SORBONNE UNIVERSITÉ

LCT Laboratoire de Chimie Théorique

Workshop on model systems in quantum mechanics

1D Dirac-delta interaction model for 3D quantum systems with Coulomb-potential interaction

Diata Traore

January 2024

Thesis work with Julien Toulouse & Emmanuel Giner

Table of Contents

The many-electron Schrödinger equation with Coulomb potential

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

where (in the Born-Oppenheimer approximation)

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

- A divergent Coulomb interaction which leads to a electron-electron cusp:

$$\hat{W}_{\text{ee}} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \Psi(r_{12}) = \Psi(r_{12} = 0)(1 + \frac{1}{2} r_{12} + ...)$$

The many-electron Schrödinger equation with Coulomb potential

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

where (in the Born-Oppenheimer approximation)

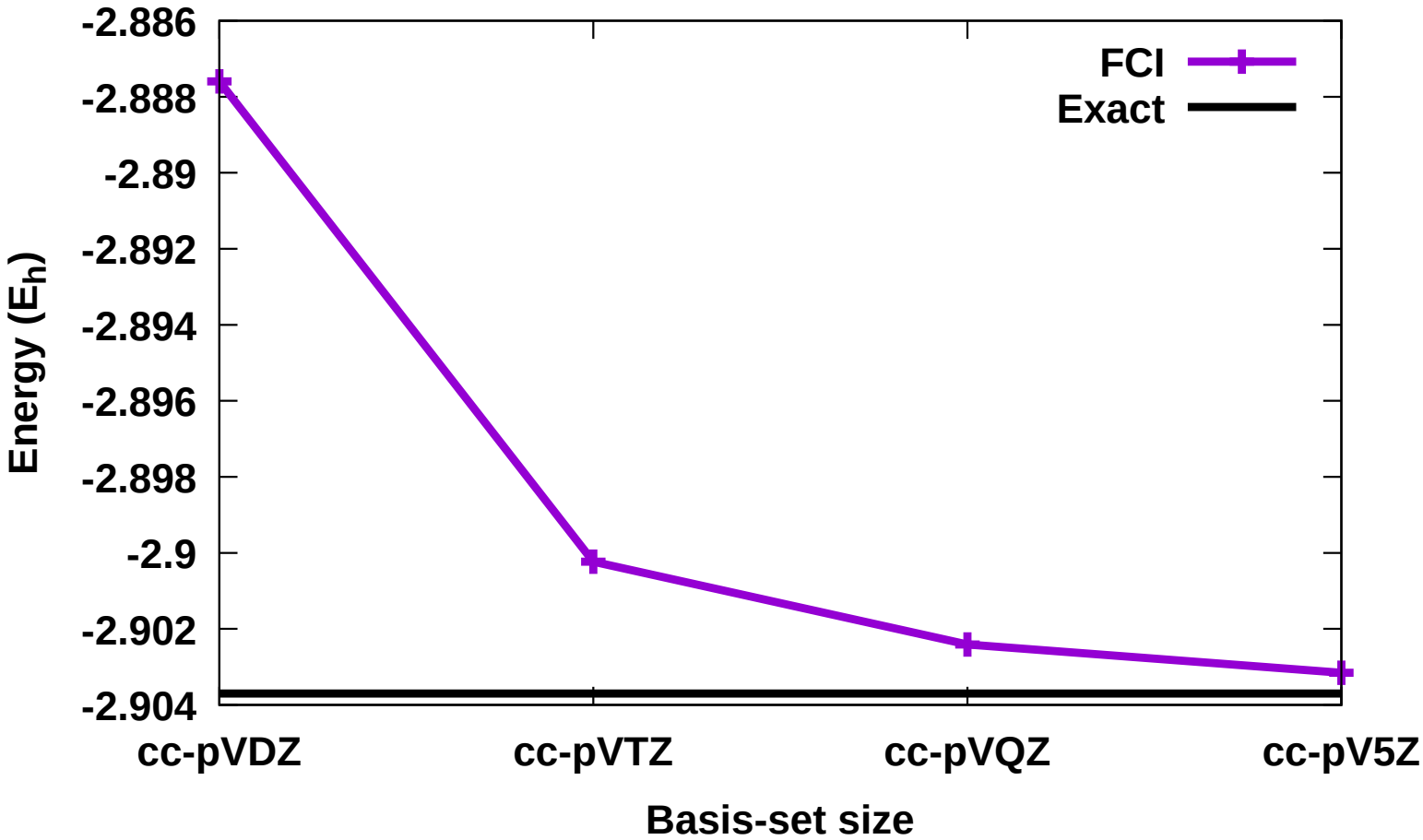
$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}$$

- A divergent Coulomb interaction which leads to a electron-electron cusp:

$$\hat{W}_{\text{ee}} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \Psi(r_{12}) = \Psi(r_{12} = 0)(1 + \frac{1}{2} r_{12} + ...)$$

1. Wave-function theory (WFT) $\Leftrightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$
   - \+ Systematic way to expand Ψ on a basis-set.
   - – Difficulty in converging the cusp behaviour.
2. Density-functional theory (DFT) $\Leftrightarrow n(\mathbf{r})$
   - \+ Hide the short-range interaction and the cusp issue in a functional of the density.
   - – Approximations are not universal and not systematically improvable

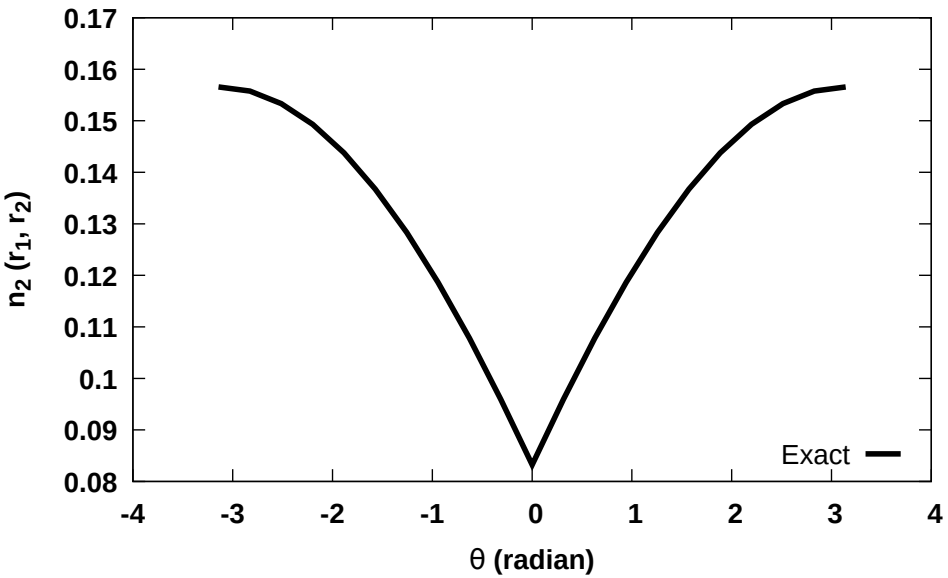
Example - Helium ground-state energy:

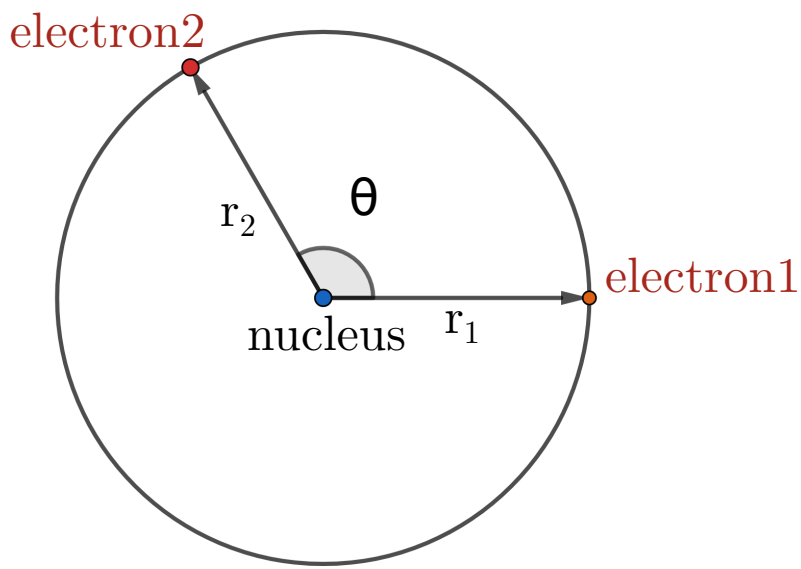


Probability of finding two electrons close to each other

- $n_2(r_1, r_2) \propto$ density of probability of finding electron 1 at r_1 when electron 2 is at r_2.
- Coulomb repulsion: electrons avoid each other.
- Slow convergence with respect to the size of B.

Electron-pair density of the Helium atom:

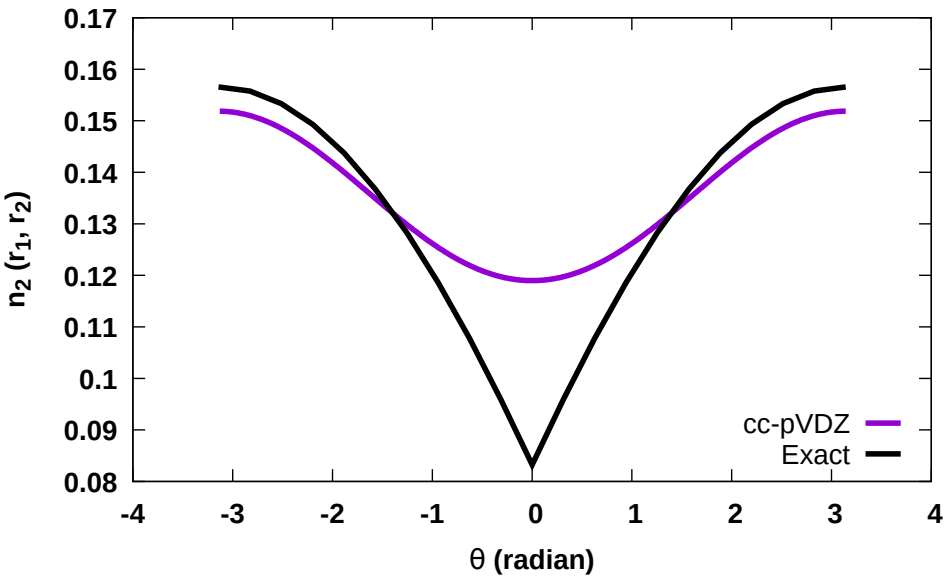


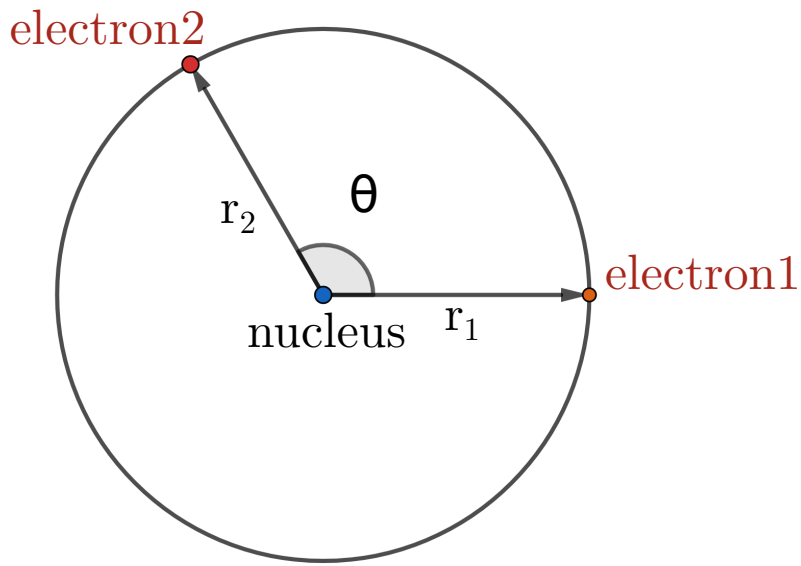


Probability of finding two electrons close to each other

- $n_2(r_1, r_2) \propto$ density of probability of finding electron 1 at r_1 when electron 2 is at r_2.
- Coulomb repulsion: electrons avoid each other.
- Slow convergence with respect to the size of B.

Electron-pair density of the Helium atom:

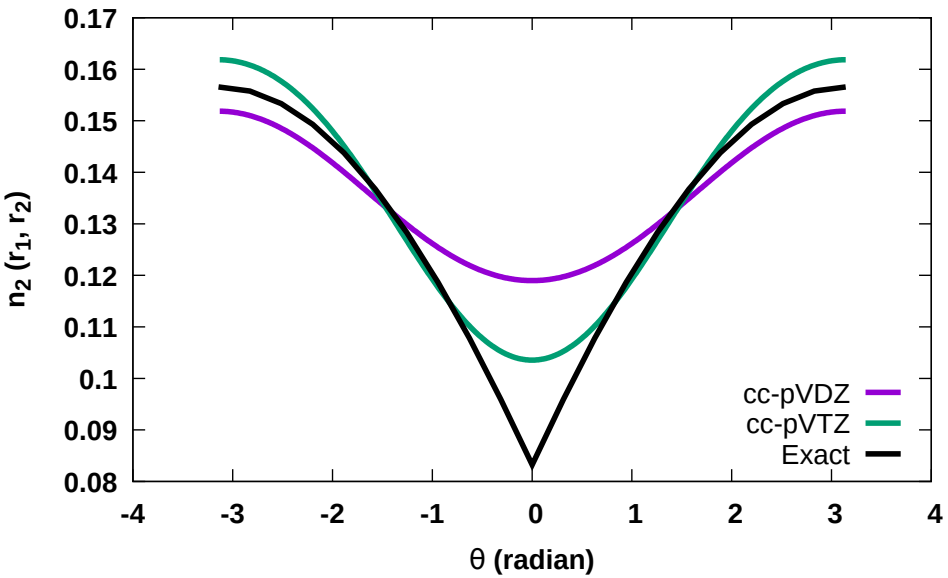


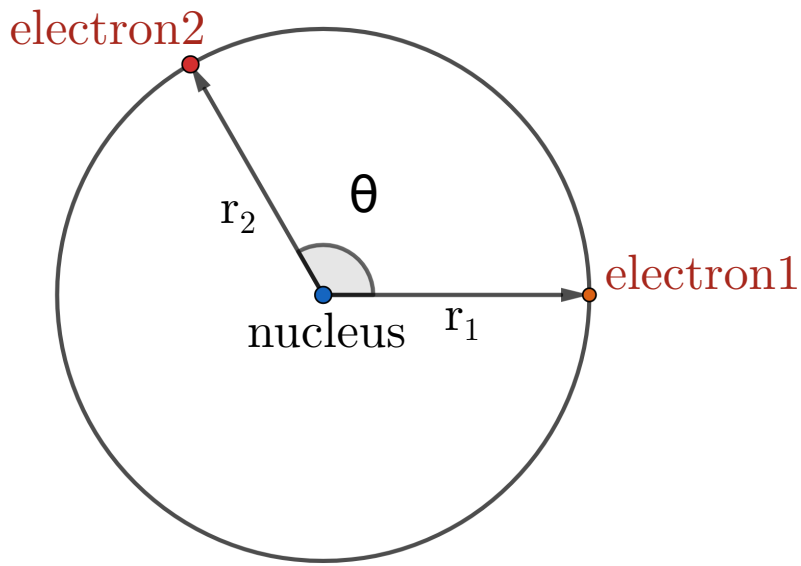


Probability of finding two electrons close to each other

- $n_2(r_1, r_2) \propto$ density of probability of finding electron 1 at r_1 when electron 2 is at r_2.
- Coulomb repulsion: electrons avoid each other.
- Slow convergence with respect to the size of B.

Electron-pair density of the Helium atom:

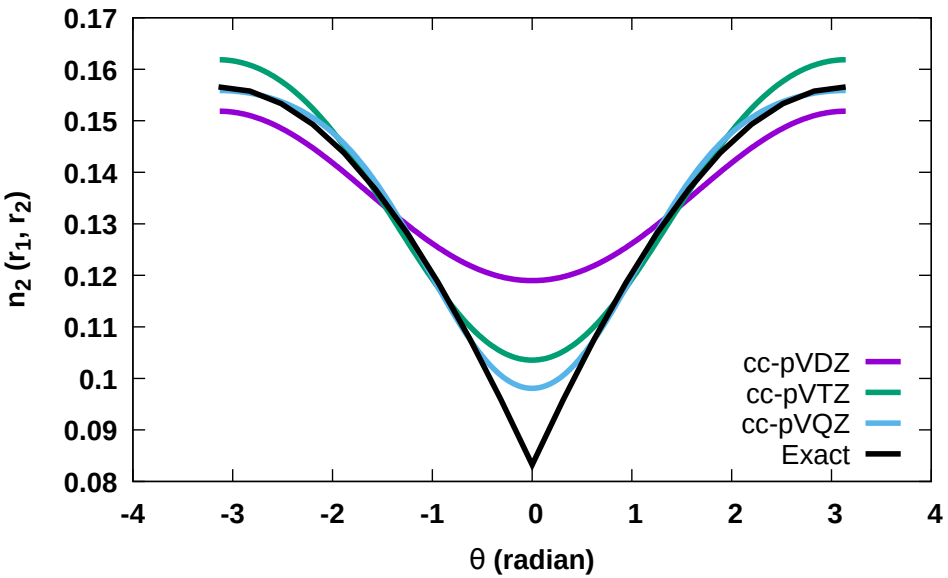


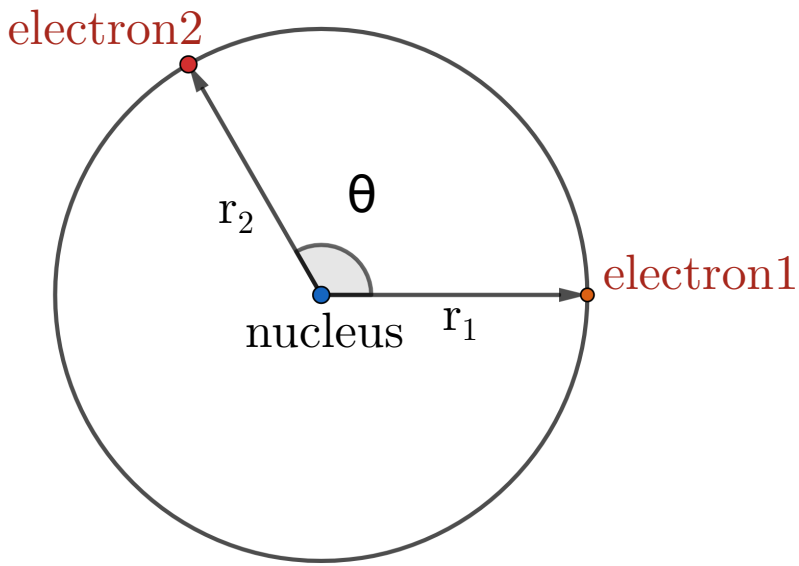


Probability of finding two electrons close to each other

- $n_2(r_1, r_2) \propto$ density of probability of finding electron 1 at r_1 when electron 2 is at r_2.
- Coulomb repulsion: electrons avoid each other.
- Slow convergence with respect to the size of B.

Electron-pair density of the Helium atom:

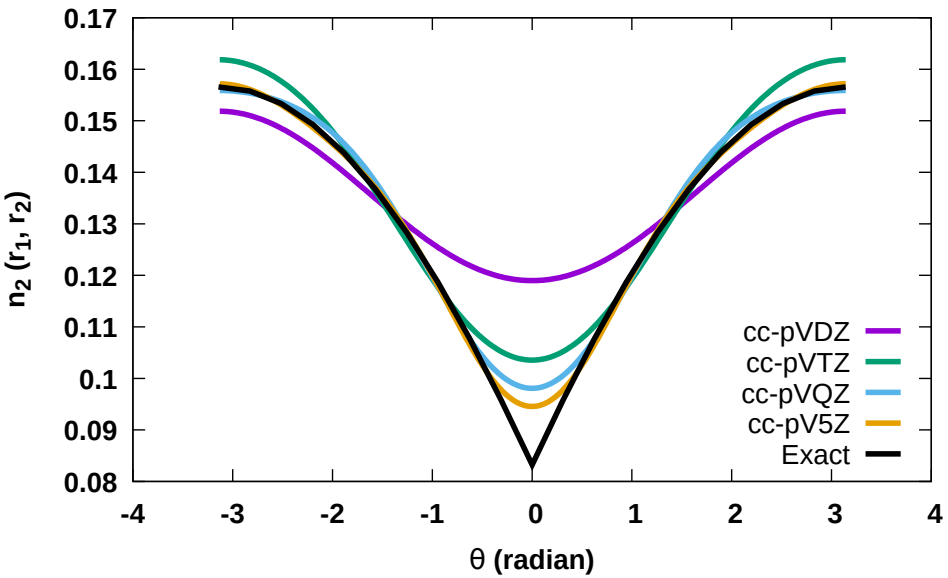


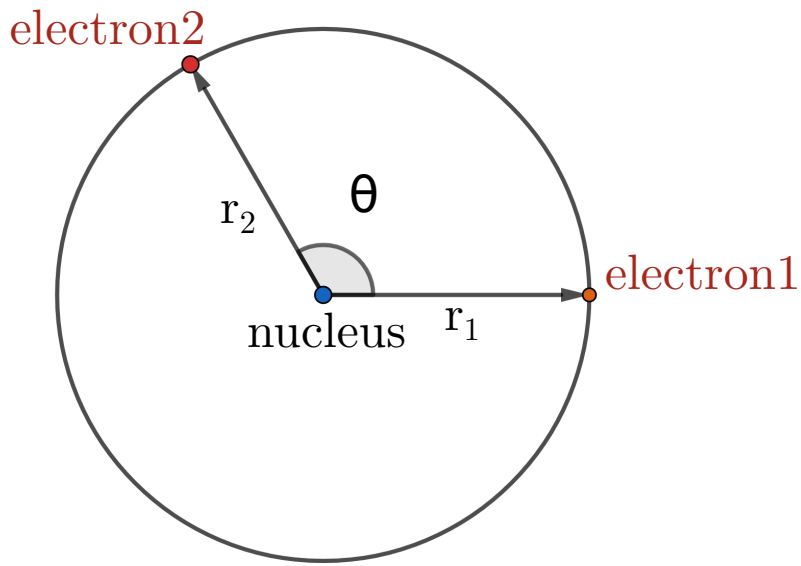


Probability of finding two electrons close to each other

- $n_2(r_1, r_2) \propto$ density of probability of finding electron 1 at r_1 when electron 2 is at r_2.
- Coulomb repulsion: electrons avoid each other.
- Slow convergence with respect to the size of B.

Electron-pair density of the Helium atom:





The many-electron Schrödinger equation with Coulomb potential

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

where (in the Born-Oppenheimer approximation)

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

- A divergent Coulomb interaction which leads to a electron-electron cusp:

$$\hat{W}_{\text{ee}} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \Psi(r_{12}) = \Psi(r_{12} = 0)(1 + \frac{1}{2} r_{12} + ...)$$

Goal

Use a model system to ease methods development and understanding.

To do list:

- ☐ To reproduce the slow basis convergence of the ground-state energy.
- ☐ To reproduce the electron-electron cusp.
- ☐ Building a functional of the density.

1D Helium-like atom Hamiltonian

2 electrons + 1 nucleus in a 1D space

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

including:

- The kinetic-energy operator of the ith electron: $\hat{T} = \sum_{i=1,2} -1/(2m)\ \partial^2/\partial x_i^2$
- The ith electron interaction with the nucleus: $\hat{V}_{\text{ne}} = \sum_{i=1,2} v_{\text{ne}}(x_i)$
- The interaction between both electrons: $\hat{W}_{\text{ee}} = \delta(x_1 - x_2)$

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

1D Helium-like atom Hamiltonian

2 electrons + 1 nucleus in a 1D space

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

including:

- The kinetic-energy operator of the ith electron: $\hat{T} = \sum_{i=1,2} -1/(2m)\ \partial^2/\partial x_i^2$
- The ith electron interaction with the nucleus: $\hat{V}_{\text{ne}} = \sum_{i=1,2} v_{\text{ne}}(x_i)$
- The interaction between both electrons: $\hat{W}_{\text{ee}} = \delta(x_1 - x_2)$

Basis for the wave function:

- Basis (Hermite-Gaussian functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

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

1D Helium-like atom Hamiltonian

2 electrons + 1 nucleus in a 1D space

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

including:

- The kinetic-energy operator of the ith electron: $\hat{T} = \sum_{i=1,2} -1/(2m)\ \partial^2/\partial x_i^2$
- The ith electron interaction with the nucleus: $\hat{V}_{\text{ne}} = \sum_{i=1,2} v_{\text{ne}}(x_i)$
- The interaction between both electrons: $\hat{W}_{\text{ee}} = \delta(x_1 - x_2)$

Basis for the wave function:

- Basis (Hermite-Gaussian functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

A model which reproduces the electron-electron cusp:

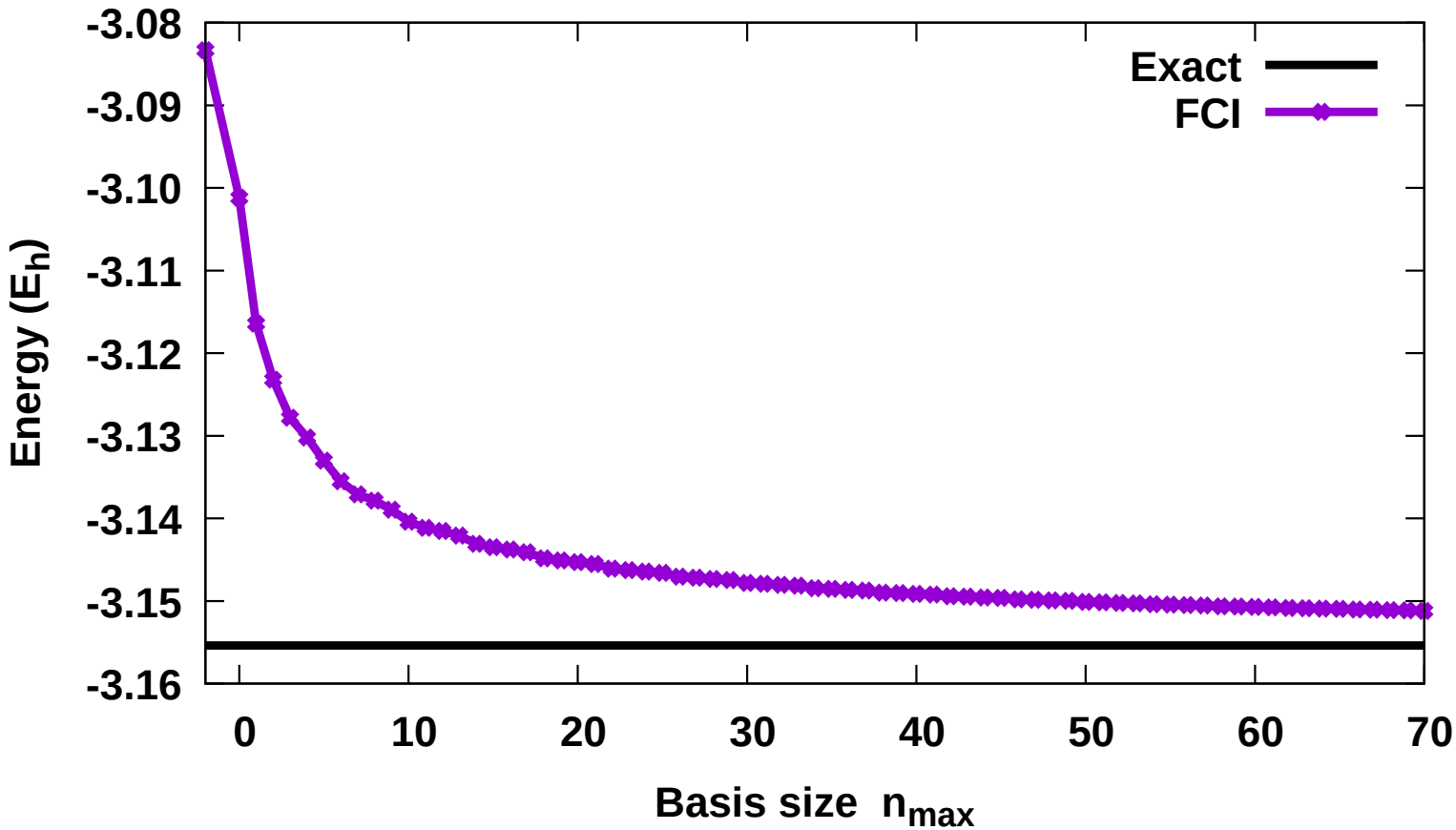
$$\hat{W}_{\text{ee}} = \delta(x_1 - x_2) \rightarrow \Psi(x_{12}) = \Psi(x_{12} = 0)(1 + \frac{1}{2} x_{12} + ...)$$

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

Basis-set convergence of the ground state energy

External potential and basis set

- External potential : $v_{\text{ne}}(x) = -Z\delta(x)$
- Basis (Hermite-Gaussian functions): $\chi_n(x) = N_n(\alpha)e^{-\alpha x^2}H_n(\sqrt{2\alpha}x)$



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

To do list check

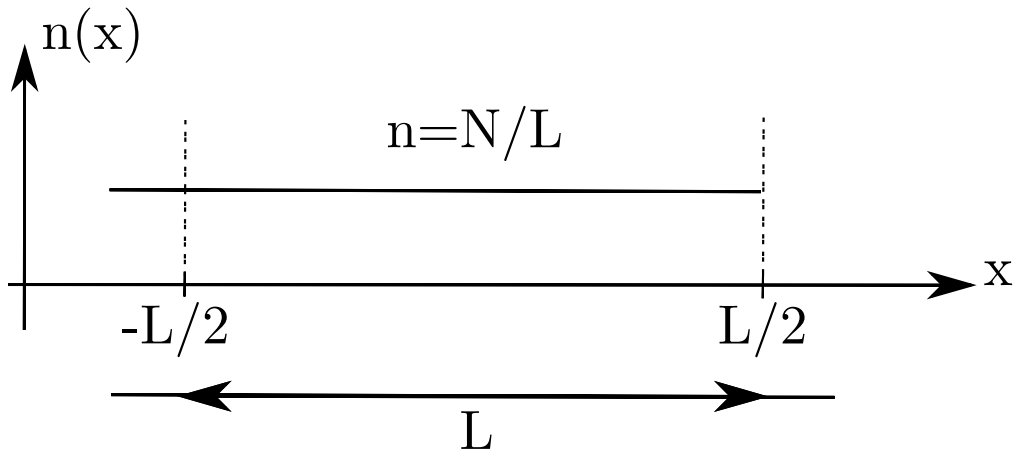
Goal

Use a model system to ease methods development and understanding.

To do list:

- ✓ To reproduce the slow basis convergence of the ground-state energy.
- ✓ To reproduce the electron-electron cusp.
- ☐ Building a functional of the density.

A 2-electron 1D uniform electron gas:



- n: Uniform density
- $N = 2$: Number of electrons
- L: size of the gas
- Periodic boundary conditions

Hamiltonian

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

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

Definition of the FCI energy and wave function

$$\hat{H}_{\text{UEG}}|\Psi_{\text{UEG}}\rangle = E|\Psi_{\text{UEG}}\rangle$$

Energy per particle

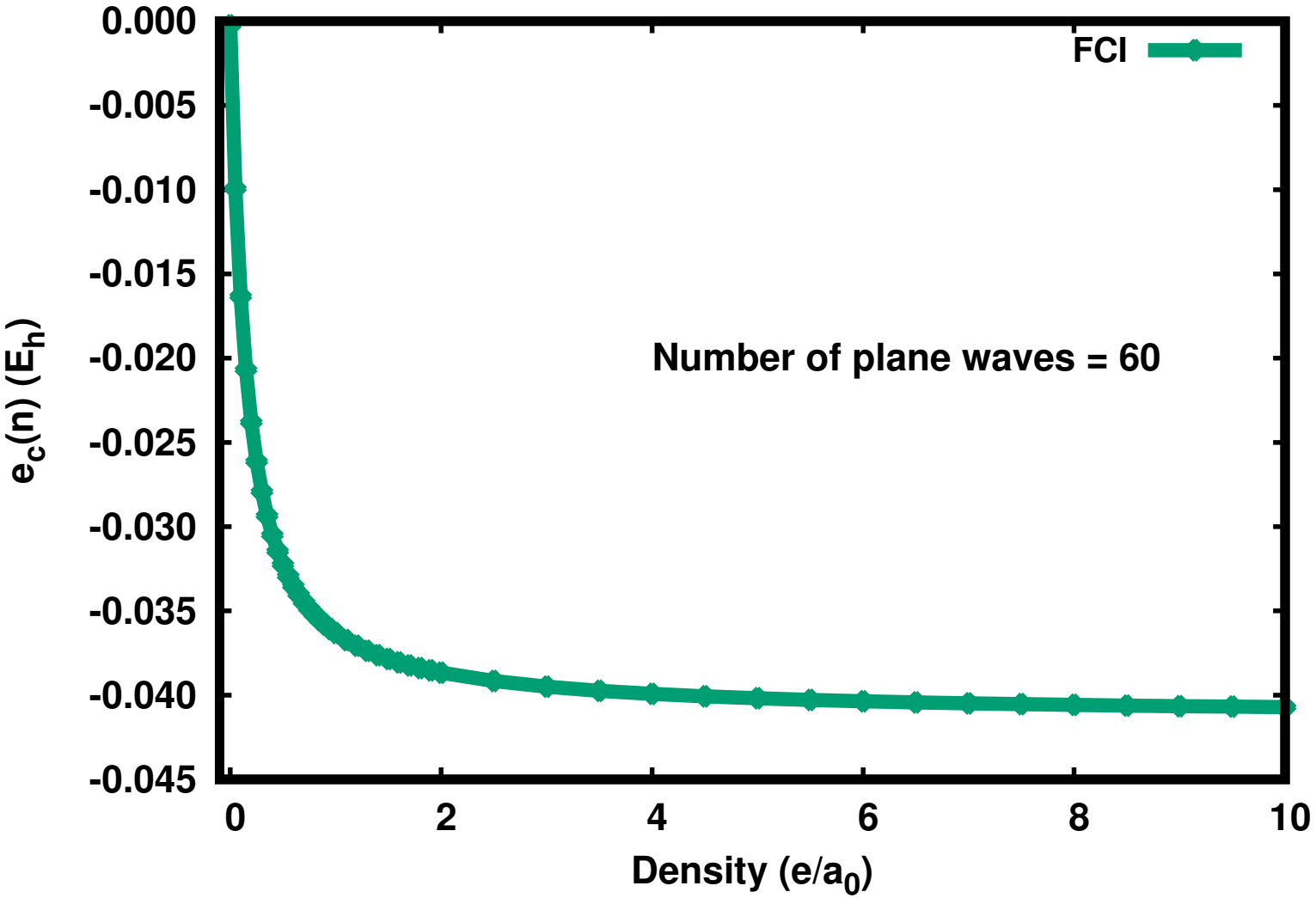
$$\epsilon^{\text{UEG}}(n) = \frac{E}{N}$$

and

$$\epsilon^{\text{UEG}}(n) = \underbrace{t_{s,\text{UEG}}(n) + \epsilon_{\text{H}}^{\text{UEG}}(n) + \epsilon_{\text{x}}^{\text{UEG}}(n)}_{\text{Exact } \checkmark} + \epsilon_{\text{c}}^{\text{UEG}}(n)$$

- $t_{s,\text{UEG}} = 0$
- $\epsilon_H^{\text{UEG}} = n/2$
- $\epsilon_x^{\text{UEG}} = -n/4$

Converged solution to the FCI correlation energy



UEG in a finite basis set:

Definition of the FCI and wave-function energy

The Hamiltonian

$$\hat{H}^B_{\mathrm{UEG}} = \hat{T} + \hat{W}^B_{\mathrm{ee}} + \hat{V}^B,$$

where

- $\hat{W}^B_{\mathrm{ee}}$: interaction projected in the Hermite-Gauss basis set B,
- $\hat{V}^B$: local potential operator keeping the density uniform.

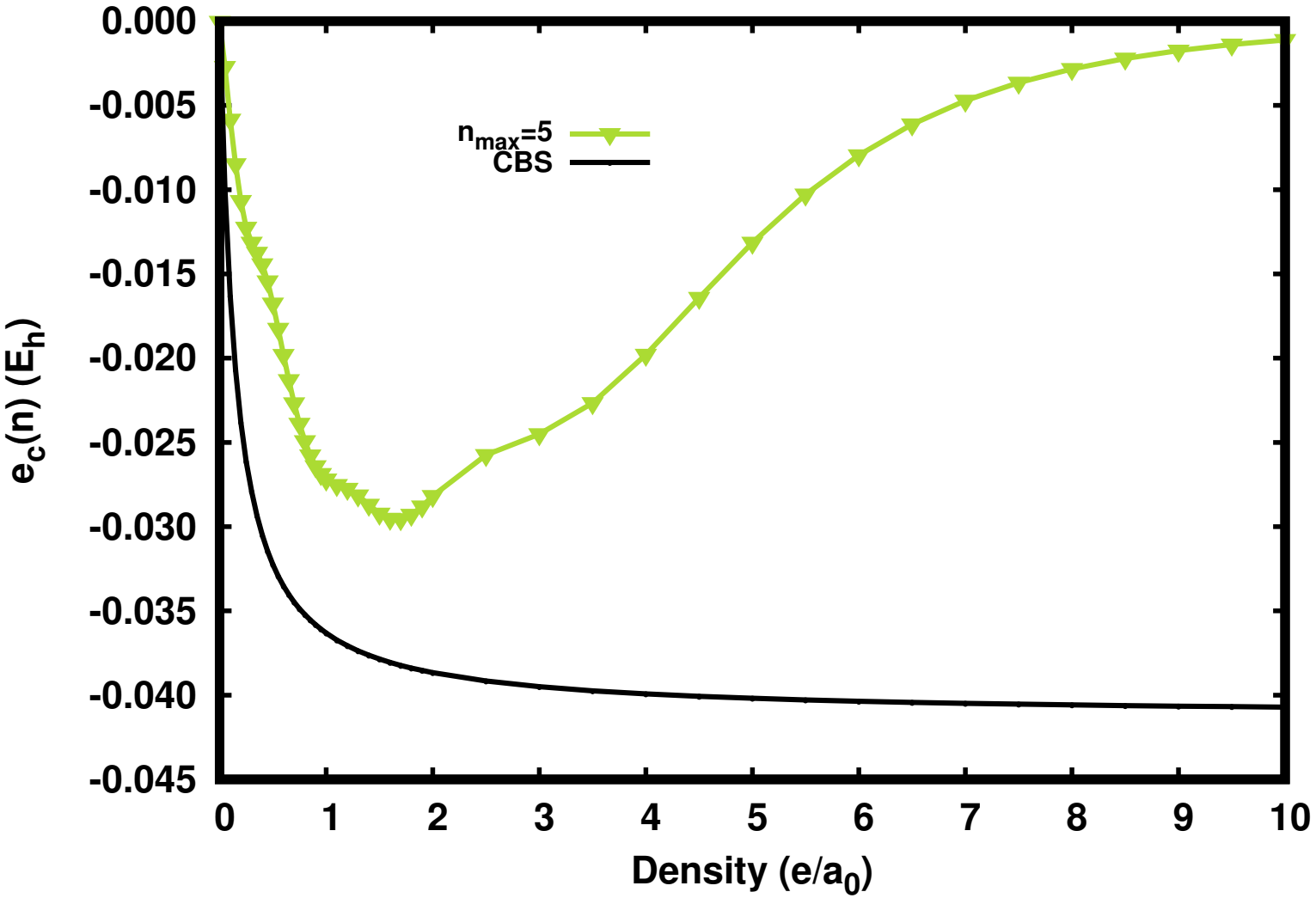
and the Schrödinger equation

$$\hat{H}^B_{\mathrm{UEG}} |\Psi^B_{\mathrm{UEG}}\rangle = E^B |\Psi^B_{\mathrm{UEG}}\rangle$$

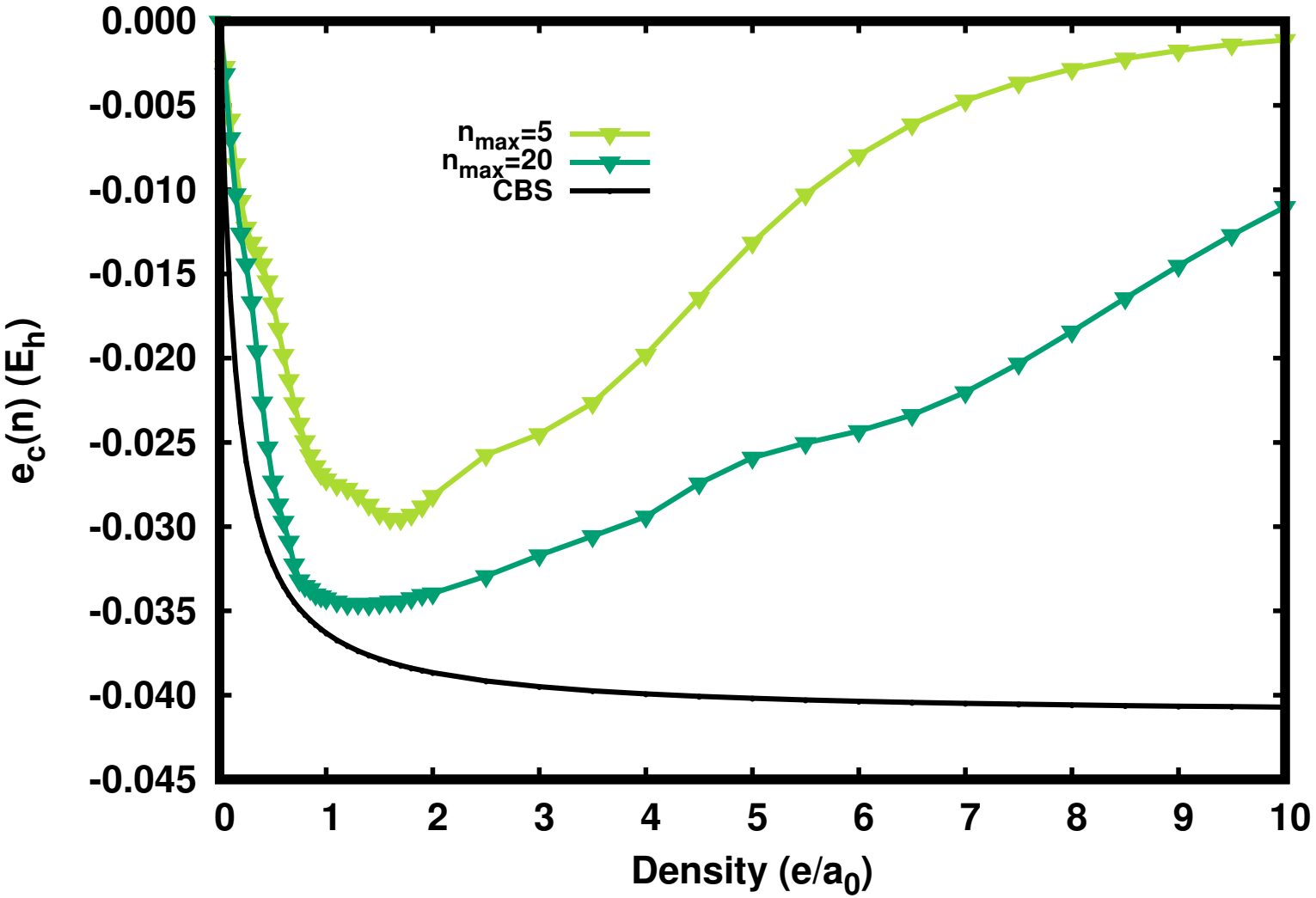
Energy per particle

$$\epsilon^{B,\mathrm{UEG}}(n) = \frac{\langle \Psi^B_{\mathrm{UEG}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi^B_{\mathrm{UEG}} \rangle}{N}$$

UEG in a finite basis set:



UEG in a finite basis set:



1D LDA-based basis-set correction

Definition of the correlation correction

$\bar{\epsilon}_c^{B,\mathrm{UEG}}(n)$: correlation energy per particle of the **uniform electron gas (UEG)** with the uniform density n:

$$\bar{\epsilon}_c^{B,\mathrm{UEG}}(n) = \epsilon^{\mathrm{UEG}}(n) - \epsilon^{B,\mathrm{UEG}}(n)$$

LDA basis-set correction

$$\bar{E}^B_{\mathrm{LDA}}[n] = \int \mathrm{d}x\, n(x)\, \bar{\epsilon}_c^{B,\mathrm{UEG}}(n(x))$$

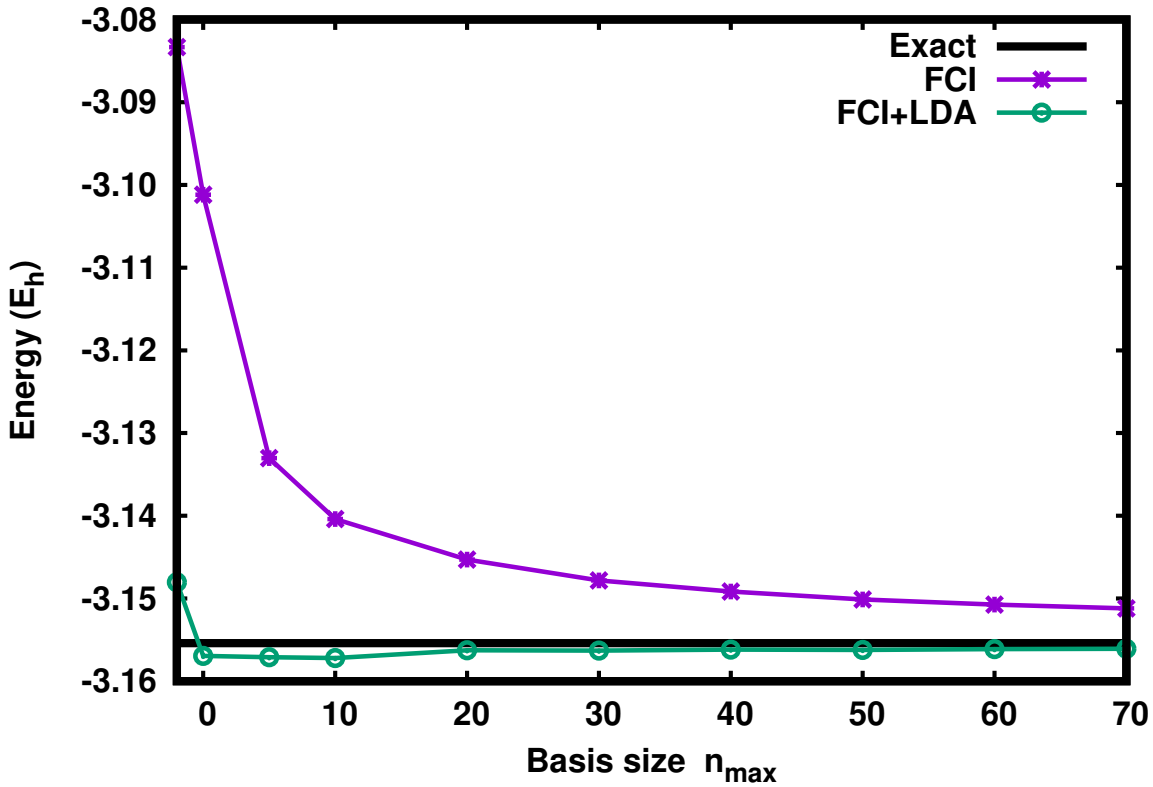
Finally,

$$E^B = \langle \Psi^B_{\mathrm{FCI}} | \hat{H} | \Psi^B_{\mathrm{FCI}} \rangle + \bar{E}^B_{\mathrm{LDA}}[n_{\Psi^B_{\mathrm{FCI}}}]$$

(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys. **156**, 044113 1-13 (2022))

External potential and basis set

- External potential : $v_{\text{ne}}(x) = -Z\delta(x)$
- Basis (Hermite-Gaussian functions): $\chi_n(x) = N_n(\alpha)e^{-\alpha x^2}H_n(\sqrt{2\alpha}x)$

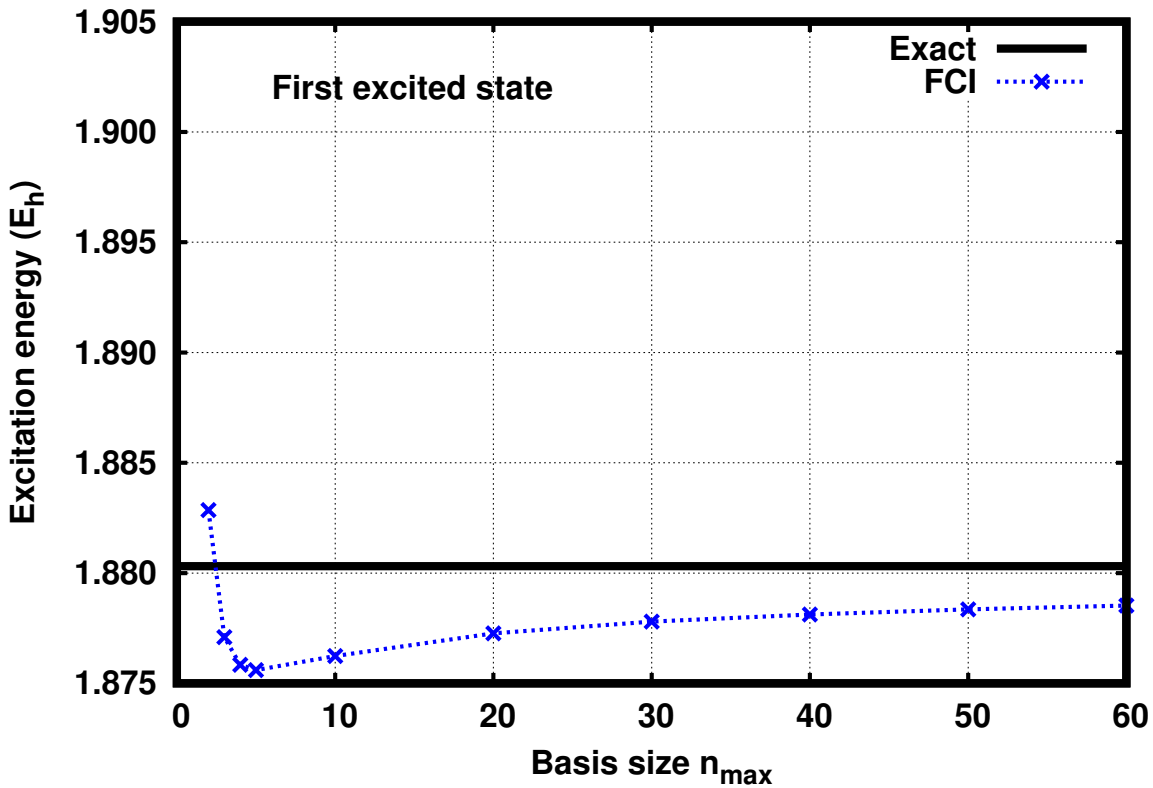


(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys. **156**, 044113 1-13 (2022))

External potential and basis set

- External potential: $v_{\text{ne}}(x) = (1/2)\omega_0^2 x^2$
- Basis (Hermite-Gauss functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

First excitation energy:

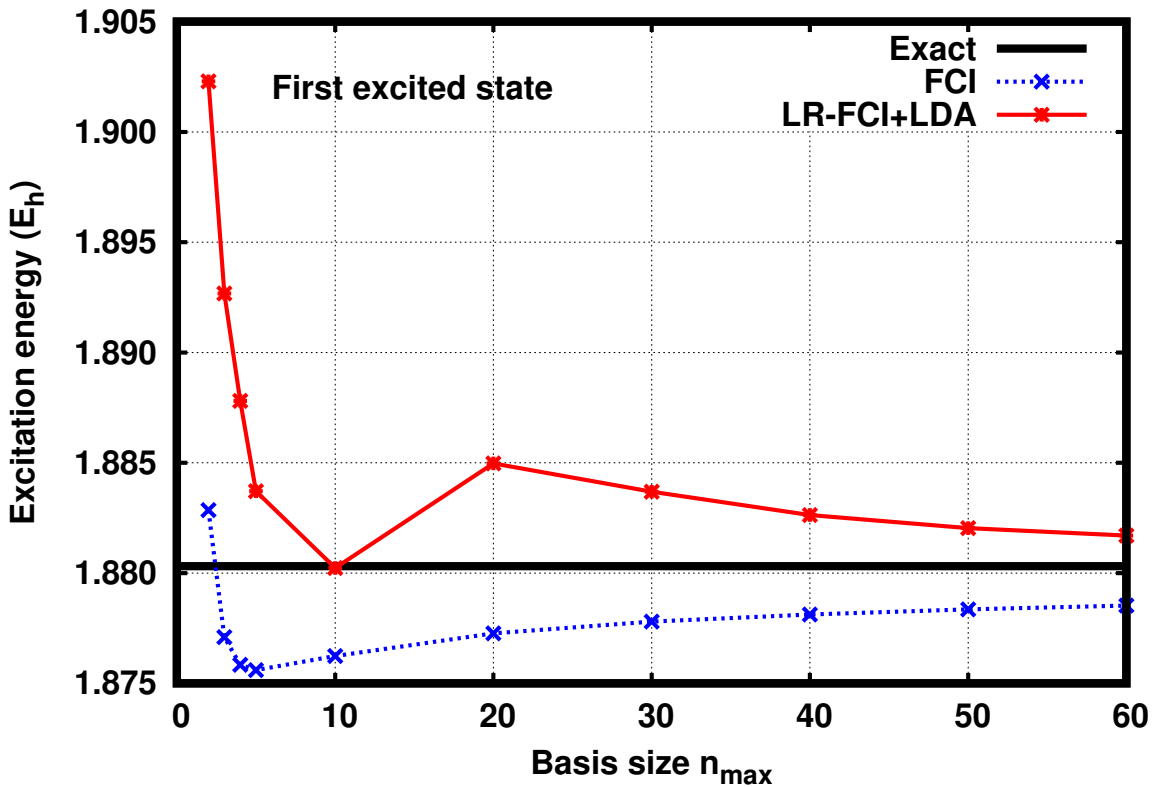


(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys **158**, 234107 (2023))

External potential and basis set

- External potential: $v_{\text{ne}}(x) = (1/2)\omega_0^2 x^2$
- Basis (Hermite-Gauss functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

First excitation energy:

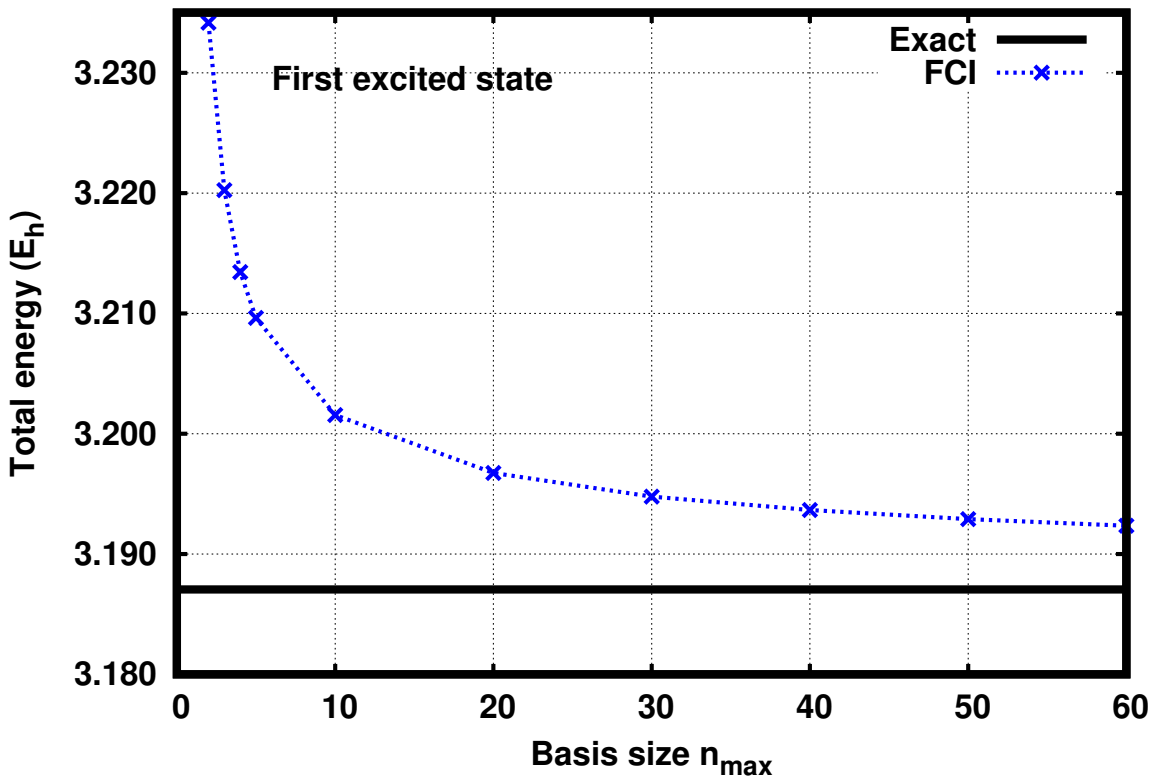


(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys **158**, 234107 (2023))

External potential and basis set

- External potential: $v_{\text{ne}}(x) = (1/2)\omega_0^2 x^2$
- Basis (Hermite-Gauss functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

First excited-state total energy:

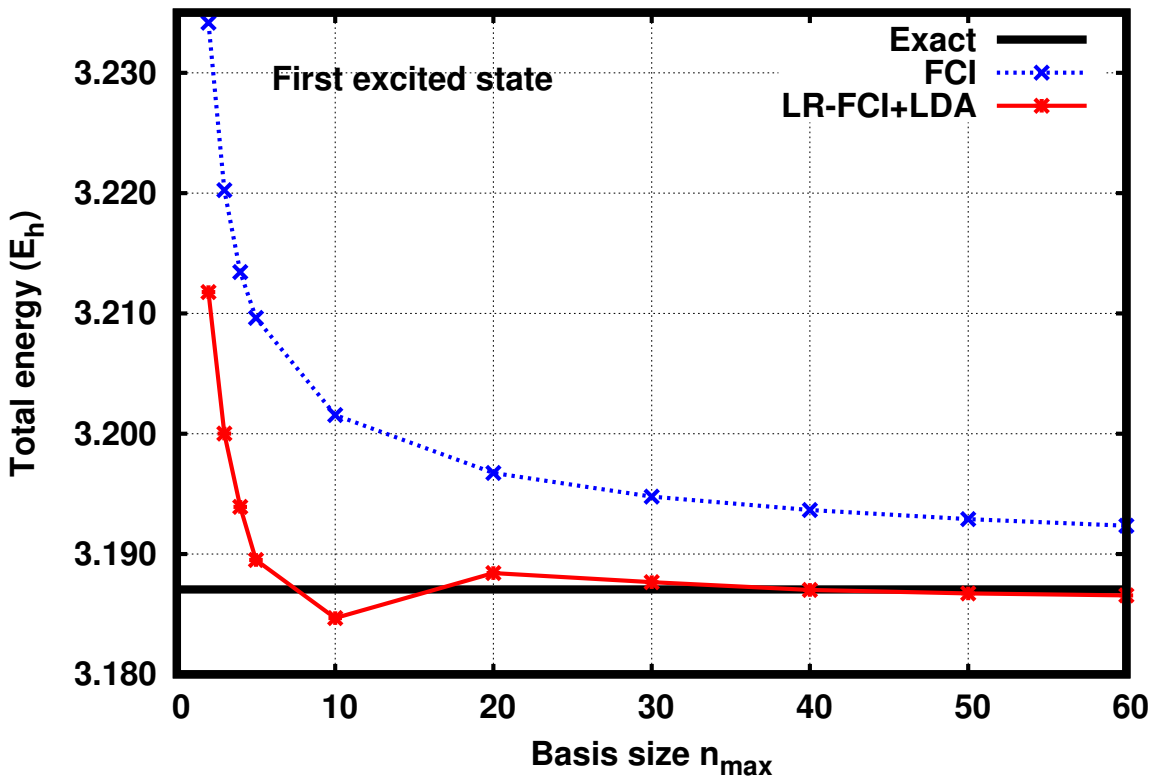


(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys **158**, 234107 (2023))

External potential and basis set

- External potential: $v_{\text{ne}}(x) = (1/2)\omega_0^2 x^2$
- Basis (Hermite-Gauss functions): $\chi_n(x) = N_n(\alpha) e^{-\alpha x^2} H_n(\sqrt{2\alpha}\, x)$

First excited-state total energy:



(D. Traore, E. Giner, J. Toulouse, J. Chem. Phys **158**, 234107 (2023))

Goal

Use a model system to ease methods development and understanding.

To do list:

- ✓ To reproduce the slow basis convergence of the ground-state energy.
- ✓ To reproduce the electron-electron cusp.
- ✓ Building a LDA correlation functional of the density.

- Understanding of the density-based basis set correction.
- Development of a strategy to apply density-based basis-set correction to excited-state energies.
- Dirac's equation with QED interactions (Timothee's talk)