Quantum Chemical Embedding Methods
— Lecture 3 —

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Structure of This Lecture

- Lecture 1: Subsystems in Quantum Chemistry
  - subsystems in wave-function- and DFT- based Quantum Chemistry
  - basics of subsystem density-functional theory
- Lecture 2: “Exact” Density-Based Embedding
  - potential reconstruction
  - projection-based embedding
  - external orthogonality and the Huzinaga equation
- Lecture 3: Embedded Wavefunctions, Density Matrices, etc.
  - wave function-in-DFT embedding: ground states
  - wave function-in-DFT embedding: excited states
  - density-matrix embedding theory and bootstrap embedding

I. Wavefunction-in-DFT Embedding

Background: sDFT vs. DFT/DFT

- sDFT energy bifunctional for given v_{ext}:

$$E^{\text{sDFT}}_{v_{\text{ext}}}[\rho_A,\rho_B] = T_s[\rho_A] + T_s[\rho_B] + J[\rho_A+\rho_B] + E_{\text{xc}}[\rho_A+\rho_B] + V_{\text{ext}}[\rho_A+\rho_B] + T_s^{\text{nad}}[\rho_A,\rho_B]$$

- note: KS energy functional for external potential v_{ext}^K is

$$E^{\text{KS}}_{v^K_{\text{ext}}}[\rho_K] \quad = \quad T_s[\rho_K] + J[\rho_K] + E_{\text{xc}}[\rho_K] + V^K_{\text{ext}}[\rho_K],$$

- hence,

$$\begin{aligned} E^{\text{sDFT}}_{v_{\text{ext}}}[\rho_A,\rho_B] &= E^{\text{KS}}_{v^A_{\text{ext}}}[\rho_A] + E^{\text{KS}}_{v^B_{\text{ext}}}[\rho_B] + J_{\text{int}}[\rho_A,\rho_B] + V^A_{\text{ext}}[\rho_B] + V^B_{\text{ext}}[\rho_A] \\ &\quad + E^{\text{nad}}_{\text{xc}}[\rho_A,\rho_B] + T_s^{\text{nad}}[\rho_A,\rho_B] \\ &= E^{\text{KS}}_{v^A_{\text{ext}}}[\rho_A] + E^{\text{KS}}_{v^B_{\text{ext}}}[\rho_B] + E^{\text{OFDFT}}_{A\leftrightarrow B}[\rho_A,\rho_B], \end{aligned}$$

where

$$E^{\text{OFDFT}}_{A\leftrightarrow B}[\rho_A,\rho_B] \quad = \quad E^{\text{OFDFT}}_{v_{\text{ext}}}[\rho_A+\rho_B] - E^{\text{OFDFT}}_{v^A_{\text{ext}}}[\rho_A] - E^{\text{OFDFT}}_{v^B_{\text{ext}}}[\rho_B]$$

Background: sDFT vs. DFT/DFT

- this energy expression has the typical additive hybrid-method form,

$$E_{A+B}^{\text{hybrid}} = E_A^{\text{method1}} + E_B^{\text{method2}} + E_{A\leftrightarrow B}^{\text{method3}}$$

  for the special case method1 = method2

- it can also be brought into the form

$$\begin{aligned} E_{v_{\text{ext}}}^{\text{sDFT}}[\rho_A, \rho_B] &= E_{v_{\text{ext}}}^{\text{OFDFT}}[\rho_A + \rho_B] + (E_{v_{\text{ext}}^A}^{\text{KS}}[\rho_A] - E_{v_{\text{ext}}^A}^{\text{OFDFT}}[\rho_A]) + \\ & (E_{v_{\text{ext}}^B}^{\text{KS}}[\rho_B] - E_{v_{\text{ext}}^B}^{\text{OFDFT}}[\rho_B]) \end{aligned}$$

  typical for subtractive hybrid-method approaches

- in the limit of exact functionals, all approaches give identical results
- but: sDFT can in fact be used in “hybrid-method fashion”

Subsystem DFT as a DFT/DFT Hybrid Method

Typical examples:

- orbital-dependent XC functionals for intra-subsystem contributions, e.g.,

$$E_{A+B}^{\text{hybrid}} = E_A^{\text{B3LYP}} + E_B^{\text{B3LYP}} + E_{A\leftrightarrow B}^{\text{BLYP}}$$

- meta-GGA for active system (A), GGA description for environment (B), and LDA for interaction, e.g.

$$E_{A+B}^{\text{hybrid}} = E_A^{\text{TPSS}} + E_B^{\text{PBE}} + E_{A\leftrightarrow B}^{\text{LDA}}$$

Note:

For orbital-dependent functionals like (double) hybrids we *have to* use different approximations for intra- and inter-subsystem contributions, since $E_{A\leftrightarrow B}$ needs to be evaluated with OFDFT

Subsystem DFT as a DFT/DFT Hybrid Method

Free variables to be optimized?

- for an energy functional

$$E^{\mathrm{sDFT}}_{v_{\mathrm{ext}}}[\rho_A,\rho_B] = E^{\mathrm{OFDFT}}_{v_{\mathrm{ext}}}[\rho_A+\rho_B] + \left(E^{\mathrm{KS}}_{v^A_{\mathrm{ext}}}[\rho_A] - E^{\mathrm{OFDFT}}_{v^A_{\mathrm{ext}}}[\rho_A]\right) + \left(E^{\mathrm{KS}}_{v^B_{\mathrm{ext}}}[\rho_B] - E^{\mathrm{OFDFT}}_{v^B_{\mathrm{ext}}}[\rho_B]\right)$$

  it seems natural to optimize $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$

- more often, subtractive hybrid methods have a form like this:

$$E^{\mathrm{KSDFT/OFDFT}}_{A+B} = E^{\mathrm{OFDFT}}_{A+B} + \left(E^{\mathrm{KS}}_{A} - E^{\mathrm{OFDFT}}_{A}\right)$$

⇒ can be considered a functional of $\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$ and ρ_A

$$E^{\mathrm{KSDFT/OFDFT}}_{v_{\mathrm{ext}}}[\rho_A,\rho] = E^{\mathrm{OFDFT}}_{v_{\mathrm{ext}}}[\rho] + \left(E^{\mathrm{KS}}_{v^A_{\mathrm{ext}}}[\rho_A] - E^{\mathrm{OFDFT}}_{v^A_{\mathrm{ext}}}[\rho_A]\right)$$

- in the latter case, $\rho_B(\mathbf{r})$ is obtained as the difference $\rho(\mathbf{r}) - \rho_A(\mathbf{r})$

⇒ can be negative in certain regions, which can cause severe problems!

WF/DFT as a Hybrid Method

Hybrid WF/DFT energy expression:

$$E_{(A+B)}^{\mathrm{WF/DFT}} = E_A^{\mathrm{WF}} + E_B^{\mathrm{DFT}} + E_{(A\leftrightarrow B)}^{\mathrm{DFT}}$$

or

$$E_{(A+B)}^{\mathrm{WF/DFT}} = E_{(A+B)}^{\mathrm{DFT}} + \left(E_A^{\mathrm{WF}} - E_A^{\mathrm{DFT}}\right)$$

(embedding potential can be identified as functional derivative $\delta E_{(A\leftrightarrow B)}^{\mathrm{DFT}} / \delta \rho_A(\mathbf{r})$ [for ρ_B fixed])

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

Questions:

- separate calculations or self-consistent energy minimization?
- if self-consistent: what are the free variables?
- which approximations enter in practice?
  (e.g. DFT part: KS or OF?)

WF/DFT: Energy Functional

- WF/DFT energy functional:

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

(ρ_A: density obtained from Ψ_A)

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

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

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!

WF/DFT: Energy Functional

- WF/DFT energy functional:

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

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

$$\left(-\frac{1}{2} \nabla^2 + v_{\mathrm{eff}}[\rho_B](\mathbf{r}) + v_{\mathrm{emb}}^{B}[\rho_B, \rho_A] \right) \phi_{i_B} = \epsilon_{i_B} \phi_{i_B} ,$$

(density ρ_B is obtained as $\sum_{i=1}^{n_B} |\phi_{i_B}(\mathbf{r})|^2$)

- full optimization: iterative freeze-and-thaw between WF and DFT part

⇒ expensive!

WF/DFT in Practice

Simple Standard Recipie:

- perform simple FDE or full sDFT optimization of $\rho_A(\mathbf{r})$ [and $\rho_B(\mathbf{r})$]
- store final embedding potential $v_{\text{emb}}^{A,\text{final}}(\mathbf{r})$ point-wise on integration grid covering system A
- evaluate $\langle \chi_\mu | v_{\text{emb}}^{A,\text{final}}(\mathbf{r}) | \chi_\nu \rangle$ numerically
- add this to one-electron part of $f_{\mu\nu}$ in HF calculation on system A
- ignore ρ_A-dependence of v_{emb}^{A} in SCF
- make sure to remove this contribution from one-electron part in energy evaluation
- get embedded orbitals and corresponding MO integrals
- use those in correlated WF treatment on system A

“Exact” WF/DFT Embedding?

Background:

- if DFT is good for densities, but not accurate enough for energies: derive highly accurate density-based embedding potential and transfer to WF part
- typical target application: transition-metal complexes
  - difficult electronic situation at metal center
  - still: DFT accurate enough for ligand system

Embedding potential by reconstruction:

- create “exact” embedding potential in sDFT calculation
- store final embedding potential $v_{\text{emb}}^{A,\text{reconstr}}(\mathbf{r})$ point-wise on integration grid covering system A
- proceed as before
- problem: convergence of reconstruction step bad for larger systems

“Exact” WF/DFT Embedding?

Embedding through projection:

- determine projection operator $\hat{P} = \sum_{i \in B} |\phi_{i_B}\rangle\langle\phi_{i_B}|$ from DFT calculation
  (as discussed before)
- again, this can be added to one-electron part in WF step
  F.R. Manby, M. Stella, J.D. Goodpaster, T.F. Miller III, *J. Chem. Theory Comput.* **8** (2012), 2564.
- problem: accurate projector requires supermolecular basis

$\Rightarrow$ fewer occupied orbitals in WF step, but all virtual orbitals of $(A + B)$

$\Rightarrow$ problem for scaling behavior of correlated WF methods [e.g., CCSD(T): $n_{\mathrm{occ}}^3 \cdot n_{\mathrm{virt}}^4$]

- another problem: DFT overdelocalization error may affect projector

$\Rightarrow$ can be solved by using HF for orbitals, DFT for energies of system B

R.C.R. Pennifold, S.J. Bennie, T.F. Miller III, F.R. Manby, *J. Chem. Phys.* **146**, 084113.

Basis Set Truncation in Projection-WF/DFT

Try to reduce no. of virtual orbitals:

- define region of border atoms
- divide system-B orbitals into $\{\phi_{i_B}^{\text{distant}}\}$ and $\{\phi_{i_B}^{\text{border}}\}$

  (based on population on border atoms)
- only include $\{\phi_{i_B}^{\text{border}}\}$ in projector
- truncate basis for WF step to include only AOs in system A and at border atoms

$\Rightarrow$ orthogonality with system B not fully enforced

T.A. Barnes, J.D. Goodpaster, F.R. Manby, T.F. Miller III, *J. Chem. Phys.* **139** (2013), 024103.

Alternative without “border atoms”:

- truncate basis set based on population in system A
- specifically: include only basis functions with Mulliken net populations

$$q_\alpha^{\text{net}} := D_{\alpha\alpha}^{A} S_{\alpha\alpha} > 10^{-4}$$

($D_{\alpha\alpha}^{A}$ = density matrix of system A)

S.J. Bennie, M. Stella, T.F. Miller III, F.R. Manby, *J. Chem. Phys.* **143** (2015), 024105.

Basis Set Truncation in Projection-WF/DFT

Correction for neglected orbitals in projector:

- define density $\rho_B^{\text{distant}}(\mathbf{r}) = \sum_{i \in B,\text{distant}} |\phi_{i_B}^{\text{distant}}(\mathbf{r})|^2$
- add density-based correction:

$$v_t^{\text{nad}}[\rho_A, \rho_B^{\text{distant}}](\mathbf{r}) = \left.\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\text{A}}+\rho_{\text{B}}^{\text{distant}}} - \left.\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\text{A}}}$$

R.C.R. Pennifold, S.J. Bennie, T.F. Miller III, F.R. Manby, *J. Chem. Phys.* **146**, 084113.

WF/DFT as a Special Kind of sDFT

Consider Multi-Configurational DFT:

- el.–el.interaction is separated into long- and short-range parts using

$$\frac{1}{r_{12}} = \frac{\mathrm{erf}(r_{12})}{r_{12}} + \frac{\mathrm{erfc}(r_{12})}{r_{12}}$$

- short-range part is treated, e.g., by LDA
- long-range part is treated through WF for interacting particles

WF/DFT as a Special Kind of sDFT

Relation to WF/DFT embedding:

- can be considered as DFT method with representation of ρ_A through a multi-determinant wave function T.A. Wesolowski, *Phys. Rev. A* **77** (2008), 012504.
- energy functional:

$$\begin{aligned} E_{v_{\text{ext}}}^{\text{WF/DFT}}[\Psi_A^{\text{MD}}, \rho_B] \quad = \quad & \langle \Psi_A^{\text{MD}} | \hat{T} + \hat{V}_{\text{ee}} | \Psi_A^{\text{MD}} \rangle + V_{\text{ext}}^A[\rho_A] + T_s[\rho_B] + J[\rho_B] \\ & + E_{\text{xc}}[\rho_B] + V_{\text{ext}}^B[\rho_B] + V_{\text{ext}}^A[\rho_B] + V_{\text{ext}}^B[\rho_A] \\ & + J_{\text{int}}[\rho_A, \rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B] + E_{\text{xc}}^{\text{nad}}[\rho_A, \rho_B], \end{aligned}$$

- full minimization w.r.t. Ψ_A^{MD} and ρ_B will lead to true ground-state energy
  (in the limit of exact functionals)
- but: only if search space for Ψ_A^{MD} includes exact wave function
- otherwise,

$$\min_{\Psi_A^{\text{MD}} \rightarrow \rho_A} \langle \Psi_A^{\text{MD}} | \hat{T} + \hat{V}_{\text{ee}} | \Psi_A^{\text{MD}} \rangle \neq T[\rho_A] + V_{\text{ee}}[\rho_A]$$

which needs to be corrected by an additional density functional

Perturbation-Theory Perspective on WF/DFT

- if only changes in system A properties due to environment are of interest, consider perturbation,

$$\hat{H}_A \longrightarrow \hat{H}_A + \sum_{i=1}^{N_A} \tilde{v}_{\mathrm{emb}}^{A}(\mathbf{r}_i),$$

- perturbation theory tells us

$$\Delta E_A^{(1)} \approx \left\langle \Psi_A^{(0)} \left| \sum_{i=1}^{N_A} \tilde{v}_{\mathrm{emb}}^{A}(\mathbf{r}_i) \right| \Psi_A^{(0)} \right\rangle ,$$

- connection to hybrid-method viewpoint (assume ρ_2 fixed):

$$\begin{aligned} E_{v_{\mathrm{ext}}}^{\mathrm{WF/DFT}}[\Psi_A, \rho_B] \quad = \quad & \langle \Psi_A | \hat{H}_A + \sum_{i=1}^{n_A} v_{\mathrm{elstat}}(\mathbf{r}_i) | \Psi_A \rangle + E_{\mathrm{xc}}[\rho_A + \rho_B] - E_{\mathrm{xc}}[\rho_A] \\ & + T_s[\rho_A + \rho_B] - T_s[\rho_A] + \text{const.} \end{aligned}$$

with const. = $E_{v_{\mathrm{ext}}^{B}}^{\mathrm{KS}}[\rho_B] + V_{\mathrm{ext}}^{A}[\rho_B] - E_{\mathrm{xc}}[\rho_B] - T_s[\rho_B]$

Perturbation-Theory Perspective on WF/DFT

$\Rightarrow$ if we want to write this as

$$E^{\mathrm{WF/DFT}}_{v_{\mathrm{ext}}}[\Psi_A, \rho_B] \quad = \quad \langle \Psi_A | \hat{H}_A + \sum_{i=1}^{n_A} v^A_{\mathrm{emb}}(\mathbf{r}_i) | \Psi_A \rangle + \text{const.'}$$

we also have to replace

$$E_{\mathrm{xc}}[\rho_A + \rho_B] - E_{\mathrm{xc}}[\rho_A] + T_s[\rho_A + \rho_B] - T_s[\rho_A]$$

by

$$\int v^{\mathrm{nad}}_{\mathrm{xc}}[\rho_A, \rho_B](\mathbf{r})\rho_A(\mathbf{r})\mathrm{d}\mathbf{r} + \int v^{\mathrm{nad}}_{t}[\rho_A](\mathbf{r}), \rho_B]\rho_A(\mathbf{r})\mathrm{d}\mathbf{r},$$

which is an additional approximation!

Excitation Energies in WF/DFT

General expression for excitation energies:

$$\Delta E \quad = \quad E^{\mathrm{WF/DFT}}_{(1+2)e} - E^{\mathrm{WF/DFT}}_{(1+2)g}$$

Case **A**: no differential polarization, ρ_2 unchanged

$$\begin{aligned}
\Delta E \quad &= \quad \Big(E_1^{\mathrm{WF}}[\Psi_1^e] + E_2^{\mathrm{KS}}[\rho_2] + E^{\mathrm{OFDFT}}_{(1\leftrightarrow 2)}[\rho_1^e, \rho_2]\Big) \\
&\quad\ - \Big(E_1^{\mathrm{WF}}[\Psi_1^g] + E_2^{\mathrm{KS}}[\rho_2] + E^{\mathrm{OFDFT}}_{(1\leftrightarrow 2)}[\rho_1^g, \rho_2]\Big) \\
&= \quad E_1^{\mathrm{WF}}[\Psi_1^e] + E^{\mathrm{OFDFT}}_{(1\leftrightarrow 2)}[\rho_1^e, \rho_2] \\
&\quad\ - E_1^{\mathrm{WF}}[\Psi_1^g] - E^{\mathrm{OFDFT}}_{(1\leftrightarrow 2)}[\rho_1^g, \rho_2]
\end{aligned}$$

Excitation Energies in WF/DFT

Expression for pure electrostatic embedding:

$$\begin{aligned}
\Delta E^{\text{elstat}} &= \left(E_1^{\text{WF}}[\Psi_1^e] - E_1^{\text{WF}}[\Psi_1^g]\right) \\
&\quad + V_{\text{nuc},2}[\rho_1^e] - V_{\text{nuc},2}[\rho_1^g] + J[\rho_1^e, \rho_2] - J[\rho_1^g, \rho_2], \\
&= \left(E_1^{\text{WF}}[\Psi_1^e] - E_1^{\text{WF}}[\Psi_1^g]\right) \\
&\quad + \left\langle \Psi_1^e \left| \sum_i v_{\text{emb},1}^{\text{elstat.}}(\mathbf{r}_i) \right| \Psi_1^e \right\rangle \\
&\quad - \left\langle \Psi_1^g \left| \sum_i v_{\text{emb},1}^{\text{elstat.}}(\mathbf{r}_i) \right| \Psi_1^g \right\rangle,
\end{aligned}$$

with

$$v_{\text{emb},1}^{\text{elstat.}}(\mathbf{r}) = v_{\text{nuc},2}(\mathbf{r}) + \int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}'$$

Excitation Energies in WF/DFT

Approximate expression based on “embedding operators”:

$$\begin{aligned}
\Delta E^{(A)}_{\text{approx}} &= E^{\text{WF}}_1[\Psi^e_1] + \langle \Psi^e_1 | \sum_i v_{\text{emb},1}(\mathbf{r}_i) | \Psi^e_1 \rangle \\
&- E^{\text{WF}}_1[\Psi^g_1] - \langle \Psi^g_1 | \sum_i v_{\text{emb},1}(\mathbf{r}_i) | \Psi^g_1 \rangle, \\
&= E^{\text{WF}}_1[\Psi^e_1] - E^{\text{WF}}_1[\Psi^g_1] \\
&\quad + V_{\text{nuc},2}[\rho^e_1] - V_{\text{nuc},2}[\rho^g_1] + J[\rho^e_1, \rho_2] - J[\rho^g_1, \rho_2] \\
&\quad + \int v^{\text{nad}}_{xc}[\rho^g_1, \rho_2](\vec{r}) \left[\rho^e_1(\vec{r}) - \rho^g_1(\vec{r})\right] \mathrm{d}\vec{r} \\
&\quad + \int v^{\text{nad}}_{t}[\rho^g_1, \rho_2](\vec{r}) \left[\rho^e_1(\vec{r}) - \rho^g_1(\vec{r})\right] \mathrm{d}\vec{r}
\end{aligned}$$

Excitation Energies in WF/DFT

True excitation energy expression for case **A**

$$
\begin{aligned}
\Delta E^{(A)} \quad = \quad & E_1^{\mathrm{WF}}[\Psi_1^e] - E_1^{\mathrm{WF}}[\Psi_1^g] \\
& + V_{\mathrm{nuc},2}[\rho_1^e] - V_{\mathrm{nuc},2}[\rho_1^g] + J[\rho_1^e, \rho_2] - J[\rho_1^g, \rho_2] \\
& + E_{xc}^{\mathrm{nad}}[\rho_1^e, \rho_2] - E_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2] \\
& + T_s^{\mathrm{nad}}[\rho_1^e, \rho_2] - T_s^{\mathrm{nad}}[\rho_1^g, \rho_2]
\end{aligned}
$$

⇒ approximation made with embedding operators:

$$
\int \left\{ v_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2](\vec{r}) + v_t^{\mathrm{nad}}[\rho_1^g, \rho_2](\vec{r}) \right\} \left[\rho_1^e(\vec{r}) - \rho_1^g(\vec{r}) \right] \mathrm{d}\vec{r} \approx
$$

$$
E_{xc}^{\mathrm{nad}}[\rho_1^e, \rho_2] - E_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2] + T_s^{\mathrm{nad}}[\rho_1^e, \rho_2] - T_s^{\mathrm{nad}}[\rho_1^g, \rho_2]
$$

similar to linearization approximation

M. Dulak, T.A. Wesolowski, *J. Chem. Theory Comput.* **2** (2006), 1538.

Differential Polarization in WF/DFT

Case **B**: ρ_2 polarized in state-specific manner

$$
\begin{aligned}
\Delta E^{(B)} &= E_1^{\mathrm{WF}}[\Psi_1^{\mathrm{pol},e}] - E_1^{\mathrm{WF}}[\Psi_1^g] \\
&+ E_2^{\mathrm{KS}}[\rho_2^{\mathrm{pol}}] - E_2^{\mathrm{KS}}[\rho_2] + V_{\mathrm{nuc},1}[\rho_2^{\mathrm{pol}}] - V_{\mathrm{nuc},1}[\rho_2] \\
&+ V_{\mathrm{nuc},2}[\rho_1^{\mathrm{pol},e}] - V_{\mathrm{nuc},2}[\rho_1^g] + J[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}] - J[\rho_1^g, \rho_2] \\
&+ E_{xc}^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}] - E_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2] \\
&+ T_s^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}] - T_s^{\mathrm{nad}}[\rho_1^g, \rho_2]
\end{aligned}
$$

Differential Polarization in WF/DFT

Use of embedding operators in state-specific embedding

$$
\begin{aligned}
\Delta E^{(B)}_{\mathrm{approx}} &= E^{\mathrm{WF}}_1[\Psi^{\mathrm{pol},e}_1] + \langle \Psi^{\mathrm{pol},e}_1 | \sum_i v^{\mathrm{pol},e}_{\mathrm{emb},1}(\mathbf{r}_i) | \Psi^{\mathrm{pol},e}_1 \rangle \\
&\quad - E^{\mathrm{WF}}_1[\Psi^{g}_1] - \langle \Psi^{g}_1 | \sum_i v_{\mathrm{emb},1}(\mathbf{r}_i) | \Psi^{g}_1 \rangle \\
&= E^{\mathrm{WF}}_1[\Psi^{\mathrm{pol},e}_1] - E^{\mathrm{WF}}_1[\Psi^{g}_1] \\
&\quad + V_{\mathrm{nuc},2}[\rho^{\mathrm{pol},e}_1] - V_{\mathrm{nuc},2}[\rho^{g}_1] + J[\rho^{\mathrm{pol},e}_1, \rho^{\mathrm{pol}}_2] - J[\rho^{g}_1, \rho_2] \\
&\quad + \int \left[v^{\mathrm{nad}}_{xc}[\rho^{\mathrm{pol},e}_1, \rho^{\mathrm{pol}}_2](\vec{r}) + v^{\mathrm{nad}}_{t}[\rho^{\mathrm{pol},e}_1, \rho^{\mathrm{pol}}_2](\vec{r}) \right] \rho^{\mathrm{pol},e}_1(\vec{r}) \mathrm{d}\vec{r} \\
&\quad - \int \left[v^{\mathrm{nad}}_{xc}[\rho^{g}_1, \rho_2](\vec{r}) + v^{\mathrm{nad}}_{t}[\rho^{g}_1, \rho_2](\vec{r}) \right] \rho^{g}_1(\vec{r}) \mathrm{d}\vec{r}
\end{aligned}
$$

C. Daday, C. König, O. Valsson, J. Neugebauer, C. Filippi, *J. Chem. Theory Comput.* **9** (2013), 2355.

Differential Polarization in WF/DFT

. . . implies the following error:

(already disregarding differential kinetic-energy and XC terms in E_1^{WF})

$$E_2^{\mathrm{KS}}[\rho_2^{\mathrm{pol}}] - E_2^{\mathrm{KS}}[\rho_2] + V_{\mathrm{nuc},1}[\rho_2^{\mathrm{pol}}] - V_{\mathrm{nuc},1}[\rho_2] \approx 0$$

Error in Coulomb terms:

$$\int \left\{ v_{\mathrm{Coul}}[\rho_2 + \Delta\rho_2/2](\vec{r}) + v_{\mathrm{nuc},1}(\vec{r}) + v_{\mathrm{nuc},2}(\vec{r}) \right\} \Delta\rho_2(\vec{r}) \mathrm{d}\vec{r} \approx 0$$

with $\Delta\rho_2(\vec{r}) = \rho_2^{\mathrm{pol}}(\vec{r}) - \rho_2(\vec{r})$

⇒ Use correction:

$$\delta E_{\mathrm{simple}}^{(\mathrm{B})} \quad = \quad E_2^{\mathrm{KS}}[\rho_2^{\mathrm{pol}}] - E_2^{\mathrm{KS}}[\rho_2] + \int v_{\mathrm{nuc},1}(\vec{r}) \Delta\rho_2(\vec{r}) \mathrm{d}\vec{r}$$

Differential Polarization in WF/DFT

Improved excitations from state-specific embedding:

$$\begin{aligned}\Delta E^{(B)} &\approx E_1^{\mathrm{WF}}[\Psi_1^{\mathrm{pol},e}] + \langle \Psi_1^{\mathrm{pol},e} | \sum_i v_{\mathrm{emb},1}^{\mathrm{pol},e}(\vec{r}_i) | \Psi_1^{\mathrm{pol},e} \rangle \\ &- E_1^{\mathrm{WF}}[\Psi_1^g] - \langle \Psi_1^g | \sum_i v_{\mathrm{emb},1}(\vec{r}_i) | \Psi_1^g \rangle + \delta E_{\mathrm{simple}}^{(\mathrm{B})}\end{aligned}$$

Remaining error: (similar to case A)

$$\begin{aligned}\delta E_{\mathrm{nadd}}^{(\mathrm{B})} &= E_{xc}^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}] - E_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2] \\ &+T_s^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}] - T_s^{\mathrm{nad}}[\rho_1^g, \rho_2] \\ &- \int \left[v_{xc}^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}](\vec{r}) + v_t^{\mathrm{nad}}[\rho_1^{\mathrm{pol},e}, \rho_2^{\mathrm{pol}}](\vec{r}) \right] \rho_1^{\mathrm{pol},e}(\vec{r}) \mathrm{d}\vec{r} \\ &- \int \left[v_{xc}^{\mathrm{nad}}[\rho_1^g, \rho_2](\vec{r}) + v_t^{\mathrm{nad}}[\rho_1^g, \rho_2](\vec{r}) \right] \rho_1^g(\vec{r}) \mathrm{d}\vec{r}\end{aligned}$$

II. Density-Matrix Embedding Theory

Decomposing Total-System States

Consider active system A and bath B:

- states of combined system can be expanded as,

$$
\begin{aligned}
|\Psi_{A\leftrightarrow B}\rangle &= \sum_{i}^{n^A_{\text{states}}} \sum_{j}^{n^B_{\text{states}}} c_{ij} |A_i\rangle |B_j\rangle = \sum_{i}^{n^A_{\text{states}}} |A_i\rangle \left(\sum_{j}^{n^B_{\text{states}}} c_{ij} |B_j\rangle \right) \\
&= \sum_{i}^{n^A_{\text{states}}} |A_i\rangle |\tilde{B}_i\rangle \qquad \text{with} \quad |\tilde{B}_i\rangle = \sum_{j}^{n^B_{\text{states}}} c_{ij} |B_j\rangle
\end{aligned}
$$

- $|\tilde{B}_i\rangle$ are not necessarily orthogonal; use

$$
|\tilde{B}^{\text{orth}}_{i'}\rangle = \sum_{i}^{n^A_{\text{states}}} c_{ii'} |\tilde{B}_i\rangle \qquad \text{such that} \quad \langle \tilde{B}^{\text{orth}}_{i'} | \tilde{B}^{\text{orth}}_{j'} \rangle = \delta_{i'j'}
$$

Decomposing Total-System States

- for simplicity, we write $|b_{i'}\rangle := |\tilde{B}^{\mathrm{orth}}_{j'}\rangle$ for these *bath states*,

$$|\Psi_{A\leftrightarrow B}\rangle \quad = \quad \sum_{i}^{n^A_{\mathrm{states}}} \sum_{i'}^{n^A_{\mathrm{states}}} |A_i\rangle|b_{i'}\rangle$$

⇒ even if $n_B \gg n_A$, exact embedding of A is possible considering only n_A bath states

- but: constructing these states requires knowledge of full $|\Psi_{A\leftrightarrow B}\rangle$
- idea of DMET:
  - construct $\{|b_{i'}\rangle\}$ from simple approximation $|\Phi\rangle$ to $|\Psi_{A\leftrightarrow B}\rangle$
  - use these bath states to embedd high-quality approx. for $\{|A_i\rangle\}$
  - try to match one-particle density matrices between low- and high-level approximations

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

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

⇒ the many-body wavefunction is expressed as a 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

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

by changing the Fock operator $\hat{f} \to \hat{f} + \sum_A \hat{\mu}_A$ with the correlation potentials $\hat{\mu}_A = \sum_{rs\in A} \mu^A_{rs}\hat{a}^\dagger_r\hat{a}_s$ in the calculation of the mean-field wavefunction $|\Phi\rangle$ (i.e., Δ is minimized w.r.t. all μ^A_{rs})

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

DMET in Practice

- total DMET energy = sum of fragment energies,

$$E = \sum_A E_A = \sum_A \left(\sum_{p \in A, s} D_{ps} h_{ps} + \frac{1}{2} \sum_{p \in A, stu} d_{pstu} g_{pstu} \right)$$

(one- and two-particle density matrices $\mathbf{D}$ and $\mathbf{d}$ here include contributions from the pure environment orbitals)

- non-integer number of electrons per fragment; total number of electrons is recovered
- important conceptual question: Can the density matrix of the high-level wave function be represented through the chosen low-level wave function?
- for HF-in-HF-embedding, the results are exact

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

Bootstrap Embedding

- concept similar to DMET, but different matching condition
- use overlapping fragments
- match one-particle density matrix of the edge of one fragment to the center of a partially overlapping fragment

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