Range-separation and Basis sets.

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Some context

- I'll talk about about ***range-separation*** (combining WFT and DFT) and about ***basis set effect*** and ***electron-electron cusp***

- I used to work on range-separation
  before joining Sandeep's group.

- When I went back to France in March,
  I talked about the latest developments in this field : it's interesting.

- **I'll be mainly talking about these two papers :**

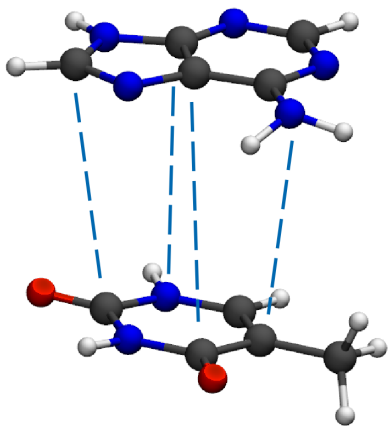
  - "Curing basis-set convergence of wave-function theory using density-functional theory : A systematically improvable approach" Giner *et al.* JCP (2018) ***JCP Editor's pick*** (link)

  - "Range-separated multideterminant density-functional theory with a short-range correlation functional of the on-top pair density" Ferté *et al.* JCP (2019) ***JCP Editor's pick*** (link)

Some context

- I'll talk about about ***range-separation*** (combining WFT and DFT) and about ***basis set effect*** and ***electron-electron cusp***

A typical example of failures of DFT
is the treatment of *long-range correlation*
(van der Waals forces, hydrogen bond, dispersion, dots)



DNA base

An idea is to rigourously couple methods

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \text{short-range (DFT)} + \text{long-range (WFT)}$$

Electronic Structure (remember ?)

- We are interested in ***energies***, ***energy differences***, ***energy derivatives***, . . .and we need the ***wavefunction***, or the ***density matrices***.

- We could do **WFT** (systematically improvable but expensive)
  or **DFT** (cheap but not systematically improvable)

We work in a basis of one-electron orbitals

$$\mathbf{B} = \{\phi_i\}$$

and in a basis of N-electrons determinants

$$\Psi_I^{\mathbf{B}} = |\phi_a \dots \phi_b|$$

on which we can expand the wavefunction

$$\Psi^{\mathbf{B}} = \sum c_I \Psi_I^{\mathbf{B}}$$

Electronic Structure (remember ?)

(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, ...
- SHCI, CIPSI, MPS, DMRG, FCIQMC, iFCIQMC, ACI, SORCI, DDCI, FOBOCI, ...
- SS-MRCC, SU-MRCC, VU-MRCC, JM-MRCC, Mk-MRCCSDT, ic-MRCC, ...

All approximate the "***FCI***" result :

$$E^{\mathbf{B}}_{\mathrm{FCI}} = \min_{\Psi^{\mathbf{B}}} \langle \Psi^{\mathbf{B}} | \hat{H} | \Psi^{\mathbf{B}} \rangle = \langle \Psi^{\mathbf{B}}_{\mathrm{FCI}} | \hat{H} | \Psi^{\mathbf{B}}_{\mathrm{FCI}} \rangle$$

The wavefunction cusp

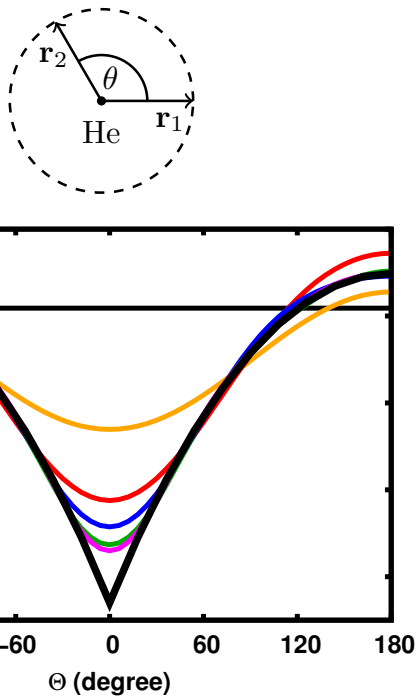
A lot of physics is lost in the approximation of the wavefunction cusp.

- **Exact wavefunction around $r_{12} \sim 0$:**

$$\Psi(\mathbf{r}_1, \mathbf{r}_{12}) = \underbrace{\Psi(\mathbf{r}_1, 0)}_{\text{system-dependant}} \underbrace{\left(1 + \frac{1}{2}\mathbf{r}_{12} + \dots\right)}_{\text{universal}}$$

- **Truncated wavefunction around $r_{12} \sim 0$:**

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



[Franck *et al.* JCP (2015)]

This is the ***short-range correlation***,
it's universal, and it's poorly described in WFT

Density Functional Theory

The problem in WFT is the slow convergence of n_2 near $\mathbf{r}_{12} \sim 0$, but n_1 converges rapidly with B !

DFT precisely works by expressing two-body quantities as one-body quantities :

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n_1(\mathbf{r}_1)\, n_1(\mathbf{r}_2) + \mathbf{n_{xc}}(\mathbf{r}_1, n_1, \nabla n_1, \ldots)$$

e.g. : $\mathbf{n_{xc}^{LDA}}(n_1)$, taken from the UEG

$\mathbf{n_{xc}}$ when $\mathbf{r}_{12} \sim 0$ is ***universal*** and performs well for **short-range correlation**

The **long-range correlation** is not so universal and is poorly described by DFT

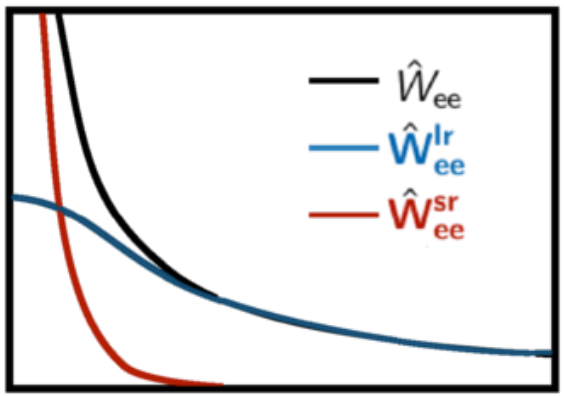
A ***"best of both words"*** scenario is shaping up :

- WFT struggles at short-range, is good for long-range
- DFT is a local approximation : is good for short-range

Range-separation

The idea is to split the e-e interaction into **long-** and **short-** range parts :

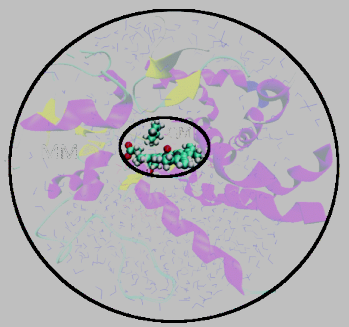
$$\hat{W}_{ee} = \hat{W}^{lr}_{ee} + \hat{W}^{sr}_{ee}$$



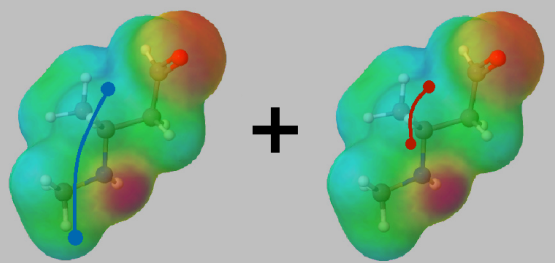
As a result, we can ***rigourously*** **mix WFT and DFT** methods

$$E = \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{ee} | \Psi \rangle + E^{sr}_{Hxc}[n_\Psi]$$

Note :
This is **not** embedding !
(where *real space regions* are receiving different treatment)



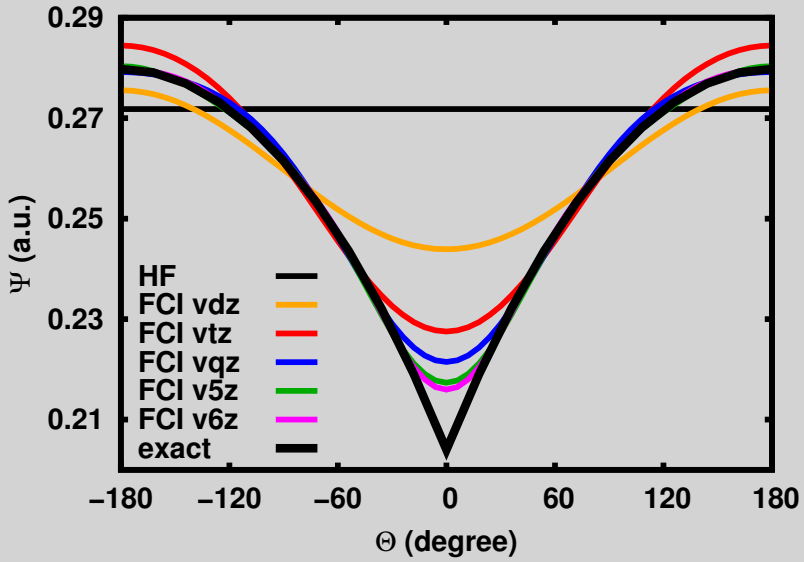
Here we separate on **range** :

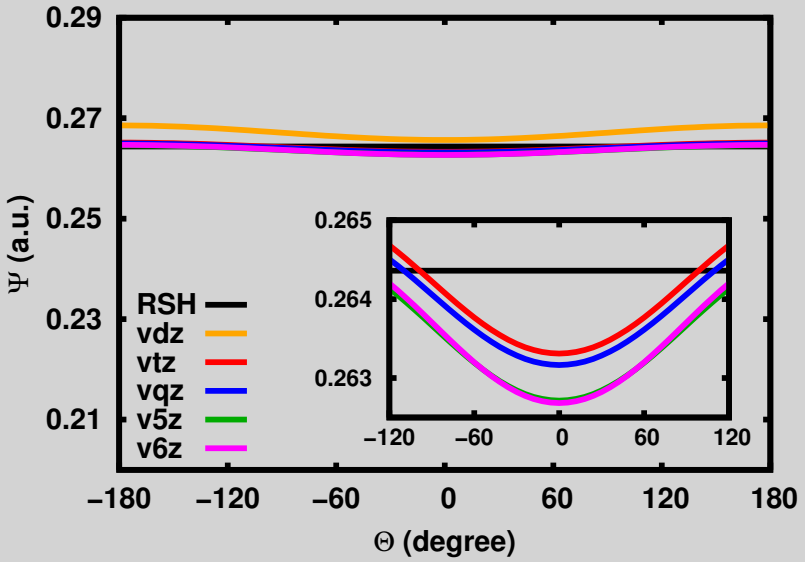


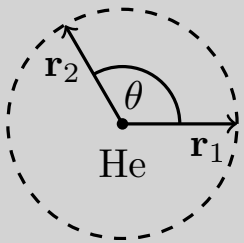
Range-separation : Illustrations

On the cusp

[Franck *et al.* JCP (2015)]





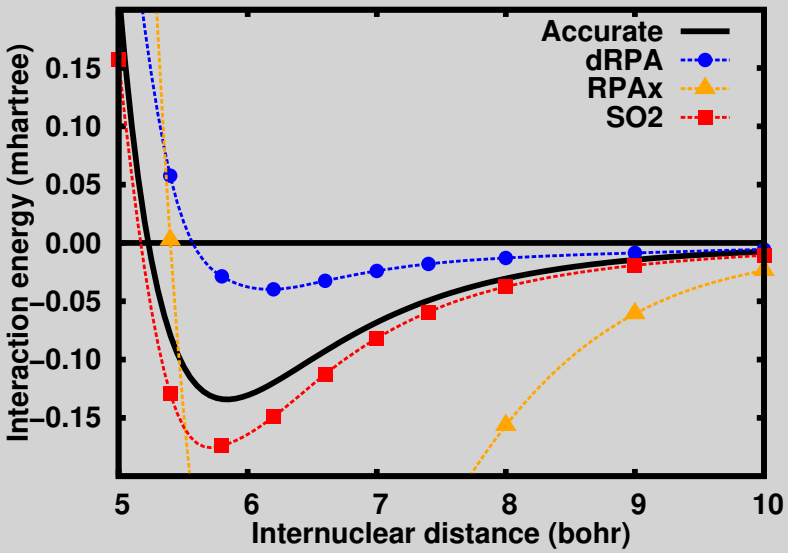


- ***Without the cusp, the wavefunction is easier to represent in B***
- The convergence goes from polynomial to weak exponential

Range-separation : Illustrations

On the Neon dimer

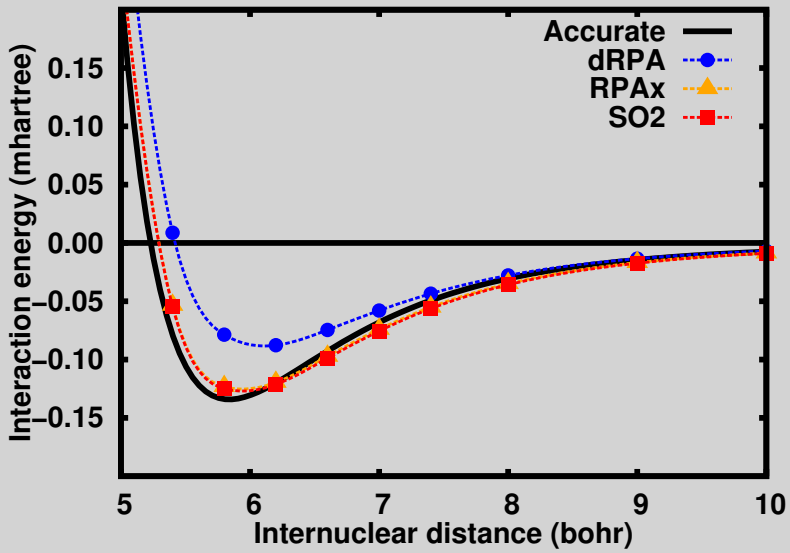
[Toulouse *et al.* JCP (2011)]



DFT+RPA calculation

>PBE, aug-cc-pV6Z

Correlation energies too negative
(and strong dependence on basis size)



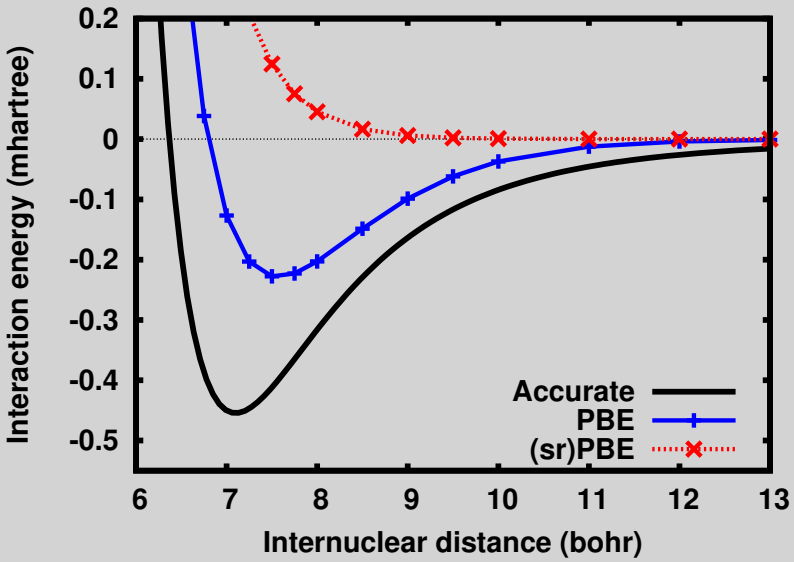
Hybrid srDFT/IrRPA

>srPBE, aug-cc-pV6Z

Range separation improves RPA
(and the basis dependence is reduced)

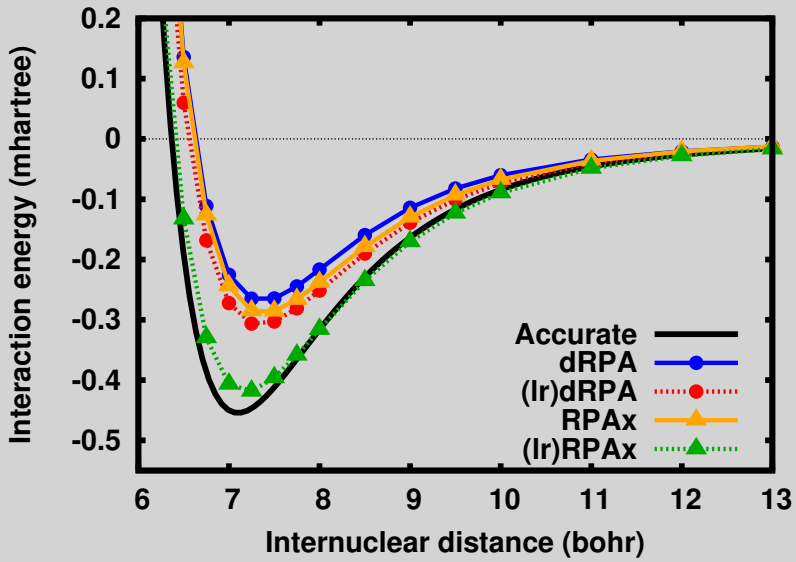
Range-separation : Illustrations

On the Argon dimer



>aug-cc-pV5Z

(sr)DFT reference contains no dispersion.



>aug-cc-pV5Z

Still important to add (lr) exchange effects to capture dispersion interactions.

DFT formalism

The ground state energy in DFT is written :

$$E_0 = \min_n \{F[n] + (v_{\text{ne}}|n)\}$$

where $F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle$ is the "Levy-Lieb" ***universal*** density functional

and $(v_{\text{ne}}|n) = \int \mathrm{d}\mathbf{r}\, v_{\text{ne}}(\mathbf{r}) n(\mathbf{r})$ is the system-dependent nuclei-electron energy

Now, in actual calculation, we search over a subset of densities $n^{\mathbf{B}}$:

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

- n_0 might not be representable in $\mathbf{B}$, *i.e.* : $E_0^{\mathbf{B}} \geq E_0$
- ***but the density converges fast*** : $n_0^{\mathbf{B}} \sim n_0$ and $E_0^{\mathbf{B}} \sim E_0$

A new take

[Giner *et al.* JCP (2018)]

Take the Levy-Lieb functional evaluated at a density represented in B :

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

and introduce a further ***restriction on the wavefunction + a correction*** :

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

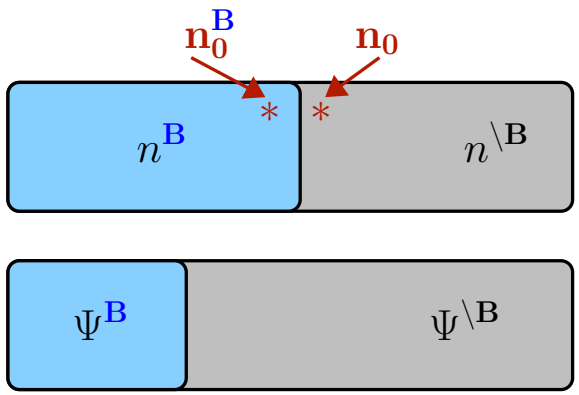
where the (unknown) complementary functional is :

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

A few notes :

Restriction on **B** is much stronger for $\Psi^{\mathbf{B}}$ than for $n^{\mathbf{B}}$!

Hence $\mathbf{E}^{\mathbf{B}}[n^{\mathbf{B}}]$ gives a ***substantial contribution*** to $F[n^{\mathbf{B}}]$, even for basis sets where indeed $n_0^{\mathbf{B}} \sim n_0$!



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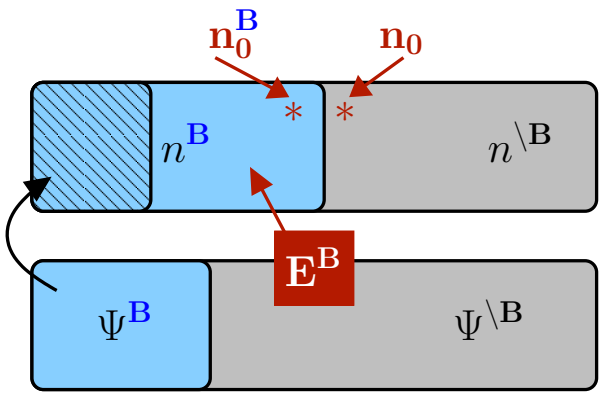


A new take

[Giner *et al.* JCP (2018)]

Now, putting the pieces together, we get :

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

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

Hence : $E_0^{\mathbf{B}} = \min_{n^{\mathbf{B}}} \left\{ \min_{\Psi^{\mathbf{B}} \to n^{\mathbf{B}}} \langle \Psi^{\mathbf{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle + \left(v_{\text{ne}} | n^{\mathbf{B}}\right) + \mathbf{E}^{\mathbf{B}}[n^{\mathbf{B}}] \right\}$

where we need to ***perform a minimization over*** $n^{\mathbf{B}}$

But the FCI densities are really good : $E_0^{\mathbf{B}}$ can be evaluated at $n^{\mathbf{B}} = n_{\Psi^{\mathbf{B}}_{\text{FCI}}}$!

$$E_0^{\mathbf{B}} \sim \langle \Psi^{\mathbf{B}}_{\text{FCI}} | \hat{H} | \Psi^{\mathbf{B}}_{\text{FCI}} \rangle + \mathbf{E}^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\text{FCI}}}]$$

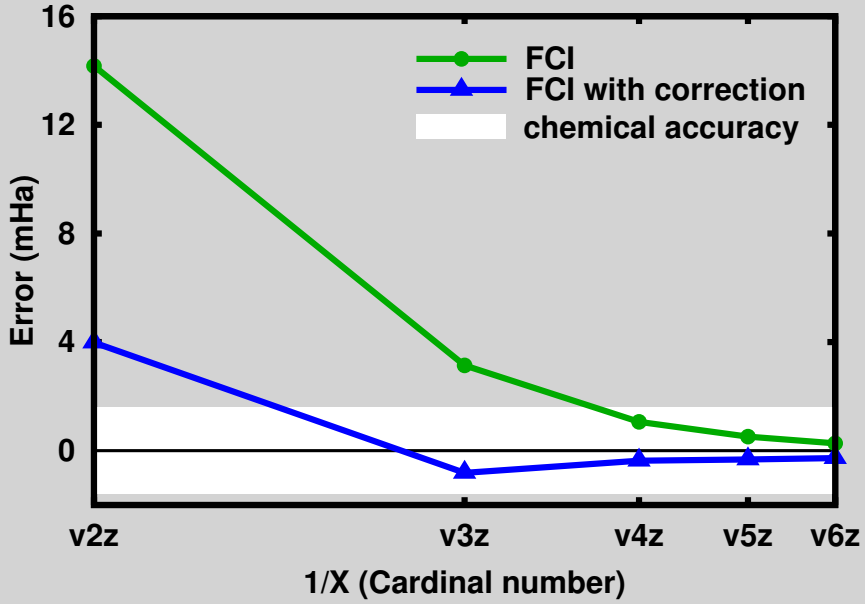
- $\mathbf{E}^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\text{FCI}}}]$ must recover what is missing in **B**
- A large part of this is ***short-range correlation effects*** !

Illustrations

[Giner *et al.* JCP (2018)]

On the Helium atom

$$E_0 \sim E^{\mathbf{B}}_{\mathrm{FCI}} + E^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\mathrm{FCI}}}]$$



Let's remember that FCI is the best exact answer in B !

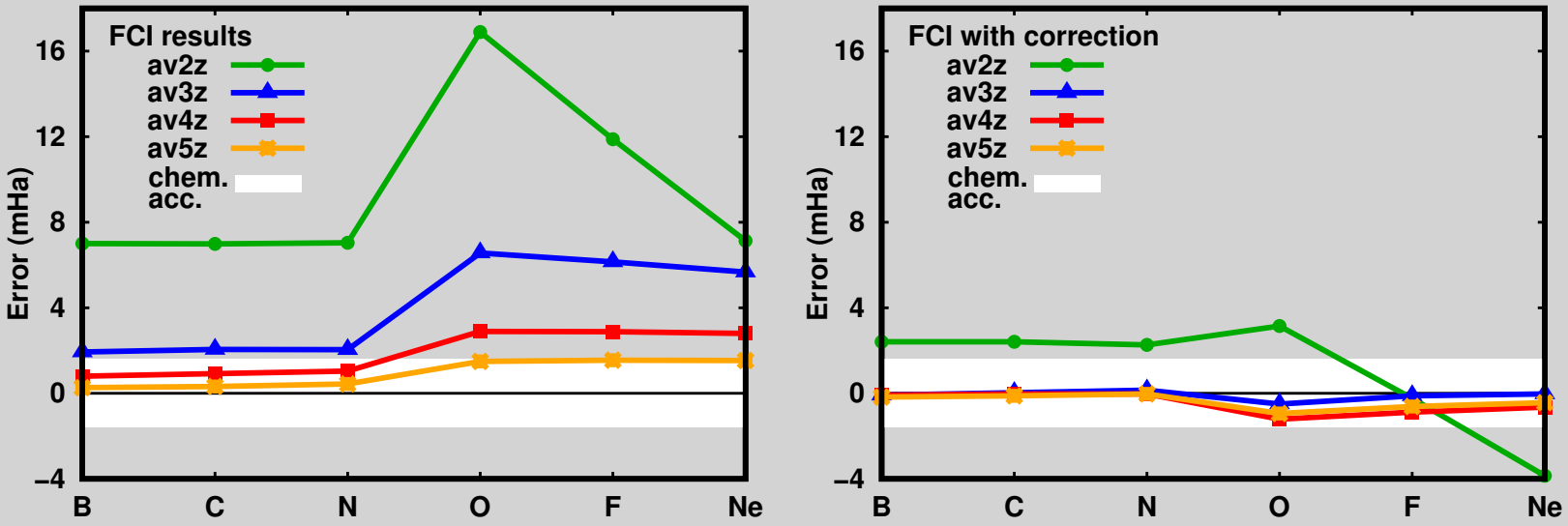
(The correction systematically improves the results.)

Illustrations

[Giner *et al.* JCP (2018)]

On the series of B-Ne atoms

$$E_0 \sim E^{\mathbf{B}}_{\mathrm{FCI}} + E^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\mathrm{FCI}}}]$$



Let's remember that FCI is the best exact answer in B !

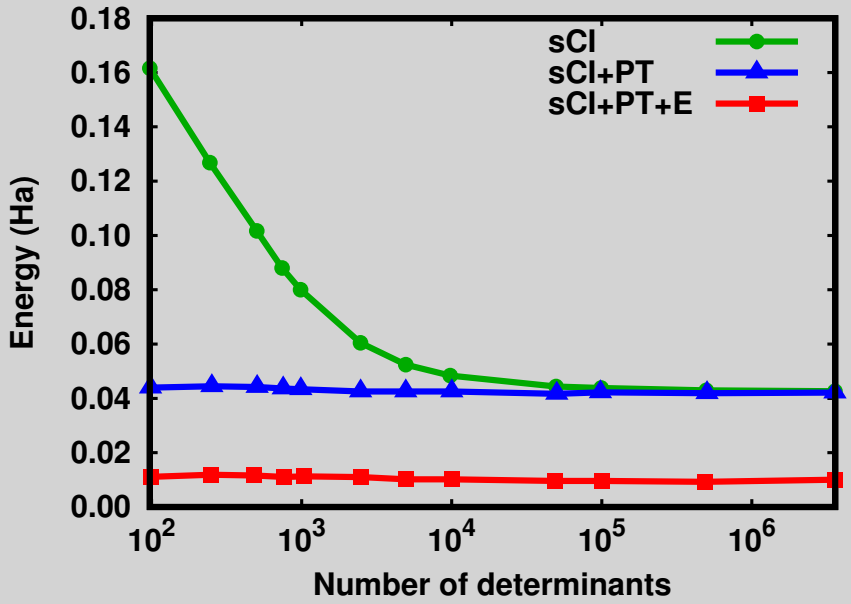
(Chemical accuracy obtained for all IP from the "avtz" basis set up.)

Illustrations

[Giner *et al.* JCP (2018)]

On the behavior with selected CI

$$E_0 \sim E^{\mathbf{B}}_{\text{FCI}} + E^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\text{FCI}}}]$$



Let's remember that FCI is the best exact answer in B !

(Oxygen ground state using the av4z basis set.)

Under the rug

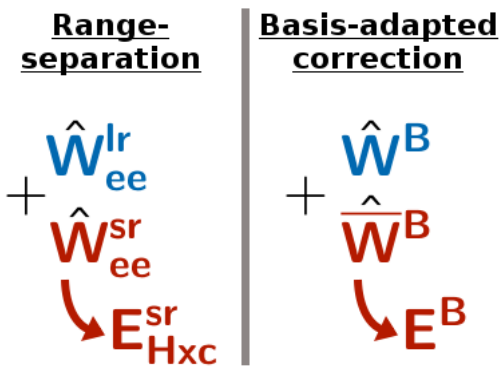
[Giner *et al.* JCP (2018)]

I have intentionally left a lot of details under the rug
and focused on final equations such as $E_0 \sim E^{\mathbf{B}}_{\mathrm{FCI}} + E^{\mathbf{B}}[n_{\Psi^{\mathbf{B}}_{\mathrm{FCI}}}]$

It probably feels like it's easy, but what exactly is $\mathbf{E}^{\mathbf{B}}$?
How to approximate it ?

$$E^{\mathbf{B}}[n^{\mathbf{B}}] = \min_{\Psi \to n^{\mathbf{B}}} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle - \min_{\Psi^{\mathbf{B}} \to n^{\mathbf{B}}} \langle \Psi^{\mathbf{B}} | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi^{\mathbf{B}} \rangle$$

As I will show, a good venue to express $\mathbf{E}^{\mathbf{B}}$
is to make a connection with the $\mathbf{E}^{\mathrm{sr}}_{\mathrm{Hxc}}$

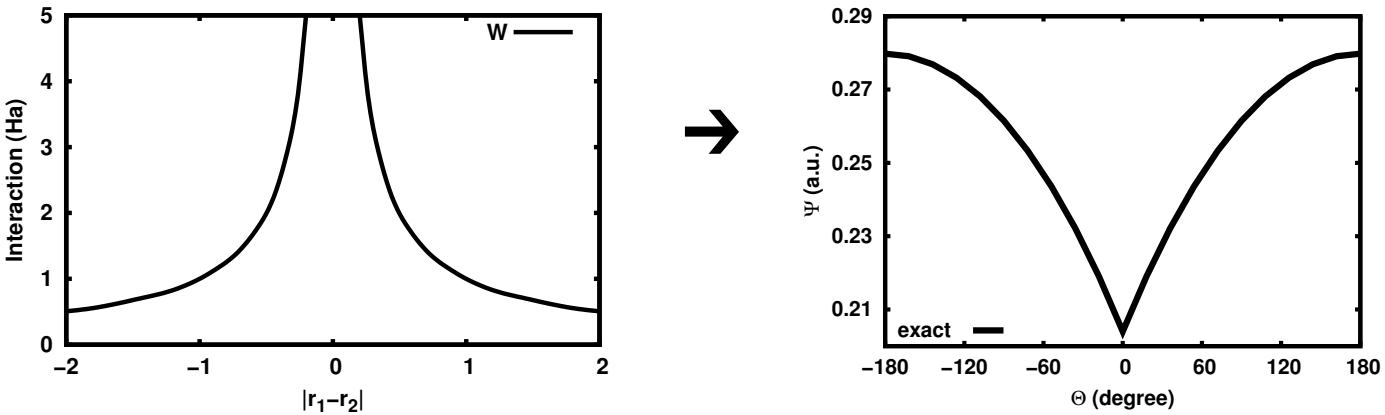


Finite basis

[Giner *et al.* JCP (2018)]

To approach E^B, we look at what it should complement

$$E_0^{\mathbf{B}} = \min_{n^{\mathbf{B}}} \left\{ \min_{\Psi^{\mathbf{B}} \to n^{\mathbf{B}}} \langle \Psi^{\mathbf{B}} | \hat{T} + \hat{W}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle \; + \mathbf{E}^{\mathbf{B}}[n^{\mathbf{B}}] + \left(v_{\text{ne}} | n^{\mathbf{B}} \right) \right\}$$



$$\hat{W}_{\text{ee}} = \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta_{\mathbf{14}} \delta_{\mathbf{23}} \; \hat{\phi}^\dagger(\mathbf{4}) \hat{\phi}^\dagger(\mathbf{3}) \hat{\phi}(\mathbf{2}) \hat{\phi}(\mathbf{1}) \qquad \langle \Psi^{\mathbf{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle = \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \; n^{(2)}_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2})$$

$$\hat{W}^{\mathbf{B}}_{\text{ee}} = \sum_{\in \mathbf{B}} V_{ij}^{kl} \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i \qquad [\dots] \qquad \langle \Psi^{\mathbf{B}} | \hat{W}^{\mathbf{B}}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle = \int W_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2}) \; n^{(2)}_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2})$$

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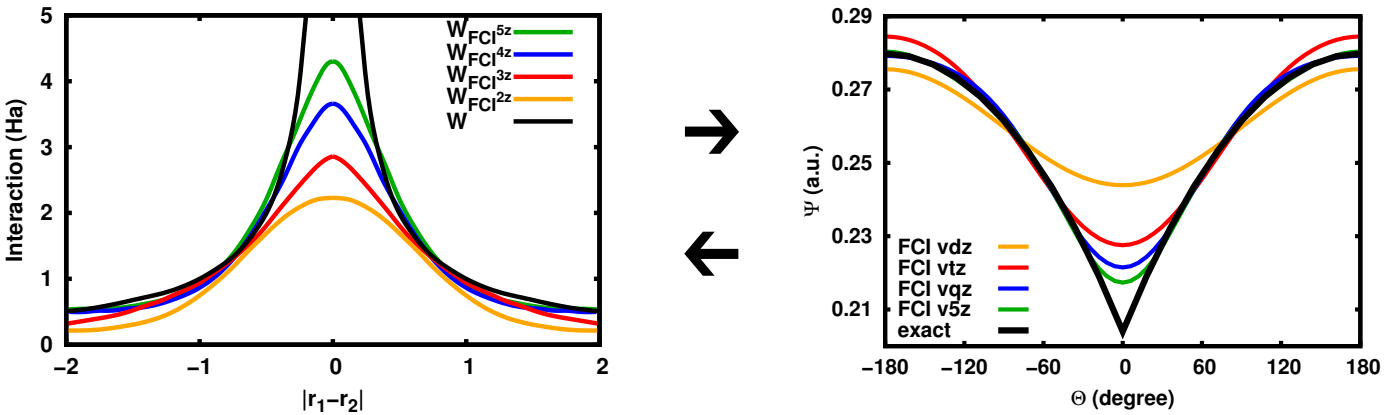


$$\hat{W}_{\text{ee}} = \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta_{14} \delta_{23} \, \hat{\phi}^\dagger(\mathbf{4}) \hat{\phi}^\dagger(\mathbf{3}) \hat{\phi}(\mathbf{2}) \hat{\phi}(\mathbf{1}) \qquad \langle \Psi^{\mathbf{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle = \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, n^{(2)}_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2})$$

$$\hat{W}^{\mathbf{B}}_{\text{ee}} = \sum_{\in \mathbf{B}} V^{kl}_{ij} \hat{a}^\dagger_k \hat{a}^\dagger_l \hat{a}_j \hat{a}_i \qquad [\dots] \qquad \langle \Psi^{\mathbf{B}} | \hat{W}^{\mathbf{B}}_{\text{ee}} | \Psi^{\mathbf{B}} \rangle = \int W_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2}) \, n^{(2)}_{\Psi^{\mathbf{B}}}(\mathbf{1}, \mathbf{2})$$

$\mathbf{W}_{\Psi^{\mathbf{B}}}$ is a ***long-range interaction***
that is finite at coalescence, much like $\mathbf{W}^{\text{lr}}$!

Preexisting approximations

(remember) $E_0 = \langle \Psi^{lr} | \hat{T} + \hat{V}_{ne} + \hat{W}^{lr}_{ee} | \Psi^{lr} \rangle + E^{sr}_{Hxc}[n_{\Psi^{lr}}]$

with : $E^{sr}_{Hxc}[n] = \langle \Psi^{lr} | \hat{W}^{sr}_{ee} | \Psi^{lr} \rangle + E^{sr}_{c,md}[n]$

so that : $E_0 = \langle \Psi^{lr} | \hat{H} | \Psi^{lr} \rangle + E^{sr}_{c,md}[n_{\Psi^{lr}}]$

i.e. : $E^{sr}_{c,md}[n_{\Psi^{lr}}] = \min_{\Psi} \langle \Psi | \hat{T} + \hat{W}_{ee} | \Psi \rangle - \langle \Psi^{lr} | \hat{T} + \hat{W}_{ee} | \Psi^{lr} \rangle$

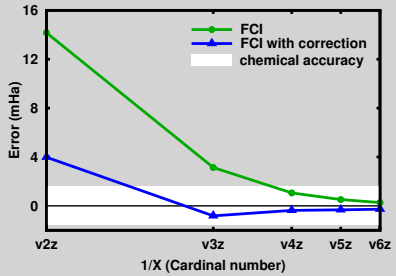
(*remember*) $E^{B}[n^{B}] = \min_{\Psi} \langle \Psi | \hat{T} + \hat{W}_{ee} | \Psi \rangle - \langle \Psi^{B} | \hat{T} + \hat{W}_{ee} | \Psi^{B} \rangle$

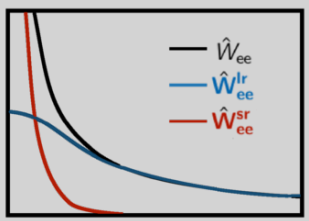
The difference between the two is the wavefunctions used for the constrained minimization.

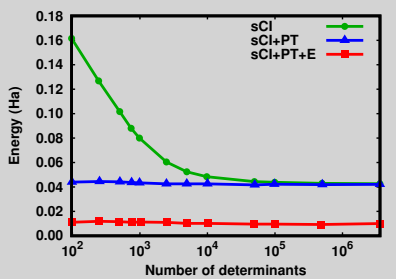
Ψ^{B} is determined by using the diverging e-e interaction expanded in a finite basis set, $\mathbf{W}_{\Psi^{B}}$.

Ψ^{lr} uses a non-diverging long-range e-e interaction defined in a complete basis set, $\mathbf{W}^{lr}$.

Hammering the take-home message







- FCI is the best variational answer one can get ***within a basis set***
- WFT suffers when having to describe ***short-range correlation***
- DFT fails at describing the ***long-range correlation***
- Range-separation offers a way to ***combine WFT and DFT*** based on range
- The $\mathbf{E^B}$ recovers basis set effets to go ***beyond FCI at a cheap cost***

$$\hat{W}_{ee} = \int_{1234} \hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta_{14}\delta_{23} \right) \hat{\psi}(2)\hat{\psi}(1)$$

$$\hat{W}^B_{ee} = \sum_{ijkl \in B} V^{ijkl} \hat{a}^\dagger_k \hat{a}^\dagger_l \hat{a}_j \hat{a}_i \qquad \text{with :} \quad \hat{a}_i = \int d1\ \phi_i(1)\hat{\psi}(1),\ \hat{a}^\dagger_i = \int d1\ \phi_i(1)\hat{\psi}^\dagger(1)$$

$$= \int_{1234} \hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3) \underbrace{\left(\sum_{ijkl \in B} V^{ijkl} \phi_l(4)\phi_k(3)\phi_j(2)\phi_i(1) \right)}_{w^B(1,2,3,4) \to \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta_{14}\delta_{23}} \hat{\psi}(2)\hat{\psi}(1)$$

$$\langle \Psi^B | \hat{W}_{ee} | \Psi^B \rangle = \int_{12} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n^{(2)}_{\Psi^B}(1,2)$$

$$\langle \Psi^B | \hat{W}^B_{ee} | \Psi^B \rangle = \int_{1234} w^B(1,2,3,4) \underbrace{\langle \Psi^B | \hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3)\hat{\psi}(2)\hat{\psi}(1) | \Psi^B \rangle}_{\sum \Gamma^{pqrs}_{\Psi^B} \phi_s(4)\phi_r(3)\phi_q(2)\phi_p(1)}$$

$$= \int_{12} W_{\Psi^B}(1,2)\ n^{(2)}_{\Psi^B}(1,2)$$

$$\text{with } W_{\Psi^B}(1,2) = \frac{\sum V^{ijkl}\Gamma^{pqkl}_{\Psi^B}\phi_i(1)\phi_j(2)\phi_q(2)\phi_p(1)}{\sum \Gamma^{pqrs}_{\Psi^B}\phi_s(1)\phi_r(2)\phi_q(2)\phi_p(1)}$$