QM/QM and QM/MM Hybrid Methods

Subsystem and Embedding Methods for Quantum Chemistry

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Lecture 2

Contents

- introduction
- energy-based embedding schemes
- many-body expansions (MBEs)
- subsystem DFT and density-based embedding
- “exact embedding” through potential reconstruction
- “exact embedding” through projection
- WF/DFT embedding
- density matrix embedding theory (DMET)

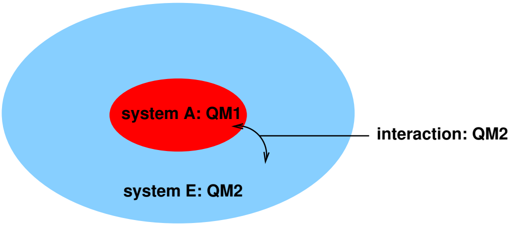
QM/QM Hybrid Methods

Partitioning is possible at different levels:

- energy partitioning
- wavefunction partitioning
- density-matrix partitioning
- Green's function partitioning
- density partitioning
- . . .

Energy-Based Partitioning and Many-Body Expansions

Simple QM/QM Hybrid Methods



- ONIOM (Morokuma): a generalization of subtractive QM/MM

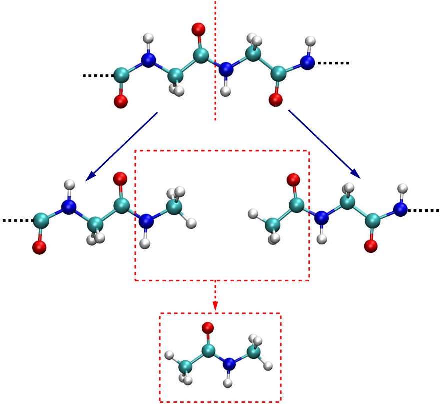
$$E_{\text{tot}}^{\text{QM/QM}} = E_{(A+E)}^{\text{QM2}} + (E_A^{\text{QM1}} - E_A^{\text{QM2}})$$

  interaction defined as

$$E_{A\leftrightarrow E}^{\text{QM2}} = E_{(A+E)}^{\text{QM2}} - E_A^{\text{QM2}} - E_E^{\text{QM2}}$$

- generalizations for many layers (QM1/QM2/MM/continuum) and electrostatic embedding
- properties require corresponding definitions

Fragmentation Methods



Molecular Fractionation with Conjugated Caps (MFCC)

- developed for proteins; partition into oligopeptides
- use model for neighboring fragments as caps
- sum up energies for capped fragments, subtract “concaps”
- no electrostatic embedding; better with larger caps

D.W. Zhang, J.Z.H. Zhang, *J. Chem. Phys.* **119** (2003), 3599.

Increment Methods

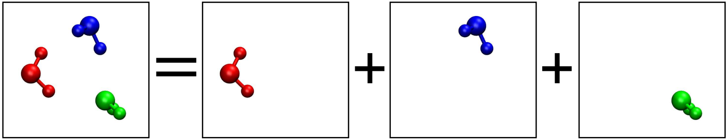
General idea:

- largest part of E_{tot} is due to energies of (isolated) subsystems
- interaction energy: mainly due to pair interactions
- general energy expression:

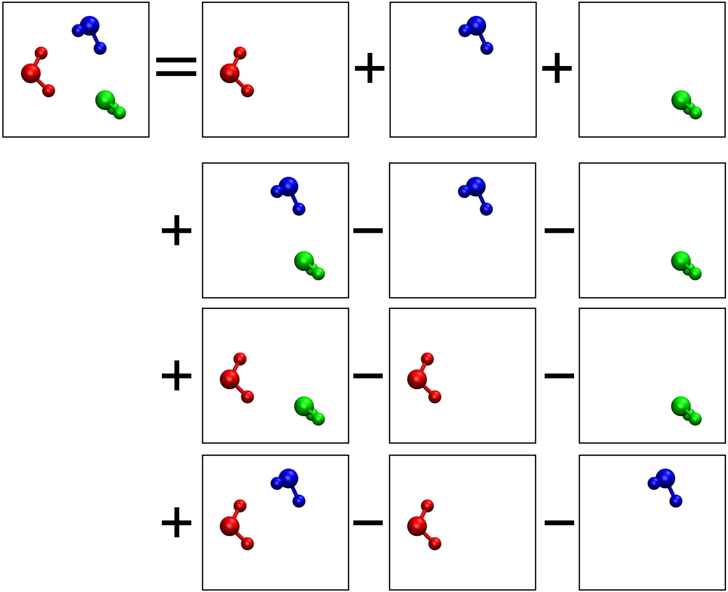
$$\begin{aligned}
E_{\text{tot}} &= \sum_{I} E_I + \sum_{I<J} E_{I\leftrightarrow J} + \sum_{I<J<K} E_{I\leftrightarrow J\leftrightarrow K} + \ldots \\
E_{I\leftrightarrow J} &= E_{IJ} - E_I - E_J \\
E_{I\leftrightarrow J\leftrightarrow K} &= E_{IJK} - E_I - E_J - E_K \\
&\quad -(E_{IJ} - E_I - E_J) - (E_{IK} - E_I - E_K) - (E_{JK} - E_J - E_K)
\end{aligned}$$

- nth-order increment method: exact for n subsystems

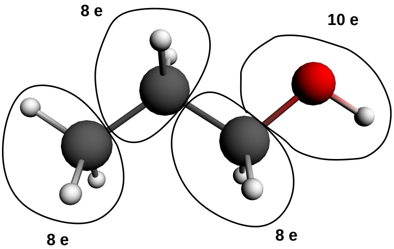
Increment Methods



Increment Methods



Fragment Molecular Orbital Method (1)

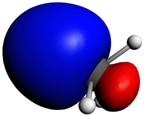


FMO-1

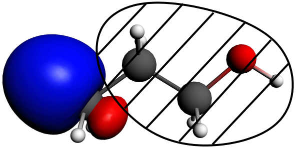
- fragmentation without separation of bond electron pairs
- fragment calculations under full electrostatic embedding
- no capping applied

K. Kitaura *et al.*, *Chem. Phys. Lett.* **313** (1999), 701.

Fragment Molecular Orbital Method (1)



generate localized MOs for capped fragment

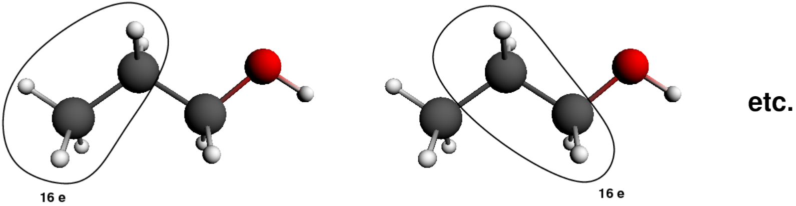


use these LMOs as basis for "true" fragments

FMO-1

- fragment orbitals are expressed through localized orbitals obtained from reference compound (capped fragment)
- minimal basis is applied ⇒ bond electron pairs have no freedom to change compared to reference compound

Fragment Molecular Orbital Method (2)



FMO-2

- 2nd order increment method
- monomers and dimers are obtained with full electrostatic embedding potential, based on localized orbitals

⇒ FMO-2 implicitly contains higher-order terms

Density Partitioning

Some Flavors of DFT

- orbital-free DFT: formulated directly in terms of $\rho(\mathbf{r})$

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- Kohn–Sham DFT: non-interacting v-representability assumed,

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

(called v_s-representability in the following)

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- Kohn–Sham DFT: non-interacting v-representability assumed,

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

(called v_s-representability in the following)

- subsystem DFT:

$$\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$$

v_s-representability assumed for every ρ_I:

$$\rho_I(\mathbf{r}) = \sum_i |\phi_{i_I}(\mathbf{r})|^2$$

(but not necessarily for the total density ⇒ different search space than in KS-DFT)

Some Flavors of DFT

Frozen-Density Embedding:

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2^{\text{fixed}}(\mathbf{r}); \qquad \rho_1(\mathbf{r}) = \sum_i |\phi_{i_1}(\mathbf{r})|^2$$

- “sDFT without optimization of $\rho_2(\mathbf{r})$” (no “freeze-and-thaw”)

Some Flavors of DFT

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- "sDFT without optimization of $\rho_2(\mathbf{r})$" (no "freeze-and-thaw")
- no orbital representation needed for ρ_2, can be taken from:
  - simple superpositions of atomic/fragment densities

    J. Neugebauer, M.J. Louwerse, E.J. Baerends, T.A. Wesolowski, *J. Chem. Phys.* **122** (2005) 094115.
  - statistically averaged densities

    J.W. Kaminski, S. Gusarov, T.A. Wesolowski, A. Kovalenko, *J. Phys. Chem. A* **114** (2010), 6082.
  - experiment

    N. Ricardi, M. Ernst, P. Macchi, T.A. Wesolowski, *Acta Cryst. A* **76** (2020), 571.

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Frozen-Density Embedding:

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- but: not well suited/not intended for total-energy calculations
- can only lead to exact solution if $\rho(\mathbf{r}) \geq \rho_2^{\text{fixed}}(\mathbf{r}) \quad \forall\, \mathbf{r}$

Subsystem DFT

- KS energy expression with partitioning $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

$$E[\rho] \quad = \quad T_s[\rho] + V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

- if ρ is given as sum of subsystem densities:

$$\begin{aligned} V_{\text{ext}}[\rho] &= V_{\text{ext}}[\rho_1 + \rho_2 + \ldots] \\ J[\rho] &= J[\rho_1 + \rho_2 + \ldots] \\ \tilde{E}_{\text{xc}}[\rho] &= \tilde{E}_{\text{xc}}[\rho_1 + \rho_2 + \ldots] \end{aligned}$$

- problem for calculations of KS energy: $T_s[\rho] = T_s[\{\phi_i^{\text{opt}}\}]$

G. Senatore, K. R. Subbaswamy, *Phys. Rev. B* **34** (1986), 5754;
P. Cortona, *Phys. Rev. B* **44** (1991), 8454;
T.A. Wesolowski, J. Weber, *Chem. Phys. Lett.* **248** (1996), 71.

Subsystem DFT

- write T_s formally exactly as

$$T_s[\rho] = \sum_I T_s[\rho_I] + \left[T_s[\rho] - \sum_I T_s[\rho_I] \right]$$

or

$$T_s[\rho] = \sum_I T_s[\rho_I] + T_s^{\mathrm{nad}}[\rho, \{\rho_J\}]$$

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- exact T_s^{nad}:

$$\begin{aligned} T_s^{\text{nad}}[\rho, \{\rho_I\}] &= \min_{\{\phi_i\} \to \rho} \sum_{i=1}^{n} \langle \phi_i | -\nabla_i^2/2 | \phi_i \rangle \\ &\quad - \sum_I \left(\min_{\{\phi_{i_I}\} \to \rho_I} \sum_{i=1}^{n} \langle \phi_{i_I} | -\nabla_i^2/2 | \phi_{i_I} \rangle \right) \end{aligned}$$

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- introduce density-dependent approximation,

$$T_s^{\mathrm{nad}}[\rho, \{\rho_J\}] \approx \tilde{T}_s^{\mathrm{nad}}[\rho, \{\rho_J\}] = \tilde{T}_s[\rho] - \sum_I \tilde{T}_s[\rho_I]$$

Subsystem DFT

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- introduce density-dependent approximation,

$$
T_s^{\mathrm{nad}}[\{\rho_J\}] \approx \tilde{T}_s^{\mathrm{nad}}[\{\rho_J\}] = \tilde{T}_s[\rho_1 + \rho_2 + \ldots] - \sum_I \tilde{T}_s[\rho_I]
$$

One-Particle Equations in Subsystem DFT

- energy functional:

$$E[\{\rho_J\}] \quad = \quad V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] + \sum_I T_s[\rho_I] + T_s^{\text{nad}}[\{\rho_J\}],$$

- choose no. of electrons per subsystem (n_J)
- construct Lagrangian

$$L[\{\rho_J\}] = E[\{\rho_J\}] - \sum_I \mu_I \left(\int \mathrm{d}^3 r \rho_I(\mathbf{r}) - n_I \right)$$

  and minimize w.r.t. ρ_K

$\Rightarrow$ Euler–Lagrange equations:

$$0 = v_{\text{ext}}(\mathbf{r}) + v_{\text{Coul}}[\rho](\mathbf{r}) + v_{\text{xc}}[\rho](\mathbf{r}) + \frac{\delta T_s[\rho_K]}{\delta \rho_K(\mathbf{r})} + \frac{\delta T_s^{\text{nad}}[\{\rho_J\}]}{\delta \rho_K(\mathbf{r})} - \mu_K$$

Frozen-Density Embedding

- assume all subsystem densities are v_s-representable

$\Rightarrow$ subsystem orbitals can be obtained from

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{sub}}[\rho, \rho_K](\mathbf{r})\right)\phi_{i_K} = \epsilon_{i_K}\phi_{i_K},$$

$\Rightarrow$ if we choose

$$v_{\text{eff}}^{\text{sub}}[\rho, \rho_K](\mathbf{r}) = v_{\text{eff}}[\rho](\mathbf{r}) + \frac{\delta T_s^{\text{nad}}[\{\rho_J\}]}{\delta \rho_K(\mathbf{r})}$$

the systems of non-interacting particles fulfill

$$v_{\text{eff}}^{\text{sub}}[\rho, \rho_K](\mathbf{r}) + \frac{\delta T_s[\rho_K]}{\delta \rho_K(\mathbf{r})} - \mu_K = 0$$

$\Rightarrow$ these are the sought-for densities

T.A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97** (1993), 8050.

Embedding Potential

- define “environmental” density for system I [complementary to $\rho_I(\mathbf{r})$]:

$$\rho_I^{\text{env}}(\mathbf{r}) = \sum_{J,J\neq I} \rho_J(\mathbf{r})$$

- one-particle equations for FDE calculation become

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho_I](\mathbf{r}) + v_{\text{emb}}[\rho_I, \rho_I^{\text{env}}](\mathbf{r})\right)\phi_{i_I} = \epsilon_{i_I}\phi_{i_I}$$

(Kohn–Sham equations with constrained electron density, KSCED)

- embedding potential

$$\begin{aligned} v_{\text{emb}}[\rho_I, \rho_I^{\text{env}}](\mathbf{r}) \quad &= \quad \sum_{J,J\neq I} v_{\text{ext}}^J(\mathbf{r}) + \sum_{J,J\neq I} v_{\text{Coul}}[\rho_J](\mathbf{r}) \\ &\quad + \{v_{\text{xc}}[\rho](\mathbf{r}) - v_{\text{xc}}[\rho_I](\mathbf{r})\} + \frac{\delta T_s^{\text{nad}}[\{\rho_J\}]}{\delta \rho_K(\mathbf{r})} \end{aligned}$$

T.A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97** (1993), 8050; T.A. Wesolowski, J. Weber, *Chem. Phys. Lett.* **248** (1996), 71.

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T.A. Wesolowski, A. Warshel, *J. Phys. Chem.* **97** (1993), 8050; T.A. Wesolowski, J. Weber, *Chem. Phys. Lett.* **248** (1996), 71.

Solution of the KSCED equations

Approximations that have to be selected:

- non-additive kinetic energy functional $\tilde{T}_s^{\text{nad}}$

  (and corresponding potential)

- XC functional:
  - either regard $E_{\text{xc}}[\rho]$ as *one* energy contribution,

$$E_{\text{xc}}[\rho] \approx \tilde{E}_{\text{xc}}[\rho_1 + \rho_2 + \ldots]$$

  - or approximate components of $E_{\text{xc}}[\rho]$,

$$\begin{aligned} E_{\text{xc}}[\rho] &= \sum_I E_{\text{xc}}[\rho_I] + E_{\text{xc}}^{\text{nad}}[\{\rho_I\}] \\ &\approx \sum_I \tilde{E}_{\text{xc}}^{(I)}[\rho_I] + \tilde{\tilde{E}}_{\text{xc}}^{\text{nad}}[\{\rho_I\}] \end{aligned}$$

(facilitates use of different XC approximations for different subsystems and/or the non-additive part)

Allows pragmatic use of hybrid XC functionals in intra-subsystem parts only

Non-additive kinetic-energy functionals

Common decomposable approximations:

- general structure: $T_s^{\mathrm{nad}}[\{\rho_I\},\rho] = T_s[\rho] - \sum_I T_s[\rho_I]$
- Thomas–Fermi approximation

$$T_s[\rho] \approx T_{\mathrm{TF}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\mathrm{d}\mathbf{r}$$

L.A. Thomas, *Proc. Camb. Phil. Soc.* **23** (1927) 542; E. Fermi, *Z. Physik* **48** (1928) 73.

exact for homogeneous electron gas (“LDA” for kinetic energy)

- von Weizsäcker approximation

$$T_s[\rho] \approx T_{\mathrm{vW}}[\rho] = \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\mathrm{d}\mathbf{r}$$

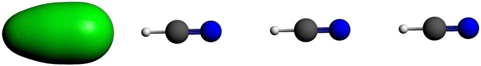
C.F. von Weizsäcker, *Z. Physik* **96** (1935) 431.

exact for one-orbital systems

Subsystem DFT at Work

Step 1

active system



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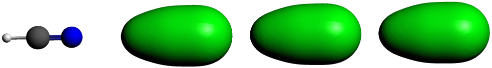
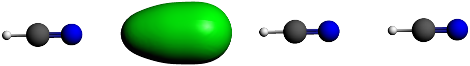


- calculate ρ_{active} with frozen environment
- iterate over all subsystems

Subsystem DFT at Work

Step 2

active system



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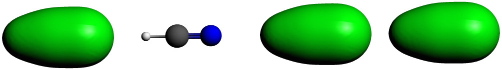

- calculate ρ_{active} with frozen environment
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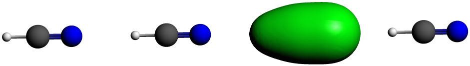
Subsystem DFT at Work

Step 3

active system



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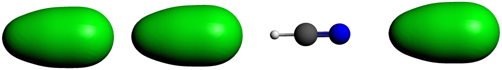
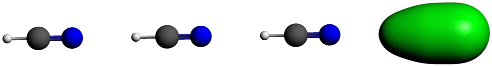


- calculate ρ_{active} with frozen environment
- iterate over all subsystems

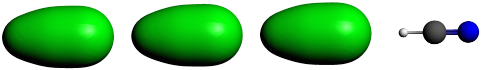
Subsystem DFT at Work

Step 4

active system



environment

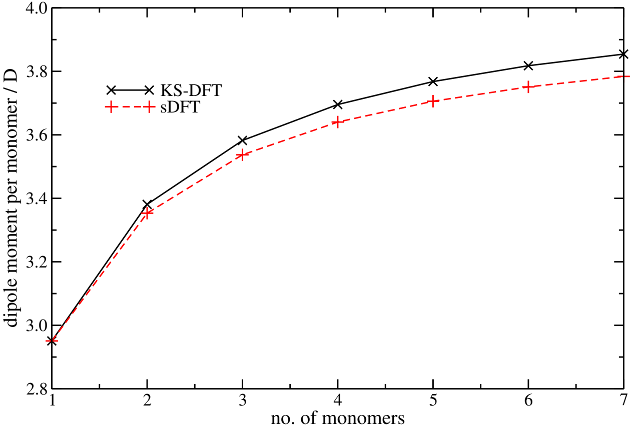


- calculate ρ_{active} with frozen environment
- iterate over all subsystems

Dipole Moment of $(HCN)_N$

Average dipole moment as a function of chain length

BP86/TZP

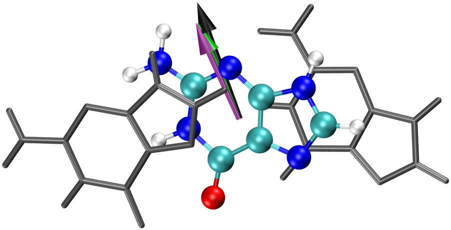


C.R. Jacob, JN, *WIREs Comput. Mol. Sci.* **4** (2014), 325.

Are Subsystem Properties Meaningful?

Dipole moment of the central guanine in a trimer

Structure: R. Sedlak *et al.*, *J. Chem. Theory Comput.* **9** (2013), 3364.



(PW91/PW91k/TZP; black: isolated; purple: sDFT; green: Bader analysis of KS-DFT)

	$\lvert\mu_{\mathrm{central}}\rvert$ / Debye	angle to $\vec{\mu}_{\mathrm{iso}}$ / $\circ$
iso	7.48	
sDFT	5.99	4.2
Bader	5.95	5.1

T. Dresselhaus, JN, *Theor. Chem. Acc.* **134** (2015), 97.

From DFT/DFT to WF/DFT embedding

DFT-in-DFT Hybrid Methods

Subsystem DFT

- fragmentation scheme,
  KS-DFT for subsystems, OF-DFT for interaction

$$E^{\mathrm{sDFT}}[\rho_{\mathrm{tot}}] \quad = \quad E^{\mathrm{KS}}[\rho_1] + E^{\mathrm{KS}}[\rho_2] + E^{\mathrm{OF}}_{(1\leftrightarrow 2)}[\rho_1, \rho_2]$$

FDE (without orbital representation of ρ_{env})

- QM/QM embedding scheme, KS-DFT/OF-DFT

$$E^{\mathrm{FDE}}[\rho_{\mathrm{tot}}] \quad = \quad E^{\mathrm{KS}}[\rho_1] + E^{\mathrm{OF}}[\rho_2] + E^{\mathrm{OF}}_{(1\leftrightarrow 2)}[\rho_1, \rho_2]$$

Wavefunction-in-DFT Hybrid Methods

Can this idea be transferred to WF-in-DFT embedding?

- within DFT, $v_{\text{emb}}(\mathbf{r})$ is formally exact
  (contains all non-electrostatic contributions)
- simple idea:
  include $\langle \chi_\mu | v_{\text{emb}}(\mathbf{r}) | \chi_\nu \rangle$ into one-electron part of WF calculation

⇒ gives access to "embedded WF" and properties

Wavefunction-in-DFT Hybrid Methods

- WF/DFT energy functional:

$$E^{\mathrm{WF/DFT}}[\Psi_A, \rho_B] \quad = \quad \langle\Psi_A|\hat{H}_A|\Psi_A\rangle + E_B^{\mathrm{KS}}[\rho_B] + E_{(A\leftrightarrow B)}^{\mathrm{OFDFT}}[\rho_A, \rho_B]$$

(ρ_A: density obtained from Ψ_A)

- minimization w.r.t. Ψ_A yields (ρ_B fixed):

$$\hat{H}'_A \Psi_A = \left(\hat{H}_A + \sum_{i=1}^{n_A} v_{\mathrm{emb}}^A[\rho_A, \rho_B](\mathbf{r}_i) \right) \Psi_A = \tilde{E}_A \Psi_A$$

where

$$v_{\mathrm{emb}}^A[\rho_A, \rho_B](\mathbf{r}) = v_{\mathrm{ext}}^B(\mathbf{r}) + v_{\mathrm{Coul}}[\rho_B](\mathbf{r}) + v_{\mathrm{xc}}[\rho](\mathbf{r}) - v_{\mathrm{xc}}[\rho_A](\mathbf{r}) + v_t^{\mathrm{nad}}[\rho_A, \rho_B](\mathbf{r})$$

$\Rightarrow$ same form as in sDFT! (but often evaluated with approximate ρ_A, ρ_B)

N. Govind, Y.A. Wang, A.J.R. da Silva, E.A. Carter, *Chem. Phys. Lett.* **295** (1998), 129.

Wavefunction-in-DFT Embedding

$$v_1^{\mathrm{emb}}[\rho_1, \rho_2](\mathbf{r}) = \sum_{A_2} -\frac{Z_{A_2}}{|\mathbf{r} - \mathbf{R}_{A_2}|} + \int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$

$$+ \left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_1+\rho_2} - \left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_1} + \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_1+\rho_2} - \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_1}$$

Wavefunction-in-DFT Embedding

$$v_1^{\mathrm{emb}}[\rho_1,\rho_2](\mathbf{r}) = \overbrace{\sum_{A_2} -\frac{Z_{A_2}}{|\mathbf{r}-\mathbf{R}_{A_2}|}}^{\text{constant}} + \overbrace{\int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'}^{\text{changes in every macroiteration}}$$

$$+ \underbrace{\left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_1+\rho_2} - \left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_1}}_{\text{changes in every microiteration}} + \underbrace{\left.\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_1+\rho_2} - \left.\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_1}}_{\text{changes in every microiteration}}$$

Wavefunction-in-DFT Embedding

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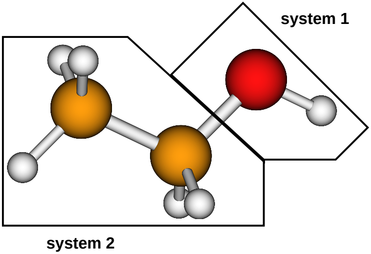
Note: Self-consistent embedding for excited states leads to non-orthogonal active-system states!

“Exact” Density-Based Embedding

Covalent Bonds through Exact Embedding Potentials

Approximations for v_t^{nad} break down for covalent bonds



- What do we know about the exact $v_t^{\mathrm{nad}}(\mathbf{r})$?
- Can we reconstruct the *exact* embedding potential for subsystems 1, 2 that reproduces $\rho_{\mathrm{super}}(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})$?

  ("exact" here excludes errors introduced by finite basis sets, errors introduced in the calculation of ρ_{super} (usually through E_{xc}), and numerical errors in the construction of the potential, e.g., due to finite grid size)

Functional Derivative of T_s^{nad}

- problems arise due to

  (here: system K = active system)

$$\frac{\delta T_s^{\mathrm{nad}}[\{\rho_I\}]}{\delta\rho_K(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta\rho_K(\mathbf{r})} - \sum_I \frac{\delta T_s[\rho_I]}{\delta\rho_K(\mathbf{r})}$$

  with $\rho(\mathbf{r}) = \sum_I \rho_I(\mathbf{r})$

- first term:

$$\begin{aligned}\frac{\delta T_s[\rho]}{\delta\rho_K(\mathbf{r})} &= \int \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r}')} \cdot \frac{\delta\rho(\mathbf{r}')}{\delta\rho_K(\mathbf{r})} \mathrm{d}\mathbf{r}' \\ &= \int \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r}')} \cdot \delta(\mathbf{r}' - \mathbf{r})\mathrm{d}\mathbf{r}' = \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\end{aligned}$$

- second term:

$$\sum_I \frac{\delta T_s[\rho_I]}{\delta\rho_K(\mathbf{r})} = \sum_I \frac{\delta T_s[\rho_K]}{\delta\rho_K(\mathbf{r})} \cdot \delta_{KI} = \frac{\delta T_s[\rho_K]}{\delta\rho_K(\mathbf{r})}$$

Functional Derivative of T_s^{nad}

⇒ we need to calculate

$$v_t^{\text{nad}}[\rho_K, \rho_{\text{super}}](\mathbf{r}) = \frac{\delta T_s^{\text{nad}}[\{\rho_I\}]}{\delta \rho_K(\mathbf{r})} \quad = \quad \frac{\delta T_s[\rho_{\text{super}}]}{\delta \rho_{\text{super}}(\mathbf{r})} - \frac{\delta T_s[\rho_K]}{\delta \rho_K(\mathbf{r})}$$

- or, in other words, we need to find

$$v_t[\rho](\mathbf{r}) = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$$

for two different densities ($\rho = \rho_{\text{super}}$ and $\rho = \rho_K$)

Euler–Lagrange Equation: Kohn–Sham Formalism

- Euler–Lagrange Equation:

$$\mu = \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_{\text{target}}} + v_s[\rho_{\text{target}}](\mathbf{r})$$

⇒ “Kinetic-energy potential:”

$$v_t[\rho_{\text{target}}](\mathbf{r}) = \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_{\text{target}}} = \mu - v_s[\rho_{\text{target}}](\mathbf{r})$$

- μ is just a constant shift in the potential (will be ignored here)

⇒ If we know the potential $v_s[\rho_{\text{target}}](\mathbf{r})$ that results in a set of orbitals $\{\phi_i^{\text{target}}\}$ such that

$$\sum_i |\phi_i^{\text{target}}(\mathbf{r})|^2 = \rho_{\text{target}}(\mathbf{r}),$$

then we also have access to $v_t[\rho_{\text{target}}](\mathbf{r})$

S. Liu, P.W. Ayers, *Phys. Rev. A* **70** (2004), 022501.

Why Use “Exact” Embedding at All?

⇒ we can obtain the exact v_t^{nad} as

$$v_t^{\mathrm{nad}}[\rho_A, \rho_{\mathrm{super}}](\mathbf{r}) = v_s[\rho_A](\mathbf{r}) - v_s[\rho_{\mathrm{super}}](\mathbf{r}) + \Delta\mu$$

(two subsystems assumed for simplicity; v_t^{nad} is given for subsystem A)

Exact embedding is expensive:

- either, we first have to solve a KS-DFT calculation for the total system
- or, we have to do (several) reconstructions of total-system potentials

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- or, we have to do (several) reconstructions of total-system potentials

Possible benefits:

- "exact" potential may serve as basis for approximations
- "exact" potential may be transferred to more expensive WF/DFT
- ground-state calculation is not the bottleneck (e.g., response)

S. Fux, C.R. Jacob, J. Neugebauer, L. Visscher, M. Reiher, *J. Chem. Phys.* **132** (2010), 164101;
J.D. Goodpaster, N. Ananth, F.R. Manby, T.F. Miller III, *J. Chem. Phys.* **133** (2010), 084103;
D. Schnieders, J. Neugebauer, *J. Chem. Phys.* **149** (2018), 054103.

Potential Reconstruction

Densities in search of Hamiltonians:

- we need to find $v_s[\rho](\mathbf{r})$ that yields a specific $\rho = \rho^{\text{target}}$

$\Rightarrow$ "inverse Kohn–Sham problem"

$\Rightarrow$ has been solved several times in the context of v_{xc} development:

  - Wang and Parr *Phys. Rev. A* **47** (1993), R1591.
  - van Leeuwen and Baerends *Phys. Rev. A* **49** (1994), 2421.
  - Zhao, Morrison and Parr *Phys. Rev. A* **50** (1994), 2138.
  - Wu and Yang *J. Chem. Phys.* **118** (2003), 2498.
  - . . .

van Leeuwen–Baerends Reconstruction

- KS-equation

$$\begin{aligned}
\epsilon_i \phi_i(\mathbf{r}) &= \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right] \phi_i(\mathbf{r}) \\
\sum_i \epsilon_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) &= \sum_i \phi_i^*(\mathbf{r}) \left[-\frac{\nabla^2}{2}\right] \phi_i(\mathbf{r}) + v_s(\mathbf{r}) \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \\
v_s(\mathbf{r})\rho(\mathbf{r}) &= \sum_i \phi_i^*(\mathbf{r}) \left[\frac{\nabla^2}{2}\right] \phi_i(\mathbf{r}) + \sum_i \epsilon_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \\
v_s(\mathbf{r}) &= \frac{1}{\rho(\mathbf{r})} \sum_i \left\{ \phi_i^*(\mathbf{r}) \left[\frac{\nabla^2}{2}\right] \phi_i(\mathbf{r}) + \epsilon_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \right\}
\end{aligned}$$

R. van Leeuwen, E.J. Baerends, *Phys. Rev. A* **49** (1994), 2421.

van Leeuwen–Baerends Reconstruction

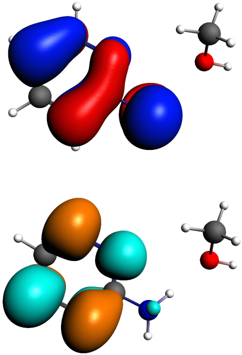
- iterative scheme, iteration $(k+1)$,

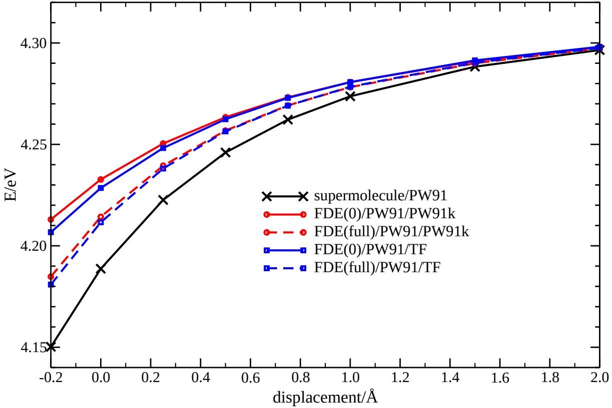
$$\begin{aligned} v_s^{(k+1)}(\mathbf{r}) &= \frac{1}{\rho^{\text{target}}(\mathbf{r})} \sum_i \left\{ \phi_i^{(k)*}(\mathbf{r}) \left[\frac{\nabla^2}{2} \right] \phi_i^{(k)}(\mathbf{r}) + \epsilon_i^{(k)} \phi_i^{(k)*}(\mathbf{r}) \phi_i^{(k)}(\mathbf{r}) \right\} \\ &= \frac{\rho^k(\mathbf{r})}{\rho^{\text{target}}(\mathbf{r})} \cdot v_s^{(k)} \end{aligned}$$

R. van Leeuwen, E.J. Baerends, *Phys. Rev. A* **49** (1994), 2421.

Excitation Energies with Reconstructed Potentials

Aminopyridine$\cdots$methanol



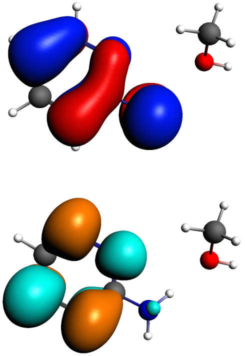


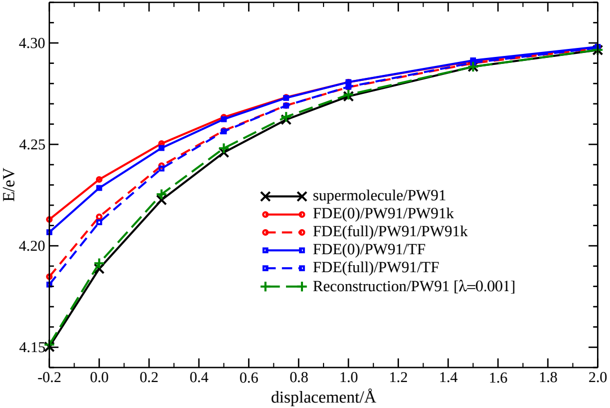
D. Artiukhin, C.R. Jacob, JN, *J. Chem. Phys.* **142** (2015), 234101.

- $\pi \rightarrow \pi^*$ excitation of aminopyridine$\cdots$MeOH (PW91/TZP)

Excitation Energies with Reconstructed Potentials

Aminopyridine$\cdots$methanol





D. Artiukhin, C.R. Jacob, JN, *J. Chem. Phys.* **142** (2015), 234101.

- $\pi \rightarrow \pi^*$ excitation of aminopyridine$\cdots$MeOH (PW91/TZP)
- reconstruction using Wu–Yang algorithm, ALDA kernel

“Exact” Projection-Based Embedding

T_s^{nad} for Orthogonal Subsystem Orbitals

- assume two-partitioning ($A + B$); determine supersystem KS orbitals
- define

$$\rho_A(\mathbf{r}) = \sum_{j=1}^{n_A} |\phi_j^{\text{super}}(\mathbf{r})|^2 \qquad \text{and} \qquad \rho_B(\mathbf{r}) = \sum_{k=n_A+1}^{n_A+n_B} |\phi_k^{\text{super}}(\mathbf{r})|^2 = \rho_{\text{env}}(\mathbf{r})$$

- kinetic energy:

$$\begin{aligned} T_s[\{\phi_i^{\text{super}}\}] &= \sum_{i=1}^{n} \left\langle \phi_i^{\text{super}} \left| -\nabla^2/2 \right| \phi_i^{\text{super}} \right\rangle \\ &= \sum_{j=1}^{n_A} \left\langle \phi_j^{\text{super}} \left| -\nabla^2/2 \right| \phi_j^{\text{super}} \right\rangle + \sum_{k=n_A+1}^{n_A+n_B} \left\langle \phi_k^{\text{super}} \left| -\nabla^2/2 \right| \phi_k^{\text{super}} \right\rangle \\ &= T_s^A + T_s^B \end{aligned}$$

⇒ apparently, no non-additive kinetic-energy approximation needed!

T_s^{nad} for Orthogonal Subsystem Orbitals

- but: even in case of orthogonal ϕ_i^{super} and exact ρ_A, ρ_B, in general

$$\begin{aligned}
&\sum_{j=1}^{n_A} \left\langle \phi_j^{\mathrm{super}} \middle| -\nabla^2/2 \middle| \phi_j^{\mathrm{super}} \right\rangle + \sum_{k=n_A+1}^{n_A+n_B} \left\langle \phi_k^{\mathrm{super}} \middle| -\nabla^2/2 \middle| \phi_k^{\mathrm{super}} \right\rangle \\
&\qquad \geq \min_{\{\phi_{i_A}\}\to\rho_A} \sum_i^{n_A} \left\langle \phi_{i_A} \middle| -\nabla^2/2 \middle| \phi_{i_A} \right\rangle + \min_{\{\phi_{i_B}\}\to\rho_B} \sum_i^{n_B} \left\langle \phi_{i_B} \middle| -\nabla^2/2 \middle| \phi_{i_B} \right\rangle
\end{aligned}$$

T_s^{nad} for Orthogonal Subsystem Orbitals

- but: even in case of orthogonal ϕ_i^{super} and exact ρ_A, ρ_B, in general

$$\sum_{j=1}^{n_A} \left\langle \phi_j^{\mathrm{super}} \left| -\nabla^2/2 \right| \phi_j^{\mathrm{super}} \right\rangle + \sum_{k=n_A+1}^{n_A+n_B} \left\langle \phi_k^{\mathrm{super}} \left| -\nabla^2/2 \right| \phi_k^{\mathrm{super}} \right\rangle$$

$$\geq \min_{\{\phi_{i_A}\}\to\rho_A} \sum_i^{n_A} \left\langle \phi_{i_A} \left| -\nabla^2/2 \right| \phi_{i_A} \right\rangle + \min_{\{\phi_{i_B}\}\to\rho_B} \sum_i^{n_B} \left\langle \phi_{i_B} \left| -\nabla^2/2 \right| \phi_{i_B} \right\rangle$$

- reason: not both subsets of $\{\phi_i^{\mathrm{super}}\}$ are, in general, ground-state of some effective potential
- still: subsets of $\{\phi_i^{\mathrm{super}}\}$ can be obtained from projected KS problem without v_t^{nad}

Externally Orthogonal Subsystem Orbitals

In sDFT, orbitals of different subsystems are not necessarily orthogonal:

$$\langle \phi_{i_I} | \phi_{j_I} \rangle = \delta_{ij}, \qquad \text{but} \quad \langle \phi_{i_I} | \phi_{j_J} \rangle \quad \text{can be} \quad \neq 0$$

How can we determine orthogonal embedded subsystem orbitals?

Three (related) strategies:

- projection-based embedding

  F.R. Manby, M. Stella, J.D. Goodpaster, T.F. Miller III, *J. Chem. Theory Comput.* 2012, **8**, 2564.

- external orthogonality through extra Lagrangian multipliers

  Y.G. Khait, M.R. Hoffmann, *Ann. Rep. Comput. Chem.* 2012, **8**, 53-70;
  P.K. Tamukong, Y.G. Khait, M.R. Hoffmann, *J. Phys. Chem. A* 2014, **118**, 9182.

- Huzinaga equation (transferred to KS-DFT)

  S. Huzinaga and A.A. Cantu, *J. Chem. Phys.* 1971, **55**, 5543;
  B. Hégely, P.R. Nagy, G.G. Ferency, M. Kállay, *J. Chem. Phys.* 2016, **145**, 064107.

Exact Embedding through Projection

Basic Idea:

- 1st step: KS-DFT calculation on $(A+B)$
- 2nd step: localization of KS orbitals $\Rightarrow \{\phi_i^A\}, \{\phi_i^B\}$
- then: construct Fock operator for electrons in subsystem A,

$$\hat{f}^A = -\frac{\nabla^2}{2} + v_{\text{nuc}}^A(\vec{r}) + v_{\text{nuc}}^B(\vec{r}) + v_{\text{Coul}}[\rho_A + \rho_B](\vec{r}) + v_{\text{xc}}[\rho_A + \rho_B](\vec{r}) + \mu \hat{P}^B$$

with projection operator $\hat{P}^B$,

$$\hat{P}^B = \sum_{i \in B} |\phi_i^B\rangle\langle\phi_i^B|$$

- for $\lim_{\mu\to\infty}$: eigenfunctions of $\hat{f}^A$ are orthogonal to $\{\phi_i^B\}$

F.R. Manby, M. Stella, J.D. Goodpaster, T.F. Miller III, *J. Chem. Theory Comput.* **8** (2012), 2564.

Externally Orthogonal Subsystem Orbitals

Enforce external orthogonality through extra constraints

- consider sDFT energy as functional of two orbital sets,

$$E^{\mathrm{sDFT}} = E^{\mathrm{sDFT}}[\{\phi_i^A\}, \{\phi_i^B\}]$$

- introduce orthonormality constraints through Lagrangian multipliers,

$$E^{\mathrm{sDFT}} \rightarrow L^{\mathrm{sDFT}} = E^{\mathrm{sDFT}} - \sum_{I=A,B} \sum_{\substack{i\in I \\ j\in I}} \lambda_{ij}^{I} \left(\langle \phi_{i_I} | \phi_{j_I} \rangle - \delta_{ij}\right) - \sum_{\substack{i\in A \\ j\in B}} \lambda_{ij}^{AB} \langle \phi_{i_A} | \phi_{j_B} \rangle - \sum_{\substack{i\in B \\ j\in A}} \lambda_{ij}^{BA} \langle \phi_{i_B} | \phi_{j_A} \rangle$$

- optimization w.r.t. ϕ_i^A yields (for ϕ_i^B fixed),

$$\left(-\frac{\nabla^2}{2} + v_{\mathrm{eff}}^{\mathrm{KS}}[\rho](\mathbf{r})\right) \phi_i^A(\mathbf{r}) = \epsilon_i^A \phi_i^A(\mathbf{r}) + \sum_{j\in B} \lambda_{ij}^{AB} \phi_j^B(\mathbf{r})$$

- multiply with $\langle \phi_k^B |$; make use of external orthogonality already,

$$\langle \phi_k^B | \hat{f}^{\mathrm{KS}} | \phi_i^A \rangle = \lambda_{ik}^{AB}$$

Y.G. Khait, M.R. Hoffmann, *Ann. Rep. Comput. Chem.* **8** (2012), 53-70;
P.K. Tamukong, Y.G. Khait, M.R. Hoffmann, *J. Phys. Chem. A* **118** (2014), 9182.

Externally Orthogonal Subsystem Orbitals

- from this it follows that,

$$
\begin{aligned}
\hat{f}^{\mathrm{KS}}|\phi_i^A\rangle &= \epsilon_i^A|\phi_i^A\rangle + \sum_{j\in B}|\phi_j^B\rangle\langle\phi_j^B|\hat{f}^{\mathrm{KS}}|\phi_i^A\rangle \\
\Rightarrow \underbrace{\left(1 - \sum_{j\in B}|\phi_j^B\rangle\langle\phi_j^B|\right)\hat{f}^{\mathrm{KS}}}_{\hat{f}'}|\phi_i^A\rangle &= \left(1 - \hat{P}^B\right)\hat{f}^{\mathrm{KS}}|\phi_i^A\rangle = \epsilon_i^A|\phi_i^A\rangle
\end{aligned}
$$

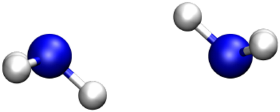
- note: $\hat{f}'$ is not Hermitian
- under external orthogonality: $(1 - \hat{P}^B)|\phi_i^A\rangle = |\phi_i^A\rangle$

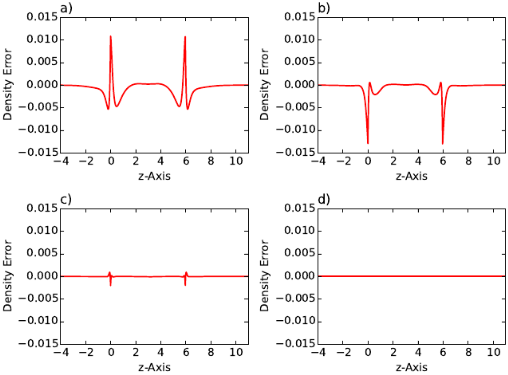
$$
\Rightarrow \underbrace{\left(1 - \hat{P}^B\right)\hat{f}^{\mathrm{KS}}\left(1 - \hat{P}^B\right)}_{\hat{f}''}|\phi_i^A\rangle = \epsilon_i^A|\phi_i^A\rangle
$$

note: $\hat{f}''$ is Hermitian!

Y.G. Khait, M.R. Hoffmann, *Ann. Rep. Comput. Chem.* **8** (2012), 53-70;
P.K. Tamukong, Y.G. Khait, M.R. Hoffmann, *J. Phys. Chem. A* **118** (2014), 9182.

Comparing Density-Based Embedding Schemes





PBE/def2-QZVP; a) sum-of-isolated densities; b) PBE-type T_s^{nad}; c) potential reconstruction d) projection

J.P. Unsleber, T. Dresselhaus, K. Klahr, D. Schnieders, M. Böckers, D. Barton, JN, *J. Comput. Chem.* **39** (2018), 788.

Density-Matrix Embedding Theory

Decomposing Total-System States

Consider active system A and environment B:

- states of combined system can be expanded as,

$$|\Psi_{A+B}\rangle = \sum_i^{n^A_{\text{states}}} \sum_j^{n^B_{\text{states}}} c_{ij} |A_i\rangle |B_j\rangle = \sum_i^{n^A_{\text{states}}} |A_i\rangle \left(\sum_j^{n^B_{\text{states}}} c_{ij} |B_j\rangle \right) = \sum_i^{n^A_{\text{states}}} |A_i\rangle |\tilde{B}_i\rangle$$

with “relative states” $|\tilde{B}_i\rangle$ (not orthonormal in general)

Schmidt Decomposition Theorem:

- any pure state $|\Psi_{A+B}\rangle$ can be written in terms of (orthonormal) *Schmidt states* $|a_i\rangle$, $|b_i\rangle$

$$|\Psi_{A+B}\rangle = \sum_k^{n_{\min}} \sqrt{p_i} |a_i\rangle |b_i\rangle$$

(where $\sqrt{p_i}$ is a real, non-negative number with $\sum_i p_i = 1$, and $n_{\min} = \min(n^A_{\text{states}}, n^B_{\text{states}})$

J. Audretsch, *Entangled Systems — New Directions in Quantum Physics*, Wiley-VCH, Weinheim, 2007, pp. 149-151;
M. Schlosshauer, *Decoherence and the Quantum-to-Classical Transition*, Springer, Berlin, 2007, p. 104.

Decomposing Total-System States

Schmidt Decomposition by SVD

- singular value decomposition of matrix $\boldsymbol{c} = \boldsymbol{U}\boldsymbol{\lambda}\boldsymbol{V}^\dagger$

$$
\begin{aligned}
|\Psi_{A+B}\rangle &= \sum_i^{n^A_\text{states}} \sum_j^{n^B_\text{states}} c_{ij} |A_i\rangle |B_j\rangle = \sum_i^{n^A_\text{states}} \sum_j^{n^B_\text{states}} \sum_k^{n_\text{min}} U_{ik} \lambda_k V^\dagger_{kj} |A_i\rangle |B_j\rangle \\
&= \sum_k^{n_\text{min}} \lambda_k |a_k\rangle |b_k\rangle
\end{aligned}
$$

⇒ even if $n^B_\text{states} \gg n^A_\text{states}$, exact embedding of A is possible with n^A_states bath states

- but: constructing bath states requires knowledge of full $|\Psi_{A+B}\rangle$

Idea of DMET

- construct bath states from simple approximation $|\Phi\rangle$ to $|\Psi_{A+B}\rangle$
- use bath states to obtain high-level approximation from embedded problem

H.-P. Breuer, F. Petruccione, *The Theory of Open Quantum Systems*, Oxford University Press, Oxford, 2006, pp. 75-76;
G. Knizia, G.K.-L. Chan, *J. Chem. Theory Comput.* 2013, **9**, 1428;
S. Wouters, C.A. Jiménez-Hoyos, Q. Sun, G.K.-L. Chan, *J. Chem. Theory Comput.* 2016, **12**, 2706.

DMET in Practice

(1) perform HF calculation on full system $(A + B)$
$\Rightarrow$ yields N_{occ} occupied orbitals $\{\phi_i\}$

(2) perform orbital rotation among $\{\phi_i\}$; specifically:

- calculate

$$S_{ij} = \sum_{p \in A} \langle \phi_i | p \rangle \langle p | \phi_j \rangle$$

(overlap matrix of orbitals projected onto the L_A ”sites” $|p\rangle$ of fragment A)

- eigenvectors of $\mathbf{S}$ define a rotation matrix; there are $N_{\text{occ}} - L_A$ eigenvectors with zero eigenvalue

$\Rightarrow$ environment orbitals $\{\phi_i^{\text{env}}\}$ without overlap with A

$\Rightarrow$ the remaining L_A “entangled” orbitals $\{\phi_i^{\text{ent}}\}$ do have overlap with A

(3) project $\{\phi_q^{\text{ent}}\}$ onto environment “sites” $\Rightarrow$ yields L_A “bath orbitals” $|b\rangle$

$$\{|b\rangle\} = \left\{ \sum_{r \in B} |r\rangle \langle r | \phi_i^{\text{ent}} \rangle \right\}$$

G. Knizia, G.K.-L. Chan, *J. Chem. Theory Comput.* **9** (2013), 1428.

DMET in Practice

- ⇒ many-body wavefunction: CAS-CI wavefunction with (half-filled) active space of $\{|p\rangle\}$ (L_A sites of fragment A) and $\{|b\rangle\}$ (L_A bath orbitals)
- (4) project total Hamiltonian $\hat{H}$ into active space, $\hat{H}^A_{\text{emb}} = \hat{P}\hat{H}\hat{P}$, and find high-accuracy approx. to $\hat{H}^A_{\text{emb}}\Psi_A = E_A\Psi_A$ (e.g., FCI)
- (5) adjust one-particle density matrix $\mathbf{D}$ to match that of Ψ_A as close as possible on fragment A. Do that for all fragments and iterate.

Note: This adjustment minimizes

$$\Delta = \sum_A \sum_{rs\in A} ||\langle\Phi|\hat{a}_r^\dagger\hat{a}_s|\Phi\rangle - \langle\Psi_A|\hat{a}_r^\dagger\hat{a}_s|\Psi_A\rangle||^2$$

by changing the Fock operator

$$\hat{f} \to \hat{f} + \textstyle\sum_A \hat{\mu}_A \qquad \text{with} \qquad \hat{\mu}_A = \textstyle\sum_{rs\in A} \mu^A_{rs}\hat{a}_r^\dagger\hat{a}_s$$

in the calculation of the mean-field wavefunction $|\Phi\rangle$
(i.e., Δ is minimized w.r.t. all μ^A_{rs})

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Conclusion

QM/QM methods

- there are several QM/QM methods available now which are (formally) exact under certain conditions
- but: using “exact” embedding directly does not lead to gain in efficiency
- however, it can be the starting point for new approximations or new (approximate) fields of application

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QM/(QM,MM) methods?

- “Polarizable Density Embedding”:
  combines elements from FDE, polarizable force fields, and Huzinaga-type embedding

  J.M.H. Olsen, C. Steinmann, K. Ruud, J. Kongsted, *J. Phys. Chem. A* 2015, **119**, 5344.