Basis convergence of range-separated density-functional theory

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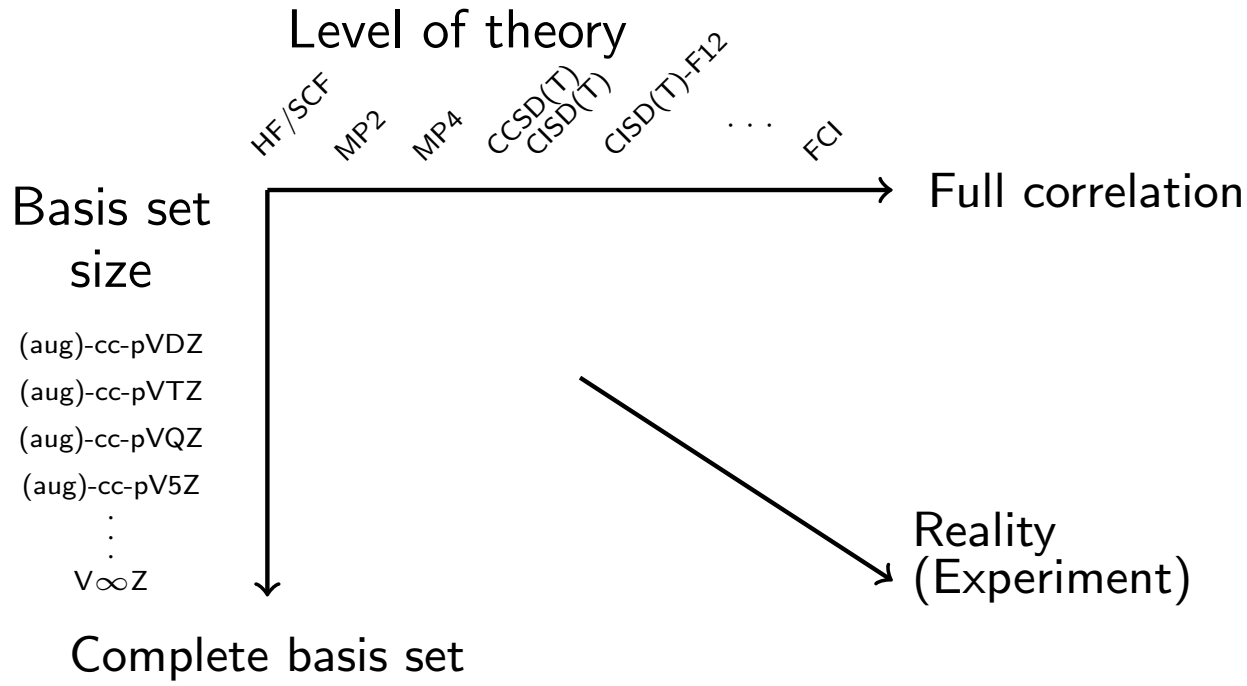
Motivation



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

Range-separated DFT

Electron-electron interaction

$$\frac{1}{r_{12}} = \frac{\mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erfc}(\mu r_{12})}{r_{12}}$$

Range-Separation

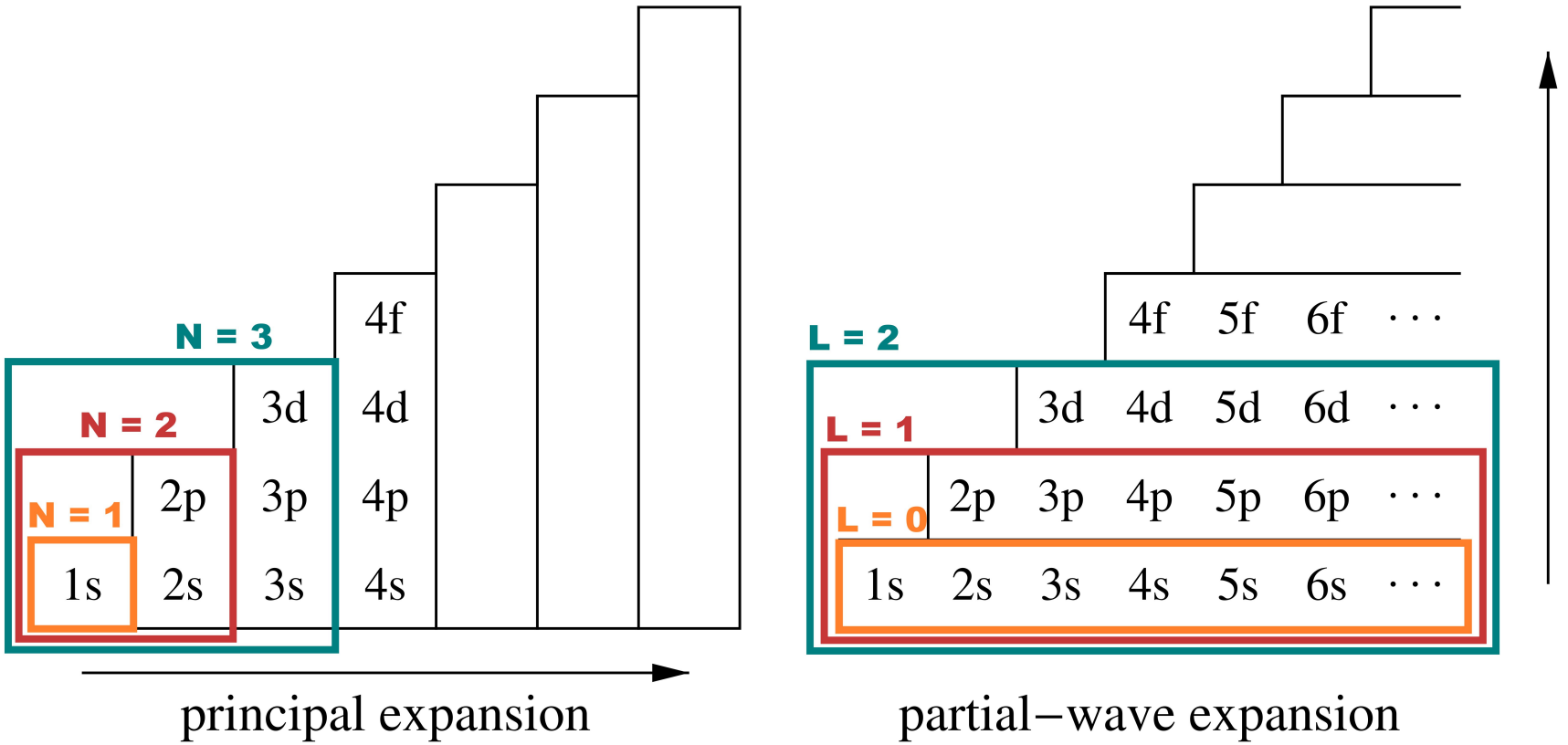
$$E^{\mu} = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_{\Psi}] \right\}$$

the minimizing wave function fulfills

$$\left(\hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}}^{\mathrm{lr},\mu} + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr},\mu} \right) |\Psi^{\mathrm{lr},\mu}\rangle = \mathcal{E}^{\mathrm{lr},\mu} |\Psi^{\mathrm{lr},\mu}\rangle$$

Outline

Partial-Wave Expansion (PWE)



W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen, and T. Helgaker, J. Phys. B **32**, R103 (1999)

T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2002)

Coulomb interaction

Wave function

Cusp condition in coulomb case imposes linearity in r_{12} of Ψ

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

T. Kato, Comm. Pure Appl. Math., **10**, 151 (1957)

Expansion in basis of Legendre polynomials

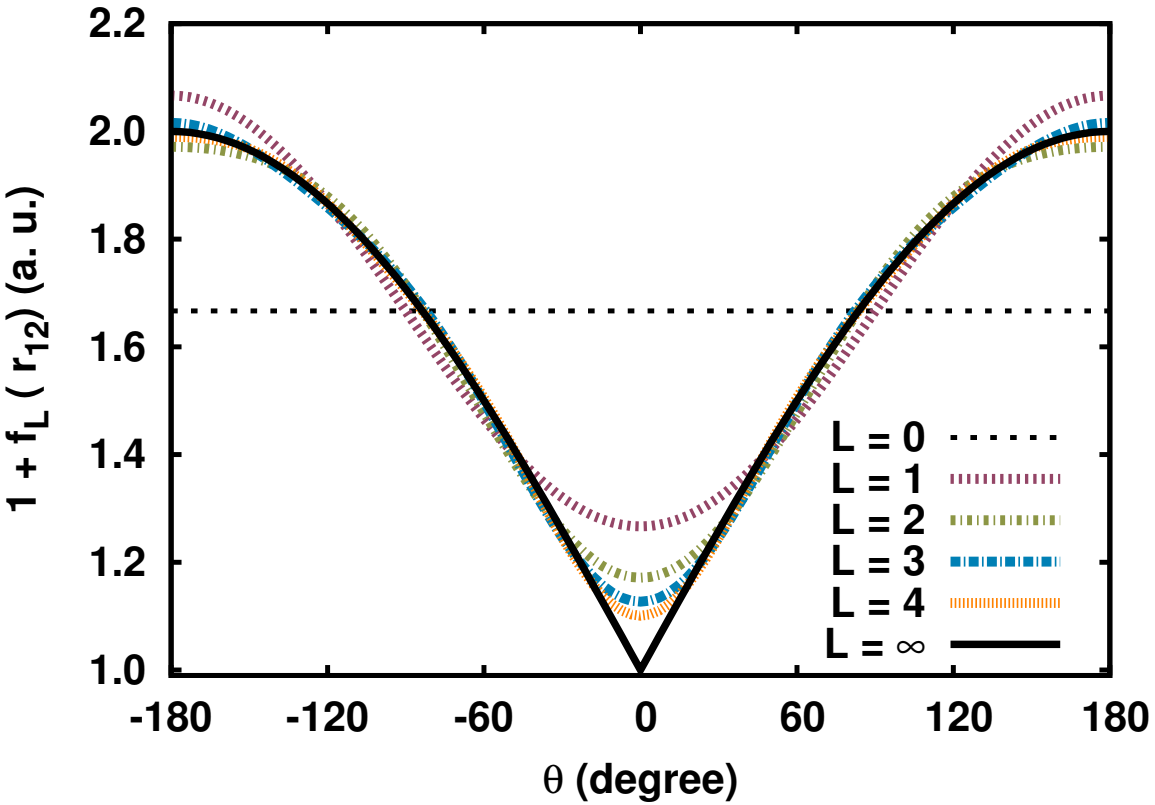
wave function in basis of Legendre polynomials

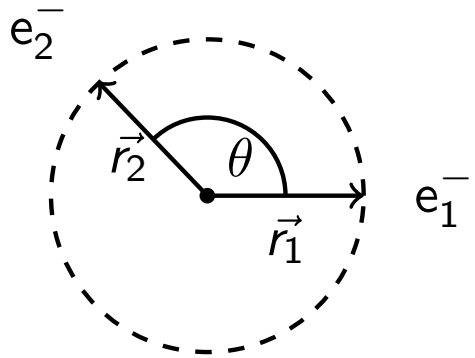
$$\left(\frac{\Psi(r_{12})}{\Psi(0)}\right)_L = 1 + \sum_{\ell=0}^{L} f_\ell \, P_\ell(\cos\theta)$$

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

W. Kutzelnigg, Theor. Chim. Acta, **68**, 445 (1985)

Coulomb interaction





Slow convergence $\longrightarrow$ slow L^{-3} convergence of the correlation energy

Long-range interaction

Wave function

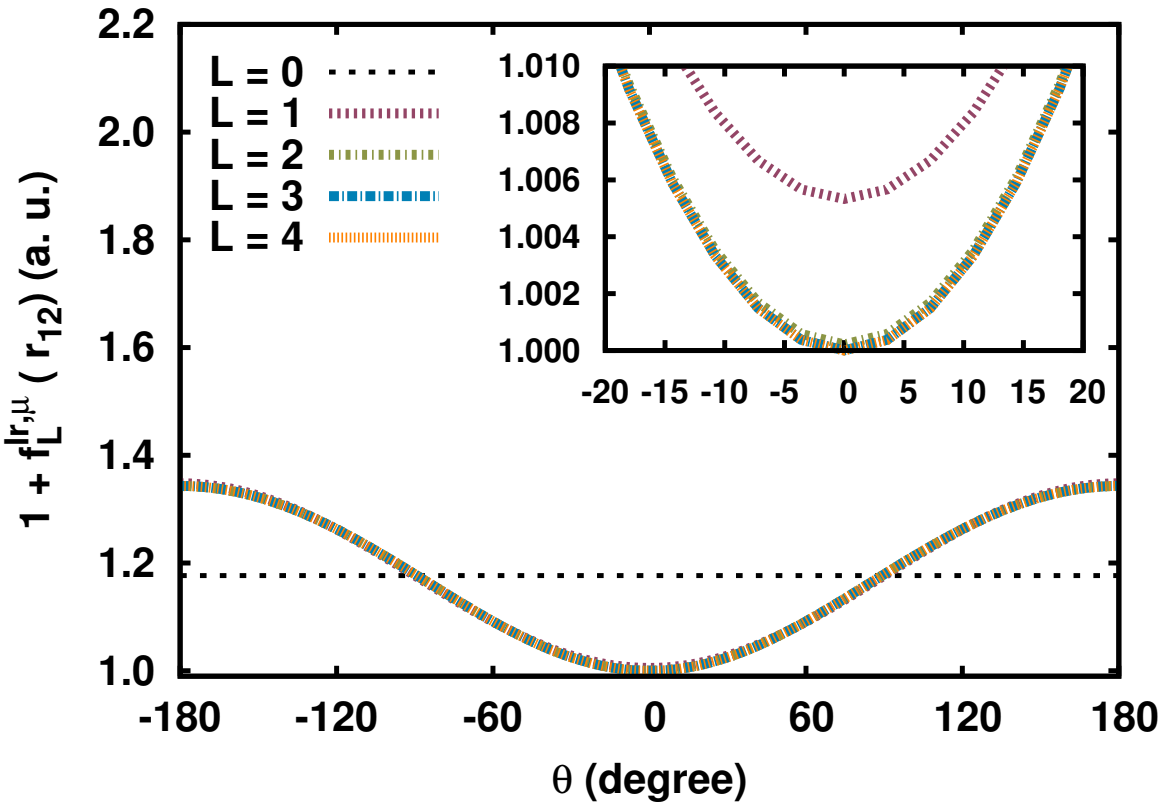
We use the behavior of $\Psi^{\mathrm{lr},\mu}$ at $r_{12} \longrightarrow 0$ studied by Gori-Giorgi and Savin

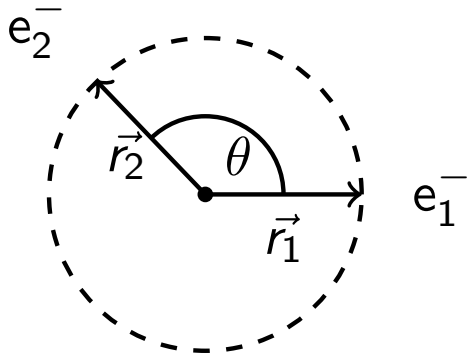
$$\frac{\Psi^{\mathrm{lr},\mu}(r_{12})}{\Psi^{\mathrm{lr},\mu}(0)} = 1 + \underbrace{r_{12} p_1(\mu r_{12})}_{f^{\mathrm{lr},\mu}(r_{12})} + O(r_{12}^4),$$

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

P. Gori-Giorgi and A. Savin, Phys. Rev. A, **73**, 032506 (2006)

Long-range interaction

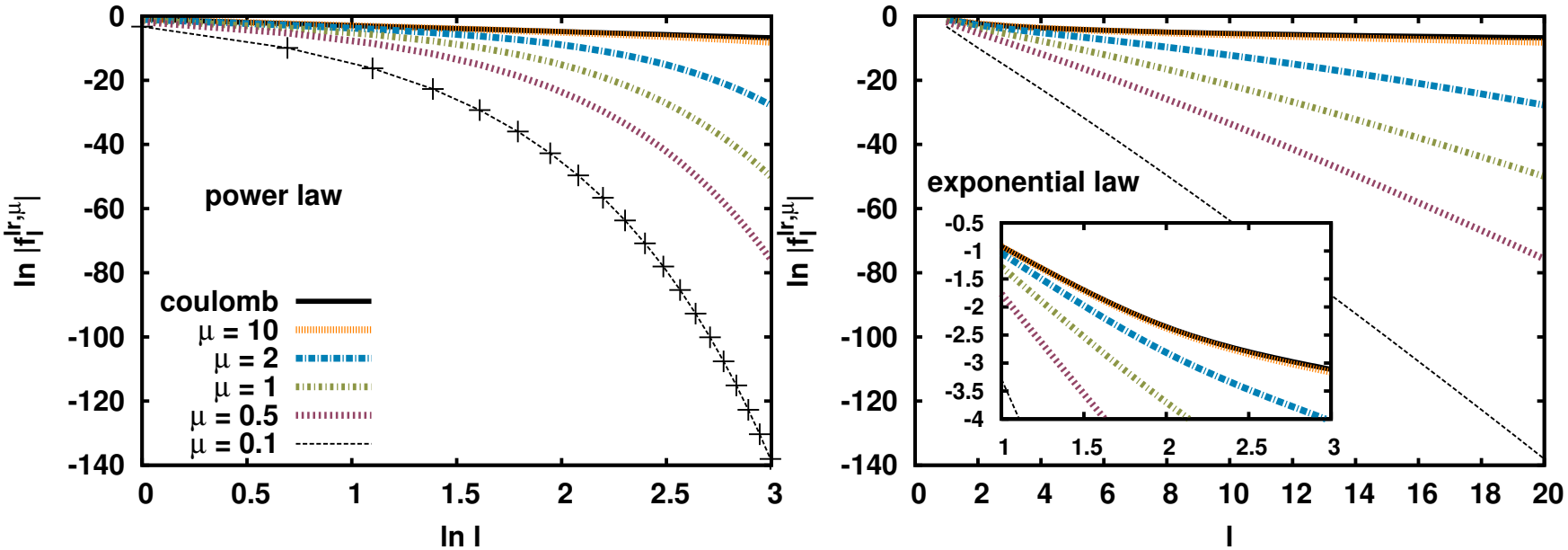




- $\mu = 0.5\ a_0^{-1}$
- The singularity disappears
- the convergence is faster (essentially converged at $L = 2$)

Convergence rate

$$f_\ell^{\mathrm{lr},\mu} = A\,\ell^{-\alpha} \qquad f_\ell^{\mathrm{lr},\mu} = B\,\exp(-\beta\ell)$$



- coulomb and $\mu = 10$: power convergence
- $\mu \leq 2$: $\Psi^{\mathrm{lr},\mu}$ 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

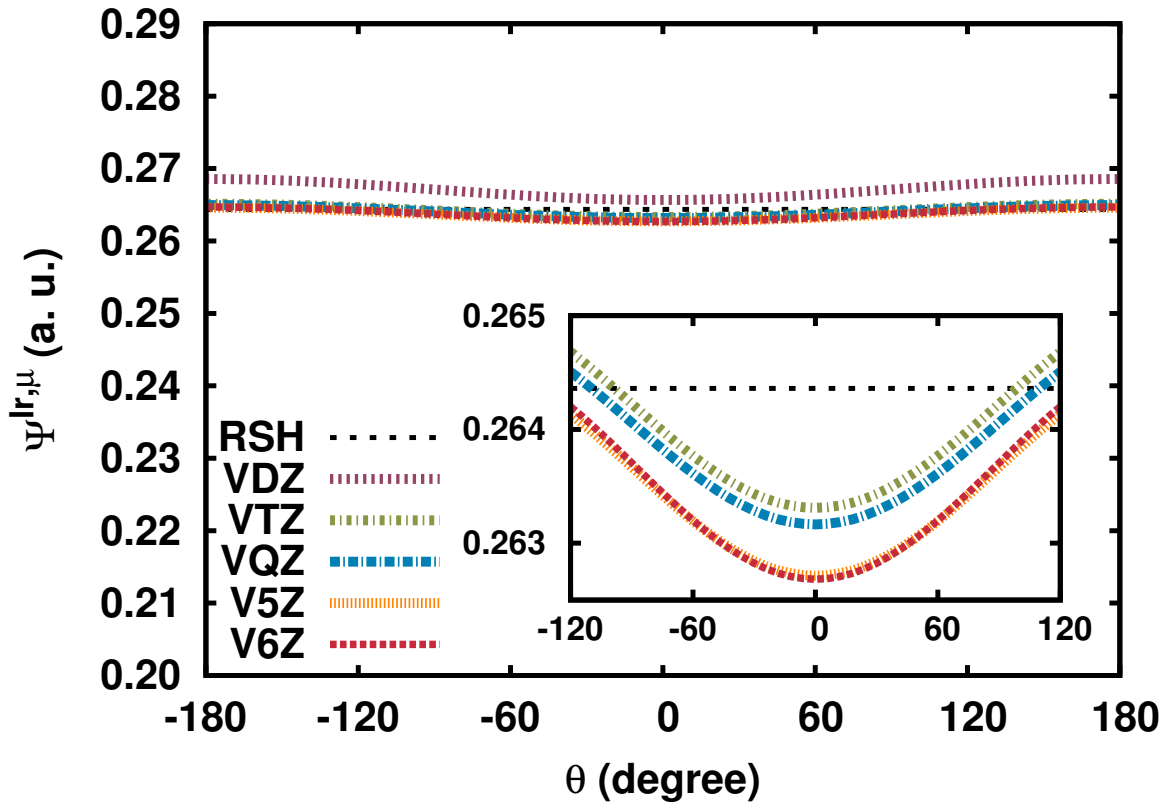
PWE can be obtained from a one-particle atomic basis if the basis **saturates the radial degree**

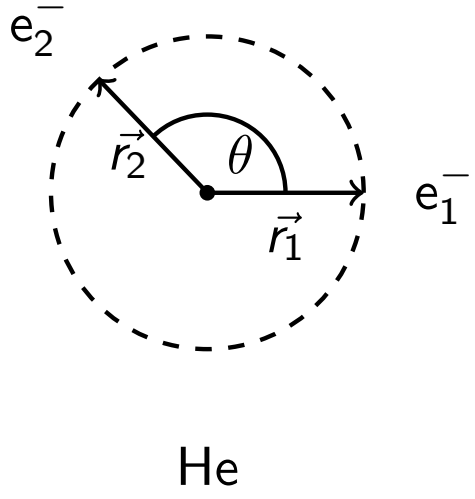
Correspondence between L and X

- 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 $\longrightarrow$ Duning basis sets not optimal for long-range interaction

Convergence of the MP2 correlation energy

Coulomb interaction

$$\Delta E_{\mathrm{c},X} = E_{\mathrm{c},X} - E_{\mathrm{c},\infty}$$

with $E_{\mathrm{c},\infty}$ the MP2 CBS limit.

Long-range interaction

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

$$\Delta E_{\mathrm{c},X}^{\mathrm{lr},\mu} = E_{\mathrm{c},X}^{\mathrm{lr},\mu} - E_{\mathrm{c},6}^{\mathrm{lr},\mu}$$

Convergence of the correlation energy

Coulomb case

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

	Power law			Exponential law		
	α	A	r^2	β	B	r^2
He	2.902	104.00	99.97	0.669	29.51	99.19
Ne	2.754	1169.90	99.93	0.636	355.28	99.37
N_2	2.693	923.76	99.98	0.621	286.90	99.16
H_2O	2.988	1051.28	99.92	0.690	288.61	99.39

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 $X \in [3, 5]$

	Power law			Exponential law		
	α	A	r^2	β	B	r^2
He	3.997	8.16	99.11	1.028	2.13	99.95
Ne	4.257	101.51	98.27	1.098	24.57	99.65
N_2	4.997	211.13	99.44	1.283	39.08	99.99
H_2O	4.686	196.20	97.63	1.210	41.50	99.33

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

	μ	$\Delta E^{\mu}_{\mathrm{D}}$	$\Delta E^{\mu}_{\mathrm{T}}$	$\Delta E^{\mu}_{\mathrm{Q}}$	ΔE^{μ}_{5}	$\Delta E^{\mu}_{\mathrm{DTQ}}$
He	0.5	8.488	0.781	0.245	0.078	0.205
Ne	0.5	74.523	20.337	5.763	0.751	0.401
N_2	0.5	51.581	13.406	4.090	0.810	1.083
H_2O	0.5	55.850	14.736	4.499	0.726	1.105

Extrapolation method for range-separated DFT

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

	μ	$\Delta E^{\mu}_{\mathrm{D}}$	$\Delta E^{\mu}_{\mathrm{T}}$	$\Delta E^{\mu}_{\mathrm{Q}}$	ΔE^{μ}_{5}	$\Delta E^{\mu}_{\mathrm{DTQ}}$
He	0.5	8.488	0.781	0.245	0.078	0.205
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H_2O	0.5	55.850	14.736	4.499	0.726	1.105

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

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