Multiplicative embedding potentials for multi-scale simulations of electronic properties: exact properties and approximations:

Beyond the frontiers of standard applications of FDET eigenvalue equation

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Frozen-Density Embedding Theory (FDET) approach to the quantum embedding problem

Hohenberg-Kohn functional

$$E_v^{HK}[\rho] \equiv \min_{\Psi \to \rho} \left\langle \Psi \left| \hat{H}_v \right| \Psi \right\rangle$$

The second Hohenberg-Kohn Theorem

[Hohenberg & Kohn, *Phys.* Rev. **136** B 864 (1964)]

$$\min_{\rho \to N_{AB}} E_v^{HK}[\rho] \quad = \quad E_v^{HK}\left[\rho^o_{N_{AB}}\right] = E_v^o$$

Constrained minimisation of Hohenberg-Kohn energy functional

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

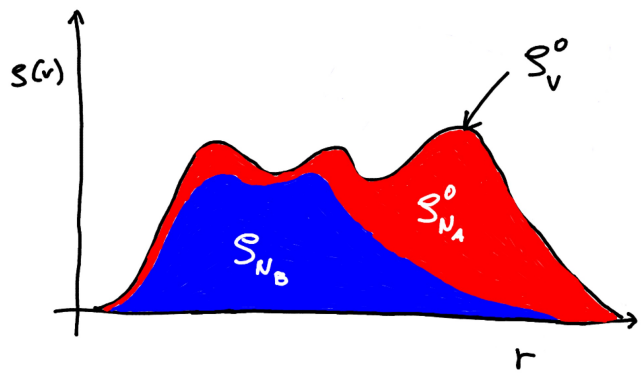
$$\min_{\substack{\rho \to N_{AB} \\ \forall_{\mathbf{r}} \rho(\mathbf{r}) \geq \rho_{N_B}(\mathbf{r})}} E_v^{HK}[\rho] \quad = \quad \min_{\rho \to N_A} E_v^{HK}[\rho + \rho_{N_B}]$$

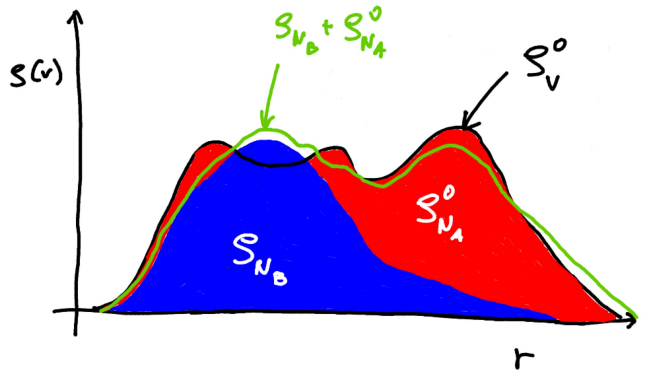
$$= \quad E_v^{HK}\left[\rho^o_{N_A} + \rho_{N_B}\right] \geq E_v^o$$

Frozen-Density Embedding Theory (FDET) approach to the quantum embedding problem

Constrained minimisation of Hohenberg-Kohn energy functional [Wesolowski, *Phys. Rev. A* **77** (2008) 012504)]

$$\min_{\substack{\rho \to N_{AB} \\ \forall_{\mathbf{r}} \rho(\mathbf{r}) \geq \rho_{N_B}(\mathbf{r})}} E_v^{HK}[\rho] = \min_{\rho \to N_A} E_v^{HK}[\rho + \rho_{N_B}] = E_v^{HK}\left[\rho^o_{N_A} + \rho_{N_B}\right] \geq E_v^o$$





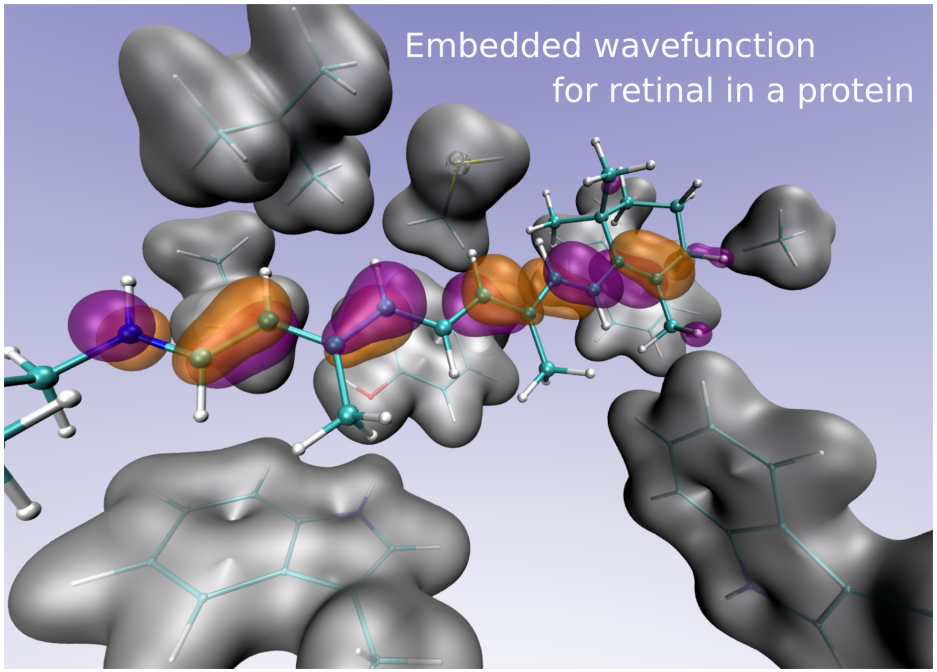
Constrained minimisation of Hohenberg-Kohn energy functional [Wesolowski, *Phys. Rev. A* **77** (2008) 012504)]

$$\min_{\substack{\rho \to N_{AB} \\ \forall_{\mathbf{r}} \rho(\mathbf{r}) \geq \rho_{N_B}(\mathbf{r})}} E_v^{HK}[\rho] = \min_{\rho \to N_A} E_v^{HK}[\rho + \rho_{N_B}]$$

$$= \min_{\Psi \to N_A} E_v^{FDET}[\Psi, \rho_{N_B}]$$

$$= E_v^{HK}\left[\rho^o_{N_A} + \rho_{N_B}\right] \geq E_v^o$$

N_A-electron density Ψ is introduced as an auxiliary object subject to optimisation which can be performed using variational methods of Molecular Quantum Mechanics.



↓

no charges, no vdW radii, no polarisabilities:
just ρ_{N_B}

Dual descriptor for $N_{AB} = N_A + N_B$ electrons: $\left[\Psi_{N_A}, \rho_{N_B}\right]$:

Ψ_{N_A}: N_A-electron wavefunction

$\rho_{N_B}(\mathbf{r})$: non-negative real function integrating to $N_B = N_{AB} - N_A$

The bifunctional $E_{xct}^{nad}[\rho_1, \rho_2]$

Constrained search definition of density functionals

[M. Levy, *Proc. Natl. Acad. Sci. USA*, **76** (1972) 6062]

$$
\begin{aligned}
F^L[\rho] &\equiv \min_{\Psi \to \rho} < \Psi | \hat{T} + \hat{V}_{ee} | \Psi > \\
&= < \Psi^{min} | \hat{T} + \hat{V}_{ee} | \Psi^{min} > \\
&= \overbrace{< \Psi[\rho] | \hat{T} | \Psi[\rho] >}^{T[\rho]} + \overbrace{< \Psi[n] | \hat{V}_{ee} | \Psi[\rho] >}^{V_{ee}[\rho]}
\end{aligned}
$$

$$F^L[\rho] = T[\rho] + V_{ee}[\rho] \equiv E_{xcT}[\rho] + J[\rho]$$

where $J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \cdot \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$

Universal bi-functional $E_{xct}^{nad}[\rho_1, \rho_2]$

$$\mathbf{E_{xct}^{nad}}[\rho_1, \rho_2] = \mathbf{E_{xct}}[\rho_1 + \rho_2] - \mathbf{E_{xct}}[\rho_1] - \mathbf{E_{xct}}[\rho_2]$$

$F^L[\rho]$ vs $F^{HK}[\rho]$

The first HK theorem defines the universal functional

$$F^{HK}[\rho] \equiv E_v^0[\rho] - \int v((\mathbf{r})) \cdot \rho(\mathbf{r}) \, d\mathbf{r}$$

- $F^{HK}[\rho]$ exists only for ρ is v-representable
- Domain of ρ for which $F^L[\rho]$ is defined is larger (N-representable densities)
- If ρ is v-representable $F^L[\rho] = F^{HK}[\rho]$

FDET energy functional for interacting embedded wavefunction

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

$$E_v^{FDET}[\Psi_A, \rho_{N_B}] \equiv \langle \Psi_A | \hat{H}_v^{N_A} | \Psi_A \rangle + E_{xct}^{nad}[\rho^{\Psi_A}, \rho_{N_B}] + J_{AB}[\rho^{\Psi_A}, \rho_{N_B}] + E_v^{HK}[\rho_{N_B}]$$

The bi-functionals $E_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$ and $J_{AB}[\rho_{N_A}, \rho_{N_B}]$ are non-additive components of the functional $F^L[\rho]$.

Basic FDET equality

$$\min_{\Psi_{N_A} \to N_A} E_v^{FDET}[\Psi_{N_A}, \rho_{N_B}] = \mathbf{E_v^{FDET}[\Psi_A^o, \rho_{N_B}] = E_v^{HK}[\rho^{\Psi_A^o} + \rho_{N_B}]} \geq E_v^o$$

where $\rho^{\Psi_{N_A}}(\mathbf{r}) \equiv \langle \Psi_{N_A} | \sum_{i=1}^{N_A} \delta(\mathbf{r}_i - \mathbf{r}) | \Psi_{N_A} \rangle$

- **FDET is not an alternative formulation of DFT!** The objective is not the ground-state energy (it cannot be guaranteed for any arbitrary ρ_{N_B}).
- The objective is the embedded wavefunction corresponding to **the lowest energy of the total system for a given ρ_{N_B}.**

FDET eigenvalue equation

$$\min_{\Psi_A \to N_A} E_v^{FDET}[\Psi_A, \rho_{N_B}] = E_v^{FDET}[\Psi_A^o, \rho_{N_B}] = E_v^{HK}[\rho^{\Psi_A^o} + \rho_{N_B}]$$

$$\downarrow$$

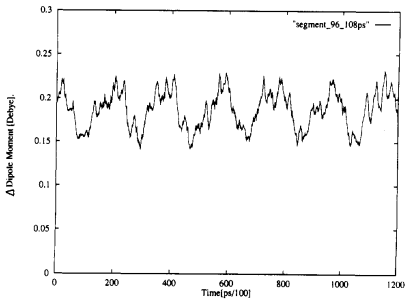
$$\frac{\delta E_v^{FDET}[\Psi_A, \rho_{N_B}]}{\delta \Psi_A} = \lambda \cdot \frac{\delta C[\Psi_A]}{\delta \Psi_A}$$

$$\downarrow$$

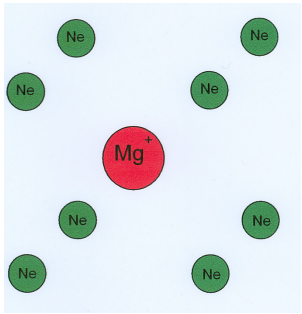
$$\left[\hat{H}_v^{N_A} + \hat{v}_{FDET}^{N_A}[\rho^{\Psi_A}, \rho_{N_B}]\right] \Psi_A = \lambda \cdot \Psi_A$$

with $\hat{v}_{FDET}^{N_A}\left[\rho^{\Psi_A}, \rho_{N_B}\right] = \sum_i^{N_A} \delta(\mathbf{r} - \mathbf{r}_i) v_{emb}^{FDET}\left[\rho^{\Psi_A}, \rho_{N_B}\right](\mathbf{r})$

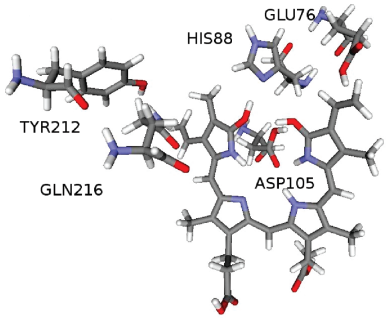
Targets for FDET based simulations: ground-state properties (examples form our own work)



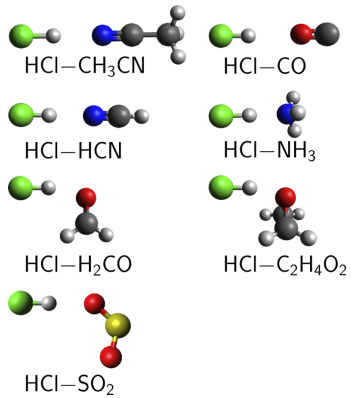
Dipole moment of a water molecule in liquid phase
[TAW &Warshel, *J. Phys. Chem.* 1994]



$\mathbf{A}_{iso}$: radical in noble gas matrices
[TAW, *Chem. Phys. Lett.* 1999]



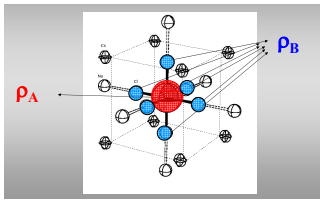
g-tensor: radical in a protein
[Fradelos&TAW, *J. Chem. Theor. &Comput.* 2011]



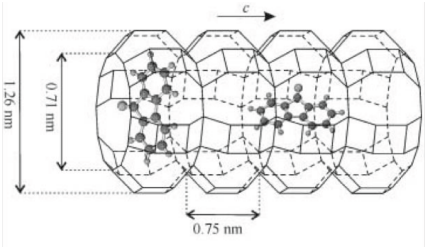
EFG: weak intermolecular complexes
[Gimbal-Zofka et al. *J. Chem. Theor. &Comput.* 2023]

Targets for FDET-based simulations: excited states (examples from our own work)

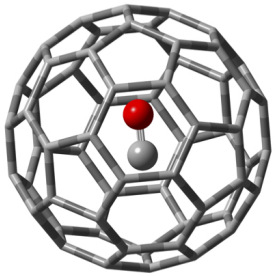
a) Ligand-field splitting of f-levels [Zbiri et al. CPL2004]



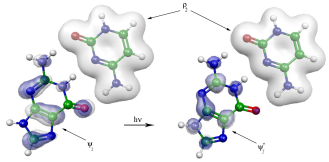
b) chromophores in porous solids [Zhou et al., PCCP2013]



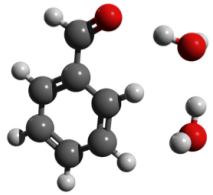
c) core excitations [Prager et al., JCTC2017]



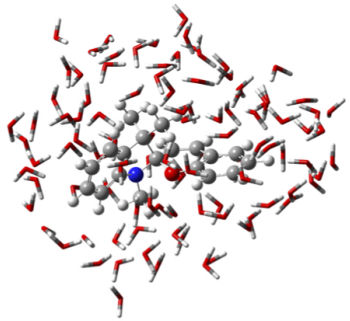
e) chromophores in clusters
[Wesolowski, JACS2004]



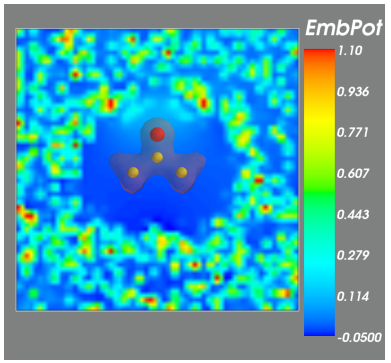
[Zech et al., JCP2015]



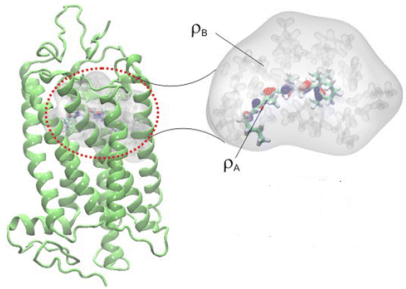
f) UV/Vis excitations for solvated chromophores
[Prager et al., JCTC2017]



[Laktyonov et al. PCCP 2016]



h) UV/Vis excitations for chromophores in proteins [Zhou et al., JACS2015]



FDET embedding potential

$$v_{emb}^{FDET}[\rho_{N_A}, \rho_{N_B}](\mathbf{r}) \equiv \int \frac{\rho_{N_B}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \overbrace{\left.\frac{\delta E_{xct}^{nad}\left[\rho, \rho_{N_B}\right]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_{N_A}}}^{v_{xct}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right](\mathbf{r})}$$

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

$v_{xct}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right]$ represents the exchange and correlation effects of electron density ρ_{N_B} on ρ_{N_A}. The analytic form of this bi-functional is not known. It must be approximated in practice.

It is convenient to divide it into its kinetic and exchange-correlation components:

$$v_{xct}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right] \equiv v_{xc}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right] + v_{t}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right]$$

The meaning of the Lagrange multiplier in $\left(\hat{H}_A + \hat{v}_{emb}^{FDET}[\rho_{N_A}, \rho_{N_B}]\right)\Psi_A^0 = \lambda^0 \cdot \Psi_A^0$

$$E_v^{FDET}\left[\Psi_A^0, \rho_{N_B}\right] = \overbrace{\left\langle \Psi_A^0 \middle| \hat{H}_A + \hat{v}_{emb}^{FDET} \middle| \Psi_A^0 \right\rangle}^{\lambda^0} + \overbrace{E_v^{HK}\left[\rho_{N_B}\right]}^{\text{Constant term}} \quad \leftarrow \text{We cannot stop here !}$$

$$+ \quad E_{xcT}^{nad}\left[\rho_{N_A}^0, \rho_{N_B}\right] - \int v_{xcT}^{nad}\left[\rho_{N_A}^{\Psi_A^0}, \rho_{N_B}\right](\mathbf{r})\rho_{N_A}^0(\mathbf{r})d\mathbf{r} \quad \leftarrow \text{Inhomogeneity !}$$

If other then the lowest-energy solutions (Ψ_A^I) exist, the vertical excitation energy is equal to the difference of the corresponding eigenvalues but only after neglecting higher than linear components of $E_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$.

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

Notion of "subsystem" in FDET and in other embedding methods

in FDET, neither the total energy nor density depend on the partition: $v(\mathbf{r}) = v_A(\mathbf{r}) + v_B(\mathbf{r})$.

$$\textbf{FDET} \longrightarrow \quad \left[\hat{H}^{N_A}_{v=v_A+v_B} + \hat{v}^{N_A}_{FDET}[\rho^{\Psi_A}, \rho_{N_B}]\right]\Psi_A = \lambda^{FDET}\cdot\Psi_A$$

In common QM/MM methods, the partition is made by the modeller ("intuition" or numerical tests), and the eigenvalue equation has the form:

$$\textbf{QM/MM} \longrightarrow \quad \left[\hat{H}^{N_A}_{v_A} + \hat{v}^{N_A}_{emb}\right]\Psi_A = \lambda^{QM/MM}\cdot\Psi_A$$

Notion of "subsystem" in FDET and in other embedding methods

- **QM/MM:**
  The localisation of ρ_{N_A} is usually **imposed by the modeller** by the way the total external potential is partitioned into $v(\mathbf{r}) = v_A(\mathbf{r}) + v_B(\mathbf{r})$, which leads to the localisation of $\rho_{N_A}(\mathbf{r})$ corresponding to the partitioning (**Monomer Expansion Approximation, MEA**). MEA implies that:

  Subsystem $\equiv$ *atoms defining* v_A *and basis sets centered on these atoms*

- **FDET:**
  The localisation of ρ_{N_A} is **the result of the optimisation of for a modeller chosen** ρ_{N_B}**.** In FDET-based methods, the localisation is a combined effect of error in the used approximant for $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$ and the monomer expansion approximation (if used). See later in this talk!

Notion of polarisation of ρ_{N_B} in FDET

"Frozen" ρ_{N_B} does not mean that the subsystem interpreted as "environment" in FDET calculations is not electronically polarised.
The optimal ρ_{N_A} obtained form the FDET eigenvalue equation might overlap with $\rho_{N_B}(\mathbf{r})$.

"Environment polarisation" is implicitly included in FDET based methods at least partially unless the densities $\rho_{N_A}(\mathbf{r})$ and $\rho_{N_B}(\mathbf{r})$ are localised in non-overlapping regions.[1]

[1] [Ricardi *et al.*, *Phys. Chem. Chem. Phys.* **20**, 26053 (2018)]

FDET energy functionals for various descriptors for ρ_{N_A} [Wesolowski, *Phys. Rev. A* **77** (2008) 012504)]

These functional satisfy the basic FDET equality: $E_v^{FDET}\left[X_A^{opt}, \rho_{N_B}\right] = E_v^{HK}[\rho_{N_A}^{X_A^{opt}} + \rho_{N_B}]$

$$E_v^{FDET}[\Psi_A, \rho_{N_B}] \equiv \langle \Psi_A | \hat{H}_v^{N_A} | \Psi_A \rangle + E_{xct}^{nad}[\rho^{\Psi_A}, \rho_{N_B}] + J_{AB}[\rho^{\Psi_A}, \rho_{N_B}] + E_v^{HK}[\rho_{N_B}]$$

$$E_v^{FDET(HF)[\Phi_A, \rho_{N_B}]} \equiv \langle \Phi_A | \hat{H}_v^{N_A} | \Phi_A \rangle + E_{xct}^{nad}[\rho^{\Phi_A}, \rho_{N_B}] + E_c[\rho^{\Phi_A}] + J_{AB}[\rho^{\Phi_A}, \rho_{N_B}] + E_v^{HK}[\rho_{N_B}]$$

$$E_v^{FDET(tCI)}[\Psi_A^{tCI}, \rho_{N_B}] \equiv \langle \Psi_A^{tCI} | \hat{H}_v^{N_A} | \Psi_A^{tCI} \rangle + E_{xct}^{nad}[\rho^{\Phi_A^{tCI}}, \rho_{N_B}] + E_c^{tCI}[\rho^{\Phi_A^{tCI}}] + J_{AB}[\rho^{\Phi_A^{tCI}}, \rho_{N_B}] + E_v^{HK}[\rho_{N_B}]$$

$$\begin{aligned} E_v^{FDET(KS)}[\Phi_A, \rho_{N_B}] &\equiv \langle \Phi_A | \hat{T}^{N_A} + \hat{v}^{N_A} + \hat{v_J}^{N_A} | \Phi_A \rangle + E_{xc}[\rho^{\Phi_A}] + E_{xct}^{nad}[\rho^{\Phi_A}, \rho_{N_B}] \\ &+ J_{AB}[\rho^{\Phi_A}, \rho_{N_B}] + E_v^{HK}[\rho_{N_B}] \end{aligned}$$

For $E_v^{FDET(\gamma)}[\gamma_A, \rho_{N_B}]$, see [Pernal & TAW, *IJQC*, **109** (2009) 2520]

Statement of the problem

It is tempting to optimise the embedded function of truncated CI form (including single-reference) and use the obtained states ti evaluate the correlation non-variationally. For instance, instead of

$$\left[\hat{T} + \hat{V}_{ee} + \hat{V} + \hat{V}_{emb}^{FDET(HF)}[\rho_{N_A}^{\Phi_A}, \rho_{N_B}]\right]\Phi_A \quad = \quad \lambda_A \cdot \Phi_A$$

use

$$\left[\hat{T} + \hat{V}_{ee} + \hat{V} + \hat{V}_{emb}^{FDET}[\rho_{N_A}^{\Phi_A}, \rho_{N_B}]\right]\Phi_A \quad = \quad \lambda_A \cdot \Phi_A$$

This would correspond to neglecting the correlation component of the FDET(HF) embedding potential. (Only the upper eigenvalue equation assures that the basic FDET equality is satisfied!)

How to use the non-variationally obtained correlation energy and assure consistency of the total energy with $E_v^{HK}[\rho]$?

From the definition of $E_v^{\mathrm{FDET}}[\Psi_A, \rho_{N_B}]$ it follows that $E_v^{\mathrm{FDET}}[\tilde{\Phi}_A^0, \rho_{N_B}] \geq E_v^{HK}[\tilde{\rho}_A^0 + \rho_{N_B}]$ but also

$$E_v^{\mathrm{FDET}}[\tilde{\Phi}_A^0, \rho_{N_B}] \geq \min_{\Psi} E_v^{\mathrm{FDET}}[\Psi_A, \rho_{N_B}] = E_v^{\mathrm{FDET}}[\Psi_A^0, \rho_{N_B}] = E_v^{HK}[\rho_A^0 + \rho_{N_B}]$$

where: $\tilde{\rho}_A^o(\mathbf{r}) = \left\langle \tilde{\Phi}_A^o | \hat{n} | \tilde{\Phi}_A^o \right\rangle$ and $\rho_A^o(\mathbf{r}) = \langle \Psi_A^o | \hat{n} | \Psi_A^o \rangle$

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

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

where,

$$v'(\mathbf{r}) = v(\mathbf{r}) + v_{emb}^{\mathrm{FDET}}[\tilde{\rho}_A^o, \rho_{N_B}](\mathbf{r})$$

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

and where $\Delta\tilde{\rho}_{v'}^c(\mathbf{r})$ 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 $v'(\mathbf{r})$.

Methods using FDET eigenvalue equation

There is no single "FDET method"!

Not only there are different FDET eigenvalue equations and FDET energy functionals depending on what descriptors are used for embedded N_A electrons, but many researchers developed methods using the FDET eigenvalue equation, see Carter et al. (1998), Neugebauer et al. (2006), Visscher et al. (2007), Miller et al. (2011), etc., for instance [2]

[2] These methods use a) additional simplifications/approximations for $E_v^{FDET}[\Psi_A, \rho_{N_B}]$, $v_{xcT}^{nad}\left[\rho_{N_A}, \rho_{N_B}\right]$, b) methods to solve the FDET eigenvalue equations, c) choices for generating ρ_{N_B}. See the review: [TAW, Shedge, Zhou, *Chemical Reviews* **115** (2015) 5891]

The "standard FDET" protocol for excited states

The "standard FDET" protocol is the entry level set of approximations in FDET equations:

- **Monomer expansion approximation (MEA)**
  The same set of atomic basis functions as the one in the absence of the environment.
- **Linearisation:** $E_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}] \approx E_{xct}^{nad}[\rho_{N_A}^{ref}, \rho_{N_B}] + \int v_{xct}^{nad}[\rho_{N_A}^{ref}, \rho_{N_B}](\mathbf{r}) \left(\rho_{N_A}(\mathbf{r}) - \rho_{N_A}^{ref}(\mathbf{r})\right) d\mathbf{r}$
  with $\rho_{N_A}^{ref}$ being the ground-state density of the isolated chromophore
- **Local density approximation:** $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}] \approx \tilde{v}_{xct}^{nad(LDA)}[\rho_{N_A}, \rho_{N_B}]$
- **Implicit electronic polarisation of** ρ_{N_B}
  (for "explicit" and "state-specific" see [Fu&TAW, *J. Phys. Chem. A.*, **127**, 535-545 (2023)])

\+ Accuracy of the solvent induced effect on excitation energies below 50 meV in **a well defined domain of applicability**

\+ Non-empirical approximant for the bi-functional $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$

\- **Not possible to treat:** Rydberg excitations, solvent-to chromophore charge transfer excitations, solvents which absorb in the same spectral range as the embedded species

\- **Expected errors above 50 meV for:** intramolecular charge-transfer excitations or chromophore-to-solvent charge-transfer excitations

Chromophores

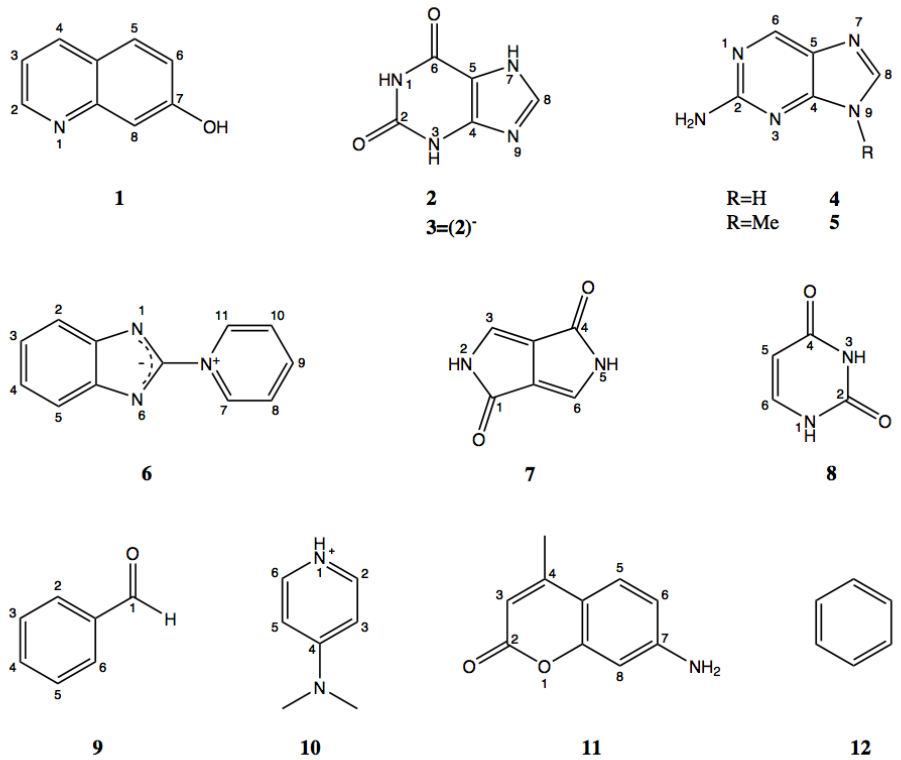


Figure 1: Chromophores considered in this work are (**1**) 7-hydroxyquinoline, (**2**) xanthine, (**3**) xanthinide, (**4**) 2-aminopurine, (**5**) 7-methyl-2-aminopurine, (**6**) pyridiniumyl benzimidazolide, (**7**) diketopyrrolopyrrole, (**8**) uracil, (**9**) benzaldehyde, (**10**) 4-dimethylaminopyridine,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

[Zech et al., J. Chem. Theor. & Comput. (2018) **14** 4028]

Environments

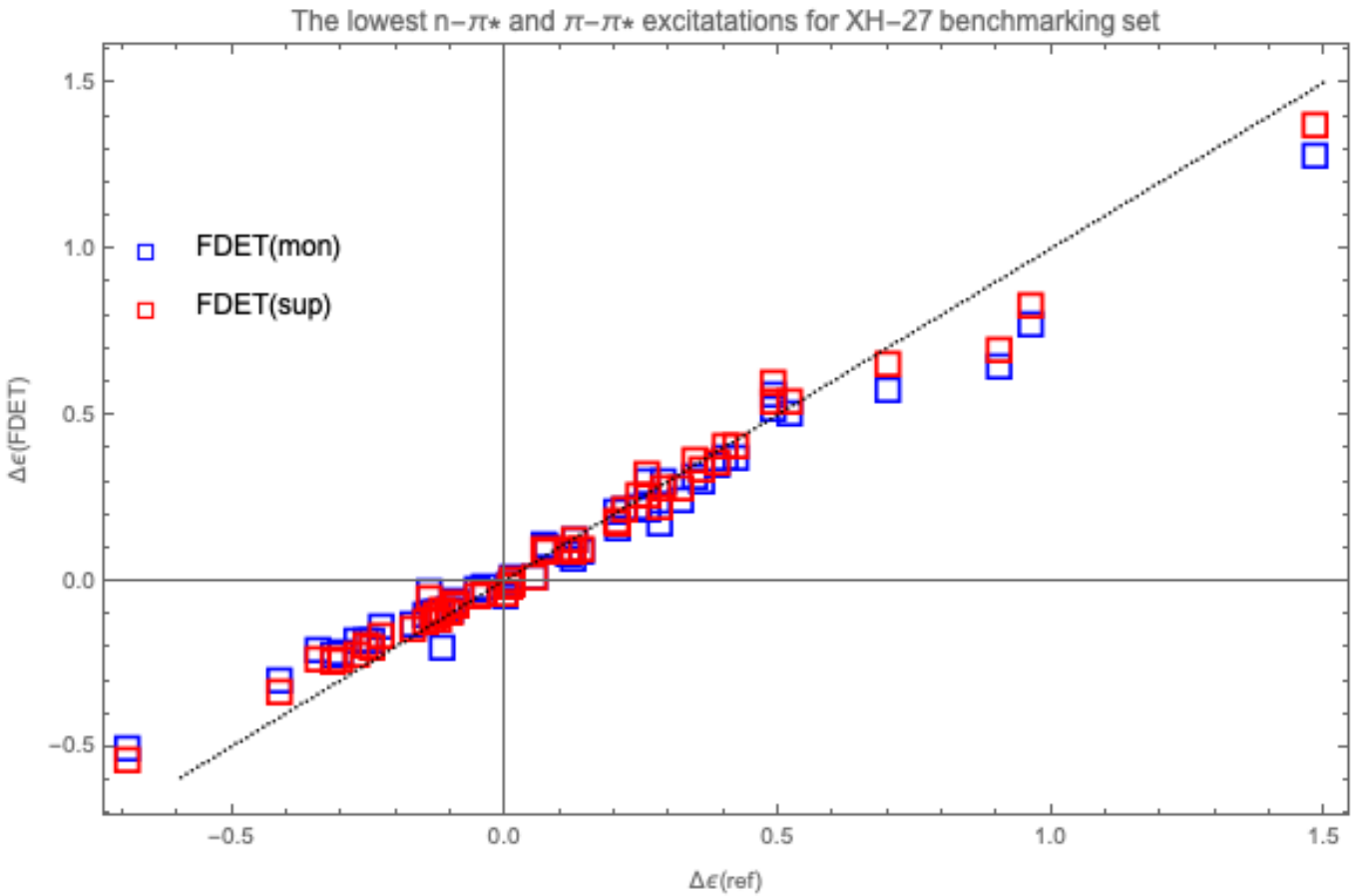
$(H_2O)_n$ n=1,10
$(NH_3)_n$, n=1,4
mixed (H_2O, NH_3)
$(HCOOH)_n$, n=1,2
$(MeOH)_n$, n=1,3
formamide, formimidamide, guanidine, acetamide, pyridine, $HCOO^-$

Statistics: 351 electronic excitations

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

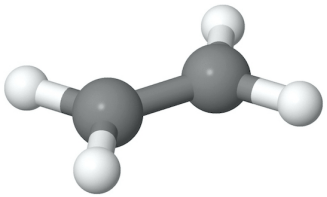
ME=39meV (0.9kcal/mol),
SD=43meV (1.0kcal/mol)

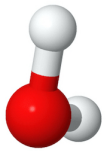
Benchmarking vertical excitation energies



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

One- and two-photon absorption properties from conventional methods





$$M_{ab} = \sum_k [\frac{\langle 0|\hat{\mu}^a|k\rangle\langle k|\hat{\mu}^b|n\rangle}{\omega_k - \omega_1} + \frac{\langle 0|\hat{\mu}^b|k\rangle\langle k|\hat{\mu}^a|n\rangle}{\omega_k - \omega_2}]$$

Method	$\Delta\epsilon_1^{\pi\pi}$ [eV]	$\Delta\epsilon_2^{\pi\pi}$ [eV]	$\Delta\delta_{TPA}^{\pi\pi 1}$ [a.u.]	$\Delta\delta_{TPA}^{\pi\pi 2}$ [a.u.]
ADC(2)	-0.083	-0.184	35.9	-23.2
FDET/ADC(2)	-0.087	-0.207	24.1	-20.7

d-aug-cc-pVQZ basis set (monomer expansion in FDET)

[Fu & Wesolowski, *J.Chem. Theor. & Comput.* (2021), **17** 3652]

more on FDET derived TPA properties in: [Fu & Wesolowski, *Mol. Phys.* (2025), e244914]

FDET in "comfort zone": electronic transitions

Electron. Struct. **7** (2025) 015007 https://doi.org/10.1088/2516-1075/adc055

Electronic Structure

PAPER

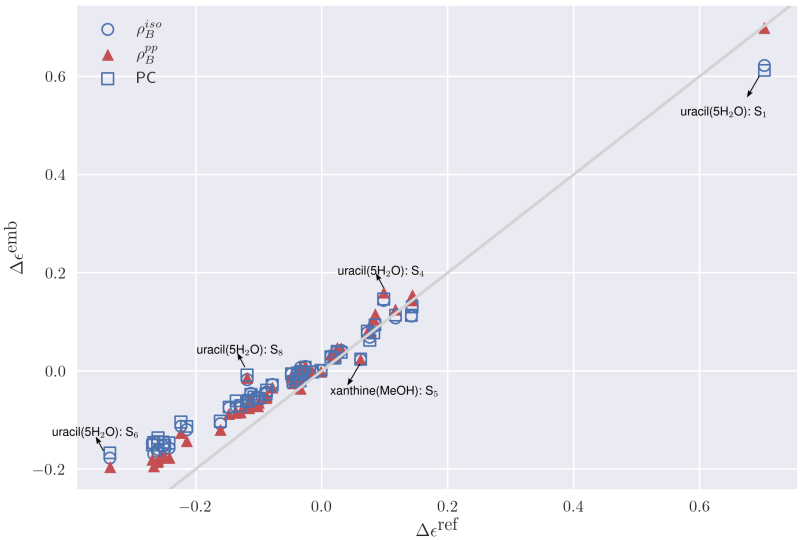
Oscillator strengths from Frozen Density Embedding Theory based calculations

Mingxue Fu and Tomasz A Wesolowski*

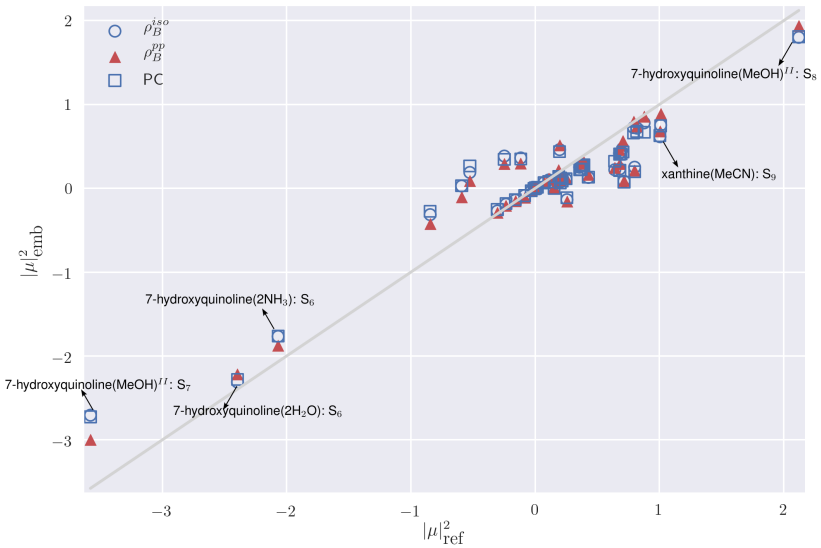
Department of Physical Chemistry, University of Geneva, 30, Quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

ADC(2) vs FDET/ADC(2)

Transition energy [eV]



Transition Moment [Debye^2]



[Fu & TAW, *Electronic Structure*, **7**, 015007 (2025)]

FDET in "comfort zone": Electric-Field Gradient

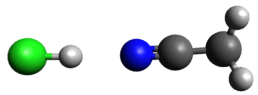
Assessment of Approximations to the Embedding Potential in Frozen-Density Embedding Theory for the Calculation of Electric Field Gradients

Yann Gimbal-Zofka, Cristina E. González-Espinoza, Christopher A. Rumble,* and Tomasz A. Wesolowski*

Cite This: *J. Chem. Theory Comput.* 2024, 20, 348–356

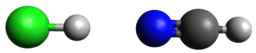
Read Online

V_{zz} for HCl-X complexes

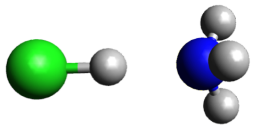


(a) Hydrogen chloride and Acetonitrile

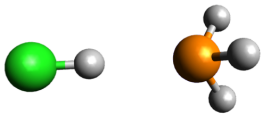
(b) Hydrogen chloride and Carbon Monoxid



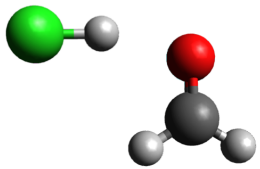
(c) Hydrogen chloride and Formonitrile



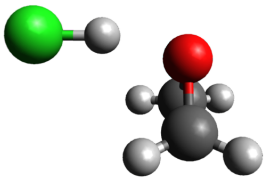
(d) Hydrogen chloride and Ammonia



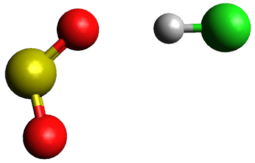
(e) Hydrogen chloride and Phosphane



(f) Hydrogen chloride and Formaldehyde

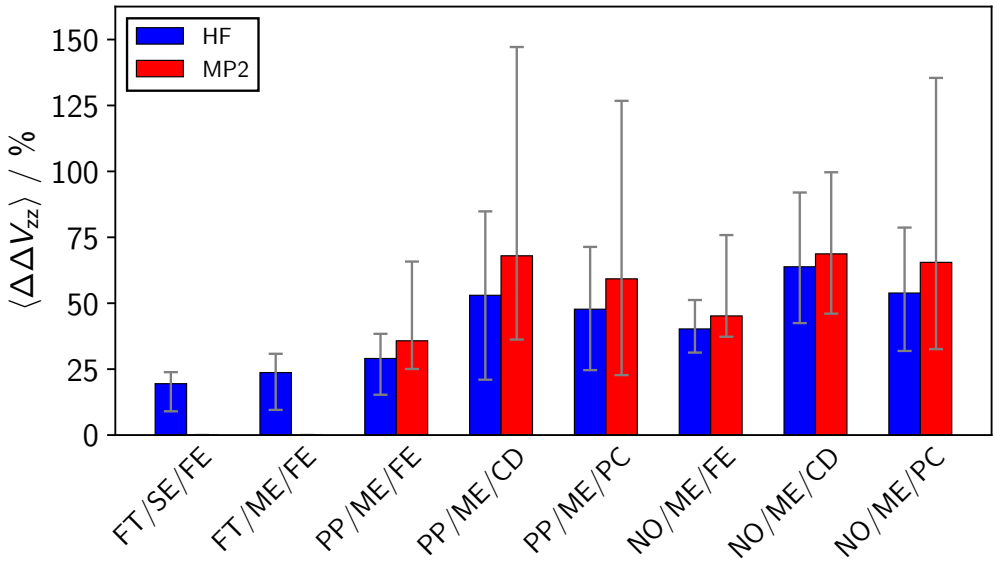


(g) Hydrogen chloride and Oxyrane



(h) Hydrogen chloride and Sulfur dioxide

EFG on **Cl** of embedded HCl



cc-pcvtz basis set

[Gimbal-Zofka et al. , *J. Chem. Theor.& Comp.*, **20**, 348 (2024)]

"Comfort Zone" for methods based on FDET

- Lack of covalent interactions between embedded species and environment
- Possible *a priori* determination of N_A and N_B
- Dispersion interactions not crucial compared to electrostatic and induction
- For electronic excitations additionally: a) negligible overlap between the spectra of the embedded chromophore and the environment and b) lack of chromophore to/from environment excitations

Rule of thumb: $$\frac{\left|\text{Error of}\left\langle \Psi_A^{emb}|\hat{O}|\Psi_A^{emb}\right\rangle - \left\langle \Psi_A^{0}|\hat{O}|\Psi_A^{0}\right\rangle\right|}{\left|\left\langle \Psi_A^{emb}|\hat{O}|\Psi_A^{emb}\right\rangle - \left\langle \Psi_A^{0}|\hat{O}|\Psi_A^{0}\right\rangle\right|} \approx 10-25\%.$$

- Dipole Moment [Jacob 2005, Krzeminska2025]
- ESR couplings [Wesolowski1999, Neugebauer2005,Englert2026]
- Electric-Field Gradient [Gimbal-Zofka2024]
- One-photon absorption: transition energies [Zech2018], transition moments [Fu2025]
- Two-Photon Absorption Cross-sections [Fu2021]

Beyond the comfort zone of well-working semi-local approximants for $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$

Can Semilocal Approximations to the Embedding Potential Tackle Charge-Transfer-to-Solvent Excitations? An Aqueous Thiocyanate Example

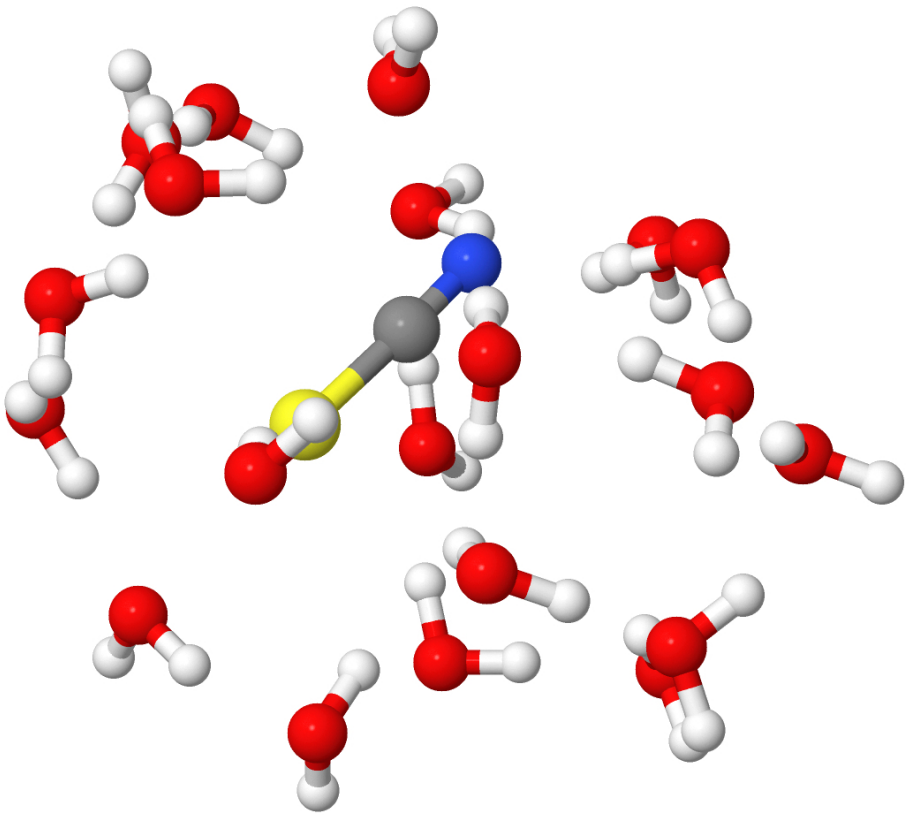
Pierre-Olivier Roy, Mingxue Fu, Ronit Sarangi, Anna I. Krylov,* and Tomasz A. Wesolowski*

Cite This: *J. Chem. Theory Comput.* 2025, 21, 10452–10465 Read Online

POR, MF, & TAW: Université de Genève

AIK &RS: University of Southern California

SCN^--20·H_2O cluster



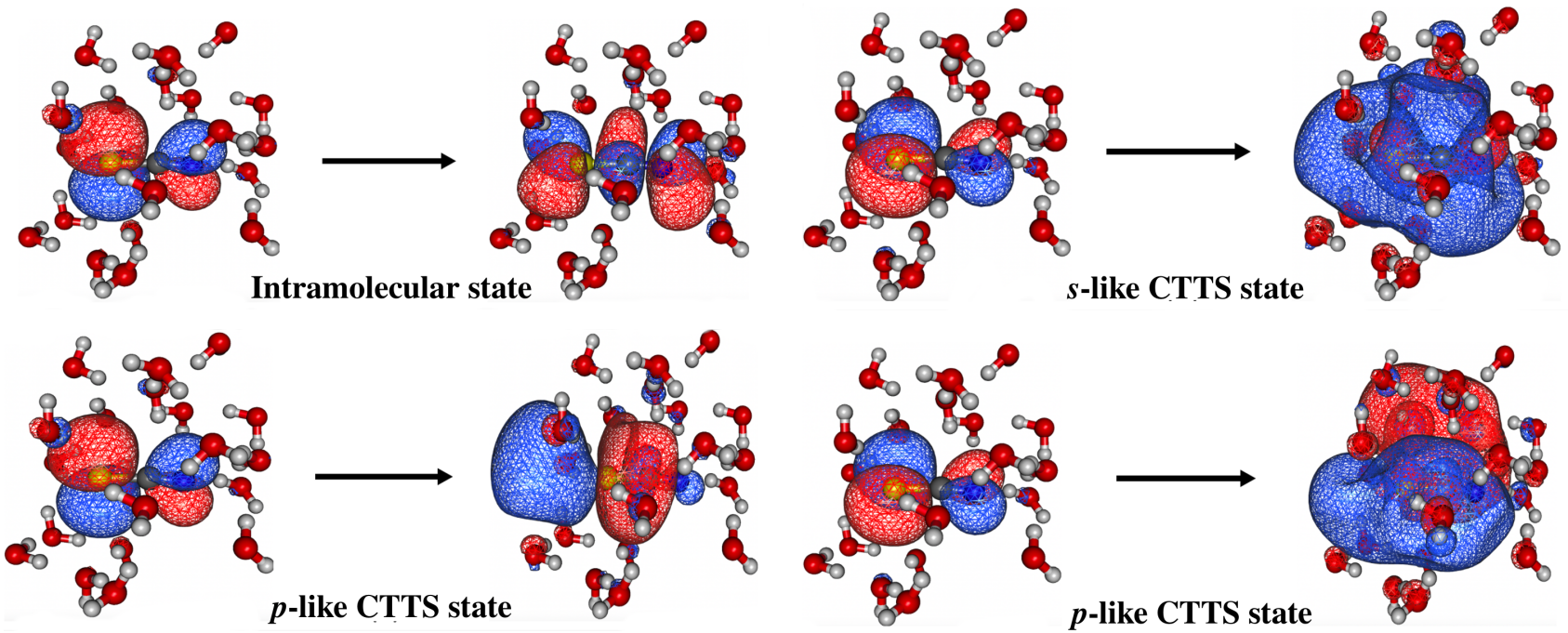
- *In the gas phase:*

  the first excited state of SCN^- lies in the continuum

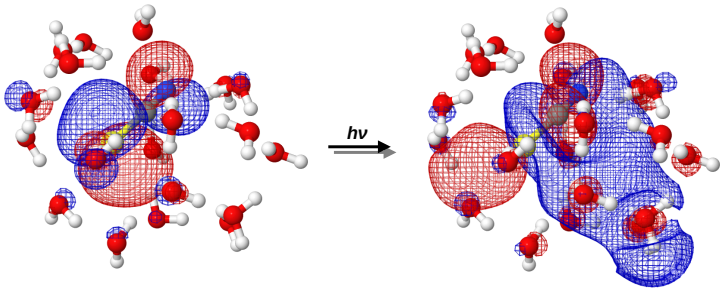
- *In liquid water (experiment) and in small clusters in water (EOM-CC or ADC(2) simulations):*

  the lowest excited states are localised on SCN^-

Natural Transition Orbitals for excited states in SCN^--20·H_2O clusters



CHARGE-TRANSFER-TO-SOLVENT EXCITATIONS

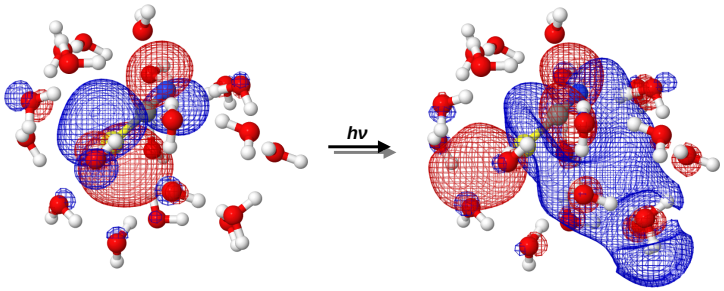


A CHALLENGE FOR EMBEDDING METHODS

How to deal with such excitations?

- **Abandon the embedding strategy:** use the wave-function description level on the whole cluster.
- **Face the challenge:** do not increase the number of electrons in the embedded part, i.e. keep the wave-function description level for the chromophore only.

CHARGE-TRANSFER-TO-SOLVENT EXCITATIONS



A CHALLENGE FOR EMBEDDING METHODS

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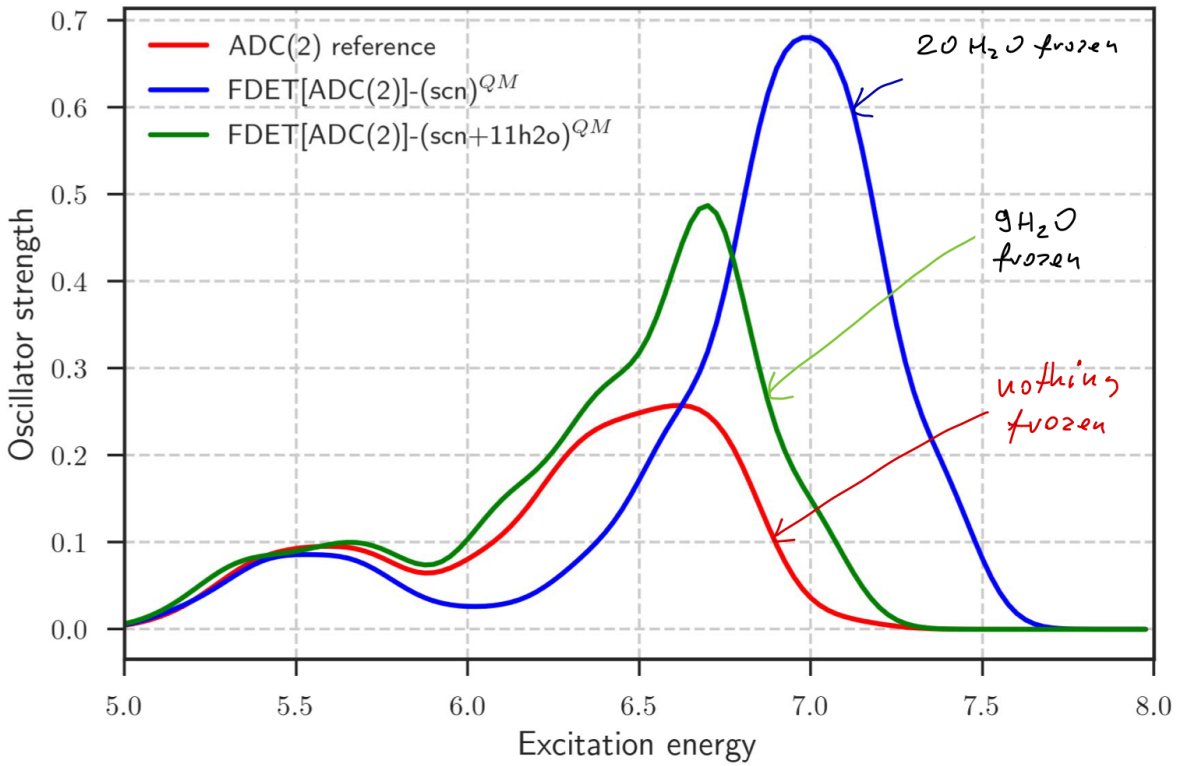
- **Abandon the embedding strategy:** use the wave-function description level on the whole cluster.

- **Face the challenge:** do not increase the number of electrons in the embedded part, i.e. keep the wave-function description level for the chromophore only.

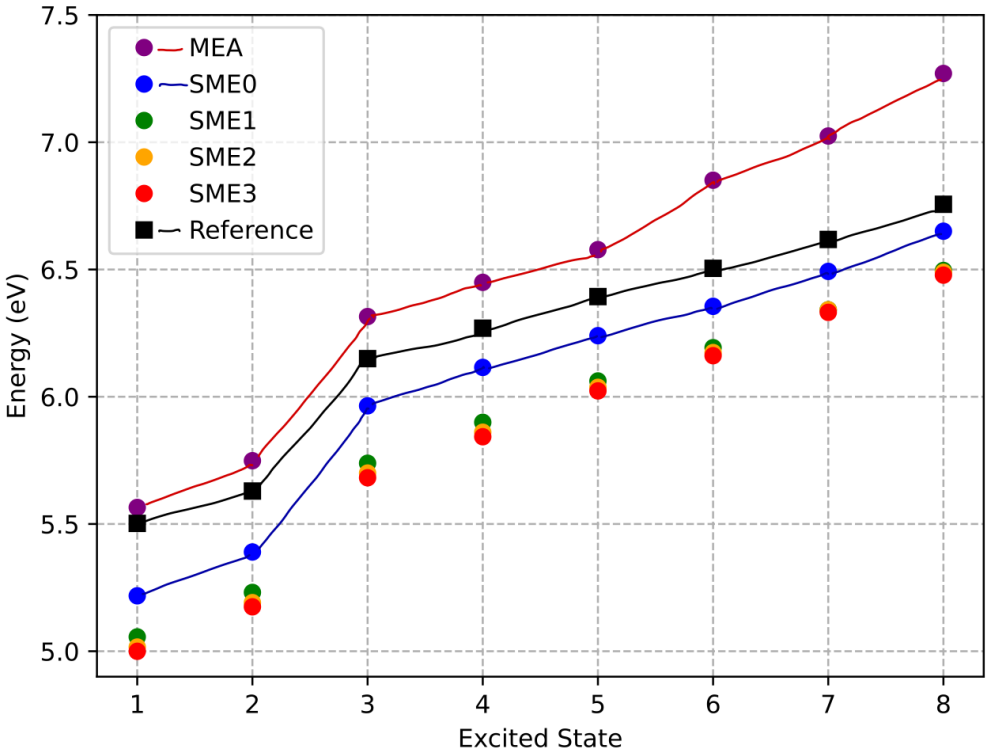
Necessary conditions for FDET:
- Basis sets for Ψ_A: must allow its localisation far from the chromophore (diffuse functions)
- $\tilde{v}_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$: describes correctly $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$ near the nuclei in the environment.

Failure of the "standard FDET protocol"



Above 6.0 eV, energies and oscillator strengths overestimated!!
Improvement possible but at the cost of increasing the number of electrons in the embedded part.

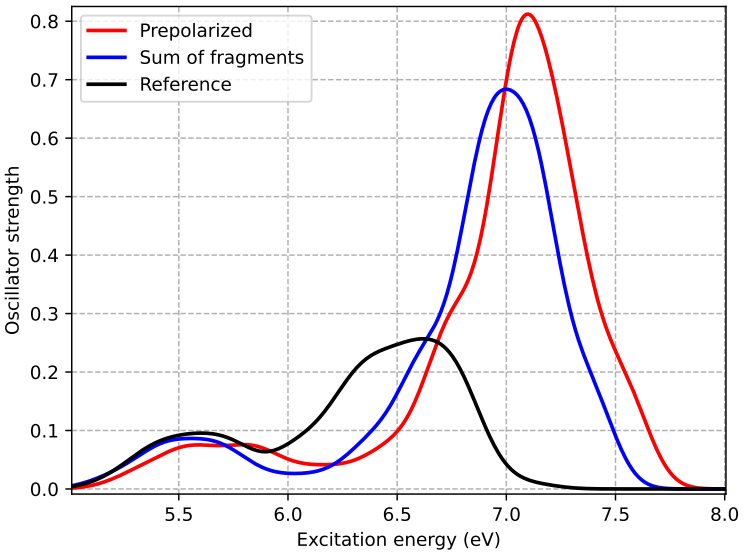
Beyond monomer-expansion approximation (MEA) in FDET with $\tilde{v}_{xct}^{nad(LDA)}[\rho_{N_A}, \rho_{N_B}]$



SME1, SME2, SME3, is a series of basis sets used for the embedded wavefunction with increasing number of functions localised in the environment (ghosts). In addition to the bass functions used in MEA, SM0 use diffuse functions centered on the atoms in the environment which are expected to describe better the excited wavefunction than the diffuse functions localised on the chromophore. SM2 and SM3 use additionally the functions representing inner shells of the solvent atoms.

For $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}] \approx \tilde{v}_{xct}^{nad(LDA)}[\rho_{N_A}, \rho_{N_B}]$, if the basis set allows to localise the excited-state wavefunction in the environment:
- **higher excitations improve**,
- **lower excitations worsen**.

Failure of the "standard FDET protocol"

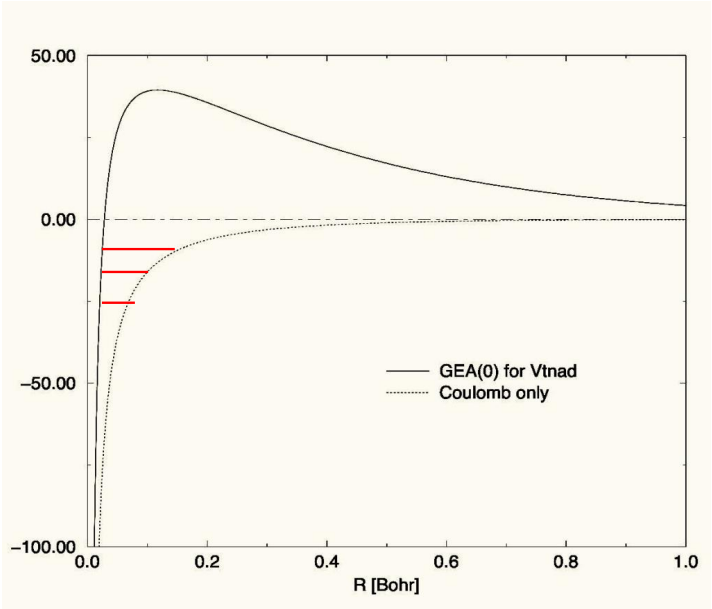


Can the failure of the LDA approximant for $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$ (and other decomposable semi-local approximants) in describing hydration effect on excitations above 6.0 eV, due violation of some exact properties of $v_{xct}^{nad}[\rho_{N_A}, \rho_{N_B}]$?

Exact property of $v_t^{nad}[\rho_{N_A}, \rho_{N_B}](\mathbf{r})$

$$\mathbf{v_t^{nad}}[\rho_{\mathbf{N_A}}, \rho_{\mathbf{N_B}}](\mathbf{r}) \xrightarrow{\text{for } \rho_{N_A}(\mathbf{r})\to 0 \text{ and } \int \rho_{N_B}(\mathbf{r})d\mathbf{r}=2} \mathbf{v_t^{nad(limit)}}[\rho_{\mathbf{N_B}}](\mathbf{r}) = -\frac{\mathbf{1}}{\mathbf{4}}\frac{\nabla^2\rho_{\mathbf{N_B}}(\mathbf{r})}{\rho_{\mathbf{N_B}}(\mathbf{r})} + \frac{\mathbf{1}}{\mathbf{8}}\frac{|\nabla\rho_{\mathbf{N_B}}(\mathbf{r})|^2}{\rho_{\mathbf{B}}^2(\mathbf{r})}$$

Any gradient expansion approximation or generalised gradient approximation based approximant to $v_t^{nad}[\rho_{N_A}, \rho_{N_B}]$, violates it. It results in emergence of artificial bund states localised on any atom in the environment. [3]



Desired relevant property of the functional $v_t^{nad(limit)}[\rho_{N_B}](\mathbf{r})$**:**

$$v_t^{nad(limit)}[\rho_{N_B} = Ae^{-2\zeta r}](\mathbf{r}) = \overbrace{-\frac{\zeta^2}{2}}^{constant} + \overbrace{\frac{\zeta}{r}}^{repulsive}$$

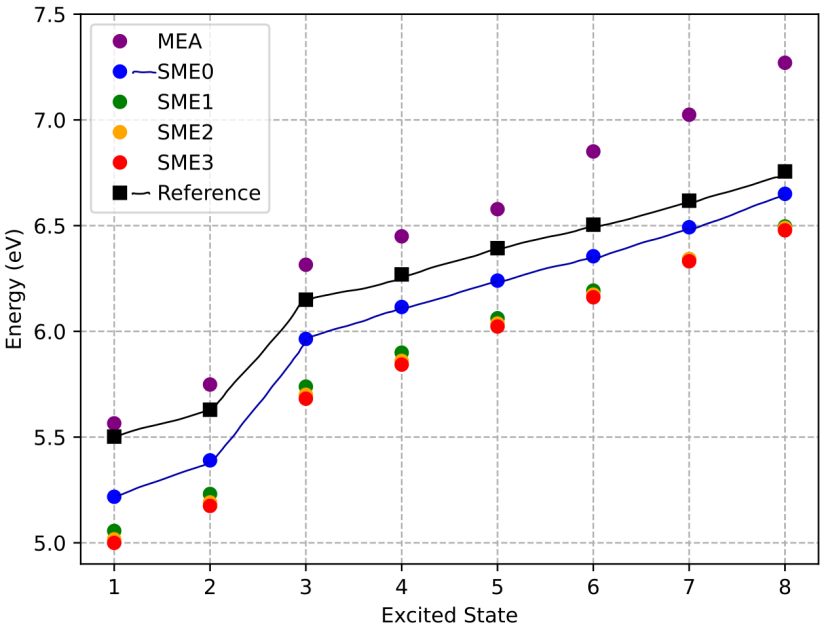
is imposed on NDSD [a] and NDCS [b] approximants

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

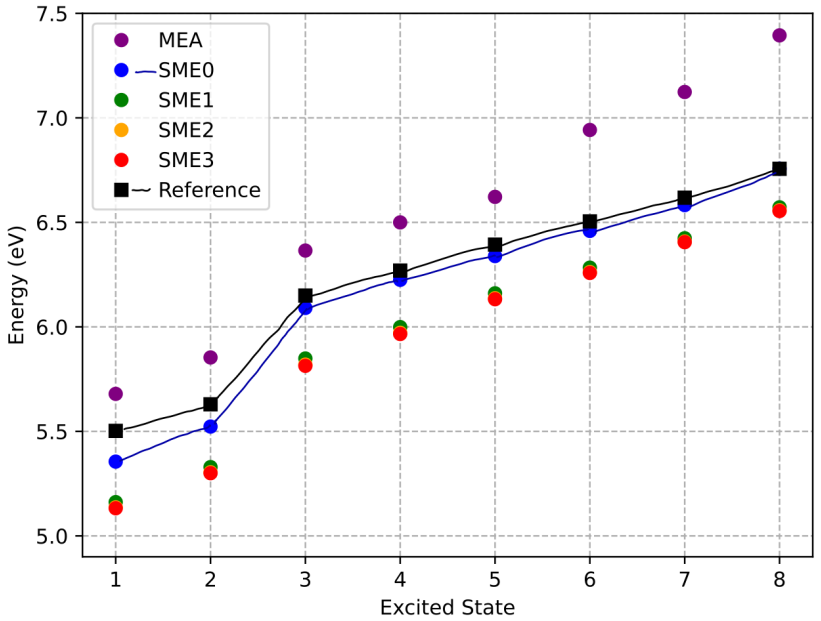
[b] NDCS [Polak et al., *J. Chem. Phys.* **156** 044103 (2022)]

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

LDA


MEA
SME0
SME1
SME2
SME3
Reference
Energy (eV)
Excited State
7.5
7.0
6.5
6.0
5.5
5.0
1
2
3
4
5
6
7
8

NDCS


MEA
SME0
SME1
SME2
SME3
Reference
Energy (eV)
Excited State
7.5
7.0
6.5
6.0
5.5
5.0
1
2
3
4
5
6
7
8

Imposing exact properties of $v_t^{nad}[\rho_{N_A}, \rho_{N_B}](\mathbf{r})$

Spin localization in intermolecular complexes: A challenge for semi-local approximants for the embedding potential

Special Collection: Quantum Embedding for Molecules and Materials

Tanguy Englert; Pierre-Olivier Roy ; Tomasz A. Wesolowski

J. Chem. Phys. 164, 084122 (2026)

Exact property of $v_t^{nad}[\rho_{N_A}, \rho_{N_B}](\mathbf{r})$

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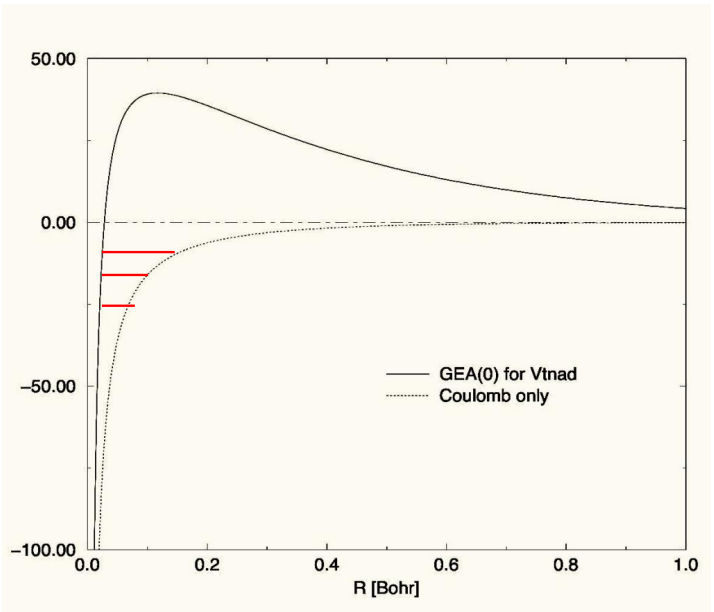

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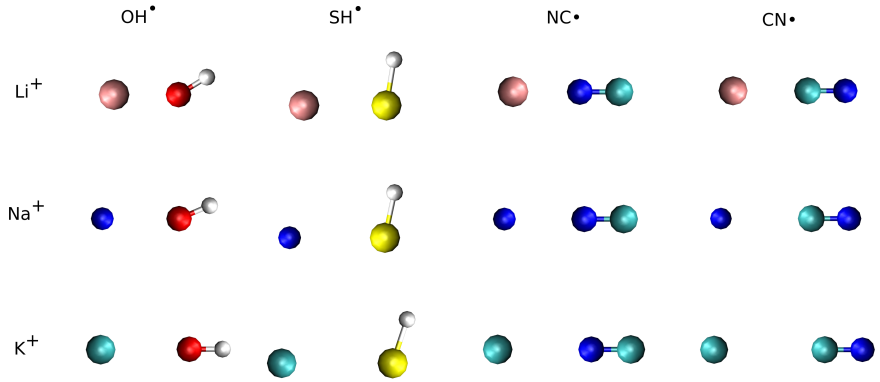
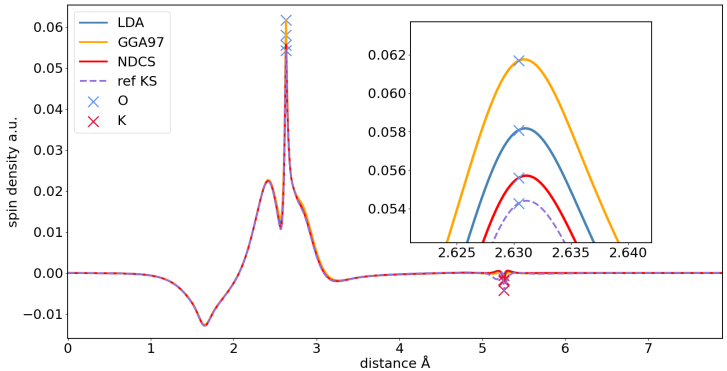


Spin-Density along the K-O axis in K^+ $OH^\bullet$



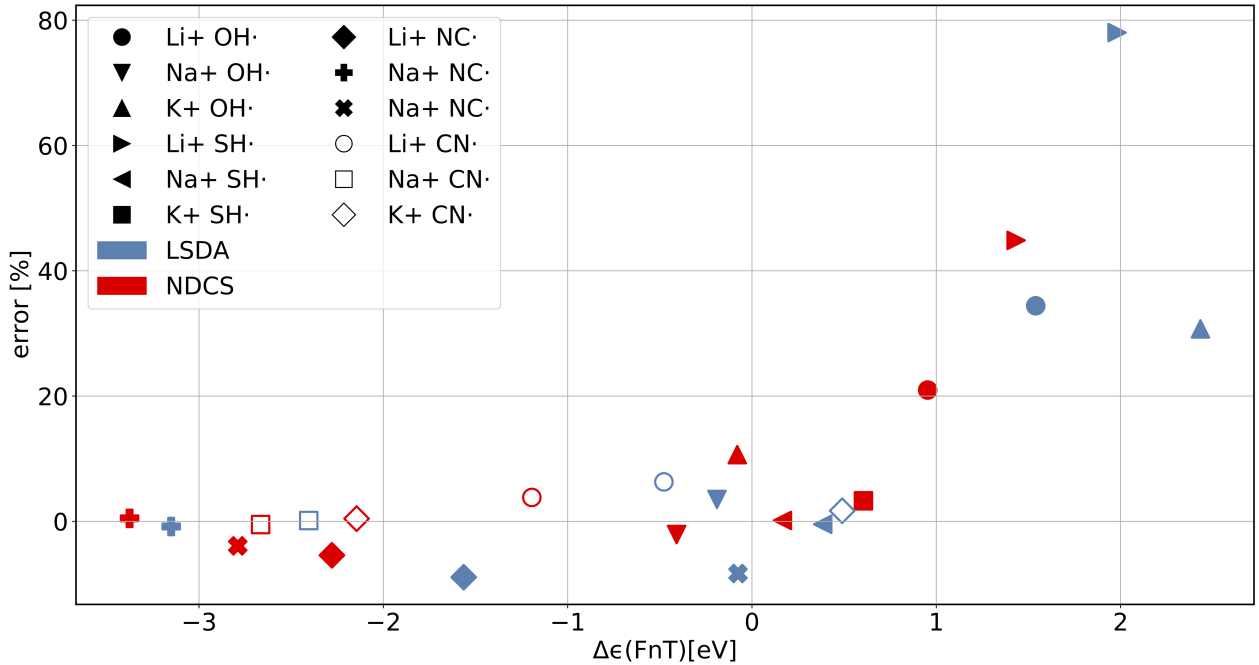
Ref.≡ Kohn-Sham PBE/cc-pcvtz

Cation	Radical	$\epsilon_{LUMO}(cation)$	ϵ_{SOMO} (radical)	$\Delta\epsilon$
K^+	$CN^\bullet$	-6.06	-9.27	-3.21
Li^+	$CN^\bullet$	-6.79	-9.29	-2.50
Na^+	$CN^\bullet$	-7.15	-9.28	-2.13
K^+	$OH^\bullet$	-6.06	-6.65	-0.59
K^+	$SH^\bullet$	-6.06	-6.19	-0.13
Li^+	$OH^\bullet$	-6.79	-6.65	0.14
Na^+	$OH^\bullet$	-7.15	-6.65	0.50
Li^+	$SH^\bullet$	-6.79	-6.18	0.60
Na^+	$SH^\bullet$	-7.15	-6.19	0.96

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.*, **164**, 084122 (2026)]

Relation between the relative errors in A_{iso} and the *a posteriori* evaluated indicator $\Delta\epsilon(FnT)$

$$\Delta\epsilon(FnT) = \epsilon^{SOMO(FDET)}_{radical} - \epsilon^{LUMO(FDET)}_{cation(\infty)}$$



FDET eigenvalue use either $\tilde{v}_t^{nad(LSDA)}[\rho_{N_A}, \rho_{N_B}]$ or $\tilde{v}_t^{nad(NDCS)}[\rho_{N_A}, \rho_{N_B}]$.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.*, **164**, 084122 (2026)]

The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

The bi-functional for the non-additive kinetic potential at dissociation

Cite as: J. Chem. Phys. 165, 000000 (2026); doi: 10.1063/5.0349436
Submitted: 23 June 2026 • Accepted: 24 August 2026 •
Published Online: 9 99 9999

Tanguy Englert, Pierre-Olivier Roy, and Tomasz A. Wesolowski[a)]

AFFILIATIONS

Département de Chimie Physique, Université de Genève, 30, Quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

Note: This paper is part of the Special Topic on Electron Densities: From Algorithms and Functionals to Molecular Modeling and Chemical Insights.

[a)]**Author to whom correspondence should be addressed:** tomasz.wesolowski@unige.ch

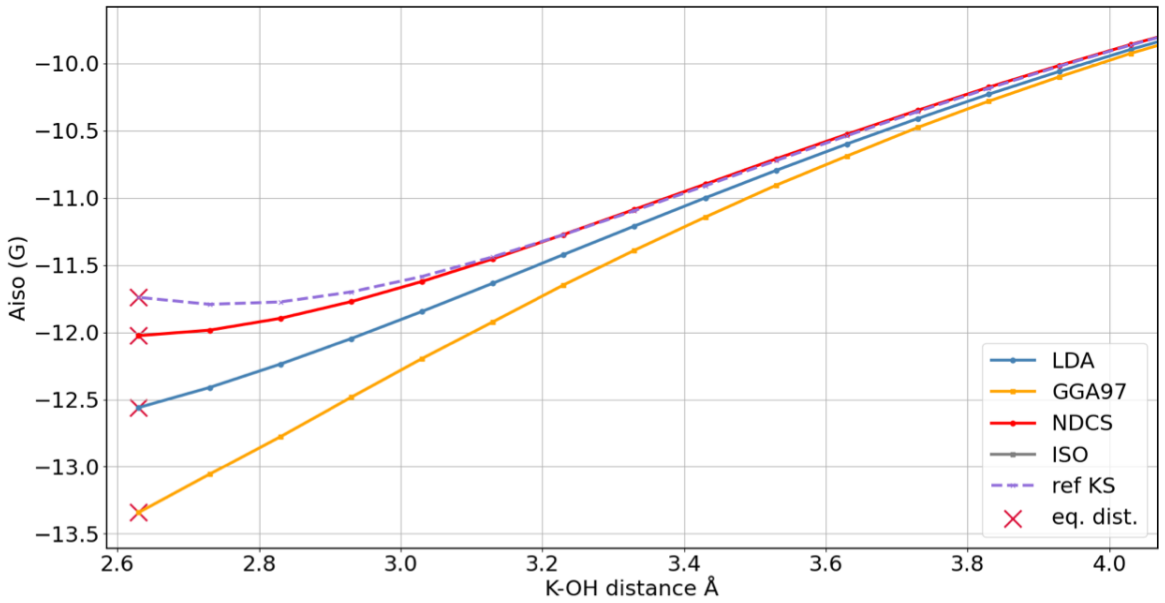
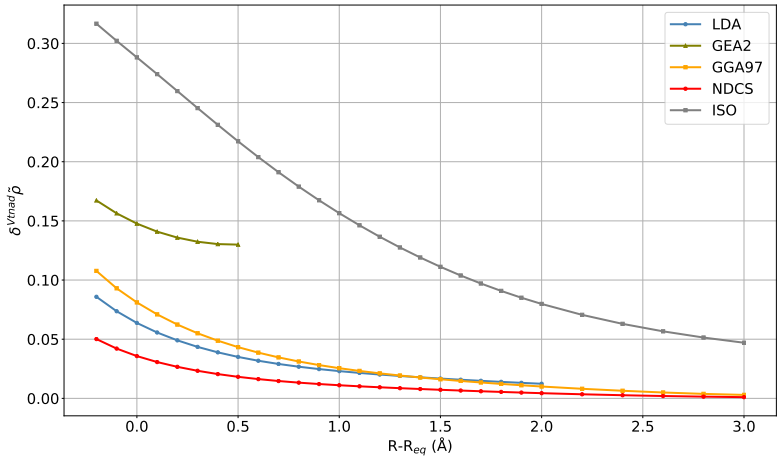
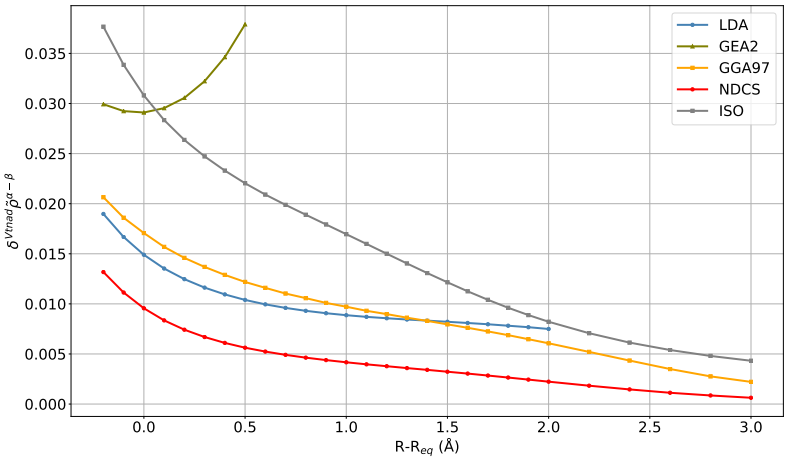


Figure 2: (zoomed in) A_{iso} values in G calculated from FnT optimized spin densities in a K^+-$OH^\bullet$ complexe and increasing distances between K^+ and $OH^\bullet$. results are shown for the $\tilde{v}_t^{nad(LSDA)}[\rho_A, \rho_B]$, $\tilde{v}_t^{nad(GGA97)}[\rho_A, \rho_B]$ or $\tilde{v}_t^{nad(NDCS)}[\rho_A, \rho_B]$ approximants together with results from the reference Kohn-Sham calculations and isolated radical.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



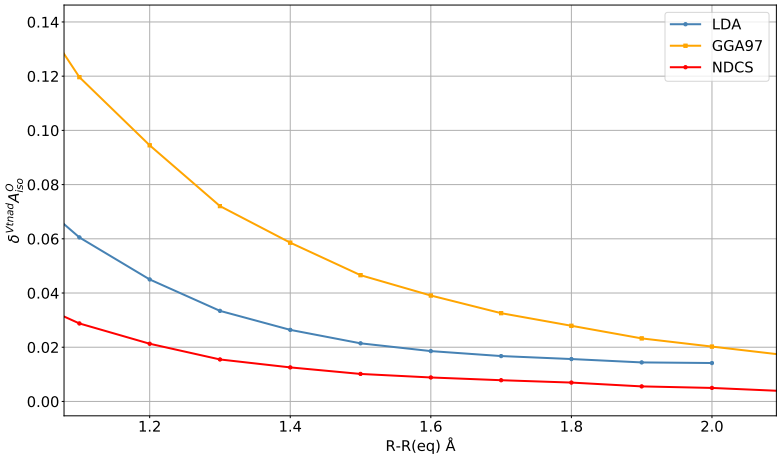
(a)



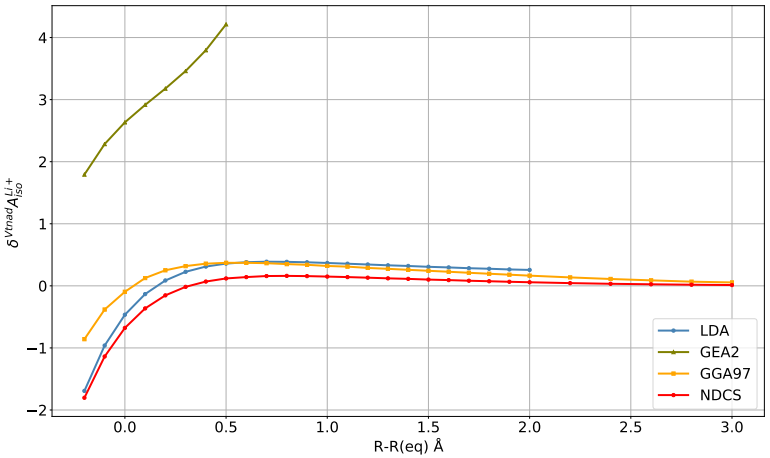
(b)

Norms of a) the total density error, $\delta^{v_t^{nad}}\tilde{\rho}$ (in e), and b) the total spin-density error in the Li^{+}–$OH^{\bullet}$ case as a function of the Li-O separation. The equilibrium Li-O distance is 1.90 Å, at which $\Delta^{compl}\rho = 0.288e$ and $\Delta^{compl}\rho^{\alpha-\beta} = 0.031e$.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



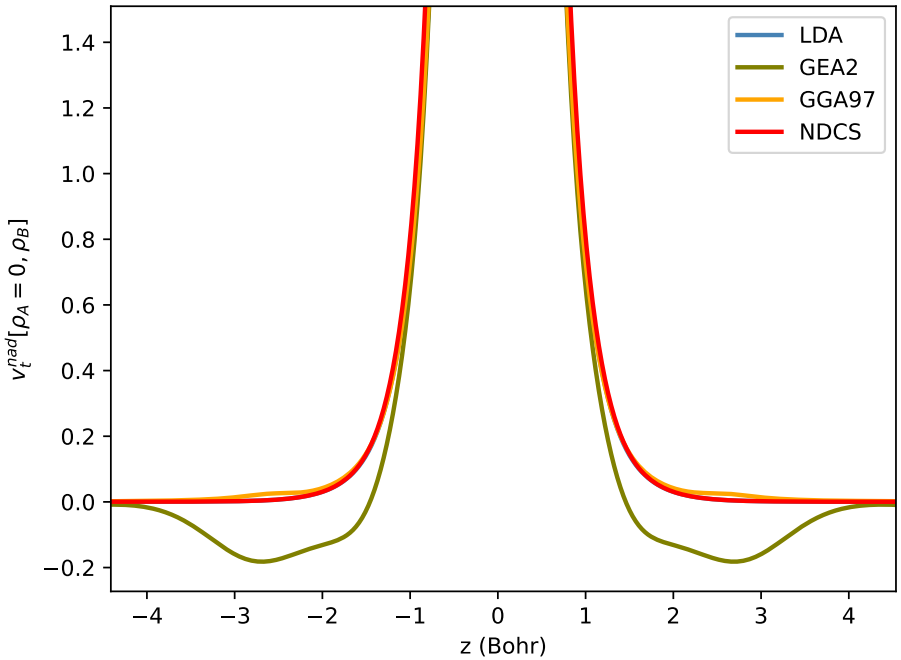
(a)



(b)

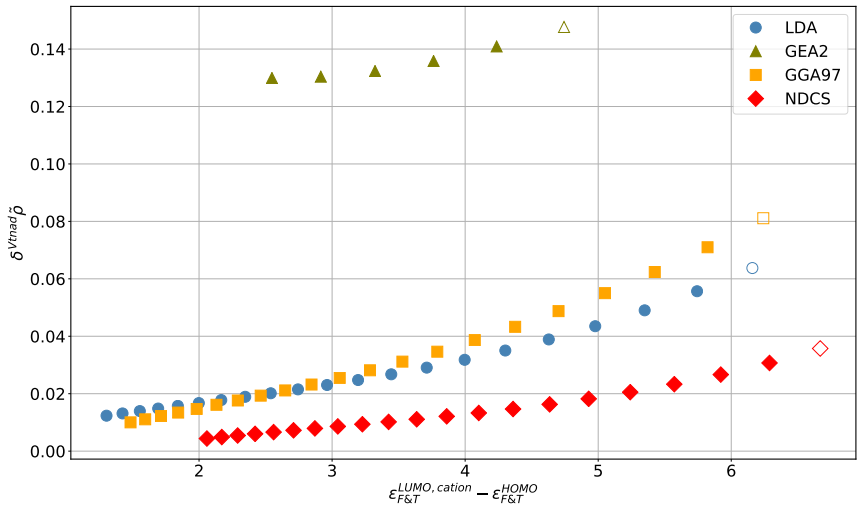
Errors in a) the oxygen hyperfine coupling constant, $\delta^{v_t^{nad}} A^O_{iso}$ and b) the lithium hyperfine coupling constant, $\delta^{v_t^{nad}} A^{Li}_{iso}$ in the Li^+–$OH^\bullet$ case as a function of the Li-O separation. The equilibrium Li-O distance is 1.90 Å, at which $\Delta^{compl} A^O_{iso} = -3.928$ Gauss and $\Delta^{compl} A^{Li}_{iso} = -1.868$ Gauss.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



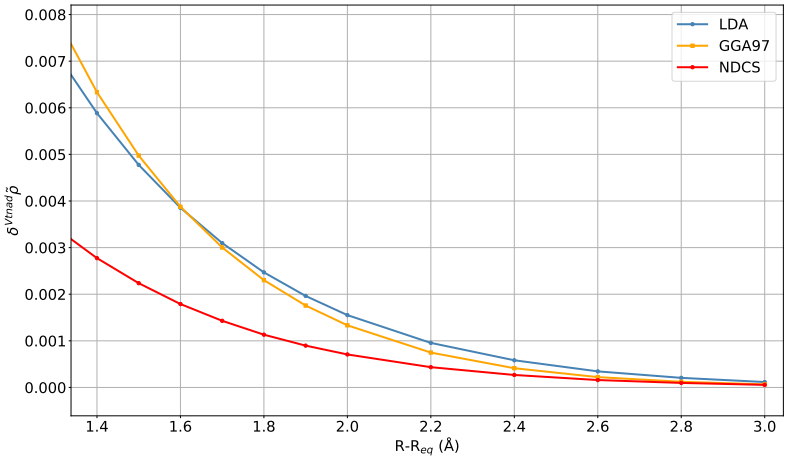
Limiting non-additive kinetic potential, $\tilde{v}_t^{nad}[\rho_{N_A} = 0, \rho_{N_B}]$ for an isolated Li^+ cation, shown along an arbitrary axis passing through the Li nucleus, obtained using the LDA, GEA2, GGA97, and NDCS approximants.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]

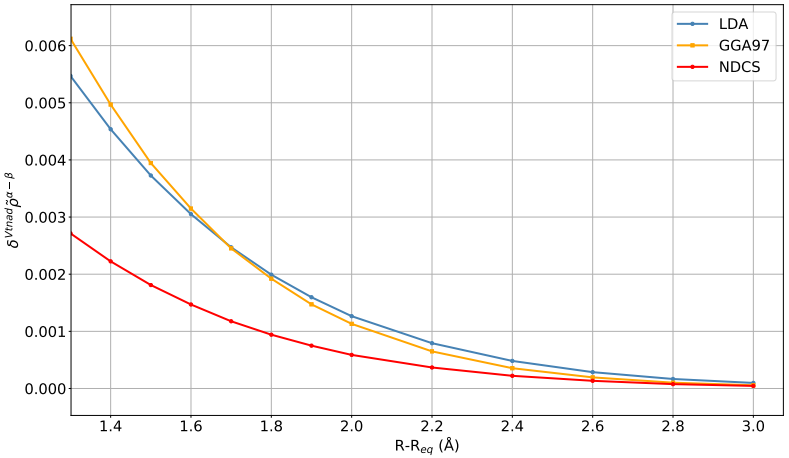


Norm of the total density error, $\delta^{V_t^{nad}}\tilde{\rho}$ in the Li^+–$OH^\bullet$ case as a function of the gap between the energy of the embedded radical HOMO and the lowest unoccupied orbital located on the cation (in eV) for different Li-O separations. The equilibrium Li-O distance is 1.90 Å. Empty symbols indicate the values evaluated at equilibrium geometry.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



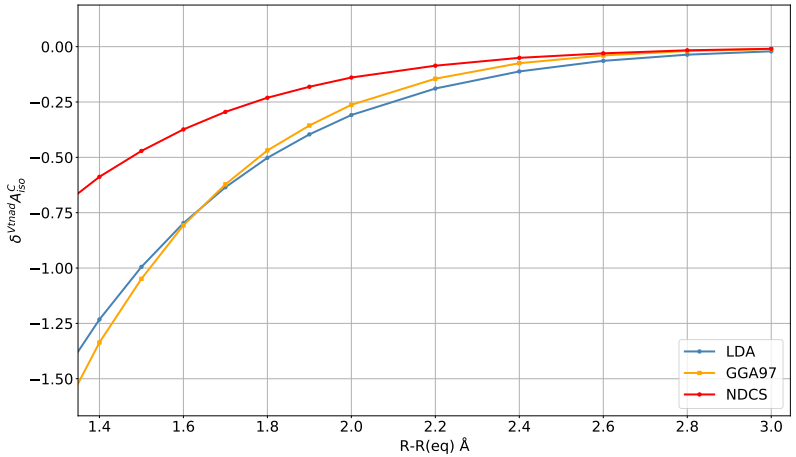
(a)



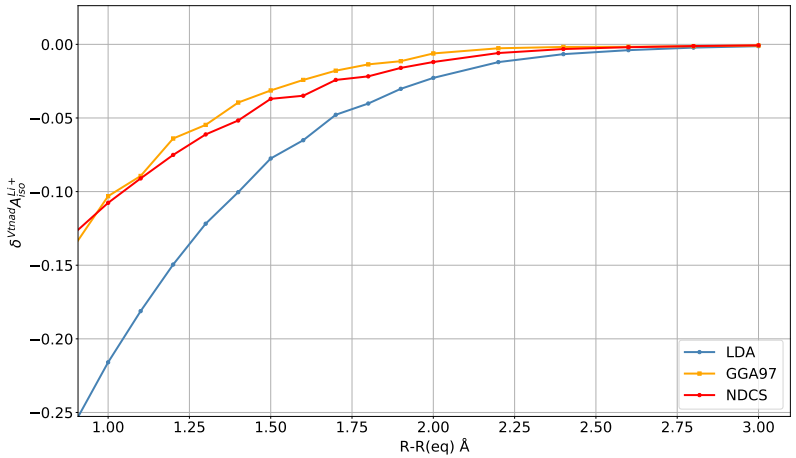
(b)

Norms of a) the total density error, $\delta^{v_t^{nad}}\tilde{\rho}$, and b) the total spin-density error, in the Li^+–$NC^\bullet$ case as a function of the Li-N separation. The equilibrium Li-N distance is 2.06 Å, at which $\Delta^{compl}\rho = 0.485e$ and $\Delta^{compl}\rho^{\alpha-\beta} = 0.446e$.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



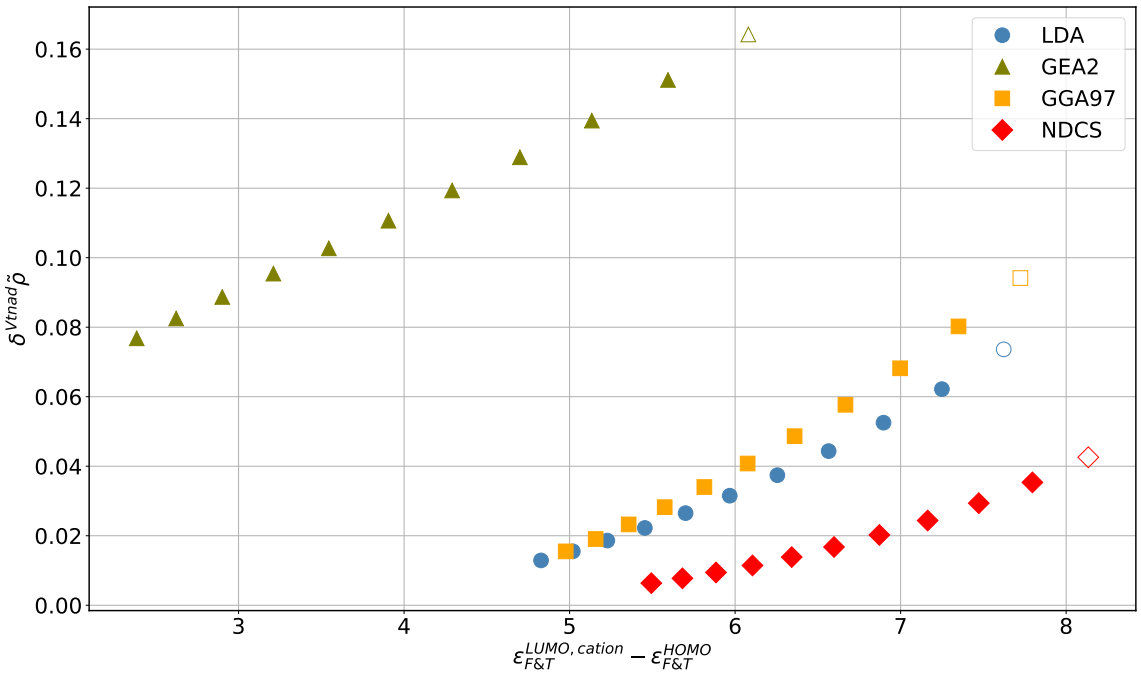
(a)



(b)

Errors in a) the carbon hyperfine coupling constant, $\delta^{v_t^{nad}} A^C_{iso}$, and b) the lithium hyperfine coupling constant, $\delta^{v_t^{nad}} A^{Li}_{iso}$, in the Li^+–$NC^\bullet$ case as a function of the Li-N separation. The equilibrium Li-N distance is 2.06 Å, at which $\Delta^{compl} A^C_{iso} = 179.59$ Gauss and $\Delta^{compl} A^{Li}_{iso} = 3.803$ Gauss.

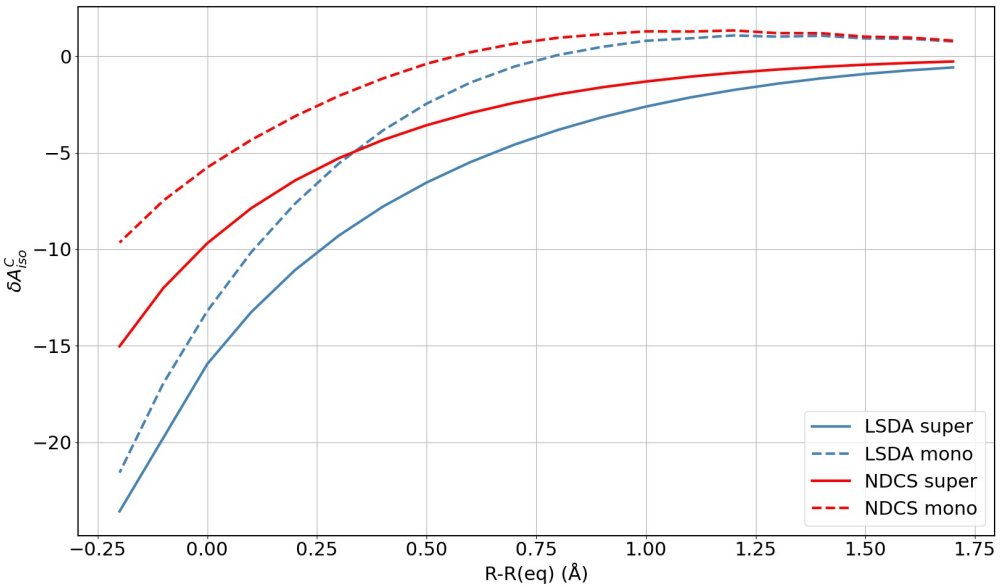
[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]



Norm of the total spin-density error for Li^{+}–$NC^{\bullet}$ as a function of the gaps between the energy of the embedded radical HOMO and the lowest unoccupied orbital located on the cation (in eV) at different Li-N separations. The equilibrium Li-N distance is 2.06 Å. The norm of the target complexation-induced change of the total spin-density at the equilibrium geometry equals 0.446. Empty symbols indicate the values evaluated at equilibrium geometry.

[T. Englert, Pierre-Olivier Roy, TAW , *J. Chem. Phys.* (2026) *accepted for publication*]

Interplay between incompleteness of the basis sets and approximations for the bi-functional for the non-additive kinetic potential in Frozen-Density Embedding Theory



Error in the carbon hyperfine coupling constant (in Gauss), $\delta^{v_t^{nad}} \tilde{A}_{iso}$ for Li^+–$NC^\bullet$ as a function of the Li-N separation. The equilibrium Li-N distance is 2.06 Å, at which $\Delta^{compl} A_{iso}(C) = 179.596$ Gauss.

[T. Englert, Pierre-Olivier Roy, TAW , *Electronic Structure* (2026) *submitted*]

The second argument in the FDET energy functional $E_v^{FDET}[\Psi_A, \rho_{N_B}]$

The function $\rho_{N_B}(\mathbf{r})$ can be generated using any physical model not necessarily based on electronic Schrödinger equation!

FDET as the formal basis for "multi-physics simulations"

Ensemble averaged observable $\hat{O}$

- Let Ψ_{A_i} is obtained at ρ_{B_i} corresponding to one geometry of the system i
- From FDET, it follows that Ψ_{A_i} is uniquely (up to unitary transformation) determined by ρ_{B_i}
- $O_i = \left\langle \Psi_{A_i} | \hat{O} | \Psi_{A_i} \right\rangle$ is uniquely determined by $\rho_{B_i} \longrightarrow O_i = O[\rho_{B_i}]$
- $\left\langle O[\rho_{B_i}] \right\rangle^{ensemble}$ is ensemble averaged observable

Proposed Approximation:

$$\langle O_i \rangle^{ensemble} = \left\langle O[\rho_{B_i}] \right\rangle^{ensemble} \approx O\left[\left\langle \rho_{B_i} \right\rangle^{ensemble} \right]$$

The quantity $\left\langle \rho_{B_i} \right\rangle^{ensemble}$ is more general then the electron density obtained from Schrödinger equation within Born-Oppenheimer approximation considered so far. $\left\langle \rho_{B_i} \right\rangle^{ensemble}$ **is a well defined quantity at any scale and in both and classical and quantum laws of physics.**

$$\langle O_i]\rangle^{ensemble} \approx O\left[\left\langle \rho_{B_i} \right\rangle^{ensemble}\right]$$

Examples of $\left\langle \rho_{B_i} \right\rangle^{ensemble}$

- From Ornstein-Zernicke theory based continuum models of Classical liquids (3D-RISM with Hirata-Kovalenko closure, "Molecular DFT"):
  - absorption for acetone and aminocoumarine in water

    [Kaminski, Gusarov, TAW, Kovalenko, J. Phys. Chem A, **114** (2010) 6082]
  - absorption for aminocoumarin 153 in various solvents

    [Zhou, Kaminski, TAW, PCCP, **13** (2011) 10565]
  - solvatochromism of emission

    [Shedge, TAW, Chem. Phys. Chem., **15** (2014) 329]
- From atomistic MD simulations:
  - Absorption for hydrated acetone

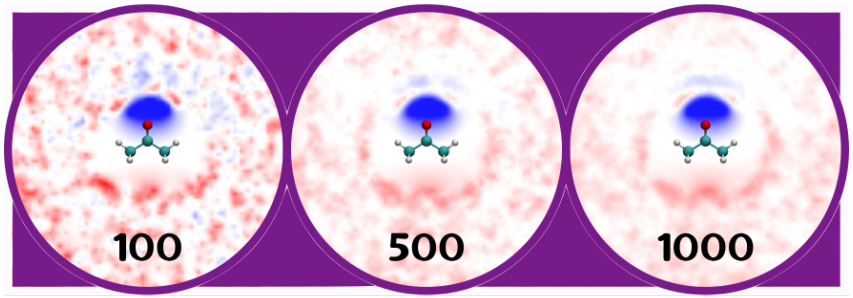
    [Lyaktonov, Chalaye, TAW, *PCCP*, **18** (2016) 21069]

    [Gonzalez-Espinoza, Rumble, Borgis, & TAW, *J. Chem. Theor. & Comput.* **18** (2022) 1072]

Quantifying Fluctuations of Average Solvent Environments for Embedding Calculations

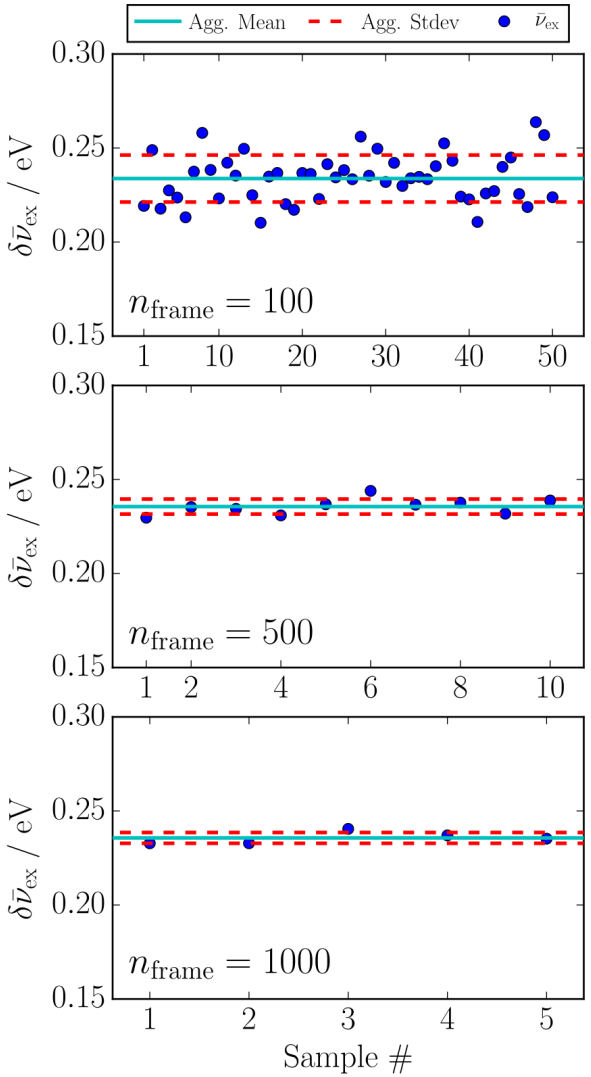
[C.E. Gonzalez-Espinoza, C. Rumble, D. Borgis, & T.A. Wesolowski, *J. Chem. Theor. & Comput.* **18** (2022) 1072]

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]



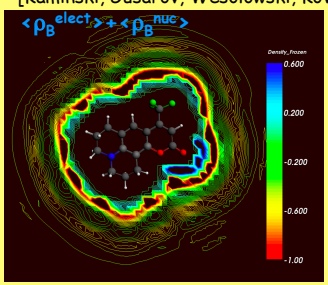
Multi-level simulations based on Frozen Density Embedding Theory

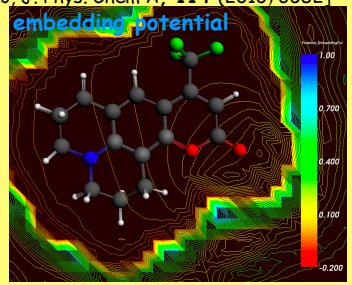
FDET for excitation energies of embedded chromophores

Solvatochromism

Implicit treatment of the solvent in FDET
(embedding potential evaluated at averaged solvent density $\langle\rho_B\rangle$

[Kaminski, Gusarov, Wesolowski, Kovalenko, J. Phys. Chem A, **114** (2010) 6082]



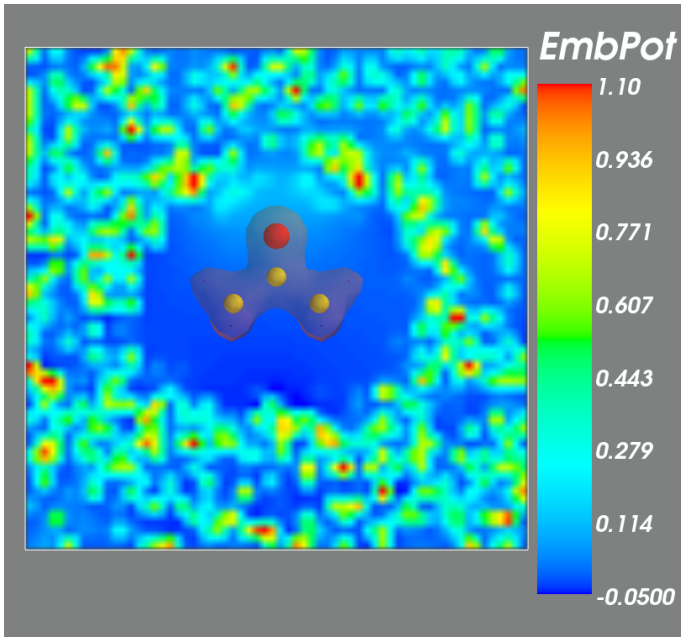


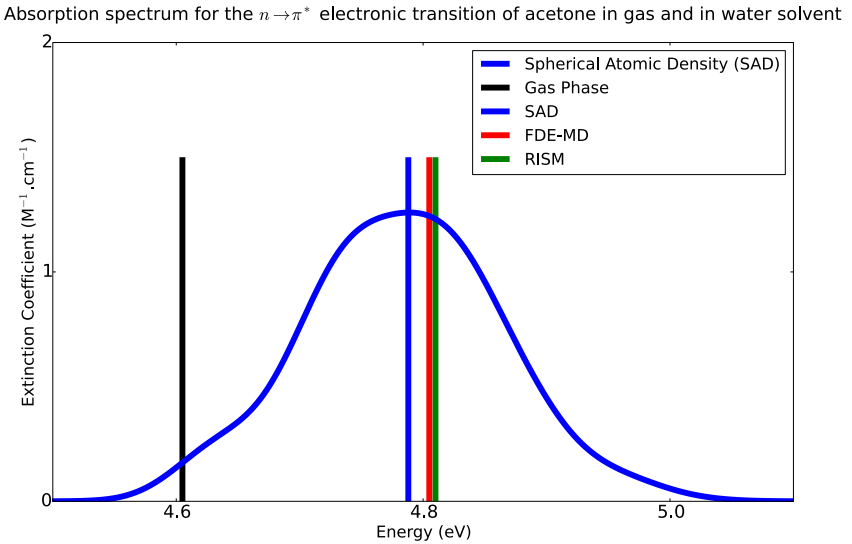
$\pi \rightarrow \pi^*$ transition in coumarin 153

[X. Zhou, J. Kaminski, Wesolowski, Phys.Chem.Chem.Phys., **13** (2011) 10565]

Solvent	Dielectric constant	Solvatochromic shift (FDET) [eV]	Solvatochromic shift (Exp) [eV]
Water	78	-0.29	-0.27
Methanol	33	-0.24	-0.24
Ethanol	25	-0.21	-0.24
1-propanol	20	-0.20	-0.23
2-propanol	20	-0.18	-0.23
Dimethyl ether	4	-0.11	-0.10
Cyclohexane	2	0.00	0.00

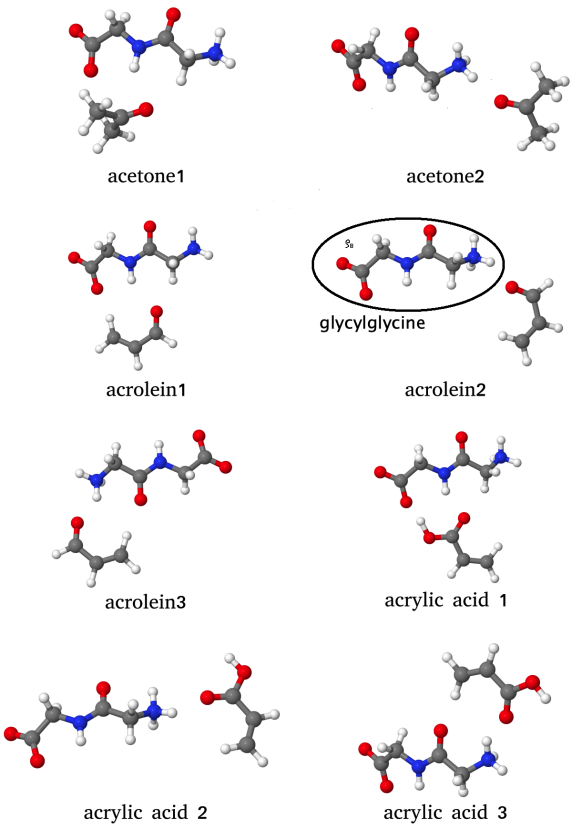
(**) Acetone in water: FDET with averaged $\rho_{N_B}(\mathbf{r})$ from MD simulations

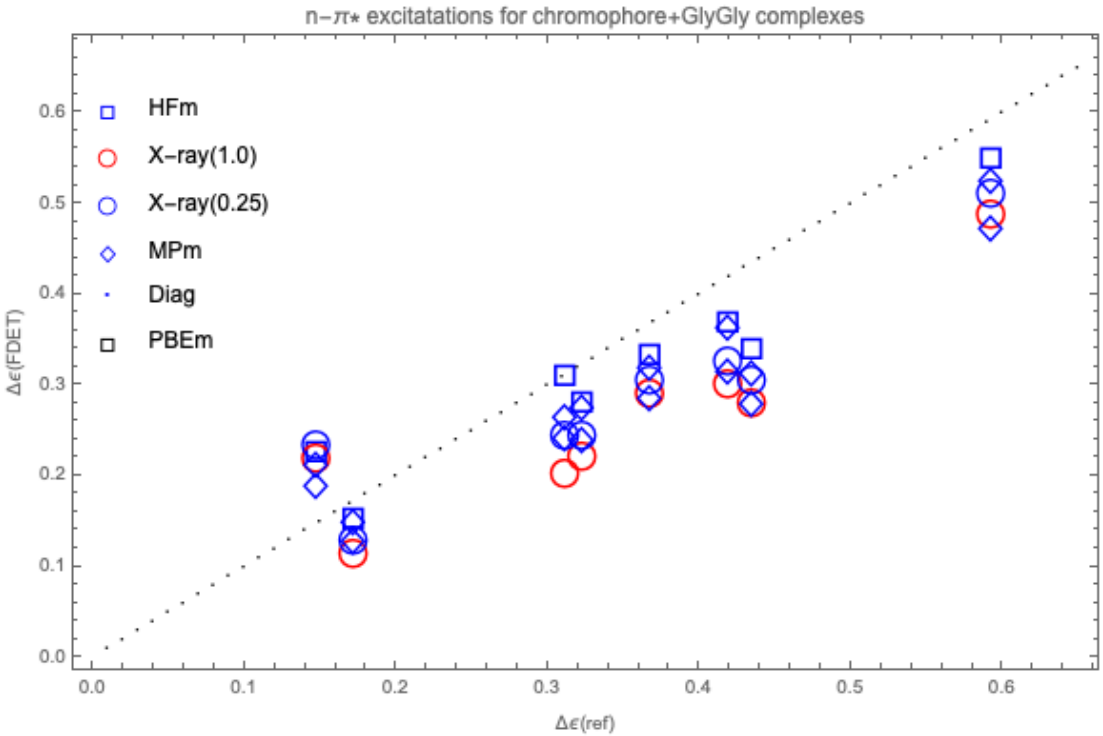




[Lyaktonov, Chalaye, TAW, *PCCP*, **18** (2016) 21069]

FDET with $\langle \rho_{N_B} \rangle$ taken from X-ray diffraction data for glycylglycine





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

[Ricardi et al. *Acta Crystallographica - Foundation and Advances* **A76** 57 (2020)]

Density dependent embedding potentials for piecewise exact densities

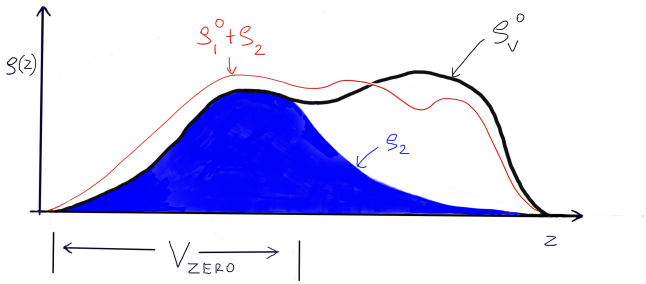
Cite as: J. Chem. Phys. 163, 164112 (2025); doi: 10.1063/5.0279936
Submitted: 9 May 2025 • Accepted: 5 October 2025 •
Published Online: 23 October 2025

View Online

Tomasz A. Wesolowski[a)]

Non-existence of the FDET embedding potential $v_{emb}[\rho_1,\rho_2] = \int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}' + \left.\frac{\delta E_{xcT}^{nad}[\rho,\rho_2]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_1}$

Example of density ρ_2 belonging to $\mathcal{A}$
i.e. $\rho_2(\mathbf{r}) = \rho_v^0(\mathbf{r})$ for $\mathbf{r} \in V_{zero}$



Lemma A: For a system of N-electrons in a Coulombic potential v, the potential $v_{xct}^{nad}[\rho_1^o[\rho_2],\rho_2](\mathbf{r})$ does not exist for $\rho_2 \in \mathscr{A}$.

FDET eigenvalue equation

$$\left(\hat{T}^{N'} + \hat{V}^{N'} + \hat{V}_{ee}^{N'} + \hat{V}_{emb}^{N'}\right)\Psi^{Eq.\ (4)} = \lambda^{Eq.\ (4)} \cdot \Psi^{Eq.\ (4)}, \qquad (4)$$

Theorem I: If the solution of Eq. (4) exists for $\rho_2 \in \mathscr{A}$ and a Coulombic external potential v,

$$\forall_{\mathbf{r}\in V_{zero}} \rho_1^{Eq.\ (4)}[\rho_2](\mathbf{r}) > 0. \qquad (22)$$

Theorem II. If the solution of Eq. (4) exists for $\rho_2 \in \mathscr{A}$ and a Coulombic external potential v,

$$E_v^{HK}\left[\rho_1^{Eq.\ (4)}[\rho_2] + \rho_2\right] > E_v^{HK}\left[\rho_v^o\right] = E_v^o. \qquad (23)$$

[TAW *J. Chem. Phys.* **163**, (2025) 164112]

Lemma A and Theorems I & II: Partitioning vs embedding context

- Non-existence of $v_{emb}^{FDET}[\rho_{N_A}, \rho_{N_B}]$ in the considered case originates form the fact that FDET restricts embedding operator to be multiplicative.
- For ρ_{N_B}, which is equal to the exact total ground-state density on a measurable volume, FDET eigenvalue equation yields the total density such that **the total energy lies above** E_v^0.
- Optimisation of both ρ_{N_A} and ρ_{N_B} (subsystem based formulation of DFT[5]) yields a pair of densities ($\rho_{N_A}^0$ and $\rho_{N_B}^0$) such that none of them is zero on a measurable volume.

[5] [Cortona, *Phys. Rev. B*, **44** (1991) 8454]

The Team

Recently left

- Dr. Cristina Elisabeth Gonzalez Espinoza (chem.): *approximations, multi-scale methods, code development and integrating*
- Dr. Alexander Zech (chem.): *FDET Linearization, code development*
- Dr. Elias Polak (math.): *NDCS approximant*
- Ds. Mingxue Fu (phys.): *electronic excitations, TPA*
- Dr. Nicolo Ricardi (chem.): *electronic excitations (benchmarking and applications), experimental* ρ_{N_B}
- Dr. Yann Gimbal-Zofka (phys.): *EFG parameters*

Current:

Dr. Pierre-Olivier Roy

Mr. Tanguy Englert