Intermolecular Interactions: RPA *et al.*

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Xinguo Ren

Patrick Rinke

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Matthias Scheffler

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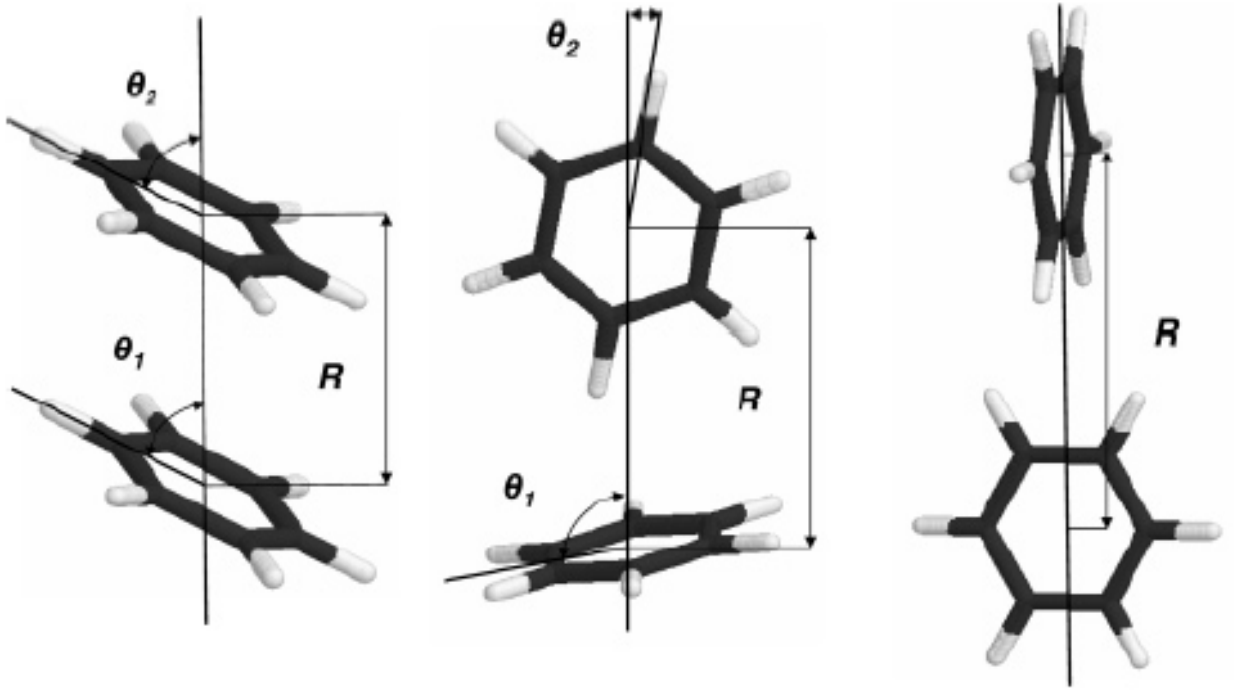
V. Blum et al. ***Comp. Phys. Comm.*** (2009).

Mission: Intermolecular Interactions

Benzene dimer



Podeszwa, Bukowski, Szalewicz, J. Phys. Chem. A (2006)

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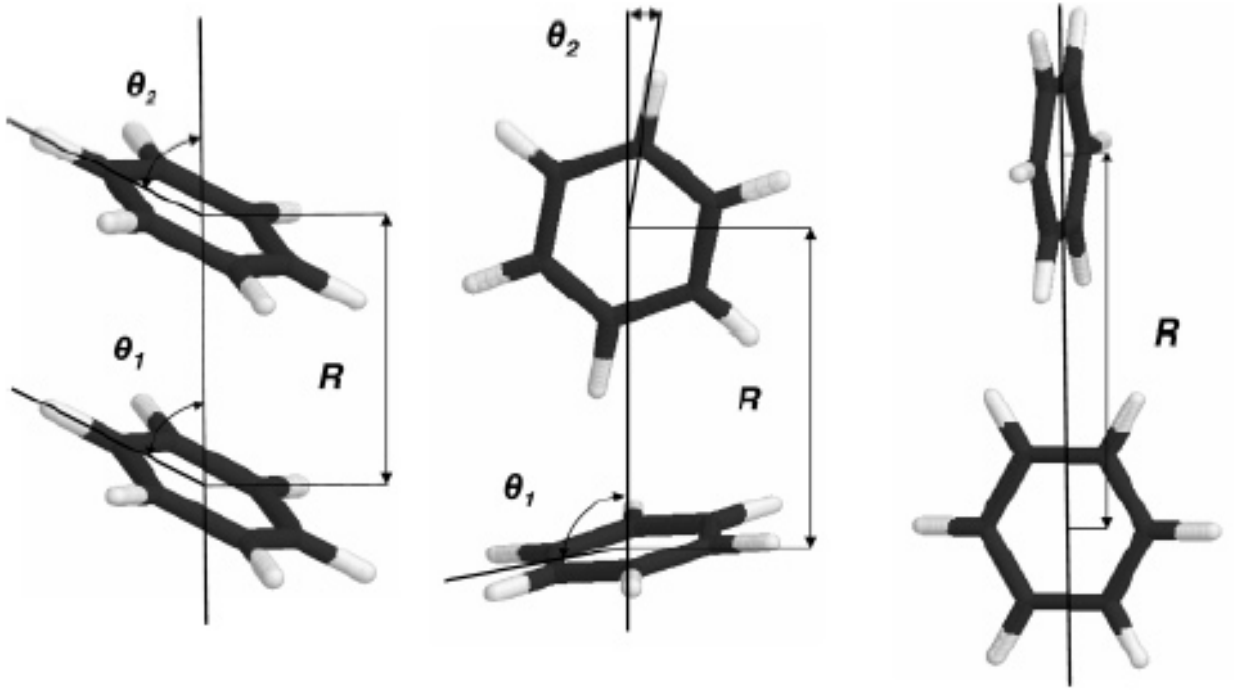

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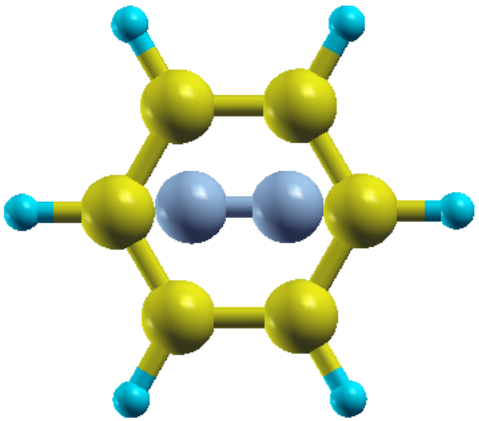
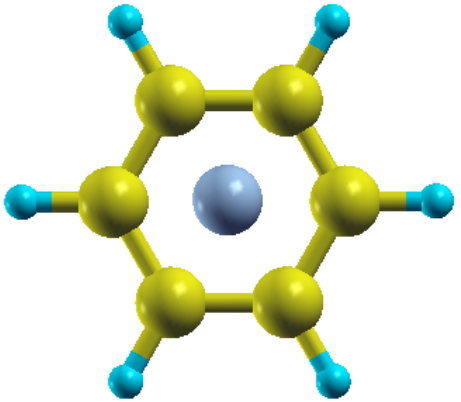
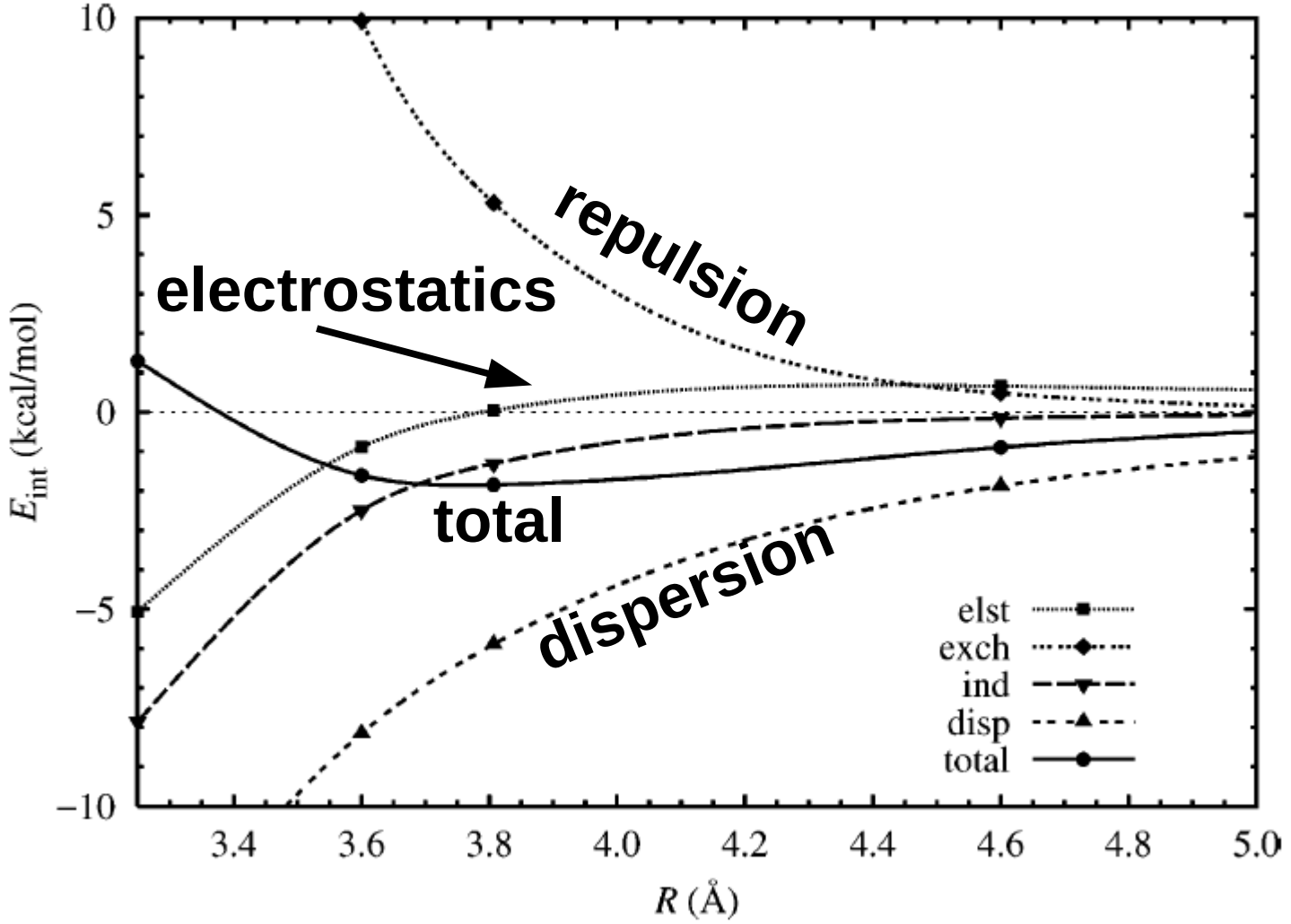


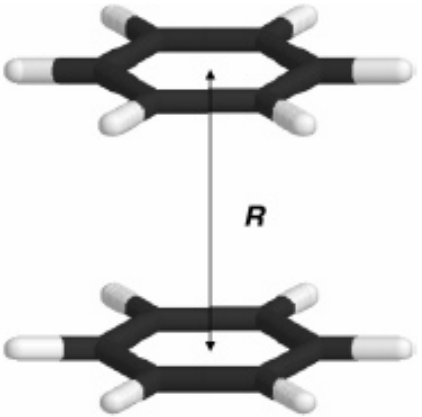
or



Nitrogen – benzene

Intermolecular Interactions: Interplay of *Repulsion*, *Electrostatics*, and *Dispersion*





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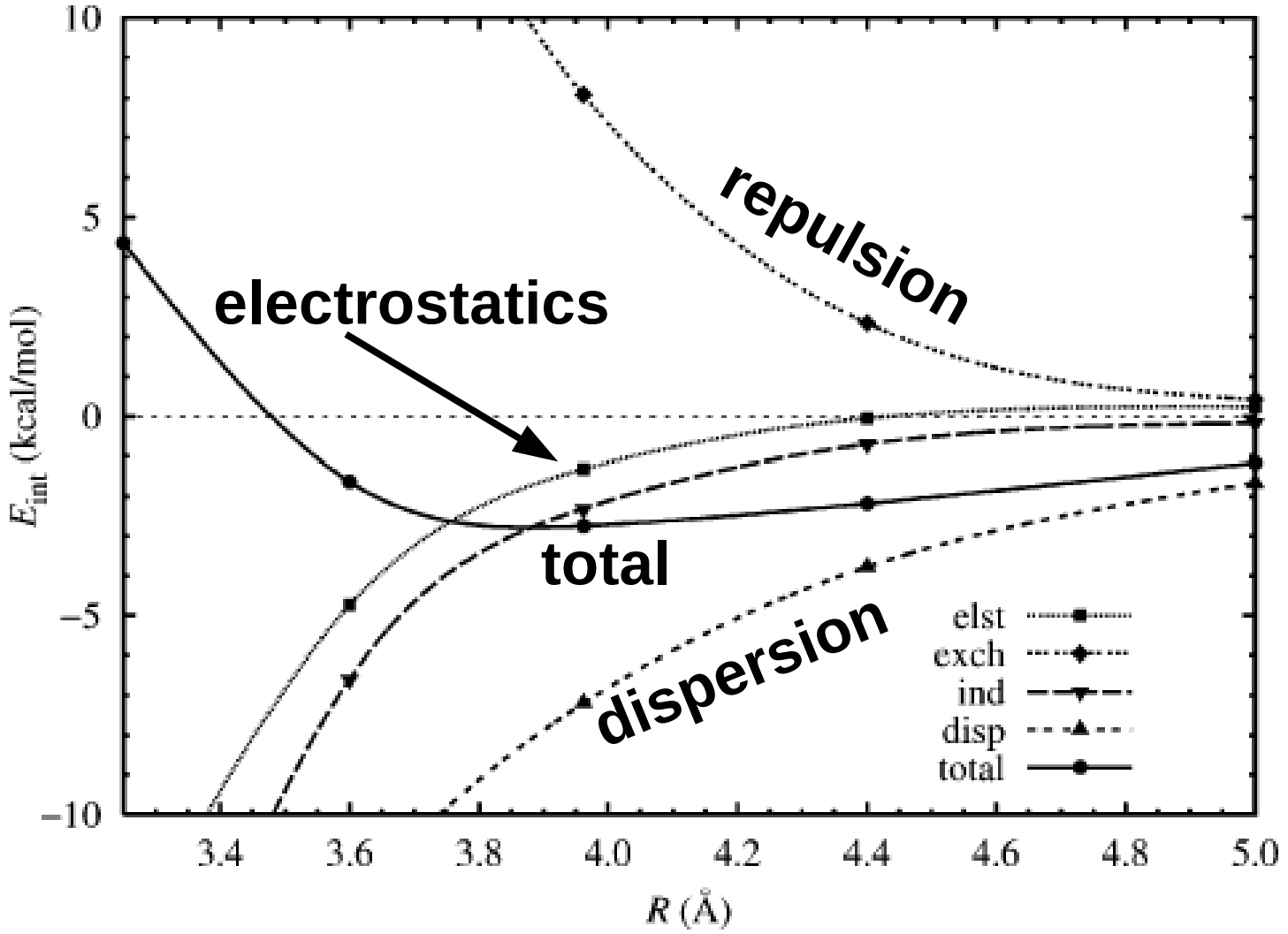

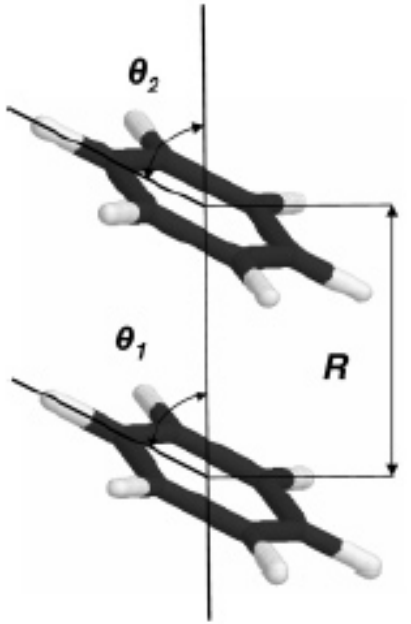

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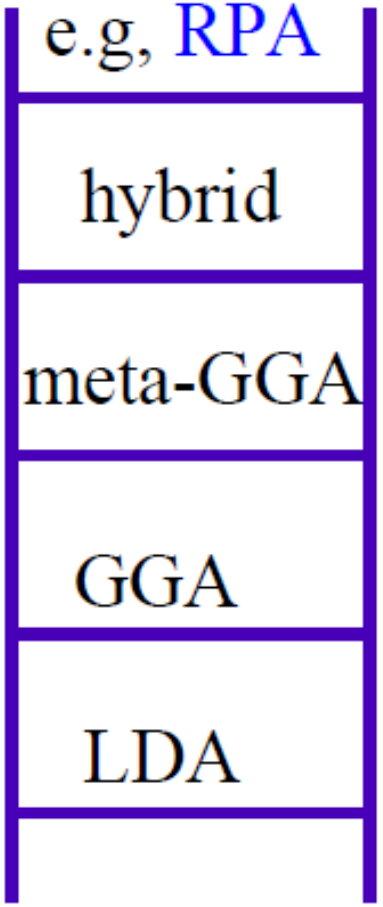
Electronic structure methods

Jacob's ladder



- LDA / GGA / meta-GGA / hybrid

  Very successful, but have several deficiencies:

  - Self-interaction error
  - No long-range dispersion interaction
  - and more …
- Attractive features of RPA
  - Exact exchange greatly reduces self-interaction
  - Dispersion interaction included
  - Electronic screening taken into account

RPA within adiabatic-connection in DFT

Exact exchange-correlation energy from ACFDT:

$$E_{XC} = -\frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' v(\mathbf{r}-\mathbf{r}') \left[\frac{1}{\pi}\int_0^\infty d\omega \chi_\lambda(i\omega) + n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \right]$$

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In practice, RPA calculation performed as post LDA/GGA correction:

$$E_{RPA} = E_{LDA/GGA} - E^{XC}_{LDA/GGA} + E_{EXX} + E^{c}_{RPA}$$

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Exact-exchange using LDA/GGA orbitals:

$$E_{EXX} = -\frac{1}{2}\sum_\sigma \sum_{i,j}^{occ} \int d\mathbf{r} \int d\mathbf{r}' \frac{\psi^*_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r})\psi^*_{j\sigma}(\mathbf{r}')\psi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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RPA correlation energy within ACFDT:

$$E^{c}_{RPA} = \frac{1}{2\pi}\int_0^\infty d\omega \, Tr\left[\ln(1-\chi_0(i\omega)v) + \chi_0(i\omega)v \right]$$

RPA: Exchange and correlation

- In principle, both exchange and correlation have to be calculated self-consistently, but this is too computationally expensive.
- Exchange:
  - Different input orbitals can lead to different results
  - Self-consistency could matter and feasible
- Correlation:
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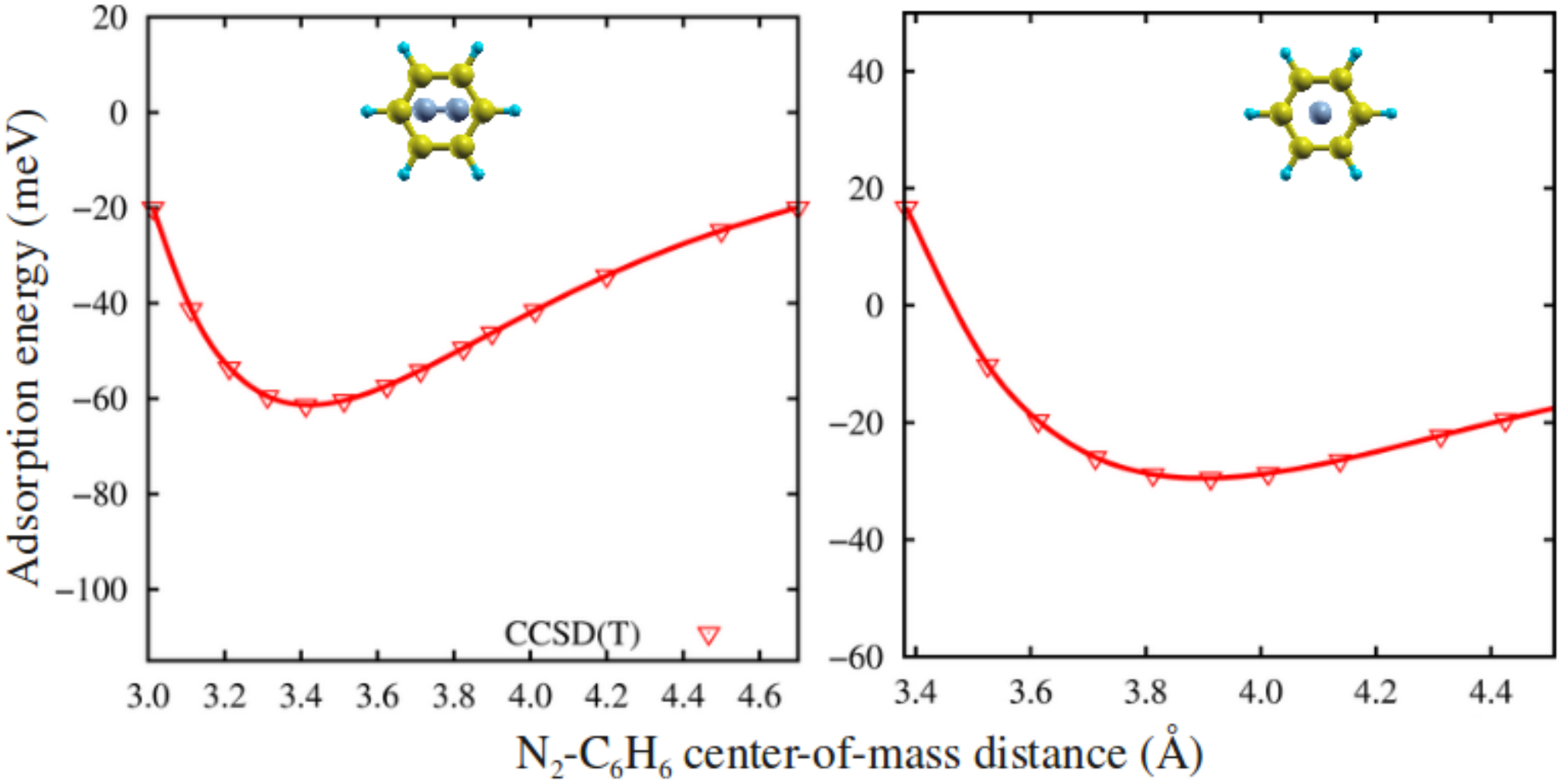
What is usually done: Compute DFT wavefunction. Then calculate EX and RPA correlation *in one shot.*

N_2–benzene: Challenging test case



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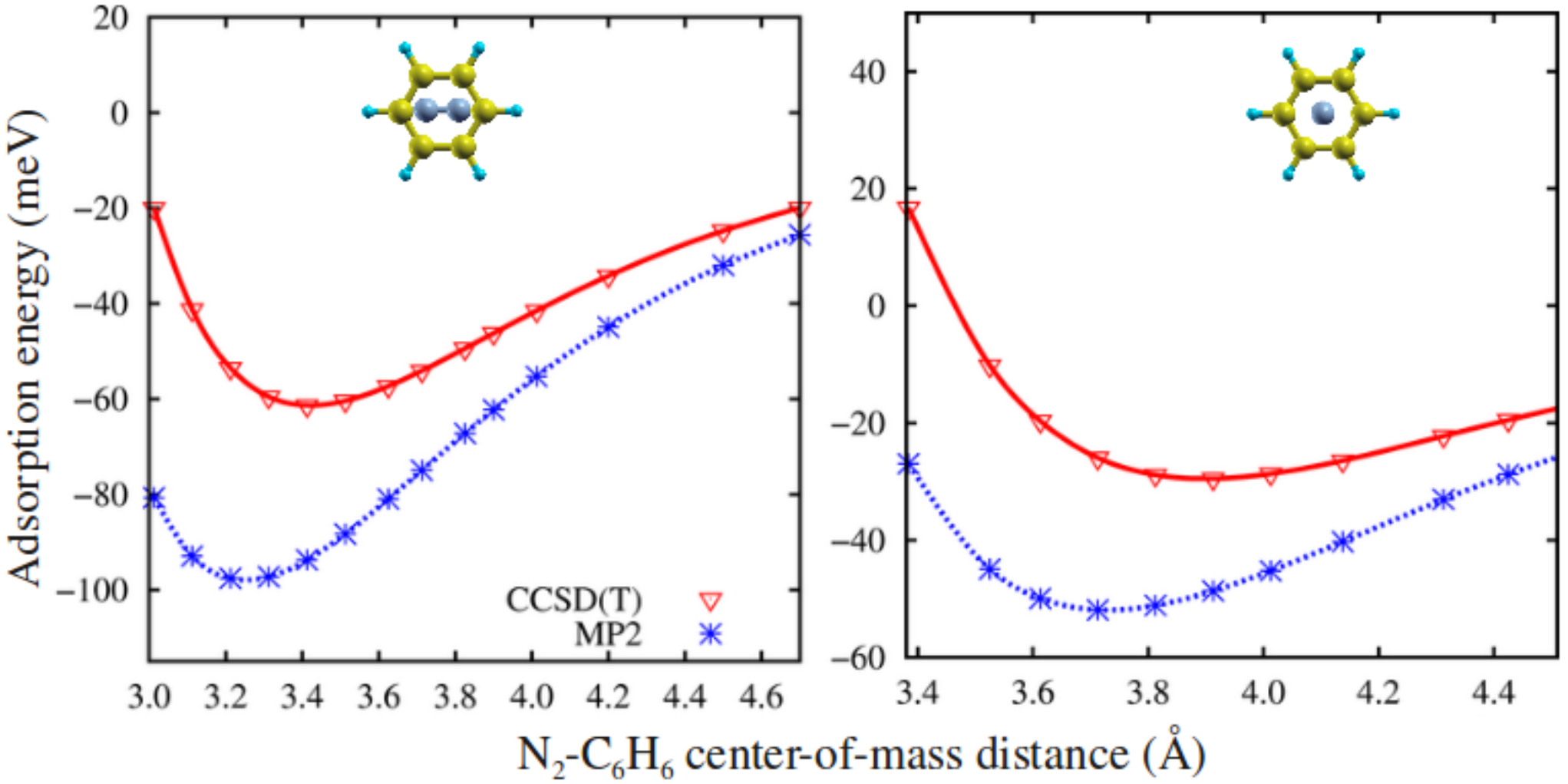

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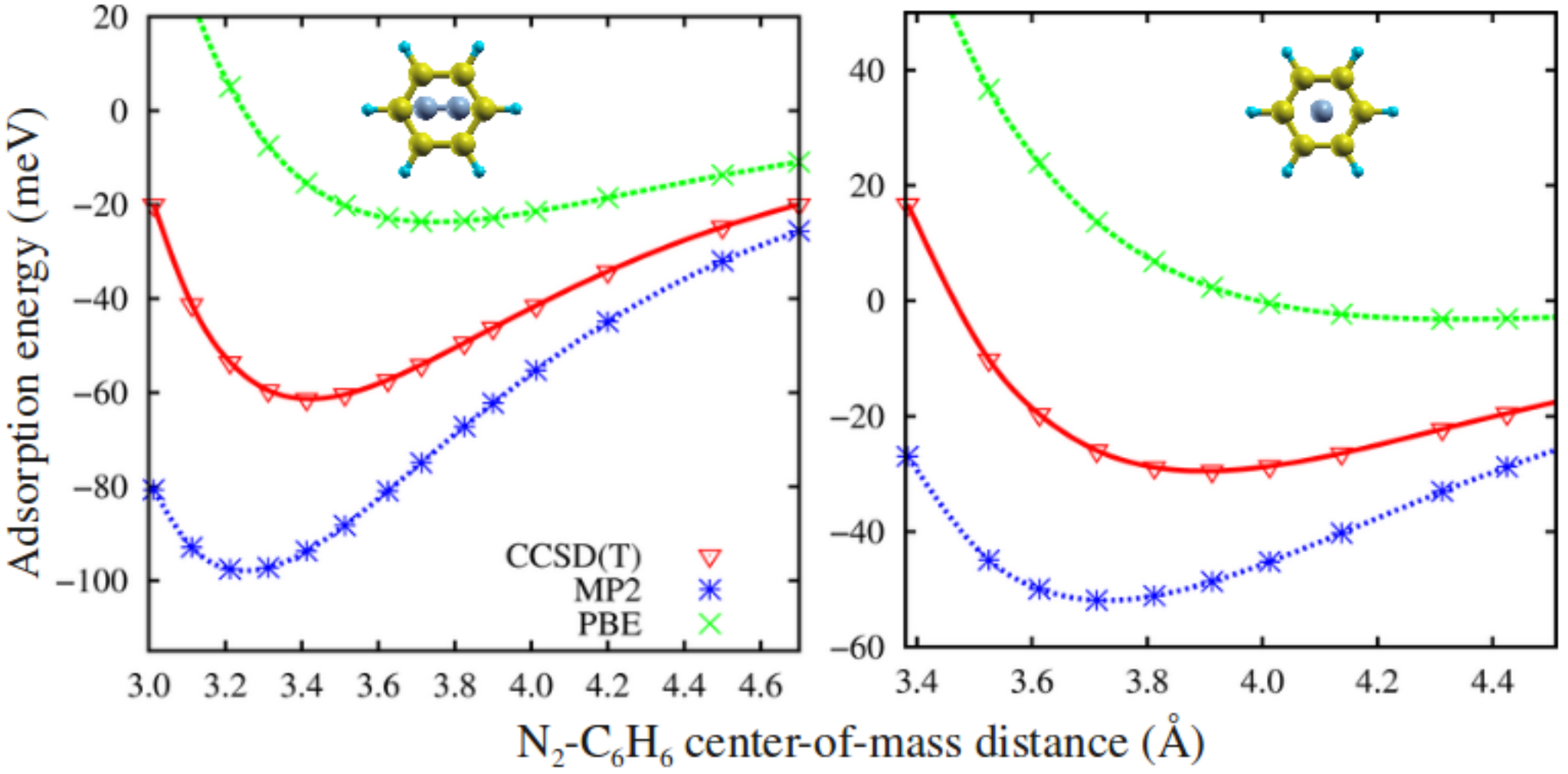

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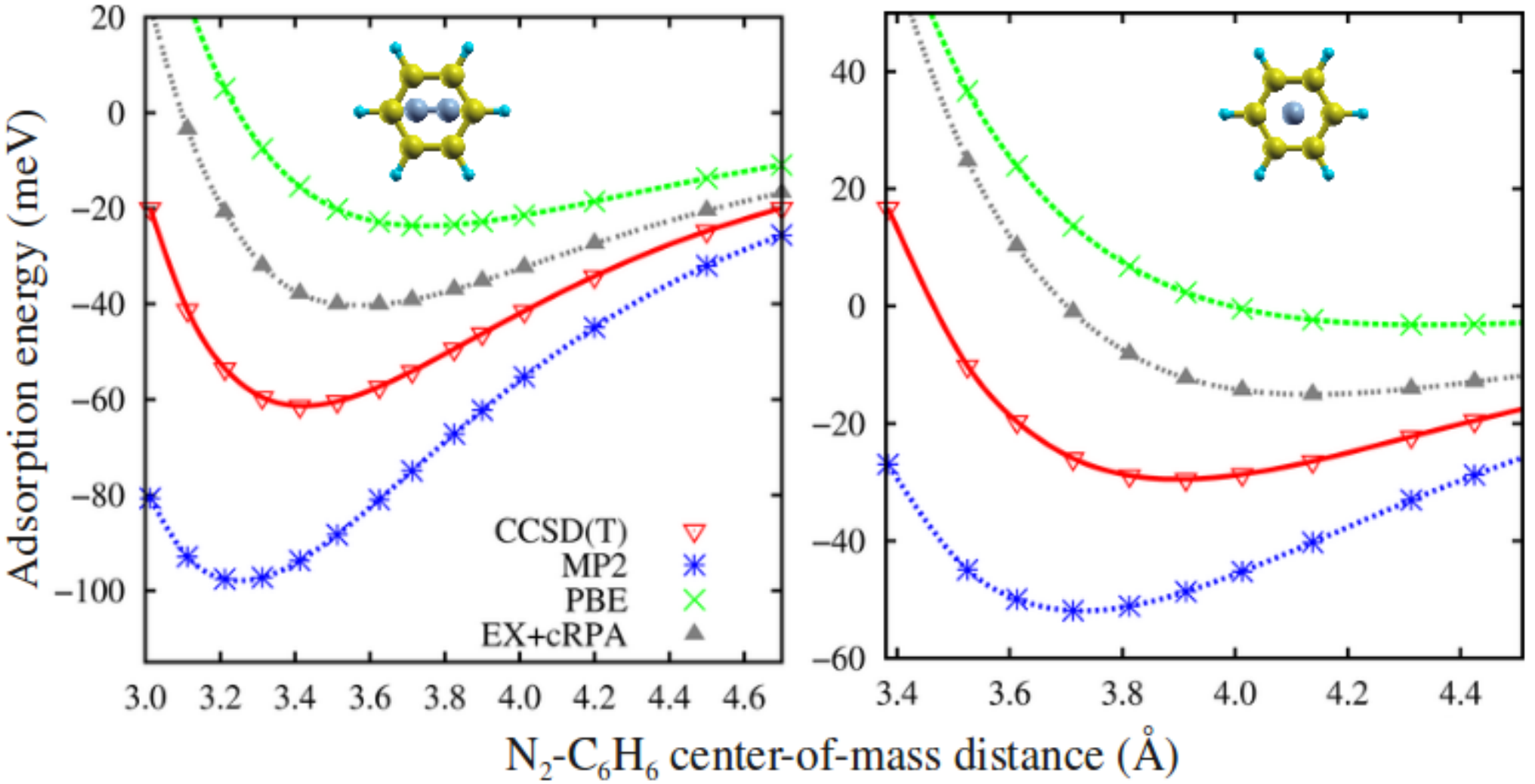

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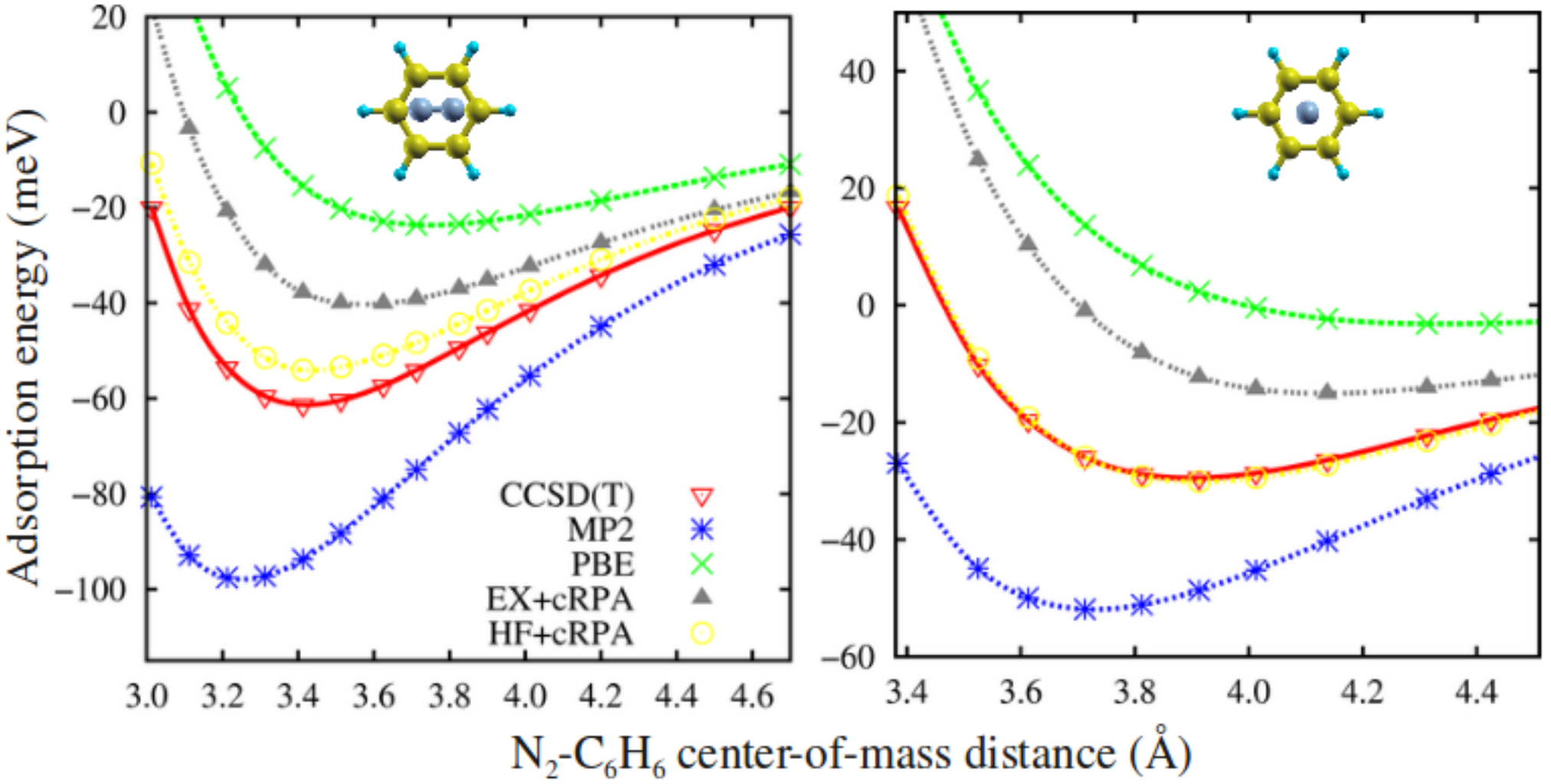

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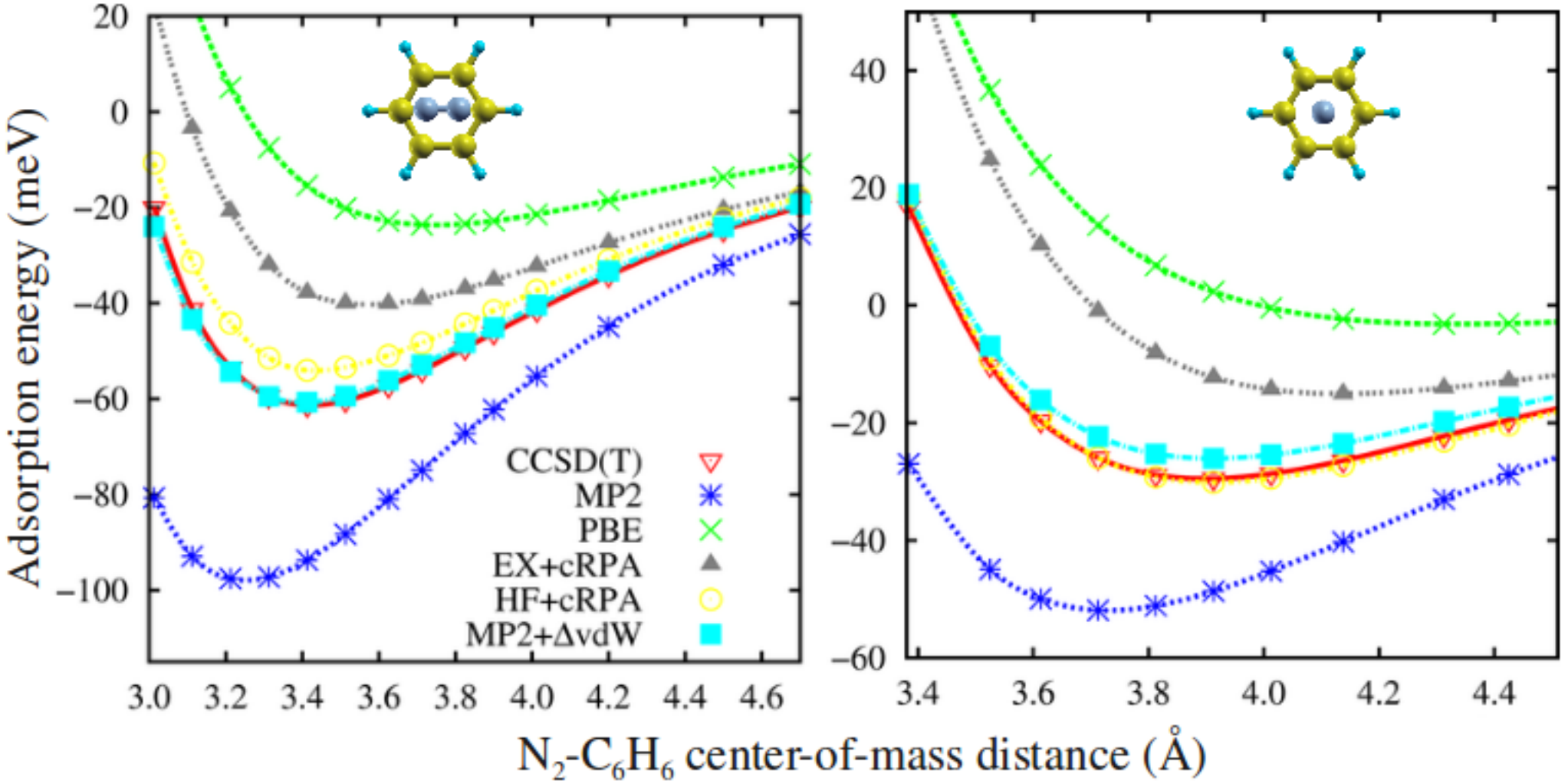
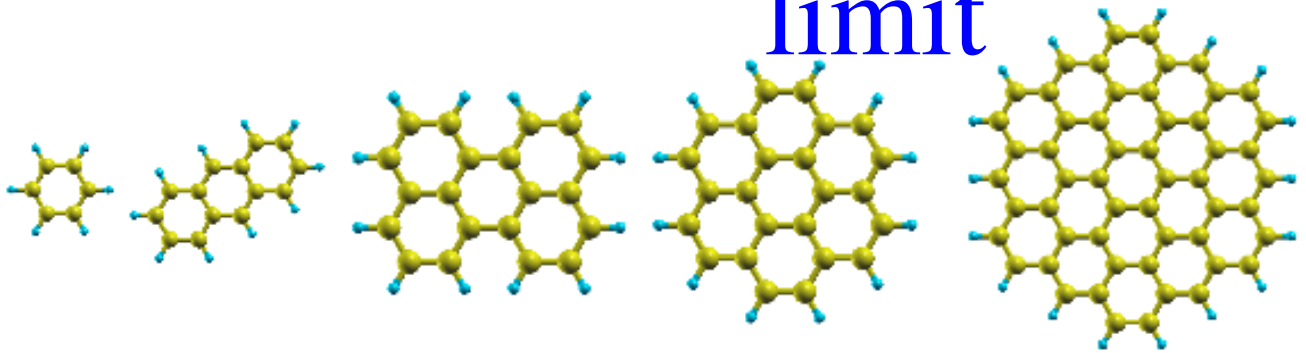
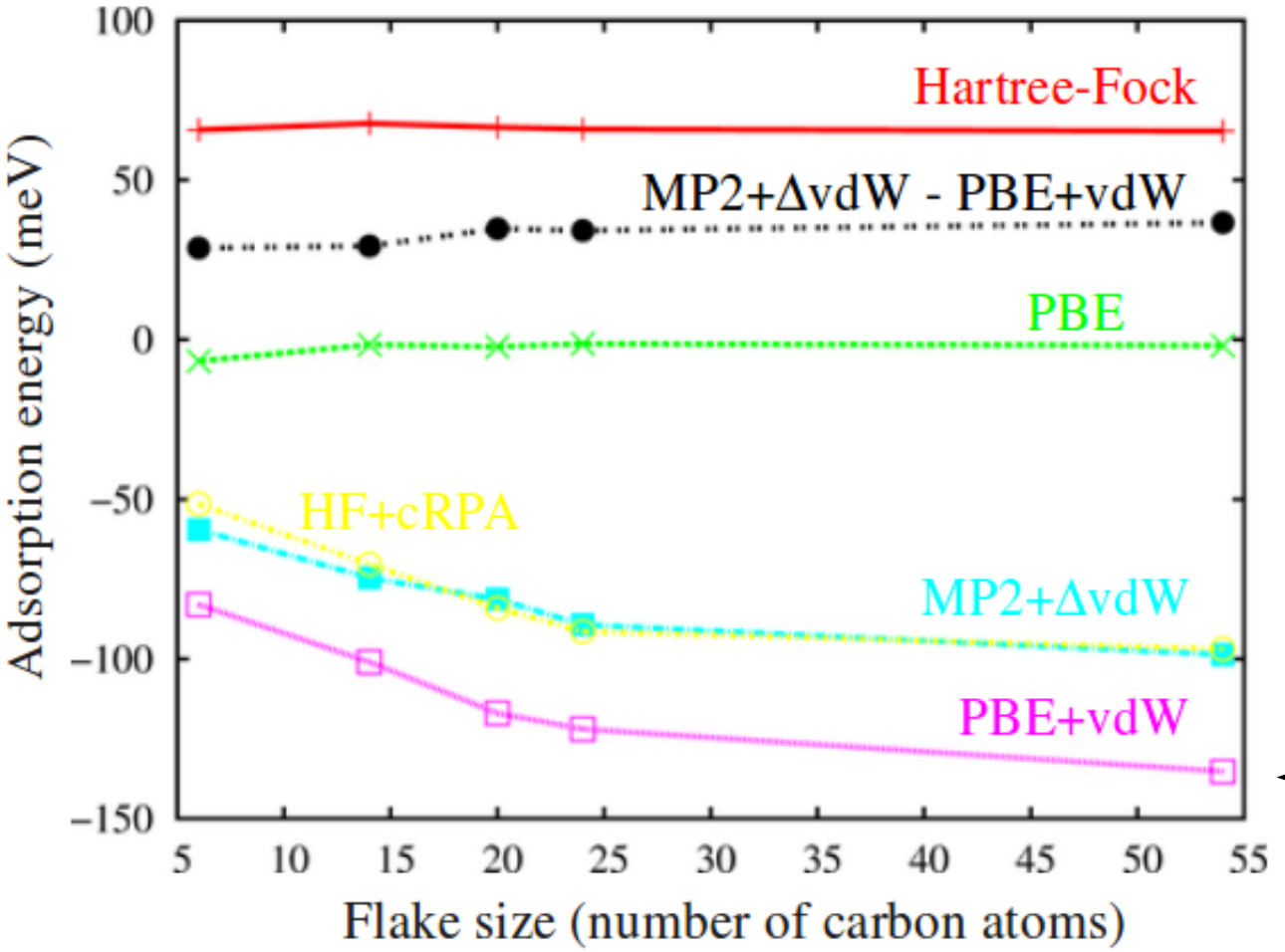


MP2+ΔvdW: *Tkatchenko, DiStasio Jr., Head-Gordon, Scheffler*, ***JCP*** (2009).

N_2@graphene: Reaching the periodic limit





Lying down (parallel) configuration

143 meV = PBE+vdW periodic limit

Hu, Reuter, Scheffler ***PRL*** 98, 176103 (2007)

N_2@graphite: Comparison with experimental desorption enthalpy

Experimental $\mathbf{N_2}$ H_{des} (extrap. to zero coverage) : 100 – 108 meV[(1)]

MP2+ΔvdW (HF+cRPA): 105 meV – 8 meV ZPE

+ 10 meV (graphite) : 107 meV

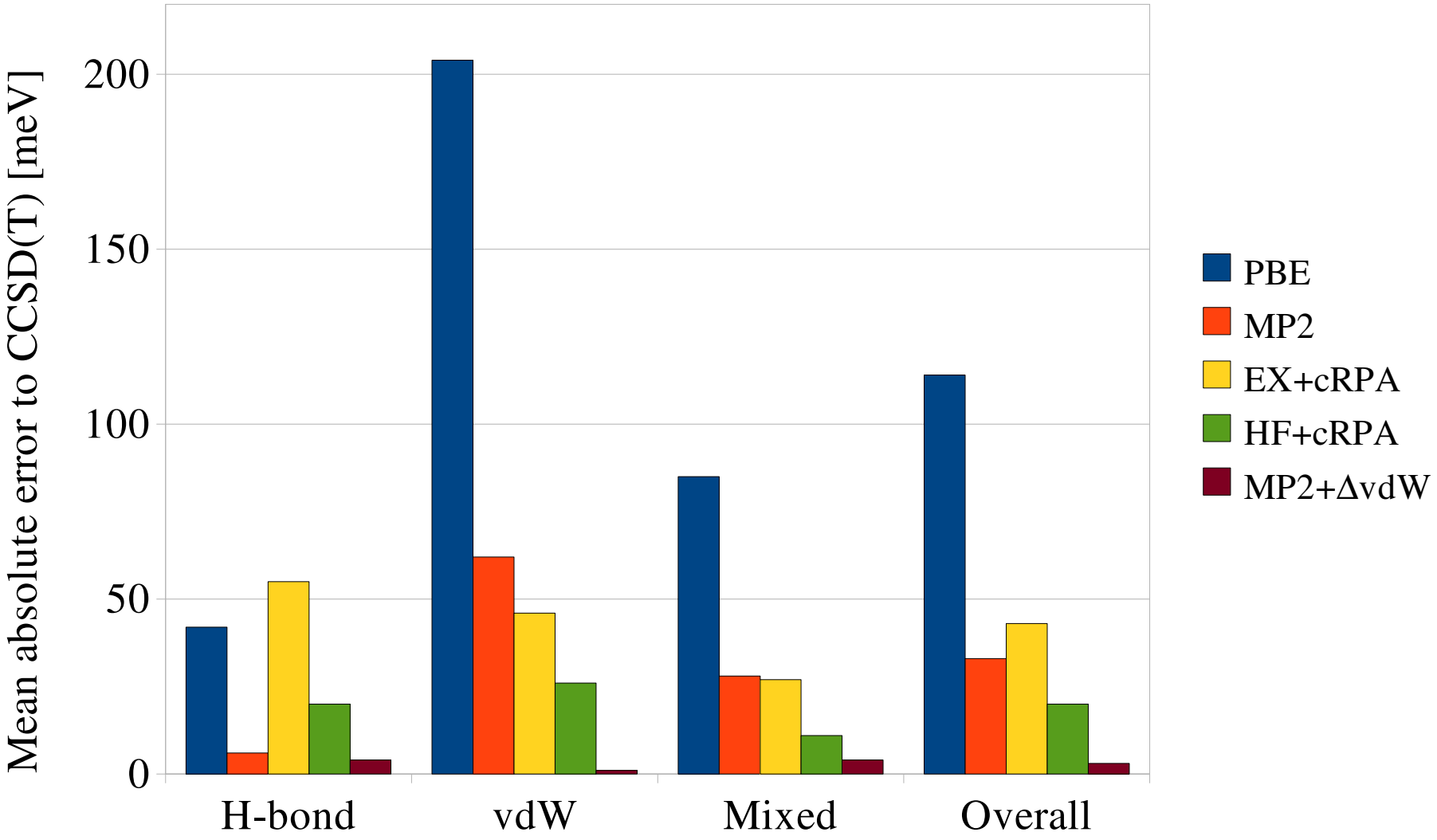
PBE+vdW: 143 meV – 8 meV ZPE

+ 10 meV (graphite) : 145 meV

MP2+ΔvdW, HF+cRPA and PBE+vdW predict the binding distance as 3.3 Å

[(1)] *Grillet et al.* ***J. Phys. (Paris) Colloq.*** (1977); *Bojan, Steele,* ***Langmuir*** (1987); *Piper et al.* ***J. Chem. Soc Faraday Trans.*** (1983).

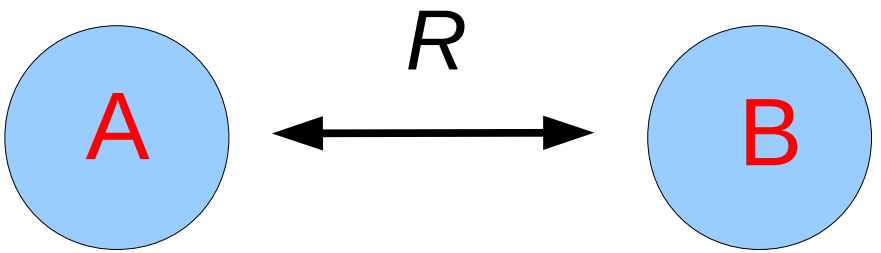
Method performance for intermolecular interactions: S22 database



S22: *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006).

How good RPA is for long-range dispersion ?

Dispersion energy asymptotics



No orbital overlap (large enough ***R***):

$$E_{\mathrm{A-B}}(R) = -\left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \ldots\right)$$

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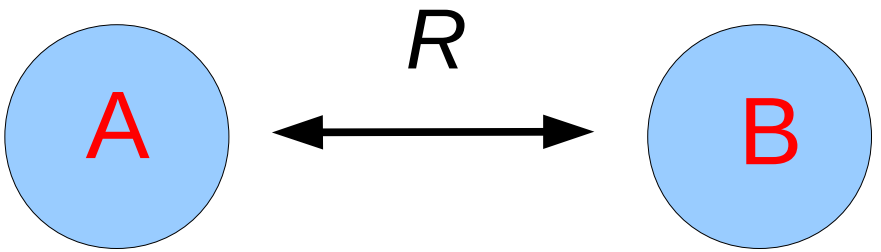

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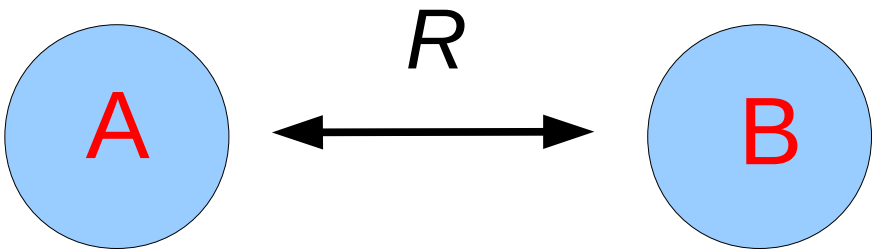

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$$C_{6AB} = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)d\omega$$

Accurate experimental C_6 database for comparison with theory

$$S(k) = \int_{E_0}^{\infty} E^k \left(\frac{df}{dE} \right) dE$$

Differential dipole oscillator strength (DOS)

Transition energy (ground state--excited state)

[1] *W. J. Meath and co-workers (1977-present)*

Accurate experimental C_6 database for comparison with theory

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Experimental data (DOSD)

$$S(k) = \sum_{i=1}^{n} \epsilon_i^k f_i, \quad k = 0, -1, \ldots, -2n+1$$

Theory (pseudo-DOSD)

$$C_{6AB} = \frac{3}{2} \sum_{i,j} \frac{f_i^A f_j^B}{\epsilon_i^A \epsilon_j^B (\epsilon_i^A + \epsilon_j^B)}$$

Using different sets of exp. *S(k)* data, C_{6AB} is typically accurate to 1-2%

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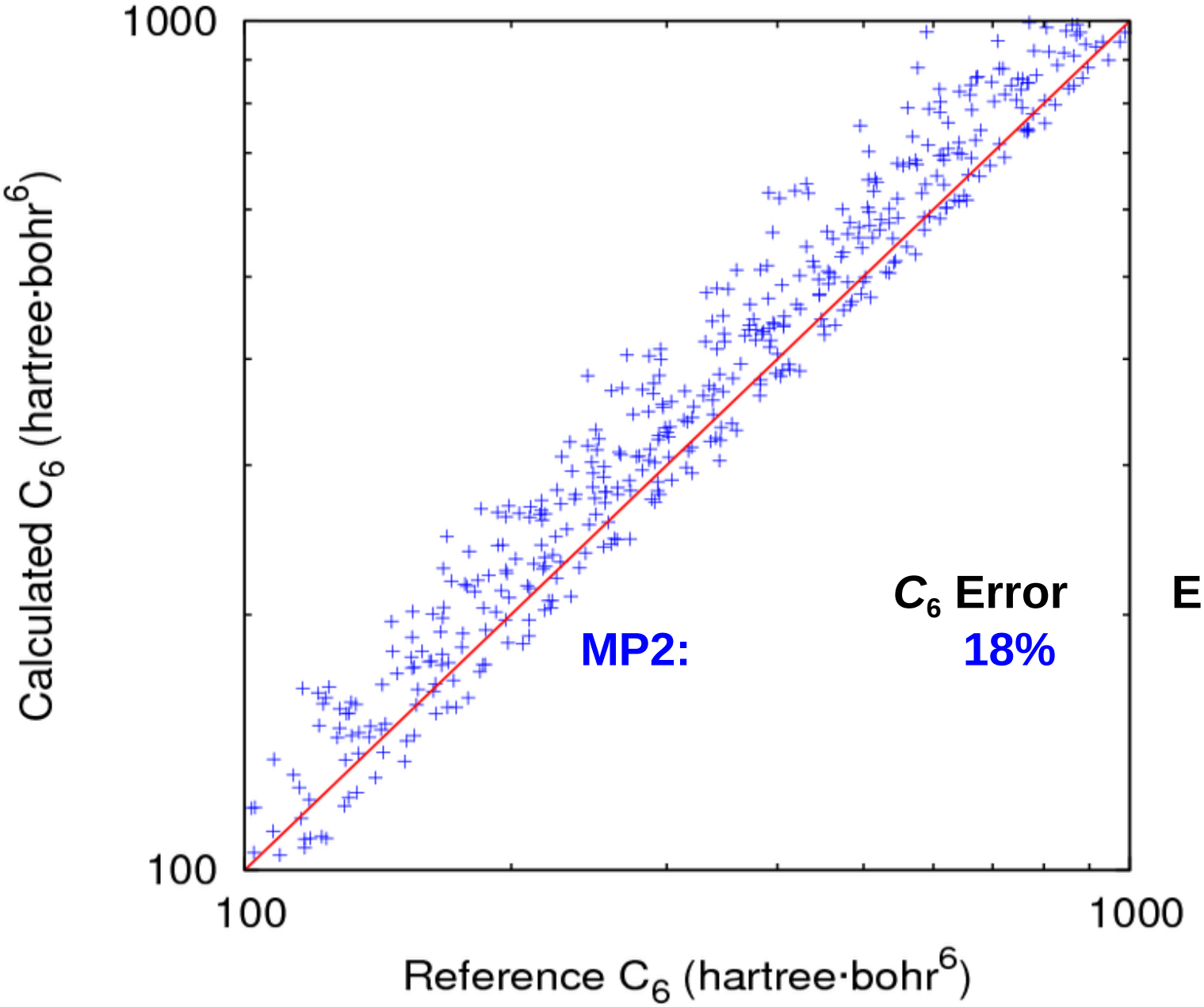
Data obtained for atoms, alkanes, alkenes, alkynes, alcohols, H_2, N_2, H_2S, NH_3, SO_2, COS, CO_2, CS_2, SiH_4, CCl_4, etc.
(50 atoms and molecules – 1225 interaction pairs)

Tkatchenko and Scheffler, ***PRL*** (2009).

C_6 coefficients: Performance of different theories



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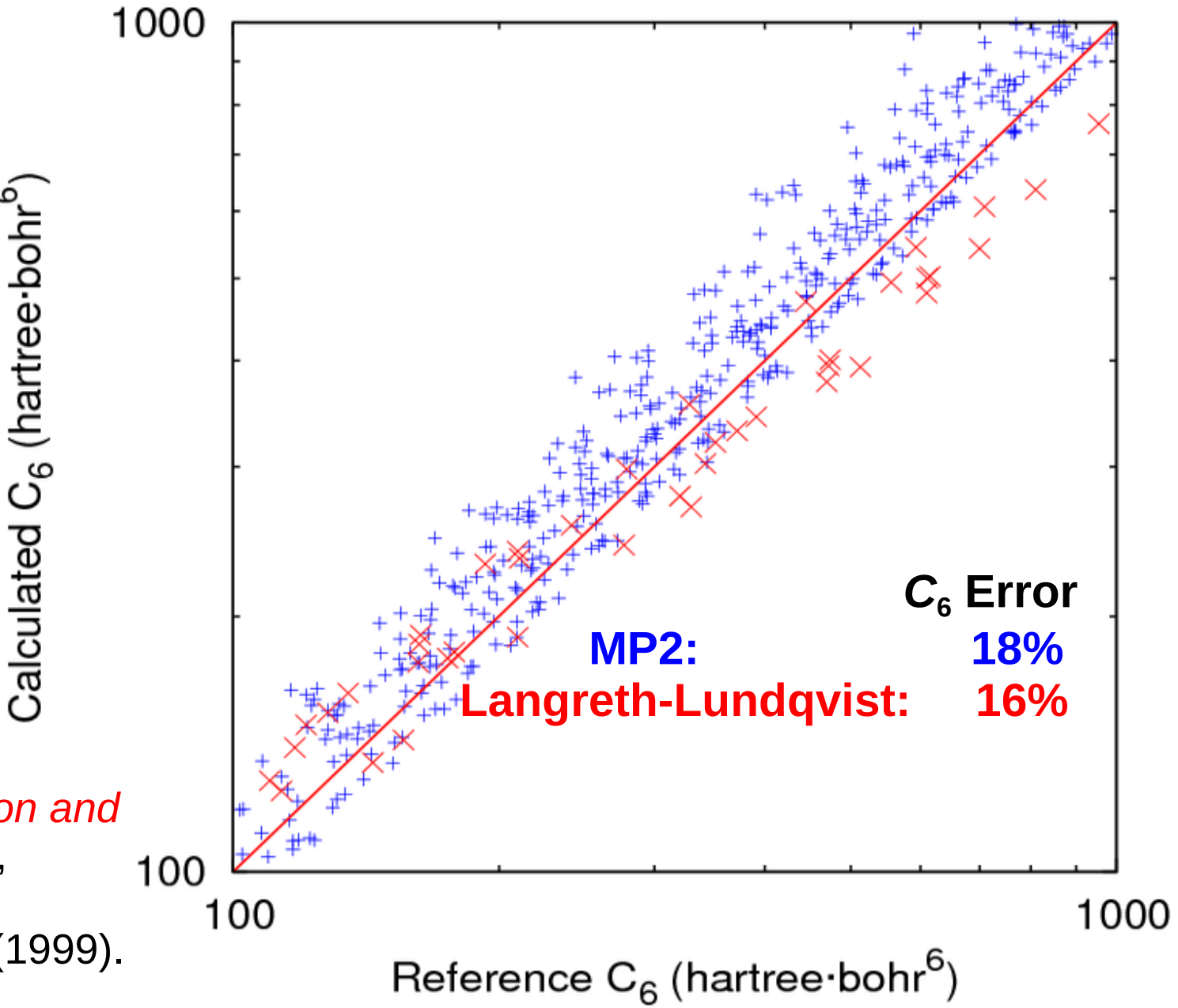

	C_6 Error	Energy Error
MP2:	18%	~ 36%
Langreth-Lundqvist:	16%	~ 32%

LL: *Andersson and Rydberg*, ***Physica Scripta*** (1999).

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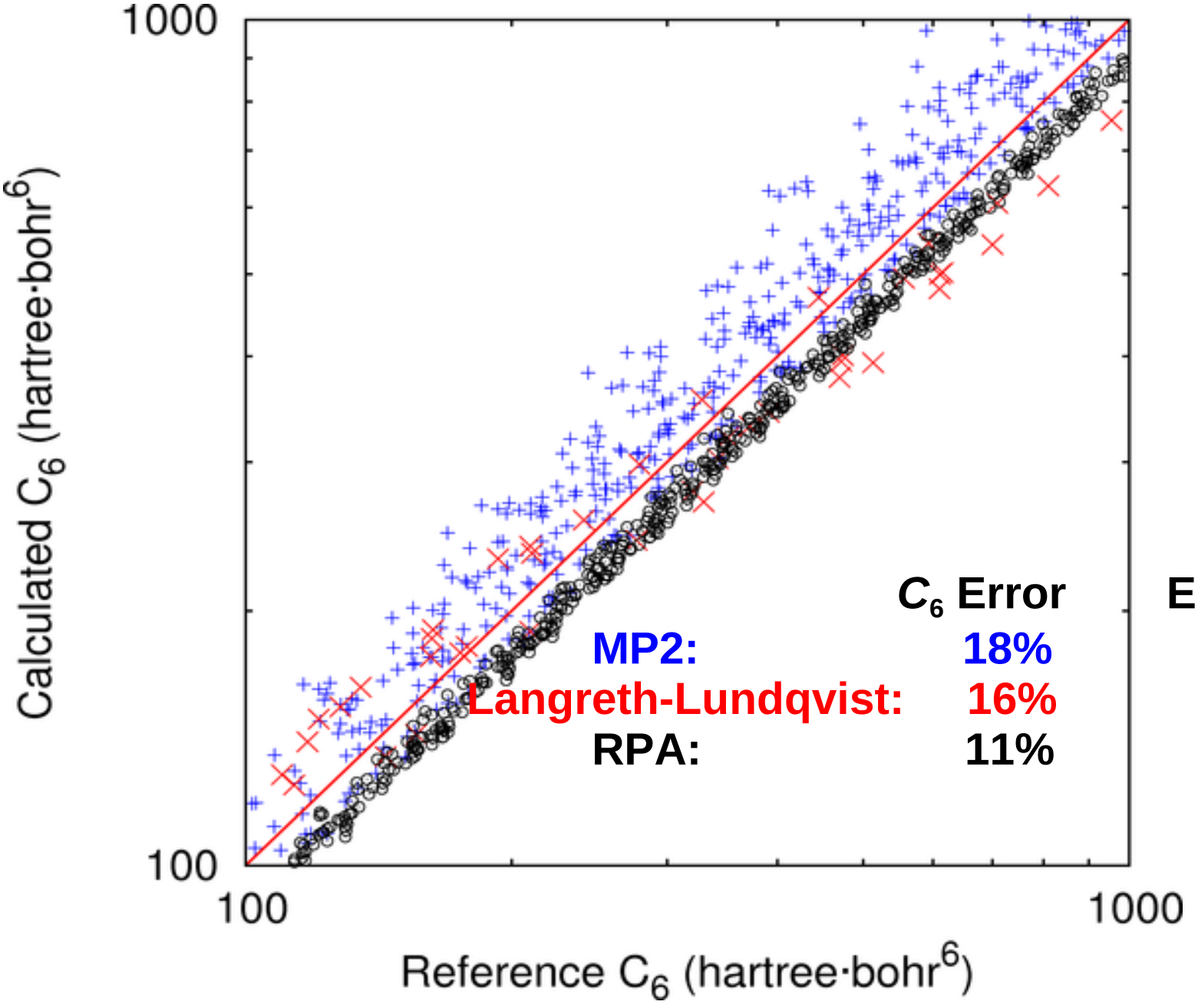

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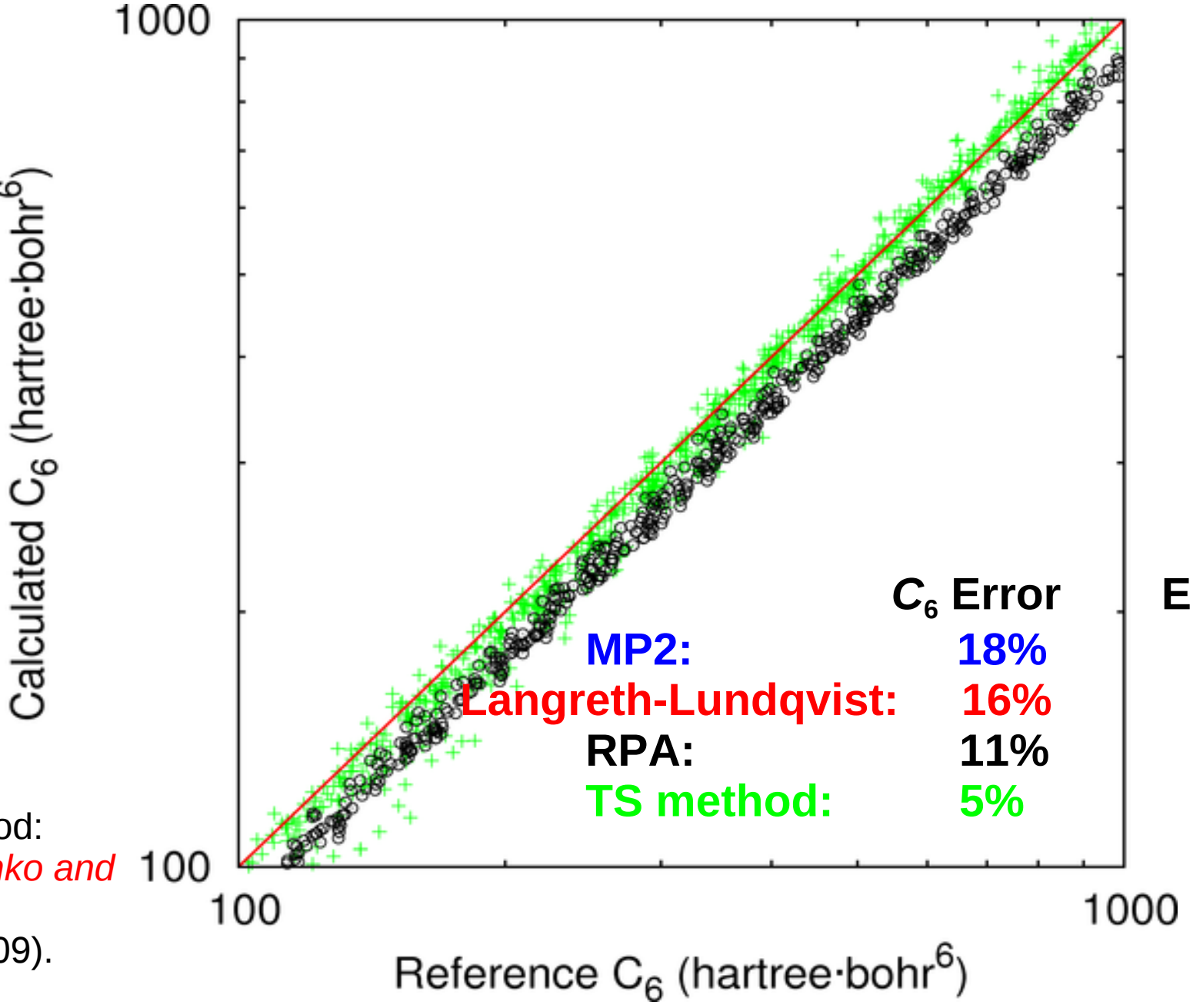

	C_6 Error	Energy Error
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RPA:	11%	~ 22%
TS method:	5%	~ 10%

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Tkatchenko and Scheffler
PRL (2009).

Take-home messages

- Intermolecular interactions: Hard nut to crack. Only CCSD(T) and beyond yield consistently accurate results.
- Understanding is emerging about shortcomings of different methods (DFT, MP2, RPA, …)
- RPA is very promising, but HF exchange has to be used for accurate electrostatics.
- Asymptotic dispersion interaction is underestimated in RPA, but is highly consistent !

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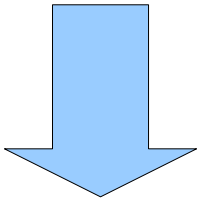

Bright future for Us and RPA ! (and some work still left ...)