Basis convergence of range-separated density-functional theory

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Previous studies show the slow $X^{-3}$ convergence

Different solutions were proposed:

- extrapolation methods
- methods including explicitly the correlation: $F_{12}$ MP2, $F_{12}$ CC, ...
- range separation, the short-range interaction is no longer treated in wave-function theory
Electron-electron interaction

\[
\frac{1}{r_{12}} = \frac{\text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erfc}(\mu r_{12})}{r_{12}}
\]

Range-Separation

\[E^\mu = \min_{\psi} \left\{ \langle \psi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr},\mu} | \psi \rangle + E^{\text{sr},\mu}_{\text{Hxc}}[n_\psi] \right\}\]

the minimizing wave function fulfills

\[
\left( \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr},\mu} + \hat{V}_{\text{Hxc}}^{\text{sr},\mu} \right) | \psi^{\text{lr},\mu} \rangle = \mathcal{E}^{\text{lr},\mu} | \psi^{\text{lr},\mu} \rangle
\]
1. Convergence in Partial-Wave Expansion (PWE)
   1.1 Coulomb interaction
   1.2 Long-range interaction
   1.3 Convergence rate

2. Convergence in one-electron atomic basis sets
   2.1 Convergence of the MP2 correlation energy
   2.2 Extrapolation method for range-separated DFT
Partial-Wave Expansion (PWE)


Coulomb interaction

Wave function

Cusp condition in coulomb case imposes linearity in $r_{12}$ of $\Psi$

$$\frac{\Psi(r_{12})}{\Psi(0)} = 1 + \frac{1}{2} r_{12} + O(r_{12}^2).$$


Expansion in basis of Legendre polynomials

Wave function in basis of Legendre polynomials

$$\left( \frac{\Psi(r_{12})}{\Psi(0)} \right)_L = 1 + \sum_{\ell=0}^{L} f_\ell \ P_\ell(\cos \theta)$$

$$f_\ell = \frac{1}{2} \left( \frac{1}{2\ell + 3} \frac{r_{\ell}^{\ell+2}}{r_{>\ell+1}} - \frac{1}{2\ell - 1} \frac{r_{\ell}^{\ell}}{r_{>\ell-1}} \right)$$

Coulomb interaction

Slow convergence $\rightarrow$ slow $L^{-3}$ convergence of the correlation energy
We use the behavior of \( \psi^{lr,\mu} \) at \( r_{12} \to 0 \) studied by Gori-Giorgi and Savin

\[
\frac{\psi^{lr,\mu}(r_{12})}{\psi^{lr,\mu}(0)} = 1 + r_{12}p_1(\mu r_{12}) + O(r_{12}^4),
\]

with \( p_1(y) = \frac{e^{-y^2}-2}{2\sqrt{\pi}y} + \left( \frac{1}{2} + \frac{1}{4y^2} \right) \text{erf}(y) \).

Long-range interaction

\[ 1 + f^{\mu}_{L}(r_{12}) \text{ (a. u.)} \]

- \( L = 0 \)
- \( L = 1 \)
- \( L = 2 \)
- \( L = 3 \)
- \( L = 4 \)

- \( \mu = 0.5 \ a_0^{-1} \)
- The singularity disappears
- the convergence is faster (essentially converged at \( L = 2 \))
Convergence rate

\[ f_{lr,\mu} = A \, \ell^{-\alpha} \]

\[ f_{lr,\mu} = B \, \exp(-\beta \ell) \]

- **coulomb and \( \mu = 10 \): power convergence**
- **\( \mu \leq 2 \): \( \Psi_{lr,\mu} \) converges exponentially**
From PWE to one-electron basis sets

In this work we considered the Dunning correlation consistent basis sets cc-pVXZ

**Correspondence between N and X**
- X cardinal number of the basis
- Maximal quantum number in the basis set
  - He: \( N = X \)
  - Li to Ne: \( N = X + 1 \)

\( N \) the highest principal quantum number

PWE can be obtained from a one-particle atomic basis if the basis **saturates the radial degree**

**Correspondence between L and X**
- He: \( L = X + 1 \)
- Li to Ne: \( L = X \)
Convergence of the FCI wave function

Long-range interaction

- Similar results as in PWE
- Convergence less systematic than for coulomb case → Duning basis sets not optimal for long-range interaction
Convergence of the MP2 correlation energy

Coulomb interaction

\[ \Delta E_{c,X} = E_{c,X} - E_{c,\infty} \]

with \( E_{c,\infty} \) the MP2 CBS limit.

Long-range interaction

We choose energy calculated in cc-pV6Z as reference energy for the error

\[ \Delta E_{c,X}^{\text{lr},\mu} = E_{c,X}^{\text{lr},\mu} - E_{c,6}^{\text{lr},\mu} \]
Convergence of the correlation energy

Coulomb case

Table: Fits for coulomb interaction for $X \in [3, 6]$

<table>
<thead>
<tr>
<th></th>
<th>Power law</th>
<th>Exponential law</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$A$</td>
</tr>
<tr>
<td>He</td>
<td>2.902</td>
<td>104.00</td>
</tr>
<tr>
<td>Ne</td>
<td>2.754</td>
<td>1169.90</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.693</td>
<td>923.76</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.988</td>
<td>1051.28</td>
</tr>
</tbody>
</table>

Polynomial behavior in accordance with results in PWE

$$E_{c,X} = E_{c,\infty} + AX^{-\alpha}$$
Convergence of the correlation energy
Long-range case

Table: Fits for long-range interaction at $\mu = 0.5$ for $X \in [3, 5]$

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<tr>
<td></td>
<td>$\alpha$</td>
<td>$A$</td>
<td>$r^2$</td>
<td>$\beta$</td>
<td>$B$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>He</td>
<td>3.997</td>
<td>8.16</td>
<td>99.11</td>
<td>1.028</td>
<td>2.13</td>
<td>99.95</td>
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<tr>
<td>Ne</td>
<td>4.257</td>
<td>101.51</td>
<td>98.27</td>
<td>1.098</td>
<td>24.57</td>
<td>99.65</td>
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<tr>
<td>N$_2$</td>
<td>4.997</td>
<td>211.13</td>
<td>99.44</td>
<td>1.283</td>
<td>39.08</td>
<td>99.99</td>
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<tr>
<td>H$_2$O</td>
<td>4.686</td>
<td>196.20</td>
<td>97.63</td>
<td>1.210</td>
<td>41.50</td>
<td>99.33</td>
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Exponential behavior in accordance with results in PWE

$$E_{c,X}^{lr,\mu} = E_{c,\infty}^{lr,\mu} + B \exp(-\beta X)$$
Extrapolation method for range-separated DFT

RSH and long-range correlation energy converge exponentially \( \rightarrow \) extrapolation scheme for total energy

3-points extrapolation scheme

\[
E_X = E_\infty + B \exp(-\beta X)
\]
\[
E_Y = E_\infty + B \exp(-\beta Y)
\]
\[
E_Z = E_\infty + B \exp(-\beta Z)
\]

with \( X, Y = X + 1 \) and \( Z = Y + 1 \)

\[
E_\infty = E_{XYZ} = \frac{E_Y^2 - E_X E_Z}{2E_Y - E_X - E_Z}
\]
Extrapolation method for range-separated DFT

Errors with respect to $X = 6$ given in mHartree

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<tr>
<th>µ</th>
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<th>$\Delta E^\mu_Q$</th>
<th>$\Delta E^\mu_5$</th>
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<td>4.090</td>
<td>0.810</td>
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<td>H₂O</td>
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<td>14.736</td>
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Extrapolation method for range-separated DFT

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- Similar results obtained when including the excitations from core electrons in the calculations
- We propose to extrapolate separately the $E_{RSH}$ and $E^{1r,\mu}_{c,\text{MP2}}$ but gives no significant differences.
- 2-point extrapolation was investigated but difficulty in finding a global value for $\beta$
Conclusion

- Exponential convergence of the long-range wave function at small $r_{12}$ in partial-wave expansion
- Exponential convergence of the long-range MP2 correlation energy with respect to the cardinal number of the Dunning basis-sets
- CBS extrapolation method for range-separated DFT was proposed

- Same convergence behavior expected for range-separated DFT methods with other methods for long-range contribution (CI, RPA, ...)
- Basis set constructed for long-range interaction could give faster and more systematic convergence