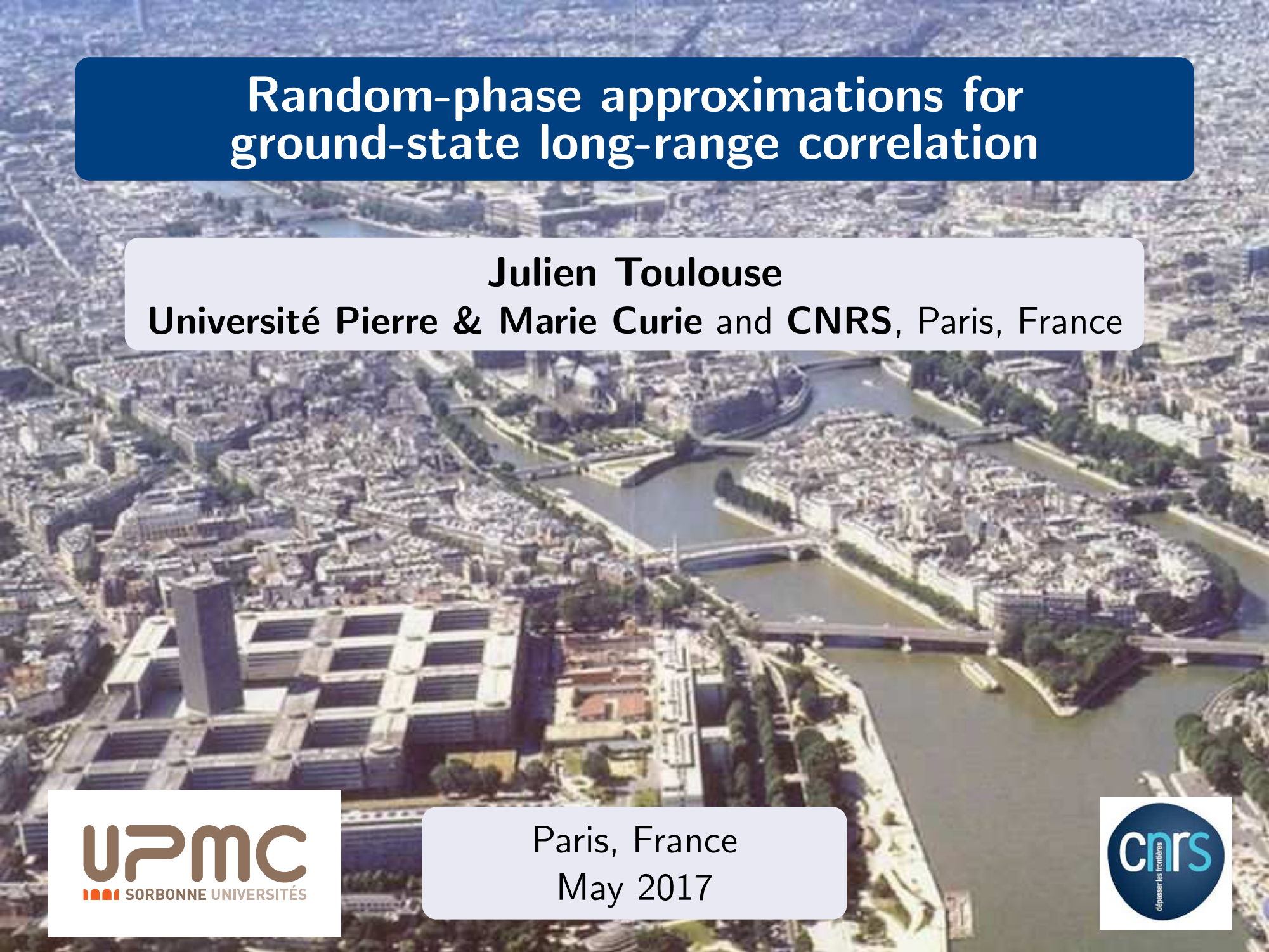
Random-phase approximations for ground-state long-range correlation

Julien Toulouse
Université Pierre & Marie Curie and **CNRS**, Paris, France



Paris, France
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Two main families of electronic-structure methods

- **Wave-function theory (WFT)**

$$E = \min_{\mathbf{\Psi}} \langle \mathbf{\Psi} | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}} | \mathbf{\Psi} \rangle$$

  - variational approximations (HF, MCSCF, CI) or non-variational approximations (MP, CC, RPA)
  - quite systematic and accurate
  - description of short-range e-e interaction is computationally costly

- **Kohn-Sham density-functional theory (DFT)**

$$E = \min_{\mathbf{\Phi}} \left\{ \langle \mathbf{\Phi} | \hat{T} + \hat{V}_{\text{ne}} | \mathbf{\Phi} \rangle + E_{\text{Hxc}}[n_{\mathbf{\Phi}}] \right\}$$

  - approximations for $E_{\text{xc}}[n]$: LDA, GGAs, ...
  - low computational cost
  - description of long-range e-e interaction is inaccurate

$\Longrightarrow$ combine **long-range WFT** with **short-range DFT**

Outline

1. Long-range WFT + short-range DFT

2. Long-range RPA
   - Adiabatic-connection fluctuation-dissipation approach
   - Coupled-cluster approach

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Long-range WFT + short-range DFT

- Derivation by constrained-search formalism (Savin, 1996)

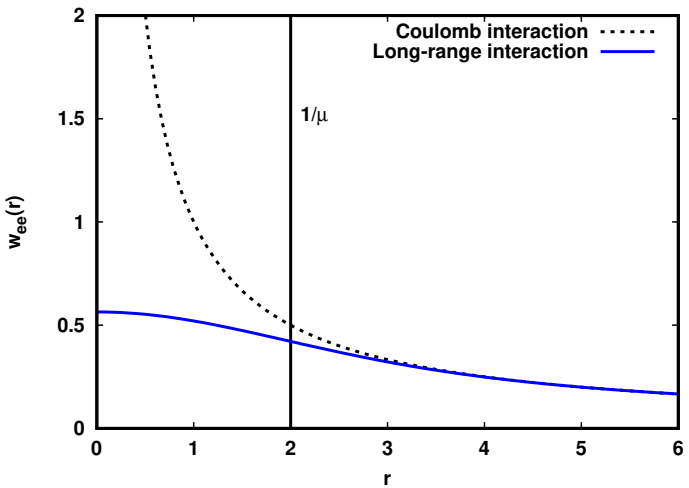
$$
\begin{aligned}
E &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \\
&= \min_{n} \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \\
&= \min_{n} \left\{ \min_{\Psi^{\mathrm{lr}} \to n} \langle \Psi^{\mathrm{lr}} | \hat{T} + \hat{V}_{\mathrm{ne}} + \hat{W}^{\mathrm{lr}}_{\mathrm{ee}} | \Psi^{\mathrm{lr}} \rangle + E^{\mathrm{sr}}_{\mathrm{Hxc}}[n] \right\}
\end{aligned}
$$

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

- **Long-range e-e interaction**

$$
\hat{W}^{\mathrm{lr}}_{\mathrm{ee}} = \sum_{i<j} \frac{\mathrm{erf}(\mu r_{ij})}{r_{ij}}
$$

with $1/\mu$ acting as a cutoff radius



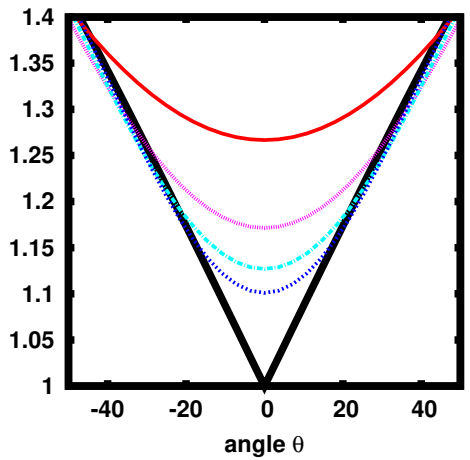
Fast basis convergence with long-range interaction

Behavior of the wave function at small interelectronic distance $r_{12} \to 0$:

Coulomb interaction

$$\frac{\Psi(r_{12})}{\Psi(0)} = 1 + \frac{r_{12}}{2} + \cdots$$

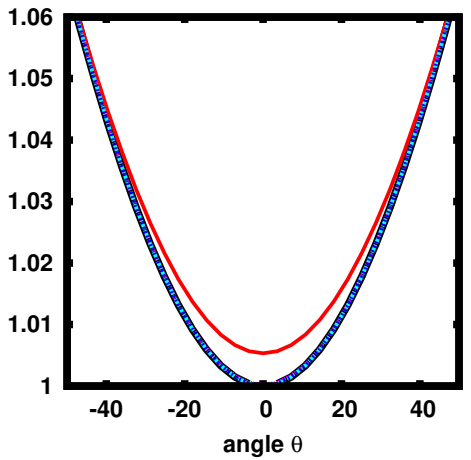
$$= \sum_{\ell=0}^{\infty} c_\ell P_\ell(\cos\theta) \text{ with } \mathbf{c_\ell \sim \ell^{-2}}$$



Long-range interaction

$$\frac{\Psi^{\text{lr}}(r_{12})}{\Psi^{\text{lr}}(0)} = 1 + \frac{\mu r_{12}^2}{3\sqrt{\pi}} + \cdots$$

$$= \sum_{\ell=0}^{\infty} c_\ell P_\ell(\cos\theta) \text{ with } \mathbf{c_\ell \sim e^{-\alpha \ell}}$$



$\mu = 0.5$ bohr^{-1}

Gori-Giorgi, Savin, PRA, 2006; Franck, Mussard, Luppi, Toulouse, JCP, 2015

The short-range density functional

- Decomposition into Hartree and exchange-correlation contributions:

$$E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] = E_{\mathrm{H}}^{\mathrm{sr}}[n] + E_{\mathrm{xc}}^{\mathrm{sr}}[n]$$

  where $E_{\mathrm{H}}^{\mathrm{sr}}[n] = (1/2) \iint n(\mathbf{r}_1) n(\mathbf{r}_2) w_{\mathrm{ee}}^{\mathrm{sr}}(r_{12}) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$

- Semilocal density-functional approximations (srLDA, srGGAs) for $E_{\mathrm{xc}}^{\mathrm{sr}}[n]$:

$$E_{\mathrm{xc}}^{\mathrm{sr}}[n] \approx \int e_{\mathrm{xc}}^{\mathrm{sr}}(n(\mathbf{r}), \nabla n(\mathbf{r})) \, \mathrm{d}\mathbf{r}$$

- In the limit of a very short-range interaction, i.e. $\mu \to \infty$, the short-range exchange energy becomes a local functional of the density:

$$E_{\mathrm{x}}^{\mathrm{sr}}[n] = -\frac{\pi}{4\mu^2} \int n(\mathbf{r})^2 \mathrm{d}\mathbf{r} + \cdots$$

  and the short-range correlation energy becomes a local functional of the on-top pair density:

$$E_{\mathrm{c}}^{\mathrm{sr}}[n] = \frac{\pi}{2\mu^2} \int n_{2,\mathrm{c}}(\mathbf{r}, \mathbf{r}) \mathrm{d}\mathbf{r} + \cdots$$

Toulouse, Colonna, Savin, PRA, 2004

Long-range single-reference perturbation theory

- Single-determinant approximation: **lrHF+srDFT**

$$E_{\text{lrHF+srDFT}} = \min_{\Phi}\left\{\langle\Phi|\hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}}|\Phi\rangle + E_{\text{Hxc}}^{\text{sr}}[n_\Phi]\right\}$$

with minimizing single-determinant Φ_0 given by

$$\left(\hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hx,HF}}^{\text{lr}} + \hat{V}_{\text{Hxc}}^{\text{sr}}\right)|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle$$

- **Adiabatic connection** between the single-determinant reference ($\lambda = 0$) and the exact energy ($\lambda = 1$):

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

with the long-range MP perturbation operator $\hat{W}^{\text{lr}} = \hat{W}_{\text{ee}}^{\text{lr}} - \hat{V}_{\text{Hx,HF}}^{\text{lr}}$

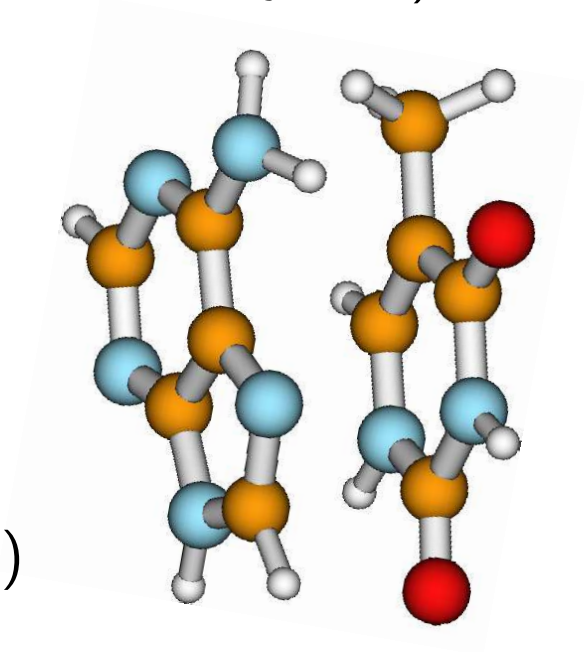
- Total energy by adding the **long-range correlation energy** E_{c}^{lr}

$$E = E_{\text{lrHF+srDFT}} + E_{\text{c}}^{\text{lr}} \quad \text{with} \quad E_{\text{c}}^{\text{lr}} = \sum_{n=2}^{\infty} E^{(n)}$$

Ángyán, Gerber, Savin, Toulouse, PRA, 2005

Test on van der Waals dispersion interactions

Interaction energy between DNA base pairs (adenine - thymine) in "stacking" configuration:



	E_{int} (kcal/mol)
CCSD(T)/CBS	**11.66**
lrMP2+srDFT/aVDZ	15.11

Zhu, Toulouse, Savin, Ángyán, JCP, 2010
Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Outline

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Adiabatic-connection fluctuation-dissipation (ACFD) approach

- **Long-range correlation energy** from **adiabatic connection formula**

$$E_c^{\rm lr} = \int_0^1 d\lambda \Big\{ \langle \Psi_\lambda^{\rm lr} | \hat{W}^{\rm lr} | \Psi_\lambda^{\rm lr} \rangle - \langle \Phi_0 | \hat{W}^{\rm lr} | \Phi_0 \rangle \Big\} = \frac{1}{2} \int_0^1 d\lambda \, {\rm tr}[\mathbf{w}^{\rm lr} \, \mathbf{P}_{c,\lambda}^{\rm lr}]$$

- Two-particle density matrix $\mathbf{P}_{c,\lambda}^{\rm lr}$ from **fluctuation-dissipation theorem**

$$\mathbf{P}_{c,\lambda}^{\rm lr} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \, \left[\boldsymbol{\chi}_\lambda^{\rm lr}(\omega) - \boldsymbol{\chi}_0(\omega) \right] e^{i\omega 0^+} + \Delta_\lambda^{\rm lr}$$

where $\Delta_\lambda^{\rm lr} = \Gamma[G_\lambda^{\rm lr}] - \Gamma[G_0]$

- **Long-range one-particle Green function $\mathbf{G}_\lambda^{\rm lr}(\omega)$** from Dyson equation

$$\left(\mathbf{G}_\lambda^{\rm lr}\right)^{-1} = \mathbf{G}_0^{-1} - \left(\boldsymbol{\Sigma}_{{\rm Hxc},\lambda}^{\rm lr}[G_\lambda^{\rm lr}] - \boldsymbol{\Sigma}_{{\rm Hx},\lambda}^{\rm lr}[G_0] \right) - \Delta_\lambda^{\rm sr}$$

where $\Delta_\lambda^{\rm sr} = \mathbf{v}_{\rm Hxc}^{\rm sr}[G_\lambda^{\rm lr}] - \mathbf{v}_{\rm Hxc}^{\rm sr}[G_0]$

- **Long-range response function $\chi_\lambda^{\rm lr}(\omega)$** from Bethe-Salpeter equation

$$\left(\chi_\lambda^{\rm lr}\right)^{-1} = \left(\chi_{{\rm IP},\lambda}^{\rm lr}\right)^{-1} - \mathbf{f}_{{\rm Hxc},\lambda}^{\rm lr}$$

where $\chi_{{\rm IP},\lambda}^{\rm lr} = -i \mathbf{G}_\lambda^{\rm lr} * \mathbf{G}_\lambda^{\rm lr}$ and $\mathbf{f}_{{\rm Hxc},\lambda}^{\rm lr} = i \delta \boldsymbol{\Sigma}_{{\rm Hxc},\lambda}^{\rm lr} / \delta \mathbf{G}_\lambda^{\rm lr}$

Toulouse, Zhu, Ángyán, Savin, PRA, 2010

direct random-phase approximation (dRPA)

- We keep only the Hartree part in the long-range self-energy

$$\boldsymbol{\Sigma}^{\text{lr}}_{\text{Hxc},\boldsymbol{\lambda}} \approx \boldsymbol{\Sigma}^{\text{lr}}_{\text{H},\boldsymbol{\lambda}} = -i\boldsymbol{\lambda}\mathbf{w}^{\text{lr}}_{\text{ee}}\mathbf{G}^{\text{lr}}_{\boldsymbol{\lambda}}$$

which implies

$$\mathbf{G}^{\text{lr}}_{\boldsymbol{\lambda}} \approx \mathbf{G}_0 \quad \text{and} \quad \mathbf{f}^{\text{lr}}_{\text{Hxc},\boldsymbol{\lambda}} \approx \boldsymbol{\lambda}\mathbf{w}^{\text{lr}}_{\text{ee}}$$

- The dRPA long-range correlation energy is

$$E^{\text{lr}}_{\text{c,dRPA}} = \frac{-1}{2}\int_0^1 d\boldsymbol{\lambda} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \text{tr}\left[\mathbf{w}^{\text{lr}}_{\text{ee}} \left(\boldsymbol{\chi}^{\text{lr}}_{\boldsymbol{\lambda}}(\omega) - \boldsymbol{\chi}_0(\omega)\right)\right] e^{i\omega 0^+}$$

where $\boldsymbol{\chi}^{\text{lr}}_{\boldsymbol{\lambda}}(\omega)$ is obtained in a spin-orbital basis

$$\boldsymbol{\chi}^{\text{lr}}_{\boldsymbol{\lambda}}(\omega)^{-1} = \boldsymbol{\chi}_0^{-1}(\omega) - \boldsymbol{\lambda}\mathbf{w}^{\text{lr}}_{\text{ee}} = -\left[\begin{pmatrix} \mathbf{A}_{\boldsymbol{\lambda}} & \mathbf{B}_{\boldsymbol{\lambda}} \\ \mathbf{B}^*_{\boldsymbol{\lambda}} & \mathbf{A}^*_{\boldsymbol{\lambda}} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}\right]$$

with $(A_{\boldsymbol{\lambda}})_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \boldsymbol{\lambda}\left\langle aj|w^{\text{lr}}_{\text{ee}}|ib\right\rangle$ and $(B_{\boldsymbol{\lambda}})_{ia,jb} = \boldsymbol{\lambda}\left\langle ab|w^{\text{lr}}_{\text{ee}}|ij\right\rangle$

Toulouse, Zhu, Ángyán, Savin, PRA, 2010

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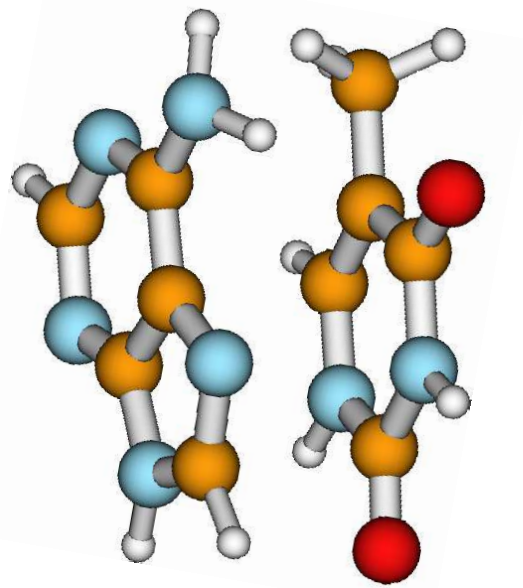

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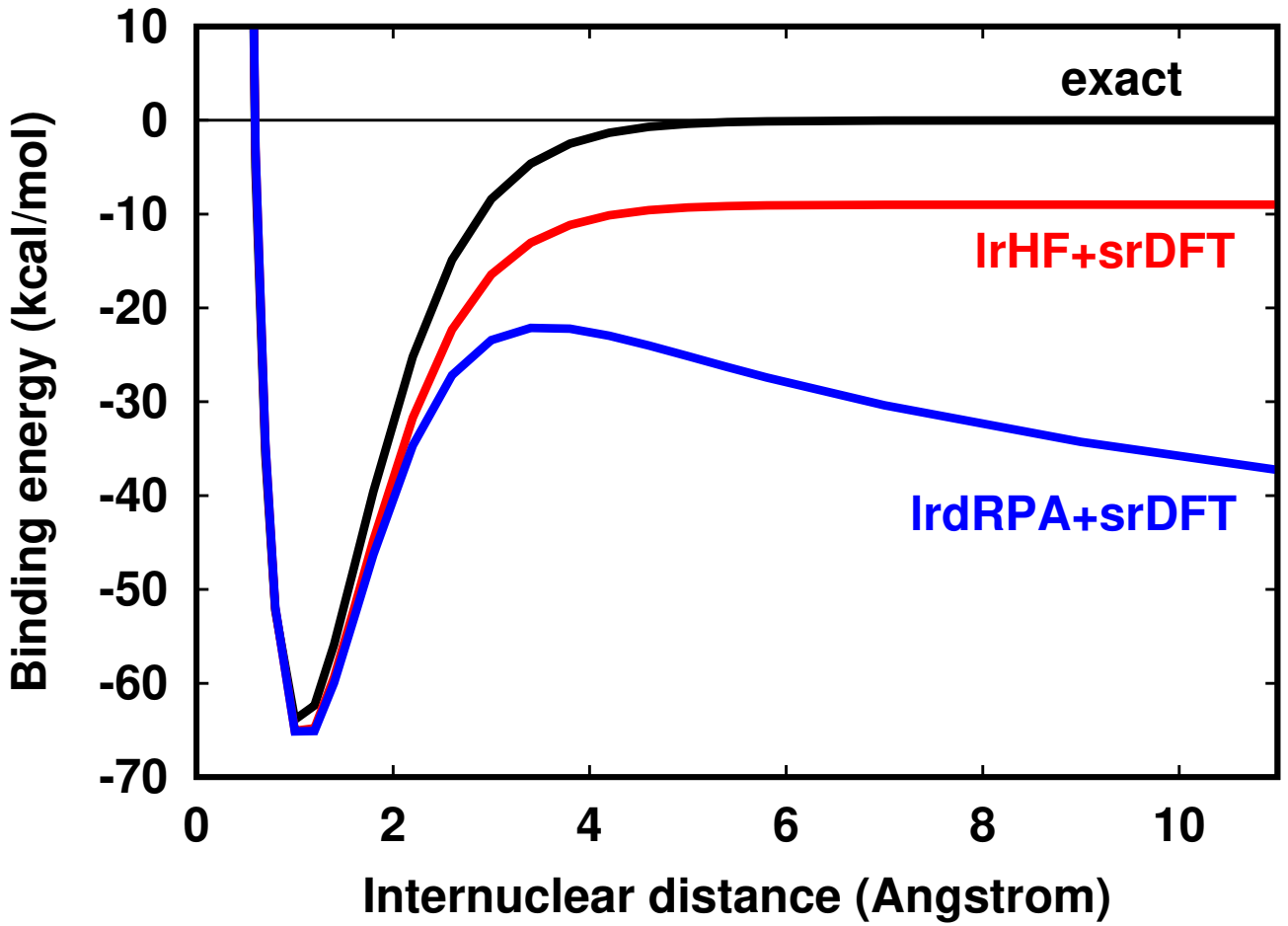
Zhu, Toulouse, Savin, Ángyán, JCP, 2010
Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Self-interaction error in lrdRPA+srDFT

Dissociation of H_2^+ molecule: $H_2^+ \longrightarrow H^{+0.5} + H^{+0.5}$



Mussard, Toulouse, MP, 2017

Random-phase approximation with exchange (RPAx)

- We keep the Hartree-Fock part in the long-range self-energy

$$\Sigma^{\text{lr}}_{\text{Hxc},\lambda} \approx \Sigma^{\text{lr}}_{\text{Hx},\lambda} = -i\lambda \bar{\mathbf{w}}^{\text{lr}}_{\text{ee}} \mathbf{G}^{\text{lr}}_{\lambda}$$

where $\bar{\mathbf{w}}^{\text{lr}}_{\text{ee}}$ is the antisymmetrized e-e interaction, which implies

$$\mathbf{G}^{\text{lr}}_{\lambda} \approx \mathbf{G}_0 \quad \text{and} \quad \mathbf{f}^{\text{lr}}_{\text{Hxc},\lambda} \approx \lambda \bar{\mathbf{w}}^{\text{lr}}_{\text{ee}}$$

- The RPAx long-range correlation energy is

$$E^{\text{lr}}_{\text{c,RPAx}} = \frac{-1}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \text{tr} \left[\mathbf{w}^{\text{lr}}_{\text{ee}} \left(\bar{\chi}^{\text{lr}}_{\lambda}(\omega) - \chi_0(\omega) \right) \right] e^{i\omega 0^+}$$

where $\bar{\chi}^{\text{lr}}_{\lambda}(\omega)$ is obtained in a spin-orbital basis

$$\bar{\chi}^{\text{lr}}_{\lambda}(\omega)^{-1} = \chi_0^{-1}(\omega) - \lambda \bar{\mathbf{w}}^{\text{lr}}_{\text{ee}} = - \left[\begin{pmatrix} \bar{\mathbf{A}}_{\lambda} & \bar{\mathbf{B}}_{\lambda} \\ \bar{\mathbf{B}}^*_{\lambda} & \bar{\mathbf{A}}^*_{\lambda} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]$$

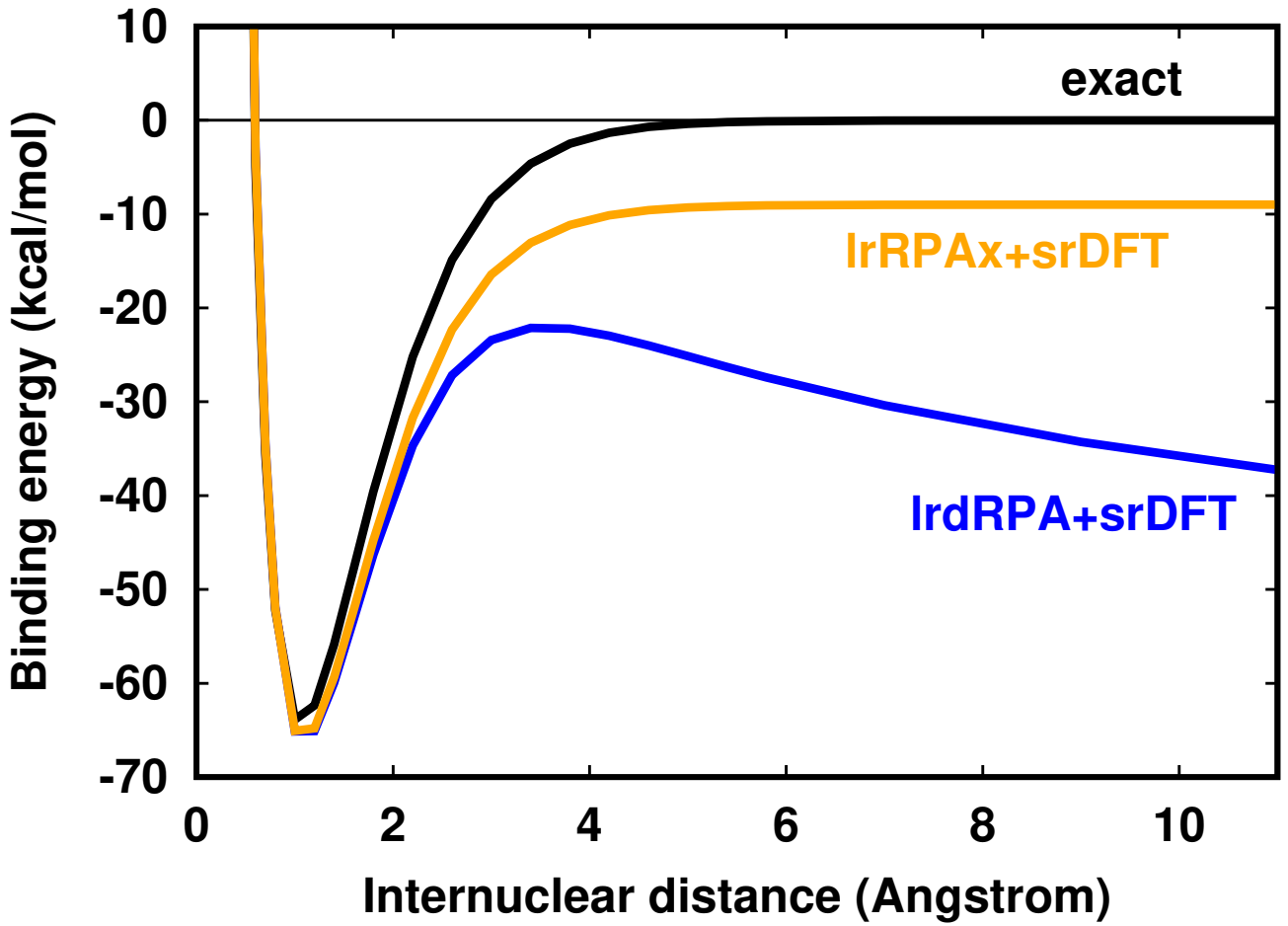
with $(\bar{A}_{\lambda})_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \lambda \left(\langle aj | w^{\text{lr}}_{\text{ee}} | ib \rangle - \langle aj | w^{\text{lr}}_{\text{ee}} | bi \rangle \right)$

and $(\bar{B}_{\lambda})_{ia,jb} = \lambda \left(\langle ab | w^{\text{lr}}_{\text{ee}} | ij \rangle - \langle ab | w^{\text{lr}}_{\text{ee}} | ji \rangle \right)$

Toulouse, Zhu, Ángyán, Savin, PRA, 2010

Self-interaction error in lrRPAx+srDFT

Dissociation of H_2^+ molecule: $H_2^+ \longrightarrow H^{+0.5} + H^{+0.5}$



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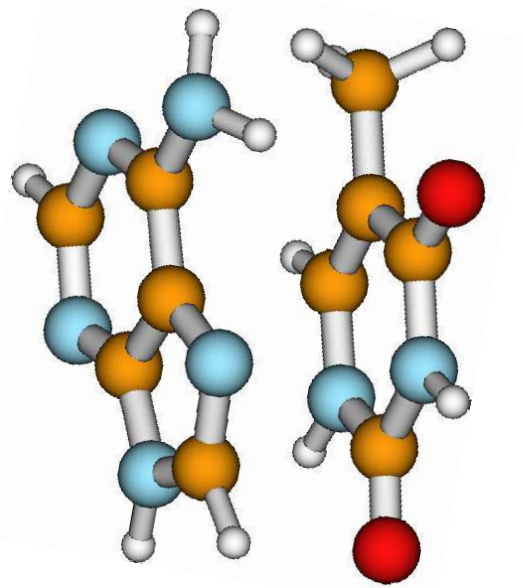

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Coupled-cluster (CC) approach

- **Long-range correlation energy** from transition formula

$$E_c^{\text{lr}} = \langle \Phi_0 | \hat{H}^{\text{lr}} | \Psi^{\text{lr}} \rangle - \langle \Phi_0 | \hat{H}^{\text{lr}} | \Phi_0 \rangle + \Delta^{\text{sr}}$$

where $\hat{H}^{\text{lr}} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} + \hat{V}_{\text{Hxc}}^{\text{sr}}$ and Δ^{sr} comes from the variation of the density

$$\Delta^{\text{sr}} = E_{\text{Hxc}}^{\text{sr}}[n_{\Psi^{\text{lr}}}] - E_{\text{Hxc}}^{\text{sr}}[n_{\Phi_0}] - \int v_{\text{Hxc}}^{\text{sr}}[n_{\Psi^{\text{lr}}}](\mathbf{r}) \left(n_{\Psi^{\text{lr}}}(\mathbf{r}) - n_{\Phi_0}(\mathbf{r}) \right) d\mathbf{r}$$

- **Long-range coupled-cluster wave function**

$$|\Psi^{\text{lr}}\rangle = e^{\hat{T}} |\Phi_0\rangle$$

where $\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N$ are excitation operators with amplitudes found from the CC equations

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H}^{\text{lr}} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H}^{\text{lr}} e^{\hat{T}} | \Phi_0 \rangle = 0$$

$$\langle \Phi_{ijk}^{abc} | e^{-\hat{T}} \hat{H}^{\text{lr}} e^{\hat{T}} | \Phi_0 \rangle = 0$$

etc...

Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

dRPA as direct ring CCD

- If we restrict $\hat{T}$ to double excitations (CCD)

$$\hat{T} \approx \hat{T}_2 = \frac{1}{4} \sum_{k,l}^{\text{occ}} \sum_{c,d}^{\text{vir}} T_{kc,ld}\, \hat{a}_c^\dagger \hat{a}_d^\dagger \hat{a}_l \hat{a}_k$$

- use the direct ring approximation in the CC amplitude equations, i.e.

$$T_{kc,ld} \to T_{kc,ld} \left(\delta_{ik}\delta_{ac} + \delta_{jl}\delta_{bd} \right)$$

in $\langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{H}^{\text{lr}} e^{\hat{T}_2} | \Phi_0 \rangle = 0$ and remove exchange terms,
giving a simple Riccati equation

$$\mathbf{B}^* + \mathbf{A}^*\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0}$$

- and neglect the density variation $n_{\Psi^{\text{lr}}}(\mathbf{r}) \approx n_{\Phi_0}(\mathbf{r})$
- we obtain another expression for the dRPA correlation energy

$$E_{\text{c,dRPA}}^{\text{lr}} = \frac{1}{2} \text{tr} \left[\mathbf{w}_{\text{ee}}^{\text{lr}} \mathbf{T} \right]$$

Scuseria, Henderson, Sorensen, JCP, 2008
Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Another RPAx variant from ring CCD

- If we keep the exchange terms in the Riccati equation

$$\bar{\mathbf{B}}^{*} + \bar{\mathbf{A}}^{*}\bar{\mathbf{T}} + \bar{\mathbf{T}}\bar{\mathbf{A}} + \bar{\mathbf{T}}\bar{\mathbf{B}}\bar{\mathbf{T}} = \mathbf{0}$$

- we obtain a new RPAx variant for the correlation energy

$$E^{\mathrm{lr}}_{\mathrm{c,RPAxSO2}} = \frac{1}{2}\,\mathrm{tr}\left[\mathbf{w}^{\mathrm{lr}}_{\mathrm{ee}}\,\overline{\mathbf{T}}\,\right]$$

  which was first proposed by Szabo and Ostlund as a zero iteration of self-consistent RPA.

Szabo, Ostlund, JCP, 1977
Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

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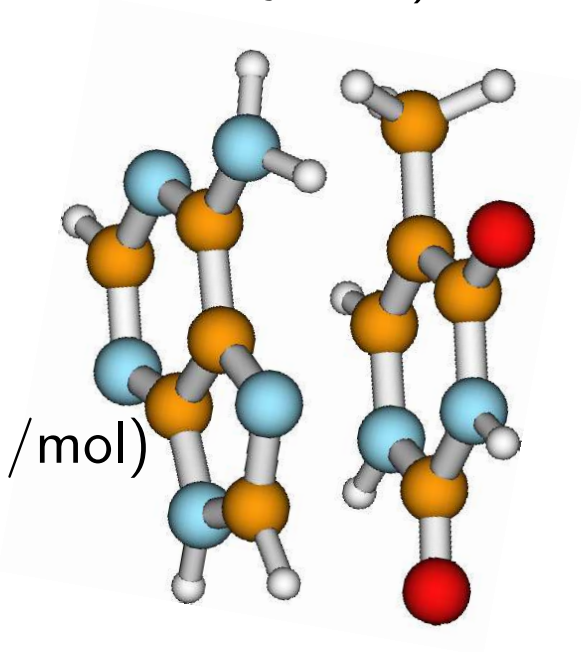

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lrRPAx+srDFT/aVDZ	10.97
lrRPAxSO2+srDFT/aVDZ	12.02

Zhu, Toulouse, Savin, Ángyán, JCP, 2010
Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011

Summary and perspectives

Summary

combination of long-range RPA with short-range DFT

- **lrRPA** has a fast basis convergence
- different **lrdRPA/lrRPAx** variants from ACFD or CC approaches
- **lrRPAx** accounts well for van der Waals dispersion interactions

For references: `www.lct.jussieu.fr/pagesperso/toulouse`

Perspectives

development of a (multireference) lrRPA variant for strong correlation?

Acknowledgments

J. Ángyán, O. Franck, I. Gerber, G. Jansen, E. Luppi, B. Mussard, P. Reinhardt, A. Savin, W. Zhu

János G. Ángyán (1956 - 2017)