Quantum Chemical Embedding Methods
— Lecture 1 —

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Workshop on Theoretical Chemistry, Mariapfarr, 20–23.02.2018

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. Introduction

Setting the Stage

General problem: Solving the Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

. . . for a really big system

Necessary steps:

(1) construct the Hamiltonian

(for this specific system)

(2) find the wavefunction that solves the SE

(or at least the best possible approximation to it)

The Molecular Hamiltonian

Total Hamiltonian:

$$\hat{H}_{\text{tot}} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{el}} + \hat{V}_{\text{nuc,nuc}} + \hat{V}_{\text{el,el}} + \hat{V}_{\text{nuc,el}}$$

Kinetic-energy operators:

$$\hat{T}_{\text{nuc}} = -\sum_{I}^{N} \frac{\nabla_I^2}{2m_I}, \qquad \hat{T}_{\text{el}} = -\sum_{i}^{n} \frac{\nabla_i^2}{2}$$

Potential-energy operators

$$\hat{V}_{\text{el,el}} = \sum_{i<j}^{n} \frac{1}{r_{ij}}, \qquad \hat{V}_{\text{nuc,nuc}} = \sum_{I<J}^{N} \frac{Z_I Z_J}{R_{IJ}}, \qquad \hat{V}_{\text{nuc,el}} = \sum_{i}^{n} \sum_{I}^{N} \frac{-Z_I}{R_{Ii}}$$

note: $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = |\vec{r}_i - \vec{r}_j|$, and $R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J| = |\vec{R}_I - \vec{R}_J|$, and $R_{Ii} = |\mathbf{R}_I - \mathbf{r}_i| = |\vec{R}_I - \vec{R}_i|$

$\mathbf{r}$ = electronic coordinates, $\mathbf{R}$ = nuclear coordinates, Z = nuclear charges

Units and Notation

Atomic units:

$$\begin{aligned} e &\equiv 1 \text{ a.u. of charge} \\ m_{\text{el}} &\equiv 1 \text{ a.u. of mass} \\ \hbar &\equiv 1 \text{ a.u. of action} \\ 4\pi\varepsilon_0 &\equiv 1 \text{ a.u. of permittivity} \end{aligned}$$

Bra-Ket Notation:

$$\begin{aligned} |\Psi_i\rangle &\equiv |i\rangle \equiv \Psi_i \\ \langle\Psi_i| &\equiv \langle i| \equiv \Psi_i^* \\ \langle i|j\rangle = \langle\Psi_i|\Psi_j\rangle &\equiv \int \Psi_i^* \Psi_j \mathrm{d}\mathbf{r} \\ \langle i|\hat{H}|j\rangle = \langle\Psi_i|\hat{H}|\Psi_j\rangle &\equiv \int \Psi_i^* \hat{H} \Psi_j \mathrm{d}\mathbf{r}. \end{aligned}$$

Electronic Hamiltonians

- assume “clamped nuclei” (nuclei fixed at $\mathbf{R}$; $T_{\text{nuc}} = 0$)

$$\hat{H}_{\text{tot}} \longrightarrow \hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{nuc,el}} + \hat{V}_{\text{el,el}} + \underbrace{\hat{V}_{\text{nuc,nuc}}}_{\text{constant}}$$

- solve electronic SE

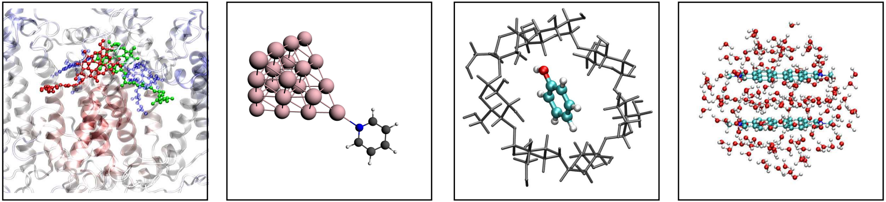
$$\hat{H}_{\text{el}} \Psi_{\text{el},i}(\mathbf{r};\mathbf{R}) = E_{\text{el},i}(\mathbf{R}) \Psi_{\text{el},i}(\mathbf{r};\mathbf{R})$$

(Nuclear coordinates do not appear as an actual argument in $\Psi_{\text{el},i}$, but the solution of the electronic SE depends on the choice of $\mathbf{R}$)

- from now on, we will only consider

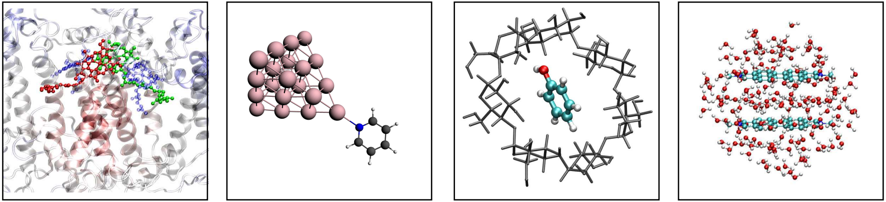
$$\hat{H} := \hat{T}_{\text{el}} + \hat{V}_{\text{nuc,el}} + \hat{V}_{\text{el,el}}$$

Why Embedding?



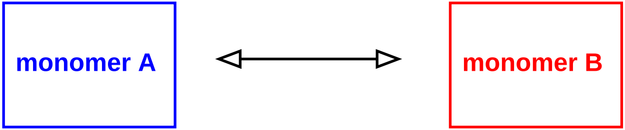
- many interesting (physico-)chemical processes take place in complex environments
- environments modulate active-system properties
- but: main characteristics are similar to isolated active systems
- brute-force approach: calculate the entire system!

Why Embedding?



- standard QC methods feature unfavorable scaling behavior
- e.g.: N^3 (DFT), N^5 (MP2), N^7 (CCSD(T))
- huge amount of CPU time would be spent on the small (but maybe important!) “modulating effect” of the environment
- sometimes the environment does not change anything . . .

Interacting Subsystems: Some initial thoughts



- isolated monomers can be described by individual Hamiltonians:

$$\begin{aligned} \hat{H}_A \Psi_A &= E_A \Psi_A \\ \hat{H}_B \Psi_B &= E_B \Psi_B \end{aligned}$$

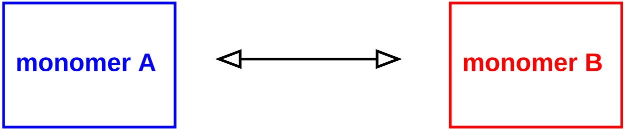
- assuming zero interaction, the total wavefunction can be factorized,

$$(\hat{H}_A + \hat{H}_B)\Psi_A \cdot \Psi_B = (E_A + E_B)\Psi_A \cdot \Psi_B$$

- true dimer Hamiltonian including interaction:

$$\hat{H}_{(A+B)} = \hat{H}_A + \hat{H}_B + \hat{H}_{A \leftrightarrow B}$$

Interacting Subsystems: Some initial thoughts



monomer A

monomer B

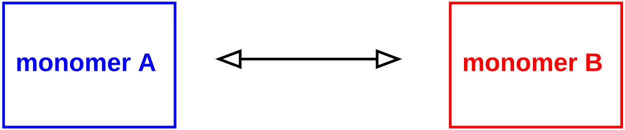
- if interaction is weak: use perturbation theory

$$E^{(1)} = \langle \Psi_A \Psi_B | \hat{H}_{A\leftrightarrow B} | \Psi_A \Psi_B \rangle$$

- form of the interaction Hamiltonian:

$$\hat{H}_{A\leftrightarrow B} = -\sum_{I\in A}^{N_A} \sum_{i\in B}^{n_B} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} - \sum_{I\in B}^{N_B} \sum_{i\in A}^{n_A} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{i\in A}^{n_A} \sum_{j\in B}^{n_B} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Interacting Subsystems: Some initial thoughts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- conceptual problem: electrons are indistinguishable particles!

Interacting Subsystems: Some initial thoughts

- wave function for N independent subsystems:

$$\Psi^{\text{tot}}(\mathbf{r}_{1_1}, \mathbf{r}_{2_1}, \ldots, \mathbf{r}_{n_N}) = \Psi_1(\mathbf{r}_{1_1} \ldots) \cdot \Psi_2(\mathbf{r}_{1_2} \ldots) \ldots \cdot \Psi_N(\mathbf{r}_{1_N} \ldots \mathbf{r}_{n_N})$$

- non-interacting subsystems: product ansatz

Interacting Subsystems: Some initial thoughts

- wave function for N independent subsystems:

$$\Psi^{\text{tot}}(\mathbf{r}_{1_1}, \mathbf{r}_{2_1}, \ldots, \mathbf{r}_{n_N}) = \Psi_1(\mathbf{r}_{1_1} \ldots) \cdot \Psi_2(\mathbf{r}_{1_2} \ldots) \ldots \cdot \Psi_N(\mathbf{r}_{1_N} \ldots \mathbf{r}_{n_N})$$

- non-interacting subsystems: product ansatz
- weak interaction: perturbation theory

Interacting Subsystems: Some initial thoughts

- wave function for N independent subsystems:

$$\Psi^{\mathrm{tot}}(\mathbf{r}_{1_1}, \mathbf{r}_{2_1}, \ldots, \mathbf{r}_{n_N}) = \hat{A}\Psi_1(\mathbf{r}_{1_1} \ldots) \cdot \Psi_2(\mathbf{r}_{1_2} \ldots) \ldots \cdot \Psi_N(\mathbf{r}_{1_N} \ldots \mathbf{r}_{n_N})$$

- non-interacting subsystems: product ansatz
- weak interaction: perturbation theory
- antisymmetrisation necessary

Interacting Subsystems: Some initial thoughts

- wave function for N independent subsystems:

$$\Psi^{\text{tot}}(\mathbf{r}_{1_1}, \mathbf{r}_{2_1}, \ldots, \mathbf{r}_{n_N}) = \sum_{\{K_I\}} c_{\{K_I\}} \hat{A} \Psi_{K_1}(\mathbf{r}_{1_1} \ldots) \cdot \Psi_{K_2}(\mathbf{r}_{1_2} \ldots) \ldots \cdot \Psi_{K_N}(\mathbf{r}_{1_N} \ldots \mathbf{r}_{n_N})$$

- non-interacting subsystems: product ansatz
- weak interaction: perturbation theory
- antisymmetrisation necessary
- maybe: configuration interaction

Interacting Subsystems: Some initial thoughts

- wave function for N independent subsystems:

$$\Psi^{\text{tot}}(\mathbf{r}_{1_1}, \mathbf{r}_{2_1}, \ldots, \mathbf{r}_{n_N}) = \sum_{\{K_I\}} c_{\{K_I\}} \hat{A} \Psi_{K_1}(\mathbf{r}_{1_1} \ldots) \cdot \Psi_{K_2}(\mathbf{r}_{1_2} \ldots) \ldots \cdot \Psi_{K_N}(\mathbf{r}_{1_N} \ldots \mathbf{r}_{n_N})$$

- non-interacting subsystems: product ansatz
- weak interaction: perturbation theory
- antisymmetrisation necessary
- maybe: configuration interaction
- conceptually simpler: subsystem density-functional theory

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{I=1}^{N} \rho_I(\mathbf{r})$$

II. Subsystem DFT and Frozen-Density Embedding

Subsystem DFT

- total density:

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

- partition into subsystem contributions:

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

- write each ρ_I in terms of subsystem orbitals

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

- assume all ϕ_{i_I} are known (but not ϕ_i^{super})

Subsystem DFT

- reminder: KS energy expression

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

- if ρ is given as sum of subsystem densities:

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

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

G. Senatore, K. R. Subbaswamy, *Phys. Rev. B* **34** (1986), 5754; P. Cortona, *Phys. Rev. B* **44** (1991), 8454.

Subsystem DFT

- write T_s formally exactly as

$$T_s[\{\phi_i^{\text{super}}\}] = \sum_I T_s[\{\phi_{i_I}\}] + \left[T_s[\{\phi_i^{\text{super}}\}] - \sum_I T_s[\{\phi_{i_I}\}] \right]$$

or

$$T_s[\{\phi_i^{\text{super}}\},\{\{\phi_{i_J}\}\}] = \sum_I T_s[\{\phi_{i_I}\}] + T_s^{\text{nad}}[\{\phi_i^{\text{super}}\},\{\{\phi_{i_J}\}\}]$$

- introduce density-dependent approximation,

$$T_s^{\text{nad}}[\{\phi_i^{\text{super}}\},\{\{\phi_{i_J}\}\}] \approx T_s^{\text{nad}}[\{\rho_J\}] = T_s[\rho] - \sum_I T_s[\rho_I]$$

G. Senatore, K. R. Subbaswamy, *Phys. Rev. B* **34** (1986), 5754; P. Cortona, *Phys. Rev. B* **44** (1991), 8454.

One-Particle Equations in Subsystem DFT

- energy functional:

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

- 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. all ρ_K

$\Rightarrow$ Euler–Lagrange equations:

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

Frozen-Density Embedding

- assume all subsystem densities are v_s-representable

⇒ subsystem orbitals can be obtained from

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

⇒ if we choose

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

the systems of non-interacting particles fulfill

$$v_{\text{eff}}^{\text{sub}}[\rho, \rho_I](\mathbf{r}) + \frac{\delta T_s[\{\phi_{i_I}\}]}{\delta\rho_I(\mathbf{r})} + \mu_I = 0$$

⇒ these are the sought-for densities

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

Embedding Potential

- define complementary density to $\rho_I(\mathbf{r})$

$$\rho_I^{\text{compl.}}(\mathbf{r}) = \sum_{J,J\neq I} \rho_J(\mathbf{r}) = \rho(\mathbf{r}) - \rho_I(\mathbf{r})$$

- one-particle equations become

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

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

- embedding potential

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

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

Solution of the KSCED equations

1. define subsystems ($\mathbf{R}_A$, Z_A, $A \in I$, and N_I)
2. provide density guess for each subsystem; most common: solve KS equations for all isolated subsystems
3. loop over all subsystems:
    - calculate embedding potential due to all other subsystems
    - solve KSCED equations for currently active subsystem I
    - update density ρ_I
    - if density change in system I is negligible: stop
    - otherwise: next cycle in loop

Note: step 2 is crucial for the definition of the subsystems

III. Kinetic Energy in different DFT variants

Kinetic Energy in DFT

Kohn–Sham DFT:

$$T \rightarrow T_s[\{\psi_i\}] \qquad \text{; actually:} \quad \min_{\{\psi_i\}\rightarrow\rho} \left(\sum_i \langle \phi_i | -\nabla^2/2 | \phi_i \rangle \right)$$

Orbital-free DFT:

$$T \rightarrow T[\rho] \qquad \text{(density-dependent approximation)}$$

Subsystem DFT:

$$T \rightarrow \sum_I T_s[\{\phi_i\}] + T_s^{\text{nad}}[\{\rho_J\}] \qquad \text{(density-dependent approx. for } T_s^{\text{nad}} \text{ only)}$$

Cluster expansion:

$$T \rightarrow \sum_I T_s[\{\phi_i\}] + \sum_{I<J} \Delta T_s^{IJ} + \sum_{I<J<K} \Delta T_s^{IJK} + \dots$$

$$\text{with} \quad \Delta T_s^{IJ} = T_s[\{\phi_i^{I+J}\}] - T_s[\{\phi_{i_I}\}] - T_s[\{\phi_{j_I}\}] \quad \text{etc.}$$

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

Kinetic-Energy Functionals: An Example

- assume one-orbital system, $\rho(\mathbf{r}) = n \cdot |\phi(\mathbf{r})|^2$

$$\begin{aligned}
T = T[\phi] &= -n \cdot \frac{1}{2} \int \phi(\mathbf{r}) \nabla^2 \phi(\mathbf{r}) \mathrm{d}\mathbf{r} \\
&= \frac{n}{2} \int (\nabla \phi(\mathbf{r}))(\nabla \phi(\mathbf{r})) \mathrm{d}\mathbf{r} \\
&= \frac{1}{2} \int \left(\nabla \sqrt{\rho(\mathbf{r})}\right) \left(\nabla \sqrt{\rho(\mathbf{r})}\right) \mathrm{d}\mathbf{r} \\
&= \frac{1}{2} \int \left(\frac{1}{2\sqrt{\rho(\mathbf{r})}} \nabla \rho(\mathbf{r})\right) \left(\frac{1}{2\sqrt{\rho(\mathbf{r})}} \nabla \rho(\mathbf{r})\right) \mathrm{d}\mathbf{r} \\
&= \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \mathrm{d}\mathbf{r}
\end{aligned}$$

$\Rightarrow$ von Weizsäcker functional $T_{\mathrm{vW}}[\rho]$, exact for one-orbital systems

Non-additive kinetic-energy functionals

- systematic gradient expansion of kinetic energy:

  $$T_s[\rho] \approx T_{\mathrm{TF}}[\rho] + \lambda T_{\mathrm{vW}}[\rho]$$

  with $\lambda = 1/9$
- empirically: $\lambda = 1/5$ gives better results
- GGA-type kinetic-energy functionals:

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

with $s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2\rho(\mathbf{r})k_F}$ (reduced density gradient) and $k_F = [3\pi^2\rho(\mathbf{r})]^{1/3}$

Non-additive kinetic-energy functionals

- conjointness hypothesis: choose $F(s)$ as in GGA-X functionals

  H. Lee, C. Lee, R.G. Parr, *Phys. Rev. A* **44** (1991), 768.

- original LLP functional: conjoint to B88 exchange
- popular example: “PW91k” with $F(s)$ conjoint to PW91-X

  (reparametrized by Lembarki and Chermette)

$$F_{\mathrm{PW91k}} = \frac{1 + 0.093907 s \operatorname{arcsinh}(76.32 s) + \left(0.26608 - 0.0809615 e^{-100 s^2}\right) s^2}{1 + 0.093907 s \operatorname{arcsinh}(76.32 s) + 0.57767 \cdot 10^{-4} s^4}$$

  A. Lembarki, H. Chermette, *Phys. Rev. A* **50** (1994), 5328.

- Huang–Carter functionals contain non-local contributions

  J. Xia, C. Huang, I. Shin, E.A. Carter, *J. Chem. Phys.* **136** (2012), 084102.

IV. Technical Aspects

Technical Aspects

Additional matrix elements needed:

$$\langle \chi_i \left| v_{\text{emb}} \right| \chi_j \rangle = \int \chi_i^*(\mathbf{r}) v_{\text{emb}}(\mathbf{r}) \chi_j(\mathbf{r}) \, d\mathbf{r}$$

- Coulomb part of $v_{\text{emb}}(\mathbf{r})$ is linear in the density:

$$v_{\text{emb}}^{\text{Coul}}(\mathbf{r}) = \int \frac{\rho_I^{\text{compl.}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}'$$

⇒ is calculated only once in every subsystem calculation

- XC and non-add. kinetic energy contributions are non-linear in ρ
- example: Thomas–Fermi non-add. kinetic-energy potential:

$$v_{\text{tsnad}}^{\text{TF}}(\mathbf{r}) = \frac{5}{3} C_F \left\{ \left[\rho_I(\mathbf{r}) + \rho_I^{\text{compl.}}(\mathbf{r}) \right]^{2/3} - \left[\rho_I(\mathbf{r}) \right]^{2/3} \right\}$$

⇒ re-calculated in every SCF cycle

Monomer vs. Supermolecular Expansion

of subsystem densities

- main computational advantage with monomer basis sets:

$$\phi_{i_1} = \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1}, \qquad \phi_{i_2} = \sum_{\nu_2} c_{i_1\nu_2}\chi_{\nu_2}$$

$$\rho = \sum_{i_1}^{\mathrm{occ}_1} \left| \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1} \right|^2 + \sum_{i_2}^{\mathrm{occ}_2} \left| \sum_{\nu_2} c_{i_2\nu_2}\chi_{\nu_2} \right|^2$$

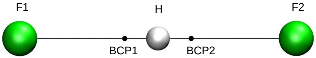
- properties may converge faster with supermolecular basis:

$$\phi_{i_{1/2}} = \sum_{\nu_1} c_{i_{1/2}\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_{1/2}\nu_2}\chi_{\nu_2}$$

$$\rho = \sum_{i_1}^{\mathrm{occ}_1} \left| \sum_{\nu_1} c_{i_1\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_1\nu_2}\chi_{\nu_2} \right|^2 + \sum_{i_2}^{\mathrm{occ}_2} \left| \sum_{\nu_1} c_{i_2\nu_1}\chi_{\nu_1} + \sum_{\nu_2} c_{i_2\nu_2}\chi_{\nu_2} \right|^2$$

- sometimes helpful: monomer + buffer region basis

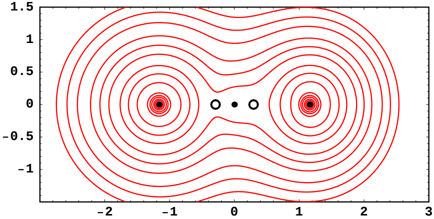
Electron Densities from FDE: F$-$H$-$F$^-$



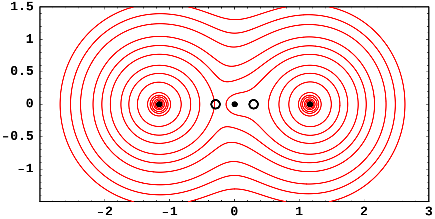
- strong, symmetric hydrogen bonds
- ρ_1: H$-$F2, ρ_2: F1$^-$ $\Rightarrow$ asymmetric fragments, strong polarization

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

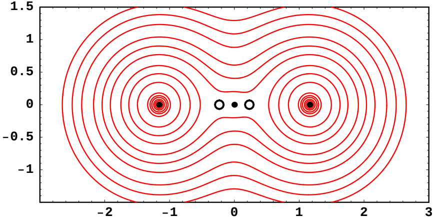
Electron Densities from FDE: F$-$H$-$F$^-$



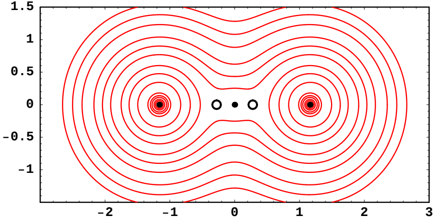
sum−of−fragments



FDE, monomer basis



FDE, supermolecular basis

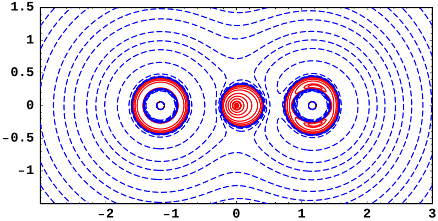


supermolecular calculation

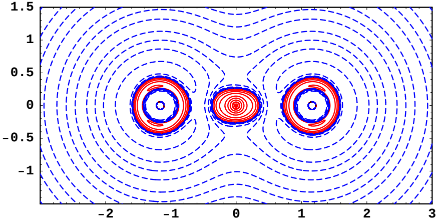
K. Kiewisch, G. Eickerling, M. Reiher, J. Neugebauer, *J. Chem. Phys.* **128** (2008), 044114.

F−H−F⁻: negative Laplacian L

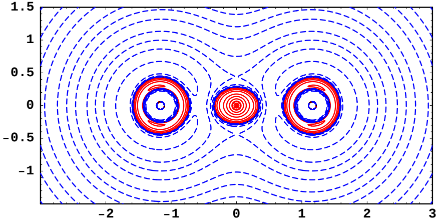
L_{frag}



L_{emb}



L_{super}



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

Linearizing the Non-Additive Parts

Non-additive kinetic energy:

- example: 2 subsystems, Thomas–Fermi (LDA)

$$T_s^{\mathrm{nad,TF}}[\rho_A,\rho_B] = C_F \int \Big[(\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}))^{5/3} - \rho_A^{5/3}(\mathbf{r}) - \rho_B^{5/3}(\mathbf{r}) \Big] \, \mathrm{d}\mathbf{r}$$

- linear approximation for T_s^{nad} based on reference density $\rho_{A,0}$
  (e.g., from isolated system A)

$$T_s^{\mathrm{nad}}[\rho_A,\rho_B] \quad \approx \quad T_s^{\mathrm{nad}}[\rho_{A,0},\rho_B] + \int \left.\frac{\delta T_s^{\mathrm{nad}}[\rho,\rho_B]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{A,0}} (\rho_A(\mathbf{r}) - \rho_{A,0}(\mathbf{r})) \, \mathrm{d}\mathbf{r}$$

$\Rightarrow$ functional derivative of $T_s^{\mathrm{nad}}[\rho_A,\rho_B]$ in linearization approximation:

$$\left.\frac{\delta T_s^{\mathrm{nad}}[\rho,\rho_B]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_A} \approx \left.\frac{\delta T_s^{\mathrm{nad}}[\rho,\rho_B]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{A,0}}$$

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

Linearizing the Non-Additive Parts

kinetic-energy potential:

- TF case:

$$v_{\text{tsnad}}^{\text{TF}}[\rho_A, \rho_B](\mathbf{r}) = \left.\frac{\delta T_s^{\text{nad}}[\rho, \rho_B]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_A} = \frac{5}{3} C_F \int \left[(\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}))^{2/3} - \rho_A^{2/3}(\mathbf{r}) \right] \mathbf{dr}$$

⇒ needs to be updated whenever ρ_A changes (every SCF cycle)

- with linearization approximation for T_s^{nad}

$$v_{\text{tsnad}}^{\text{TF}}[\rho_A, \rho_B](\mathbf{r}) \approx \left.\frac{\delta T_s^{\text{nad}}[\rho, \rho_B]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_{A,0}} = v_{\text{tsnad}}^{\text{TF}}[\rho_{A,0}, \rho_B](\mathbf{r}) = \frac{5}{3} C_F \int \left[(\rho_{A,0}(\mathbf{r}) + \rho_B(\mathbf{r}))^{2/3} - \rho_{A,0}(\mathbf{r})^{2/3} \right] \mathbf{dr}$$

⇒ independent of ρ_A, can be pre-calculated before SCF

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Effects of the Linearization Approximation for T_s^{nad}

Relative Errors:

- shifts in orbital energies: typically $\mathcal{O}(10^{-2})$
- shifts in dipole moments: typically < 0.06
- non-additive kinetic energies: typically < 0.001
- exception:
  Charge-transfer complexes with large density rearrangement,
  e.g., for $\mathrm{NH_3 \cdots ClF}$:

$$|\delta\Delta\mu/\Delta\mu| = 287.6/983.1 = 29.3\%$$

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