Overview of selected configuration interaction ~~and its coupling with DFT~~

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WFT in a nutshell ..

- Basis set $\mathcal{B}$ ⇔ **Hydrogen-like** functions **centered on atoms**
- Use **Slater determinants** for the N_e-particle basis set:

$$\Psi^{\mathcal{B}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) = \sum_{\mathrm{I}} c_{\mathrm{I}} \, \psi_{\mathrm{I}}^{\mathcal{B}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e})$$

- **Try to solve**

$$\hat{H} \, \Psi^{\mathcal{B}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) = E \, \Psi^{\mathcal{B}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e})$$

- **A clear target:** the **FCI**

$$\boxed{E_{\mathrm{FCI}}^{\mathcal{B}} = \min_{\Psi^{\mathcal{B}}} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{v}_{ne} | \Psi^{\mathcal{B}} \rangle}$$

$\Psi^{\mathcal{B}}$ a is a fully flexible wave function **within** $\mathcal{B}$

- **Approximated WFT methods :**
  - **Who are** $\psi_{\mathrm{I}}^{\mathcal{B}}$ **?**
  - **How to find** c_{I} **?**
  - **How to determine** E **?**

3 questions leads to MANY WFT methods ...

(Some) **Acronyms for Wave Function Theory ...**

- HF, MP2, CEPA-*n*, CISD(SC)^2, CCSD(T), BCCD(T), EOM-CCSD(T), PNO-CCSD(T), DLPNO-CCSD(T), ...
- CASCI, CASSCF, MCSCF, MRMP2, XMCQDPT, CASPT2, MS-CASPT2, NEVPT2, SC-NEVPT2, PC-NEVPT2, QD-NEVPT2, JMMRPT2, ...
- CIPSI, HBCI, MPS, DMRG, FCIQMC, *i*FCIQMC, ACI, SORCI, DDCI, FOBOCI, ...
- SS-MRCC, SU-MRCC, VU-MRCC, JM-MRCC, Mk-MRCCSDT, ic-MRCC, ...

Why so many acronyms ?

- Do theoretical chemists **love** to produce more ? (ego issue ?)
- Chemistry is very **heterogeneous**:
  - Different **properties** to compute (E, $\vec{\nabla}E$, etc ...)
  - Different **size of systems** ($10^1 \rightarrow 10^3$ electrons)
  - Different **states** (ground/excited state, spin symmetry ...)
  - Different **correlation** (weak and/or strong)
  - **Chemical accuracy** ($\approx$ 1 mH, 0.02 eV, 300 K)
- **Within $\mathcal{B}$:** what is the answer of selected CI to
  - **Who are $\psi_{\mathrm{I}}^{\mathcal{B}}$?**
  - **How to find c_{I} ?**
  - **How to determine E ?**
  - **What computational scaling with $N_{\mathcal{B}}$?**
- **What outside $\mathcal{B}$?**

  ⇒ **chemical accuracy** and link with DFT

Some history of selected CI in quantum chemistry

Selected CI: use a **selection** based on $\hat{H}$

Natural idea (re)**discovered** and (slightly) improved **MANY** times

- Bender, Davidson, 1969
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- Malrieu *et al*, 1973 (CIPSI)
- Buenker *et al*, 1978
- Malrieu *et al*, 1983 (CIPSI)
- Cimiraglia, 1985 (CIPSI)
- Angeli *et al*, 1997 (CIPSI)
- Hanrath *et al*, 2001
- Sherill *et al*, 2005
- Bunge *et al*, 2006
- Ruedenberg *et al*, 2009 (CEEIS)
- Toulouse group, 2013-2020 (CIPSI for QMC and stochastic PT2)
- Umrigar *et al*, 2016-2020 (HCI and stochastic PT2)
- Liu *et al*, 2016 (iCI)
- Evangelista *et al*, 2017 (ACI: CIPSI with another name ... ?)
- Hasegawa *et al*, 2017
- ...

The concept of selection in WFT

- Selection **a priori**:
  - You **can predict exactly** who are the $\psi_{\mathrm{I}}^{\mathcal{B}}$
  - Ex: all singles and doubles on top of HF, CASCI space, etc ...
  - Ex: CISD, CCSD, CCSD(T), MP2, CASSCF, NEVPT2, ...
- Selection **without a priori**
  - You **cannot predict** who are the $\psi_{\mathrm{I}}^{\mathcal{B}}$
  - Ex: selection by perturbation, random walk in $\psi_{\mathrm{I}}^{\mathcal{B}}$ space, etc ...
  - Ex: selected CI (CIPSI, HCI, blablabla), FCI-QMC, etc ...

Selection *with "A priori"*

- Not always adapted : **user dependency** ☹
  - Strong / weak correlation and their coupling ? (CCSD(T) enough/adapted ?)
  - Choice of the active space ? (Am I missing physics ?)

- Targets essentially a **polynomial subspace** of FCI

- Clear target: **mathematical optimization** ☺
  - Compute only $\langle\psi_{\rm I}|\hat{H}|\psi_{\rm J}\rangle \neq 0$ (exploit strong sparsity of $\hat{H}$)
  - Complex parametrization ($e^{\hat{T}}|{\rm HF}\rangle$, $\sum_{\rm I} c_{\rm I} e^{\hat{T}_{\rm I}}|\psi_{\rm I}\rangle$, etc ...)
  - **Good properties**: size extensivity/spin multiplet degeneracy
    Ex: CISD died, CCSD took over because of size extensivity

Selection *without ”A priori”*

- When affordable: **essentially the FCI solution** ☺
  - **Very trusty and black box**
  - Handle strong / weak correlation and their coupling
- Targets the **whole FCI space** ☹
  - Exponentially large target
  - But ”not so many” $|\psi_{\mathrm{I}}\rangle$ matter at the end ...
- No *A priori* knowledge: **Linear parametrization**
  - *i.e.* CI expansion, not CC expansion
  - Simple equations (CI + MRPT2 for instance)
  - Much less simple to make it efficient
- If not converged:
  - Size consistency issue
  - Bad error cancellations for energy differences

The CIPSI-like algorithm (1)

Starting with a guess WF: $|\Psi^{(0)}\rangle = \sum_{\mathrm{I}=1}^{N^{(0)}} c_{\mathrm{I}}|\psi_{\mathrm{I}}\rangle$

do k = 0, $N_{iterations}$

1. Look at all **connected** determinants $|\mu\rangle$: $\langle\mu|\hat{H}|\Psi^{(k)}\rangle \neq 0$
   $\Rightarrow$ single or double excitation on top of any $|\psi_{\mathrm{I}}\rangle$
2. Compute the **perturbative energy** contribution ϵ_μ
3. **Sort all the** $|\mu\rangle$ by energy contribution ϵ_μ
4. **Select** the "n" most important ones
5. **Diagonalize** $\hat{H}$ in the **new set of determinants** :
   $N^{(k+1)} = N^{(k)} + n$
6. You have a **new reference WF** :
   $|\Psi^{(k+1)}\rangle = \sum_{\mathrm{I}=1}^{N^{(k+1)}} c_{\mathrm{I}}|\psi_{\mathrm{I}}\rangle$

end do

The perturbative and variational energy

At a given **iteration**, one has a given $|\Psi\rangle$:

- **Variational** energy

$$E_{Var} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

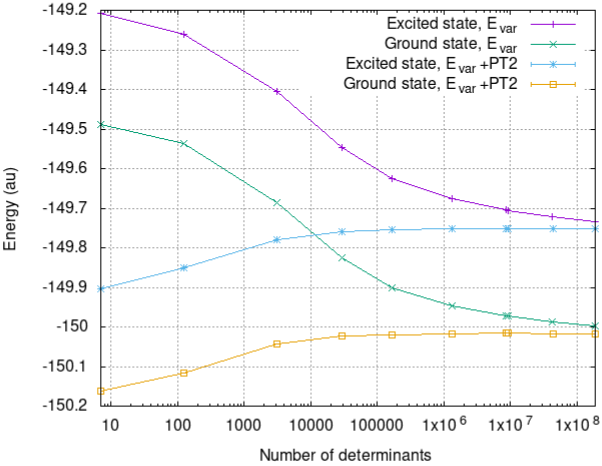
- Second order **Perturbative** energy

$$E_{PT2} = \sum_{\mu} \epsilon_{\mu}$$

$$\epsilon_{\mu} = \frac{\left(\langle\mu|\hat{H}|\Psi\rangle\right)^2}{E_{Var} - \langle\mu|\hat{H}|\mu\rangle}$$

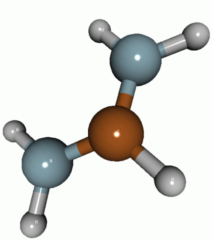
- **CIPSI** energy $\equiv E_{Var} + E_{PT2}$
  $\Rightarrow$ approximation of the **FCI energy**

Example: a cyanine ground and excited state



Frozen core FCI:

- 18 e in 111 MOs
- FCI space: $\approx 10^{24}\ \psi_{\mathrm{I}}$
- ΔE stabilized within 0.02 eV $\approx 2 \times 10^{6}\ \psi_{\mathrm{I}}$



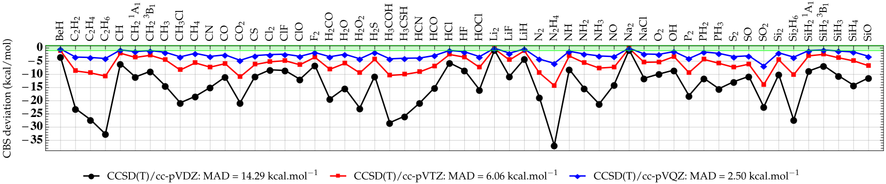
What can you obtain with CIPSI-like algorithms

- **FCI quality** whatever the **level of correlation** for gd/excited
- Modest basis (DZ) and molecules (4/5 non-hydrogen atoms) (See Loos *et al* 2018, 2019 with ≈ 400 FCI transition energies)
- Validation of methods in complex situations (Loos *et al* 2019 for doubly exc states and Giner *et al* 2019 for Cu^{2+} systems)
- QMC trial wave functions (a lot of litterature)
- Large CASSCF calculations (Umrigar *et al*)
- Caffarel / Chicago go in the direction of solid state

CIPSI available in QP2: stand-alone open source program
`https://quantum-package.readthedocs.io/en/master/`

- A lot of WFT tools
- All ingredients for DFT
- Developer friendly
- Check the Youtube videos :)

Example: the CCSD(T) atomization energies for the G2 set



Method	MAD	RMSD	MAX	CA
CCSD(T)/cc-pVDZ	14.29	16.21	36.95	2
CCSD(T)/cc-pVTZ	6.06	6.84	14.25	2
CCSD(T)/cc-pVQZ	2.50	2.86	6.75	9
CCSD(T)/cc-pV5Z	1.28	1.46	3.46	21

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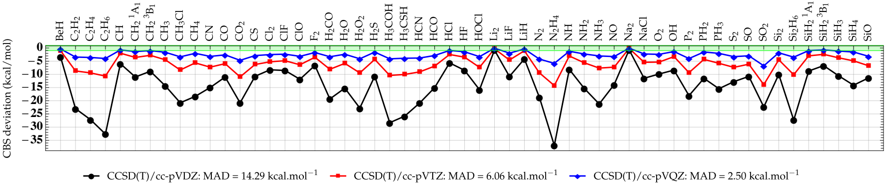

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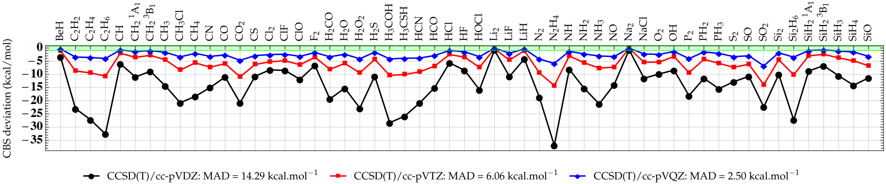

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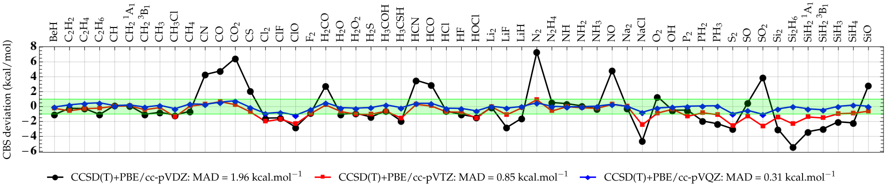

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Collaborators on selected CI and WFT/DFT

- selected CI
  - Anthony Scemama (LCPQ)
  - Michel Caffarel (LCPQ)
  - P. F. Loos (LCPQ)
  - Yan Garniron (LCPQ)
  - Anouar Benali (Chicago)
  - Kevin Gasperich (Chicago)
  - Anthony Ferté (LCPMR)
- coupling WFT/DFT
  - Julien Toulouse (LCT)
  - P. F. Loos (LCPQ)
  - Barthélémy Pradines (LCT)
  - Anthony Ferté (LCPMR)
  - Rolland Assaraf (LCT)
  - Anthony Scemama (LCPQ)

Exact conditions in WFT: the electron-electron cusp

- **Exact** wave function $\Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$ satisfies $\forall\ (\mathbf{r}_1,\dots,\mathbf{r}_N)$

$$H\ \Psi(\mathbf{r}_1,\dots,\mathbf{r}_N) = E\ \Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$$

$$\left(-\frac{1}{2}\sum_{i=1}^{N}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} v_{ne}(\mathbf{r}_i) + \sum_{i>j}\frac{1}{r_{ij}}\right)\Psi(\mathbf{r}_1,\dots,\mathbf{r}_N) = E\ \Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$$

- **Divergence** of coulomb interaction **near** $r_{12} \approx 0$

$$\lim_{r_{12}\to 0}\frac{1}{r_{12}} = +\infty$$

- $H\ \Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$ must remain **finite** $\forall\ (\mathbf{r}_1,\dots,\mathbf{r}_N)$:
  $\Rightarrow$ The kinetic energy must compensate !
  $\Rightarrow$ **Discontinuity** in first-derivative !
- **Cusp** in the electronic **wave function**

Exact conditions in WFT: the electron-electron cusp

- Expansion of **the exact Ψ** around $r_{12} \approx 0$:

$$\Psi(\mathbf{r}_1, r_{12}) = \underbrace{\Psi(\mathbf{r}_1, 0)}_{\text{System dependant}} \left(1 + \underbrace{\frac{1}{2}\,\mathbf{r_{12}}}_{\text{Universal !}} + \dots\right)$$

- Valid for any **fermionic systems**
- For instance the **U**niform **E**lectron **G**az
- Expansion of **truncated $\Psi^{\mathcal{B}}$** around $r_{12} \approx 0$

$$\Psi^{\mathcal{B}}(\mathbf{r}_1, r_{12}) = \Psi^{\mathcal{B}}(\mathbf{r}_1, 0)(1 + \underbrace{\mathbf{0} \times \mathbf{r_{12}}}_{\text{no cusp !}} + \dots)$$

- **One solution**: F_{12} methods

$$\Psi^{\mathcal{B}}_{\mathrm{F}_{12}}(\mathbf{r}_1, r_{12}) = f(r_{12})\Psi^{\mathcal{B}}(\mathbf{r}_1, r_{12})$$

An aternative point of view on the cusp

- **Finite** basis-set ⇔ $\Psi^{\mathcal{B}}$ **no cusp**

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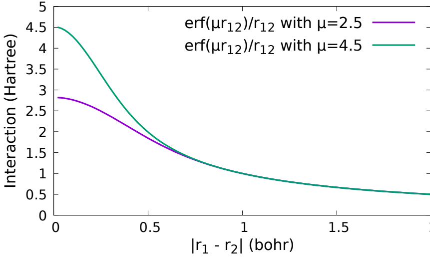
- **Truncation of** $\mathcal{B}$ ⇔ $\hat{W}_{ee}^{\mathcal{B}}$ **does not diverge !!**
- We know a **DFT framework which looks like that !** :)
  ⇒ **Range Separated DFT (RS-DFT)**

RS-DFT in a nutshell ...

- Hybrid WFT/DFT scheme
  (ex: range-separated hybrid)



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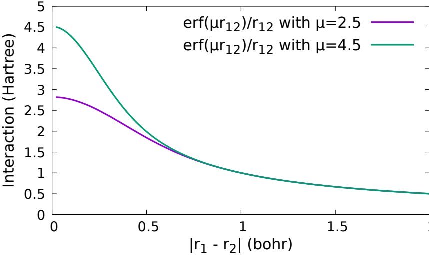
$$w_{ee}^{\mathrm{lr}}(r_{12};\mu) = \frac{\mathrm{erf}(\mu\, r_{12})}{r_{12}}$$

μ: **tunable** parameter



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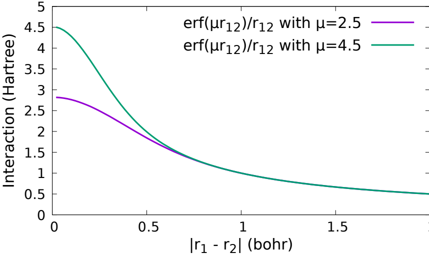

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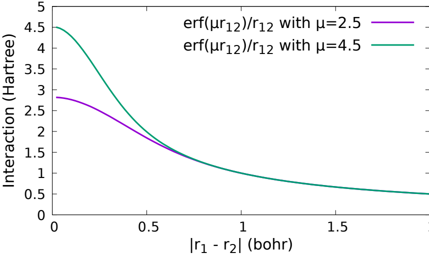

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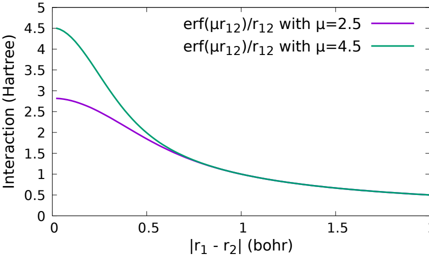

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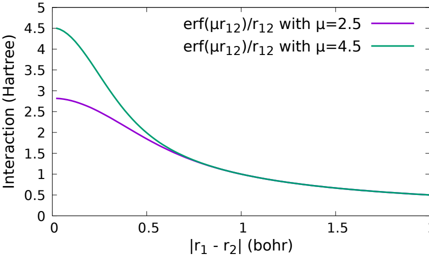

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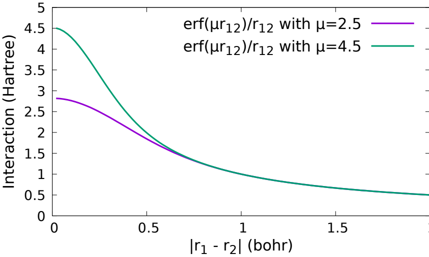
  - Self-interaction errors .. ?



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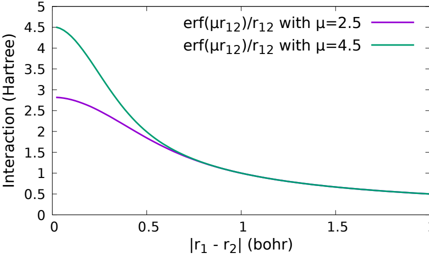

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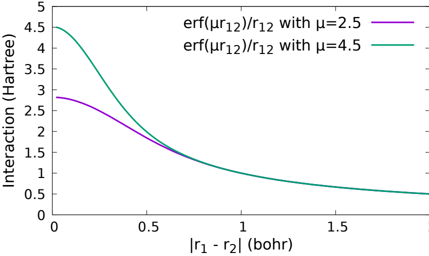
  - which μ .. ?
  - choice of the functional .. ?



Where we are going

Idea: taking RS-DFT only for **basis set error**

In practice

- Formalism to **merge WFT in $\mathcal{B}$ and DFT**
- Define properly a non diverging interaction within $\mathcal{B}$
- Fit it with the interaction used in RS-DFT
- Use RS-DFT functionals ! :)

The Levy-Lieb formalism of DFT

$$E_0 = \min_{n(\mathbf{r})} \Big\{ \underbrace{F[n(\mathbf{r})]}_{\textit{positive}} + \underbrace{(v_{\text{ne}}|n)}_{\textit{negative}} \Big\}$$

- Nuclei-electron interaction energy:

$$(v_{\text{ne}}|n) = \int \text{d}\mathbf{r}\ v_{\text{ne}}(\mathbf{r})\ n(\mathbf{r})$$

$\Rightarrow$ **system dependent**

- Levy-Lieb universal density functional:

$$F[n(\mathbf{r})] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle$$

  - **universal** : holly grail of DFT !
  - Here Ψ is developed in a **complete basis set**

Decomposition of $F[n^{\mathcal{B}}(\mathbf{r})]$

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

- We **split** $F[n(\mathbf{r})]$ **using** $\mathcal{B}$:

$$\boxed{F[n(\mathbf{r})] = \underbrace{\min_{\Psi^{\mathcal{B}} \rightarrow n(\mathbf{r})} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle}_{\text{within } \mathcal{B}} + \underbrace{\bar{E}^{\mathcal{B}}[n(\mathbf{r})]}_{\text{outside } \mathcal{B}}} \qquad (1)$$

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$\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$ is **the complementary density functional for $\mathcal{B}$**:

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

$\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$ must **recover what is missing in $\Psi^{\mathcal{B}}$**

Decomposition of $F[n^{\mathcal{B}}(\mathbf{r})]$

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

- We **split $F[n(\mathbf{r})]$ using $\mathcal{B}$**:

$$\boxed{F[n(\mathbf{r})] = \underbrace{\min_{\Psi^{\mathcal{B}} \rightarrow n(\mathbf{r})} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle}_{\text{within } \mathcal{B}} + \underbrace{\bar{E}^{\mathcal{B}}[n(\mathbf{r})]}_{\text{outside } \mathcal{B}}} \qquad (1)$$

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$\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$ must **recover what is missing in $\Psi^{\mathcal{B}}$**

- $\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$ not universal, but **a functional of the density !**

Approximation of the FCI density

- Using the previous decomposition:

$$E_0 = \min_{n(\mathbf{r})} \left\{ \min_{\Psi^{\mathcal{B}} \rightarrow n(\mathbf{r})} \langle \Psi^{\mathcal{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle + (v_{\text{ne}} | n) + \bar{E}^{\mathcal{B}} [n(\mathbf{r})] \right\} \quad (2)$$

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- But **FCI densities are really good !**
- Evaluation of (2) at $n(\mathbf{r}) = n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})$: final equation

$$\boxed{E_0 \approx \langle \Psi^{\mathcal{B}}_{\text{FCI}} | H | \Psi^{\mathcal{B}}_{\text{FCI}} \rangle + \bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})]} \quad (3)$$

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- Only approximation here :

$$\boxed{n_0(\mathbf{r}) \approx n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})} \ \textbf{much weaker than } \Psi_0 \approx \Psi^{\mathcal{B}}_{\text{FCI}}$$

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- $\bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})]$ must recover **what is missing in $\mathcal{B}$**
  ⇒ a large part is **short-range correlation effects !**

Approximation of the FCI density

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- $\bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})]$ must recover **what is missing in $\mathcal{B}$**
  $\Rightarrow$ a large part is **short-range correlation effects !**
- Question: how to find $\bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})]$?

Where we are going

Idea: taking RS-DFT only for **basis set error**

In practice

- **Formalism to merge WFT in $\mathcal{B}$ and DFT ☺**
- **Define properly a non diverging interaction within $\mathcal{B}$**
- Fit it with the interaction used in RS-DFT
- Use RS-DFT functionals

The effective e-e interaction within $\mathcal{B}$

- Expectation value of $\hat{W}_{\text{ee}}$ over $\Psi^{\mathcal{B}}$ as an integral **real space**

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iint \text{d}\mathbf{r}_1 \, \text{d}\mathbf{r}_2 \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2)$$

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- Consider $\hat{W}_{\text{ee}}^{\mathcal{B}} = \frac{1}{2} \sum_{ijkl \, \in \, \mathcal{B}} V_{ij}^{kl} \, \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i$ in **real space** (operator in Fock space ⇔ distributions in real space)

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- Do some more math (distributions again ...) and end-up with

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iint d\mathbf{r}_1 \, d\mathbf{r}_2 \, f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2),$$

$$f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ijklmn} V_{ij}^{kl} \Gamma_{mn}^{kl} \; \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_m(\mathbf{r}_1) \phi_n(\mathbf{r}_2)$$

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- as $\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle = \langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle$ one can write

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$$\iint \text{d}\mathbf{r}_1 \, \text{d}\mathbf{r}_2 \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \; n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) = \iint \text{d}\mathbf{r}_1 \, \text{d}\mathbf{r}_2 \; W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2) n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1, \mathbf{r}_2)$$

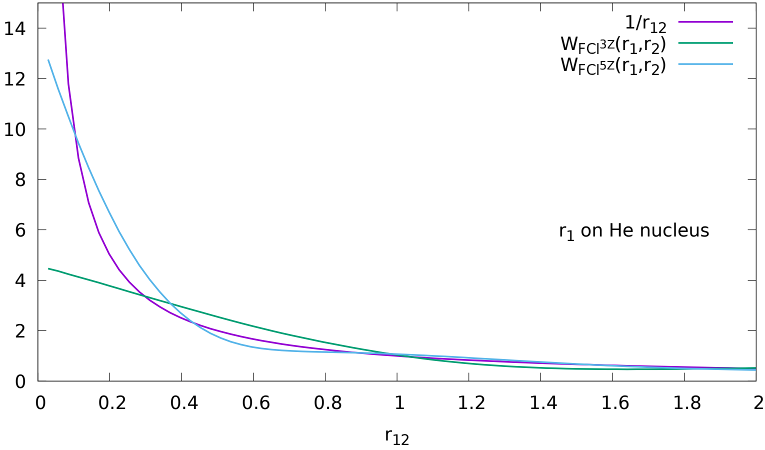
A few properties of $W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2) = \begin{cases} \frac{f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)}{n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)}, & \text{if } n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2) \neq 0, \\ \infty, & \text{otherwise,} \end{cases}$$

- $W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$ **depends on** $\Psi^{\mathcal{B}}$
- necessary **finite at** $r_{12} = 0$ when $\mathcal{B}$ is incomplete
- Because of its very construction

$$\boxed{\lim_{\mathcal{B}\to\infty} W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{r_{12}} \ \forall \ \Psi^{\mathcal{B}}}$$

Example Hellium with $\Psi^{\mathcal{B}}$ =FCI



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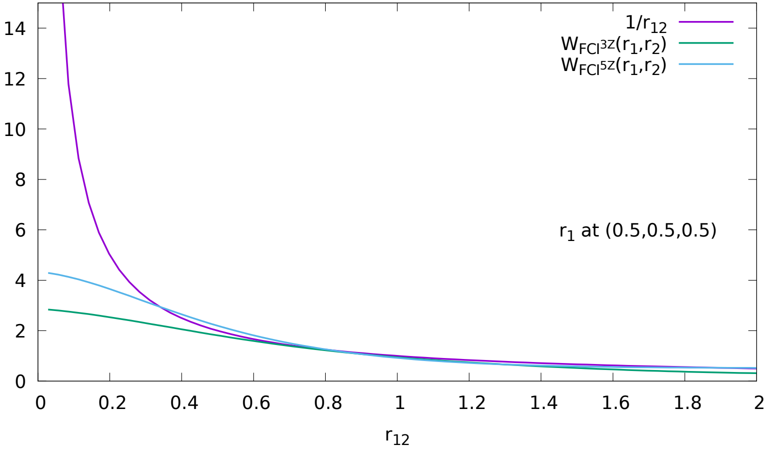
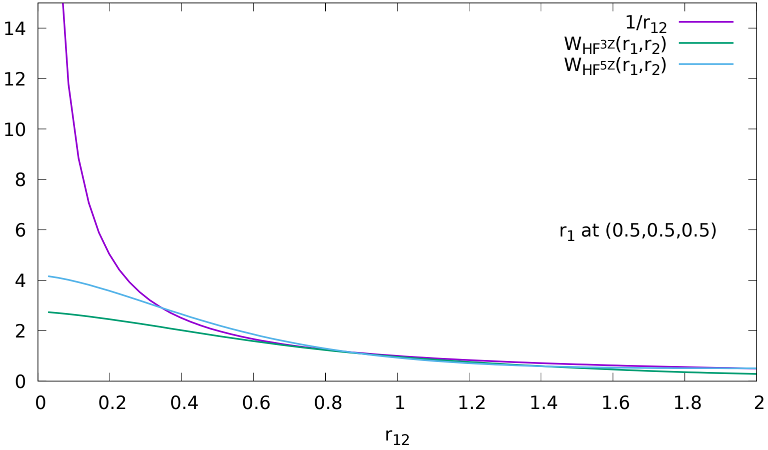


Example Hellium with $\Psi^{\mathcal{B}}$ =HF



Where we are going

Idea: taking RS-DFT only for **basis set error**

In practice

- **Formalism to merge WFT in $\mathcal{B}$ and DFT ☺**
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Fit $W_{\Psi_{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$ with RS-DFT interaction

- RS-DFT uses **non diverging interaction** tuned by μ

$$w_{ee}^{\text{lr}}(\mathbf{r}_1,\mathbf{r}_2;\mu) = \frac{\text{erf}(\mu\, r_{12})}{r_{12}}$$

- **Fit** $W_{\Psi_{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$ at **coalescence**, *i.e.* $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$

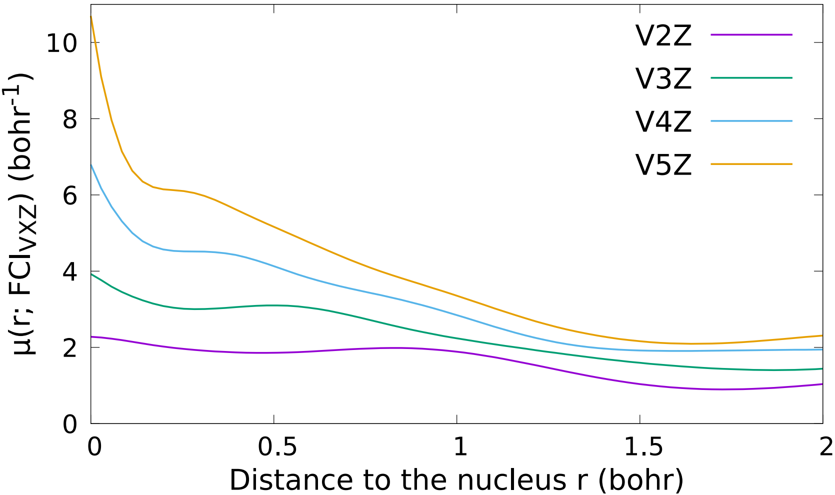
$$W_{\Psi_{\mathcal{B}}}(\mathbf{r},\mathbf{r}) = w_{ee}^{\text{lr}}(\mathbf{r},\mathbf{r};\mu)$$

- Leads to $\mu(\mathbf{r})$ varying in space

$$\boxed{\mu_{\Psi_{\mathcal{B}}}(\mathbf{r}) = \frac{\sqrt{\pi}}{2} W_{\Psi_{\mathcal{B}}}(\mathbf{r},\mathbf{r})}$$

$$\lim_{\mathcal{B}\to\infty} \mu_{\Psi_{\mathcal{B}}}(\mathbf{r}) = +\infty \quad \forall\, \Psi_{\mathcal{B}} \text{ and } \forall\, \mathbf{r}$$

Example Hellium with $\Psi^{\mathcal{B}}$ =FCI



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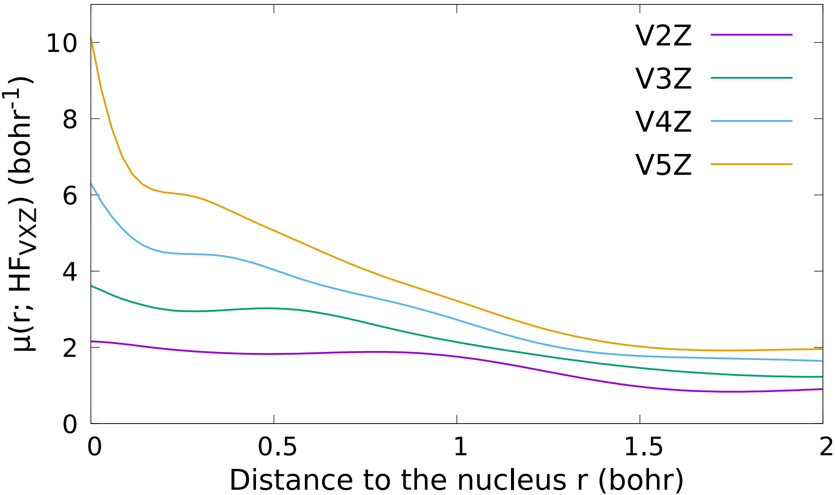

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Approximation for the functional

Using RSDFT functionals

- Use the **multi determinantal correlation** functionals $\epsilon_c^{\text{md}}(n;\mu)$ (Toulouse *et al*)

$$E_c^{\text{md}} = \int \text{d}\mathbf{r} \;\; \epsilon_c^{\text{md}}(n(\mathbf{r});\mu)$$

$$\lim_{\mu\to\infty} \epsilon_c^{\text{md}}(n;\mu) = 0$$

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$$\lim_{\mu\to\infty} \epsilon_c^{\text{md}}(n;\mu) = 0$$

- Use the range separation parameter $\mu_{\Psi_{\mathcal{B}}}(\mathbf{r})$

$$\bar{E}^{\mathcal{B}}[n(\mathbf{r})] \approx \int d\mathbf{r}\ \ \epsilon_c^{\text{md}}(n(\mathbf{r});\mu_{\Psi_{\mathcal{B}}}(\mathbf{r}))$$

- $\epsilon_c^{\text{md}}(n;\mu)$: LDA already existed, new PBE version recently proposed (JCP, 2019)

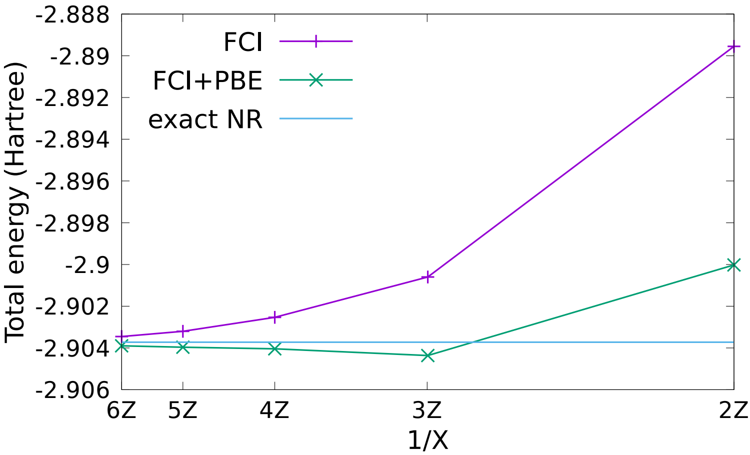
Final working equations

$$E_0 \approx E_{\text{FCI}}^{\mathcal{B}} + \int \mathrm{d}\mathbf{r} \;\; \epsilon_c^{\text{md}}\left(n_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r}); \mu_{\Psi^{\mathcal{B}}_{\text{FCI}}}(\mathbf{r})\right)$$

At the end of the day

- $\mu_{\Psi_{\mathcal{B}}}(\mathbf{r})$ **Automatically** adapts to $\mathcal{B}$
- **Correct limit** at the **Complete Basis Set limit**
- Use **pre-existing DFT methodology**

The total energy of the He atom



Systematically improve the results !

Generalization to any wave function method

- Exact framework works with FCI **energies**, **densities** and **WF**

$$E_0 \approx E_{\mathbf{FCI}}^{\mathcal{B}} + \int \mathrm{d}\mathbf{r} \;\; \epsilon_c^{\mathrm{md}}\left(n_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r}); \mu_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r})\right)$$

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Generalization to any wave function method

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$$E_0 \approx E^{\mathcal{B}}_{\mathbf{FCI}} + \int \mathrm{d}\mathbf{r} \;\; \epsilon_c^{\mathrm{md}}\big(n_{\Psi^{\mathcal{B}}_{\mathrm{FCI}}}(\mathbf{r}); \mu_{\Psi^{\mathcal{B}}_{\mathrm{FCI}}}(\mathbf{r})\big)$$

- What do you need is:

$$\boxed{E_0 \approx E^{\mathcal{B}}_{\mathbf{X}} + \int \mathrm{d}\mathbf{r} \; \epsilon_c^{\mathrm{md}}\big(n_{\mathrm{Y}}(\mathbf{r}); \mu_{\Psi^{\mathcal{B}}}(\mathbf{r})\big)}$$

Generalization to any wave function method

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$$E_0 \approx E_{\mathbf{FCI}}^{\mathcal{B}} + \int \mathrm{d}\mathbf{r} \;\; \epsilon_c^{\mathrm{md}}\big(n_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r}); \mu_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r})\big)$$

- What do you need is:

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- CIPSI calculations:

Generalization to any wave function method

- Exact framework works with FCI **energies**, **densities** and **WF**

$$E_0 \approx E_{\mathbf{FCI}}^{\mathcal{B}} + \int \mathrm{d}\mathbf{r} \;\; \epsilon_c^{\mathrm{md}}(n_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r}); \mu_{\Psi_{\mathrm{FCI}}^{\mathcal{B}}}(\mathbf{r}))$$

- What do you need is:

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- CIPSI calculations:
  - $E_{\mathbf{X}}^{\mathcal{B}}$: **CIPSI energy** $\approx E_{\mathbf{FCI}}^{\mathcal{B}}$

Generalization to any wave function method

- Exact framework works with FCI **energies**, **densities** and **WF**

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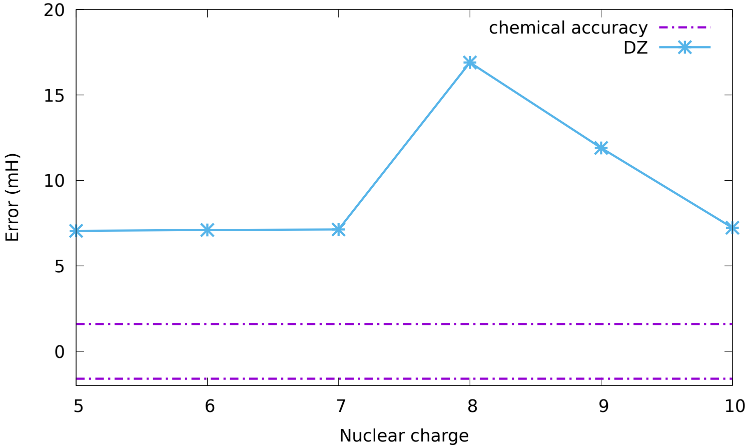
Example: CIPSI ionization potentials of the B-Ne series



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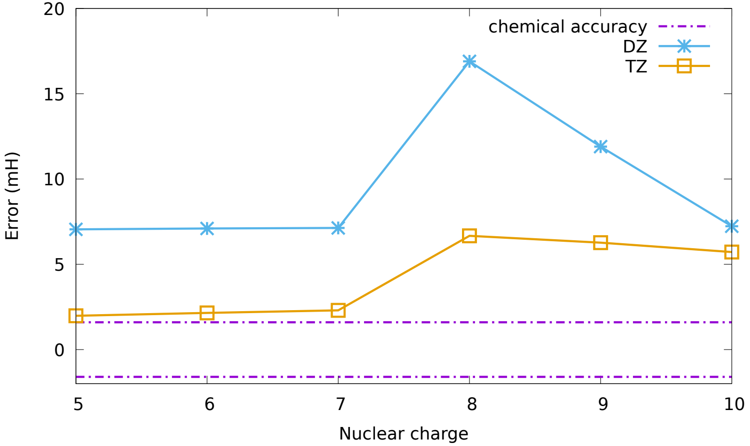

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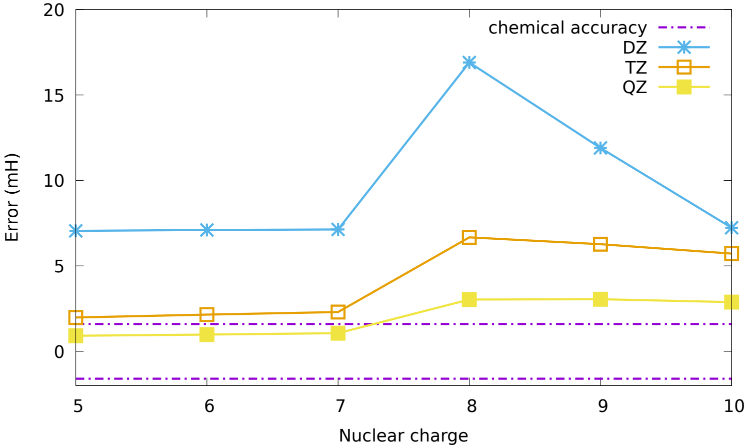

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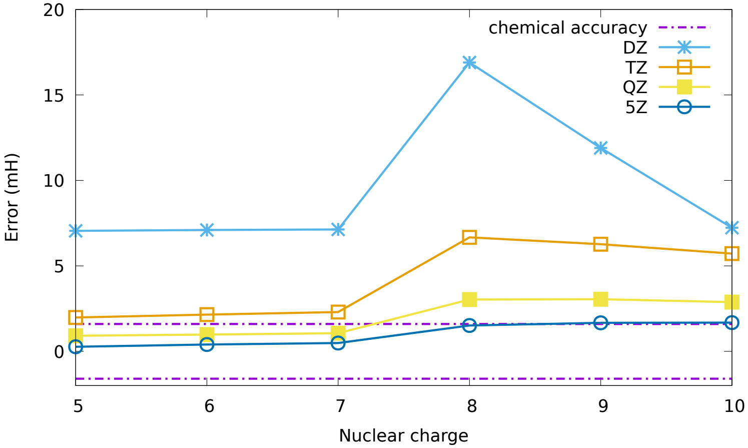

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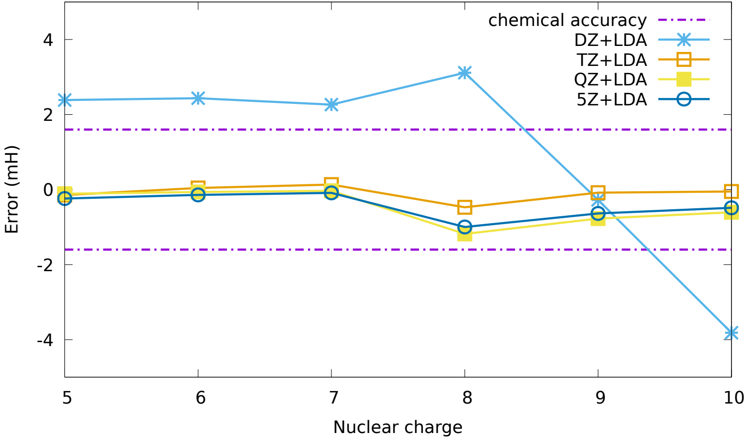
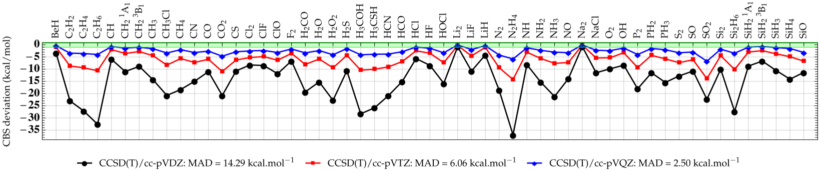


The G2 set with CCSD(T) and CCSD(T)+PBE



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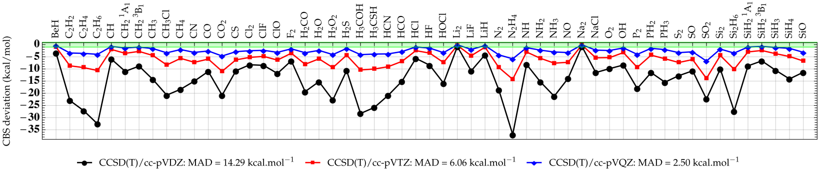

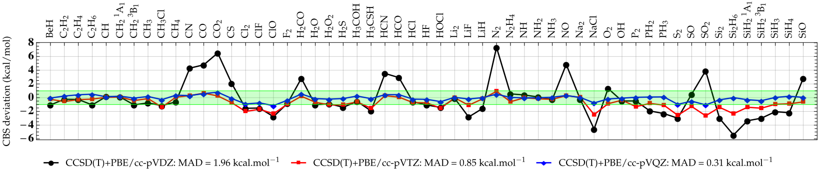

Statistical analysis of the G2 set with CCSD(T)+PBE

Method	MAD	RMSD	MAX	CA
CCSD(T)/cc-pVDZ	14.29	16.21	36.95	2
CCSD(T)/cc-pVTZ	6.06	6.84	14.25	2
CCSD(T)/cc-pVQZ	2.50	2.86	6.75	9
CCSD(T)/cc-pV5Z	1.28	1.46	3.46	21

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CCSD(T)+PBE/cc-pVDZ	1.96	2.59	7.33	19
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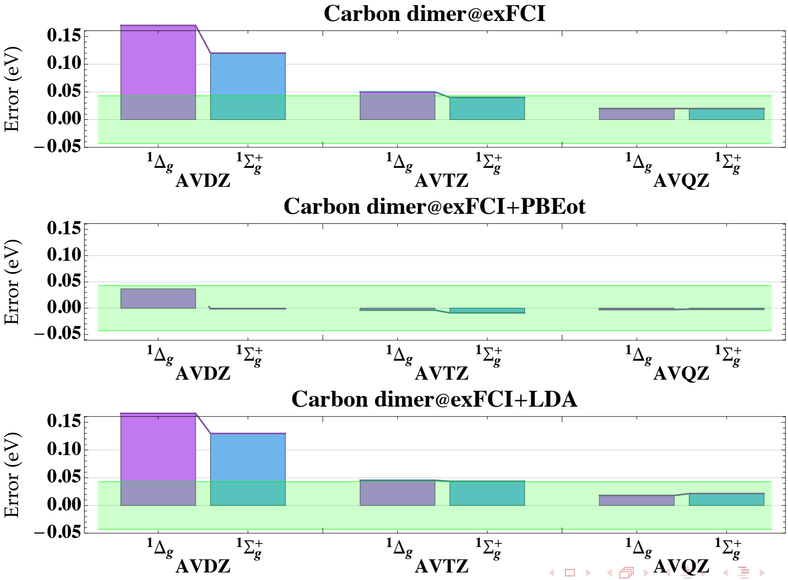
To compute the DFT part we need only

- The HF **one body density**
- The HF **two body density for α/β pairs**
- The **MP2 integrals**

very cheap compared to CCSD(T)

Application to excited states: doubly excited states



Conclusion and work in progress

What we obtained

- **Proper theory** to link **basis set error and DFT**
  J. Chem. Phys. 149, 194301 (2018)
  - **No cusp ⇔ non divergent interaction !**
  - **Automatic, simple and cheap**
  - **Correct limit when $\mathcal{B}$ is complete**
- Application to **weak correlation, CCSD(T) and CIPSI**
  J. Phys. Chem. Let., 10, 2931-2937 (2019)
- Application to **excited states**, J. Chem. Phys. 151, (2019)

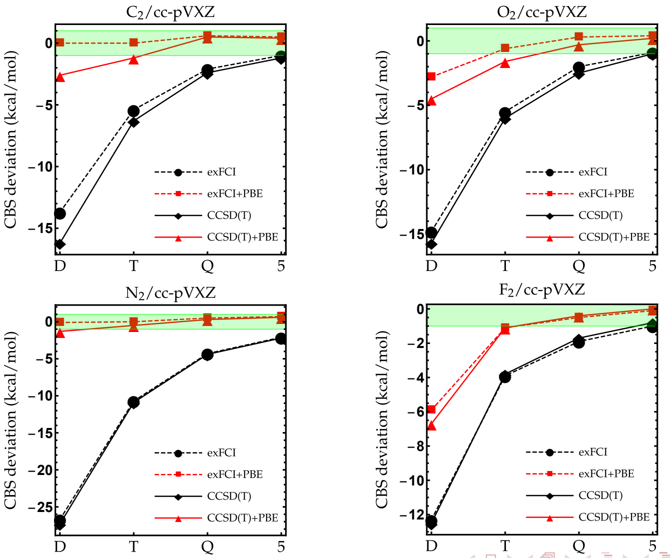
What we're doing now

- Development of **new functionals** for **strong correlation**
- Self-consistent formalism, properties, GW
- Formal aspects, new formalisms to connect $\mathcal{B}$ and DFT

Collaborators

- **Julien Toulouse** (introduction to DFT, enthousiasm ...)
- Roland Assaraf (distributions ...)
- Barthelemy Pradines (self consistent version, GW ...)
- PF Loos (excited states, GW ...)
- Andreas Savin (stimulating discussions ...)

Atomization energies with CIPSI/CCSD(T)



Link with the ECMD functionals in RSDFT

- Definition of $\bar{E}^{\mathcal{B}}[n(\mathbf{r})]$

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

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- Make a link between $\Psi^{\mathcal{B}}$ and Ψ^{μ}

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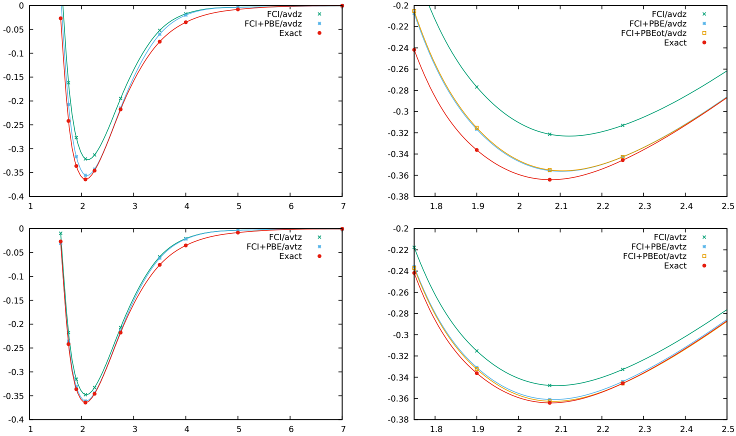
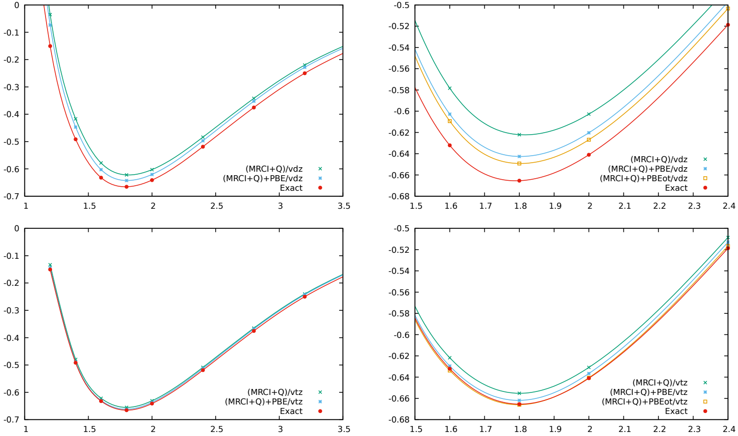
- Make a link between $\Psi^{\mathcal{B}}$ and Ψ^{μ}
- The way to make a link: connect $\hat{W}_{\text{ee}}^{\mathcal{B}}$ and $\hat{W}_{\text{ee}}^{\mu}$

PES of N_2 in AVXZ (X=D,T)



PES of H_{10} in VXZ (X=D,T)



The effective operator in practice

$$\hat{W}_{\rm ee}^{\mathcal{B}} = \frac{1}{2} \sum_{ijkl\,\in\,\mathcal{B}} V_{ij}^{kl}\ \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i, \quad \hat{a}_k^\dagger = \int d\mathbf{r}_1 \phi_k(\mathbf{r}_1) \hat{\Psi}^\dagger(\mathbf{r}_1)$$

$$\hat{W}_{\rm ee}^{\mathcal{B}} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_{1'} d\mathbf{r}_{2'} w_{ee}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{1'}, \mathbf{r}_{2'}) \hat{\Psi}^\dagger(\mathbf{r}_1) \hat{\Psi}^\dagger(\mathbf{r}_2) \hat{\Psi}(\mathbf{r}_{2'}) \hat{\Psi}(\mathbf{r}_{1'})$$

$$w_{ee}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{1'}, \mathbf{r}_{2'}) = \sum_{ijkl\,\in\,\mathcal{B}} V_{ij}^{kl}\ \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2) \phi_j(\mathbf{r}_{2'}) \phi_i(\mathbf{r}_{1'})$$

Here $w_{ee}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{1'}, \mathbf{r}_{2'})$ MUST NOT be considered as function as

$$\lim_{\mathcal{B}\to\infty} w_{ee}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{1'}, \mathbf{r}_{2'}) = \delta(\mathbf{r}_1 - \mathbf{r}_{1'}) \delta(\mathbf{r}_2 - \mathbf{r}_{2'}) \frac{1}{r_{12}}$$

The diagonal elements $w_{ee}^{\mathcal{B}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$ do not make sense ...

The effective operator in practice

$w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'},\mathbf{r}_{2'})$ MUST be considered as a **distribution**
Therefore, one MUST integrate $w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'},\mathbf{r}_{2'})$ over functions

$$\begin{aligned}\langle\Psi^{\mathcal{B}}|\hat{W}_{\text{ee}}^{\mathcal{B}}|\Psi^{\mathcal{B}}\rangle &= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_{1'} d\mathbf{r}_{2'}\ w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'},\mathbf{r}_{2'}) \\ &\qquad \langle\Psi^{\mathcal{B}}|\hat{\Psi}^\dagger(\mathbf{r}_1)\hat{\Psi}^\dagger(\mathbf{r}_2)\hat{\Psi}(\mathbf{r}_{2'})\hat{\Psi}(\mathbf{r}_{1'})|\Psi^{\mathcal{B}}\rangle \\ &= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_{1'} d\mathbf{r}_{2'}\ w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'}\mathbf{r}_{2'}) n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'}\mathbf{r}_{2'})\end{aligned}$$

Apply the distribution $w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'},\mathbf{r}_{2'})$, integrate over $\mathbf{r}_{1'}$ and $\mathbf{r}_{2'}$

$$\begin{aligned}\langle\Psi^{\mathcal{B}}|\hat{W}_{\text{ee}}^{\mathcal{B}}|\Psi^{\mathcal{B}}\rangle &= \int d\mathbf{r}_1 d\mathbf{r}_2 \left(\int d\mathbf{r}_{1'} d\mathbf{r}_{2'} w_{ee}^{\mathcal{B}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'}\mathbf{r}_{2'}) n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{1'}\mathbf{r}_{2'}) \right) \\ &= \int d\mathbf{r}_1 d\mathbf{r}_2 \quad f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)\end{aligned}$$

Why HF is such a good approximation for μ ?

$$W_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)}{n_2^{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)}$$

- Everything is within $f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$
- The explicit form for $f_{\Psi^{\mathcal{B}}}(\mathbf{r}_1,\mathbf{r}_2)$ for $\Psi^{\mathcal{B}}$ =HF for α/β electrons

$$f_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k\in\alpha}\sum_{l\in\beta}\sum_{ij\in\mathcal{B}} V_{ij}^{kl}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2) \tag{4}$$

- $\sum_{ij\in\mathcal{B}} \Leftrightarrow$ one sees "all the basis $\mathcal{B}$"
- Integrals involved V_{ij}^{ab} like in usual MP2 calculations
- Dominant effect to quantify the quality of the basis set

Finite basis-set approximation for the exact density

- In actual calculation: **finite one-electron basis set $\mathcal{B}$**
  $\Rightarrow$ search over a **subet of densities $n^{\mathcal{B}}(\mathbf{r})$**

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

- $n_0^{\mathcal{B}}(\mathbf{r})$ is the density giving the lowest energy
- $n_0(\mathbf{r})$ might not be representable within $\mathcal{B}$
  $\Rightarrow E_0^{\mathcal{B}} \geq E_0$
- In practice **fast convergence of the density with $\mathcal{B}$**

$$\boxed{\begin{array}{l} n_0(\mathbf{r}) \approx n_0^{\mathcal{B}}(\mathbf{r}) \\ E_0 \approx E_0^{\mathcal{B}} \end{array}}$$

What about DFT and the basis set ?

- How does **DFT** works ?
    - expresses the **two-body density** with **one-body density**

$$n_2(\mathbf{r}_1,\mathbf{r}_2) = \underbrace{n(\mathbf{r}_1)n(\mathbf{r}_2)}_{\text{System dependant}} + \underbrace{n_{\text{xc}}(\mathbf{r}_1,\mathbf{r}_2,n,\nabla n,...)}_{\text{quite universal}}$$

    - Example: LDA $n_{\text{xc}}(n)$ is taken from the electron gas

- $n_{\mathbf{xc}}(\mathbf{r}_1,\mathbf{r}_2)$ **when** $r_{12} \approx 0$ ⇔ electron cusp ⇔ **universal !**
  ⇒ short-range correlation effects well reproduced !

- n **converges rapidly with** $\mathcal{B}$

- Long-range correlation effects are less universal ...