DFT basée sur le théorème de fluctuation-dissipation avec séparation de portée pour les interactions de van der Waals

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1. Kohn-Sham DFT and ACFDT approach
2. Range-separated ACFDT approach
3. Some results

1 Kohn-Sham DFT and ACFDT approach

2 Range-separated ACFDT approach

3 Some results

Kohn-Sham DFT

Kohn-Sham (KS) scheme

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

$\mathbf{\Phi}$: **single-determinant** wave function

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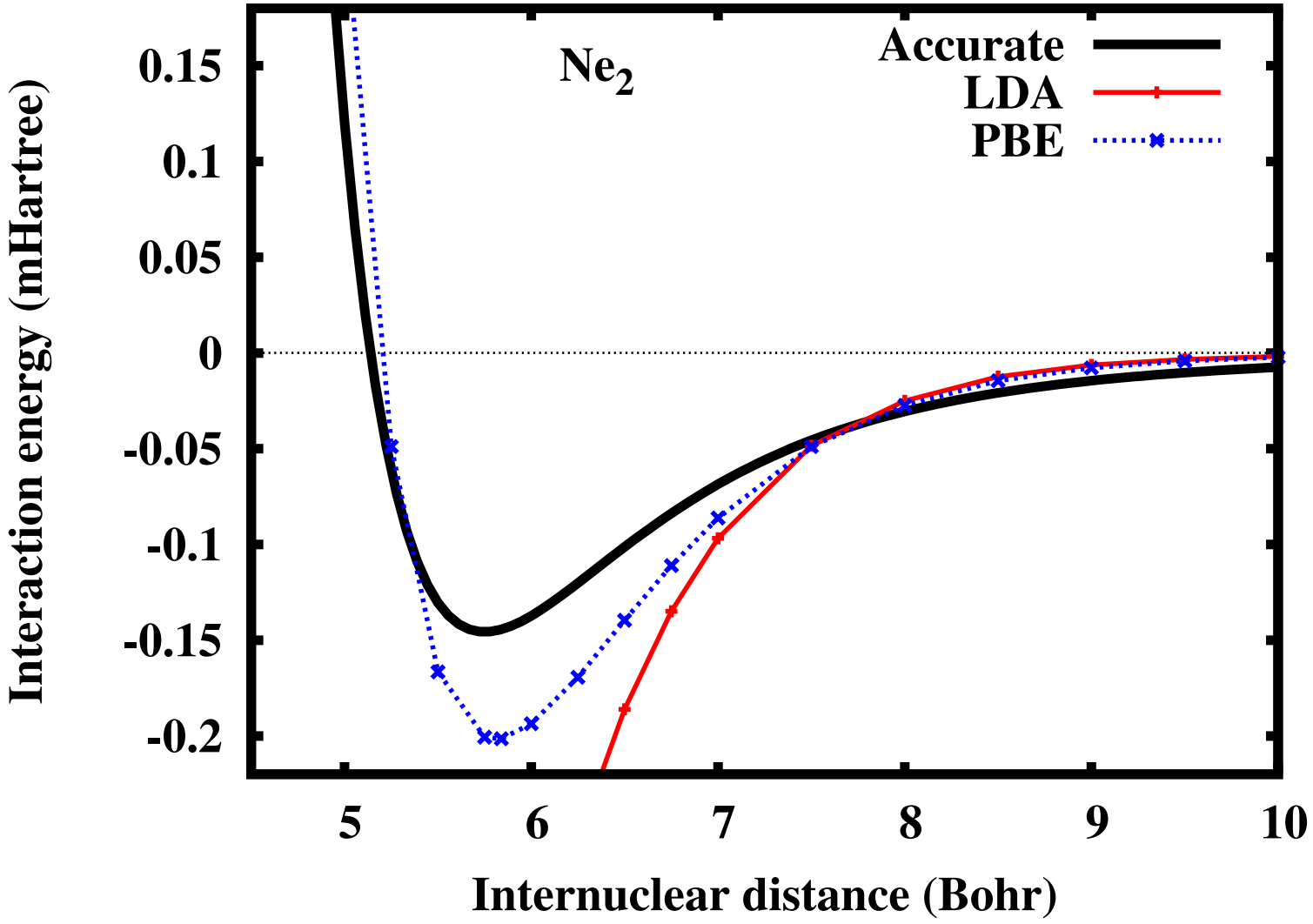
One problem (among others):
Usual approximations for exchange-correlation functional $E_{xc}[n]$ (LDA, GGA, ...) **do not describe well (long-range) van der Waals dispersion forces**

Example: interaction energy curve of Ne_2

LDA and PBE functionals, aug-cc-pV5Z basis:



ACFDT approach to DFT

Adiabatic connection formula for correlation energy:

$$E_c = \int_0^1 d\boldsymbol{\lambda} \left\{ \langle \boldsymbol{\Psi}_{\boldsymbol{\lambda}} | \hat{W}_{ee} | \boldsymbol{\Psi}_{\boldsymbol{\lambda}} \rangle - \langle \boldsymbol{\Phi}_{\mathrm{KS}} | \hat{W}_{ee} | \boldsymbol{\Phi}_{\mathrm{KS}} \rangle \right\}$$

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or, with a compact notation,

$$E_c = \frac{1}{2} \int_0^1 d\boldsymbol{\lambda} \ \mathrm{Tr}\left[w_{ee} * P_{c,\boldsymbol{\lambda}} \right]$$

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$$P_{c,\boldsymbol{\lambda}} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \; \left[\chi_{\boldsymbol{\lambda}}(i\omega) - \chi_{\mathrm{KS}}(i\omega) \right]$$

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$$\chi_{\boldsymbol{\lambda}}(i\omega)^{-1} = \chi_{\mathrm{KS}}(i\omega)^{-1} - f_{\mathrm{H}xc,\boldsymbol{\lambda}}(i\omega)$$

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- consistent with exact exchange
- correct dispersion forces at (very) large separation
- good cohesive energies and lattice constants of solids
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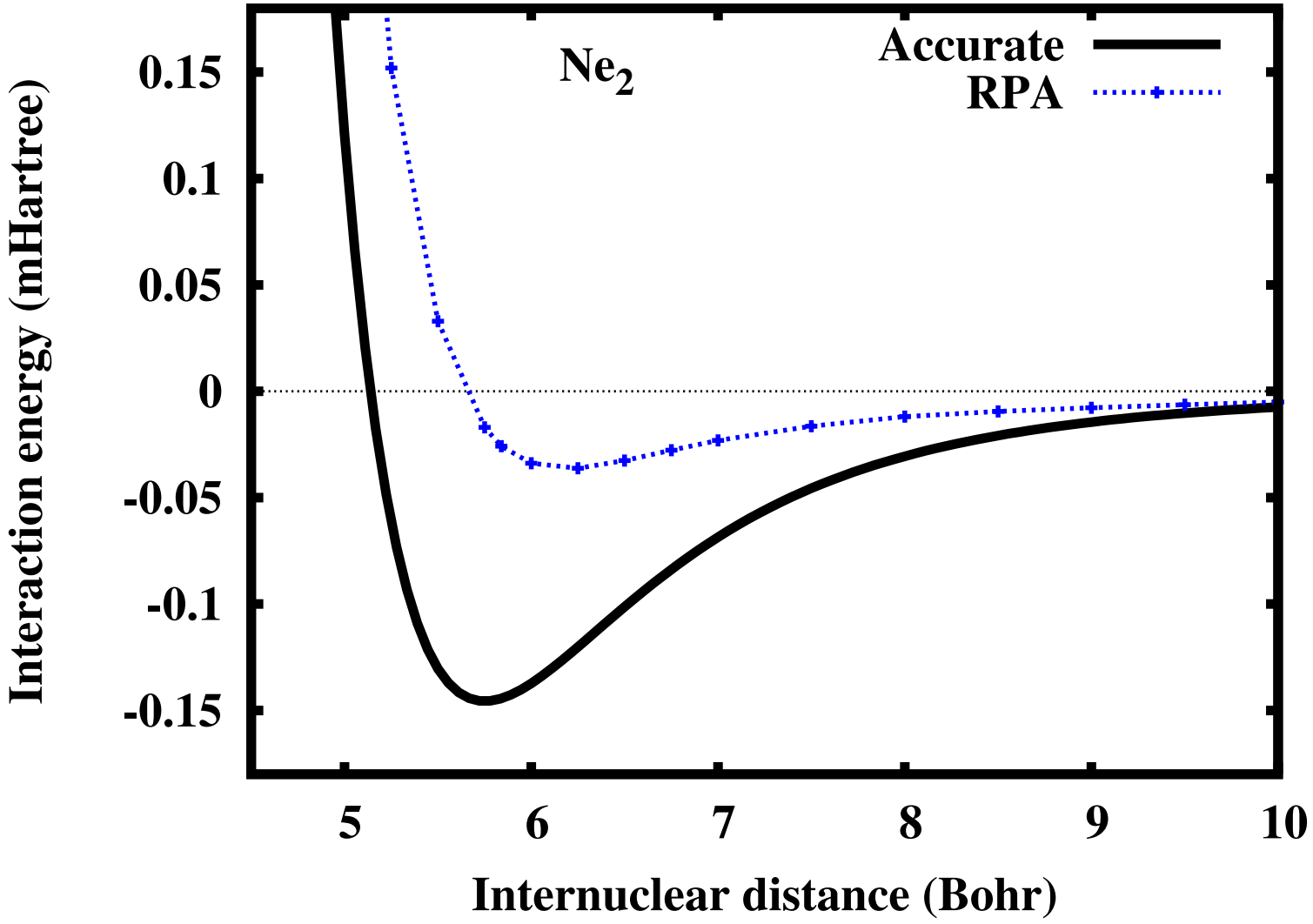
But several unsatisfactory aspects:

- correlation energies far too negative
- strong dependence on basis size
- bump at intermediate distances in some dissociation curves
- embarrassing results for simple van der Waals dimers!

Example: interaction energy curve of Ne_2

RPA (with PBE orbitals), aug-cc-pV5Z basis:



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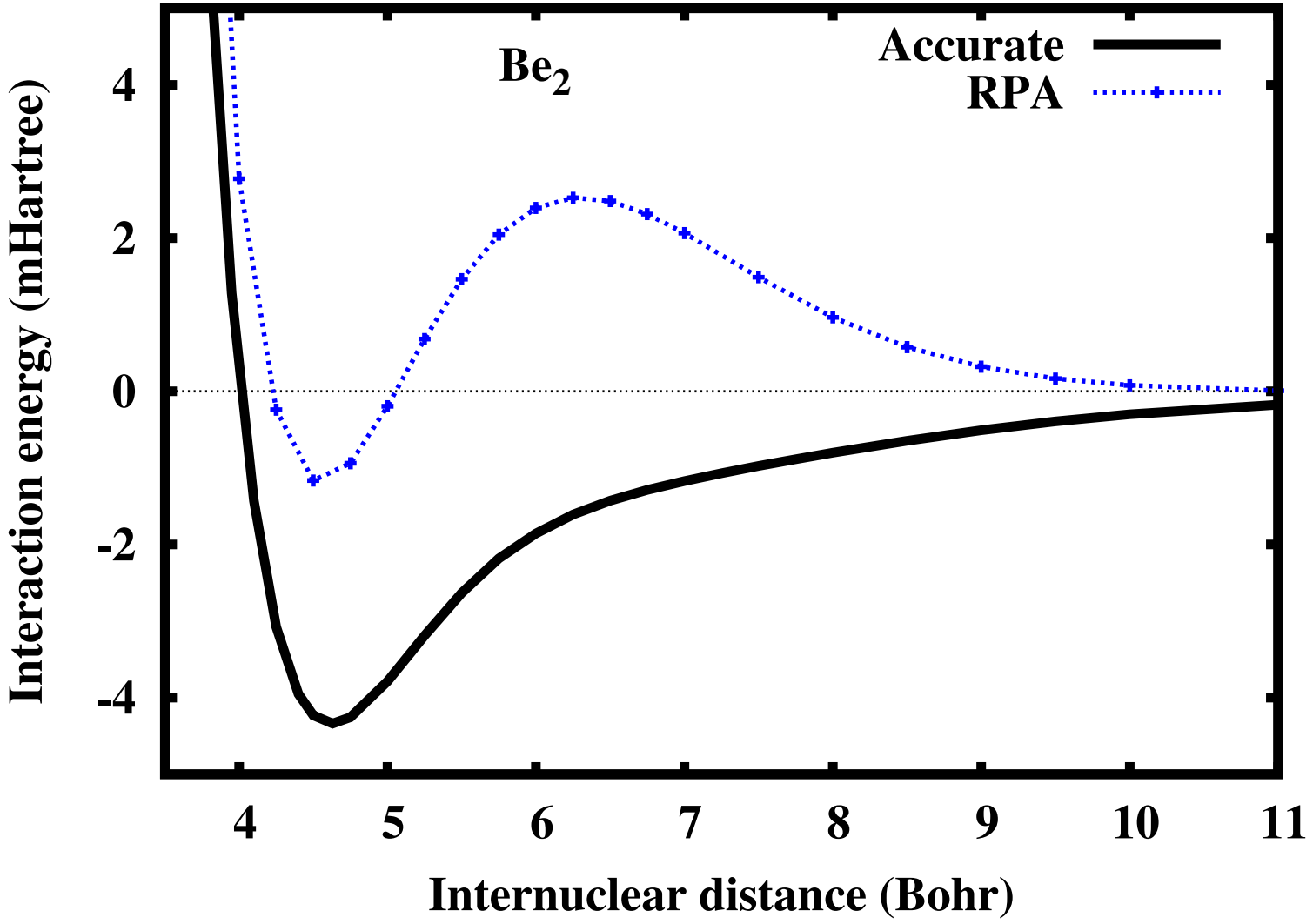

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Range-separated DFT

Multideterminant extension of KS scheme with range separation

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

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  Limiting cases:
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- **In principle: exact**
- **In practice: approximations** are necessary for Ψ^{lr} and $E_{xc}^{\mathrm{sr}}[n]$

Range-separated DFT: approximations

Approximations for $E_{xc}^{sr}[n]$

- short-range LDA
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Approximations for Ψ^{lr}

- **single-determinant** $\Longrightarrow$ RSH method
- **MP2** $\Longrightarrow$ RSH+MP2 method
- **RPA** $\Longrightarrow$ RSH+RPA method
- ...

Range-separated hybrid (RSH) scheme

Restriction to single-determinant wave functions $\mathbf{\Phi}$:

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

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The minimizing RSH determinant Φ_{RSH} is given by

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So the RSH energy is

$$E_{\mathrm{RSH}} = \langle \Phi_{\mathrm{RSH}} | \hat{T} + \hat{V}_{ne} | \Phi_{\mathrm{RSH}} \rangle + E_{\mathrm{H}} + E_{x,\mathrm{HF}}^{\mathrm{lr}} + E_{xc}^{\mathrm{sr}}$$

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Exact energy = RSH energy + **long-range correlation energy**

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Adiabatic connection from RSH reference to exact system:

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where $\Delta_{\boldsymbol{\lambda}}^{\mathrm{lr}}$ comes from the variation of the density.

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Approximation: $f_{c,\lambda}^{\mathrm{lr}} = 0 \Longrightarrow$ **RSH+RPAx method**

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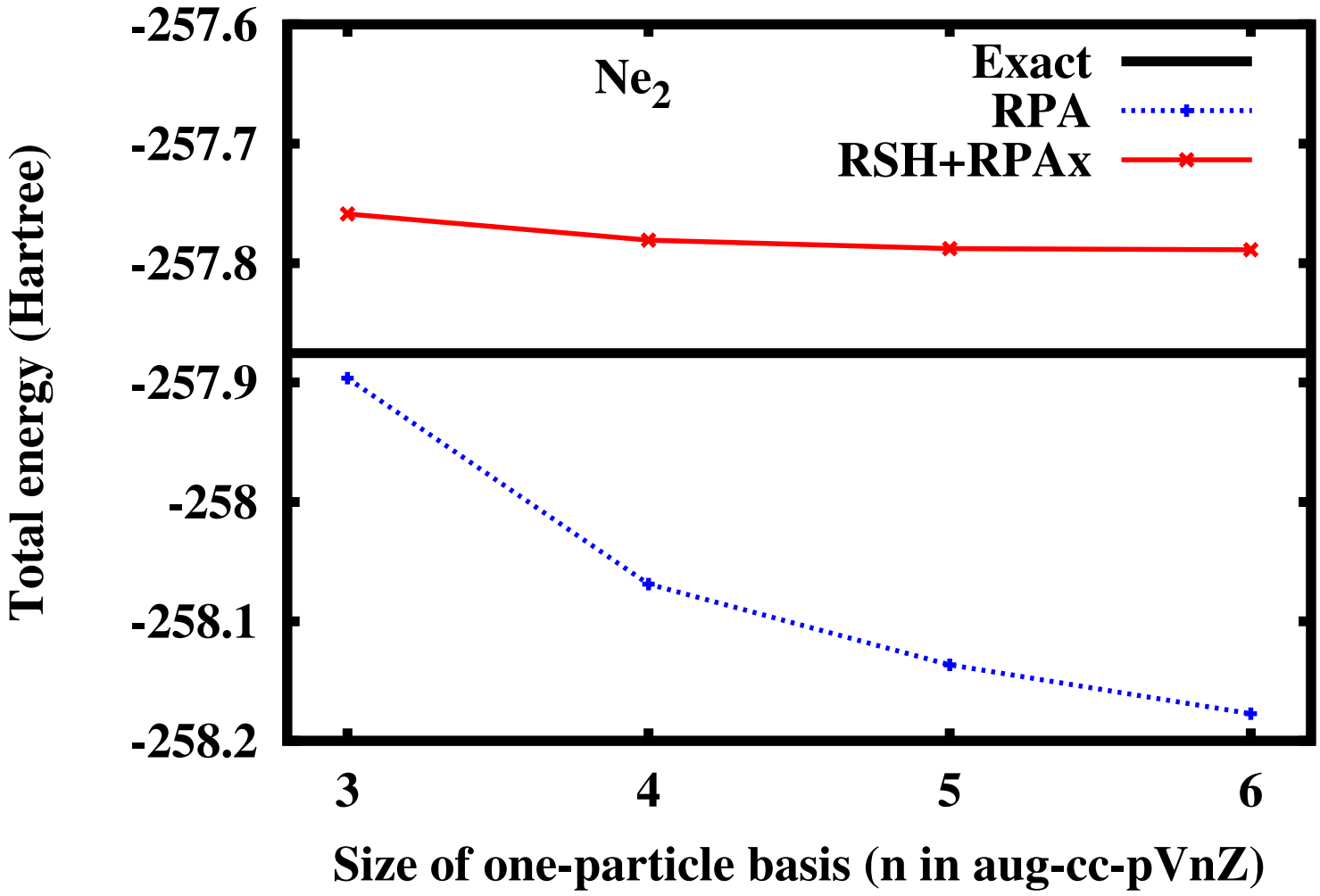
Dependence on basis size: Ne_2

Total energy (aug-cc-pVnZ basis, $\mu = 0.5$, sr-PBE functional):



$\Longrightarrow$ **RSH+RPAx has a small basis dependence**

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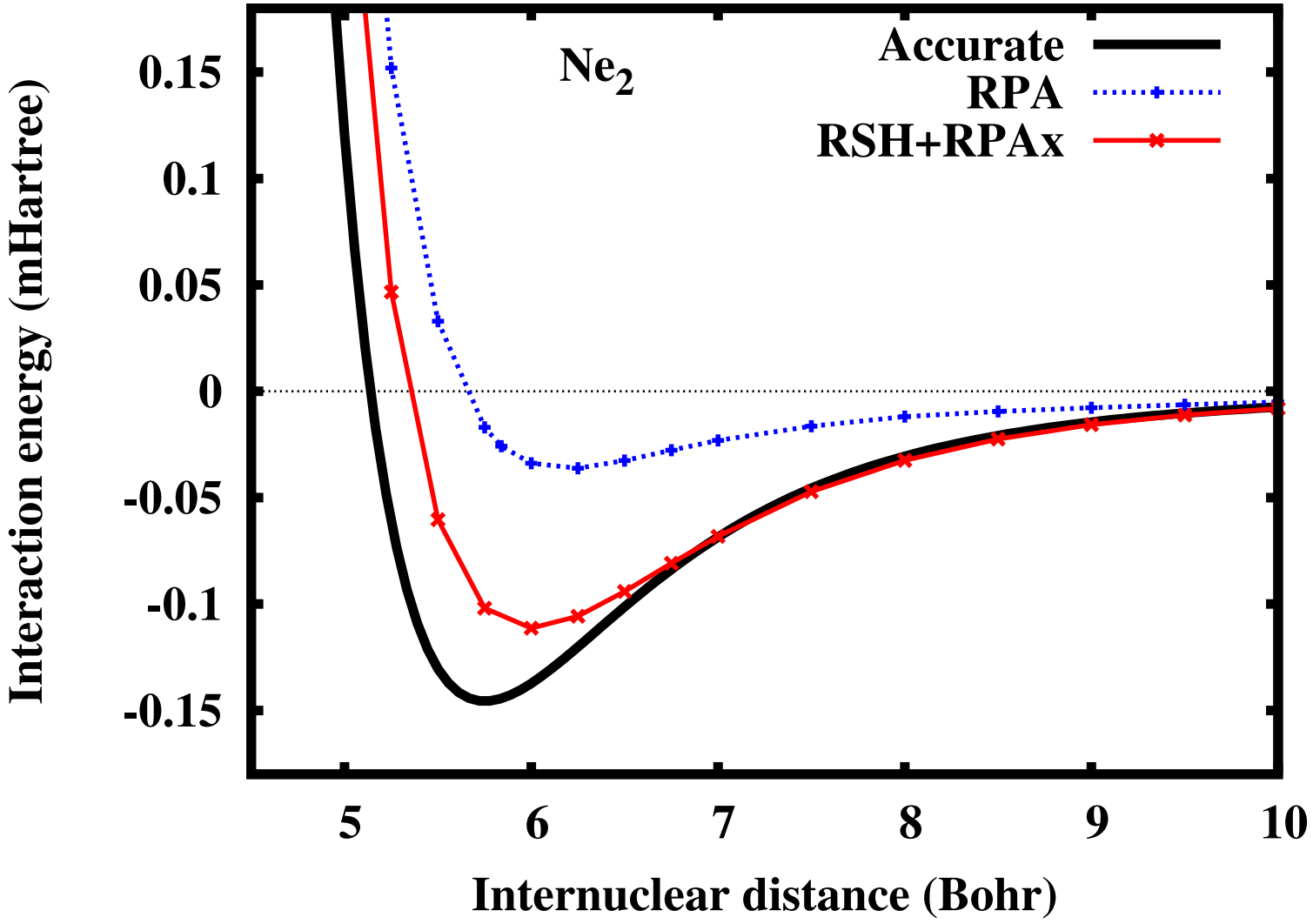

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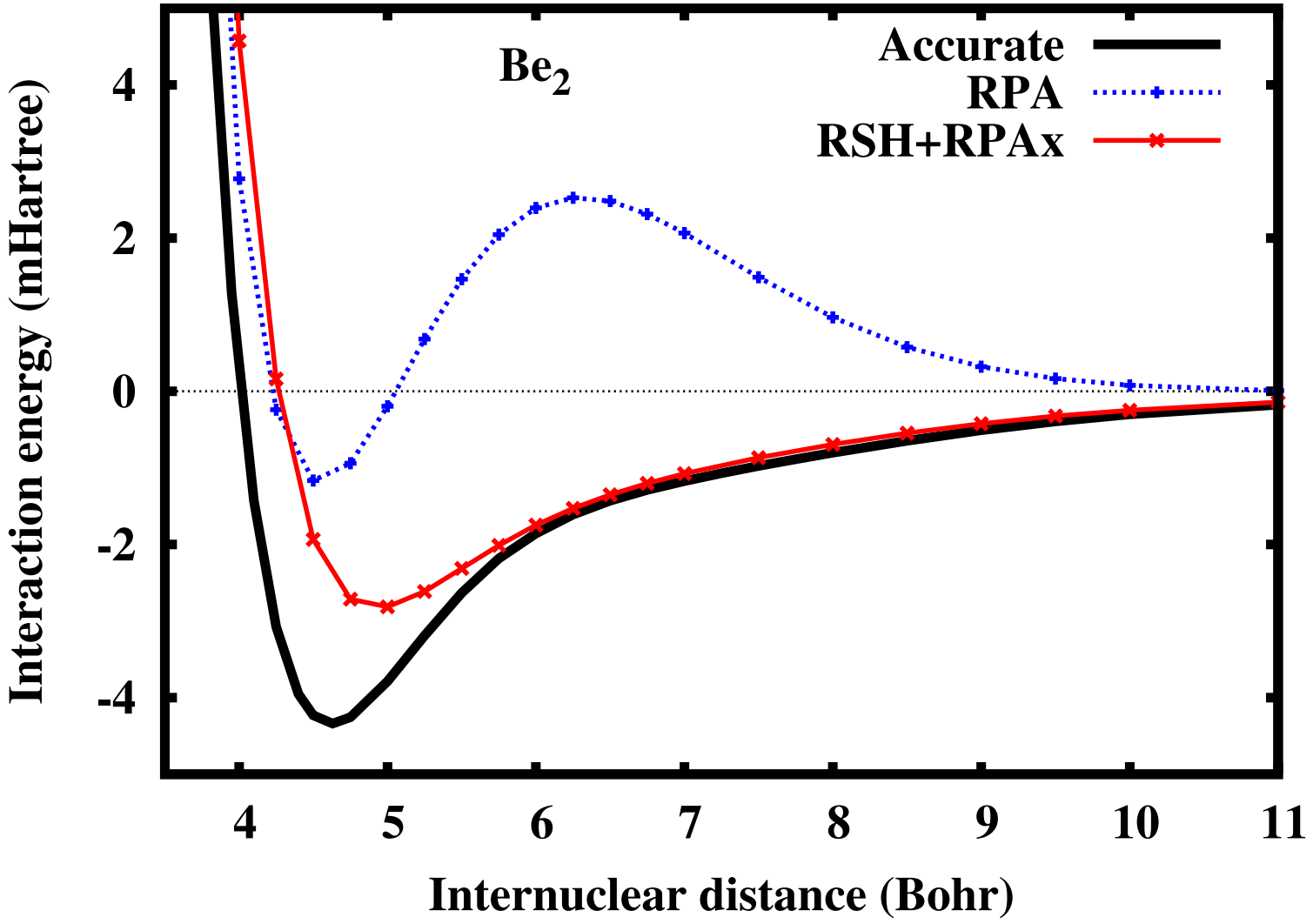

Conclusions and perspectives

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- RSH+RPAx method overcomes many problems of standard RPA
- RSH+RPAx method seems well suited for van der Waals systems
- RSH+RPAx method has also problems (e.g., dissociation)

Toulouse, Gerber, Jansen, Savin, Ángyán, arXiv:0812.3302

Perspectives

- exploration of other variants of the method
- application to larger molecular systems (benzene dimer, ...)
- application to solids

Web page: www.lct.jussieu.fr/pagesperso/toulouse/