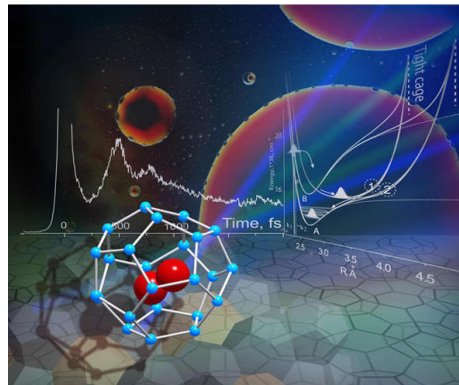


Density division + Embedding Potential Inversion method for spectroscopy in clathrates ?

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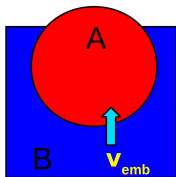


Outline:

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Partition techniques

- **A** : primary region → high accuracy
- **B** : Substrate → low accuracy
- V_{emb} : Embedding potential



Covalent

“cluster” method
saturation of bonds

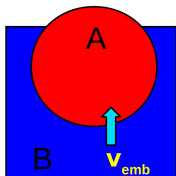
Ionic

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}

$$v_{emb} = \frac{\delta E_{int}}{\delta \rho_A}$$

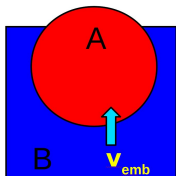
$$E_{int} = E[\rho] - E_A[\rho_A] - E_B[\rho_B]$$

$$\rho_A \approx 0 \quad \text{in } B \quad \rightarrow \quad \frac{\delta E_B}{\delta \rho_A} \approx 0$$

$$v_{emb} = v_T + v_J + v_{xc} + v_{ion}$$

Exchange Correlation
Coulomb Nuclear

Frozen Density Method (Wesolowski & Warshel, 1993)



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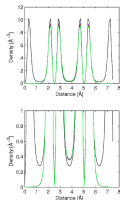
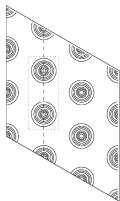
$$\rho_A \approx 0 \quad \text{in } B \quad \rightarrow \quad \frac{\delta E_B}{\delta \rho_A} \approx 0$$

$$\left. \begin{array}{l} v_{emb} = \frac{\delta E_{int}}{\delta \rho_A} \\ E_{int} = E[\rho] - E_A[\rho_A] - E_B[\rho_B] \\ \rho_A \approx 0 \quad \text{in } B \quad \rightarrow \quad \frac{\delta E_B}{\delta \rho_A} \approx 0 \end{array} \right\} v_{emb} = v_T + v_J + v_{xc} + v_{ion}$$

$$\text{Kinetic} = \frac{\delta T_s[\rho]}{\delta \rho} - \frac{\delta T_s[\rho_A]}{\delta \rho_A}$$

Beyond DFT in A (Govind, Wang & Carter, 1999)

- 1 FDE used to obtain v_{emb} and ρ_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 ($\mathcal{F} = \hat{F} + v_{emb}$) conventional *ab initio* methods are used

- 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

Approximate character of the kinetic energy functional

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

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

ρ_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 $\sum_l \langle \Lambda_l \Lambda_l | (\mathbf{r}_1 - \mathbf{r}_2)^2 | \Lambda_l \Lambda_l \rangle$
- ② Pipek and Mezey: projection maximization \hat{P}_A
- ③ Edmiston and Ruedenberg: maximization of self-repulsion $\frac{1}{\mathbf{r}_1 - \mathbf{r}_2}$

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Localized orbitals satisfy (Edmiston & Ruedenberg, '63)

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

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 Φ_k^A and Φ_k^B

- local terms: $V \alpha(\mathbf{r}) \Phi_k = \alpha(\mathbf{r}) V \Phi_k$
- non local terms: $-\frac{1}{2} \nabla^2 \alpha(\mathbf{r}) \Phi_k = \alpha(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 \right] \Phi_k + \mathcal{V}_T \Phi_k$

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$$\alpha - \frac{1}{2} (\nabla^2 \alpha) - (\nabla \alpha) \cdot \nabla$$



$$\mathcal{V}_T \Phi_k$$

Kinetic energy term

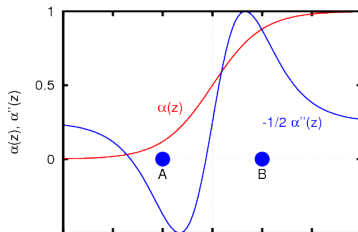
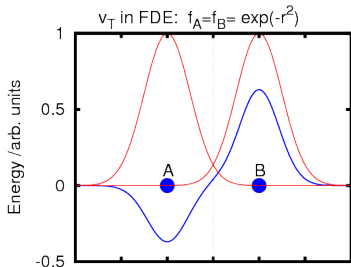
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$$\alpha - \frac{1}{2} (\nabla^2 \alpha)$$



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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

$\mathcal{F}_A = F_A + \mathcal{V}_A$ whose solution is ρ_A

Functionals from reference densities in DFT

Leeuwen & Baerends Phys. Rev. A ('94)

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

Similar to Govind, Wang & Carter, J. Chem. Phys. ('99)

Self-repulsion and embedding potential

For a reference density ρ_A we define

$$\Delta_A^k = \rho_A^k - \rho_A$$

- $\Delta_A^k > 0 \rightarrow$ repulsive potential
 - $\Delta_A^k < 0 \rightarrow$ attractive potential
- $$\left. \vphantom{\begin{matrix} \bullet \\ \bullet \end{matrix}} \right\} \mathcal{V}_A^k \propto \Delta_A^k \text{ or } \mathcal{V}_A^k \equiv \mathcal{V}_A^k[\Delta_A^k]$$

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

$$v_{rep}^k = \int d\mathbf{r} \frac{\Delta_A^k}{\mathbf{r} - \mathbf{r}'} \equiv J[\Delta_A^k]$$

the embedding potential is obtained iteratively as

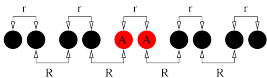
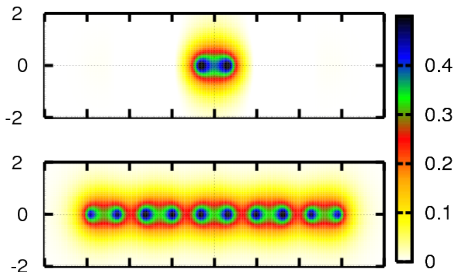
$$\mathcal{V}_A^{k+1} = \mathcal{V}_A^k + \lambda v_{rep}^k$$

where λ minimize $\delta^{k+1} = \int d\mathbf{r} (\Delta^{k+1})^2$

H₁₀ chain example: procedure

- Density partition: Mulliken's method

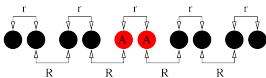
$$R = r = 1.3 \text{ a.u.}$$

 ρ_A  ρ_{AB}

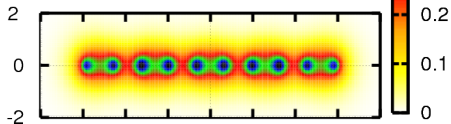
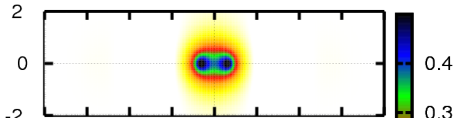
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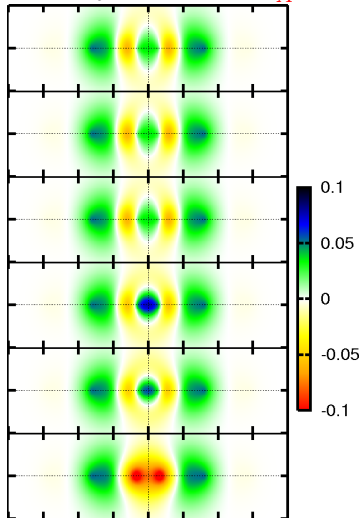
ρ_A



ρ_{AB}

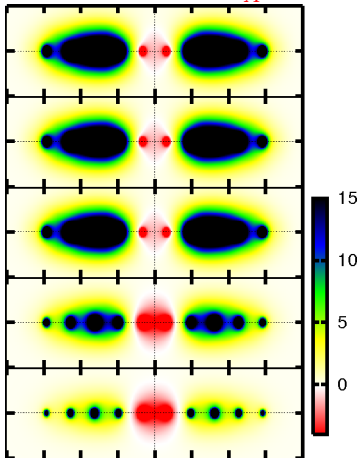


Density difference Δ^k_A

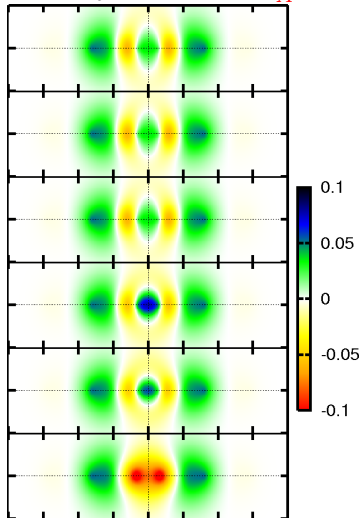


H₁₀ chain example: procedure

●

Embedding pot. \mathcal{V}_A^k 

●

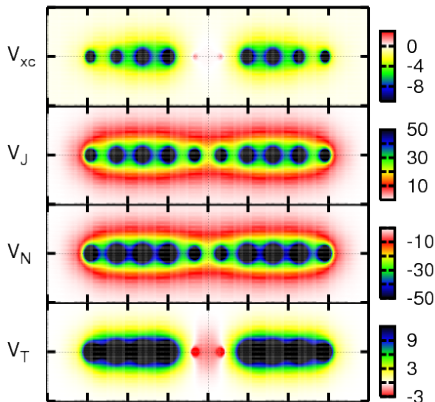
Density difference Δ_A^k 

H₁₀ chain example: comparison with FDE

FDE potential using ρ and ρ_A

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

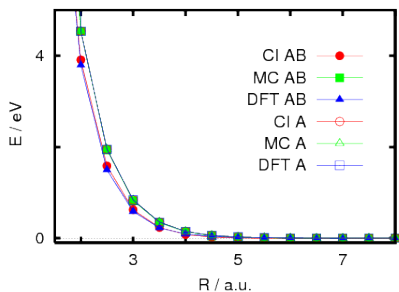
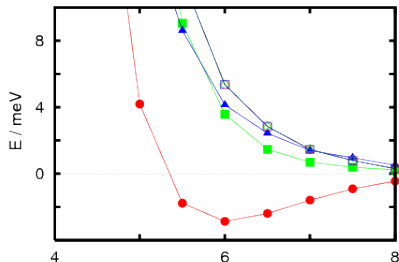
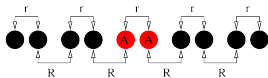
The two V_{emb} are similar



H₁₀ chain example: Energies

- Electronic Correlation
 - Full symbols:
in whole H₁₀ system
 - Open symbols:
in "A" embedded

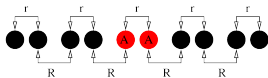
● $r = 1.3$ a.u.



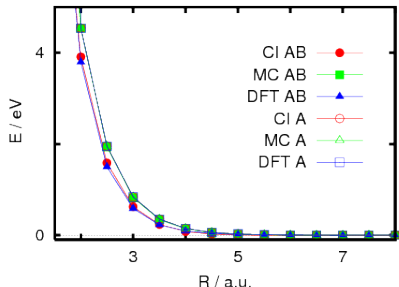
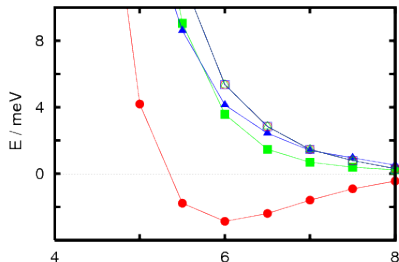
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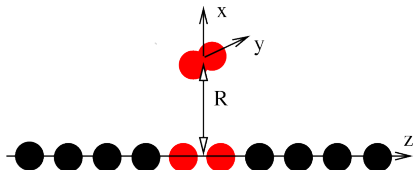
- $r = 1.3$ a.u.



- Only with **A** the repulsion of environment is described !!
- The van der Waals well requires **AB** and a **CI** method



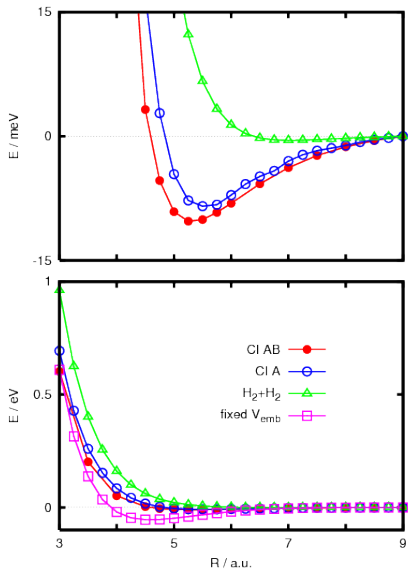
$H_{10} + H_2$ van der Waals interactions



Comparison of CI calculations:

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

Roncero, *et al.*, J. Chem Phys. **129** ('08)



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Problems of the inversion of embedding potentials

- The reference density ρ_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 $\rho = \rho_A + \rho_B$

$$\textcircled{1} \quad \Delta^k = \rho - \rho_A^k + \rho_B^k$$

with ρ_C^k being obtained from a MFE

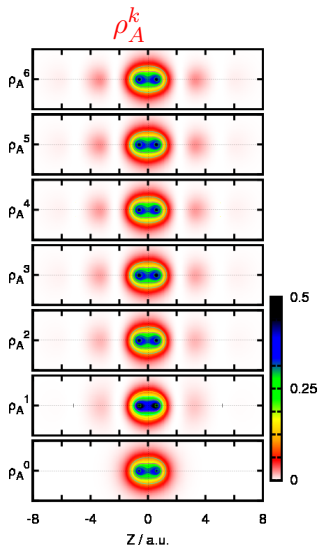
$$[F_C + V_C^k] \phi_C^k = \epsilon_C \phi_C^k$$

$$\textcircled{2} \quad v_{rep}^k = \frac{1}{2} \sum_{m,l} \Delta_{m,l}^k (im|lj) \equiv K[\Delta^k]$$

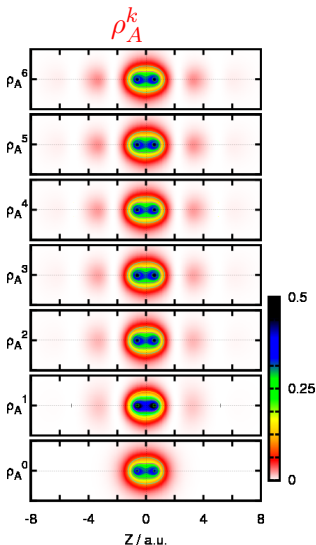
$$\textcircled{3} \quad V_C^{k+1} = V_C^k + \lambda v_{rep}^k[\Delta^k]$$

where λ minimizes $\delta^{k+1} = \int d\mathbf{r} (\Delta^k)^2$

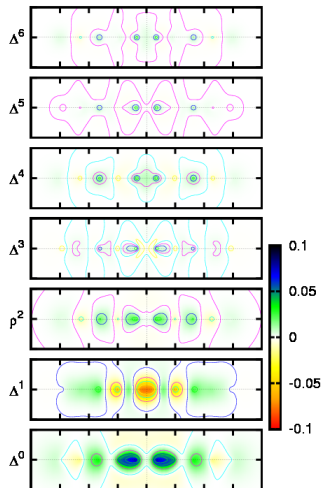
The H_{10} example



The H_{10} example

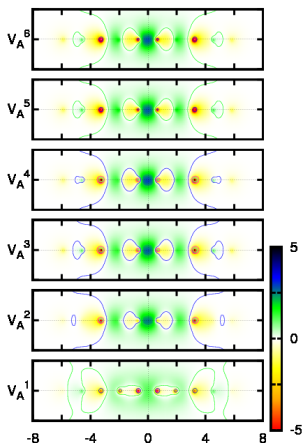


Density difference Δ^k



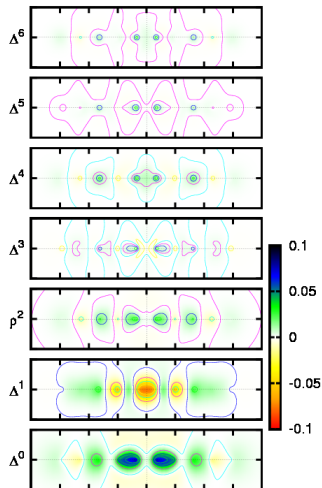
The H_{10} example

- Embedding pot. \mathcal{V}_A^k

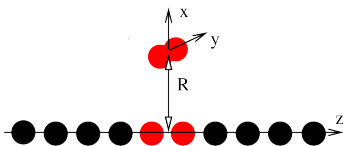


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Density difference Δ^k

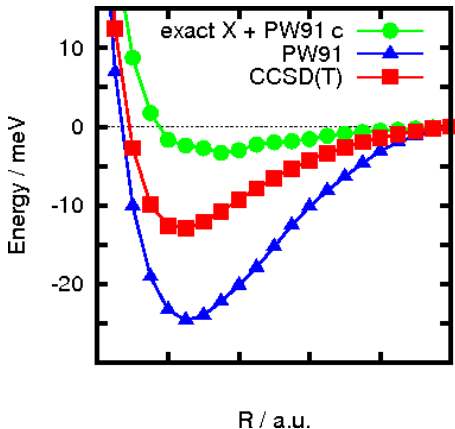


$H_{10} + H_2$ van der Waals interactions

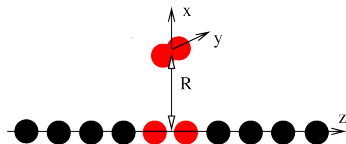


- Comparing different DFT functionals for the full system

Roncero, *et al.*, J. Chem Phys. **131** ('09)

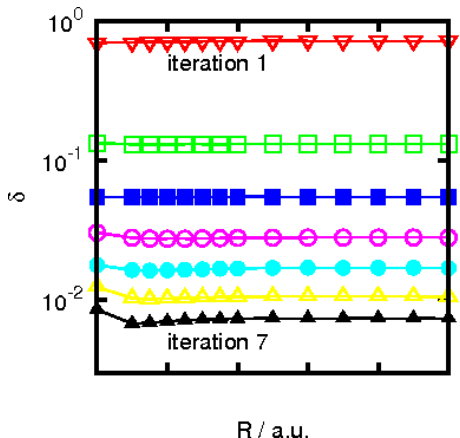


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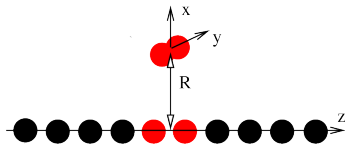


- Comparing different DFT functionals for the full system
- The density difference Δ^k converges fast
- The convergence depends on the DFT functional used for ρ

Roncero, *et al.*, J. Chem Phys. **131** ('09)

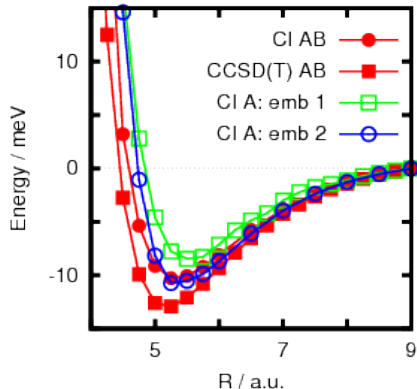


$H_{10} + H_2$ van der Waals interactions



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

Roncero, *et al.*, J. Chem Phys. **131** ('09)



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Conclusions

- An alternative to the FDE embedding method in which ρ_A and ρ_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 ρ can be obtained from any method, DFT or not.
- It can be combined with the most traditional FDE method by using ρ_A and ρ_B

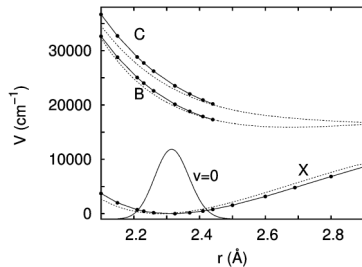
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- It can be combined with the most traditional FDE method by using ρ_A and ρ_B
- More work is needed to solve convergence problems and to design new v_{rep}

What about impurities in clathrates?

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

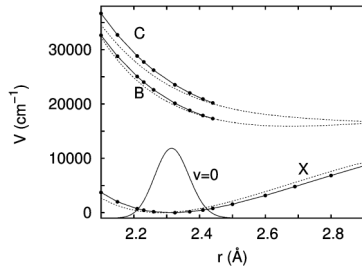
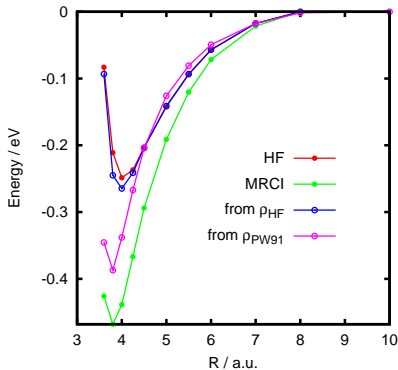
Franklin-Mergarejo *et al*
J. Phys. Chem. A **115**, (2011)



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Franklin-Mergarejo *et al*
J. Phys. Chem. A **115**, (2011)



Ramón Hernández-Lamonedada

What DFT functional to use?

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