Basis-set correction based on density-functional theory

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

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`www.lct.jussieu.fr/pagesperso/toulouse/presentations/presentation_dft_24.pdf`

Outline

1. Slow basis-set convergence of wave-function theory

2. Basis-set correction based on DFT

3. Benchmarks and extensions

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The roots of slow basis-set convergence

- The space of one-electron states $\mathfrak{H} = L^2(\mathbb{R}^3 \times \{\uparrow,\downarrow\}, \mathbb{C})$ and the space of N-electron states $\mathcal{H} = \bigwedge^N \mathfrak{H}$ are **infinite-dimensional** Hilbert spaces.

- In practice, we use a **finite one-electron basis set** $\mathcal{B} = \{\chi_\nu\}_{\nu=1,\dots,N_{\text{basis}}}$ to span the one-electron space $\mathfrak{H}^{\mathcal{B}} = \text{span}(\mathcal{B})$ and the N-electron space $\mathcal{H}^{\mathcal{B}} = \bigwedge^N \mathfrak{H}^{\mathcal{B}}$, and we must try to approach the **complete-basis-set (CBS) limit** $N_{\text{basis}} \to \infty$.

- In the molecular electronic Hamiltonian

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

  the **Coulomb electron-electron interaction** $\hat{W}_{\text{ee}} = \sum_{i<j} 1/r_{ij}$ is singular as $r_{ij} \to 0$, leading to the **electron-electron cusp** (derivative discontinuity) in the eigenfunctions

  $$\Psi(r_{ij}) = \Psi(0)\left[1 + \frac{1}{2} r_{ij} + \cdots\right]$$

  Kato, CPAM, 1957

- This leads to a **slow basis-set convergence of energies and many properties due to short-range correlation**

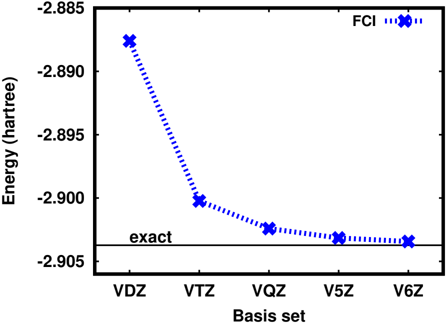
Slow basis-set convergence of the FCI ground-state energy

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

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

where $\mathcal{W}^{\mathcal{B}} = \{\Psi \in \mathcal{H}^{\mathcal{B}} \mid \langle \Psi | \Psi \rangle = 1\}$.

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



- **Systematic but slow basis-set convergence**

Two main strategies to deal with slow basis-set convergence

- **Extrapolation of the correlation energy to the CBS limit** using an inverse cubic law in X:

$$E_\text{c}^{X} = E_\text{c}^{\text{CBS}} + \frac{A}{X^3}$$

Helgaker, Klopper, Koch, Noga, JCP, 1997

- **Explicitly correlated R12/F12 methods** consisting in augmenting the two-electron Hilbert space by geminals of the form:

$$g_{i,j}(\mathbf{x}_1, \mathbf{x}_2) = \hat{Q}_{12} f(r_{12}) \hat{S}_{12}\ \phi_i(\mathbf{x}_1) \wedge \phi_j(\mathbf{x}_2)$$

where $f(r_{12})$ is a correlation factor, $\hat{S}_{12}$ is the rational generator ensuring the singlet and triplet cusp conditions, and $\hat{Q}_{12}$ is the strong-orthogonality projector

Reviews: Ten-no, Noga, WIREs, 2012; Hättig, Klopper, Köhn, Tew, CR, 2012; Kong, Bischoff, Valeev, CR, 2012; Shiozaki, Werner, MP, 2013

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Basis-set correction based on DFT (1/2)

- In **standard DFT** (complete basis set), the **exact ground-state energy** is expressed as

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

  where $\mathcal{D}^{\text{CBS}} = \{\rho \mid \exists \Psi \in \mathcal{W}^{\text{CBS}} \text{ s.t. } \rho_\Psi = \rho\}$ is the set of N-representable densities, and $F[\rho]$ is the **Levy-Lieb universal density functional**

$$F[\rho] = \min_{\substack{\Psi \in \mathcal{W}^{\text{CBS}} \\ \Psi \to \rho}} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle$$

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

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

  where $\mathcal{D}^{\mathcal{B}} = \{\rho \mid \exists \Psi \in \mathcal{W}^{\mathcal{B}} \text{ s.t. } \rho_\Psi = \rho\}$.

- **The restriction to densities representable in $\mathcal{B}$ is much weaker than the restriction to wave functions representable in $\mathcal{B}$**, so we expect

$$E_{\text{FCI}}^{\mathcal{B}} \gg E_0^{\mathcal{B}} \gtrsim E_0$$

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018

Basis-set correction based on DFT (2/2)

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

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

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

- The energy $E_0^{\mathcal{B}}$ can then be obtained **self-consistently** as

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

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

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

- We can also add the DFT basis-set correction to any **approximate wave-function theory (WFT) method**:

$$E_{\text{WFT+DFT}}^{\mathcal{B}} = E_{\text{WFT}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[\rho_{\Psi_{\text{WFT}}^{\mathcal{B}}}]$$

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018

The complementary basis-set correction functional $\bar{E}^{\mathcal{B}}[\rho]$

- We start by defining an **electron-electron interaction projected in the basis set $\mathcal{B}$**

$$w_{\text{ee}}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2)$$

- **We fit this projected interaction by the long-range interaction used in range-separated DFT:**

$$w_{\text{ee}}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{\text{erf}(\mu^{\mathcal{B}}(\mathbf{r}_1) r_{12})}{r_{12}}$$

  with a local range-separation parameter $\mu^{\mathcal{B}}(\mathbf{r})$.

- The obtained $\mu^{\mathcal{B}}(\mathbf{r})$ is a **local measure of the incompleteness of the basis set $\mathcal{B}$**.
- We then approximate the basis-set correction functional by a **short-range PBE correlation functional** previously developed for range-separated DFT:

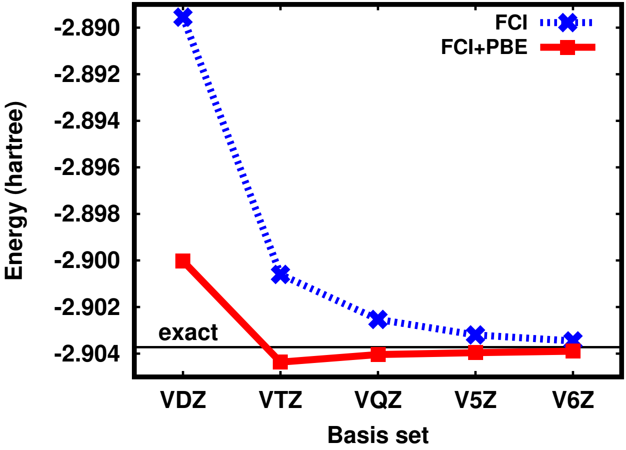
$$\bar{E}_{\text{PBE}}^{\mathcal{B}}[\rho] = \int e_{\text{c}}^{\text{srPBE}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \mu^{\mathcal{B}}(\mathbf{r}))\, \text{d}\mathbf{r}$$

- **This approximate basis-set correction functional contains the physics of the electron-electron cusp, automatically adapts to each basis set $\mathcal{B}$, and correctly vanishes in the CBS limit**

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018
Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

Convergence of the total energy with respect to the basis set

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



- **Much faster basis-set convergence without altering the CBS limit**

Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, JCP, 2018

Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

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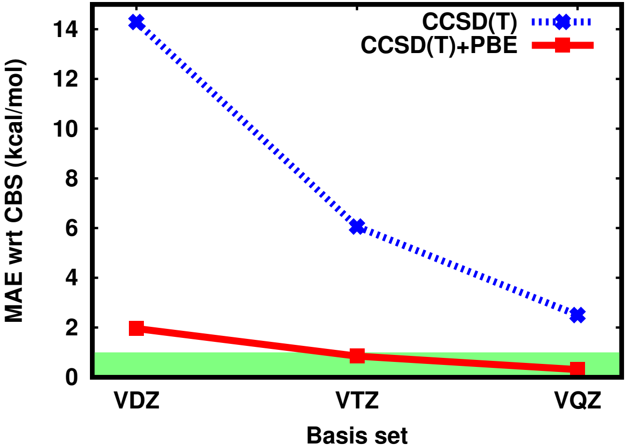
Benchmark on atomization energies of small molecules

- **Atomization energies of 55 small molecules** (G2 set) with cc-pVXZ basis sets:

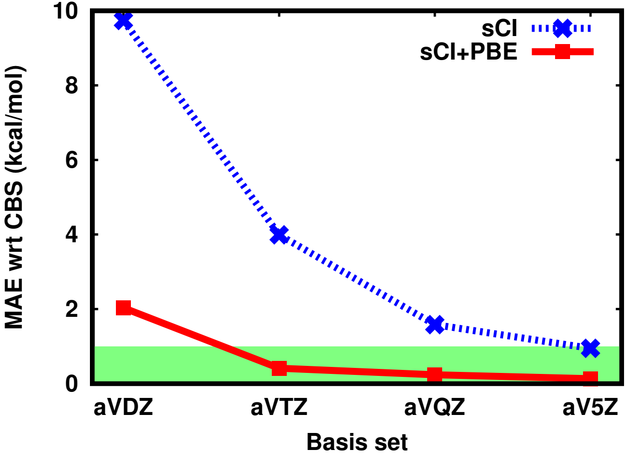


- **MAE wrt CBS is below 1 kcal/mol already with the triple-zeta basis set**

Loos, Pradines, Scemama, Toulouse, Giner, JPCL, 2019

Benchmark on dissociation energies of transition metal monoxides

- **Dissociation energies of transition metal monoxides** (ScO, TiO, VO, CrO, MnO, FeO, CuO) with selected CI calculations with aug-cc-pVXZ basis sets and pseudopotentials:



- **MAE wrt CBS is below 1 kcal/mol already with the triple-zeta basis set**

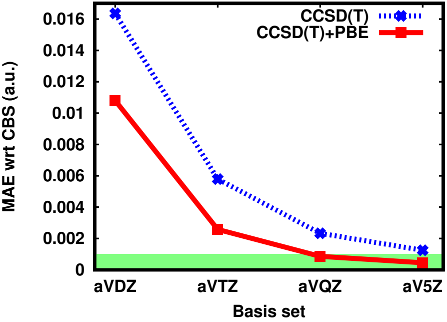
Yao, Giner, Anderson, Toulouse, Umrigar, JCP, 2021

Benchmark on dipole moments of small molecules

- Calculation of the **dipole moment** by response to an electric field $\mathcal{E}$:

$$\boxed{E_0^{\mathcal{B}}(\mathcal{E}) = E_{\mathrm{WFT}}^{\mathcal{B}}(\mathcal{E}) + \bar{E}^{\mathcal{B}}[\rho_{\Psi_{\mathrm{WFT}}^{\mathcal{B}}(\mathcal{E})}]} \implies \boxed{d_0^{\mathcal{B}} = -\left.\frac{\mathrm{d}E_0^{\mathcal{B}}(\mathcal{E})}{\mathrm{d}\mathcal{E}}\right|_{\mathcal{E}=0}}$$

- **Dipole moments of 14 small molecules** with aug-cc-pVXZ basis sets:



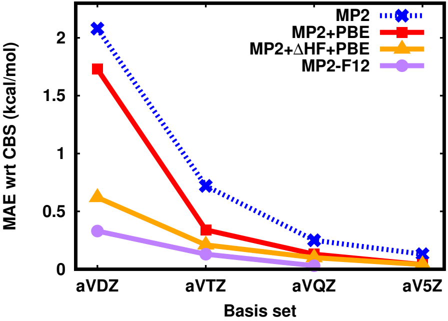
- **The basis-set correction also accelerates the convergence of dipole moments, albeit to a lesser extent**

Giner, Traore, Pradines, Toulouse, JCP, 2021; Traore, Toulouse, Giner, JCP, 2022

Density-fitting implementation and benchmark on reaction energies

- Implementation in MOLPRO with **density-fitting calculation of the local range-separation parameter** $\mu^{\mathcal{B}}(\mathbf{r})$ with scaling $O(N_{\text{occ}} N_{\text{basis}} N_{\text{fit}} N_{\text{grid}})$

- **51 reaction energies** (FH51 set) with aug-cc-pV(X+d)Z basis sets:



- **The HF basis-set correction (ΔHF) is important for small basis sets**

- **MP2-F12 is more accurate, especially for the double-zeta basis set**

Heßelmann, Werner, Knowles, Giner, Reinhardt, Toulouse, JCC, 2024
(see also Mester, Kállay, JCTC, 2023)

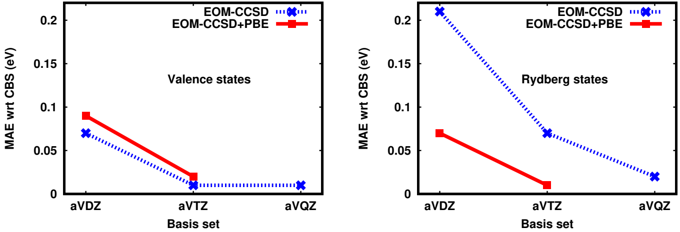
Benchmark on excitation energies

- The self-consistent formulation leads to an **effective Hamiltonian with a DFT basis-set correction potential**:

$$E_0^{\mathcal{B}} = \min_{\Psi \in \mathcal{W}^{\mathcal{B}}} \left\{ \langle \Psi | \hat{H} | \Psi \rangle + \bar{E}^{\mathcal{B}}[\rho_\Psi] \right\} \Longrightarrow \left(\hat{H} + \hat{\bar{V}}^{\mathcal{B}}[\rho_{\Psi^{\mathcal{B}}}] \right) |\Psi^{\mathcal{B}}\rangle = \mathcal{E}^{\mathcal{B}} |\Psi^{\mathcal{B}}\rangle$$

  and excitation energies are obtained with EOM-CCSD applied to this effective Hamiltonian.

- **28 excitation energies** of small molecules with aug-cc-pVXZ basis sets:



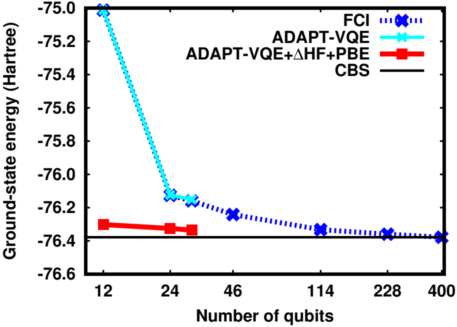
- **The basis-set correction accelerates the convergence of the Rydberg excitations energies but not the valence ones.**

Traore, Toulouse, Giner, Faraday Discussions, 2024

DFT basis-set correction to the rescue of quantum computing

- In **quantum computing**, there is a strong limitation on the size of the basis set since it corresponds to the **number of qubits**.

- **Ground-state energy of H_2O with ADAPT-VQE emulated calculations:**



- **The basis-set correction helps the convergence of quantum-computing calculations.**

Traore, Adjoua, Feniou, Lygatsika, Maday, Posenitski, Hammernik, Peruzzo, Toulouse, Giner, Piquemal, arXiv 2405.11567, 2024

Conclusions

- **Summary:**
  - DFT basis-set correction which automatically adapts to each basis set
  - based on pre-existing short-range correlation functional
  - accelerates basis-set convergence of energies and properties
  - implemented in **QUANTUM PACKAGE** and **MOLPRO**

- **Outlook:**
  - Analysis of the exact basis-set correction functional
  - Construction of better approximations to it

- **Contributors to this work:**

  Paris: O. Adjoua, R. Assaraf, C. Feniou, A. Ferté, **E. Giner**, J.-P. Piquemal, B. Pradines, P. Reinhardt, A. Savin, D. Traore

  Toulouse: P.-F. Loos, A. Scemama

  Cornell: Y. Yao, T. Anderson, C. Umrigar

  Molpro team: A. Heßelmann, P. Knowles, H.-J. Werner

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