Basis-set correction method

Application to a molecular property
the dipole moment

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General introduction about quantum chemistry

Quantum chemistry :

- provides methods to solve the many-body Schrödinger equation

The many-body Schrödinger equation

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

where

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_i v(\vec{r}_i)$$

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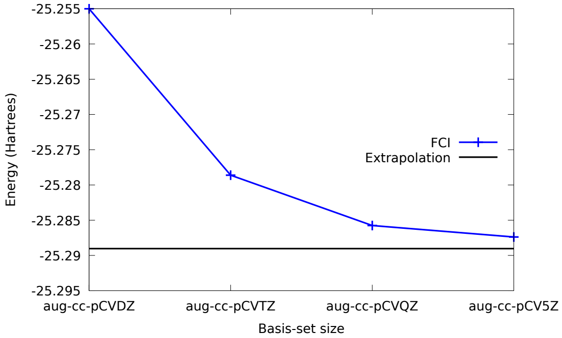
Main approaches :

- Wave-function theory (Hartree-Fock, Configuration Interaction, CCSD(T), Perturbation Theory, ...)
- Density functional theory (LDA, GGA, Meta-GGA, ...)
- **Hybrid methods** (example : basis-set correction)

Wave-function theory - slow convergence of molecular properties

System : Boron monohydride (BH)



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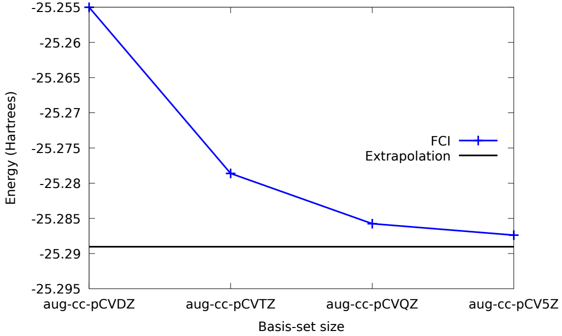

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- Slow convergence with basis-set size due to short-range correlation

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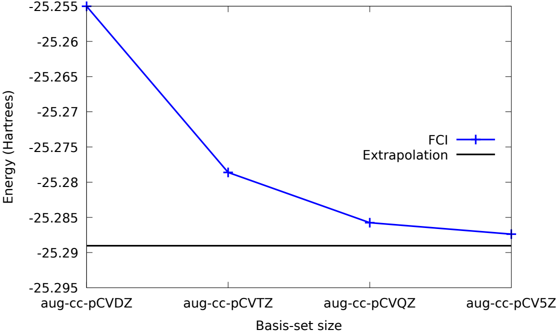

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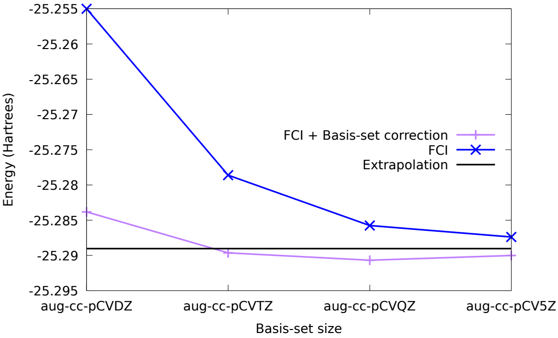

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Outline

1. Basis-set correction
2. Applications
3. Conclusion and perspectives

Outline

Levy-Lieb constrained-search formulation

Standard Levy-Lieb constrained-search universal density functional

$$E_0 = \min_n \left\{ F[n] + \int \mathrm{d}\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

where

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle$$

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Restriction of the density on a finite basis-set

(Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, J. Chem. Phys. 149, *(2018))*

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

Decomposition of the universal density functional

Decomposition of the universal functional

(Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, J. Chem. Phys. 149, *(2018))*

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

- Ψ^{B} : Expended on a finite basis set
- $\bar{E}^{\mathcal{B}}[n^{\mathcal{B}}]$ = Complementary density functional
- Complete Basis Set (CBS) limit : $F[n]$ is exact, and $\bar{E}^{\mathcal{B}}[n^{\mathcal{B}}] = 0$

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

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

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$$\begin{aligned} E_0^{\mathcal{B}} &= \min_{n^{\mathcal{B}}} \left\{ F[n^{\mathcal{B}}] + \int \mathrm{d}\mathbf{r}\, v_{\text{ne}}(\mathbf{r}) n^{\mathcal{B}}(\mathbf{r}) \right\} \\ &= \min_{\Psi^{\mathcal{B}}} \left\{ \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi^{\mathcal{B}} \rangle + \bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}}] \right\} \end{aligned}$$

⟶ Quantum Package (`https://quantumpackage.github.io/qp2/`) ⟵

Two approaches

Variational approach : Self-consistent formalism

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

- Correction to the wave function
- Computation of properties as expectation values or analytical derivatives

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Non-variational approach : non-self-consistent formalism

$$E_0^{\mathcal{B}} \simeq \underbrace{\langle\Psi_{\text{FCI}}^{\mathcal{B}}|\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}|\Psi_{\text{FCI}}^{\mathcal{B}}\rangle}_{\text{Variational principle}} + \underbrace{\bar{E}^{\mathcal{B}}[n_{\Psi_{\text{FCI}}^{\mathcal{B}}}]}_{\text{DFT}}$$

- Correction to the energy
- Computation of properties using numerical derivatives

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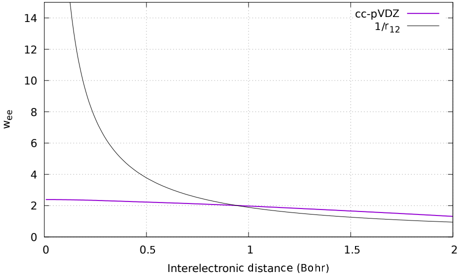
$$E_0^{\mathcal{B}} \simeq E^{\mathcal{B}}_{\text{WFT1}} + \bar{E}^{\mathcal{B}}[n^{\mathcal{B}}_{\text{WFT2}}]$$

- Correction to the energy
- Computation of properties using numerical derivatives

How to approximate the complementary functional ?

Projection of the electron-electron interaction in the basis set $\mathcal{B}$

$\hat{P}^{\mathcal{B}}\hat{W}_{ee}\hat{P}^{\mathcal{B}} \rightarrow$ A non-diverging electronic interaction



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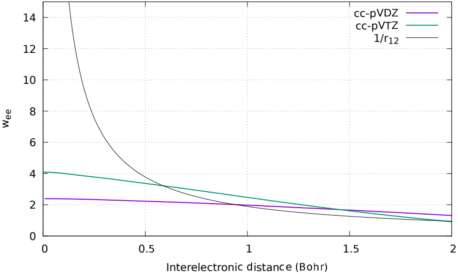

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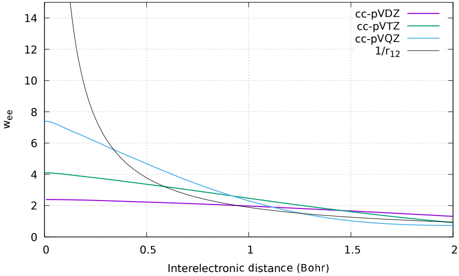

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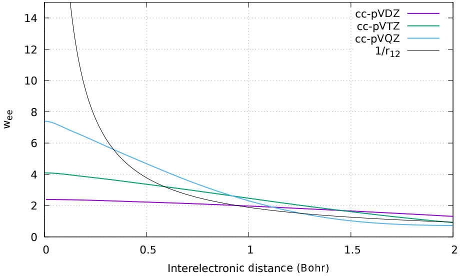


Possible comparison with the **range-separated DFT** method ?

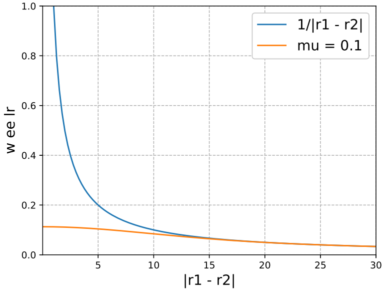
How to approximate the complementary functional ?

From the long-range electron-electron interaction in RS-DFT ...

$$\hat{W}_{ee}^{lr} = \sum_{i<j} w_{ee}^{lr}(|r_i - r_j|)$$

with

$$w_{ee}^{lr}(|r_i - r_j|) = \frac{\mathrm{erf}(\mu|r_i - r_j|)}{|r_i - r_j|}$$



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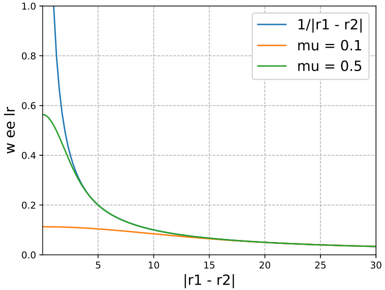

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From the long-range electron-electron interaction in RS-DFT …

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… to an expression for the electron-electron interaction projected in the basis set $\mathcal{B}$

$$\hat{P}^{\mathcal{B}} \hat{W}_{\text{ee}} \hat{P}^{\mathcal{B}}$$

→ after comparisons :

$$w_{\text{ee}}^{\mathcal{B}}(r_i, |r_i - r_j|) \simeq \frac{\text{erf}(\mu^{\mathcal{B}}(r_i)|r_i - r_j|)}{|r_i - r_j|}$$

How to approximate the complementary functional ?

Approximation of the complementary functional

Mapping between the physics of **range-separated DFT** and **basis-set correction** :

$$\bar{E}^{\mathcal{B}}_{\mathrm{PBEUEG}}[n] \simeq \int \mathrm{d}\mathbf{r}\, \bar{e}^{\mathrm{sr},\mu}_{\mathrm{c,PBEUEG}}(n, \nabla n(\mathbf{r}), \mu^{\mathcal{B}}(\mathbf{r}))$$

$\bar{e}^{\mathrm{sr},\mu}_{\mathrm{c,\ PBEUEG}}$ → Complementary short-range *(sr)* correlation *(c)*

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Applications of the basis-set correction method

Non-self-consistent basis-set correction

- Ground state energies [1][2]
- Energy differences : atomization energies [2]

[1] *Giner, Pradines, Ferté, Assaraf, Savin, Toulouse, J. Chem. Phys. (2018)*
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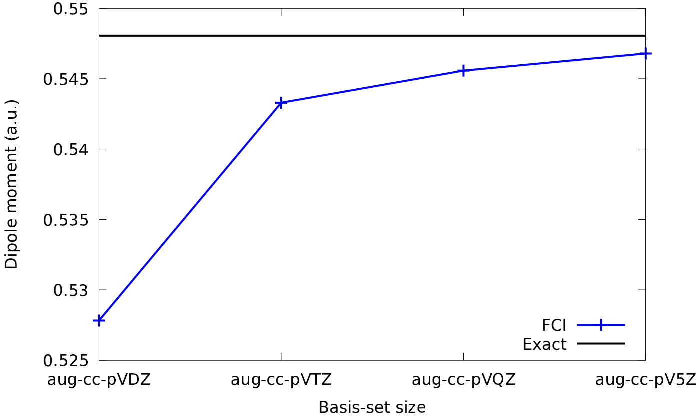
BH dipole moment - using self-consistent framework



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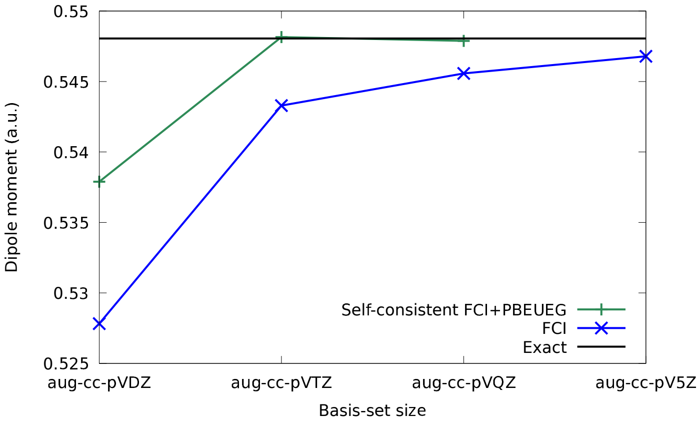

Non variational approach - CCSD(T)

Definition of the dipole moment :

$$\hat{H}(\epsilon) = \hat{H} - \epsilon \hat{d}$$

then

$$d = - \left. \frac{\partial E}{\partial \epsilon} \right|_{\epsilon=0} \simeq - \left. \frac{E(\epsilon) - E(-\epsilon)}{2\epsilon} \right|_{\epsilon=0}$$

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Correction of the CCSD(T) dipole moment

$$E_0^{\mathcal{B}} \simeq E_{\mathrm{WFT1}}^{\mathcal{B}} + \bar{E}^{\mathcal{B}}[n_{\mathrm{WFT2}}^{\mathcal{B}}] \longrightarrow d_0^{\mathcal{B}} \simeq d_{\mathrm{WFT1}}^{\mathcal{B}} + \bar{d}^{\mathcal{B}}[n_{\mathrm{WFT2}}^{\mathcal{B}}]$$

$$d_{\mathrm{CCSD(T)+PBEUEG}}^{\mathcal{B}} = d_{\mathrm{CCSD(T)}}^{\mathcal{B}} + \bar{d}^{\mathcal{B}}[n_{\mathrm{HF}}^{\mathcal{B}}]$$

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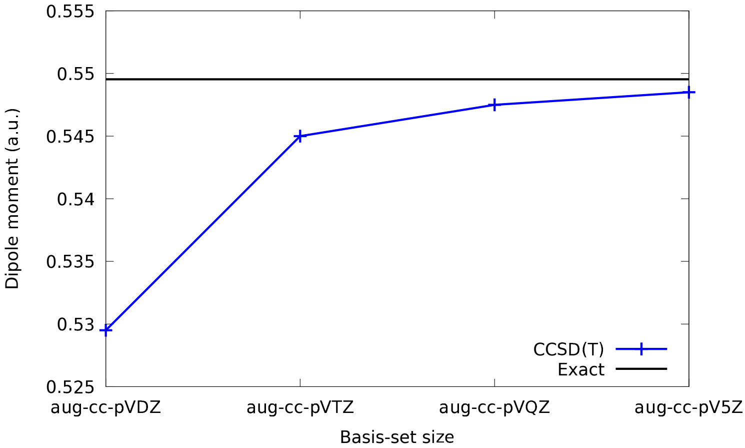
Basis-set correction of the dipole moment

Solve the Hartree-Fock equation with a field operator to compute $n_{\mathrm{HF}}(\epsilon)$. Then :

$$\bar{d}^{\mathcal{B}} = -\frac{\bar{E}_{\mathrm{PBE\text{-}UEG}}^{\mathcal{B}}[n_{\mathrm{HF}}(\epsilon)] - \bar{E}_{\mathrm{PBE\text{-}UEG}}^{\mathcal{B}}[n_{\mathrm{HF}}(-\epsilon)]}{2\epsilon}$$

BH dipole moment - CCSD(T)



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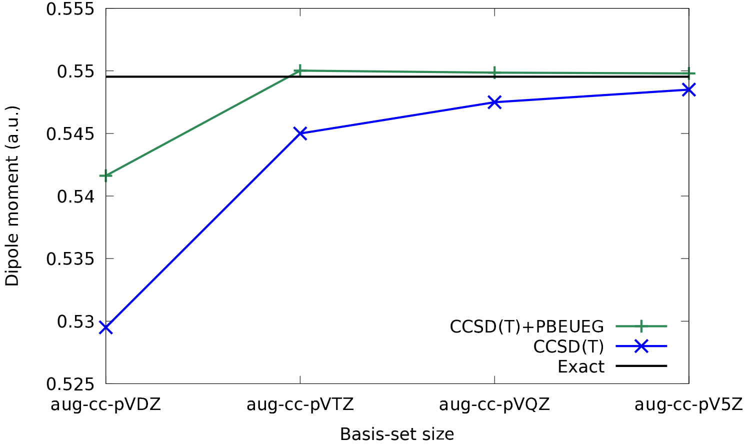
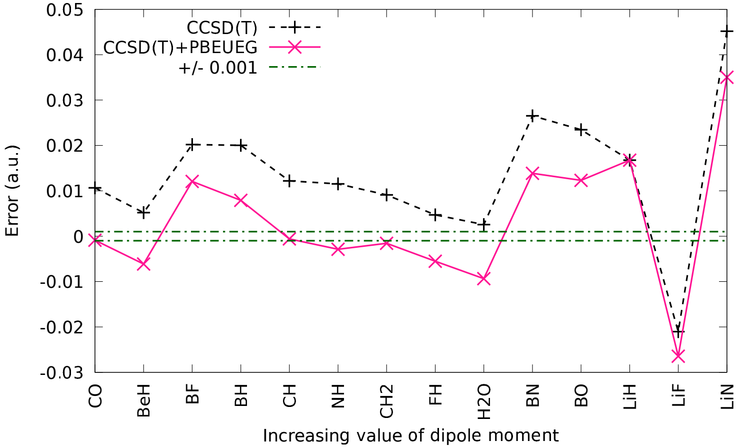


CCSD(T)+PBEUEG errors

aug-cc-pVDZ basis set



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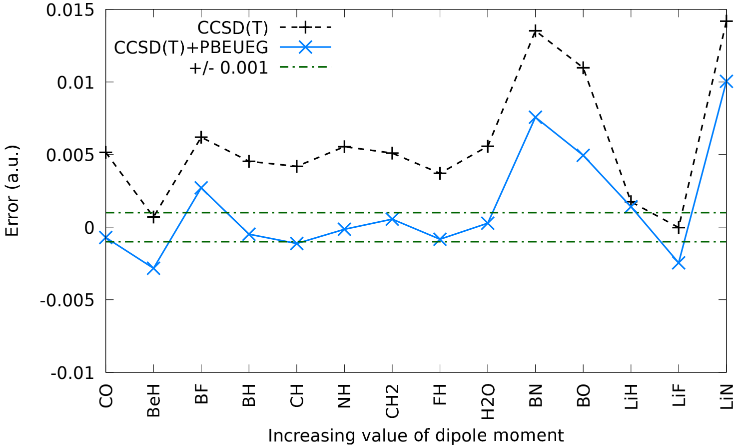

CCSD(T)+PBEUEG errors

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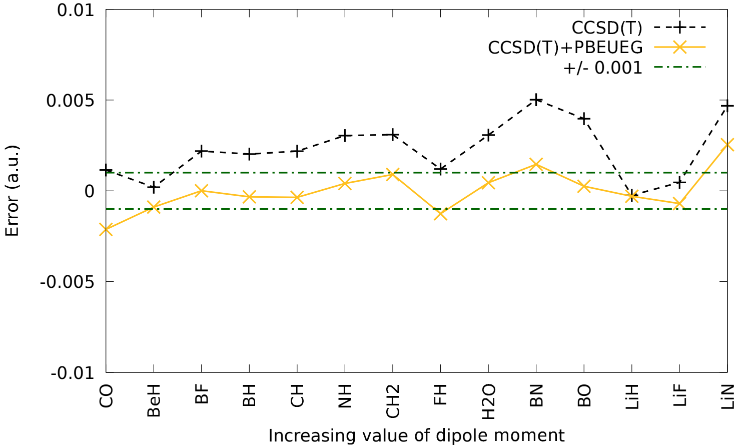

CCSD(T)+PBEUEG errors

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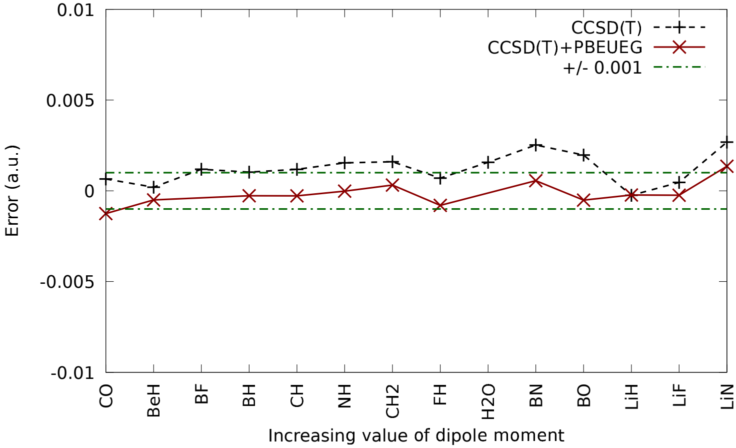

Conclusion and perspectives

Summary

- Test of the self-consistent and non-self-consistent basis set correction for the dipole moment

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- Study of the approximation used for the complementary functional $\bar{E}^{\mathcal{B}}[n]$ using a simplified one-dimensional model (Julien Toulouse's poster)

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Perspectives

- Study of the approximation used for the complementary functional $\bar{E}^{\mathcal{B}}[n]$ using a simplified one-dimensional model (Julien Toulouse's poster)
- Extension of the basis-set correction to higher order molecular properties / linear response theory

Mapping between RS-DFT and basis-set correction

Range-separated DFT : *(J. Toulouse, P. Gori-Giorgi, and A. Savin, Theor. Chem. Acc., 114, 305, (2005))*

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

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$$☞ \ \Psi^{\mathcal{B}}[n] = \text{arg} \min_{\Psi \to n^{\mathcal{B}}} \langle \Psi | \hat{P}^{\mathcal{B}} \left(\hat{T} + \hat{W}_{\text{ee}} \right) \hat{P}^{\mathcal{B}} | \Psi \rangle$$

Mapping between RS-DFT and basis-set correction

Range-separated DFT : *(J. Toulouse, P. Gori-Giorgi, and A. Savin, Theor. Chem. Acc., 114, 305, (2005))*

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

$$☞ \ \Psi^{\text{lr}}[n] = \text{arg} \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}^{\text{lr}}_{\text{ee}} | \Psi \rangle$$

Basis-set correction :

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

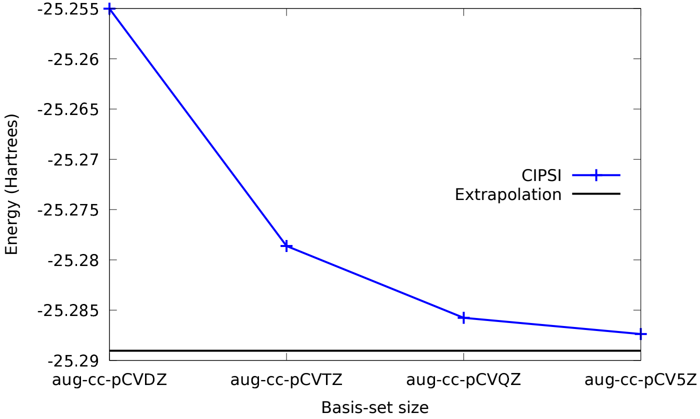
$$☞ \ \Psi^{\mathcal{B}}[n] = \text{arg} \min_{\Psi \rightarrow n^{\mathcal{B}}} \langle \Psi | \hat{P}^{\mathcal{B}} \left(\hat{T} + \hat{W}_{\text{ee}} \right) \hat{P}^{\mathcal{B}} | \Psi \rangle$$

Mapping between RS-DFT and basis-set correction electronic interaction

$$\hat{P}^{\mathcal{B}} \hat{W}_{\text{ee}} \hat{P}^{\mathcal{B}} \simeq \hat{W}^{\text{lr}}_{\text{ee}}$$

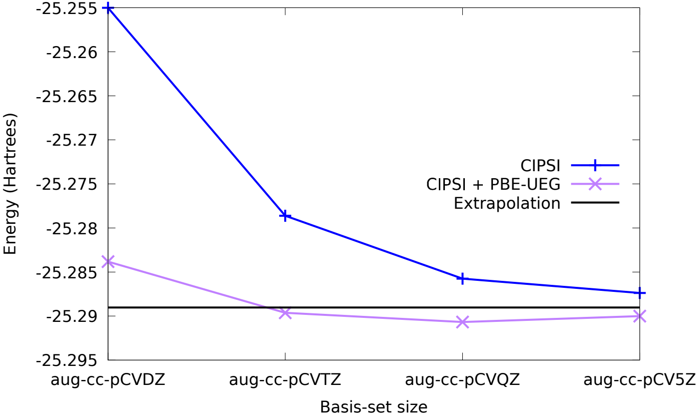
☞ **Non-diverging interactions**

BH ground state energy



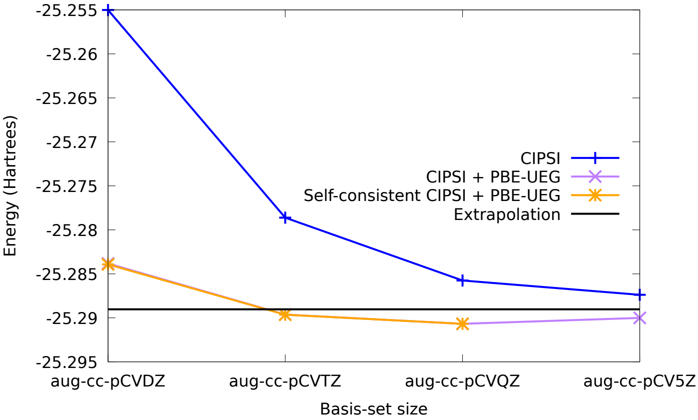
BH ground state energy

Procedure #1 : $E_0^{\mathcal{B}} \simeq \langle \Psi_{\text{FCI}}^{\mathcal{B}} | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \Psi_{\text{FCI}}^{\mathcal{B}} \rangle + \bar{E}_{\text{PBE-UEG}}^{\mathcal{B}}[n_{\Psi_{\text{FCI}}^{\mathcal{B}}}]$



BH ground state energy

Procedure #2 : $\hat{P}^{\mathcal{B}} \left(\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} + \hat{V}^{\mathcal{B}}_{\text{PBE-UEG}}[n_{\Psi^{\mathcal{B}}}] \right) |\Psi^{\mathcal{B}}\rangle = \mathcal{E}^{\mathcal{B}} |\Psi^{\mathcal{B}}\rangle$



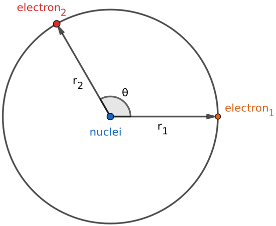
Coulomb cusp condition

Electronic pair density

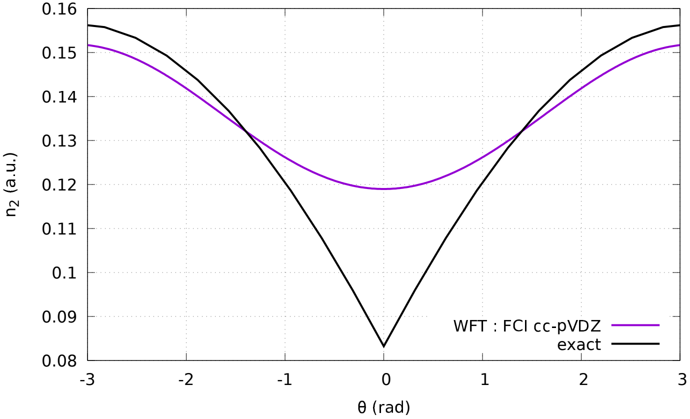
Density of probability to find electron 1 at position $\vec{r}_1$ while electron 2 is at position $\vec{r}_2$

$$n_2(\vec{r}_1, \vec{r}_2) = 2|\Psi(\vec{r}_1, \vec{r}_2)|^2$$

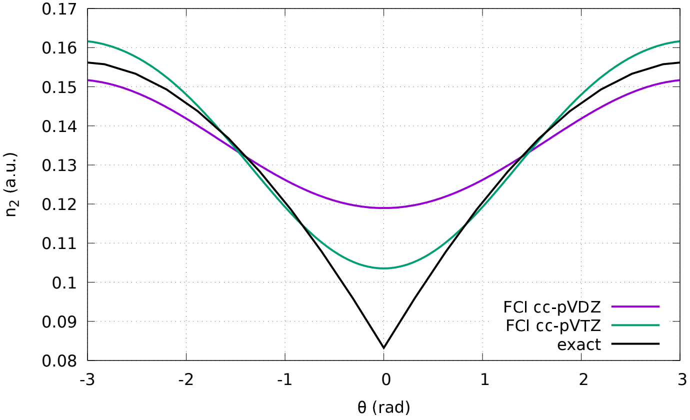
$r_1 = r_2 = 0.5$ a.u., $\theta \in [-\pi, \pi]$



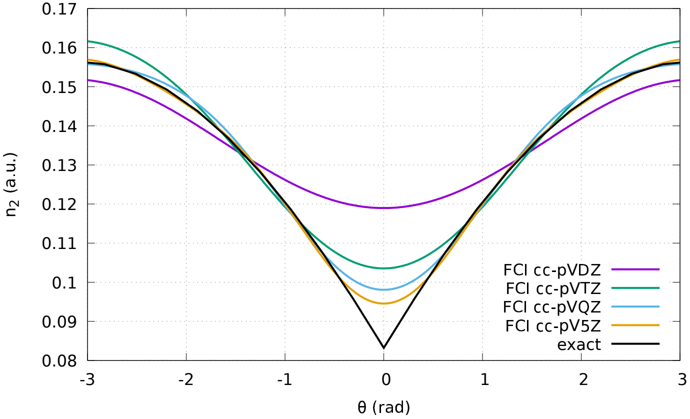
Helium pair density



Helium pair density



Helium pair density



WFT approaches

Hartree-Fock approximation :
A Slater determinant :

$$\Psi^{\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_{\mathrm{N}}) = (N!)^{-1/2} \begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_j(\mathbf{x}_1) & \dots & \phi_k(\mathbf{x}_1) \\ \phi_i(\mathbf{x}_2) & \phi_j(\mathbf{x}_2) & \dots & \phi_k(\mathbf{x}_1) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(\mathbf{x}_{\mathrm{N}}) & \phi_j(\mathbf{x}_{\mathrm{N}}) & \dots & \phi_k(\mathbf{x}_{\mathrm{N}}) \end{vmatrix}$$

where

$$\phi_i(\mathbf{r},\omega) = \alpha(\omega) \sum_\mu c_{\mu i} \chi_\mu(\vec{r})$$

$$\phi_i(\mathbf{r},\omega) = \beta(\omega) \underbrace{\sum_\mu c_{\mu i} \chi_\mu(\vec{r})}_{\psi_i(\mathbf{r})}$$

with Gaussian-type basis functions :

$$\chi_\mu(\vec{r}) = r^{l_\mu} \left(\sum_i d_{\mu,i} e^{-\alpha_\mu r^2} \right) \mathcal{Y}_{l_\mu,m_\mu}(\theta,\phi)$$

WFT approaches

Hartree-Fock approximation :

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Hartree-Fock equation :

$$E_0^{\mathrm{HF}} = \min_{\Psi^{\mathrm{HF}}} \langle \Psi^{\mathrm{HF}} | \hat{H} | \Psi^{\mathrm{HF}} \rangle$$

Euler-Lagrange with the constraint $\langle \phi_i | \phi_j \rangle = \delta_{ij}$:

$$\hat{f} \phi_i(\mathbf{x}) = \epsilon_i \phi_j(\mathbf{x})$$

Hartree-Fock estimation of the ground state energy :

$$\underbrace{E^{\text{correlation}}}_{\text{☹}} = E^{\text{exact}} - E^{\mathrm{HF}}$$

WFT approaches

Hartree-Fock approximation :
A Slater determinant :

$$\Psi^{\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_{\mathrm{N}}) = (N!)^{-1/2} \begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_j(\mathbf{x}_1) & \dots & \phi_k(\mathbf{x}_1) \\ \phi_i(\mathbf{x}_2) & \phi_j(\mathbf{x}_2) & \dots & \phi_k(\mathbf{x}_1) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(\mathbf{x}_{\mathrm{N}}) & \phi_j(\mathbf{x}_{\mathrm{N}}) & \dots & \phi_k(\mathbf{x}_{\mathrm{N}}) \end{vmatrix}$$

$\longrightarrow$ **Configuration interaction** methods

FCI approach

The full configuration interaction (FCI) wave function :

$$|\Psi^{\mathrm{FCI}}\rangle = c_{\mathrm{HF}}|\psi^{\mathrm{HF}}\rangle + \sum_{ar} c_a^r|\psi_a^r\rangle + \sum_{a>b,\, r<s} c_{ab}^{rs}|\psi_{ab}^{rs}\rangle + \sum_{a<b<c,\, r<s<t} c_{abc}^{rst}|\psi_{abc}^{rst}\rangle + \dots$$

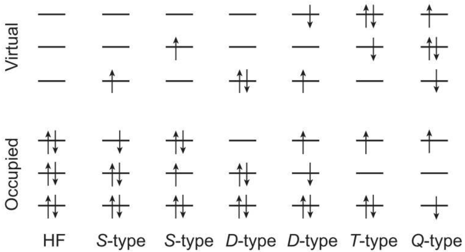

FIGURE 3.18 Excited Slater determinants generated from a ground state HF reference configuration.

(V.P. Gupta, Principles and applications of quantum chemistry, Elsevier (2016))

Approximations of the FCI

The full configuration interaction (FCI) wave function :

$$|\Psi^{\mathrm{FCI}}\rangle = c_{\mathrm{HF}}|\psi^{\mathrm{HF}}\rangle + \sum_{ar} c_a^r|\psi_a^r\rangle + \sum_{a>b,\, r<s} c_{ab}^{rs}|\psi_{ab}^{rs}\rangle + \sum_{a<b<c,\, r<s<t} c_{abc}^{rst}|\psi_{abc}^{rst}\rangle + \ldots$$

☹ Number of determinants scales exponentially with the size of the system

Truncation of the CI space :

- CIS (configuration interaction with simple excitations)
- CISD (configuration interaction with simple and double excitations)

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Truncation of the CI space :

- CIS (configuration interaction with simple excitations)
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- ☞ **CIPSI** : **C**onfiguration **I**nteraction **P**erturbatively **S**elected **I**teratively

(B. Huron, J. P. Malrieu, and P. Rancurel, J. Chem. Phys. 58, *5745, (1973))*
(E. Giner, A. Scemama, M. Caffarel, Canadian J. Chem., 91, *879-885 (2013))*

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Configuration-**I**nteraction **P**erturbatively **S**elected **I**teratively algorithm

Step 1 :

$$|\Psi^{(k)}\rangle = \sum_{I \in \mathcal{R}^{(k)}} c_I^{(k)} |I\rangle$$

☞ Quantum Package (`https://quantumpackage.github.io/qp2/`)

(B. Huron, J. P. Malrieu, and P. Rancurel, J. Chem. Phys. 58, *5745, (1973))*
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Configuration-Interaction Perturbatively Selected Iteratively algorithm

Step 1 :

$$|\Psi^{(k)}\rangle = \sum_{I \in \mathcal{R}^{(k)}} c_I^{(k)} |I\rangle$$

Step 2 :

$$\epsilon_{P,\mathrm{PT2}}^{(k)} = -\frac{|\langle \Psi^{(k)}|\hat{H}|P\rangle|^2}{\langle P|\hat{H}|P\rangle - \langle \Psi^{(k)}|\hat{H}|\Psi^{(k)}\rangle}$$

→ Selection of the largest contributions $|\epsilon_{P,\mathrm{PT2}}^{(k)}|$.

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Configuration-Interaction Perturbatively Selected Iteratively algorithm

Step 1 :

$$|\Psi^{(k)}\rangle = \sum_{I \in \mathcal{R}^{(k)}} c_I^{(k)} |I\rangle$$

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$$\epsilon^{(k)}_{P,\mathrm{PT2}} = -\frac{|\langle \Psi^{(k)}|\hat{H}|P\rangle|^2}{\langle P|\hat{H}|P\rangle - \langle \Psi^{(k)}|\hat{H}|\Psi^{(k)}\rangle}$$

→ Selection of the largest contributions $|\epsilon^{(k)}_{P,\mathrm{PT2}}|$.

Step 3 :

$$\text{If } |\sum_P \epsilon^{(k)}_{P,\mathrm{PT2}}| > \text{threshold} \rightarrow \text{Step 1}$$

☞ Quantum Package (`https://quantumpackage.github.io/qp2/`)