Density division + Embedding Potential Inversion method for spectroscopy in clathrates

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Outline:

1. Introduction
2. Localization vs. Embedding potential
3. Inversion of embedding potentials
4. Density division and embedding potential inversion
5. Conclusions
**Partition techniques**

- A : primary region $\rightarrow$ high accuracy
- B : Substrate $\rightarrow$ low accuracy
- $V_{emb}$ : Embedding potential

**Covalent**
- “cluster” method
- saturation of bonds

**Ionic**
- cations by core pseudopotential
- anions by point charges
- polarization of the substrate

**Metallic**
- Wave function partition
- electronic density partition
Frozen Density Method  (Wesolowski & Warshel, 1993)

Total density factorizes as \( \rho = \rho_A + \rho_B \)

and energy as \( E[\rho] = E_A[\rho_A] + E_B[\rho_B] + E_{int} \)

The embedding potential is obtained by minimizing \( E_{int} \)

\[ v_{emb} = \frac{\delta E_{int}}{\delta \rho_A} \]

\[ E_{int} = E[\rho] - E_A[\rho_A] - E_B[\rho_B] \]

\( \rho_A \approx 0 \) in \( B \) \( \rightarrow \frac{\delta E_B}{\delta \rho_A} \approx 0 \)

\[ v_{emb} = v_T + v_J + v_{xc} + v_{ion} \]

Exchange Correlation

Coulomb

Nuclear
Frozen Density Method  
(Wesolowski & Warshel, 1993)

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Kinetic = $\frac{\delta T_s[\rho]}{\delta \rho} - \frac{\delta T_s[\rho_A]}{\delta \rho_A}$
Beyond DFT in A (Govind, Wang & Carter, 1999)

1. FDE used to obtain $v_{emb}$ and $\rho_A$ iteratively by setting $\rho_B = \rho - \rho_A$

Kondo state in Co/Cu(111)

A: cluster of CoCu$_7$

Huang & Carter (’06)

2. In subsystem A, with a modified Fock operator ($\mathcal{F} = \hat{F} + v_{emb}$)

   - to include dynamical correlation in A (CoCu$_7$)
   - calculate excited electronic states localized in A
   - etc
Kinetic energy functional

Approximate character of the kinetic energy functional

\[ v_T = \frac{\delta T_s[\rho]}{\delta \rho} - \frac{\delta T_s[\rho_A]}{\delta \rho_A} \]

Break down of the FDE procedure for covalent bonds (Fux, et al. 2010)
Kinetic energy functional

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Intense work

1. Developing new functionals (Wesolowski, since ’97)
2. :
3. Exact no additive kinetic potentials (Goodpaster, et al.’10)
4. Numerical calculations of accurate \( v_T \) (Jacob and co-workers, ’10)
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Density partition and localization

\( \rho_A \) related to local orbitals, obtained by an unitary transformation

\[
| \Lambda_l \rangle = \sum_k | \phi_k \rangle U_{kl}
\]

1. Boys: minimization of spacial extension
   \[
   \sum_l \langle \Lambda_l \Lambda_l | (r_1 - r_2)^2 | \Lambda_l \Lambda_l \rangle
   \]

2. Pipek and Mezey: projection maximization
   \( \hat{P}_A \)

3. Edmiston and Ruedenberg: maximization of self-repulsion
   \[
   \frac{1}{r_1 - r_2}
   \]
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Localized orbitals satisfy

(Edmiston & Ruedenberg, ’63)

\[
\left[ \hat{F} + \mathcal{V} \right] \Lambda_l = \lambda_l \Lambda \rightarrow \text{Modified Fock equation}
\]

where \( \mathcal{V} \) includes terms analogue to the embedding potential
Kinetic energy term

Let’s partition the molecular orbitals as

$$\Phi_k = \alpha \Phi_k + (1 - \alpha) \Phi_k \equiv \Phi_k^A + \Phi_k^B$$

Two coupled Fock equations, for $\Phi_k^A$ and $\Phi_k^B$

- local terms: $V \alpha(r) \Phi_k = \alpha(r) V \Phi_k$
- non local terms: $-\frac{1}{2} \nabla^2 \alpha(r) \Phi_k = \alpha(r) \left[ -\frac{1}{2} \nabla^2 \right] \Phi_k + \mathcal{V}_T \Phi_k$
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![Graph for $V_T$ in FDE: $f_A = f_B = \exp(-r^2)$](image1.png)

![Graph for $\alpha(z)$, $\alpha''(z)$](image2.png)
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Inversion of embedding potential method (Roncero et al.’08)

- **Density partition**
  \[ \rho = \rho_A + \rho_B \]
  E.g.: minimizing
  \[ \langle \rho_A | \frac{1}{r_{12}} | \rho_B \rangle \]

- **Inversion of the embedding potential**
  \[ \mathcal{F}_A = F_A + V_A \]
  whose solution is \( \rho_A \)

Functionals from reference densities in DFT
- Zhao, Morrison & Parr Phys. Rev. A (’94)
- Yang & Wu Phys. Rev. Lett. (’02)

- Use \( \mathcal{F}_A \) to calculate
  \[ E_A^{cor} = E_A^{CI} - E_A^{HF} \]

Total energy:
\[ E^{HF}[\rho_A + \rho_B] + E_A^{cor} \]

Self-repulsion and embedding potential

For a reference density $\rho_A$ we define

$$\Delta^k_A = \rho^k_A - \rho_A$$

- $\Delta^k_A > 0 \rightarrow$ repulsive potential
- $\Delta^k_A < 0 \rightarrow$ attractive potential

Defining a repulsive potential as (Zhao, Morrison & Parr ’94)

$$v^k_{rep} = \int dr \frac{\Delta^k_A}{r - r'} \equiv J[\Delta^k_A]$$

the embedding potential is obtained iteratively as

$$\mathcal{V}^{k+1}_A = \mathcal{V}^k_A + \lambda v^k_{rep}$$

where $\lambda$ minimize $\delta^{k+1} = \int dr (\Delta^{k+1})^2$
H$_{10}$ chain example: procedure

- Density partition: Mulliken’s method
- $R = r = 1.3$ a.u.
H$_{10}$ chain example: procedure

- Density partition: Mulliken’s method
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$$\Delta^k_A$$

Density difference

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Water-Ice-Clathrate, Toulouse, Nov.3-4$^{th}$
H$_{10}$ chain example: procedure

Embedding pot. $\mathcal{V}^k_A$

Density difference $\Delta^k_A$
H$_{10}$ chain example: comparison with FDE

FDE potential using $\rho$ and $\rho_A$

- $V_J \approx -V_N$
- The dominant term is $V_T$

The two $V_{emb}$ are similar
H$_{10}$ chain example: Energies

- Electronic Correlation
  - Full symbols: in whole H$_{10}$ system
  - Open symbols: in “A” embedded

$r = 1.3$ a.u.

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H$_{10}$ chain example: Energies

- Electronic Correlation
  - Full symbols: in whole H$_{10}$ system
  - Open symbols: in “A” embedded

- $r = 1.3$ a.u.

- Only with A the repulsion of enviroment is described !!

- The van der Waals well requires AB and a CI method
**H_{10} + H_2** van der Waals interactions

Comparison of CI calculations:

- **Full H_{10}+H_2 system**
- **H_2+H_2**
- **embedded H_2+H_2**

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Problems of the inversion of embedding potentials

- The reference density \( \rho_A \) may not be v-representable
  - Mulliken’s method yields fractional charges
  - Any renormalization is arbitrary

- The procedure depends on:
  - Initial guess:
  - Self-repulsion potential \( v_{rep} \)
  - Optimization procedure

- Convergence is always a problem: 3 iterative procedures
Density division + embedding potential inversion

All in one single step

(Roncero et al’09)

To obtain the density partition \( \rho = \rho_A + \rho_B \)

\[ \Delta^k = \rho - \rho_A^k + \rho_B^k \]

with \( \rho_C^k \) being obtained from a MFE

\[ [F_C + V_C^k] \phi_C^k = \epsilon_C \phi_C^k \]

\[ \nu_{rep}^k = \frac{1}{2} \sum_{m,l} \Delta^k_{m,l}(imlj) \equiv K[\Delta^k] \]

\[ V_C^{k+1} = V_C^k + \lambda \nu_{rep}^k[\Delta^k] \]

where \( \lambda \) minimizes \( \delta^{k+1} = \int dr (\Delta^k)^2 \)
The H$_{10}$ example
The $H_{10}$ example

$\rho^k_A$

Density difference $\Delta^k$

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The $H_{10}$ example

- Embedding pot. $V_A^k$
  
  \begin{align*}
  &V_A^8 \\
  &V_A^5 \\
  &V_A^4 \\
  &V_A^3 \\
  &V_A^2 \\
  &V_A^1
  \end{align*}

- Density difference $\Delta^k$
  
  \begin{align*}
  &\Delta^6 \\
  &\Delta^5 \\
  &\Delta^4 \\
  &\Delta^3 \\
  &\Delta^2 \\
  &\Delta^1 \\
  &\Delta^0
  \end{align*}
Comparing different DFT functionals for the full system

$H_{10} + H_2$ van der Waals interactions

- Comparing different DFT functionals for the full system
- The density difference $\Delta^k$ converges fast
- The convergence depends on the DFT functional used for $\rho$

$H_{10} + H_2$ van der Waals interactions

- Comparing different DFT functionals for the full system
- The density difference $\Delta^k$ converges fast
- The convergence depends on the DFT functional used for $\rho$
- This new method yields better results

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- An alternative to the FDE embedding method in which $\rho_A$ and $\rho_B$ are $v$-representable.
- It has **not** the problem of the kinetic energy functional; **but** different $v_{rep}$ should be tested for different functionals.
- Initial $\rho$ can be obtained from any method, DFT or not.
- It can be combined with the most traditional FDE method by using $\rho_A$ and $\rho_B$. 

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Conclusions

- An alternative to the FDE embedding method in which $\rho_A$ and $\rho_B$ are $v$-representable.
- It has not the problem of the kinetic energy functional but different $v_{rep}$ should be tested for different functionals.
- Initial $\rho$ can be obtained from any method, DFT or not.
- It can be combined with the most traditional FDE method by using $\rho_A$ and $\rho_B$.
- More work is needed to solve convergence problems and to design new $v_{rep}$.
What about impurities in clathrates?

First check: \( \text{Br}_2 + \text{H}_2\text{O} \)

Franklin-Mergarejo \textit{et al}
What about impurities in clathrates?

First check: Br$_2$ + H$_2$O

Franklin-Mergarejo et al

Ramón Hernández-Lamoneda

What DFT functional to use?
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