Accelerating quantum-chemistry wave-function calculations with density-functional theory

Julien Toulouse
Laboratoire de Chimie Théorique
Sorbonne Université and **CNRS**, Paris, France

Fields Institute, Toronto, April 2019

www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_toronto_19.pdf

Outline

1. Quantum-chemistry wave-function methods
2. Long-range wave-function methods + short-range DFT
3. Wave-function methods + DFT basis correction

Outline

1. Quantum-chemistry wave-function methods
2. Long-range wave-function methods + short-range DFT
3. Wave-function methods + DFT basis correction

The quantum many-electron problem

- ***N*-electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The quantum many-electron problem

- N-**electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- We will only consider the **time-independent Schrödinger equation**:

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

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a **wave function** written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i \in \{\uparrow, \downarrow\}$), and E is the associated energy.

The quantum many-electron problem

- N-**electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- We will only consider the **time-independent Schrödinger equation**:

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

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a **wave function** written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i \in \{\uparrow, \downarrow\}$), and E is the associated energy.

- Because electrons are fermions, the wave function must be **antisymmetric** with respect to the exchange of two coordinates:

$$\Psi(..., \mathbf{x}_i, ..., \mathbf{x}_j, ...) = -\Psi(..., \mathbf{x}_j, ..., \mathbf{x}_i, ...)$$

The quantum many-electron problem

- ***N*-electron Hamiltonian** in the Born-Oppenheimer and non-relativistic approximations:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{\text{ne}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- We will only consider the **time-independent Schrödinger equation**:

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

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a **wave function** written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i \in \{\uparrow, \downarrow\}$), and E is the associated energy.

- Because electrons are fermions, the wave function must be **antisymmetric** with respect to the exchange of two coordinates:

$$\Psi(..., \mathbf{x}_i, ..., \mathbf{x}_j, ...) = -\Psi(..., \mathbf{x}_j, ..., \mathbf{x}_i, ...)$$

- The first quantity of interest is the **ground-state energy** E_0 which can be expressed with the **variational theorem** (using Dirac notations)

$$E_0 = \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle$$

where the wave-function space is $\mathcal{W} = \{\Psi \in \mathcal{H}^1_N \mid \|\Psi\|_2 = 1, \Psi \text{ antisymmetric}\}$.

Wave-function methods in a basis set

- In an **one-electron basis set** $\mathcal{B} = \{\chi_\nu\}_{\nu=1,M}$, we obtain the **full configuration interaction (FCI)** energy

$$E_{\mathrm{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \geq E_0$$

where $\mathcal{W}^{\mathcal{B}} = \{\Psi \in \bigwedge^N w^{\mathcal{B}} \mid \|\Psi\|_2 = 1\}$ where $\bigwedge^N w^{\mathcal{B}}$ is the N-fold antisymmetric tensor product of one-electron spaces $w^{\mathcal{B}} = \mathrm{span}(\mathcal{B})$.

Wave-function methods in a basis set

- In an **one-electron basis set** $\mathcal{B} = \{\chi_\nu\}_{\nu=1,M}$, we obtain the **full configuration interaction (FCI)** energy

$$E_{\text{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle \geq E_0$$

where $\mathcal{W}^{\mathcal{B}} = \{\Psi \in \bigwedge^N w^{\mathcal{B}} \mid \|\Psi\|_2 = 1\}$ where $\bigwedge^N w^{\mathcal{B}}$ is the N-fold antisymmetric tensor product of one-electron spaces $w^{\mathcal{B}} = \text{span}(\mathcal{B})$.

- A wave function $\Psi \in \mathcal{W}^{\mathcal{B}}$ can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}} \Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

where $\Phi_{\mathbf{I}}$ are **determinants of orthonormal spin-orbitals**

$$\Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \psi_{\mathrm{I}_1}(\mathbf{x}_1) \wedge \psi_{\mathrm{I}_2}(\mathbf{x}_2) \wedge ... \wedge \psi_{\mathrm{I}_N}(\mathbf{x}_N)$$

and the spin-orbitals are expanded on the basis

$$\psi_i(\mathbf{x}) = \sum_{\nu=1}^{M} c_{\nu,i}\, \chi_\nu(\mathbf{x})$$

with nucleus-centered basis functions: $\chi_\nu(\mathbf{x}) \propto r^{\ell_\nu} e^{-\alpha_\nu r^2} Y_{\ell_\nu}^{m_\nu}(\theta, \phi) \delta_{\sigma_\nu, \sigma}$.

Wave-function methods in a basis set

- In an **one-electron basis set** $\mathcal{B} = \{\chi_\nu\}_{\nu=1,M}$, we obtain the **full configuration interaction (FCI)** energy

$$E_{\text{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle \geq E_0$$

where $\mathcal{W}^{\mathcal{B}} = \{\Psi \in \bigwedge^N w^{\mathcal{B}} \mid \|\Psi\|_2 = 1\}$ where $\bigwedge^N w^{\mathcal{B}}$ is the N-fold antisymmetric tensor product of one-electron spaces $w^{\mathcal{B}} = \text{span}(\mathcal{B})$.

- A wave function $\Psi \in \mathcal{W}^{\mathcal{B}}$ can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}} \Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

where $\Phi_{\mathbf{I}}$ are **determinants of orthonormal spin-orbitals**

$$\Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \psi_{\mathrm{I}_1}(\mathbf{x}_1) \wedge \psi_{\mathrm{I}_2}(\mathbf{x}_2) \wedge ... \wedge \psi_{\mathrm{I}_N}(\mathbf{x}_N)$$

and the spin-orbitals are expanded on the basis

$$\psi_i(\mathbf{x}) = \sum_{\nu=1}^{M} c_{\nu,i}\, \chi_\nu(\mathbf{x})$$

with nucleus-centered basis functions: $\chi_\nu(\mathbf{x}) \propto r^{\ell_\nu} e^{-\alpha_\nu r^2} Y_{\ell_\nu}^{m_\nu}(\theta, \phi) \delta_{\sigma_\nu, \sigma}$.

- The total number of determinants is: $N_{\text{det}}^{\text{FCI}} = \binom{M}{N} = \mathcal{O}\left(M^N\right)$

Wave-function methods in a basis set

- In an **one-electron basis set** $\mathcal{B} = \{\chi_\nu\}_{\nu=1,M}$, we obtain the **full configuration interaction (FCI)** energy

$$E_{\text{FCI}}^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle \geq E_0$$

where $\mathcal{W}^{\mathcal{B}} = \{\Psi \in \bigwedge^N w^{\mathcal{B}} \mid \|\Psi\|_2 = 1\}$ where $\bigwedge^N w^{\mathcal{B}}$ is the N-fold antisymmetric tensor product of one-electron spaces $w^{\mathcal{B}} = \text{span}(\mathcal{B})$.

- A wave function $\Psi \in \mathcal{W}^{\mathcal{B}}$ can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}} \Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

where $\Phi_{\mathbf{I}}$ are **determinants of orthonormal spin-orbitals**

$$\Phi_{\mathbf{I}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \psi_{\mathrm{I}_1}(\mathbf{x}_1) \wedge \psi_{\mathrm{I}_2}(\mathbf{x}_2) \wedge ... \wedge \psi_{\mathrm{I}_N}(\mathbf{x}_N)$$

and the spin-orbitals are expanded on the basis

$$\psi_i(\mathbf{x}) = \sum_{\nu=1}^{M} c_{\nu,i}\, \chi_\nu(\mathbf{x})$$

with nucleus-centered basis functions: $\chi_\nu(\mathbf{x}) \propto r^{\ell_\nu} e^{-\alpha_\nu r^2} Y_{\ell_\nu}^{m_\nu}(\theta, \phi) \delta_{\sigma_\nu, \sigma}$.

- The total number of determinants is: $N_{\text{det}}^{\text{FCI}} = \binom{M}{N} = \mathcal{O}\left(M^N\right)$
- We must extrapolate to the **complete basis set (CBS)** limit $M \to \infty$.

Convergence of FCI with respect to the basis set

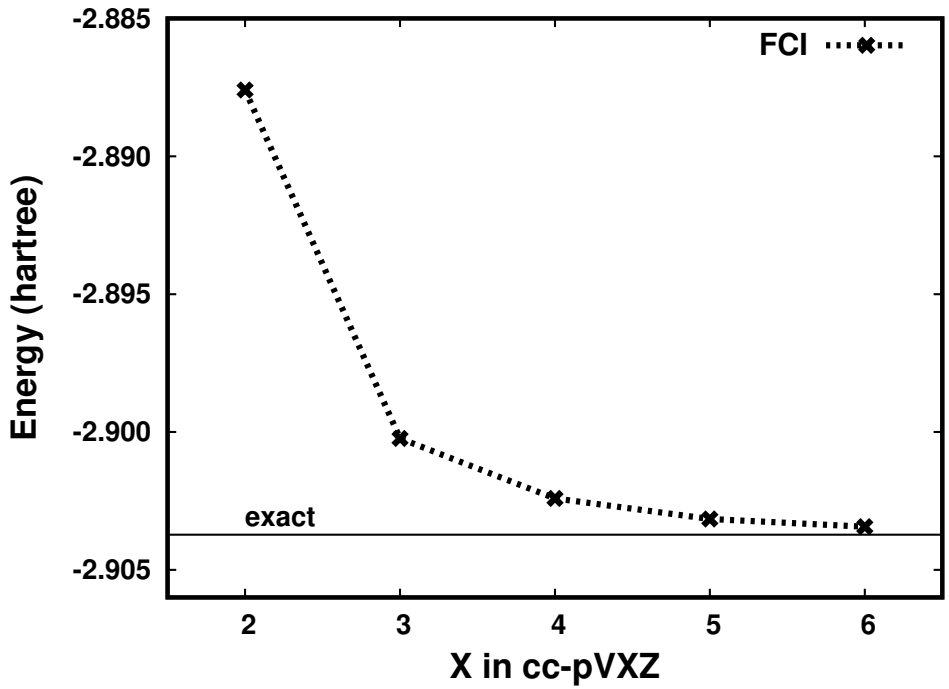
- Example of He atom ($N = 2$) with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":

X (# shells)	2	3	4	5	6
functions	2s,1p	3s,2p,1d	4s,3p,2d,1f	5s,4p,3d,2f,1g	6s,5p,4d,3f,2g,1h
$M = \mathcal{O}(X^3)$	10	28	60	110	182
$N_{\text{det}}^{\text{FCI}} = \binom{M}{N}$	45	378	1770	5996	16471

Convergence of FCI with respect to the basis set

- Example of He atom ($N = 2$) with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":

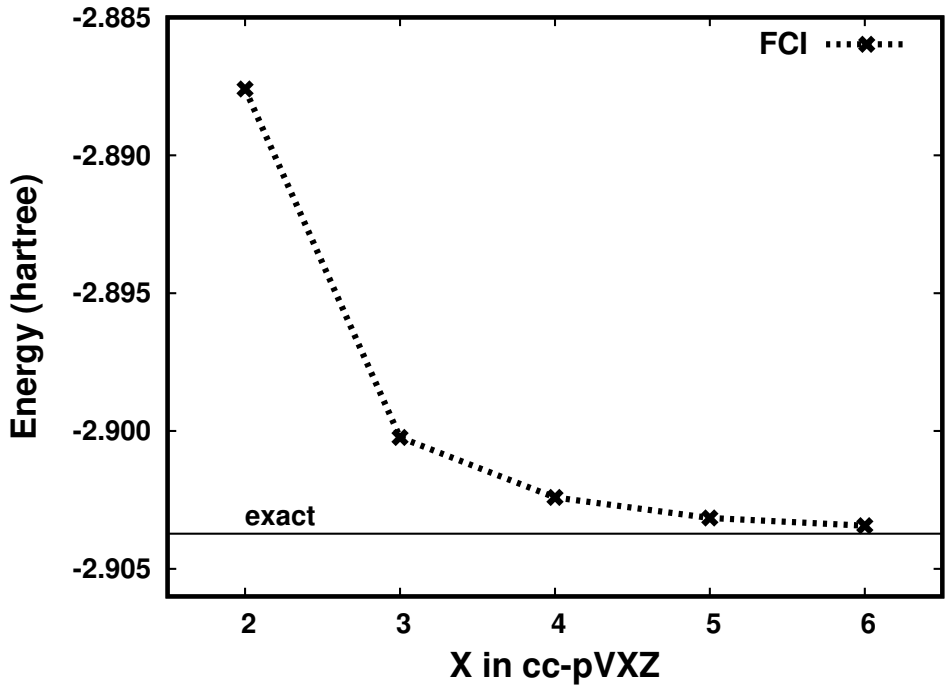
X (# shells)	2	3	4	5	6
functions	2s,1p	3s,2p,1d	4s,3p,2d,1f	5s,4p,3d,2f,1g	6s,5p,4d,3f,2g,1h
$M = \mathcal{O}(X^3)$	10	28	60	110	182
$N_{\text{det}}^{\text{FCI}} = \binom{M}{N}$	45	378	1770	5996	16471



Convergence of FCI with respect to the basis set

- Example of He atom ($N = 2$) with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":

X (# shells)	2	3	4	5	6
functions	2s,1p	3s,2p,1d	4s,3p,2d,1f	5s,4p,3d,2f,1g	6s,5p,4d,3f,2g,1h
$M = \mathcal{O}(X^3)$	10	28	60	110	182
$N_{\text{det}}^{\text{FCI}} = \binom{M}{N}$	45	378	1770	5996	16471



- Theoretical and empirical considerations indicate an **inverse cubic-law convergence**:

$$E_{\text{FCI}}^{X} = E_{\text{FCI}}^{\text{CBS}} + c\, X^{-3}$$

Origin of the slow basis-set convergence

- The exact wave function as a **cusp** as the distance between two opposite-spin electrons goes to zero, $r_{12} \to 0$,

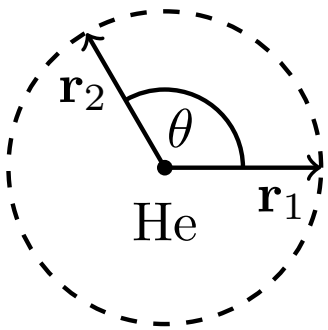
$$\Psi(r_{12}) = \Psi(0)\left[1 + \frac{r_{12}}{2} + \mathcal{O}(r_{12}^2)\right]$$

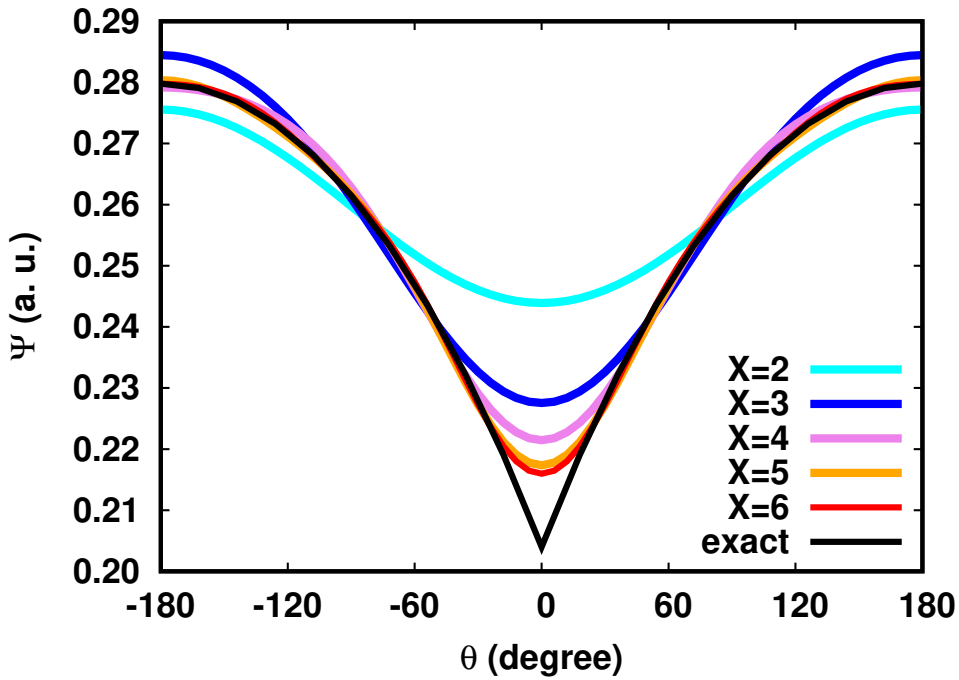
Origin of the slow basis-set convergence

- The exact wave function as a **cusp** as the distance between two opposite-spin electrons goes to zero, $r_{12} \to 0$,

$$\Psi(r_{12}) = \Psi(0)\left[1 + \frac{r_{12}}{2} + \mathcal{O}(r_{12}^2)\right]$$

- Example of He atom with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":



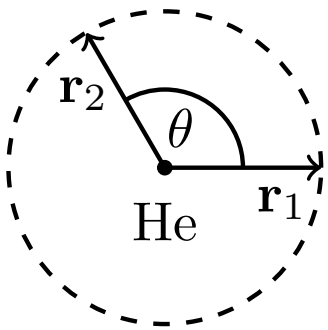


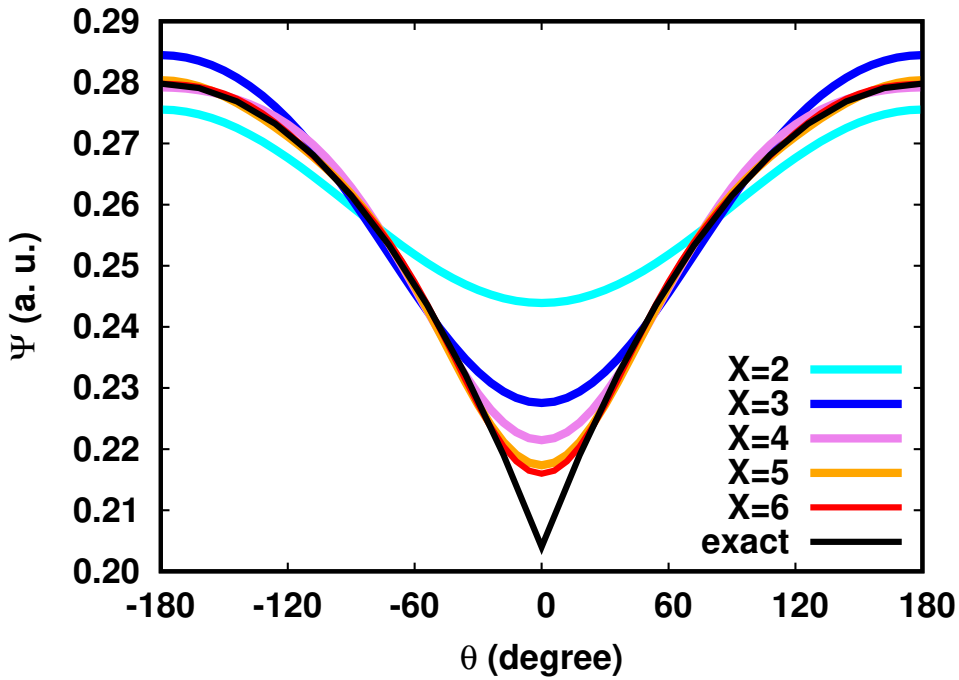
Origin of the slow basis-set convergence

- The exact wave function as a **cusp** as the distance between two opposite-spin electrons goes to zero, $r_{12} \to 0$,

$$\Psi(r_{12}) = \Psi(0)\left[1 + \frac{r_{12}}{2} + \mathcal{O}(r_{12}^2)\right]$$

- Example of He atom with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":





- **We would like to accelerate the convergence with respect to the basis set.**

Approaching FCI: selected configuration interaction (SCI)

- In practice, for most systems, even with a basis set of modest size, the number of determinants in the FCI space is too large!

Approaching FCI: selected configuration interaction (SCI)

- In practice, for most systems, even with a basis set of modest size, the number of determinants in the FCI space is too large!

- We can approach the FCI by a **selected configuration interaction (SCI) algorithm**:

  1. calculate initial wave function with a **subset $\mathcal{S}$** of determinants:

$$\Psi_0 = \sum_{\mathbf{I} \in \mathcal{S}} c_{\mathbf{I}} \Phi_{\mathbf{I}}$$

  2. expand subset $\mathcal{S}$ by **selecting determinants** $\{\Phi_K\}$ with largest second-order perturbative corrections:

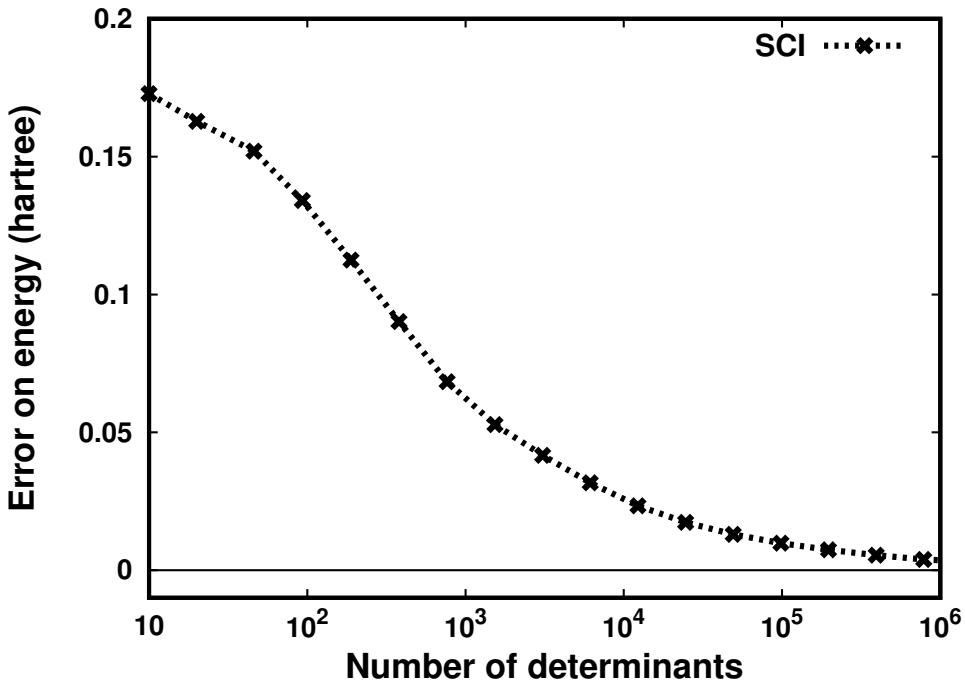
$$E_K^{(2)} = -\frac{|\langle \Phi_K | \hat{H} | \Psi_0 \rangle|^2}{\langle \Phi_K | \hat{H} | \Phi_K \rangle - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle}$$

  3. calculate new wave function Ψ_0 in larger $\mathcal{S}$ and iterate until $|\sum_K E_K^{(2)}| <$ threshold

Convergence of SCI with respect to the number of determinants

- Example of Be_2 molecule ($N = 8$) with basis set $\mathcal{B}$ = "aug-cc-pCVTZ" ($M = 236$)

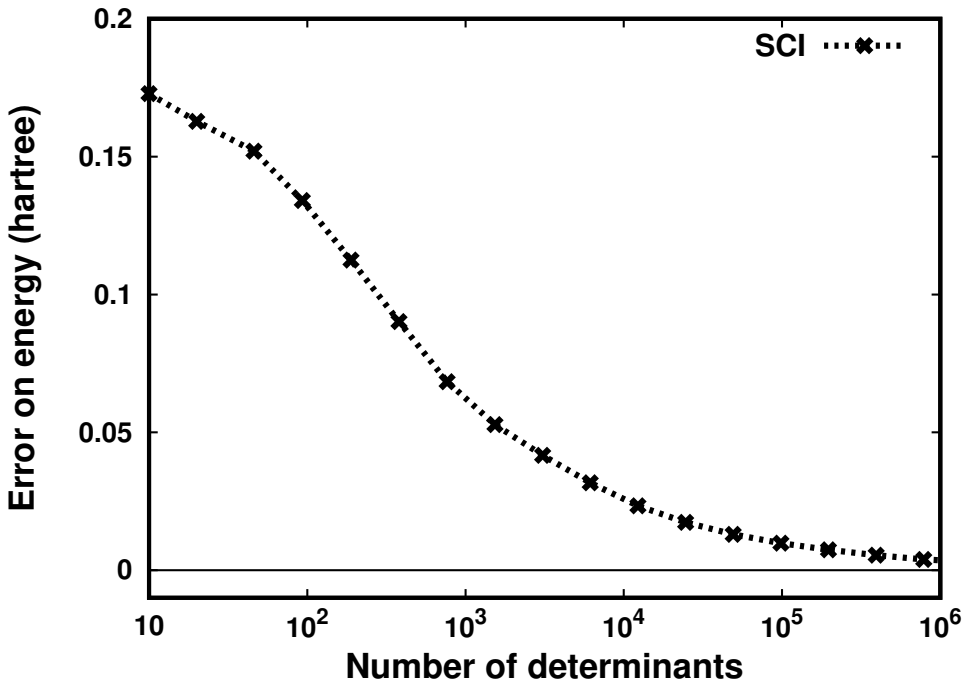
$$\Longrightarrow N_{\text{det}}^{\text{FCI}} = \binom{M}{N} \approx 10^{14} \quad \text{(without symmetry)}$$



Convergence of SCI with respect to the number of determinants

- Example of Be_2 molecule ($N = 8$) with basis set $\mathcal{B}$ = "aug-cc-pCVTZ" ($M = 236$)

$$\Longrightarrow N_{\text{det}}^{\text{FCI}} = \binom{M}{N} \approx 10^{14} \quad \text{(without symmetry)}$$



- **We would like to accelerate the convergence with respect to the number of determinants.**

Outline

1. Quantum-chemistry wave-function methods

2. Long-range wave-function methods + short-range DFT

   with Anthony Ferté and Emmanuel Giner

3. Wave-function methods + DFT basis correction

Standard density-functional theory (DFT)

- The ground-state energy can be rewritten via the **constrained-search** approach:

$$E_0 = \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle$$

Standard density-functional theory (DFT)

- The ground-state energy can be rewritten via the **constrained-search** approach:

$$
\begin{aligned}
E_0 &= \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \\
&= \min_{n \in \mathcal{D}} \left\{ \min_{\Psi \in \mathcal{W}_n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\}
\end{aligned}
$$

Standard density-functional theory (DFT)

- The ground-state energy can be rewritten via the **constrained-search** approach:

$$
\begin{aligned}
E_0 &= \min_{\Psi \in \mathcal{W}} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \\
&= \min_{n \in \mathcal{D}} \left\{ \min_{\Psi \in \mathcal{W}_n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\} \\
&= \min_{n \in \mathcal{D}} \left\{ F[n] + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\}
\end{aligned}
$$

Standard density-functional theory (DFT)

- The ground-state energy can be rewritten via the **constrained-search** approach:

$$
\begin{aligned}
E_0 &= \min_{\Psi\in\mathcal{W}} \langle\Psi|\hat{T}+\hat{V}_{\text{ne}}+\hat{W}_{\text{ee}}|\Psi\rangle \\
&= \min_{n\in\mathcal{D}}\left\{\min_{\Psi\in\mathcal{W}_n}\langle\Psi|\hat{T}+\hat{W}_{\text{ee}}|\Psi\rangle+\int v_{\text{ne}}(\mathbf{r})n(\mathbf{x})\mathrm{d}\mathbf{x}\right\} \\
&= \min_{n\in\mathcal{D}}\left\{F[n]+\int v_{\text{ne}}(\mathbf{r})n(\mathbf{x})\mathrm{d}\mathbf{x}\right\}
\end{aligned}
$$

- $\mathcal{W}_n$ is the space of wave functions giving a fixed density $n(\mathbf{x})$

$$\mathcal{W}_n = \{\Psi\in\mathcal{W} \mid \forall\,\mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x})\}$$

with

$$n_\Psi(\mathbf{x}_1) = N\int|\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2\mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N$$

Standard density-functional theory (DFT)

- The ground-state energy can be rewritten via the **constrained-search** approach:

$$\begin{aligned} E_0 &= \min_{\Psi\in\mathcal{W}} \langle\Psi|\hat{T}+\hat{V}_{\text{ne}}+\hat{W}_{\text{ee}}|\Psi\rangle \\ &= \min_{n\in\mathcal{D}}\left\{\min_{\Psi\in\mathcal{W}_n}\langle\Psi|\hat{T}+\hat{W}_{\text{ee}}|\Psi\rangle + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{x})\mathrm{d}\mathbf{x}\right\} \\ &= \min_{n\in\mathcal{D}}\left\{F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{x})\mathrm{d}\mathbf{x}\right\} \end{aligned}$$

- $\mathcal{W}_n$ is the space of wave functions giving a fixed density $n(\mathbf{x})$

$$\mathcal{W}_n = \{\Psi\in\mathcal{W} \mid \forall\,\mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x})\}$$

with

$$n_\Psi(\mathbf{x}_1) = N\int |\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2 \mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N$$

- $\mathcal{D}$ is the space of N-representable densities

$$\begin{aligned} \mathcal{D} &= \{n \mid \exists\Psi\in\mathcal{W} \text{ s.t. } \forall\,\mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x})\} \\ &= \{n\in\mathcal{L}^1 \mid n\geq 0, \int n(\mathbf{x})\mathrm{d}\mathbf{x} = N,\ n^{1/2}\in\mathcal{H}^1_1\} \end{aligned}$$

Long-range wave-function methods + short-range DFT

- We decomposition of the **universal density functional** $F[n]$ as

$$F[n] = \min_{\Psi \in \mathcal{W}_n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n]$$

where $\hat{W}_{\text{ee}}^{\text{lr}}$ is a **non-divergent long-range electron-electron interaction** and $E_{\text{Hxc}}^{\text{sr}}[n]$ is the **complementary short-range Hartree-exchange-correlation density functional**.

Long-range wave-function methods + short-range DFT

- We decomposition of the **universal density functional** $F[n]$ as

$$F[n] = \min_{\Psi \in \mathcal{W}_n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n]$$

where $\hat{W}_{\text{ee}}^{\text{lr}}$ is a **non-divergent long-range electron-electron interaction** and $E_{\text{Hxc}}^{\text{sr}}[n]$ is the **complementary short-range Hartree-exchange-correlation density functional**.

- The **exact ground-state energy** can thus be written as

$$E_0 = \min_{\Psi \in \mathcal{W}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_\Psi] \right\}$$

Long-range wave-function methods + short-range DFT

- We decomposition of the **universal density functional** $F[n]$ as

$$F[n] = \min_{\Psi \in \mathcal{W}_n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n]$$

where $\hat{W}_{\text{ee}}^{\text{lr}}$ is a **non-divergent long-range electron-electron interaction** and $E_{\text{Hxc}}^{\text{sr}}[n]$ is the **complementary short-range Hartree-exchange-correlation density functional**.

- The **exact ground-state energy** can thus be written as

$$E_0 = \min_{\Psi \in \mathcal{W}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_\Psi] \right\}$$

- The minimizing wave function Ψ^{lr} is an **effective multideterminant wave function** satisfying the nonlinear Schrödinger equation

$$\left(\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} + \hat{V}_{\text{Hxc}}^{\text{sr}}[n_{\Psi^{\text{lr}}}] \right) |\Psi^{\text{lr}}\rangle = \mathcal{E}^{\text{lr}} |\Psi^{\text{lr}}\rangle$$

where $V_{\text{Hxc}}^{\text{sr}}[n] = \sum_{i=1}^{N} \frac{\delta E_{\text{Hxc}}^{\text{sr}}[n]}{\delta n(\mathbf{x}_i)}$ is a short-range effective one-electron potential.

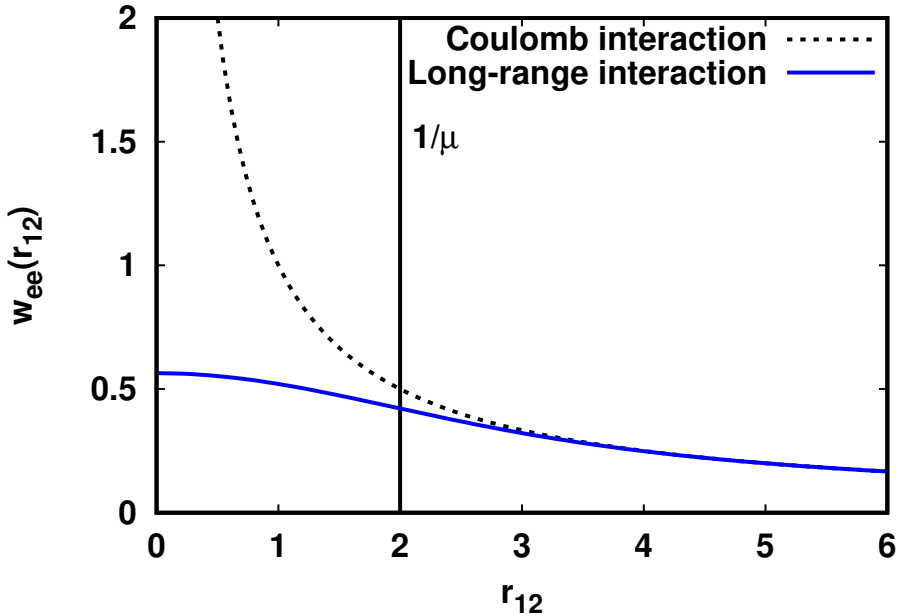
Choice of the long-range electron-electron interaction

- A convenient form of **non-divergent long-range electron-electron interaction** is

$$W_{ee}^{lr,\mu} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} w_{ee}^{lr,\mu}(r_{ij})$$

with $$w_{ee}^{lr,\mu}(r_{12}) = \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}}$$

and the range-separation parameter μ



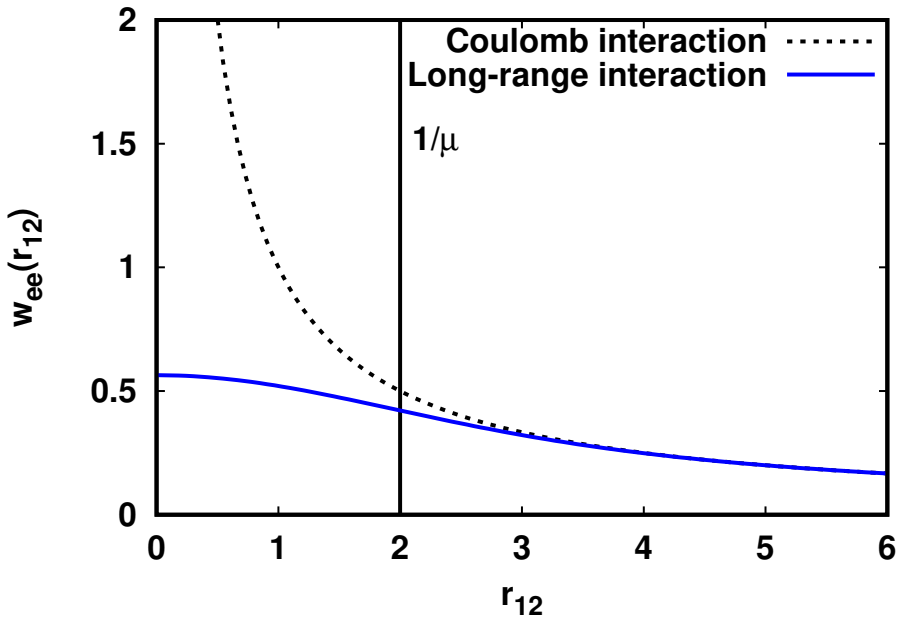
Choice of the long-range electron-electron interaction

- A convenient form of **non-divergent long-range electron-electron interaction** is

$$W_{ee}^{lr,\mu} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} w_{ee}^{lr,\mu}(r_{ij})$$

with $$w_{ee}^{lr,\mu}(r_{12}) = \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}}$$

and the range-separation parameter μ



- With Gaussian basis sets, this interaction gives integrals that can be easily calculated exactly.

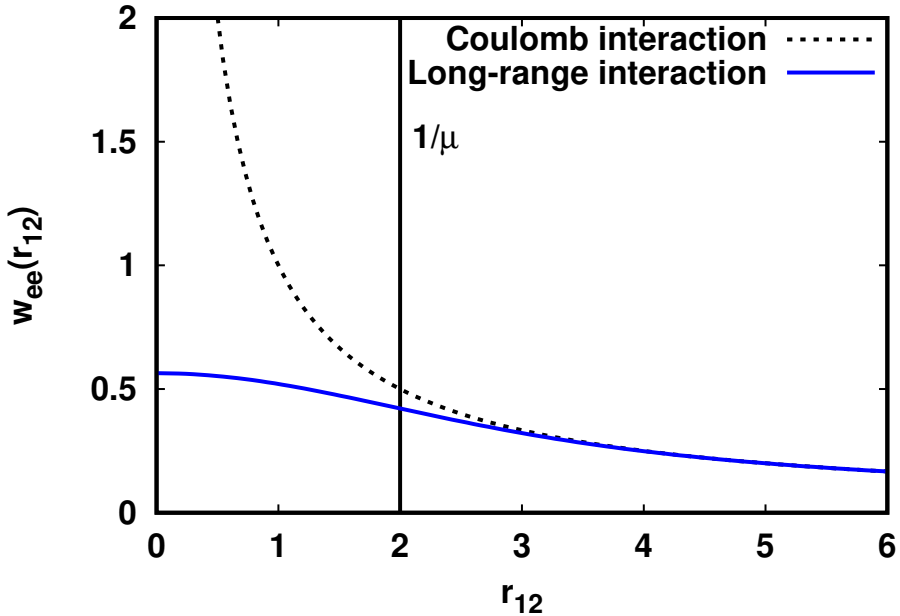
Choice of the long-range electron-electron interaction

- A convenient form of **non-divergent long-range electron-electron interaction** is

$$W_{ee}^{lr,\mu} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} w_{ee}^{lr,\mu}(r_{ij})$$

with $$w_{ee}^{lr,\mu}(r_{12}) = \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}}$$

and the range-separation parameter μ



- With Gaussian basis sets, this interaction gives integrals that can be easily calculated exactly.

- For $\mu = 0$, the interaction vanishes: $w_{ee}^{lr,\mu=0}(r_{12}) = 0$.
  For $\mu \to \infty$, we recover the Coulomb interaction: $w_{ee}^{lr,\mu\to\infty}(r_{12}) = 1/r_{12}$.

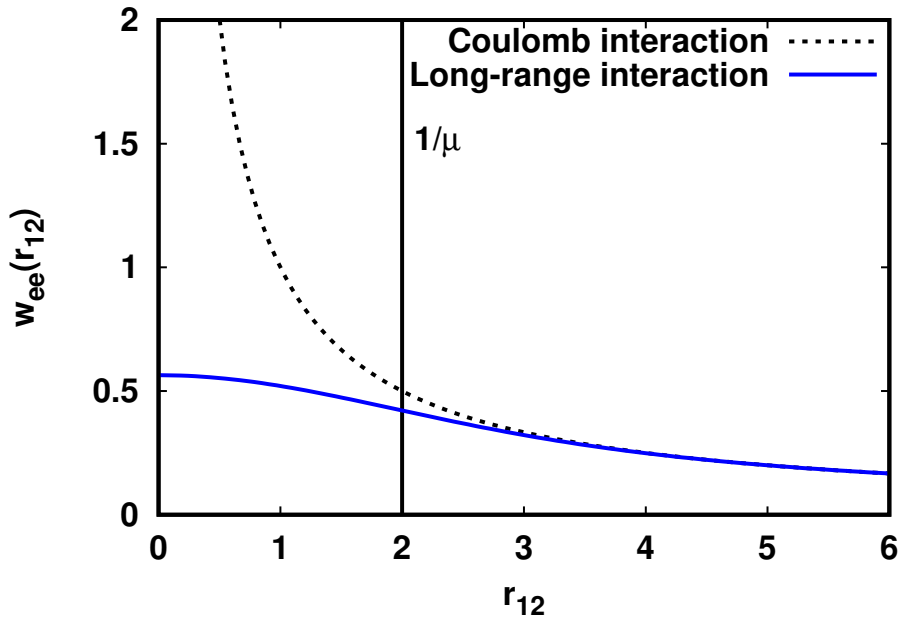
Choice of the long-range electron-electron interaction

- A convenient form of **non-divergent long-range electron-electron interaction** is

$$W_{ee}^{lr,\mu} = \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} w_{ee}^{lr,\mu}(r_{ij})$$

with $$w_{ee}^{lr,\mu}(r_{12}) = \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}}$$

and the range-separation parameter μ



- With Gaussian basis sets, this interaction gives integrals that can be easily calculated exactly.

- For $\mu = 0$, the interaction vanishes: $w_{ee}^{lr,\mu=0}(r_{12}) = 0$.
  For $\mu \to \infty$, we recover the Coulomb interaction: $w_{ee}^{lr,\mu\to\infty}(r_{12}) = 1/r_{12}$.

- In practice, we use a **range-separation parameter of** $\mu = 0.5$ **bohr**$^{-1}$, which is of the order of the inverse distance between electrons in valence regions of molecules.

The complementary short-range density functional

- The short-range Hartree-exchange-correlation energy can be written as

$$E_{\rm Hxc}^{\rm sr,\mu}[n] = \frac{1}{2}\int_{\mu}^{+\infty} {\rm d}\tilde{\mu} \iint n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)\frac{\partial w_{\rm ee}^{\rm lr,\tilde{\mu}}(r_{12})}{\partial\tilde{\mu}}{\rm d}\mathbf{x}_1{\rm d}\mathbf{x}_2$$

where $n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)$ is the **pair density** associated with the wave function $\Psi^{\rm lr,\tilde{\mu}}$

$$n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2) = N(N-1)\int |\Psi^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)|^2 {\rm d}\mathbf{x}_3...{\rm d}\mathbf{x}_N$$

The complementary short-range density functional

- The short-range Hartree-exchange-correlation energy can be written as

$$E_{\rm Hxc}^{\rm sr,\mu}[n] = \frac{1}{2}\int_{\mu}^{+\infty} {\rm d}\tilde{\mu} \iint n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)\frac{\partial w_{\rm ee}^{\rm lr,\tilde{\mu}}(r_{12})}{\partial\tilde{\mu}}{\rm d}\mathbf{x}_1{\rm d}\mathbf{x}_2$$

where $n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)$ is the **pair density** associated with the wave function $\Psi^{\rm lr,\tilde{\mu}}$

$$n_2^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2) = N(N-1)\int |\Psi^{\rm lr,\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)|^2 {\rm d}\mathbf{x}_3...{\rm d}\mathbf{x}_N$$

- In practice, we decompose it into **Hartree** and **exchange-correlation** contributions:

$$E_{\rm Hxc}^{\rm sr,\mu}[n] = E_{\rm H}^{\rm sr,\mu}[n] + E_{\rm xc}^{\rm sr,\mu}[n]$$

where $E_{\rm H}^{\rm sr,\mu}[n] = (1/2)\iint n(\mathbf{x}_1)n(\mathbf{x}_2)w_{\rm ee}^{\rm sr,\mu}(r_{12}){\rm d}\mathbf{x}_1{\rm d}\mathbf{x}_2$ is calculated exactly

The complementary short-range density functional

- The short-range Hartree-exchange-correlation energy can be written as

$$E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n] = \frac{1}{2}\int_{\mu}^{+\infty} \mathrm{d}\tilde{\mu} \iint n_2^{\mathrm{lr},\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)\frac{\partial w_{\mathrm{ee}}^{\mathrm{lr},\tilde{\mu}}(r_{12})}{\partial\tilde{\mu}}\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2$$

where $n_2^{\mathrm{lr},\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2)$ is the **pair density** associated with the wave function $\Psi^{\mathrm{lr},\tilde{\mu}}$

$$n_2^{\mathrm{lr},\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2) = N(N-1)\int |\Psi^{\mathrm{lr},\tilde{\mu}}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2 \mathrm{d}\mathbf{x}_3\ldots\mathrm{d}\mathbf{x}_N$$

- In practice, we decompose it into **Hartree** and **exchange-correlation** contributions:

$$E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n] = E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] + E_{\mathrm{xc}}^{\mathrm{sr},\mu}[n]$$

where $E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] = (1/2)\iint n(\mathbf{x}_1)n(\mathbf{x}_2)w_{\mathrm{ee}}^{\mathrm{sr},\mu}(r_{12})\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2$ is calculated exactly

- and we use a **semilocal density-functional approximation (DFA)** for $E_{\mathrm{xc}}^{\mathrm{sr},\mu}[n]$:

$$E_{\mathrm{xc,DFA}}^{\mathrm{sr},\mu}[n] = \int e_{\mathrm{xc}}^{\mathrm{sr},\mu}(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}}\, n(\mathbf{x}))\, \mathrm{d}\mathbf{r}$$

where $e_{\mathrm{xc}}^{\mathrm{sr},\mu}$ is constructed based on an uniform electron gas with modified interaction and exact constraints.

Using a basis set and selected configuration interaction

- In a basis set, we obtain the approximate lrFCI+srDFA energy

$$E^{\mathcal{B}}_{\text{lrFCI+srDFA}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}^{\text{lr},\mu}_{\text{ee}} | \Psi \rangle + E^{\text{sr},\mu}_{\text{H}}[n_\Psi] + E^{\text{sr},\mu}_{\text{xc,DFA}}[n_\Psi] \right\}$$

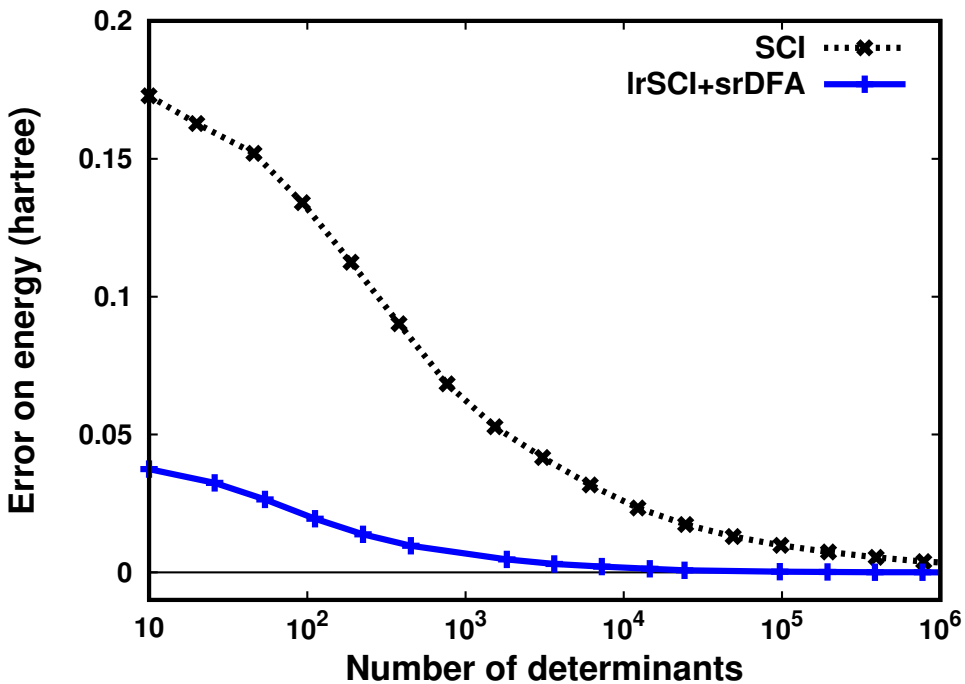
Using a basis set and selected configuration interaction

- In a basis set, we obtain the approximate lrFCI+srDFA energy

$$E^{\mathcal{B}}_{\text{lrFCI+srDFA}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}^{\text{lr},\mu}_{\text{ee}} | \Psi \rangle + E^{\text{sr},\mu}_{\text{H}}[n_\Psi] + E^{\text{sr},\mu}_{\text{xc,DFA}}[n_\Psi] \right\}$$

- We can systematically approach the lrFCI+srDFA energy by using an adapted selected configuration-interaction agorithm, referred to as lrSCI+srDFA.

  Example of Be_2 molecule ($N = 8$) with basis set $\mathcal{B}$ = "aug-cc-pCVTZ" ($M = 236$)



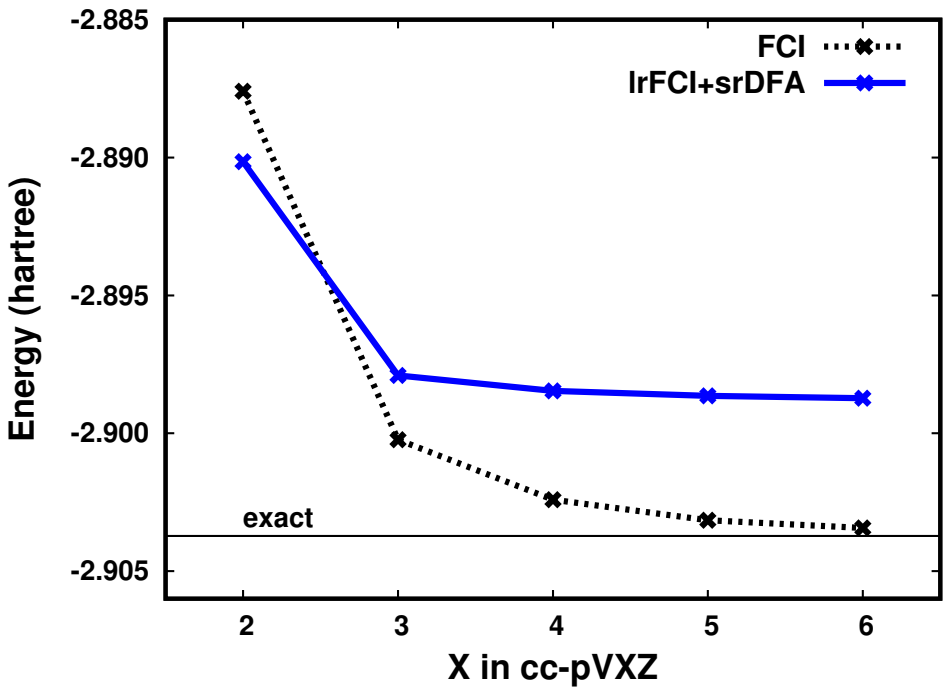
$\Longrightarrow$ **Much faster convergence of lrSCI+srDFA with the number of determinants.**

Convergence with respect to the basis set

- The long-range wave function **does not have an electron-electron cusp**:

$$\Psi^{\mathrm{lr},\mu}(r_{12}) = \Psi^{\mathrm{lr},\mu}(0)\left[1 + \frac{\mu r_{12}^2}{3\sqrt{\pi}} + \mathcal{O}(r_{12}^4)\right]$$

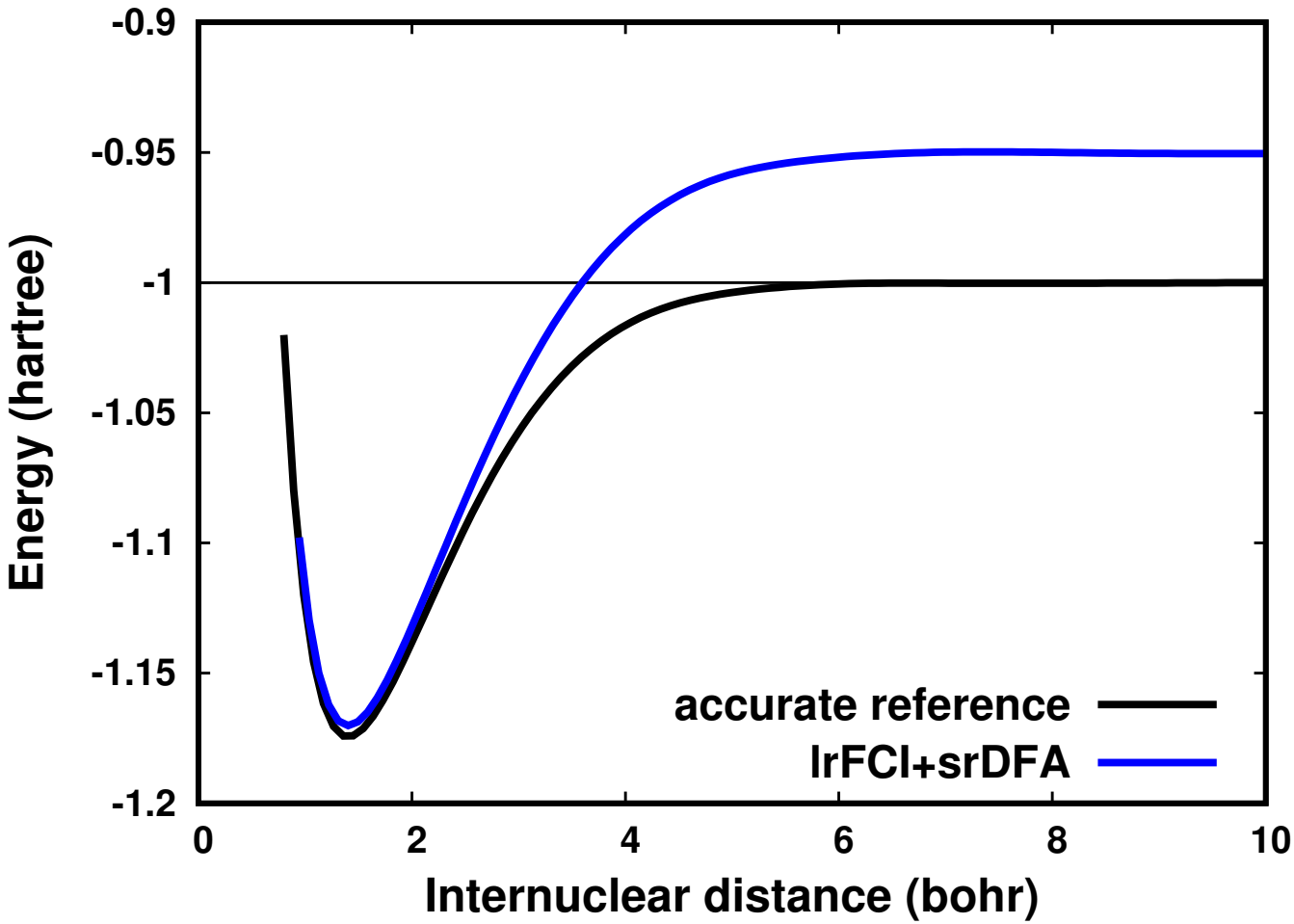
- Example of He atom ($N = 2$) with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":



$\Longrightarrow$ **Exponential basis-set convergence but there is an error coming from the short-range density-functional approximation.**

Dissociation of H_2 molecule

with cc-pVTZ basis set



$\Longrightarrow$ **lrFCI+srDFA is accurate at the equilibrium distance but gives a large error at dissociation.**

An alternative non-variational energy expression

- An alternative **non-variational expression** for the exact ground-state energy is

$$E_0 = \langle \Psi^{\mathrm{lr},\mu} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi^{\mathrm{lr},\mu} \rangle + E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$$

where $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ is a short-range correlation energy with respect to the long-range **multideterminant (md)** wave function $\Psi^{\mathrm{lr},\mu}$.

An alternative non-variational energy expression

- An alternative **non-variational expression** for the exact ground-state energy is

$$E_0 = \langle \Psi^{\mathrm{lr},\mu} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi^{\mathrm{lr},\mu} \rangle + E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$$

where $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ is a short-range correlation energy with respect to the long-range **multideterminant (md)** wave function $\Psi^{\mathrm{lr},\mu}$.

- In the limit $\mu \to \infty$, $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ becomes a local functional of the **on-top pair density** $n_2(\mathbf{r},\mathbf{r}) = n_2(\mathbf{r}\uparrow,\mathbf{r}\downarrow) + n_2(\mathbf{r}\downarrow,\mathbf{r}\uparrow)$

$$E_{\mathrm{c,md}}^{\mathrm{sr},\mu} = \frac{2\sqrt{\pi}(1-\sqrt{2})}{3\mu^3} \int n_2(\mathbf{r},\mathbf{r}) \mathrm{d}\mathbf{r} + \mathcal{O}\left(\frac{1}{\mu^4}\right)$$

An alternative non-variational energy expression

- An alternative **non-variational expression** for the exact ground-state energy is

$$E_0 = \langle \Psi^{\mathrm{lr},\mu} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi^{\mathrm{lr},\mu} \rangle + E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$$

  where $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ is a short-range correlation energy with respect to the long-range **multideterminant (md)** wave function $\Psi^{\mathrm{lr},\mu}$.

- In the limit $\mu \to \infty$, $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ becomes a local functional of the **on-top pair density** $n_2(\mathbf{r},\mathbf{r}) = n_2(\mathbf{r}\uparrow,\mathbf{r}\downarrow) + n_2(\mathbf{r}\downarrow,\mathbf{r}\uparrow)$

$$E_{\mathrm{c,md}}^{\mathrm{sr},\mu} = \frac{2\sqrt{\pi}(1-\sqrt{2})}{3\mu^3} \int n_2(\mathbf{r},\mathbf{r}) \mathrm{d}\mathbf{r} + \mathcal{O}\left(\frac{1}{\mu^4}\right)$$

- Based on this, we propose a **semilocal pair-density functional approximation (PDFA)**

$$E_{\mathrm{c,md,PDFA}}^{\mathrm{sr},\mu} = \int e_{\mathrm{c,md}}^{\mathrm{sr},\mu}(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x}), n_2(\mathbf{r},\mathbf{r})) \mathrm{d}\mathbf{r}$$

An alternative non-variational energy expression

- An alternative **non-variational expression** for the exact ground-state energy is

$$E_0 = \langle \Psi^{\mathrm{lr},\mu} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi^{\mathrm{lr},\mu} \rangle + E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$$

where $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ is a short-range correlation energy with respect to the long-range **multideterminant (md)** wave function $\Psi^{\mathrm{lr},\mu}$.

- In the limit $\mu \to \infty$, $E_{\mathrm{c,md}}^{\mathrm{sr},\mu}$ becomes a local functional of the **on-top pair density** $n_2(\mathbf{r},\mathbf{r}) = n_2(\mathbf{r}\uparrow,\mathbf{r}\downarrow) + n_2(\mathbf{r}\downarrow,\mathbf{r}\uparrow)$

$$E_{\mathrm{c,md}}^{\mathrm{sr},\mu} = \frac{2\sqrt{\pi}(1-\sqrt{2})}{3\mu^3} \int n_2(\mathbf{r},\mathbf{r}) \mathrm{d}\mathbf{r} + \mathcal{O}\left(\frac{1}{\mu^4}\right)$$

- Based on this, we propose a **semilocal pair-density functional approximation (PDFA)**

$$E_{\mathrm{c,md,PDFA}}^{\mathrm{sr},\mu} = \int e_{\mathrm{c,md}}^{\mathrm{sr},\mu}(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x}), n_2(\mathbf{r},\mathbf{r})) \mathrm{d}\mathbf{r}$$

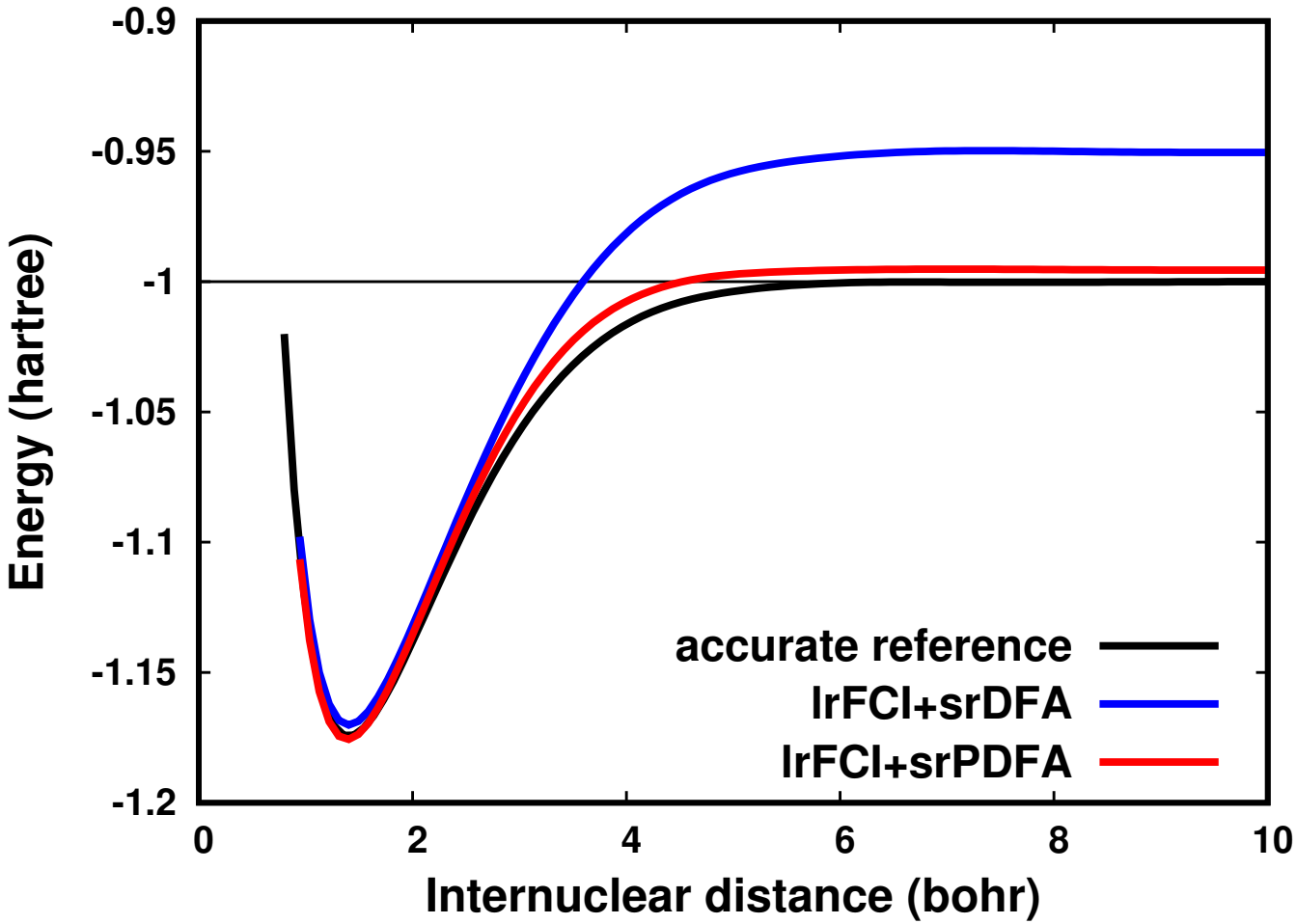
- Remark: in a basis set, the on-top pair density is calculated as

$$n_2(\mathbf{r}\uparrow,\mathbf{r}\downarrow) = \sum_{i=1}^{M}\sum_{j=1}^{M}\sum_{k=1}^{M}\sum_{l=1}^{M} \Gamma_{ij}^{kl}\, \psi_i(\mathbf{r}\uparrow)\psi_j(\mathbf{r}\downarrow)\psi_k(\mathbf{r}\uparrow)\psi_l(\mathbf{r}\downarrow)$$

where the two-electron reduced density-matrix tensor Γ_{ij}^{kl} can be efficiently approximated using low-rank approximations (work with Laura Grigori).

Dissociation of H_2 molecule

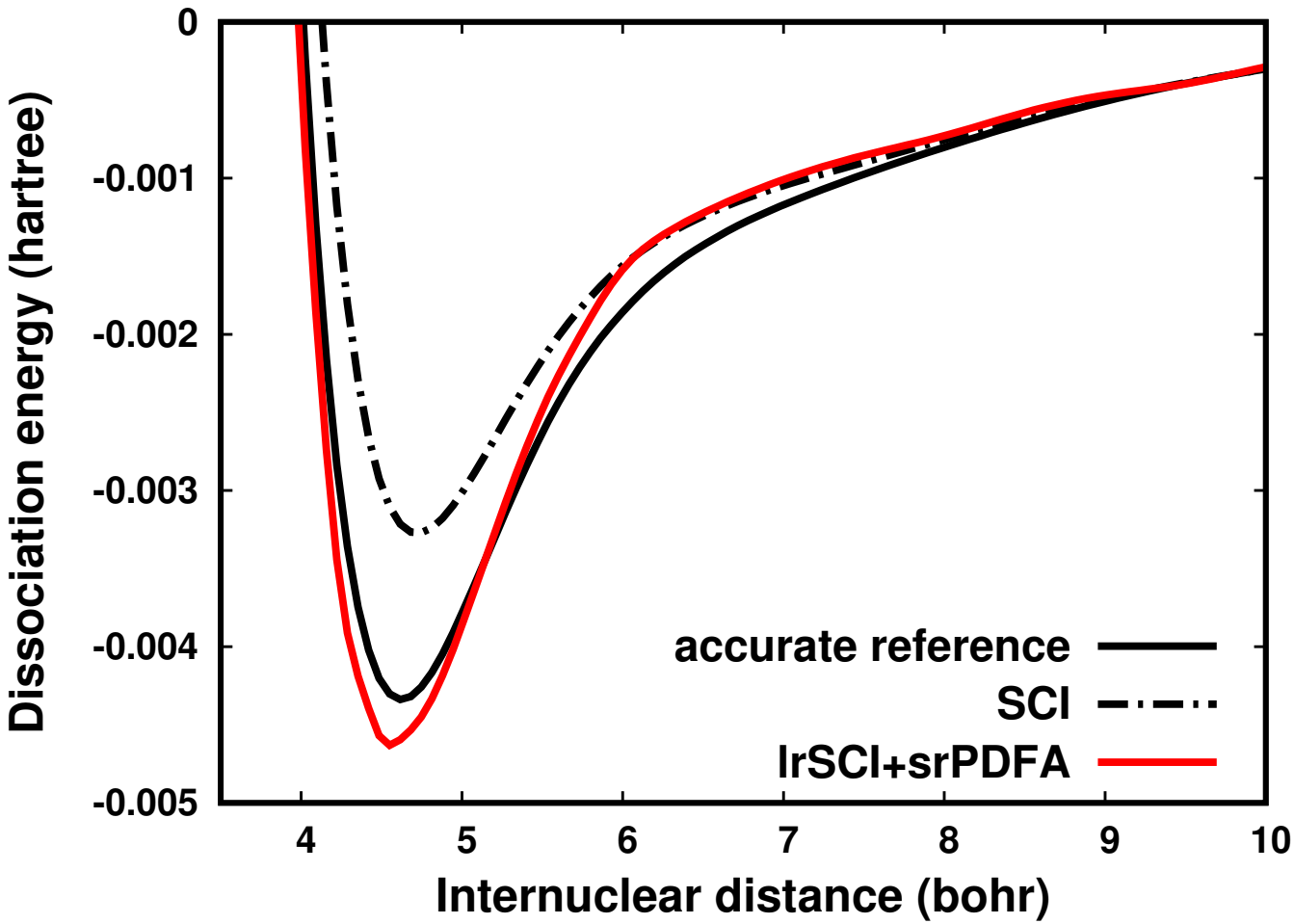
with cc-pVTZ basis set



$\Longrightarrow$ **lrFCI+srPDFA removes the error at dissociation thanks to the on-top pair density.**

A more difficult example: dissociation of Be_2 molecule

with aug-cc-pVTZ basis set



$\Longrightarrow$ **The large basis-set error of the standard SCI calculation is corrected by lrSCI+srPDFA.**

Ongoing work and outlook

- Tests on larger systems. For example, for F_2 molecule, one has to deal with spatial symmetry breaking among p-type degenerate states.
- Better approximations for the short-range Hxc density functional used at the variational level.
- Tensor-network decomposition for more efficiently calculating the long-range wave function.
- Relativistic extension based on the Dirac equation.
- Using a local range-separation parameter.
- More adapted and systematic basis sets?
- Calculation of excited states and response properties.

Outline

1 Quantum-chemistry wave-function methods

2 Long-range wave-function methods + short-range DFT

3 Wave-function methods + DFT basis correction

with Roland Assaraf, Anthony Ferté, Emmanuel Giner, Pierre-Francois Loos, Barthélémy Pradines, Andreas Savin, Anthony Scemama

Wave-function methods + DFT basis correction

- For a **basis set** $\mathcal{B}$, we define an approximation to the ground-state energy by **restriction to densities representable in** $\mathcal{B}$

$$E_0^{\mathcal{B}} = \min_{n \in \mathcal{D}^{\mathcal{B}}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\}$$

where $\mathcal{D}^{\mathcal{B}}$ is the space of densities that can be represented in the basis set $\mathcal{B}$

$$\mathcal{D}^{\mathcal{B}} = \{ n \in \mathcal{D} \mid \exists \Psi \in \mathcal{W}^{\mathcal{B}} \text{ s.t. } \forall\, \mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x}) \}$$

Wave-function methods + DFT basis correction

- For a **basis set** $\mathcal{B}$, we define an approximation to the ground-state energy by **restriction to densities representable in** $\mathcal{B}$

$$E_0^{\mathcal{B}} = \min_{n \in \mathcal{D}^{\mathcal{B}}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\}$$

where $\mathcal{D}^{\mathcal{B}}$ is the space of densities that can be represented in the basis set $\mathcal{B}$

$$\mathcal{D}^{\mathcal{B}} = \{ n \in \mathcal{D} \mid \exists \Psi \in \mathcal{W}^{\mathcal{B}} \text{ s.t. } \forall \mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x}) \}$$

- The restriction on densities representable in $\mathcal{B}$ is **much weaker** that the restriction on wave functions representable in $\mathcal{B}$, so

$$E_{\text{FCI}}^{\mathcal{B}} \geq E_0^{\mathcal{B}} \geq E_0$$

Wave-function methods + DFT basis correction

- For a **basis set** $\mathcal{B}$, we define an approximation to the ground-state energy by **restriction to densities representable in** $\mathcal{B}$

$$E_0^{\mathcal{B}} = \min_{n \in \mathcal{D}^{\mathcal{B}}} \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r}) n(\mathbf{x}) \mathrm{d}\mathbf{x} \right\}$$

where $\mathcal{D}^{\mathcal{B}}$ is the space of densities that can be represented in the basis set $\mathcal{B}$

$$\mathcal{D}^{\mathcal{B}} = \{ n \in \mathcal{D} \mid \exists \Psi \in \mathcal{W}^{\mathcal{B}} \text{ s.t. } \forall\, \mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x}) \}$$

- The restriction on densities representable in $\mathcal{B}$ is **much weaker** that the restriction on wave functions representable in $\mathcal{B}$, so

$$E_{\text{FCI}}^{\mathcal{B}} \geq E_0^{\mathcal{B}} \geq E_0$$

- We then **decompose the universal density functional** $F[n]$ as

$$F[n] = \min_{\Psi \in \mathcal{W}_n^{\mathcal{B}}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle + \bar{E}^{\mathcal{B}}[n]$$

where $\mathcal{W}_n^{\mathcal{B}}$ is the space of **wave functions representable in** $\mathcal{B}$ and giving the density n

$$\mathcal{W}_n^{\mathcal{B}} = \{ \Psi \in \mathcal{W}^{\mathcal{B}} \mid \forall\, \mathbf{x}, n_\Psi(\mathbf{x}) = n(\mathbf{x}) \}$$

and $\bar{E}^{\mathcal{B}}[n]$ is a **complementary density functional correcting for the basis-set restriction on the wave function**.

Wave-function methods + DFT basis correction

- The energy $E_0^{\mathcal{B}}$ can thus be expressed as

$$E_0^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle + \bar{E}^{\mathcal{B}}[n_\Psi] \right\}$$

Wave-function methods + DFT basis correction

- The energy $E_0^{\mathcal{B}}$ can thus be expressed as

$$E_0^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle + \bar{E}^{\mathcal{B}}[n_\Psi] \right\}$$

- The minimizing wave function $\Psi^{\mathcal{B}}$ is an **effective multideterminant wave function** satisfying the nonlinear Schrödinger equation

$$\hat{P}_{\mathcal{B}} \left(\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} + \hat{V}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}}] \right) |\Psi^{\mathcal{B}}\rangle = \mathcal{E}^{\mathcal{B}} |\Psi^{\mathcal{B}}\rangle$$

where $\hat{P}_{\mathcal{B}}$ is the projector on $\mathcal{W}^{\mathcal{B}}$ and $V^{\mathcal{B}}[n] = \sum_{i=1}^{N} \frac{\delta \bar{E}^{\mathcal{B}}[n]}{\delta n(\mathbf{x}_i)}$ is an effective one-electron potential.

Wave-function methods + DFT basis correction

- The energy $E_0^{\mathcal{B}}$ can thus be expressed as

$$E_0^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi \rangle + \bar{E}^{\mathcal{B}}[n_\Psi] \right\}$$

- The minimizing wave function $\Psi^{\mathcal{B}}$ is an **effective multideterminant wave function** satisfying the nonlinear Schrödinger equation

$$\hat{P}_{\mathcal{B}} \left(\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} + \hat{V}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}}] \right) |\Psi^{\mathcal{B}}\rangle = \mathcal{E}^{\mathcal{B}} |\Psi^{\mathcal{B}}\rangle$$

where $\hat{P}_{\mathcal{B}}$ is the projector on $\mathcal{W}^{\mathcal{B}}$ and $V^{\mathcal{B}}[n] = \sum_{i=1}^{N} \frac{\delta \bar{E}^{\mathcal{B}}[n]}{\delta n(\mathbf{x}_i)}$ is an effective one-electron potential.

- We will consider a **non-self-consistent approximation** using the FCI wave function:

$$E^{\mathcal{B}}_{\text{FCI+DFT}} = \langle \Psi^{\mathcal{B}}_{\text{FCI}} | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}}_{\text{FCI}} \rangle + \bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}]$$

and we have $E^{\mathcal{B}}_{\text{FCI}} \geq E^{\mathcal{B}}_{\text{FCI+DFT}} \geq E^{\mathcal{B}}_0$.

The complementary basis-correction density functional

- The complementary basis-correction functional $\bar{E}^{\mathcal{B}}$ has a **similar definition** than the short-range correlation functional $E_{\text{c,md}}^{\text{sr},\mu}$:

$$\bar{E}^{\mathcal{B}} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle$$

$$E_{\text{c,md}}^{\text{sr},\mu} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\text{lr},\mu} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\text{lr},\mu} \rangle$$

and they **coincide** if $\Psi^{\text{lr},\mu} = \Psi^{\mathcal{B}}$.

The complementary basis-correction density functional

- The complementary basis-correction functional $\bar{E}^{\mathcal{B}}$ has a **similar definition** than the short-range correlation functional $E_{\text{c,md}}^{\text{sr},\mu}$:

$$\bar{E}^{\mathcal{B}} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle$$

$$E_{\text{c,md}}^{\text{sr},\mu} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\text{lr},\mu} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\text{lr},\mu} \rangle$$

  and they **coincide** if $\Psi^{\text{lr},\mu} = \Psi^{\mathcal{B}}$.

- We define an **effective two-electron interaction in the basis set** $\mathcal{B}$:

$$w^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{\iint \langle \mathbf{x}_1, \mathbf{x}_2 | \hat{P}_{\mathcal{B}} \hat{W}_{\text{ee}} \hat{P}_{\mathcal{B}} | \mathbf{x}_1', \mathbf{x}_2' \rangle \; n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') \, \mathrm{d}\mathbf{x}_1' \mathrm{d}\mathbf{x}_2'}{n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2)}$$

  and we find the **local range-separation parameter** $\mu_{\mathcal{B}}(\mathbf{r})$ which makes the on-top value of the long-range interaction match the on-top value of the effective interaction

$$w_{\text{ee}}^{\text{lr},\mu_{\mathcal{B}}(\mathbf{r})}(0) = w^{\mathcal{B}}(\mathbf{r}\uparrow, \mathbf{r}\downarrow)$$

The complementary basis-correction density functional

- The complementary basis-correction functional $\bar{E}^{\mathcal{B}}$ has a **similar definition** than the short-range correlation functional $E_{\text{c,md}}^{\text{sr},\mu}$:

$$\bar{E}^{\mathcal{B}} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle$$

$$E_{\text{c,md}}^{\text{sr},\mu} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\text{lr},\mu} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\text{lr},\mu} \rangle$$

and they **coincide** if $\Psi^{\text{lr},\mu} = \Psi^{\mathcal{B}}$.

- We define an **effective two-electron interaction in the basis set** $\mathcal{B}$:

$$w^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{\iint \langle \mathbf{x}_1, \mathbf{x}_2 | \hat{P}_{\mathcal{B}} \hat{W}_{\text{ee}} \hat{P}_{\mathcal{B}} | \mathbf{x}_1', \mathbf{x}_2' \rangle \; n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') \, \mathrm{d}\mathbf{x}_1' \mathrm{d}\mathbf{x}_2'}{n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2)}$$

and we find the **local range-separation parameter** $\mu_{\mathcal{B}}(\mathbf{r})$ which makes the on-top value of the long-range interaction match the on-top value of the effective interaction

$$w_{\text{ee}}^{\text{lr},\mu_{\mathcal{B}}(\mathbf{r})}(0) = w^{\mathcal{B}}(\mathbf{r}\uparrow, \mathbf{r}\downarrow)$$

- We then a **recycle a semilocal DFA** for $E_{\text{c,md}}^{\text{sr},\mu}$ using $\mu = \mu_{\mathcal{B}}(\mathbf{r})$

$$\bar{E}_{\text{DFA}}^{\mathcal{B}} = \int e_{\text{c,md}}^{\text{sr},\mu_{\mathcal{B}}(\mathbf{r})}(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x})) \mathrm{d}\mathbf{r}$$

The complementary basis-correction density functional

- The complementary basis-correction functional $\bar{E}^{\mathcal{B}}$ has a **similar definition** than the short-range correlation functional $E_{\text{c,md}}^{\text{sr},\mu}$:

$$\bar{E}^{\mathcal{B}} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle$$

$$E_{\text{c,md}}^{\text{sr},\mu} = \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle - \langle \Psi^{\text{lr},\mu} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\text{lr},\mu} \rangle$$

  and they **coincide** if $\Psi^{\text{lr},\mu} = \Psi^{\mathcal{B}}$.

- We define an **effective two-electron interaction in the basis set** $\mathcal{B}$:

$$w^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2) = \frac{\iint \langle \mathbf{x}_1, \mathbf{x}_2 | \hat{P}_{\mathcal{B}} \hat{W}_{\text{ee}} \hat{P}_{\mathcal{B}} | \mathbf{x}_1', \mathbf{x}_2' \rangle \; n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') \, \mathrm{d}\mathbf{x}_1' \mathrm{d}\mathbf{x}_2'}{n_2^{\mathcal{B}}(\mathbf{x}_1, \mathbf{x}_2)}$$

  and we find the **local range-separation parameter** $\mu_{\mathcal{B}}(\mathbf{r})$ which makes the on-top value of the long-range interaction match the on-top value of the effective interaction

$$w_{\text{ee}}^{\text{lr},\mu_{\mathcal{B}}(\mathbf{r})}(0) = w^{\mathcal{B}}(\mathbf{r}\uparrow, \mathbf{r}\downarrow)$$

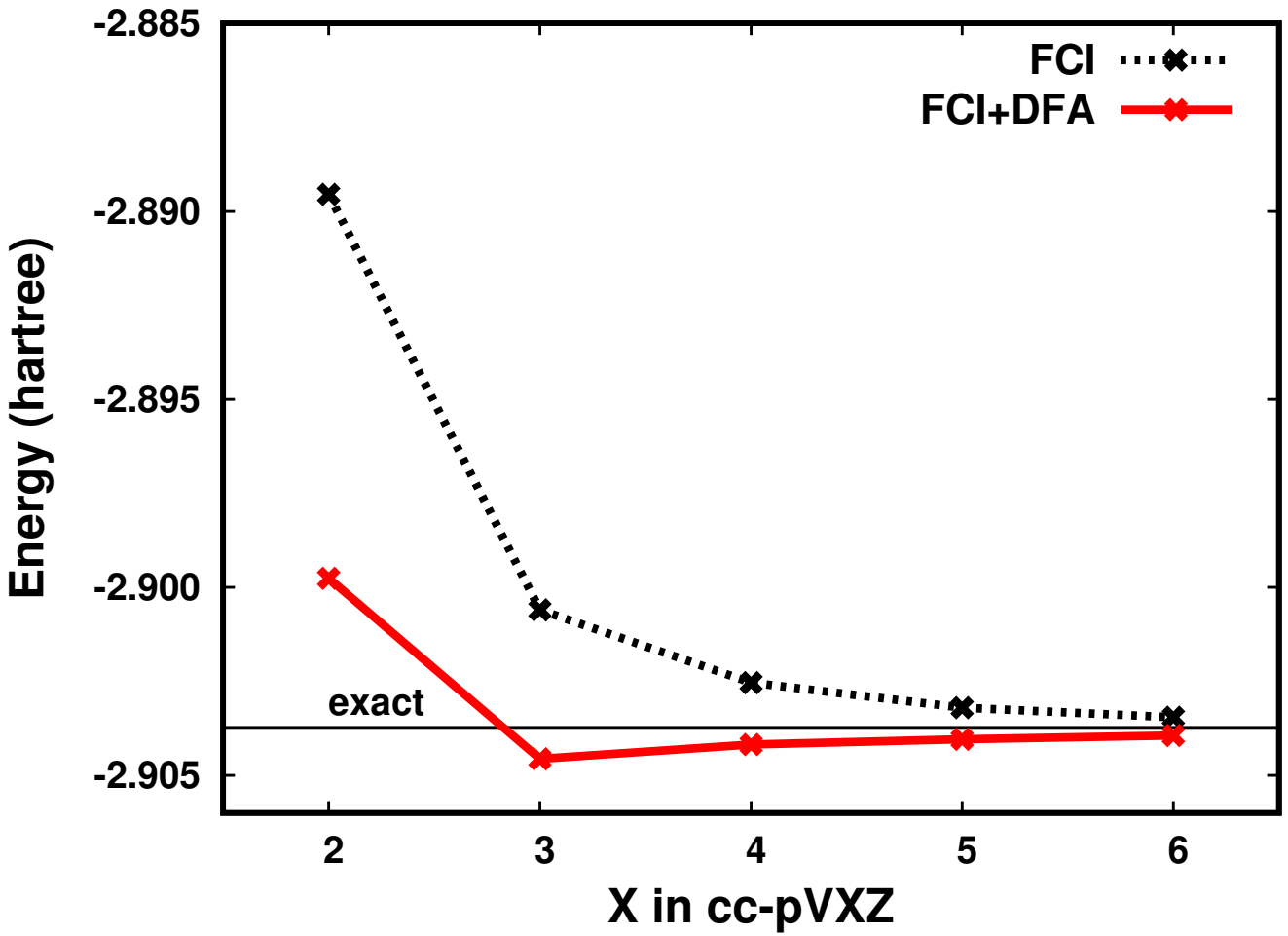
- We then a **recycle a semilocal DFA** for $E_{\text{c,md}}^{\text{sr},\mu}$ using $\mu = \mu_{\mathcal{B}}(\mathbf{r})$

$$\bar{E}_{\text{DFA}}^{\mathcal{B}} = \int e_{\text{c,md}}^{\text{sr},\mu_{\mathcal{B}}(\mathbf{r})}(n(\mathbf{x}), \boldsymbol{\nabla}_{\mathbf{r}} n(\mathbf{x})) \mathrm{d}\mathbf{r}$$

- In the **CBS limit**, we have $\mu_{\mathcal{B}}(\mathbf{r}) \to \infty$, and $\bar{E}_{\text{DFA}}^{\mathcal{B}}$ correctly vanishes.

Convergence with respect to the basis set

Example of He atom ($N = 2$) with the **series of basis sets** $\mathcal{B}$ = "cc-pVXZ":

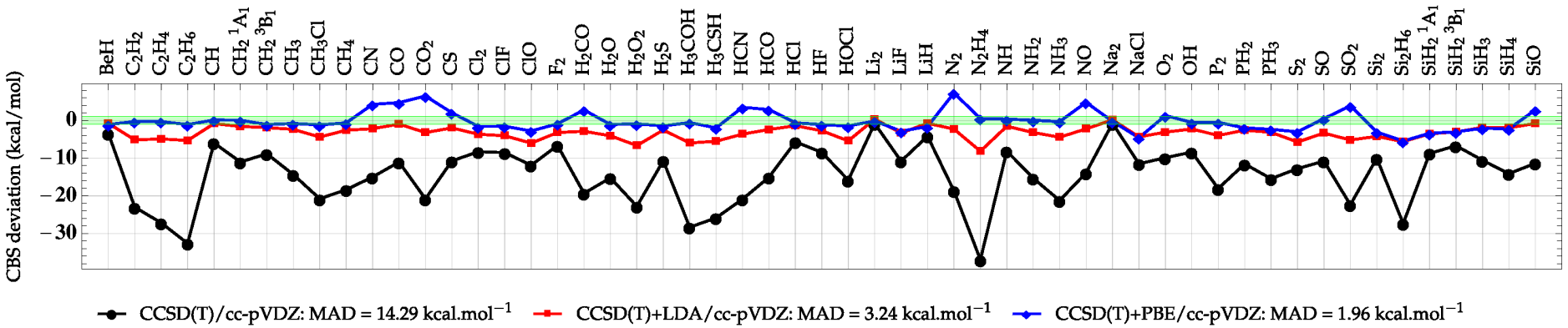


$\Longrightarrow$ **Much faster basis-set convergence without altering the CBS limit.**

Tests on atomization energies

A set of **55 atomization energies** of small molecules, e.g. $CO_2 \rightarrow C + 2\,O$, using the **CCSD(T) approximation** to FCI with cc-pVXZ basis sets.

$X = 2$:



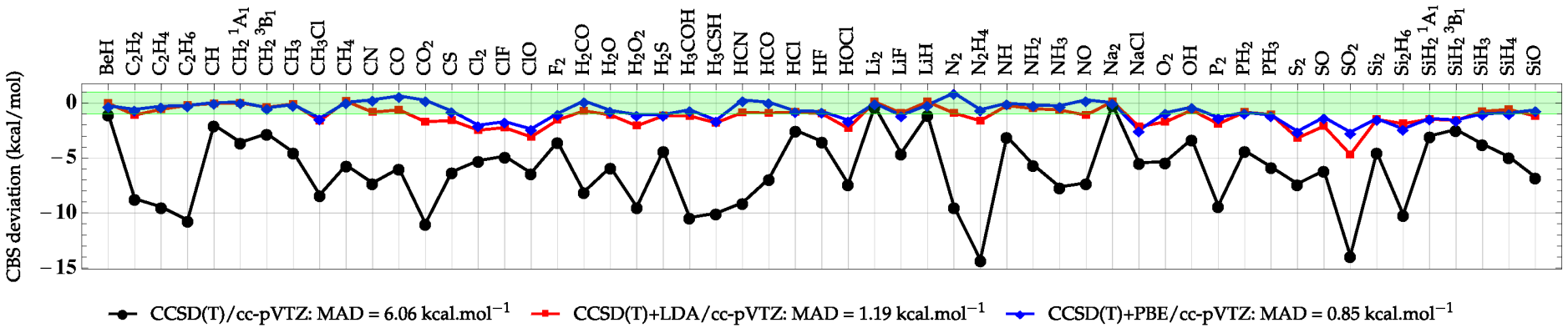
Mean absolute deviation with respect to CBS limit (in kcal/mol):

	CCSD(T)	CCSD(T)+DFA
X=2	14.29	1.96

Tests on atomization energies

A set of **55 atomization energies** of small molecules, e.g. $CO_2 \rightarrow C + 2\,O$, using the **CCSD(T) approximation** to FCI with cc-pVXZ basis sets.

$X = 3$:



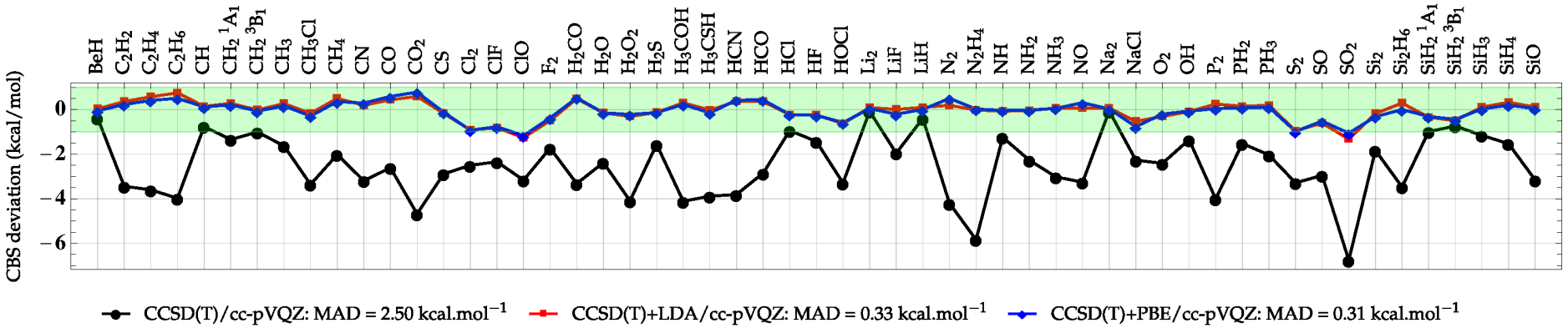
Mean absolute deviation with respect to CBS limit (in kcal/mol):

	CCSD(T)	CCSD(T)+DFA
X=2	14.29	1.96
X=3	6.06	0.85

Tests on atomization energies

A set of **55 atomization energies** of small molecules, e.g. $CO_2 \rightarrow C + 2\,O$, using the **CCSD(T) approximation** to FCI with cc-pVXZ basis sets.

$X = 4$:



Mean absolute deviation with respect to CBS limit (in kcal/mol):

	CCSD(T)	CCSD(T)+DFA
X=2	14.29	1.96
X=3	6.06	0.85
X=4	2.50	0.31

$\Longrightarrow$ **CCSD(T)+DFA quickly converges to "chemical accuracy" (1 kcal/mol).**

Ongoing work and outlook

- Use functionals of the on-top pair density for strongly correlated systems.
- Extension to calculations of excited-state energies.
- Development of more rigorous DFT basis corrections?
- Similar DFT correction for improving convergence with respect to the number of determinants?
- Correction for improving convergence of one-electron properties?
- Calculation of response properties.

Summary

Two related approaches for accelerating wave-function methods:

- **Long-range wave-function methods + short-range DFT**
  - fast convergence of long-range wave-function methods
  - accurate non-variational energy expression using the on-top pair density
  - we would like to improve the accuracy at the variational level

  Ferté, Giner, Toulouse, J. Chem. Phys., 2019

- **Wave-function methods + DFT basis correction**
  - DFT basis correction which automatically adapts to each basis set
  - presently based on recycling short-range DFT correlation functionals
  - we would like to develop more rigorous DFT basis corrections

  Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, J. Chem. Phys., 2018

  Loos, Pradines, Scemama, Toulouse, Giner, to be submitted

- Implemented in the **open-source software QUANTUM PACKAGE**
  `quantumpackage.github.io/qp2`

Garniron, Applencourt, Gasperich, Benali, Ferté, Paquier, Pradines, Assaraf, Reinhardt, Toulouse, Barbaresco, Renon, David, Malrieu, Véril, Caffarel, Loos, Giner, Scemama, arXiv:1902.08154

`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_toronto_19.pdf`