Accurate van der Waals interactions from ground-state electron density

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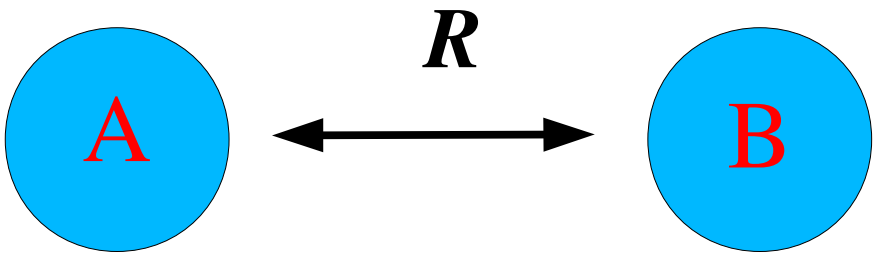
EXCITCM09, Nov 2, 2009

Back to Basics



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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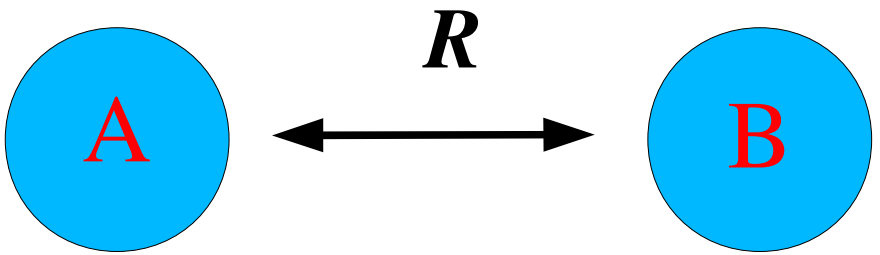

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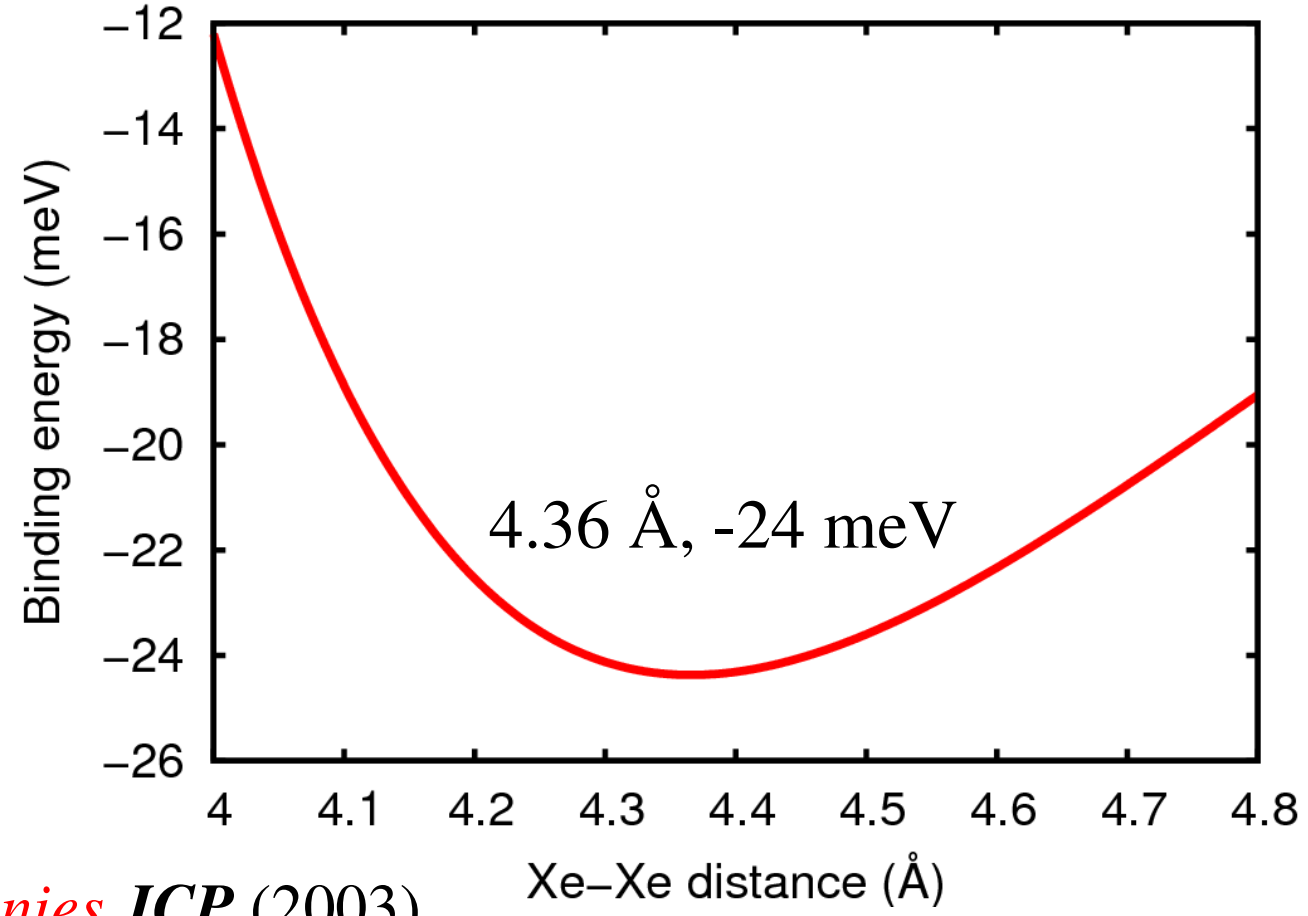
$$E_{\mathrm{A-B}}(R) = -\left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \ldots\right)$$

20% error in C_n coefficients leads to 20% error in binding energy

Role of vdW asymptotics **at equilibrium distance**

$$E_{\mathrm{Xe-Xe}}(R) = E_{\mathrm{Hartree-Fock}}(R) - \left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

Xe-Xe



Tang and Toennies ***JCP*** (2003)

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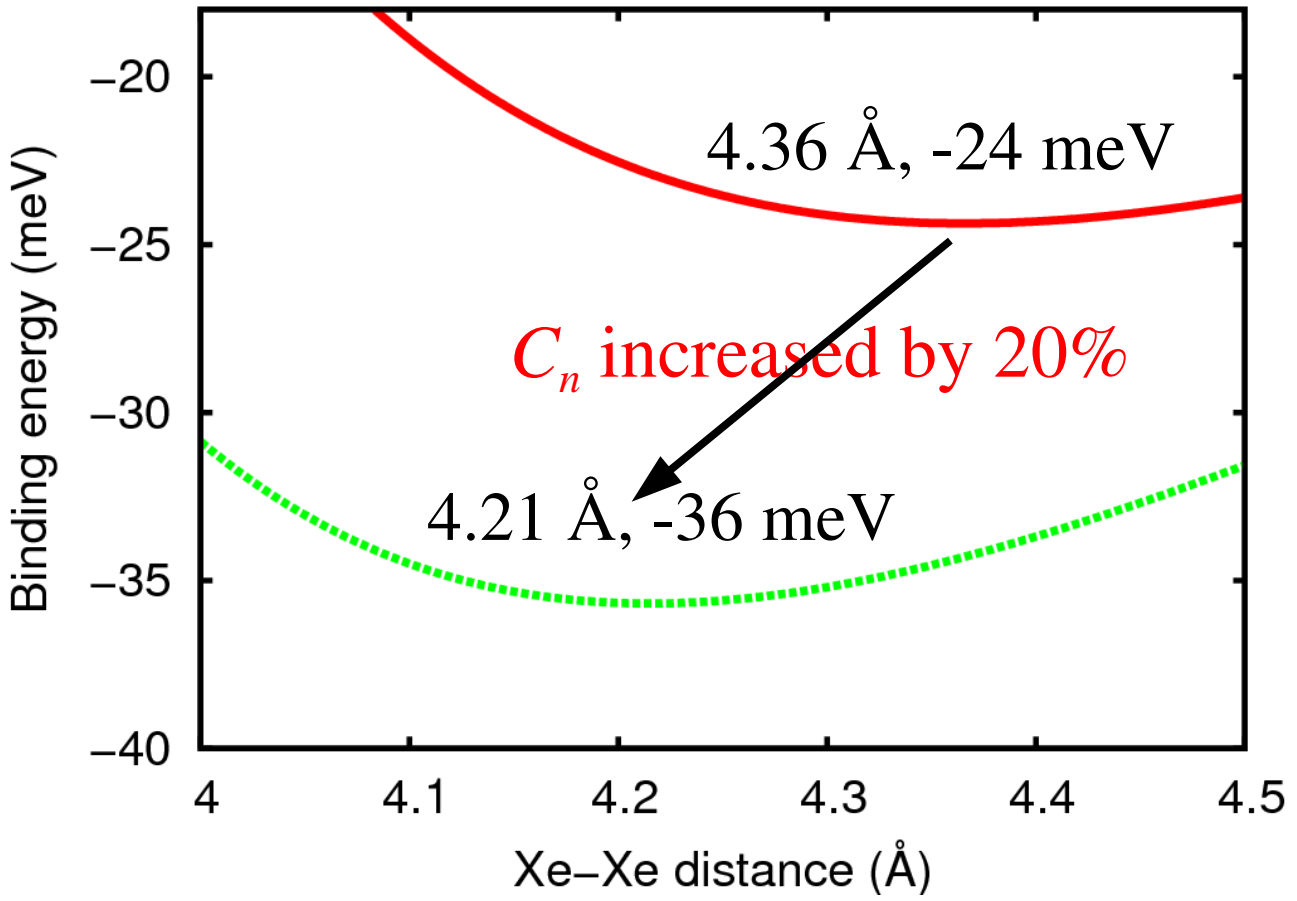

Asymptotics **do** matter: RG dimers

~ 60% ~ 30% ~ 10%

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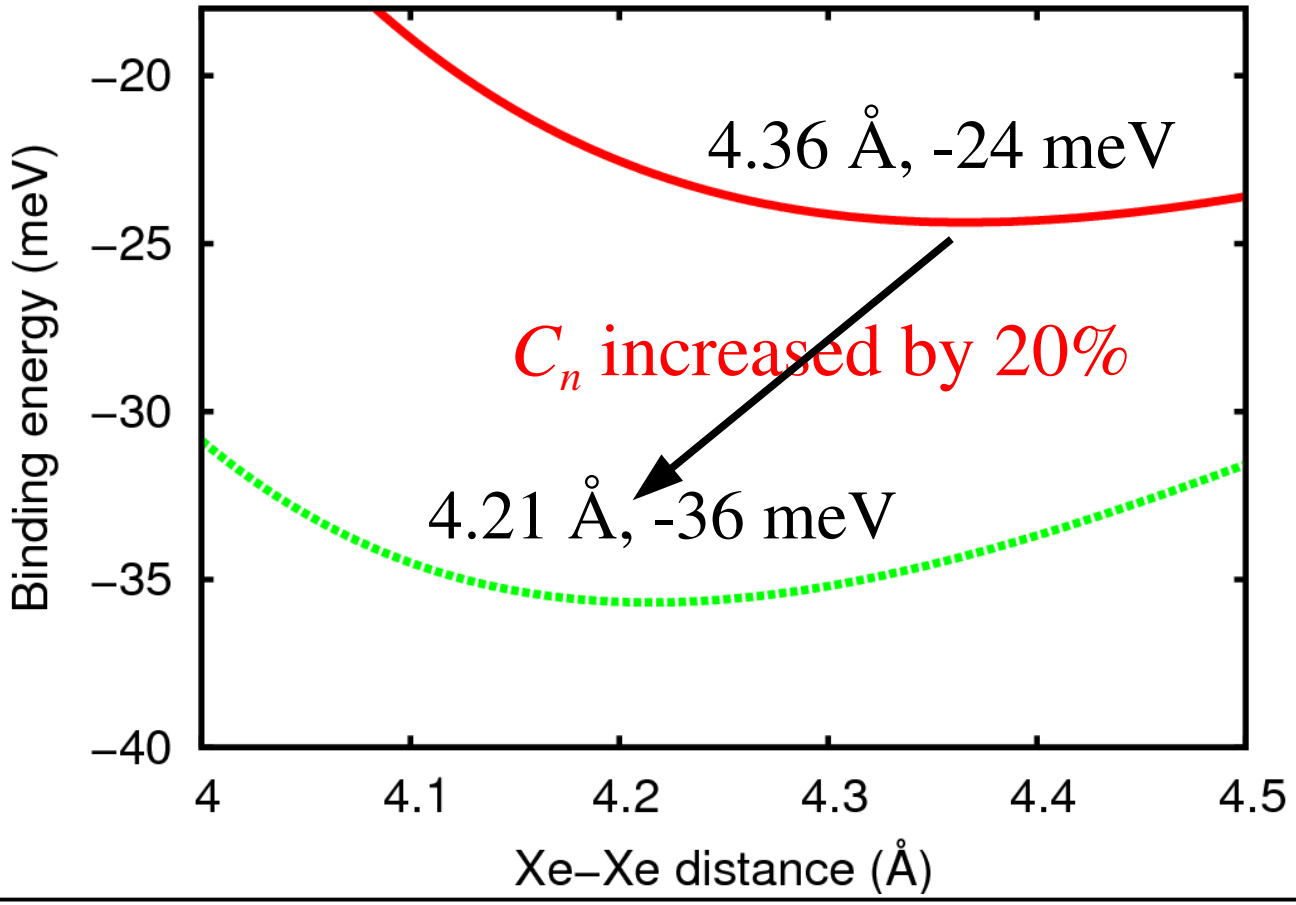
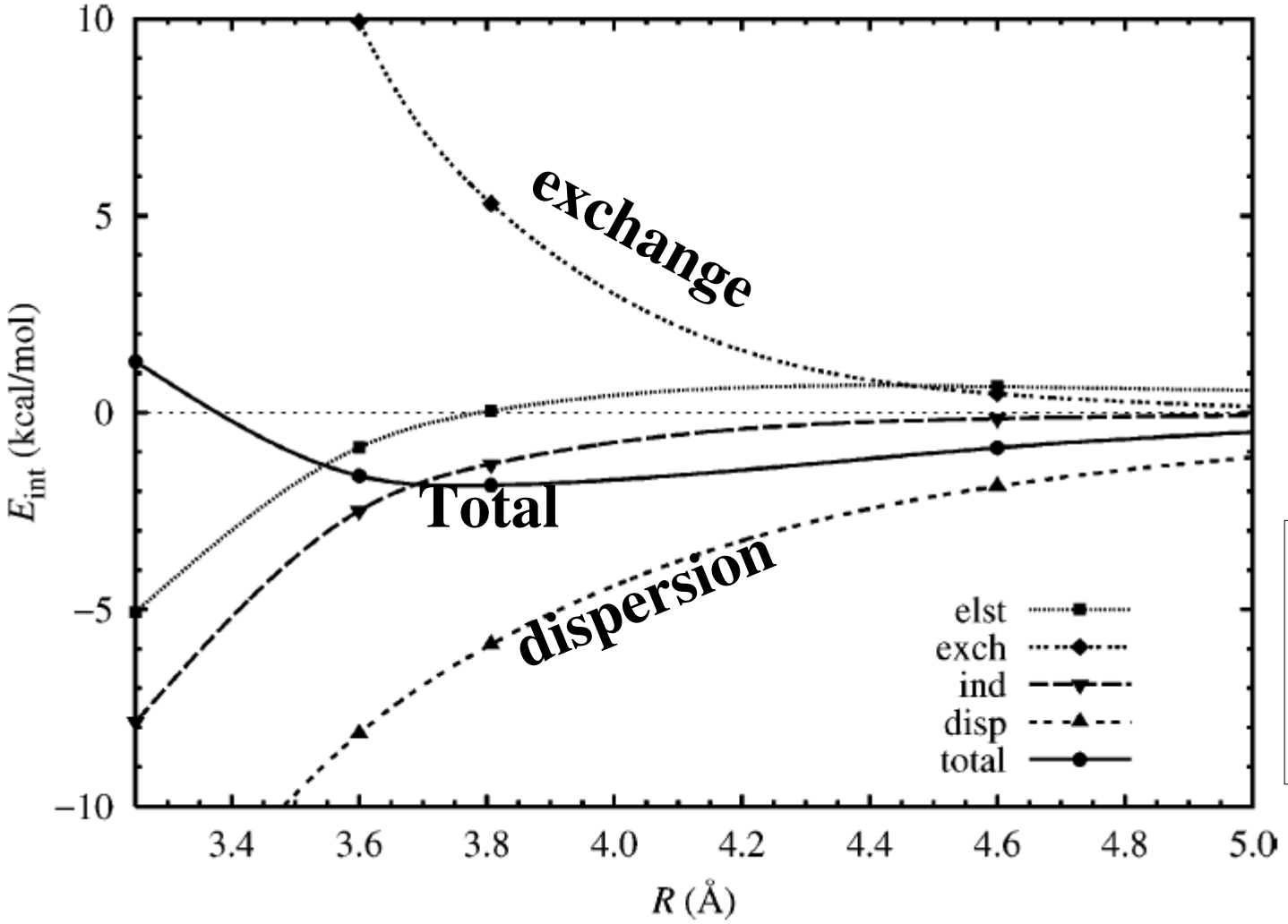
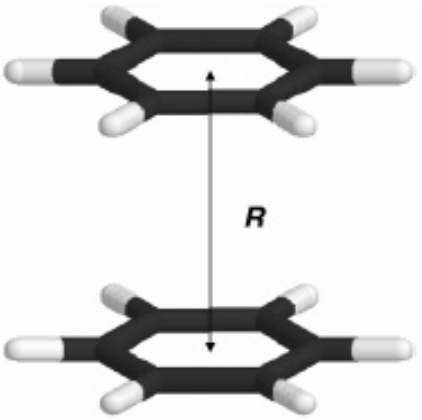


Increasing C_n by **20%** increases the binding energy by **50%**

Asymptotics **do** matter: Benzene dimer





SAPT:

Podeszwa, Bukowski, Szalewicz, JPCA (2006)

Error of **20%** in the dispersion energy leads to **50%** error in binding

Can we get dispersion coefficients
(from ground-state theory)
to better than 5% ?

Accurate reference C_6 database[1]

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

Differential dipole oscillator strength (DOS)

Transition energy (ground state--excited state)

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

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

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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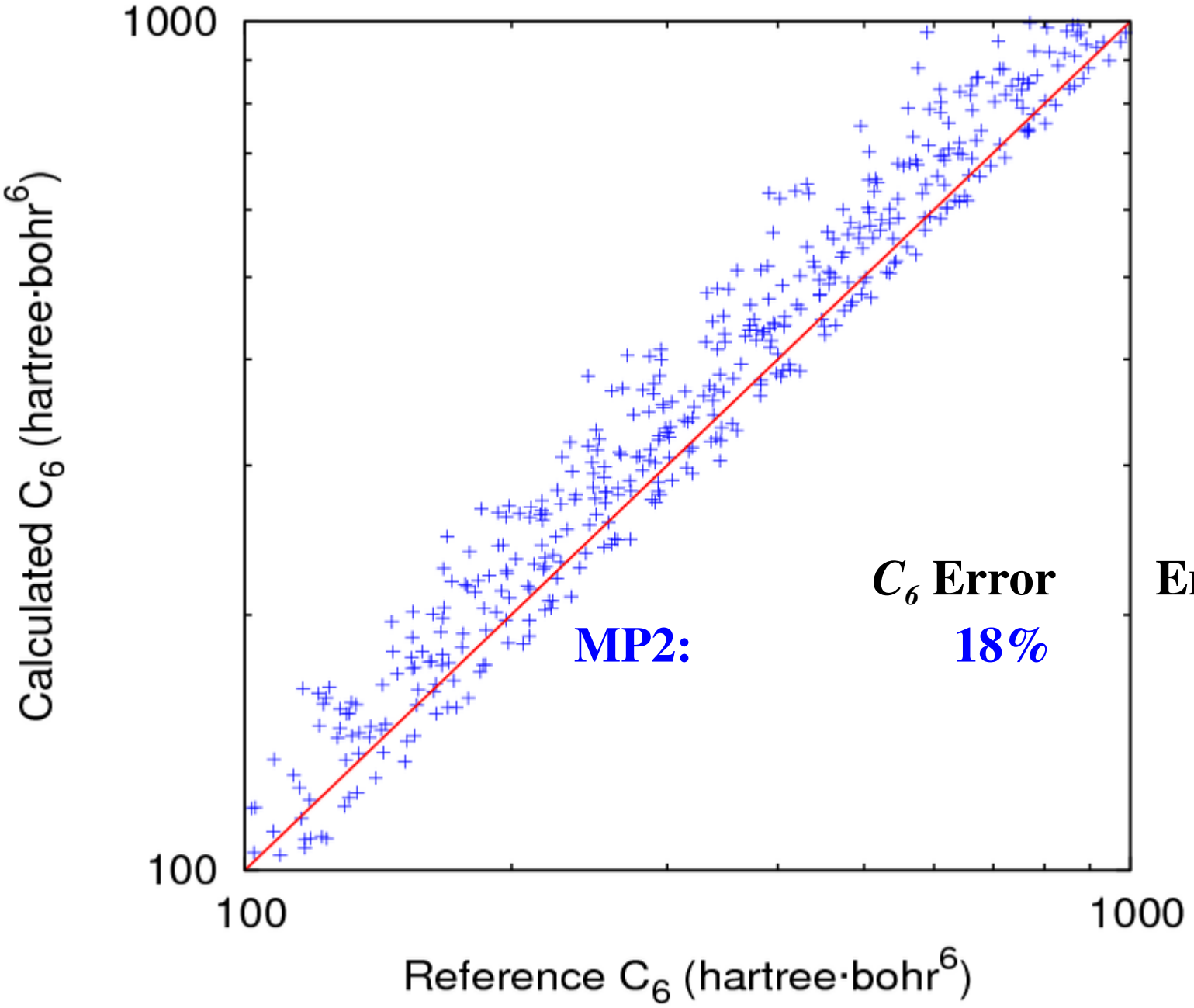
Data available for atoms, alkanes, alkenes, alkynes, alcohols, H_2, N_2, H_2S, NH_3, SO_2, COS, CO_2, CS_2, SiH_4, CCl_4, etc.

(50 atoms and molecules – 1225 interaction pairs)

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

Can we get accurate dispersion coefficients ?



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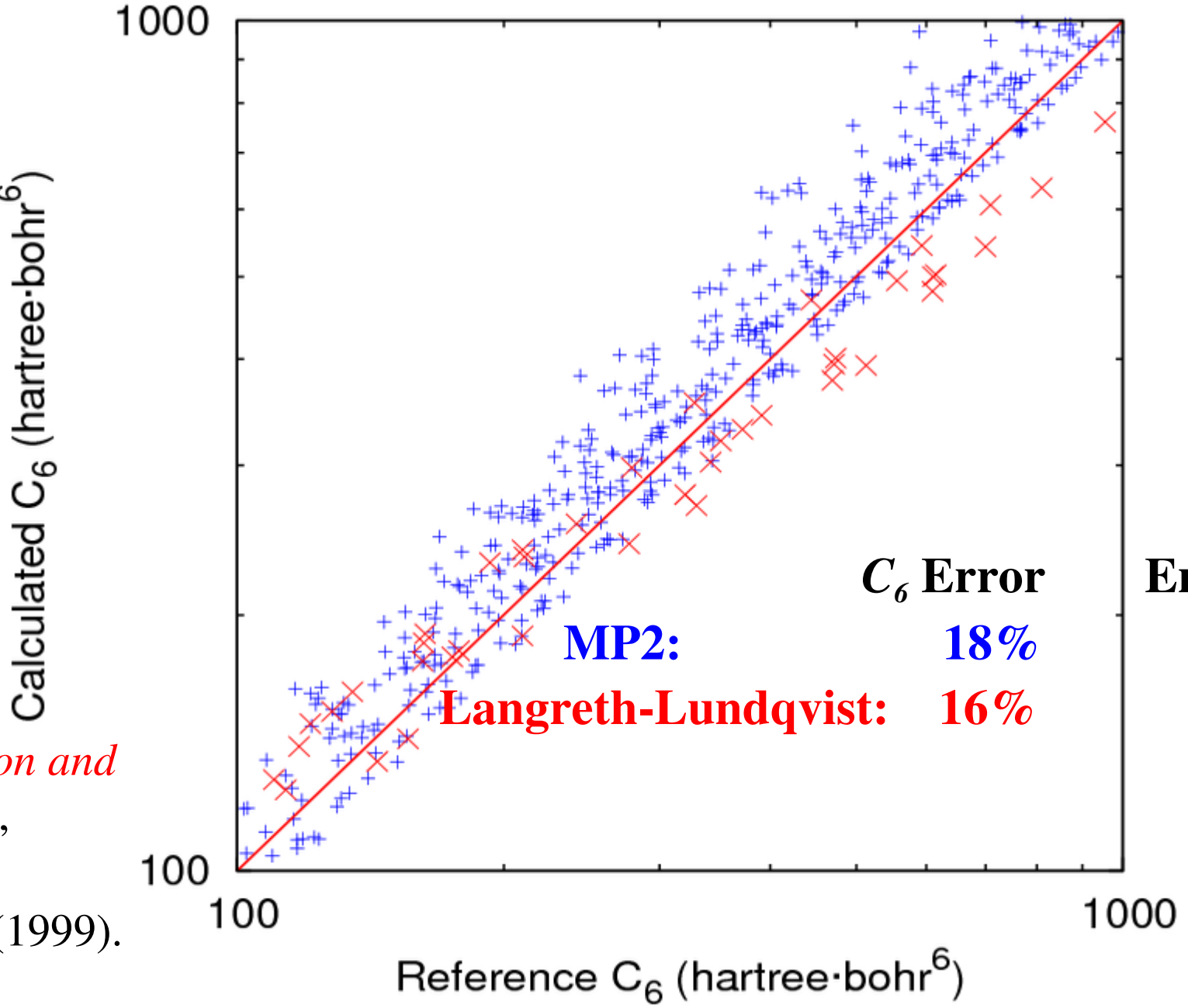

	C_6 Error	Energy Error
MP2:	**18%**	**~ 36%**
Langreth-Lundqvist:	**16%**	**~ 32%**

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

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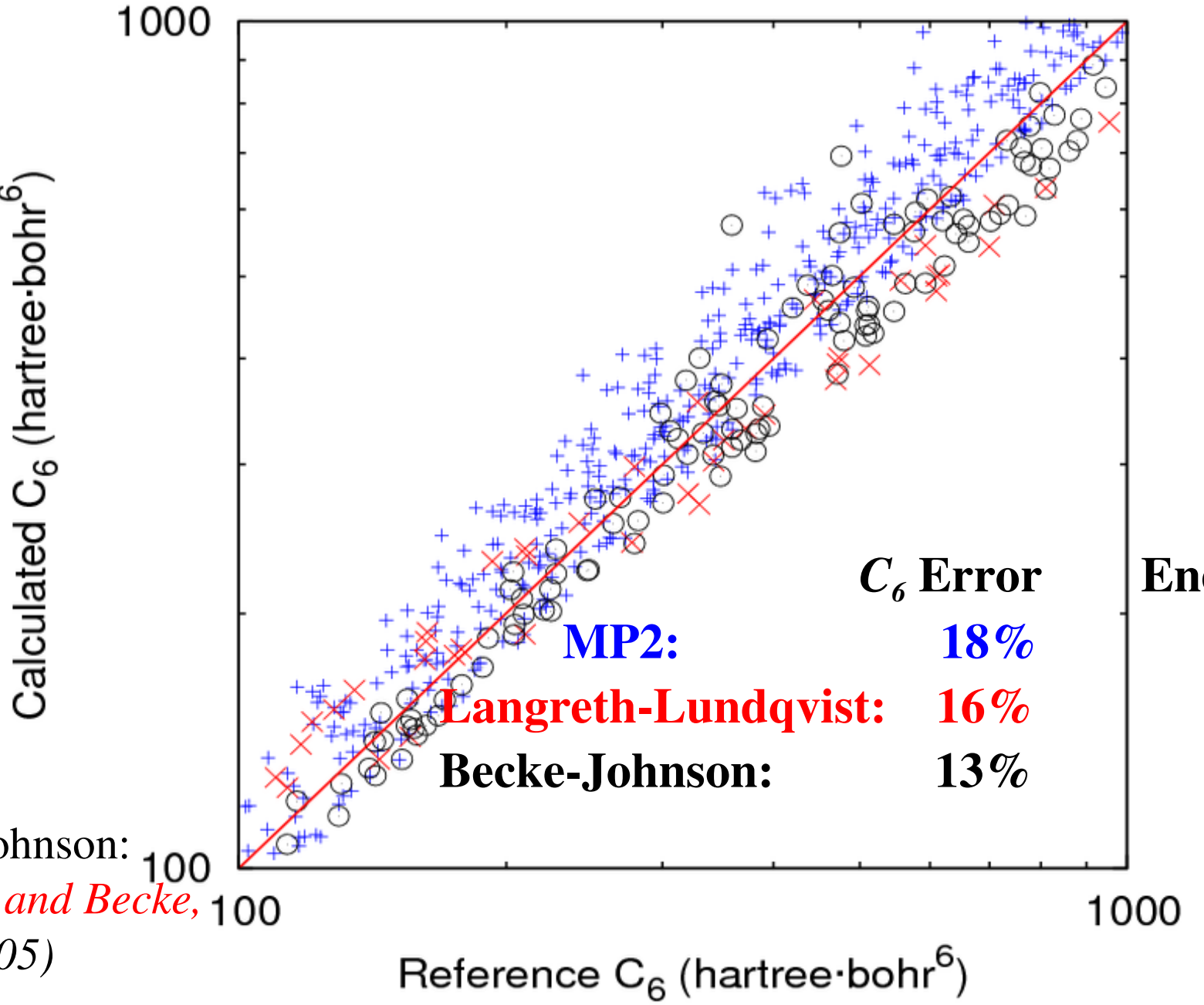


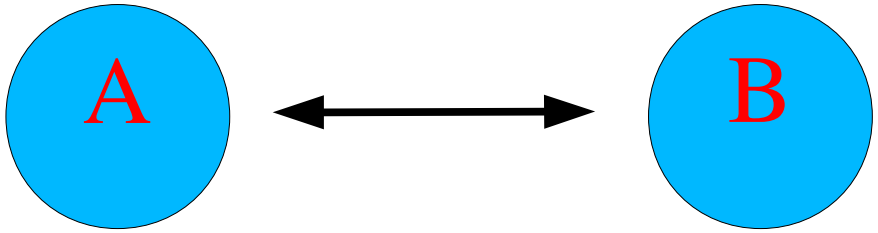
	C_6 Error	Energy Error
MP2:	**18%**	**~ 36%**
Langreth-Lundqvist:	**16%**	**~ 32%**
Becke-Johnson:	**13%**	**~ 26%**

Becke-Johnson:
Johnson and Becke, ***JCP*** *(2005)*

Let us start from
first principles ...

Atom-atom dispersion energy

$\Psi_A^{(0)}, \Psi_A^{(1)}, \Psi_A^{(2)}, \ldots, \Psi_A^{(\infty)}$



$\Psi_B^{(0)}, \Psi_B^{(1)}, \Psi_B^{(2)}, \ldots, \Psi_B^{(\infty)}$

No multipole moments on ***A*** and ***B*** $\Rightarrow$ $E_{int} = E_{disp}$

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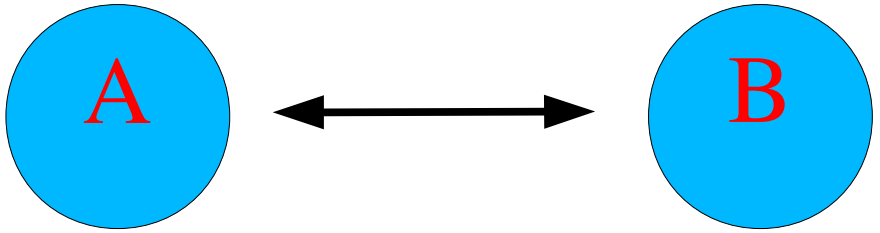

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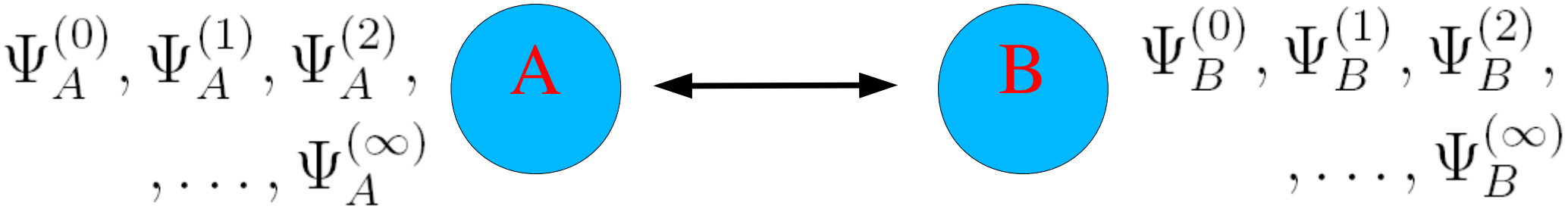
$$E_{disp} = -\sum_{i\neq 0, j\neq 0} \frac{\langle 00|\, H' \,|ij\rangle \langle ij|\, H' \,|00\rangle}{\epsilon_i^A + \epsilon_j^B - \epsilon_0^A - \epsilon_0^B} \qquad H' = \sum_{a\in A}\sum_{b\in B} \frac{Z_a Z_b}{r_{ab}}$$

To leading order (long-range approximation):

$$E_{disp}^{\infty} = -\frac{6}{R_{AB}^6} \sum_{i\neq 0, j\neq 0} \frac{\langle 0|\, \mu^A \,|i\rangle^2 \langle 0|\, \mu^B \,|j\rangle^2}{\epsilon_i^A + \epsilon_j^B - \epsilon_0^A - \epsilon_0^B}$$

Atom-atom dispersion energy



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C_6 coefficient

TS-vdW method: Basic ingredients

1) Only *relative* polarizability is used – avoiding inaccurate absolute polarizability of (semi-) local DFT or Hartree-Fock.

2) *Ab initio* reference *free-atom* C_6 coefficients (*Chu and Dalgarno*).

3) Accurate combination rule for heteronuclear coefficients.

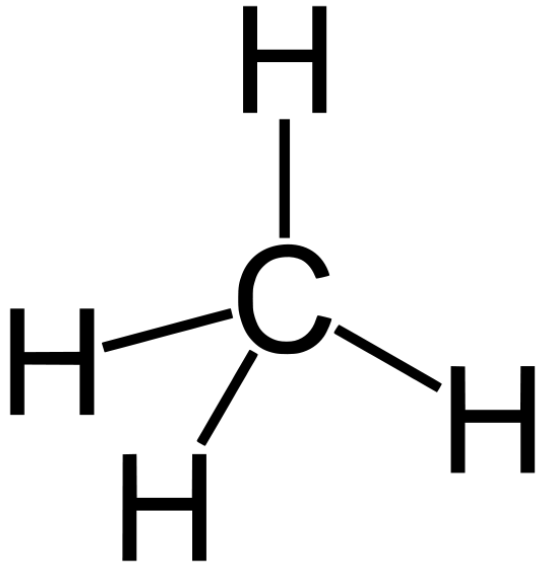
4) *Atom-in-a-molecule/solid* polarizability from Hirshfeld partitioning of the electron density (*Becke and Johnson*).

5) $C_6 = C_6[n(\boldsymbol{r})]$: C_6 becomes a functional of the electron density.

A. Tkatchenko and M. Scheffler ***PRL*** (2009).

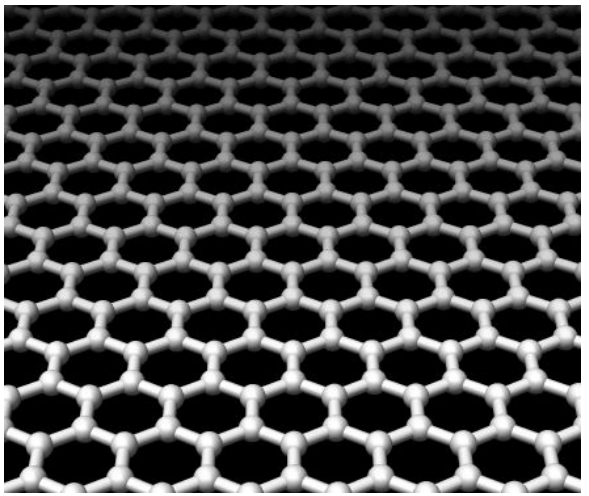
C_6 is a functional of the density

(Carbon-Carbon C_6 coefficient)



24.1 HartreeBohr^6

sp^3



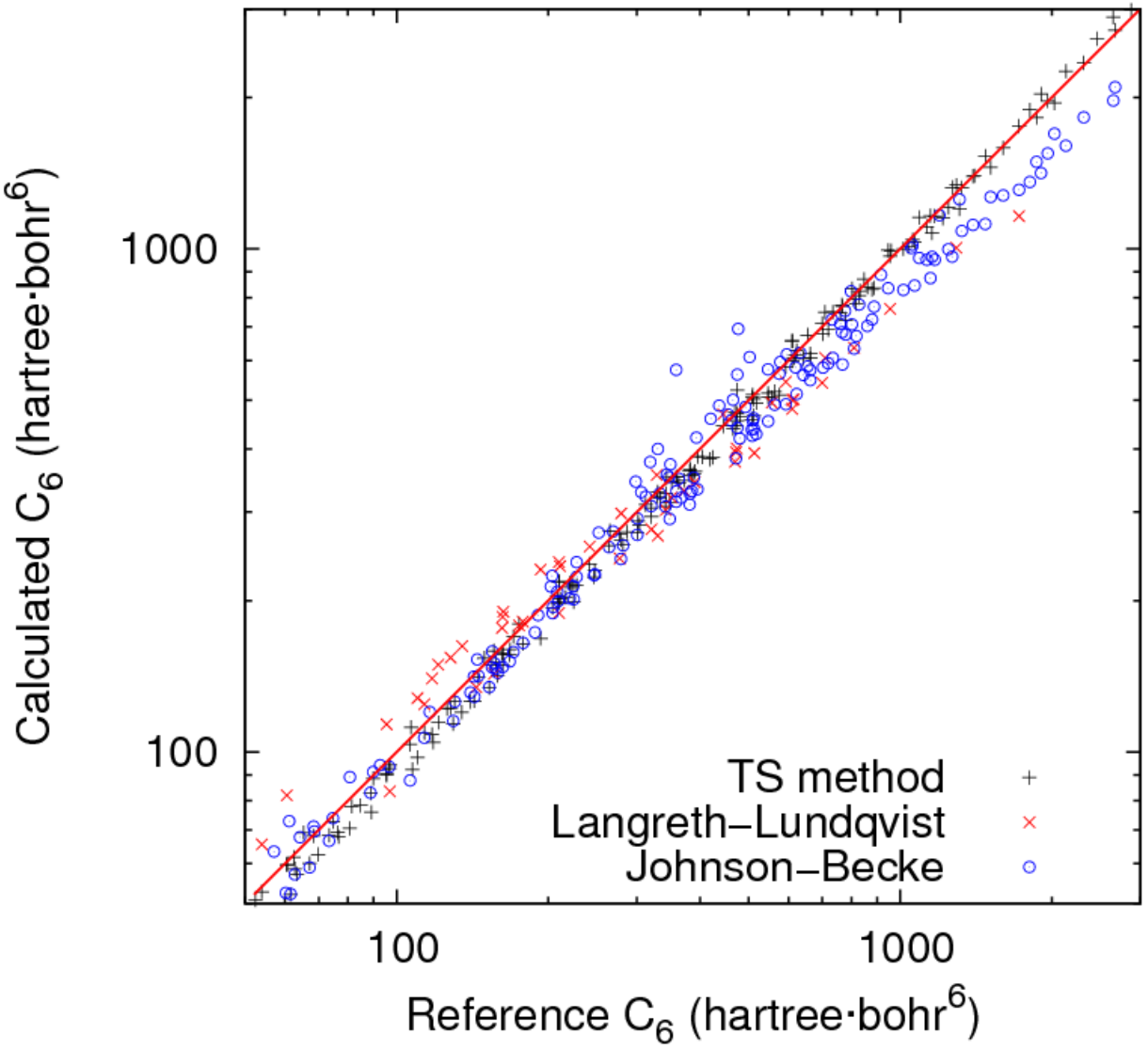
33.0 HartreeBohr^6

sp^2

38.6 HartreeBohr^6

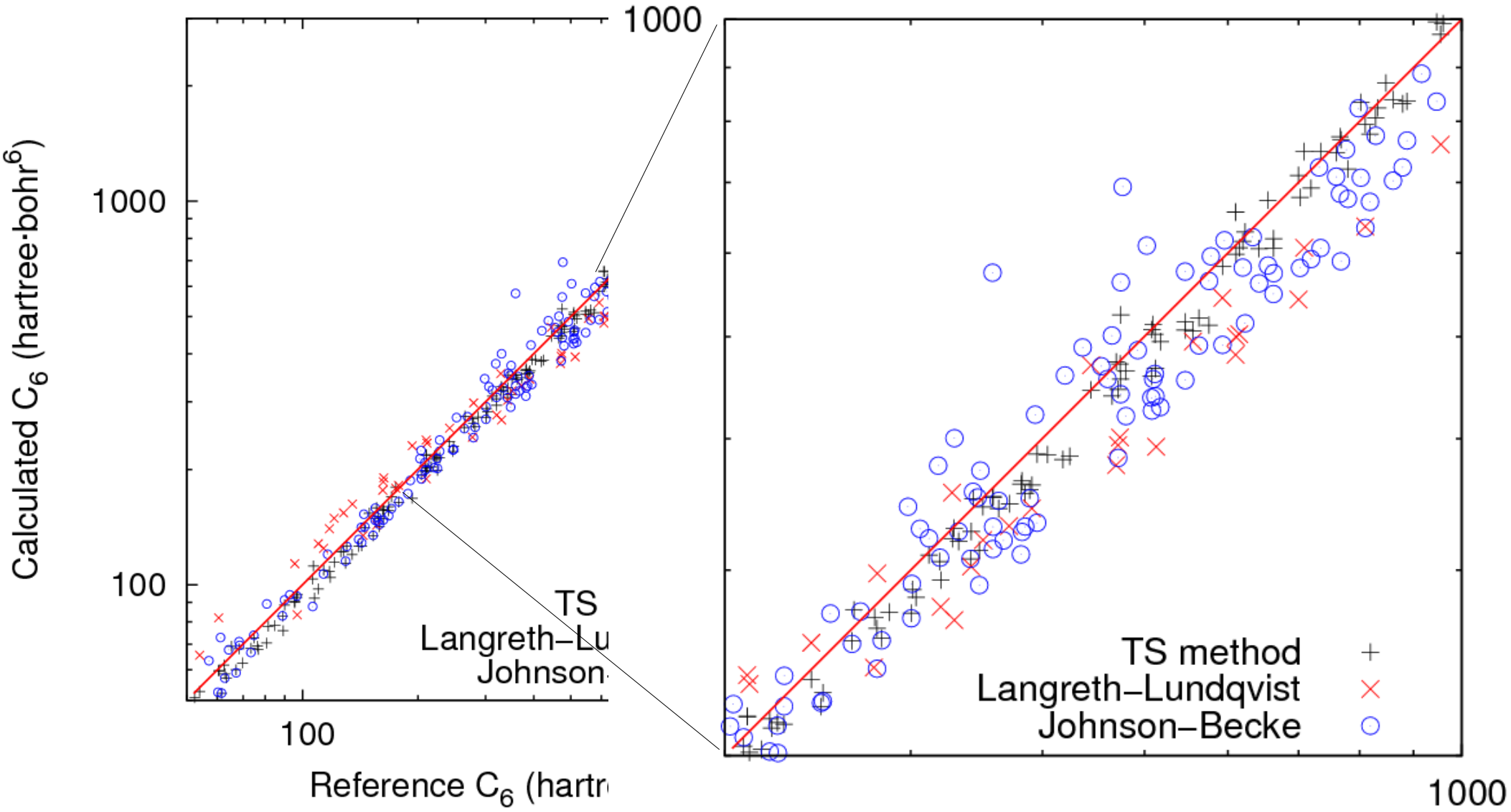
sp^3

Performance of TS-vdW for molecules



- **MAE of 5.5%** for 1225 molecular pairs from DOSD reference data of *W. J. Meath et al.*

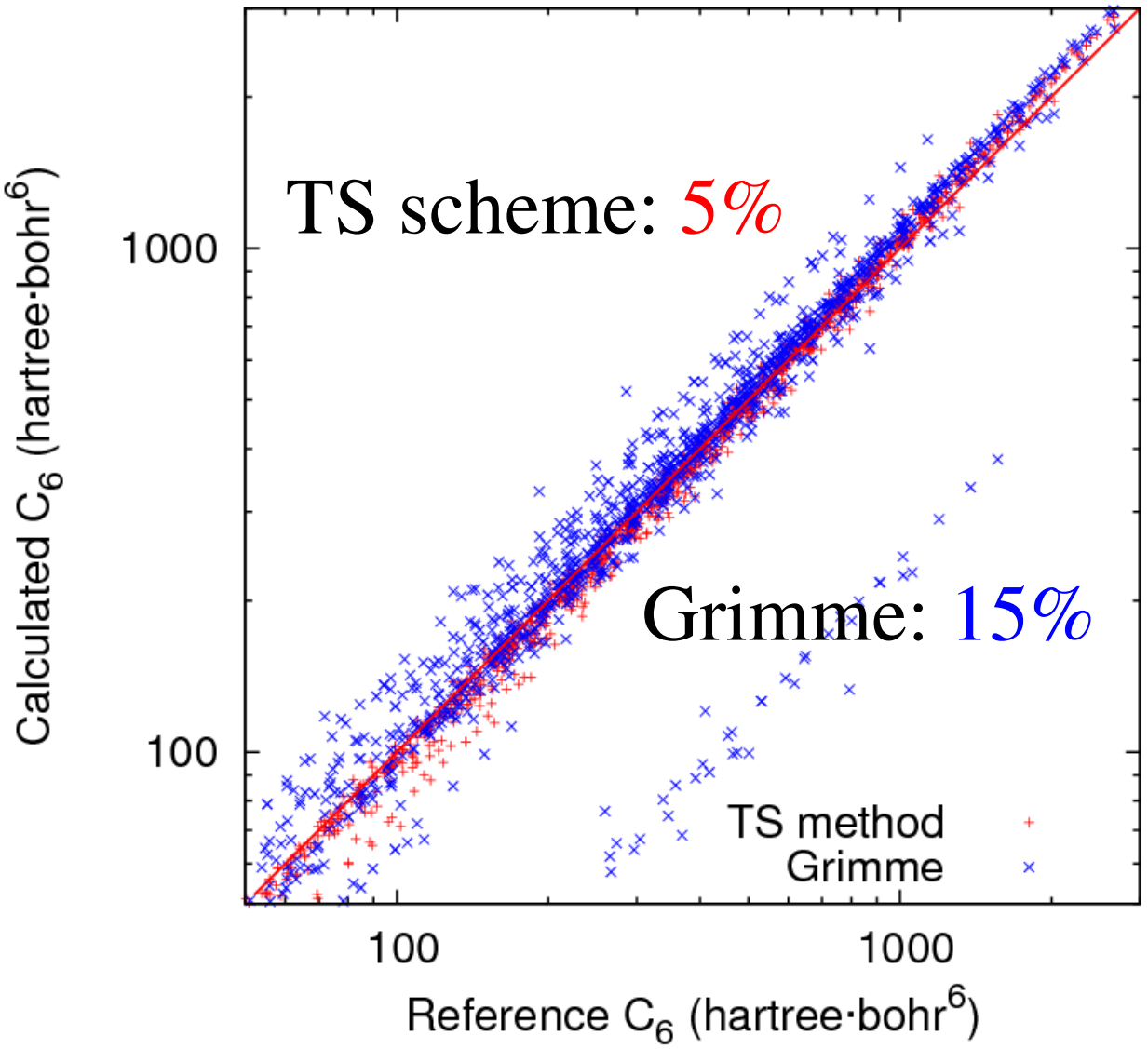
Performance of TS-vdW for molecules



Results depend negligibly (1% deviation) on the employed *xc* functional

Comparison to fixed C_6 schemes

S. Grimme ***J. Comput. Chem.*** 27, 1787 (2006)



... and we can treat all elements in the periodic table

DFT+vdW[(1)] & *MP2+ΔvdW*[(2)]

Leading dispersion term (or ΔC_6 term) is added to DFT or MP2 total energy, damped at short distances,

$$E_{vdW} = -\sum_{A}\sum_{B>A} f_{damp}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6}$$

$$R_{eff}^0 = \left(\frac{V^{eff}}{V^{free}}\right)^{1/3} R_{free}^0$$

- Effective vdW parameters are functionals of the electron density:

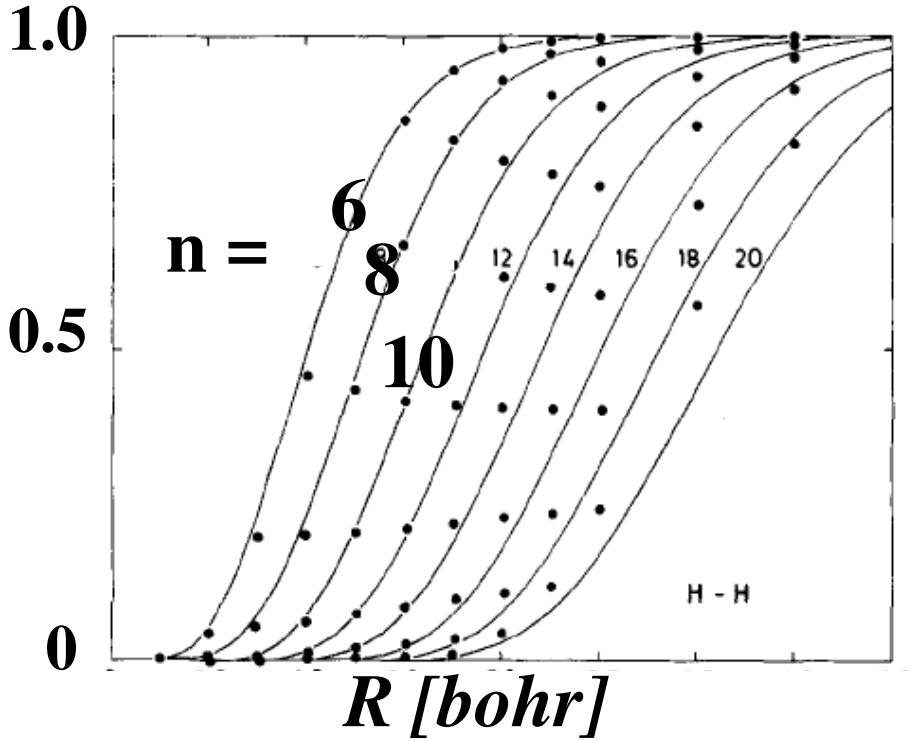
$$C_6 = C_6[n(\boldsymbol{r})], \quad R_{vdW} = R_{vdW}[n(\boldsymbol{r})]$$

- One damping parameter for DFT (for each functional), no parameters for MP2

[(1)]***DFT+vdW*:** *Tkatchenko and Scheffler* ***PRL*** (2009)
[(2)]***MP2+ΔvdW*:** *Tkatchenko, DiStasio Jr., Head-Gordon, Scheffler* ***JCP (2009)***

Short-range damping function

$f_n(R)$



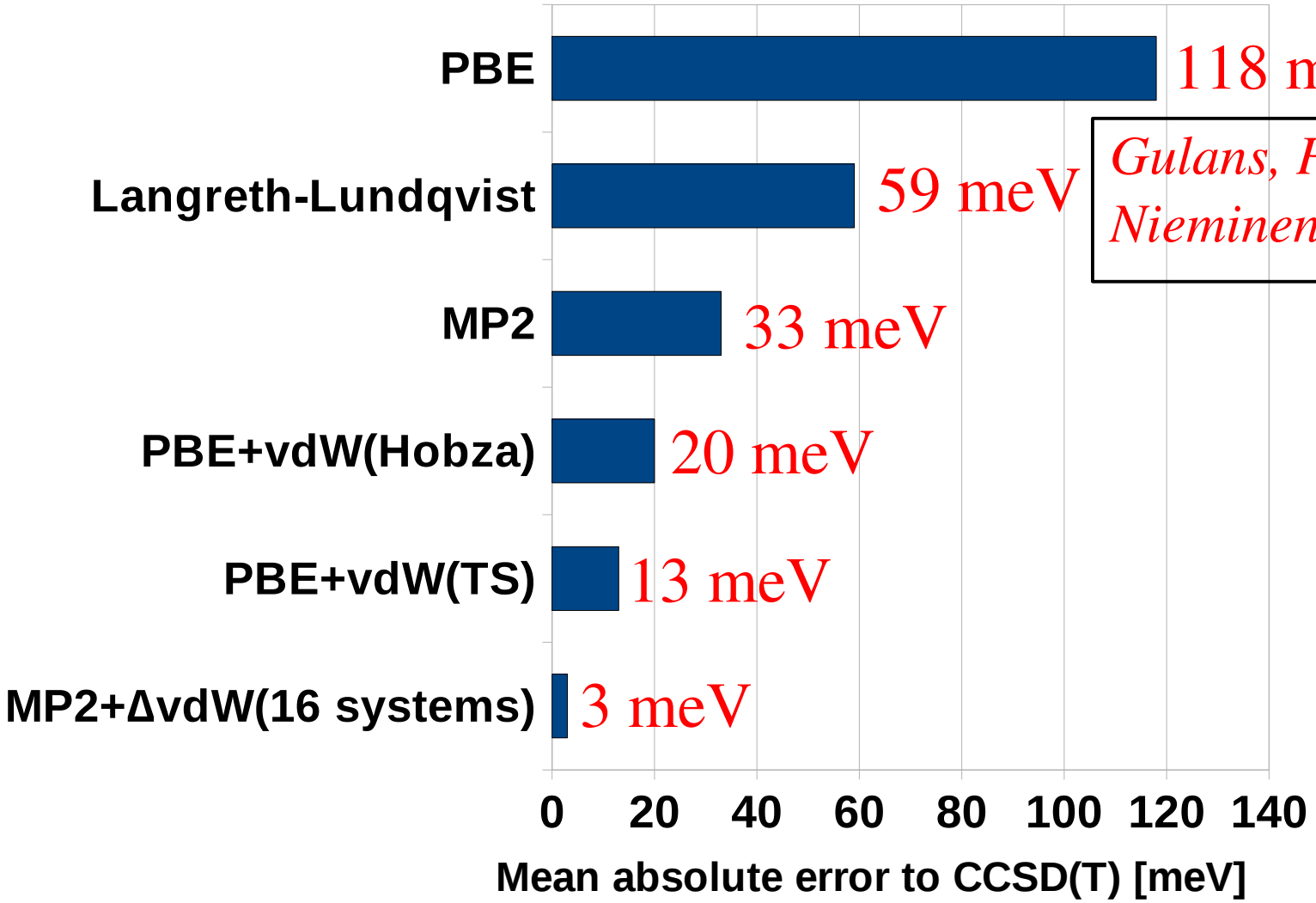
Analytic:
Aziz, Koide, Meath, Tang, Toennies, et al.

HF&DFT:
Scoles, Yang, Grimme, Bechstedt, Hobza, et al.

Damping function:

- Analytical form known *exactly* for dispersion energy in H-H
- Law of corresponding states for other spherical atoms (rare-gas, alkaline earth, mercury)
- Parameterized when used with DFT or quantum chemical methods

Performance for intermolecular interactions (S22*)

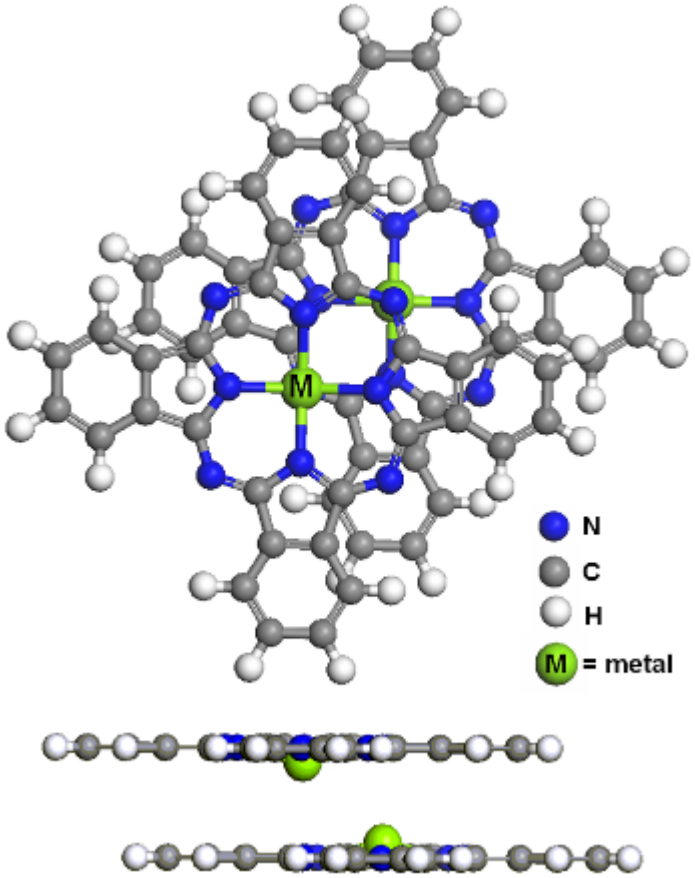


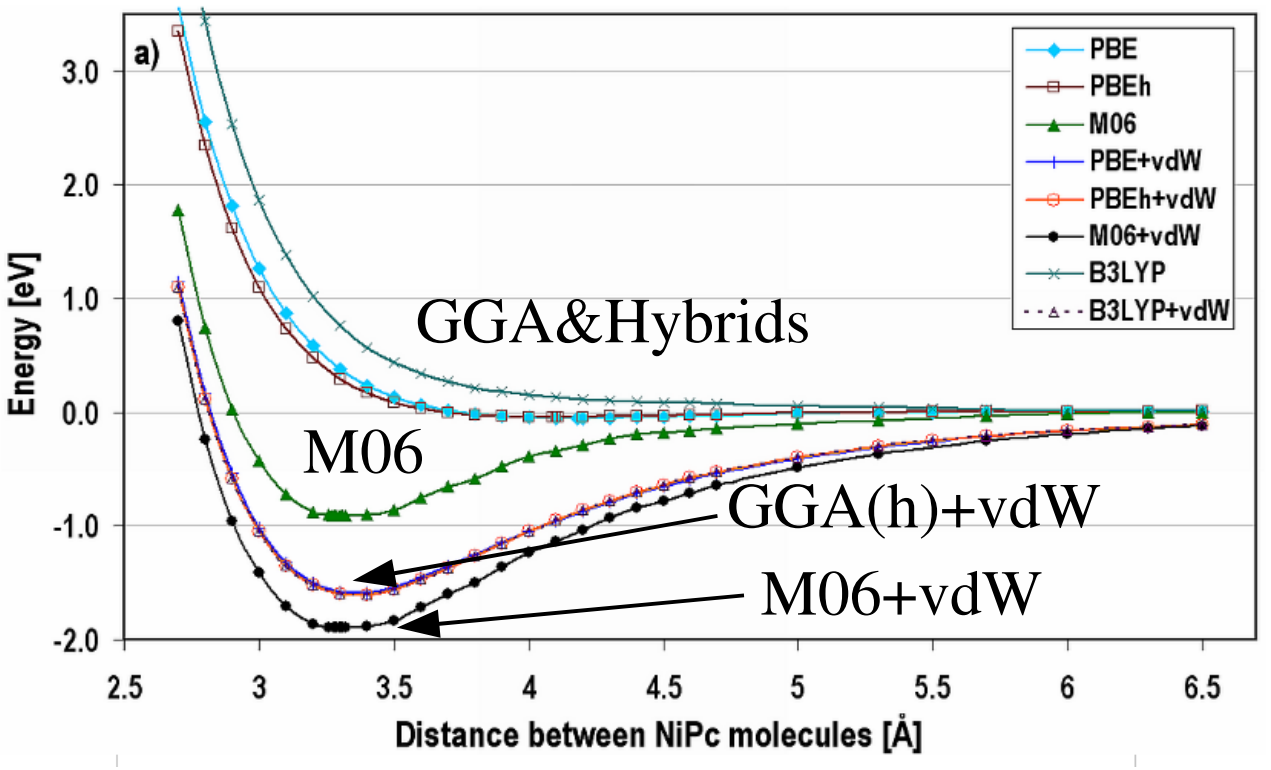
Gulans, Puska, Nieminen, ***PRB*** (2009)

S22 database:
Organic dimers, including vdW, electrostatics and H-bonding

Jurecka, Sponer, Cerny, Hobza* ***PCCP* 8, 1985 (2006)

Importance of vdW asymptotics (large molecules)





Marom, Tkatchenko, Scheffler, Kronik, ***JCTC***, submitted.

Outlook

- Extending the method to solids and adsorption (dielectric screening in **metals,** etc.)
- Short-range damping function
- Anisotropic and non-additive many-body vdW interactions

Summary

- Developed accurate *first-principles* method for the long-range van der Waals interactions

- Can be coupled to DFT (***DFT+vdW***) or MP2 (***MP2+ΔvdW***)

- Consistently accurate results for a variety of applications

- Can be coupled to hybrid functionals for improved electronic structure (*Marom, Tkatchenko, Scheffler, Kronik, submitted*)
  or followed by *GW* calculations