# Adiabatic-connection fluctuation-dissipation density-functional theory based on range separation

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January 2010

1. ACFDT approach to DFT
2. Range-separated ACFDT approach
3. Some results on van der Waals systems

1 ACFDT approach to DFT

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# Kohn-Sham density-functional theory (DFT)

## Kohn-Sham (KS) scheme

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

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

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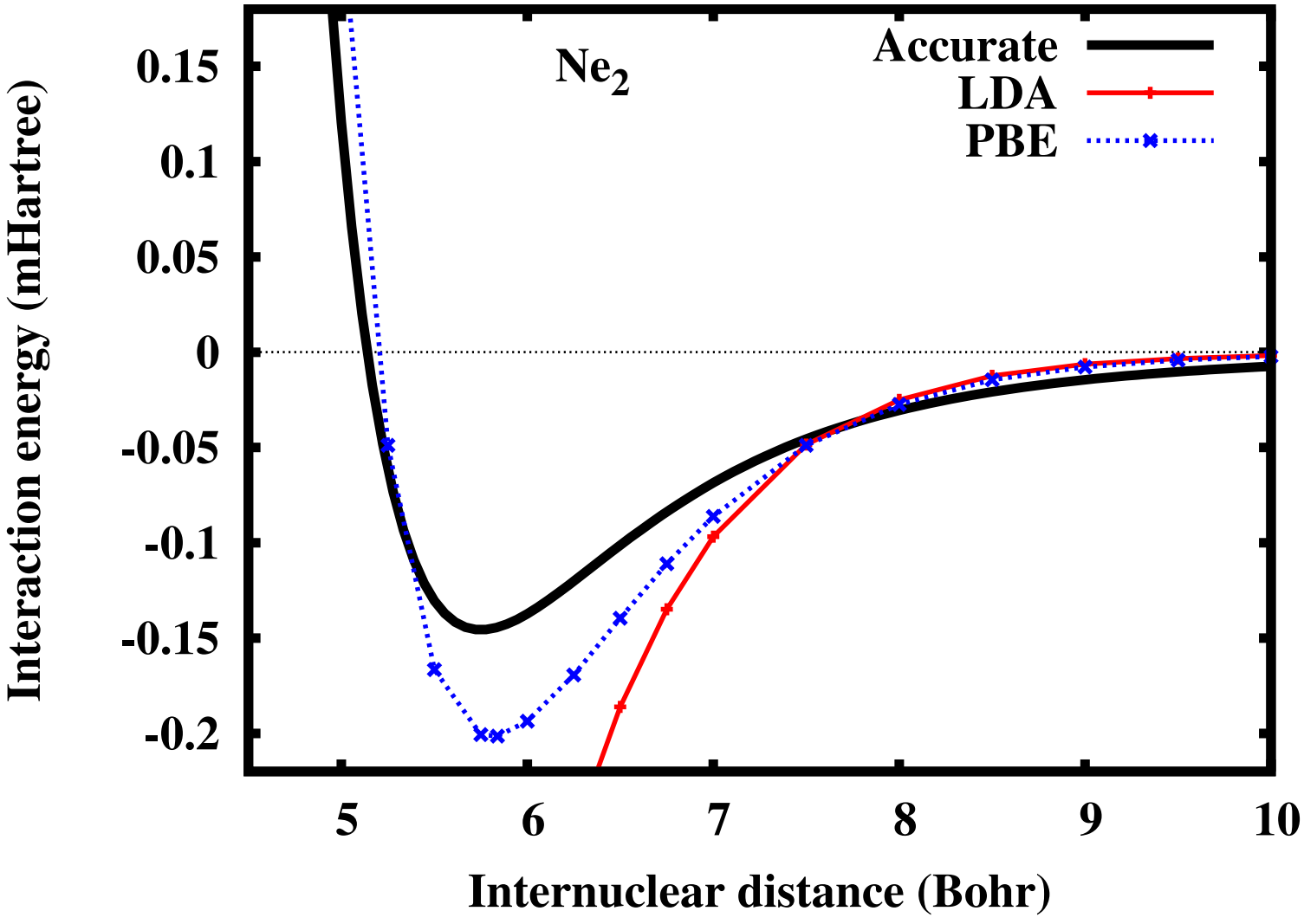
One problem (among others):
Usual approximations for exchange-correlation functional $E_{xc}[n]$ (LDA, GGA, ...) **do not describe well (long-range) van der Waals dispersion forces**

# 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,

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$P_{c,\boldsymbol{\lambda}}$ from **fluctuation-dissipation theorem**

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

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**Encouraging results:**

- consistent with the use of exact exchange
- qualitatively correct dispersion forces at (very) large separation
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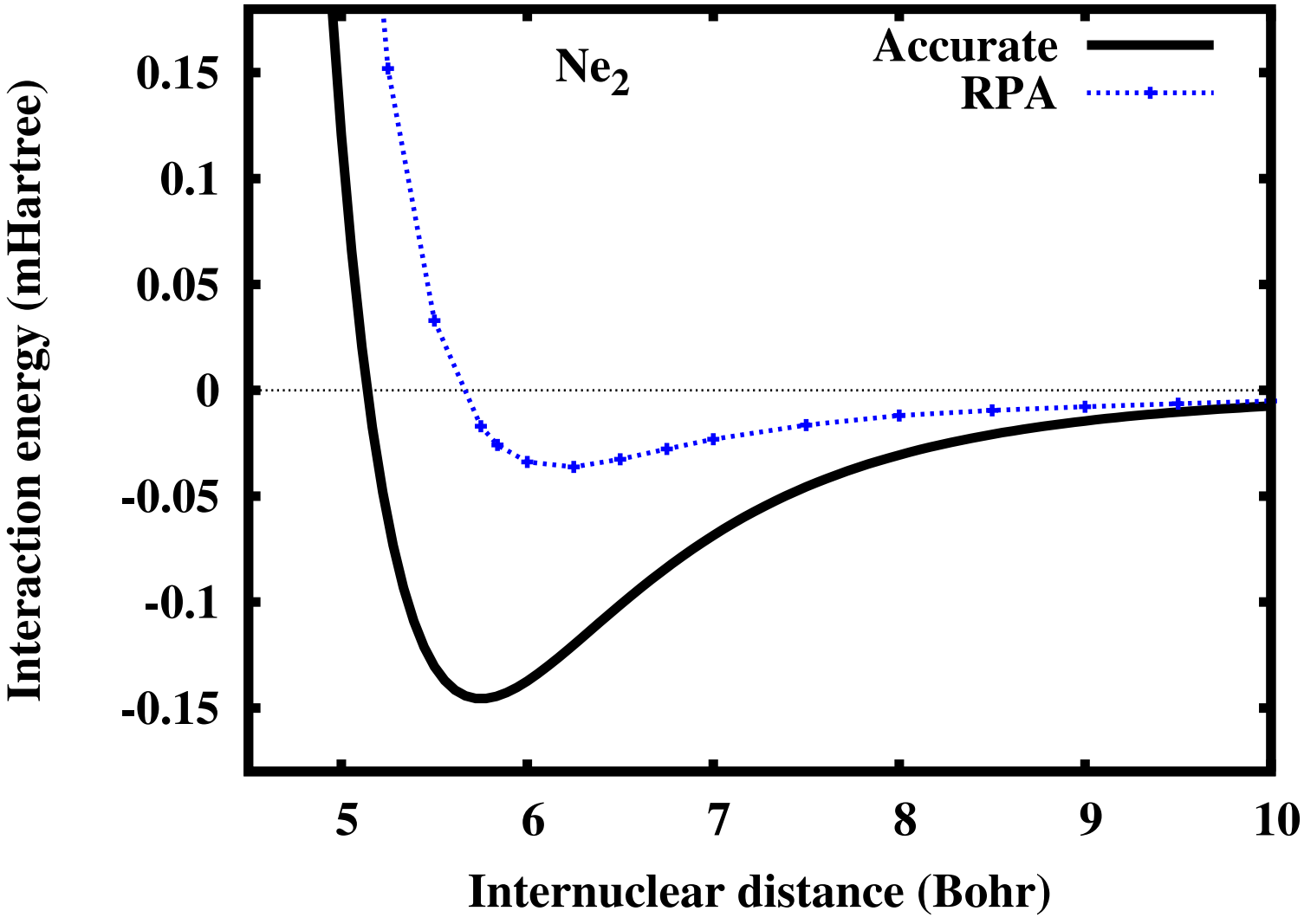
**But several unsatisfactory aspects:**

- short-range correlation energies far too negative
- strong dependence on basis size
- not good 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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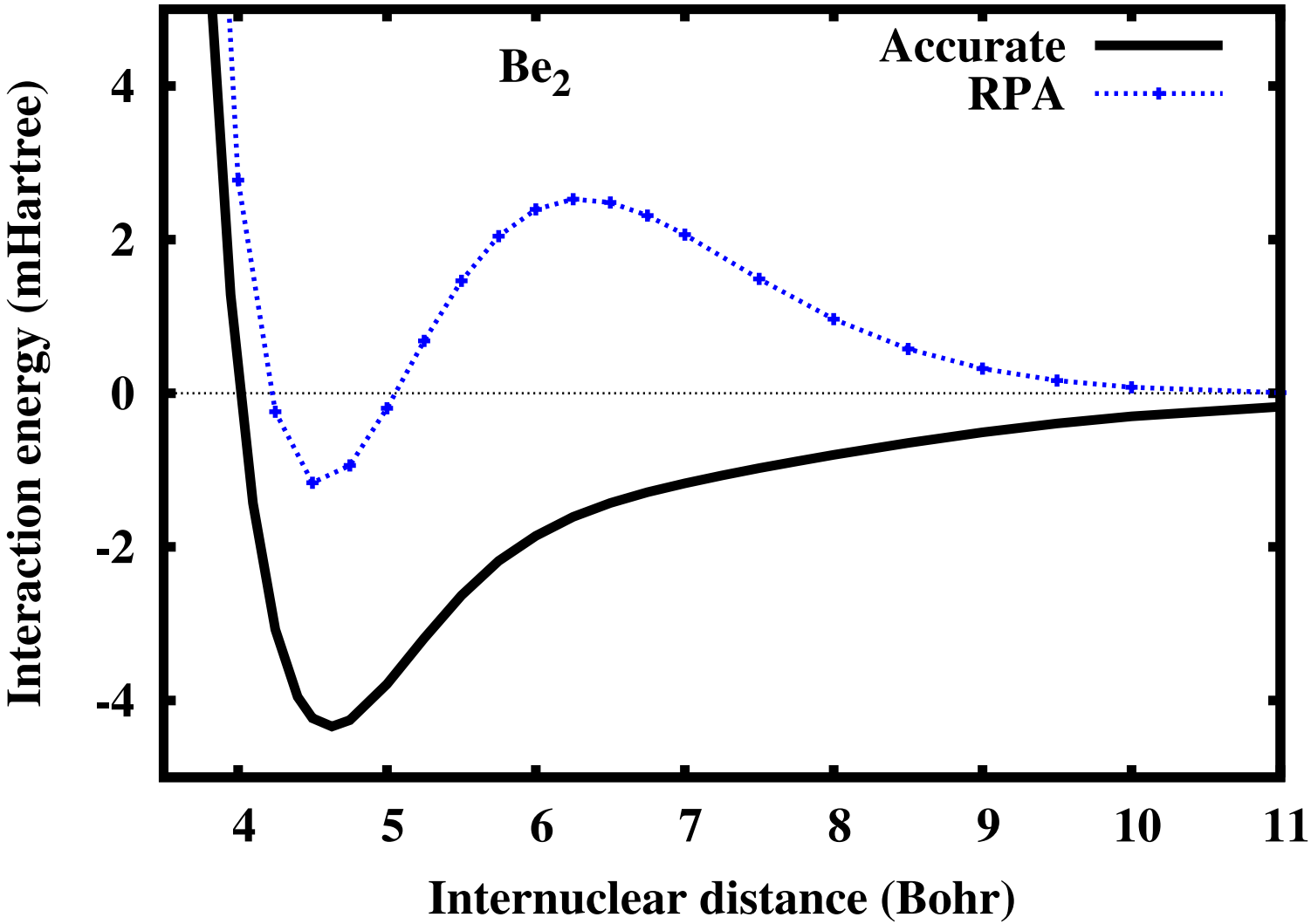

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# Range-separated DFT

## 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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- parameter $\mu$ controls the range of separation.
- **In principle: exact**
- **In practice: approximations** are necessary for $\Psi^{\mathrm{lr}}$ and $E_{xc}^{\mathrm{sr}}[n]$

# Range-separated DFT: approximations

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

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

- short-range LDA
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## Approximations for $\Psi^{lr}$

- **single-determinant** $\Longrightarrow$ RSH 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 $\Phi_{\mathrm{RSH}}$ is given by

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

This is a hybrid DFT with exact (HF) exchange at long range.

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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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$P_{c,\lambda}^{\text{lr}}$ from a **fluctuation-dissipation theorem**

$$P_{c,\lambda}^{\text{lr}} = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left[\chi_{\lambda}^{\text{lr}}(i\omega) - \chi_{\text{RSH}}(i\omega)\right] + \Delta_{\lambda}^{\text{lr}}$$

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The long-range response function $\chi_{\lambda}^{\mathrm{lr}}(i\omega)$ is given by

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Possible approximations:

- RPA approximation: $f_{xc,\lambda}^{\text{lr}} = 0 \Longrightarrow$ **RSH+RPA method**
- RPAx approximation: $f_{c,\lambda}^{\text{lr}} = 0 \Longrightarrow$ **RSH+RPAx method**

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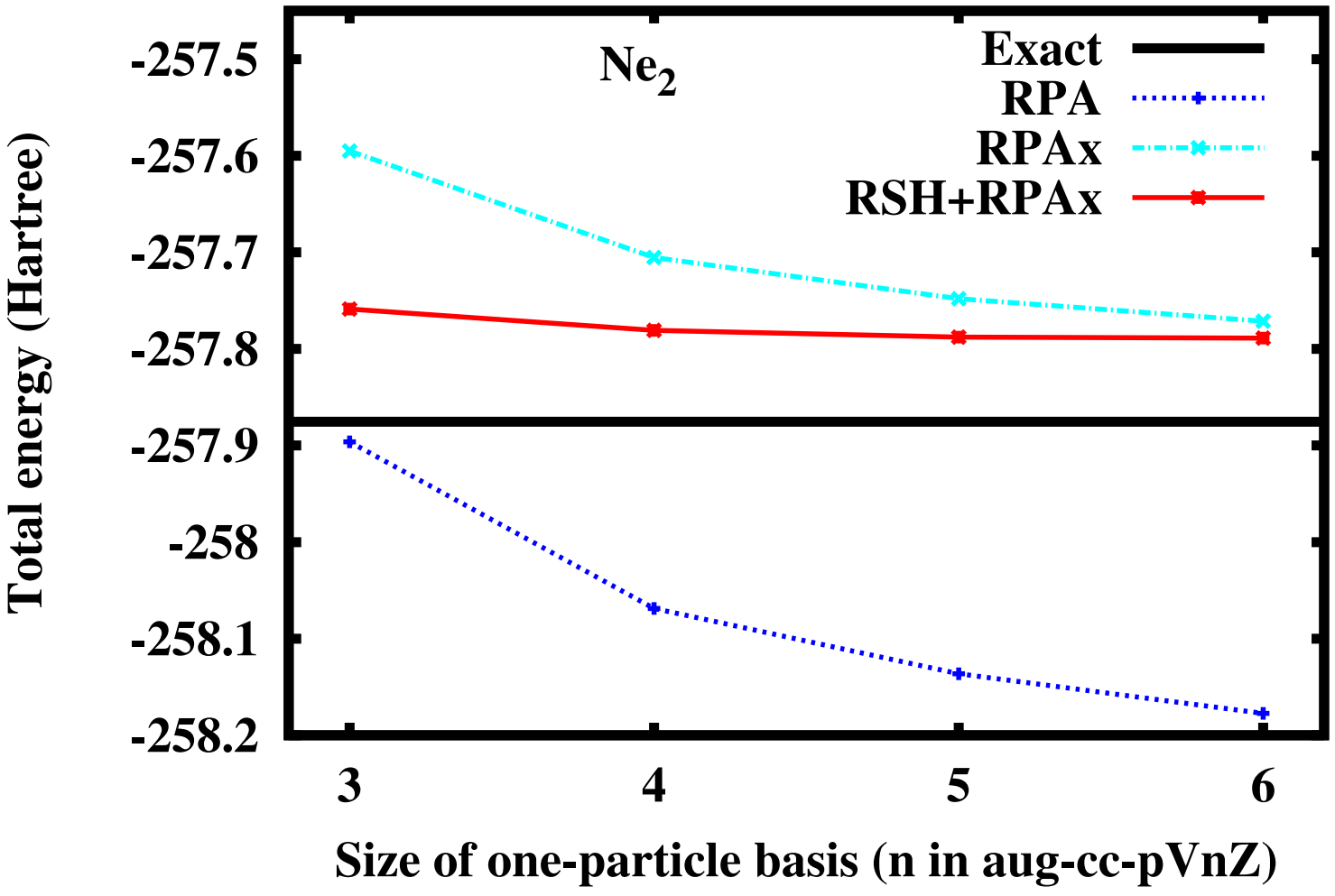
# Dependence on basis size: $Ne_2$

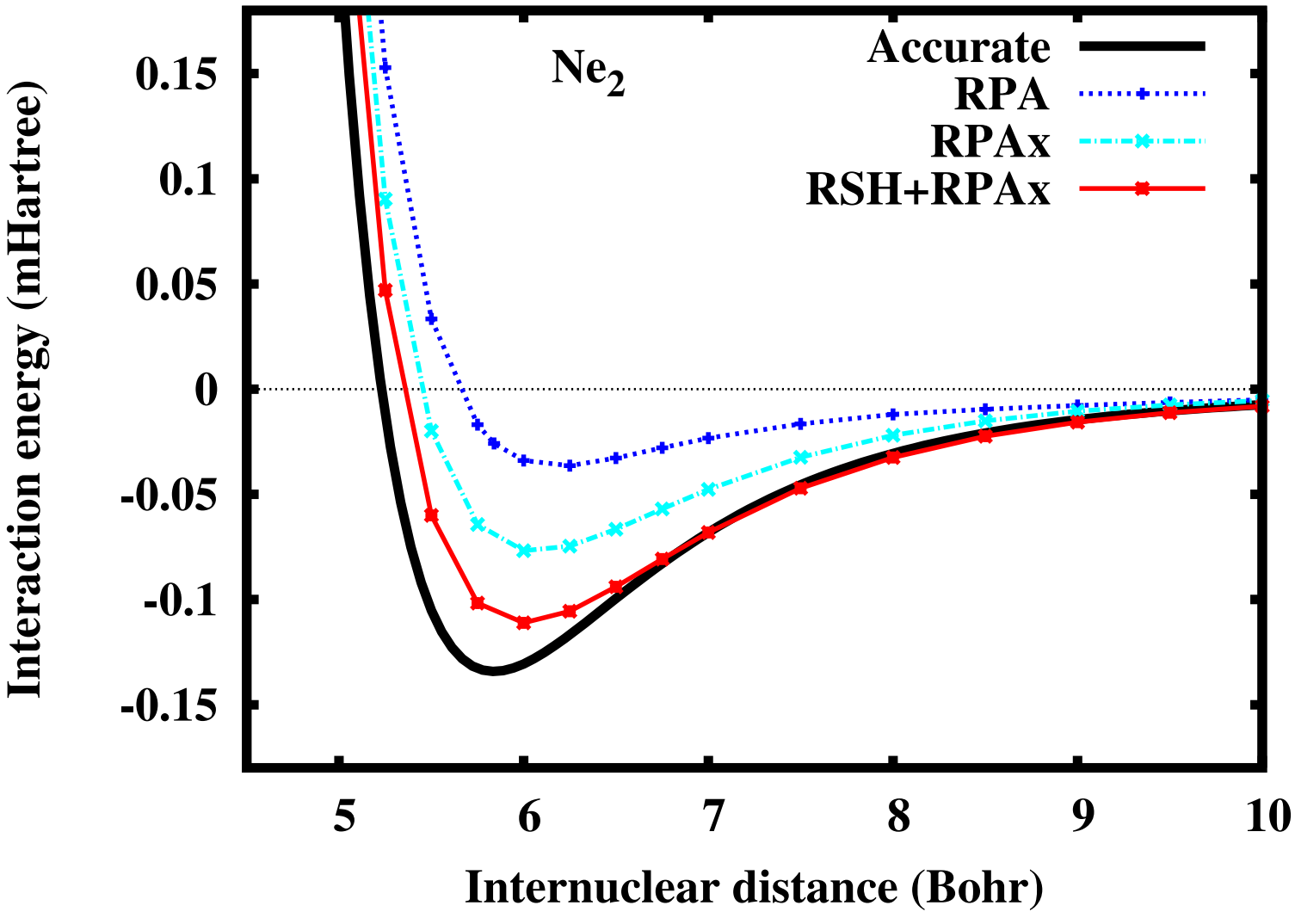
Total energy (aug-cc-pVnZ basis, $\mu = 0.5$, sr-PBE functional):




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

# Interaction energy curve of $Ne_2$

Interaction energy (aug-cc-pV5Z basis, $\mu = 0.5$, sr-PBE functional):




$\Longrightarrow$ **Range separation improves RPA(x)**

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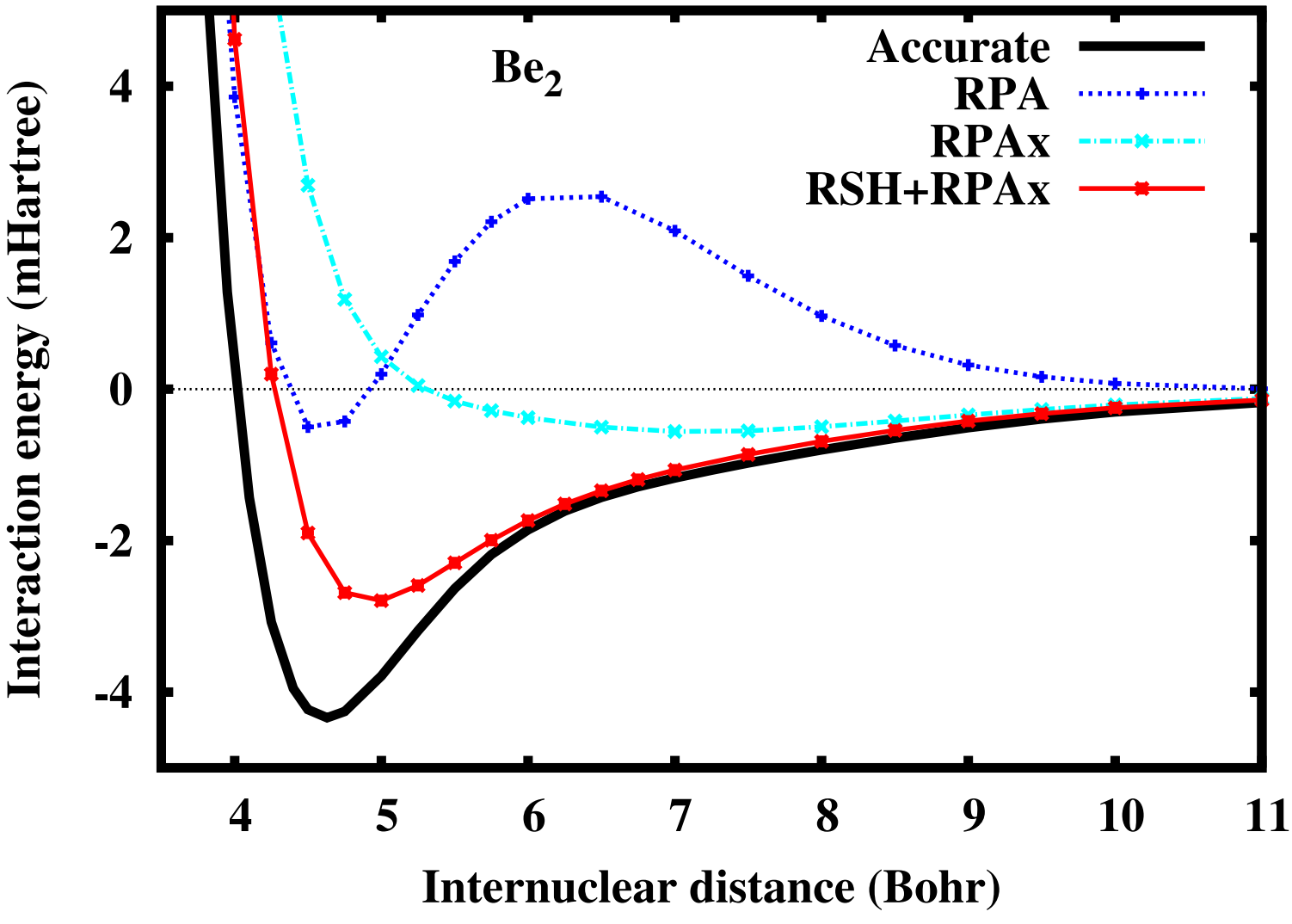


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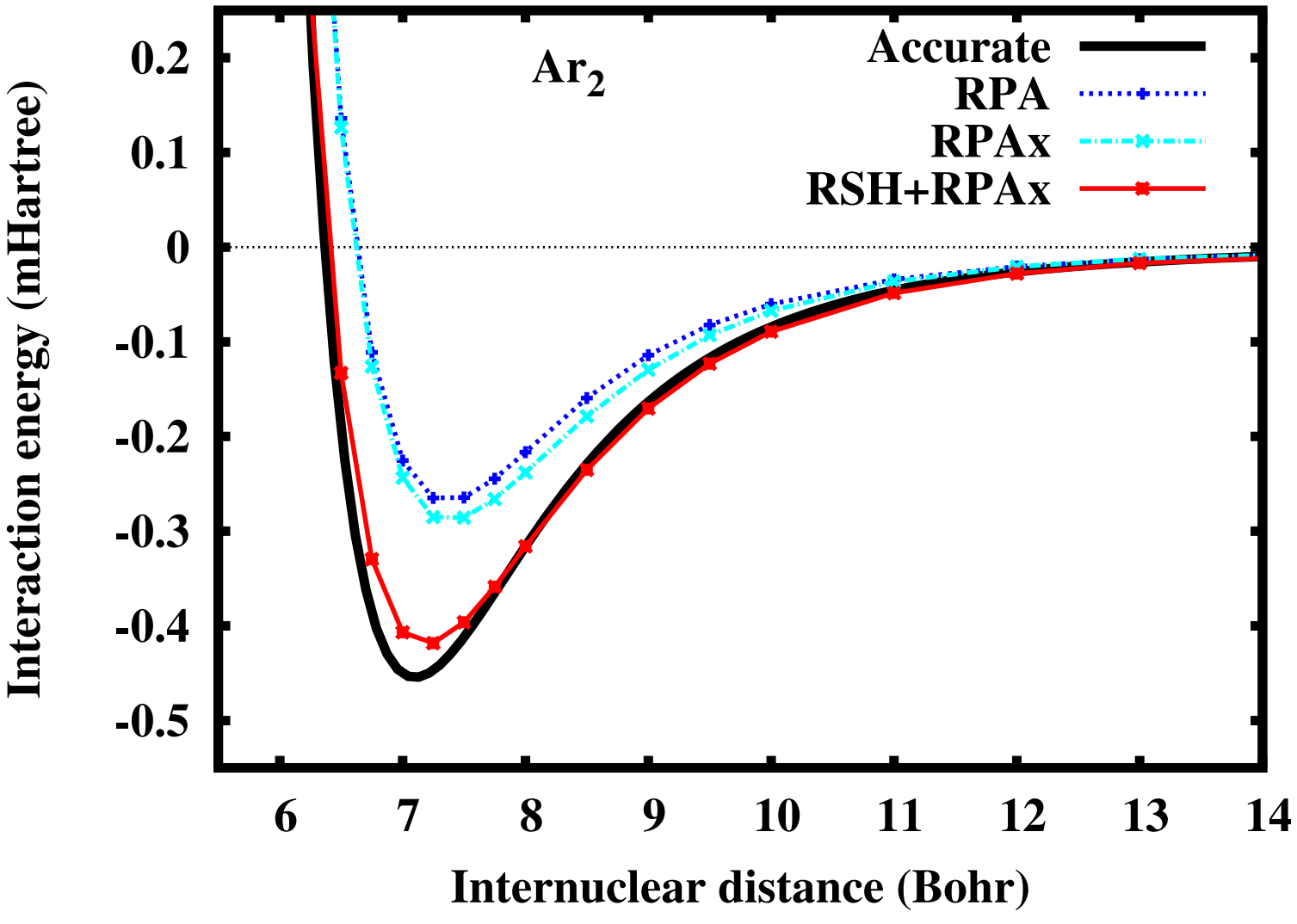


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# Interaction energy curve of $(CH_4)_2$

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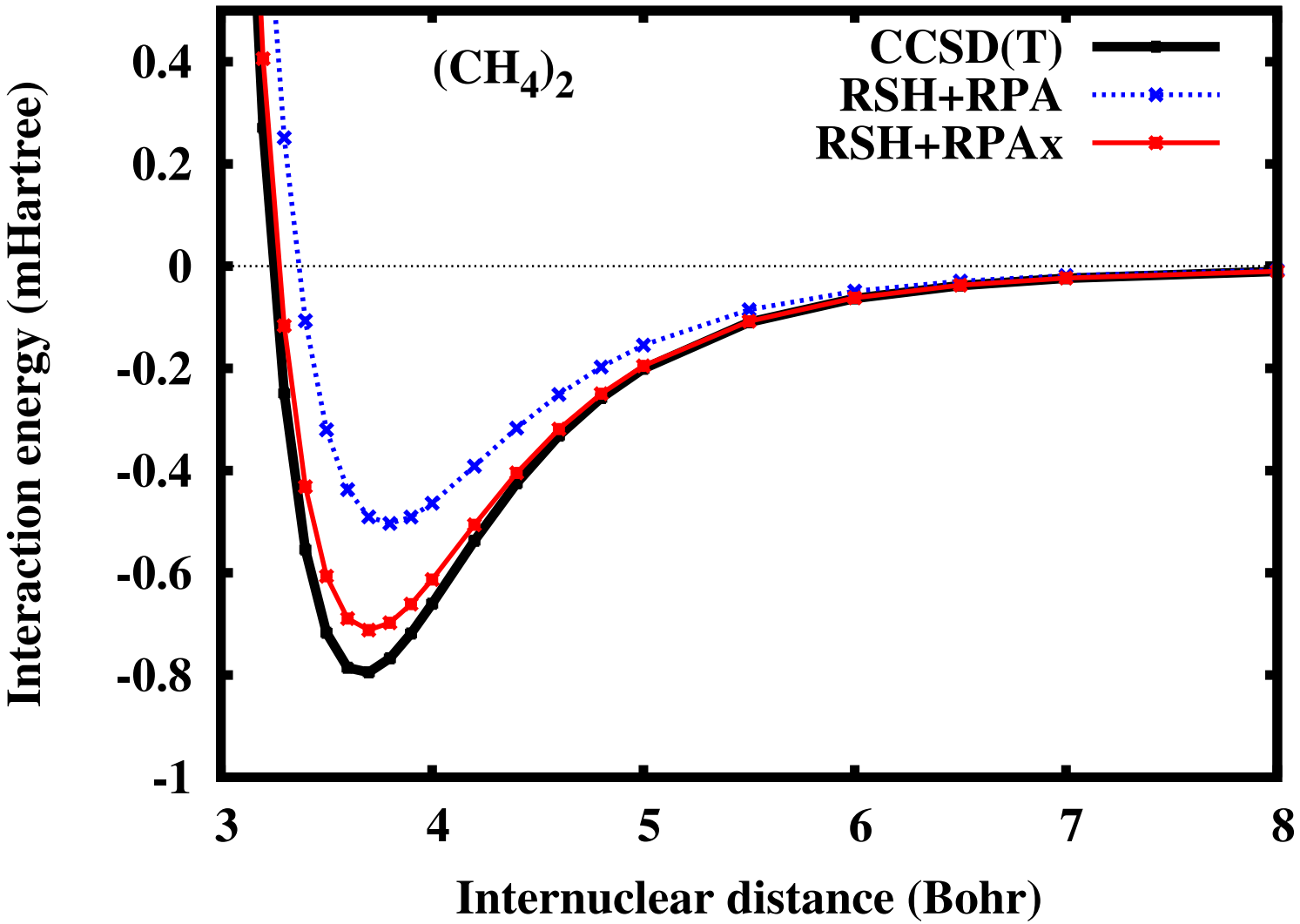
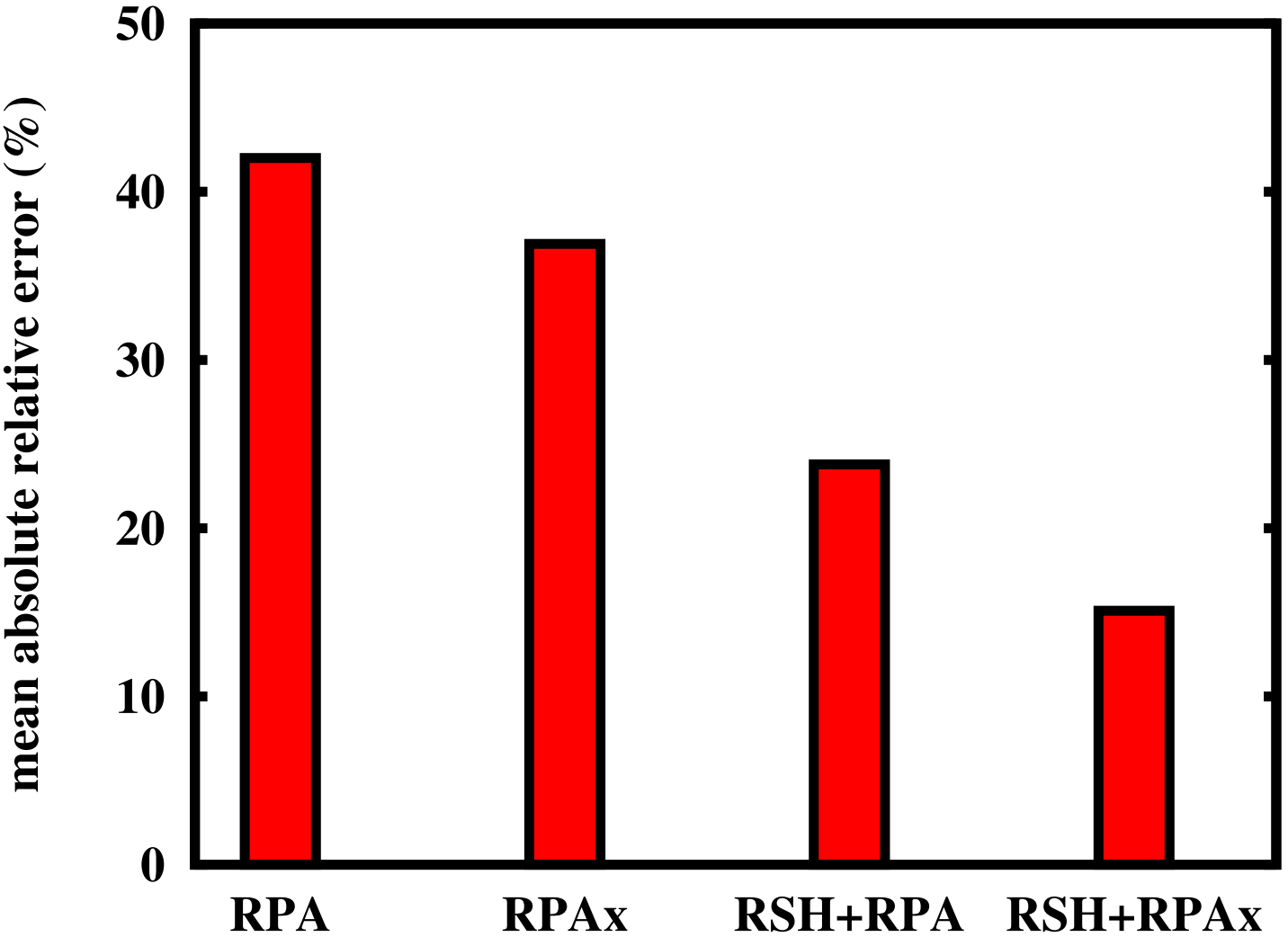



$\Longrightarrow$ **Exact exchange kernel is important**

# Equilibrium interaction energies

of a set of 22 weakly-interacting molecular systems (S22 set) from water dimer to DNA base pairs



# Summary and Conclusions

## Summary

**RSH+RPAx method = short-range DFT + long-range RPAx**

## Conclusions

- 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)

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**Phys. Rev. Lett. 102, 096404 (2009)**

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