CO ₂	0.0316	0.0797	0.0273	0.0270	0.4544
K ⁺	CO ₂	0.0197	0.0630	–	0.0173	0.2926
Li ⁺	F ₂	0.0279	0.0463	0.0222	0.0205	0.3031

TF and **GEA2** denote the approximation for $T_s[\rho]$ used in decomposable approximations for $\tilde{v}_t^{nad}[\rho_A, \rho_B]$; **NDSD** and **NDCS** are not decomposable.

Polak et al., *J. Chem. Phys.* **156** 044103 (2022)



Differences between subsystem DFT density and the reference Kohn-Sham density

$$\|(\rho_A + \rho_B - \rho_{ref})^{1/2}\|^2 = \int \left(|(\rho_A + \rho_B - \rho_{ref})^{1/2}|^2 + |\nabla(\rho_A + \rho_B - \rho_{ref})^{1/2}|^2 \right)$$

optimisation of ρ_A and ρ_B with various $\tilde{v}_t^{nad}[\rho_A, \rho_B]$

A	B	TF	GEA2	NDS	NDCS	$\ (\rho_A^{isol} + \rho_B^{isol} - \rho_{ref})^{1/2}\ ^2$
H ₂ O	H ₂ O	0.0210	0.0311	0.0209	0.0224	0.0914
Li ⁺	F ⁻	0.2044	0.2839	0.1670	0.1465	0.4440
Li ⁺	Cl ⁻	0.2623	0.3788	0.2148	0.1843	0.6088
Li ⁺	Br ⁻	0.2969	0.4300	0.2440	0.2075	0.6736
Na ⁺	F ⁻	0.0691	0.1583	0.0578	0.0479	0.3592
Na ⁺	Cl ⁻	0.0619	0.1893	0.0505	0.0416	0.5231
Na ⁺	Br ⁻	0.0615	0.2071	0.0490	0.0404	0.5926
Be ²⁺	O ²⁻	1.1169	1.2709	0.9723	0.8114	2.1072
Mg ²⁺	O ²⁻	0.2988	0.5172	0.2205	0.1531	2.1176
HF	HF	0.0537	0.0441	0.0539	0.0591	0.1504
K ⁺	Cl ⁻	– ₂	– ₂	– ₂	0.1969	0.4279
K ⁺	F ⁻	– ₂	– ₂	– ₂	0.1929	0.4916



Decomposable $\tilde{v}_t^{nad}[\rho_A, \rho_B]$ yield symmetric $\tilde{T}_s^{nad}[\rho_A, \rho_B]$.
 $\tilde{T}_s^{nad(NDCS)}[\rho_A, \rho_B]$ corresponding to $v_t^{nad(NDCS)}[\rho_A, \rho_B]$ might not be symmetric.

And it is!

Complex		Interaction energies from subsystem DFT		
A	B	$\tilde{E}_{int}^{NDCS}[\rho_A, \rho_B]$	$\tilde{E}_{int}^{NDCS}[\rho_B, \rho_A]$	E_{int}^{KS}
Li ⁺	H ₂ O	-39.82	-37.90	-37.48
Li ⁺	CO ₂	-21.87	-20.72	-21.47
Li ⁺	F ⁻	-194.80	-188.32	-187.56
Li ⁺	Cl ⁻	-162.07	-157.22	-153.57
Li ⁺	OH ⁻	-195.79	-189.80	-191.69
K ⁺	F ⁻	-131.51	-140.90	-141.83
K ⁺	Cl ⁻	-112.80	-119.64	-116.62
K ⁺	OH ⁻	-138.21	-140.80	-142.08
Mg ²⁺	O ²⁻	-696.66	-670.52	-666.35
Mg ²⁺	H ₂ O	-87.24	-83.96	-85.21
Be ²⁺	O ²⁻	-947.31	-883.99	-857.56
Be ²⁺	H ₂ O	-176.28	-153.96	-149.97

Polak et al., *J. Chem. Phys.* **158** (2023) 17410



Symmetrisation of $\tilde{T}_s^{nad(NDCS)}[\rho_A, \rho_B]$

- **Straightforward solution:**

$$\tilde{T}_s^{nad(NDCSsym)}[\rho_A, \rho_B] = \tilde{T}_s^{nad(NDCS)}[\rho_A, \rho_B] + \frac{1}{2} \tilde{T}_s^{nad(NDCSasym)}[\rho_A, \rho_B]$$

with

$$\tilde{T}_s^{nad(NDCSasym)}[\rho_A, \rho_B] = \tilde{T}_s^{nad(NDCS)}[\rho_A, \rho_B] - \tilde{T}_s^{nad(NDCS)}[\rho_B, \rho_A]$$

But this would mean modification of the potential:

$$\tilde{v}_t^{nad(NDCSsym)}[\rho_A, \rho_B] = \tilde{v}_t^{nad(NDCS)}[\rho_A, \rho_B] + \frac{\delta \tilde{T}_s^{nad(NDCS)}[\rho_B, \rho_A]}{\delta \rho_A}$$

- **Our solution** [Polak et al., *J. Chem. Phys.* **158** (2023) 17410]

$$\tilde{T}_s^{nad(NDCSsym)}[\rho_A, \rho_B] = \tilde{T}_s^{nad(NDCS)}[\rho_A, \rho_B] + C^{sym} \int \rho_A \frac{\delta \tilde{T}_s^{nad(NDCS)}[\rho_B, \rho_A]}{\delta \rho_A} dr$$

and choosing the constant C^{sym} to yield the first-order correction to $v_s^{nad(NDCS)}[\rho_A, \rho_B]$ making the whole functional symmetric.



Complex		Interaction energies from subsystem DFT [kcal/mol]		
		TF	sym-NDCS	KS
Li ⁺	H ₂ O	-40.66 (8.48)	-39.02 (4.11)	-37.48
Li ⁺	CO ₂	-22.41 (4.37)	-21.39 (0.37)	-21.47
Li ⁺	F ⁻	-196.75 (4.90)	-192.04 (2.39)	-187.56
Li ⁺	Cl ⁻	-164.08 (6.84)	-160.05 (4.22)	-153.57
Li ⁺	OH ⁻	-197.09 (2.82)	-193.20 (0.79)	-191.69
K ⁺	F ⁻	...	-136.94 (3.45)	-141.83
K ⁺	Cl ⁻	...	-116.77 (0.13)	-116.62
K ⁺	OH ⁻	...	-139.80 (1.61)	-142.08
Mg ²⁺	O ²⁻	-691.91 (3.84)	-684.44 (2.71)	-666.35
Mg ²⁺	H ₂ O	-89.21 (4.69)	-85.94 (0.85)	-85.21
Be ²⁺	O ²⁻	-954.86 (11.31)	-920.58 (7.31)	-857.86
Be ²⁺	H ₂ O	-186.51 (24.36)	-167.41 (11.63)	-149.97



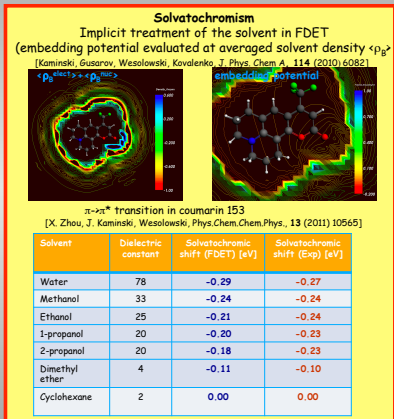
Combining physical laws for different scales in FDET

$$\overbrace{\langle \rho_B \rangle_{\text{statistical ensemble}}}^{\text{continuum at scale of } \text{\AA}}(\mathbf{r}) = \sum_i^{\text{atomtype}} \int P_i(\mathbf{r}') \rho^i(\mathbf{r} - \mathbf{r}') d\mathbf{r}'$$

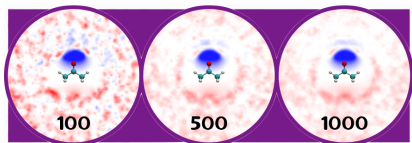
Kaminski et al.	<i>J. Phys. Chem. A</i> 114 (2010) 6082	}	P from 3D-RISM
Zhou et al.	<i>Phys. Chem. Chem. Phys.</i> 13 (2011) 10565		
Shedge et al.	<i>Chem. Phys. Chem.</i> 15 (2014) 3291		
Lyaktonov et al.	<i>Phys. Chem. Chem. Phys.</i> (2016) 18 21069	}	P from classical MD
Gonzalez-Espinoza et al.	<i>J. Chem. Theor. & Comput.</i> 18 (2022) 1072		
Ricardi et al.	<i>J. Chem. Theor. & Comput.</i> (2023) <i>in press</i>		
Gonzalez-Espinoza et al.	<i>to be published</i>	}	P from MolecularDFT
Ricardi et al.	<i>Acta Cryst. - Foundation and Advances</i> A76 57(2020)	}	P from X-ray diffraction



Multi-level simulations based on Frozen Density Embedding Theory FDET for excitation energies of embedded chromophores

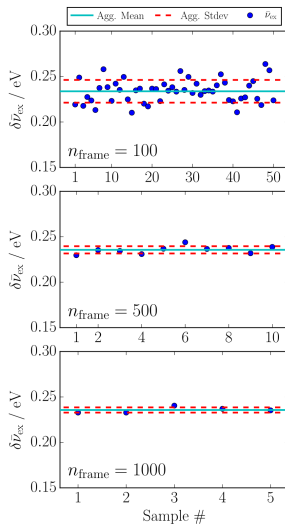


Averaged electrostatic potentials from MD



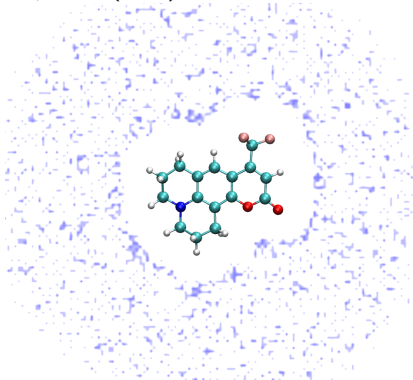
Number of frames

[C.E. Gonzalez-Espinoza, C. Rumble, D. Borgis, and T.A. Wesolowski, *J. Chem. Theor. & Comput.* **18** (2022) 1072]

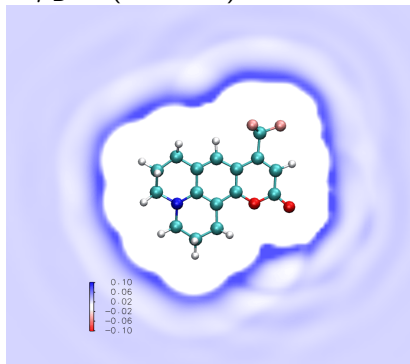


Aminocoumarin 153 in water

$\langle \rho_B \rangle$ (MD)

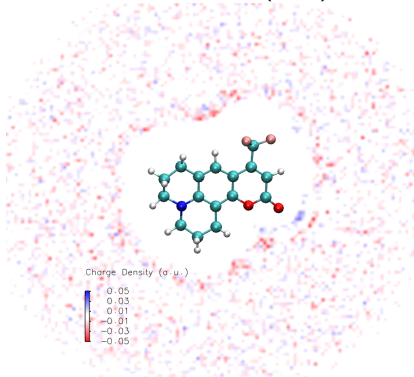


$\langle \rho_B \rangle$ (MoIDFT)

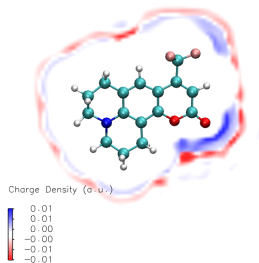


Aminocoumarin 153 in water

Total solvent charge (MD)

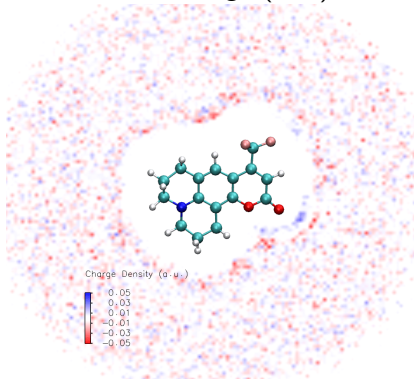


Total solvent charge (MoIDFT)

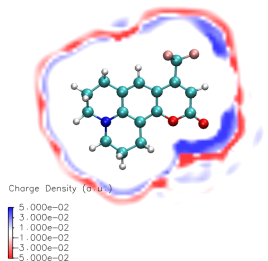


Aminocoumarin 153 in acetonitrile

Total solvent charge (MD)

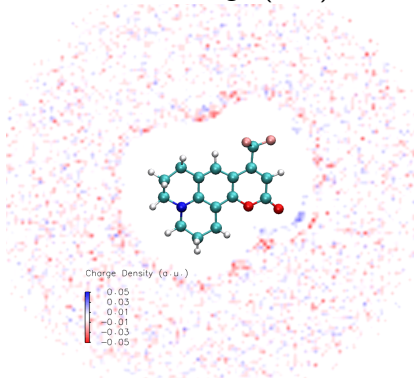


Total solvent charge (MoIDFT)

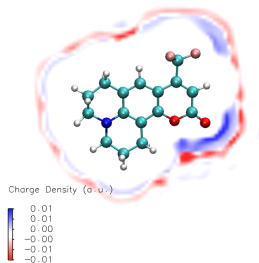


Aminocoumarin 153 in water

Total solvent charge (MD)

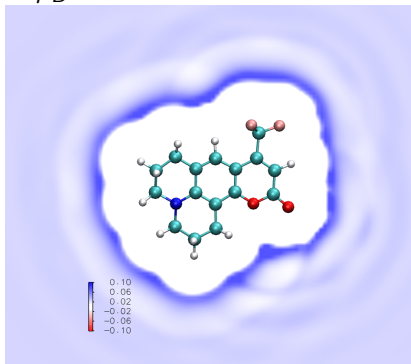


Total solvent charge (MoIDFT)

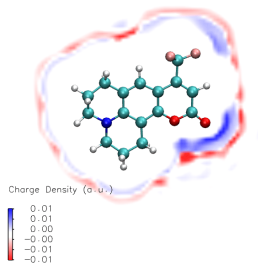


Aminocoumarin 153 in water

$\langle \rho_B \rangle$ from MolDFT

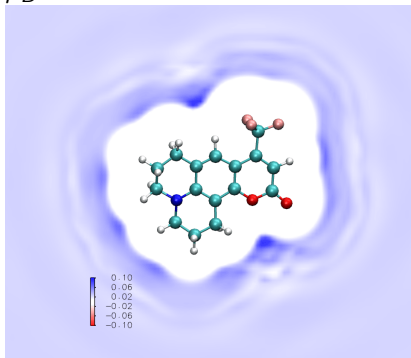


Total solvent charge (MolDFT)

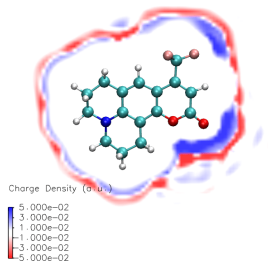


Aminocoumarin 153 in acetonitrile

ρ_B from MolDFT

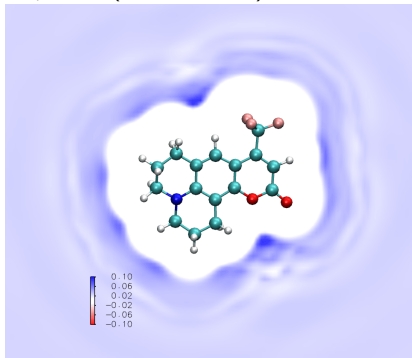


Total solvent charge (MolDFT)

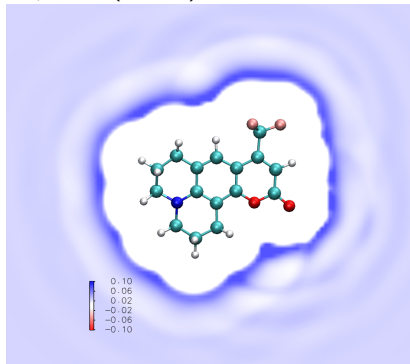


Structuring effect of the chromophore on the solvent

$\langle \rho_B \rangle$ (acetonitrile)

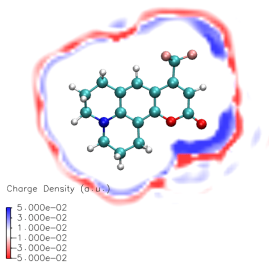


$\langle \rho_B \rangle$ (water)

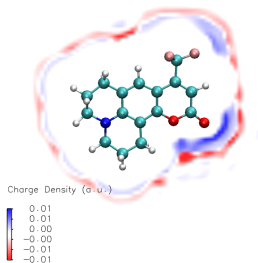


Structuring effect of the chromophore on the solvent

Total solvent charge
(acetonitrile)



Total solvent charge (water)



Performance of $\langle \rho_B \rangle^{MDFT}$ in FDET

Table: Vertical excitation energies shifts (in eV) for acetone and C153. Excitation energies of the chromophores in vacuum are 4.270 eV (acetone) and 3.135 eV (coumarin C153).

Source of $\langle \rho_B \rangle_{ens}$	Acetone		C153	
	Water	ACN	Water	ACN
MDFT	0.239	0.099	-0.250	-0.120
MD	0.230	0.118	-0.202	-0.097

Gonzalez-Espinoza, Rumble, Borgis, Wesolowski, *to be published*



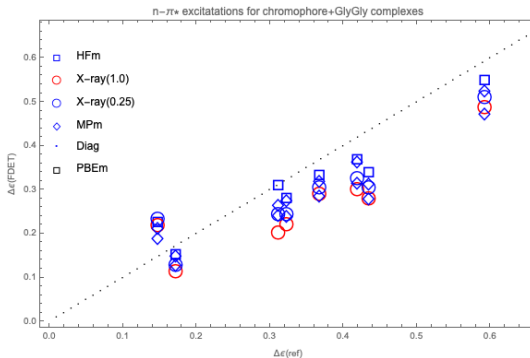
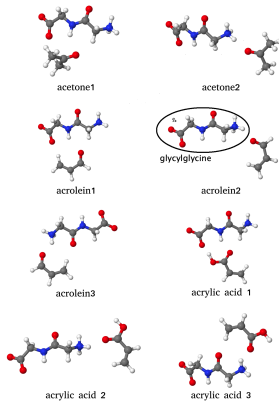
$\langle \rho_B \rangle$ from molecular crystals

Embedding-theory-based simulations using experimental electron densities for the environment

[N. Ricardi, M. Ernst, P. Macchi, and T. A. Wesolowski, *Acta Crystallographica - Foundation and Advances* **A76** 57 (2020)]



FDET with ρ_B taken from molecular crystal of glycyglycine



Complexation effect on vertical excitation energies:
 "Embedded ADC(2)" vs ADC(2) for with various
 choices for $\rho_B(\vec{r})$

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