# Quantum Chemical Embedding Methods
## — Lecture 2 —

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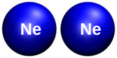
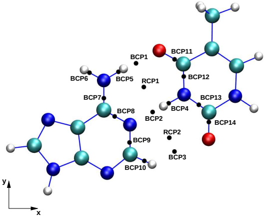
# Structure of This Lecture

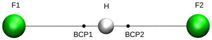
- Lecture 1: Subsystems in Quantum Chemistry
  - subsystems in wave-function- and DFT- based Quantum Chemistry
  - basics of subsystem density-functional theory
- Lecture 2: “Exact” Density-Based Embedding
  - potential reconstruction
  - projection-based embedding
  - external orthogonality and the 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

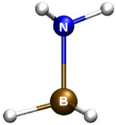
# I. Reconstructed Embedding Potentials

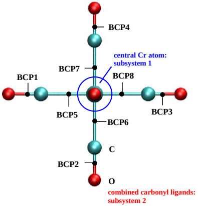
# Applicability of Approximate Subsystem DFT











- van der Waals complexes, hydrogen bonds: good results

  K. Kiewisch, G. Eickerling, M. Reiher, JN, *J. Chem. Phys.* **128** (2008), 044114.

- coordination bonds: borderline cases

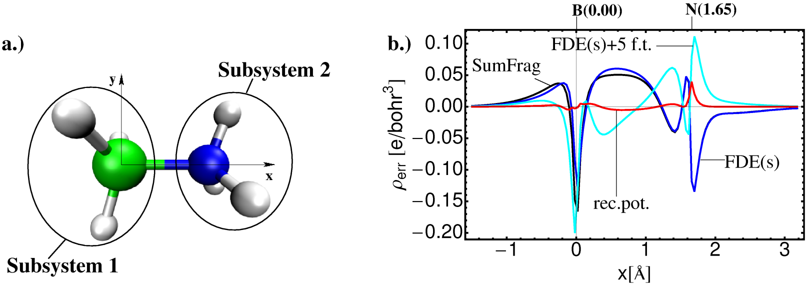
  S. Fux, K. Kiewisch, C.R. Jacob, JN, M. Reiher, *Chem. Phys. Lett.* **461** (2008), 353.

- covalent bonds: qualitatively wrong with standard approximations

  S. Fux, C.R. Jacob, JN, L. Visscher, M. Reiher, *J. Chem. Phys.* **132** (2010), 164101.

- main problem: non-additive kinetic-energy potentials

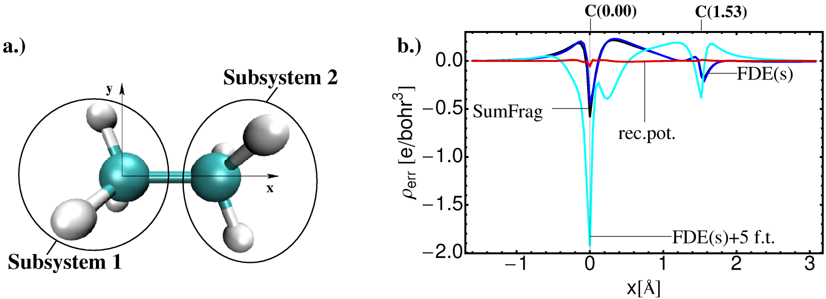
# Subsystem DFT for Donor–Acceptor Bonds



- example: ammonia borane, $BH_3$—$NH_3$, $\rho_{\mathrm{tot}}(\mathbf{r}) \approx \rho_{\mathrm{tot}}^{\mathrm{BP86/QZ4P}}(\mathbf{r})$

S. Fux, C.R. Jacob, J. Neugebauer, L. Visscher, M. Reiher, *J. Chem. Phys.* **132** (2010), 164101.

# Subsystem DFT for Covalent Bonds

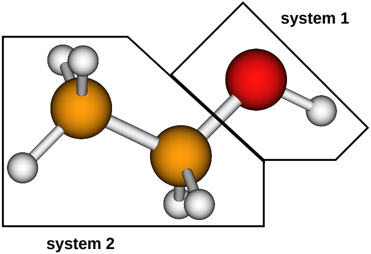


- example: ethane as “CH$_3^+$—CH$_3^-$”, $\rho_{\text{tot}}(\mathbf{r}) \approx \rho_{\text{tot}}^{\text{BP86/QZ4P}}(\mathbf{r})$

S. Fux, C.R. Jacob, J. Neugebauer, L. Visscher, M. Reiher, *J. Chem. Phys.* **132** (2010), 164101.

# Covalent Bonds through Exact Embedding Potentials

## Approximations for $v_{\text{tsnad}}$ break down for covalent bonds



- What do we know about the exact $v_t^{\text{nad}}(\mathbf{r})$ ?
- Can we reconstruct the *exact* embedding potential for subsystems $A, B$ that reproduces $\rho_{\text{tot}}(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$?
- “exact” here excludes
  - errors introduced by finite basis sets
  - errors introduced in the calculation of $\rho_{\text{tot}}$ (usually through $E_{xc}$)
  - numerical errors in the construction of the potential, e.g., due to finite grid size

# Functional Derivative of $T_s^{\mathrm{nad}}$

- 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 $T_s^{\mathrm{nad}}$

$\Rightarrow$ we need to calculate

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

- or, in other words, we need to find

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

for two different densities ($\rho = \rho_{\mathrm{tot}}$ and $\rho = \rho_K$)

# Euler–Lagrange Equation: Kohn–Sham Formalism

- Euler–Lagrange Equation:

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

⇒ “Kinetic-energy potential:”

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

- $\mu$ is just a constant shift in the potential (will be ignored here)

⇒ If we know the potential $v^{\text{eff}}[\rho_{\text{target}}](\mathbf{r})$ 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.

# “Exact” Non-additive Kinetic Potentials

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

$$v_t^{\text{nad}}[\rho_A, \rho_{\text{tot}}](\mathbf{r}) = v^{\text{eff}}[\rho_A](\mathbf{r}) - v^{\text{eff}}[\rho_{\text{tot}}](\mathbf{r}) + \Delta\mu$$

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

Two (to three) scenarios for $v^{\text{eff}}[\rho_{\text{target}}](\mathbf{r})$:

1) $\rho_{\text{target}}(\mathbf{r})$ has been obtained from Kohn–Sham-like equations
   - 1a) just save $v^{\text{eff}}[\rho_{\text{target}}](\mathbf{r})$ on a grid at the end of the SCF
   - 1b) recalculate $v^{\text{eff}}[\rho_{\text{target}}](\mathbf{r})$ from orbitals and orbital energies

     (to be discussed)

2) $\rho_{\text{target}}(\mathbf{r})$ has been obtained in a different way
   ⇒ $v^{\text{eff}}[\rho_{\text{target}}](\mathbf{r})$ needs to be reconstructed

# “Exact” Non-additive Kinetic Potentials

In “exact” embedding, usually one effective potential for $v_t^{\mathrm{nad}}$ needs to be reconstructed

- case A:
  approximations for $\rho_A$ and $\rho_B$ are obtained from KS-like equations
  - $\Rightarrow$ we know $v^{\mathrm{eff}}[\rho_A](\mathbf{r})$ and $v^{\mathrm{eff}}[\rho_B](\mathbf{r})$
  - $\Rightarrow$ we don’t know $v^{\mathrm{eff}}[\rho_{\mathrm{tot}}](\mathbf{r})$ for $\rho_{\mathrm{tot}} := \rho_A + \rho_B$
- case B:
  a target for the embedded density $\rho_A$ is constructed from a KS density $\rho_{\mathrm{tot}}$ and a predefined $\rho_B$ (e.g., from orbital localization)
  - $\Rightarrow$ we know $v^{\mathrm{eff}}[\rho_{\mathrm{tot}}](\mathbf{r})$;
    the potential $v^{\mathrm{eff}}[\rho_B](\mathbf{r})$ is actually not needed
  - $\Rightarrow$ we don’t know $v^{\mathrm{eff}}[\rho_A^{\mathrm{target}}](\mathbf{r})$ for $\rho_A^{\mathrm{target}} := \rho_{\mathrm{tot}} - \rho_A$

# Potential Reconstruction

Densities in search of Hamiltonians:

- we need to find $v^{\text{eff}}[\rho_A](\mathbf{r})$ that yields $\rho_A$

⇒ "inverse Kohn–Sham problem"

⇒ has been solved several times in the context of $v_{\text{xc}}$ 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.

# Wang–Parr Reconstruction

- goal: reconstruct potential $v_s$ that yields a given $\rho$
- KS-equation

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

Y. Wang, R. Parr, *Phys. Rev. A* **47** (1993), R1591.

# Wang–Parr Reconstruction

- solve for $v_s$

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

In practice:

- start by guessing a $v_s^0$
- solve KS equation, get orbitals $\phi_i$ and orbital energies $\epsilon_i$
- construct new $v_s$ from resulting orbitals; iterate until convergence

Y. Wang, R. Parr, *Phys. Rev. A* **47** (1993), R1591.

# 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 $(k+1)$,

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

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

# Zhao–Morrison–Parr Reconstruction

Idea:

- define $\Delta^{(k)}$ as density difference between current (iteration $k$) and target density,

$$\Delta^{(k)}(\mathbf{r}) = \rho^{\text{target}}(\mathbf{r}) - \rho^{(k)}(\mathbf{r})$$

- construct a density-difference self-repulsion potential,

$$v_{\text{emb}}^{(k)}(\mathbf{r}) = -\int \frac{\Delta^{(k)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\mathrm{d}\mathbf{r}'$$

- add this potential to the usual effective potential in order to minimize the density difference

Zhao, Morrison, Parr, *Phys. Rev. A* **50** (1994), 2138.

# Embedding Potentials from the Wu–Yang Scheme

- background: Kohn–Sham determinant has minimum kinetic energy among all determinants integrating to $\rho^{\mathrm{target}}$

⇒ minimize

$$T_s = \sum_i^n \langle \phi_i | -\nabla^2/2 | \phi_i \rangle$$

subject to constraint

$$\rho(\mathbf{r}) := \sum_i |\phi_i(\mathbf{r})|^2 \overset{!}{=} \rho^{\mathrm{target}}(\mathbf{r})$$

- use method of Lagrange multipliers ⇒ optimize

$$W_s[v_s(\mathbf{r})] = T_s + \int v(\mathbf{r})[\rho(\mathbf{r}) - \rho^{\mathrm{target}}(\mathbf{r})]\mathrm{d}\mathbf{r}$$

Wu and Yang, *J. Chem. Phys.* **118** (2003), 2498.

# Embedding Potentials from the Wu–Yang Scheme

- practical solution: expand $v$ in initial guess and correction,

$$v(\mathbf{r}) = v_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r})$$

($g_t(\mathbf{r})$ = auxiliary functions)

- first and second derivatives of $W_s$ w.r.t. $b_t$ are known analytically, e.g.

$$\begin{aligned} \frac{\partial W_s}{\partial b_t} &= \int \frac{\delta W_s}{\delta v(\mathbf{r})} \cdot \frac{\partial v(\mathbf{r})}{\partial b_t} \mathrm{d}\mathbf{r} \\ &= \int [\rho(\mathbf{r}) - \rho^{\text{target}}(\mathbf{r})] g_t(\mathbf{r}) \mathrm{d}\mathbf{r} \end{aligned}$$

- then: Newton–Raphson optimization of expansion coefficients $b_t$

Wu and Yang, *J. Chem. Phys.* **118** (2003), 2498.

# King–Handy Approach for Kinetic-Energy Potential

- can be used if $v^{\mathrm{eff}}$ has not been stored for target density, but $\{\phi_i\}, \{\epsilon_i\}$ are available
- as shown before (LB reconstruction; real orbitals assumed):

$$v_s[\rho_{\mathrm{tot}}](\mathbf{r}) = \frac{1}{\rho_{\mathrm{tot}}(\mathbf{r})} \sum_i \left[ \phi_{i_{AB}}(\mathbf{r}) \frac{\nabla^2}{2} \phi_{i_{AB}} + \epsilon_{i_{AB}} \phi^2_{i_{AB}}(\mathbf{r}) \right]$$

- therefore, we get,

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

R.A. King and N.C. Handy, *Phys. Chem. Chem. Phys.* **2** (2000), 5049.

# Kinetic-Energy Potential from a Single KS Orbital

- note that

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

- from this it follows that

$$v_s(\mathbf{r}) = \frac{1}{2}\left(\frac{\nabla^2\phi_i(\mathbf{r})}{\phi_i(\mathbf{r})}\right) + \epsilon_i$$

except at nodes of $\phi_i(\mathbf{r})$

⇒ in principle, $v_s(\mathbf{r})$ can be reconstructed from a single KS orbital

M. Levy and P. Ayers, *Phys. Rev. A* **79** (2009), 064504.

# Two Strategies for Exact Embedding

Top-down strategy:

1. do supersystem KS calculation $\Rightarrow \rho_{\text{tot}}(\mathbf{r}),\ v_s[\rho_{\text{tot}}](\mathbf{r}) \rightarrow v_t[\rho_{\text{tot}}](\mathbf{r})$
2. define suitable environment density $\rho_B(\mathbf{r})$, e.g., through localization

$$\phi_i^{\text{super,loc}} = \sum_k^n U_{ik}\phi_k^{\text{super}}$$

   and partitioning $\{\phi_i^{\text{super,loc}}\} \rightarrow \{\phi_i^{\text{super,locA}}\} \cup \{\phi_i^{\text{super,locB}}\}$
   $\Rightarrow \rho_B(\mathbf{r}) = \sum_{i\in B} |\phi_i^{\text{super,locB}}(\mathbf{r})|^2$

3. calculate target density as $\rho_A^{\text{target}}(\mathbf{r}) = \rho_{\text{tot}}(\mathbf{r}) - \rho_B(\mathbf{r})$
4. reconstruct potential $v_s[\rho_A^{\text{target}}](\mathbf{r})$ to get $v_t[\rho_A^{\text{target}}](\mathbf{r})$
5. use this to get $v_t^{\text{nad}}(\mathbf{r}) \rightarrow v_{\text{emb}}(\mathbf{r})$
6. re-calculate $\rho_A(\mathbf{r})$ using this $v_{\text{emb}}(\mathbf{r})$; compare to $\rho_A^{\text{target}}(\mathbf{r})$

S. Fux, C.R. Jacob, JN, L. Visscher, M. Reiher, *J. Chem. Phys.* **132** (2010), 164101.

# Two Strategies for Exact Embedding

Bottom-up strategy:

1. do isolated system KS calculations $\Rightarrow \rho_A^{(k=0)}(\mathbf{r}),\ \rho_B^{(k=0)}(\mathbf{r})$
   ($k$ = iteration counter)
2. calculate $\rho_{\text{tot}}^{(k)} = \rho_A^{(k)}(\mathbf{r}) + \rho_B^{(k)}(\mathbf{r})$
3. reconstruct potential $v_s[\rho_{\text{tot}}^{(k)}](\mathbf{r}) \rightarrow v_t[\rho_{\text{tot}}^{(k)}](\mathbf{r})$
4. reconstruct (or re-use from KS-like steps) potentials $v_s[\rho_{A/B}^{(k)}](\mathbf{r}) \rightarrow v_t[\rho_{A/B}^{(k)}](\mathbf{r})$
5. use these potentials to get $v_{\text{emb}}(\mathbf{r})$ for systems $A$ and $B$
6. use embedding potentials to calculate new subsystem orbitals and densities $\rho_A^{(k+1)}(\mathbf{r}),\ \rho_B^{(k+1)}(\mathbf{r})$
7. go back to step 2 and iterate until convergence

J.D. Goodpaster, N. Ananth, F.R. Manby, T.F. Miller III, *J. Chem. Phys.* **133** (2010), 084103.

# II. Exact Embedding Through Projection

# $T_s^{\mathrm{nad}}$ for Orthogonal Subsystem Orbitals

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

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

- kinetic energy:

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

⇒ $T_s^{\mathrm{nad}} = 0$, no non-additive kinetic-energy approximation needed!

# $T_s^{\mathrm{nad}}$ for Orthogonal Subsystem Orbitals

- even in case of orthogonal $\phi_i^{\mathrm{tot}}$ and exact $\rho_A$, $\rho_B$, in general

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

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

- reason: not both subsets of $\{\phi_i^{\mathrm{tot}}\}$ are, in general, ground-state of some effective potential
- for such $v^{AB}$-representable pairs of densities (closed shell), we have

$$T_s^{\mathrm{nad}}[\rho_A, \rho_B] \geq 0.$$

T.A. Wesolowski, *J. Phys. A: Math. Gen.* **36** (2003), 10607.

- but: subsets of $\{\phi_i^{\mathrm{tot}}\}$ can be obtained from projected KS problem without $v_t^{\mathrm{nad}}$

# 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.* **8** (2012), 2564.

- external orthogonality through extra Lagrangian multipliers

  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.

- Huzinaga equation (transferred to KS-DFT)

  S. Huzinaga and A.A. Cantu, *J. Chem. Phys.* **55** (1971), 5543.

# 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 $A$,

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

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

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

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

# Exact Embedding through Projection

- effective Kohn–Sham–Fock matrix:

$$\begin{aligned} f_{\lambda\nu} &= h_{\lambda\nu} + J_{\lambda\nu} + \langle\chi_\lambda|v_{\mathrm{xc}}|\chi_\nu\rangle + \mu\cdot\langle\chi_\lambda|\sum_{i\in B}\sum_{\sigma\rho} c^*_{\sigma i}c_{\rho i}|\chi_\sigma\rangle\langle\chi_\rho|\chi_\nu\rangle \\ &= f^{\mathrm{super}}_{\lambda\nu} + \mu\sum_{\sigma\rho} S_{\lambda\sigma}D^B_{\sigma\rho}S_{\rho\nu} \end{aligned}$$

($f^{\mathrm{super}}_{\lambda\nu} = h_{\lambda\nu} + J_{\lambda\nu} + \langle\chi_\lambda|v_{\mathrm{xc}}|\chi_\nu\rangle$ = supermolecular KS-Fock-matrix element, $S_{\lambda\sigma} = \langle\chi_\lambda|\chi_\sigma\rangle$ = overlap matrix element, $D^B_{\sigma\rho} = \sum_{i\in B} c^*_{\sigma i}c_{\rho i}$ = density matrix element [system $B$ only])

- effect of $\mu\hat{P}^B$: shifts orbital energies of $\phi^B_i$ to $\epsilon^B_i + \mu$
- for $\lim_{\mu\to\infty}$: eigenfunctions of $\hat{f}^A$ are orthogonal to $\{\phi^B_i\}$

$\Rightarrow$ no $v^{\mathrm{nad}}_t(\vec{r})$ needed!

- problem: numerically instable for large $\mu$

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

# Exact Embedding through Projection

## Calculate limit $\mu \to \infty$ by perturbation theory:

- define unperturbed operator

$$\hat{f}_0 = \hat{f} + \mu \hat{P}$$

and

$$\hat{f}_1 = \lim_{\nu \to \infty} (\hat{f} + \nu \hat{P})$$

- consider perturbed operator

$$\begin{aligned} \hat{f}_\zeta &= \hat{f} + \frac{\mu}{1-\zeta}\hat{P} \qquad \Rightarrow f_1 = \lim_{\zeta \to 1} \hat{f}_\zeta \\ \hat{f}_\zeta &= \hat{f} + \mu(\hat{P} + \zeta\hat{P} + \zeta^2\hat{P} + \ldots) \\ &= \hat{f}_0 + \mu(\zeta\hat{P} + \zeta^2\hat{P} + \ldots) \end{aligned}$$

- 1st order energy correction for limit $\zeta \to 1$: $E_1 = \sum_i \langle \phi_i^A | \mu \hat{P} | \phi_i^A \rangle$

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,

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

- introduce orthonormality constraints through Lagrangian multipliers,

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

- optimization w.r.t. $\phi_i^A$ yields (for $\phi_i^B$ fixed),

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

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

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

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.

# Huzinaga Equation

- original derivation: in the context of Hartree–Fock
- similar to the one by Khait and Hoffmann
- differs only in the way the Fock operator in

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

  is made Hermitian

- under external orthogonality: $(-\hat{f}^{\mathrm{KS}}\hat{P}^{B})|\phi_i^A\rangle = |\phi_i^A\rangle$

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

S. Huzinaga and A.A. Cantu, *J. Chem. Phys.* **55** (1971), 5543.

# Non-Additive Kinetic-Energy Functionals/Potentials

Is external orthogonality required for SDFT to be exact?

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{i=1}^{n_{\text{tot}}} \left|\phi_i^{\text{KS}}(\mathbf{r})\right|^2 \overset{?}{=} \sum_{i_A=1}^{n_A} \left|\phi_{i_A}^{A}(\mathbf{r})\right|^2 + \sum_{i_B=1}^{n_B} \left|\phi_{i_B}^{B}(\mathbf{r})\right|^2 = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}).$$

J.P. Unsleber, JN, C.R. Jacob, *Phys. Chem. Chem. Phys.* **18** (2016), 21001.

# Is External Orthogonality Required for exact SDFT?

- following Khait and Hoffmann, we define

$$\{\phi_i^{AB}\}_{i=1,n_{\text{tot}}} = \{\phi_{i_A}^{A}\}_{i_A=1,n_A} \cup \{\phi_{i_B}^{B}\}_{i_B=1,n_B}$$

  and create a set of explicitly orthonormalized subsystem orbitals,

$$\tilde{\phi}_i^{\text{orth}}(\mathbf{r}) = \sum_{j=1}^{n_{\text{tot}}} \left(\tilde{\boldsymbol{S}}^{-1/2}\right)_{ij} \phi_j^{AB}(\mathbf{r}), \qquad \text{with} \quad \tilde{S}_{ij} = \langle \phi_i^{AB} | \phi_j^{AB} \rangle$$

- sum of subsystem densities:

$$\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \sum_{i=1}^{n_{\text{tot}}} \left|\phi_i^{AB}(\mathbf{r})\right|^2 = \sum_{i,j=1}^{n_{\text{tot}}} \tilde{\phi}_i^{\text{orth}}(\mathbf{r})\, \tilde{S}_{ij}\, \tilde{\phi}_j^{\text{orth}}(\mathbf{r})$$

# Is External Orthogonality Required for exact SDFT?

- expand orthonormalized subsystem orbitals in KS orbitals

$$\tilde{\phi}_i^{\text{orth}}(\mathbf{r}) = \sum_{p=1}^{\infty} U_{pi} \phi_p^{\text{KS}}(\mathbf{r})$$

- this leads to

$$\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \sum_{p,q=1}^{\infty} \phi_p^{\text{KS}}(\mathbf{r})\, S_{pq}\, \phi_q^{\text{KS}}(\mathbf{r}) \qquad \text{with} \quad S_{pq} = \sum_{i,j=1}^{n_{\text{tot}}} U_{pi} \tilde{S}_{ij} U_{qj}$$

- requirement for SDFT to be exact:

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{i,j=1}^{n_{\text{tot}}} \delta_{ij} \phi_i^{\text{KS}}(\mathbf{r}) \phi_j^{\text{KS}}(\mathbf{r}) \overset{!}{=} \sum_{p,q=1}^{\infty} S_{pq}\, \phi_p^{\text{KS}}(\mathbf{r}) \phi_q^{\text{KS}}(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$$

# Is External Orthogonality Required for exact SDFT?

$$\sum_{i,j=1}^{n_{\mathrm{tot}}} \delta_{ij}\phi_i^{\mathrm{KS}}(\mathbf{r})\phi_j^{\mathrm{KS}}(\mathbf{r}) \overset{!}{=} \sum_{p,q=1}^{\infty} S_{pq}\,\phi_p^{\mathrm{KS}}(\mathbf{r})\phi_q^{\mathrm{KS}}(\mathbf{r})$$

- one might think that this requires

$$S_{ij} = \delta_{ij} \qquad \text{for} \quad i,j = 1,\ldots,n_{\mathrm{tot}}$$

(and zero otherwise)

. . . and, as a consequence, externally orthogonal subsystem orbitals

# Is External Orthogonality Required for exact SDFT?

$$\sum_{i,j=1}^{n_{\mathrm{tot}}} \delta_{ij}\phi_i^{\mathrm{KS}}(\mathbf{r})\phi_j^{\mathrm{KS}}(\mathbf{r}) \overset{!}{=} \sum_{p,q=1}^{\infty} S_{pq}\,\phi_p^{\mathrm{KS}}(\mathbf{r})\phi_q^{\mathrm{KS}}(\mathbf{r})$$

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- this implies linearly independent orbital products $\{\phi_p^{\mathrm{KS}}\phi_q^{\mathrm{KS}}\}_{p,q=1,\infty}$

# Is External Orthogonality Required for exact SDFT?

$$\sum_{i,j=1}^{n_{\text{tot}}} \delta_{ij}\phi_i^{\text{KS}}(\mathbf{r})\phi_j^{\text{KS}}(\mathbf{r}) \overset{!}{=} \sum_{p,q=1}^{\infty} S_{pq}\, \phi_p^{\text{KS}}(\mathbf{r})\phi_q^{\text{KS}}(\mathbf{r})$$

- one might think that this requires

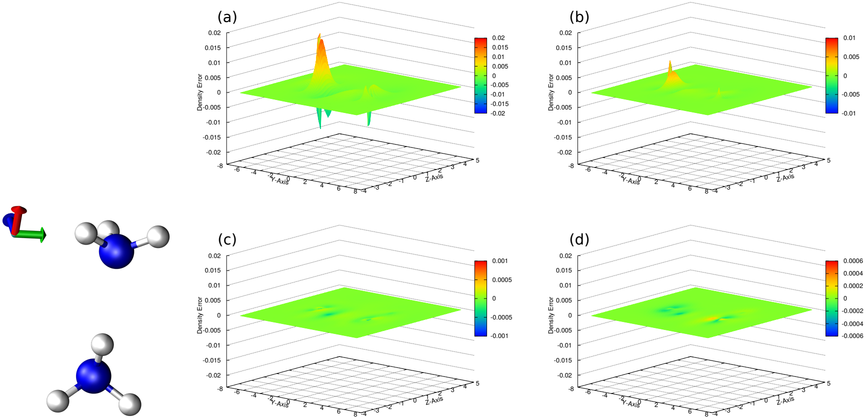
  $$S_{ij} = \delta_{ij} \qquad \text{for} \quad i,j = 1,\ldots,n_{\text{tot}}$$

  (and zero otherwise)

  . . . and, as a consequence, externally orthogonal subsystem orbitals
- this implies linearly independent orbital products $\{\phi_p^{\text{KS}}\phi_q^{\text{KS}}\}_{p,q=1,\infty}$
- but: orbital products for complete basis in one-electron Hilbert space are linearly dependent

  A. Görling, A. Heßelmann, M. Jones, M. Levy, *J. Chem. Phys.* **128** (2008), 104104.
- even for incomplete basis sets, (near-)linear dependencies may occur

# No Need for External Orthogonality in SDFT



Cut plane through N—H· · · N; (a) SumFrag/ATZP, (b) SDFT/PW91k/ATZP, (c) SDFT/RecPot/ATZP, (d) SDFT/RecPot/ET-pVQZ

J.P. Unsleber, JN, C.R. Jacob, *Phys. Chem. Chem. Phys.* **18** (2016), 21001.

# No Need for External Orthogonality in SDFT

## Overlap matrix $\tilde{S}$ of SDFT/RecPot/ET-pVQZ subsystem orbitals

| | | **A** | | | | | **B** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\phi_1^A$ | $\phi_2^A$ | $\phi_3^A$ | $\phi_4^A$ | $\phi_5^A$ | $\phi_1^B$ | $\phi_2^B$ | $\phi_3^B$ | $\phi_4^B$ | $\phi_5^B$ |
| | $\phi_1^A$ | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0003 | 0.0000 | −0.0021 | −0.0005 |
| | $\phi_2^A$ | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0002 | 0.0083 | 0.0000 | −0.0291 | −0.0030 |
| **A** | $\phi_3^A$ | 0.0000 | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0048 | 0.0001 | −0.0001 |
| | $\phi_4^A$ | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 | −0.0009 | −0.0120 | 0.0000 | 0.0226 | −0.0128 |
| | $\phi_5^A$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | −0.0075 | −0.0712 | 0.0000 | 0.0795 | 0.0147 |
| | $\phi_1^B$ | 0.0000 | 0.0002 | 0.0000 | −0.0009 | −0.0075 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | $\phi_2^B$ | 0.0003 | 0.0083 | 0.0000 | −0.0120 | −0.0712 | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 |
| **B** | $\phi_3^B$ | 0.0000 | 0.0000 | 0.0048 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 | 0.0000 |
| | $\phi_4^B$ | −0.0021 | −0.0291 | 0.0001 | 0.0226 | 0.0795 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 |
| | $\phi_5^B$ | −0.0005 | −0.0030 | −0.0001 | −0.0128 | 0.0147 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 |

J.P. Unsleber, JN, C.R. Jacob, *Phys. Chem. Chem. Phys.* **18** (2016), 21001.