Basis-set correction based on density-functional theory: Rigorous framework for a one-dimensional model

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`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_correlation_meeting_22.pdf`

Introduction: basis-set correction based on DFT

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  - **Extrapolation to the complete-basis-set (CBS) limit**
  - **Methods using an explicit correlation factor (QMC, F12, transcorrelated)**

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- Here, we **rexamine this method** more closely for a **one-dimensional model Hamiltonian with delta-potential interactions**
- We give a new **formulation of the method** and we develop an **adapted local-density approximation (LDA) for the basis-set correction functional $\bar{E}^{\mathcal{B}}[\rho]$ for any basis $\mathcal{B}$** using a **finite uniform electron gas**

Traore, Giner, Toulouse, JCP, 2022

Outline

1. One-dimensional model system
2. Basis-set correction theory based on DFT
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Description of the 1D model system

- We consider the **Hamiltonian** of $N = 2$ **electrons** in a **1D He-like atom ($Z = 2$) with delta-potential interactions**:

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}$$

with

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\frac{\partial^2}{\partial x_i^2}, \quad \hat{W}_{\text{ee}} = \delta(x_1 - x_2), \quad \hat{V}_{\text{ne}} = -Z\sum_{i=1}^{N}\delta(x_i)$$

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- The exact ground-state wave function has the same **electron-electron cusp** as the 3D one, i.e. for small interelectronic distances $x_{12} = x_1 - x_2$

$$\Psi_0(x_1, x_2) = \Psi_0(x_1, x_1)\left(1 + \frac{1}{2}|x_{12}| + O(x_{12}^2)\right)$$

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- In a finite one-electron basis set, we thus expect a **slow convergence with the basis size** very similar to the slow convergence observed in 3D quantum systems with the Coulomb electron-electron interaction

Exact ground-state energy and Hartree-Fock approximation

- The **ground-state energy** is

$$\boxed{E_0 = \min_{\Psi \in \mathcal{W}} \langle \Psi, \hat{H}\Psi \rangle}$$

where $\mathcal{W} = \left\{ \Psi \in \mathcal{H} \mid \Psi \in H^1(\mathbb{R}^2, \mathbb{C}),\ \langle \Psi, \Psi \rangle = 1 \right\}$ is the set of admissible wave functions

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- The model can be solved analytically at the **Hartree-Fock (HF) level**
  - The HF ground-state energy is

$$E_{\text{HF}} = -Z^2 + \frac{Z}{2} - \frac{1}{12} = -3.083333\ldots \text{ a.u.}$$

  - The doubly occupied HF orbital is

$$\phi_1(x) = 2\beta\sqrt{\gamma}\frac{e^{-\beta|x|}}{1 - \gamma\, e^{-2\beta|x|}}$$

with $\beta = Z - 1/2 = 3/2$ and $\gamma = 1/(4Z - 1) = 1/7$

Nogami, Vallières, van Dijk, AJP, 1976

Full-configuration interaction in a basis set

- To have a systematically improvable basis set, we use **Hermite functions** with a unique fixed exponent α

$$\forall n \in \mathbb{N},\ f_n^{\alpha}(x) = N_n^{\alpha}\ H_n(\sqrt{2\alpha}x)\ e^{-\alpha x^2}$$

  where H_n are the Hermite polynomials and N_n^{α} is a normalization constant

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  $$\mathcal{B} = \left\{\phi_1\right\} \cup \left\{f_n^\alpha\right\}_{n=0,\ldots,n_{\max}}$$

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- We now work in the **finite-dimensional two-electron Hilbert space** $\mathcal{H}^{\mathcal{B}} = \mathscr{h}^{\mathcal{B}} \otimes \mathscr{h}^{\mathcal{B}}$ where $\mathscr{h}^{\mathcal{B}} = \text{span}(\mathcal{B})$ is the one-electron Hilbert space spanned by the basis set $\mathcal{B}$

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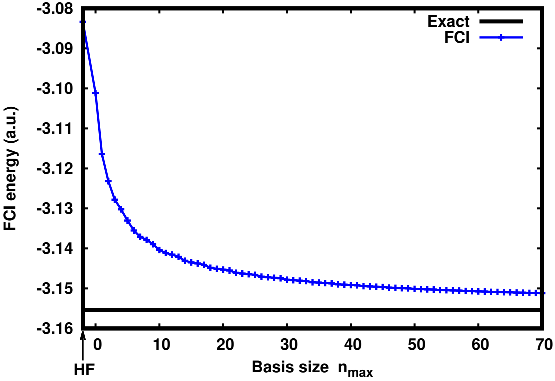
- The **full-configuration-interaction (FCI) ground-state energy** for this basis set $\mathcal{B}$ is

$$E_{\text{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi, \hat{H}\Psi \rangle$$

where $\mathcal{W}^{\mathcal{B}} = \left\{\Psi \in \mathcal{H}^{\mathcal{B}} \mid \langle \Psi, \Psi \rangle = 1\right\}$ is the set of wave functions restricted to $\mathcal{H}^{\mathcal{B}}$

Basis convergence of the FCI ground-state energy

- **Convergence** of $E_{\mathrm{FCI}}^{\mathcal{B}}$ as a function of the **basis size** $n_{\max}$



- As in the 3D Coulomb case, we find a **slow power-law convergence**:

$$E_{\mathrm{FCI}}^{\mathcal{B}} \underset{n_{\max}\to\infty}{\sim} E_0 + \frac{A}{n_{\max}^{b}} \qquad \text{with } b \approx 0.5$$

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Review of DFT for the 1D model

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$$\boxed{\hat{H}[v] = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}} \text{ where } \hat{V} = \sum_{i=1}^{N} v(x_i)$$

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  where $(v, \rho) = \int_{\mathbb{R}} v(x)\rho(x)\mathrm{d}x$

First variant of basis-set correction (1/2)

- We define the **Levy-Lieb density functional restricted to the basis set $\mathcal{B}$** as

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- We now **decompose** the exact Levy-Lieb density functional as

$$\forall \rho \in \mathcal{R}^{\mathcal{B}}, \; F[\rho] = F^{\mathcal{B}}[\rho] + \bar{E}^{\mathcal{B}}[\rho]$$

  where $\bar{E}^{\mathcal{B}}[\rho]$ is the **complementary basis-set correction density functional**

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- As the basis set is increased, $E^{\mathcal{B}}_0[v]$ **converges to** $E_0[v]$ **much faster** than $E^{\mathcal{B}}_{\text{FCI}}[v]$ does

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- The **limitations** are:
  - It does not give the exact ground-state energy even with the exact basis-set correction functional $\bar{E}^{\mathcal{B}}[\rho]$
  - The basis-set correction functional $\bar{E}^{\mathcal{B}}[\rho]$ is defined only for densities $\rho \in \mathcal{R}^{\mathcal{B}}$ $\Longrightarrow$ it is not clear how to define a local-density approximation (LDA)

Second variant of basis-set correction (1/2)

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$$\forall \rho \in \mathcal{R},\ F[\rho] = F^{\mathrm{w}\mathcal{B}}[\rho] + \bar{E}_{\mathrm{Hxc}}^{\mathrm{w}\mathcal{B}}[\rho]$$

  where $\bar{E}_{\mathrm{Hxc}}^{\mathrm{w}\mathcal{B}}[\rho]$ is the **complementary Hartree-exchange-correlation basis-set correction density functional**

Second variant of basis-set correction (1/2)

- We define a new **Levy-Lieb density functional restricted to the basis set $\mathcal{B}$** for all densities $\rho \in \mathcal{R}$ as

$$\forall \rho \in \mathcal{R}, \;\; F^{\text{w}\mathcal{B}}[\rho] = \min_{\Psi \in \mathcal{W}_\rho} \langle \Psi, (\hat{T} + \hat{W}_{\text{ee}}^{\mathcal{B}})\Psi \rangle$$

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- We can obtain the **exact ground-state energy** as

$$E_0[v] = \inf_{\rho \in \mathcal{R}} (F[\rho] + (v, \rho)) = \inf_{\Psi \in \mathcal{W}} \left(\langle \Psi, (\hat{T} + \hat{W}_{\text{ee}}^{\mathcal{B}} + \hat{V})\Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{w}\mathcal{B}}[\rho_\Psi] \right)$$

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where $\Psi[\rho]$ is the wave function minimizing $\langle \Psi, (\hat{T} + \hat{W}_{\text{ee}})\Psi \rangle$ and $\Psi^{\text{w}\mathcal{B}}[\rho]$ is the wave function minimizing $\langle \Psi, (\hat{T} + \hat{W}_{\text{ee}}^{\mathcal{B}})\Psi \rangle$

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- In practice, we will use **approximations** for $\Psi_0^{\text{w}\mathcal{B}}$ and $\bar{E}_{\text{c,md}}^{\text{w}\mathcal{B}}[\rho]$

Outline

1. One-dimensional model system
2. Basis-set correction theory based on DFT
3. LDA from finite uniform-electron gas

1D uniform-electron gas

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- We can extend this to any N and the energy per particle of the **infinite UEG** is $\varepsilon_{\text{UEG}}(\rho_0) = \lim_{N \to \infty} \varepsilon_{\text{UEG},N}(\rho_0)$ **but we may as well use the finite UEG for $N = 2$**

Gill, Loos, TCA, 2012

1D finite UEG for second variant of basis-set correction

- In the **second variant of basis-set correction**, the **Levy-Lieb density functional** is

$$\forall \rho \in \mathcal{R}_a, \;\; F_{\mathrm{a}}^{\mathrm{w}\mathcal{B}}[\rho] = \min_{\Psi \in \mathcal{W}_{a,\rho}} \langle \Psi, (\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathcal{B}})\Psi \rangle_a = \langle \Psi^{\mathrm{w}\mathcal{B}}[\rho], (\hat{T} + \hat{W}_{\mathrm{ee}}^{\mathcal{B}})\Psi^{\mathrm{w}\mathcal{B}}[\rho] \rangle_a,$$

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$$\hat{H}_{\mathrm{UEG}}^{\mathrm{w}\mathcal{B}} = \hat{T} + \hat{W}_{\mathrm{ee}}^{\mathcal{B}} + \hat{V}^{\mathrm{w}\mathcal{B}} \qquad \text{with } \hat{V}^{\mathrm{w}\mathcal{B}} = \sum_{i=1}^{N} v^{\mathrm{w}\mathcal{B}}(x_i)$$

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- According to **Lieb's convex-conjugation approach**, the potential $v^{\mathrm{w}\mathcal{B}}$ is calculated as

$$v^{\mathrm{w}\mathcal{B}} = \operatorname*{argmax}_{v \in \mathcal{V}_a} \left(E_{0,a}^{\mathrm{w}\mathcal{B}}[v] - (v, \rho_{\mathrm{unif}})_a \right)$$

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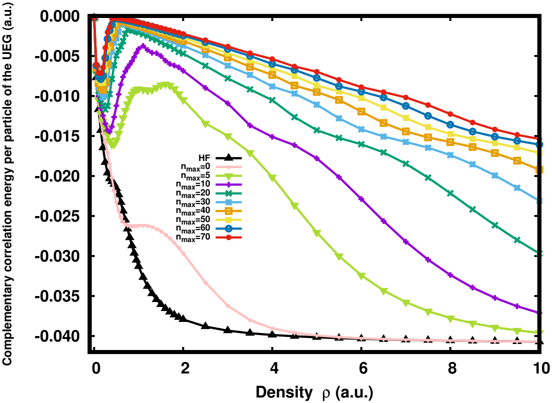
- From $\Psi^{\mathrm{w}\mathcal{B}}[\rho_{\mathrm{unif}}]$, we calculate the **complementary correlation energy per particle**

$$\bar{\varepsilon}_{\mathrm{c,md},N=2}^{\mathrm{w}\mathcal{B}}(\rho_0) = \frac{\bar{E}_{\mathrm{c,md}}^{\mathrm{w}\mathcal{B}}[\rho_{\mathrm{unif}}]}{N}$$

Complementary correlation energy per particle

- **Complementary correlation energy per particle of the finite 1D UEG $\bar{\varepsilon}^{\mathrm{w}\mathcal{B}}_{\mathrm{c,md},N=2}(\rho)$** as a function of ρ for basis sets $\mathcal{B}$ of the 1D He-like atom of increasing sizes n_{max}:



- As n_{max} increases, $\bar{\varepsilon}^{\mathrm{w}\mathcal{B}}_{\mathrm{c,md},N=2}(\rho)$ becomes smaller and must eventually vanish in the limit $n_{\mathrm{max}} \to \infty$

FCI with LDA-based basis-set correction

- Recall that in the **second variant of basis-set correction**, the exact ground-state energy can be written as

$$E_0 = \langle \Psi_0^{\mathrm{w}\mathcal{B}}, \hat{H}\Psi_0^{\mathrm{w}\mathcal{B}} \rangle + \bar{E}_{\mathrm{c,md}}^{\mathrm{w}\mathcal{B}}[\rho_{\Psi_0^{\mathrm{w}\mathcal{B}}}]$$

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- For the functional $\bar{E}_{\mathrm{c,md}}^{\mathrm{w}\mathcal{B}}[\rho]$, we use the **LDA** from our 1D finite UEG calculations for the basis set $\mathcal{B}$

$$\bar{E}_{\mathrm{c,md,LDA}}^{\mathrm{w}\mathcal{B}}[\rho] = \int_{\mathbb{R}} \rho(x)\bar{\varepsilon}_{\mathrm{c,md},N=2}^{\mathrm{w}\mathcal{B}}(\rho(x))\mathrm{d}x$$

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- We approximate the wave function $\Psi_0^{\mathrm{w}\mathcal{B}}$ by the **FCI ground-state wave function** $\Psi_{\mathrm{FCI}}^{\mathcal{B}}$ in the basis set $\mathcal{B}$

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$$\bar{E}_{\mathrm{c,md,LDA}}^{\mathrm{w}\mathcal{B}}[\rho] = \int_{\mathbb{R}} \rho(x)\bar{\varepsilon}_{\mathrm{c,md},N=2}^{\mathrm{w}\mathcal{B}}(\rho(x))\mathrm{d}x$$

- We approximate the wave function $\Psi_0^{\mathrm{w}\mathcal{B}}$ by the **FCI ground-state wave function** $\Psi_{\mathrm{FCI}}^{\mathcal{B}}$ in the basis set $\mathcal{B}$

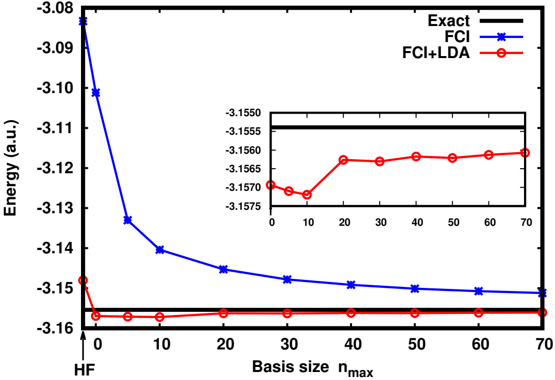
- We thus finally the **FCI energy with a LDA-based basis-set correction**

$$E_{\mathrm{FCI+LDA}}^{\mathrm{w}\mathcal{B}} = \langle \Psi_{\mathrm{FCI}}^{\mathcal{B}}, \hat{H}\Psi_{\mathrm{FCI}}^{\mathcal{B}} \rangle + \bar{E}_{\mathrm{c,md,LDA}}^{\mathrm{w}\mathcal{B}}[\rho_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}]$$

and $E_{\mathrm{FCI+LDA}}^{\mathrm{w}\mathcal{B}}$ correctly converges to E_0 in the complete-basis-set limit

Basis convergence of the FCI+LDA energy of the 1D He-like atom

- **FCI and FCI+LDA ground-state energies of the 1D He-like atom** as a function of the basis size n_{max} :



- The **LDA-based basis-set correction efficiently accelerates the basis convergence of the FCI ground-state energy**

Summary and outlook

- **Summary:**
  - The 1D model with delta-potential interactions captures the essence of the basis-set convergence problem
  - Two variants of basis-set corrections based on DFT have been rigorously developed
  - The LDA for the basis-set correction functional has been constructed from a finite uniform-electron gas

D. Traore, E. Giner, J. Toulouse, J. Chem. Phys. **156**, 044113, 2022

- **Outlook:**
  - Linear-response theory for basis-set correction of excitation energies in a 1D model
  - Extension to a relativistic 1D model
  - Density-functional approximations for the first variant of basis-set correction in the 1D model
  - Extension of the work on the 1D model to 3D molecular systems
  - Extension to solids?

`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_correlation_meeting_22.pdf`