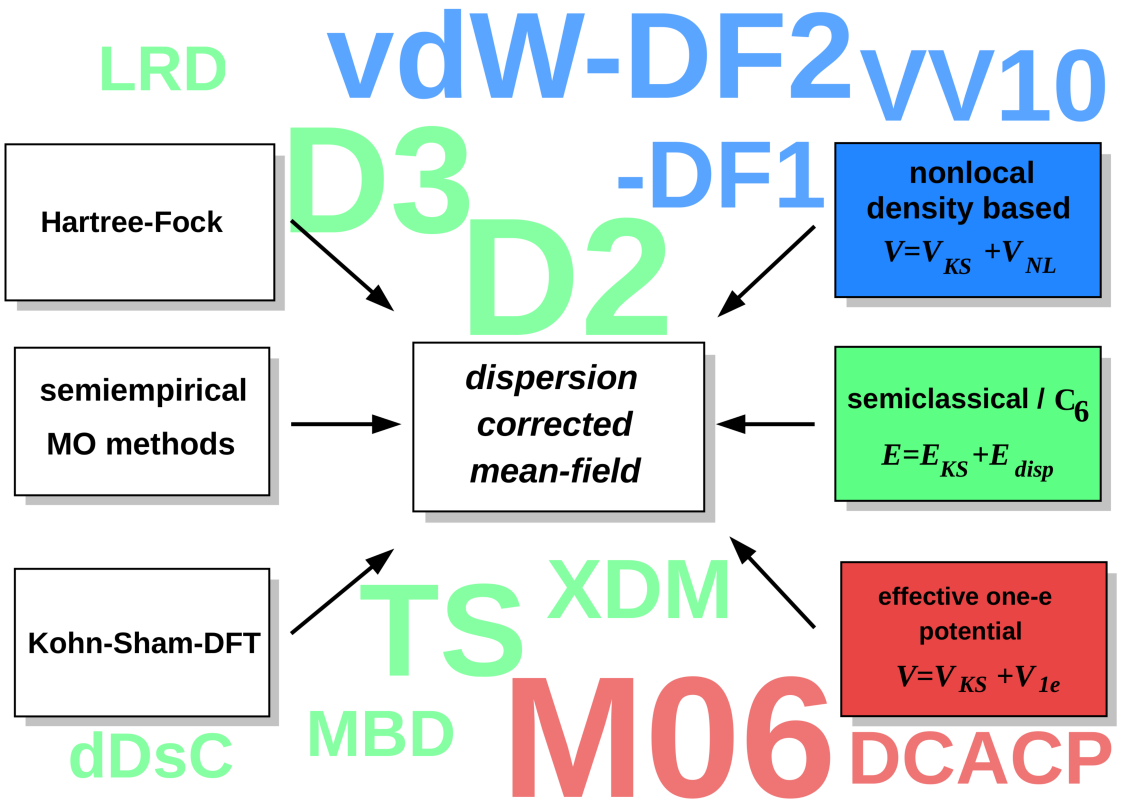
Van-der-Waals interactions: Benchmarking from clusters to solid state

Gerit Brandenburg <g.brandenburg@ucl.ac.uk> | 8th of March 2018

PHASG473 - UCL - ELECTRONIC STRUCTURE METHODS FOR MATERIALS MODELLING

Outline of talk

Many good dispersion corrections exist



- focus on D3 scheme as it can be used at all computational levels
- own work started with extension of D3 type corrections

[3] S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016)

Outline of talk

Why is benchmarking important?

- every computed or measured property needs an error bar
- possible origins: random and systematic errors
- random errors from statistics, e.g. molecular dynamics
  $\longrightarrow$ straight-forward to converge
- systematic errors from intrinsic error of theoretical model
  $\longrightarrow$ nontrivial to estimate

Benchmarking from economical perspective

(1) determine a standardized quality measure

(2) analyze what and where improvements are called for

(3) use this information to improve performance

Which properties should be tested?

Possible properties of interest

- atomization energies
- binding energies, reaction energies, barrier hight
- electron affinities, ionization potential
- geometries, covalent bonds, lattice parameter

Possible systems of interest

- organic systems
- main group elements
- transition-metals
- molecules vs. condensed systems?

What reference data can be used?

Experimental

- final goal should be to describe experimental conditions
- possible for complex systems
- measurement uncertainty
- no separation of effects

Theoretical

- straight-forward comparison
- only possible for 'small enough' systems
- uncertainty of reference method

Semi-experimental:
Combine measured properties with theoretical evaluation of secondary effects

Methods with 'benchmark quality' for noncovalent interactions

(1) CCSD(T)/CBS

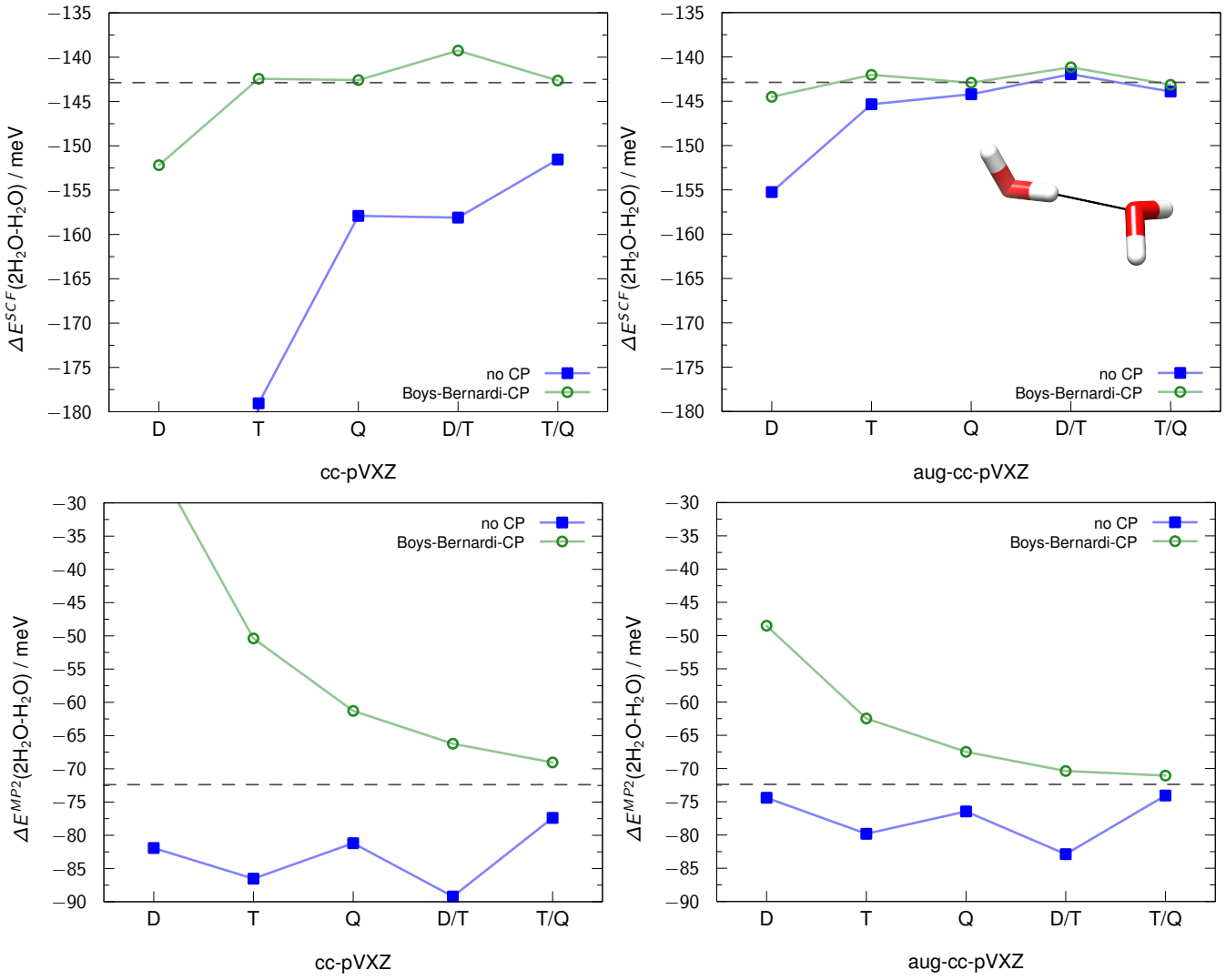
- established gold standard in quantum chemistry
- tight convergence of orbital basis set $\longrightarrow$ aug-cc-pVQZ or better
- N^7 scaling with system size $\longrightarrow$ linear-scaling variant for large systems

(2) Diffusion Monte-Carlo

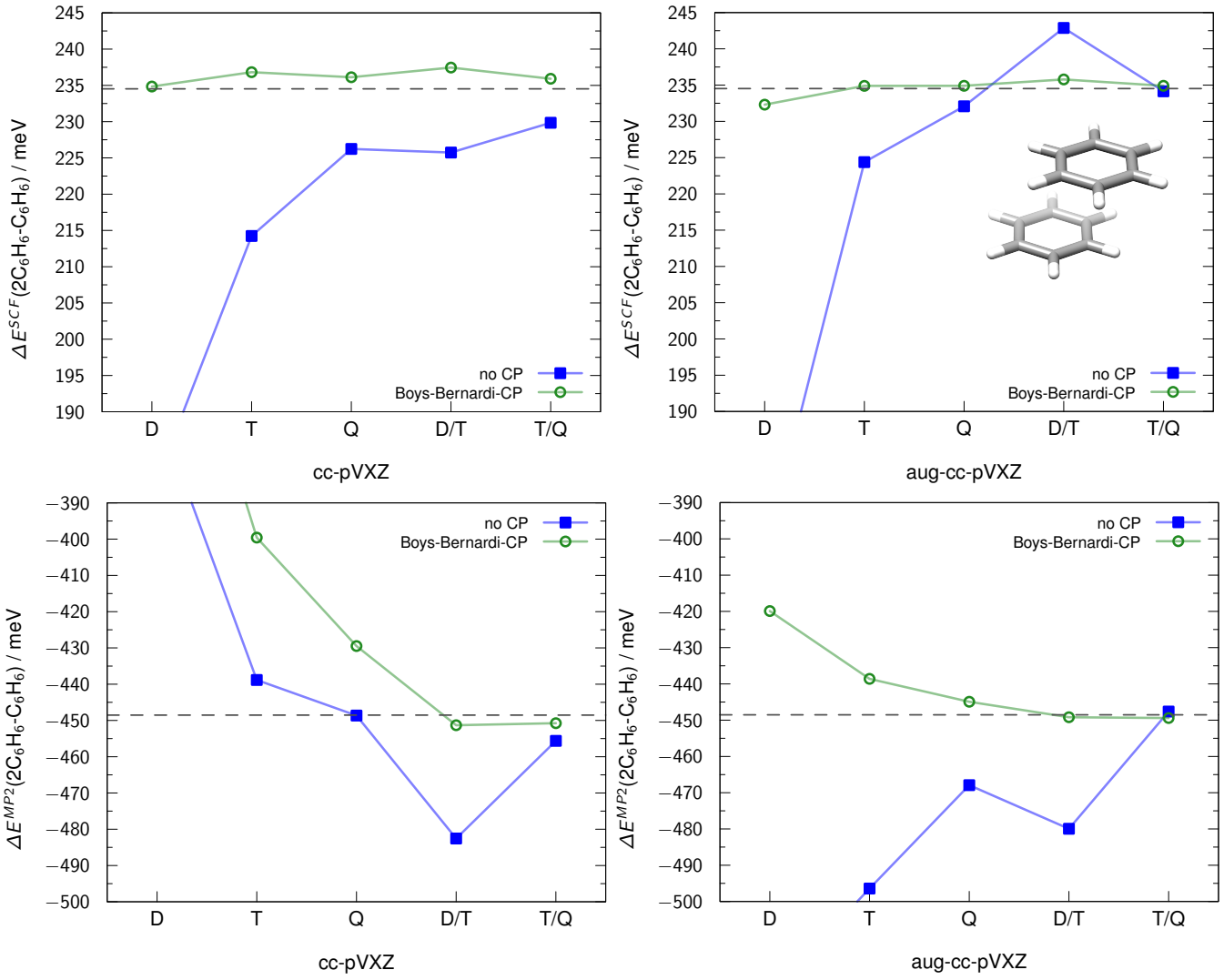
- capable of yielding CCSD(T) accuracy
- projection technique $\longrightarrow$ basis set less crucial
- N^3 scaling with system size, scaleable to HPCs
- possible problems from fixed-node error and Jastrow optimization

No benchmark quality: MP2, MP3, RPA, CCSD, CCSD(T)/cc-pVTZ

Convergence with orbital basis sets: Water dimer



Convergence with orbital basis sets: Benzene dimer



Best practices for benchmark calculations

- use the largest orbital expansion available (minimum triple-zeta)
- use a counterpoise correction for atom-centered basis functions
- use polarization and diffuse functions
- extrapolate SCF and correlation energies separately

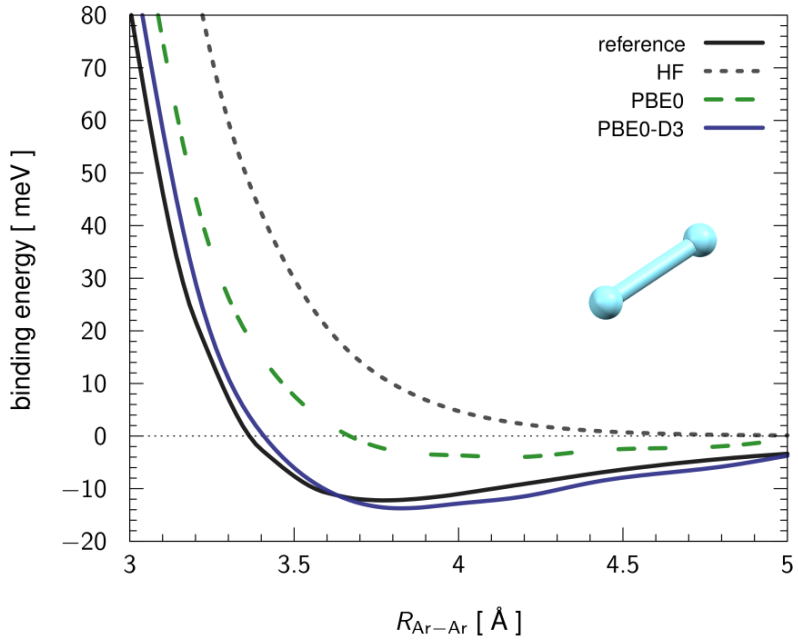
Set $\{x_1, \ldots, x_n\}$ of data points with references $\{r_1, \ldots, r_n\}$ are

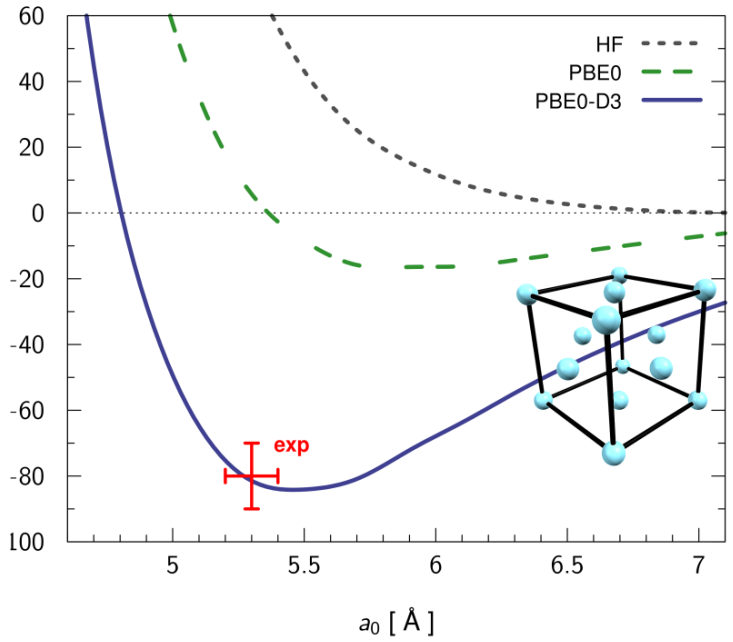
- Mean deviation (MD): $MD = \frac{1}{n} \sum_i (x_i - r_i)$
- Mean absolute deviation (MAD): $MAD = \frac{1}{n} \sum_i |x_i - r_i|$
- Standard deviation (SD): $SD = \sqrt{\frac{1}{n-1} \sum_i (x_i - r_i - MD)^2}$
- Maximum absolute deviation (MAX): $MAX = \max\{|x_i - r_i|\}$

Outline of talk

Guinea pig for testing vdW interactions

Noble gas assemblies

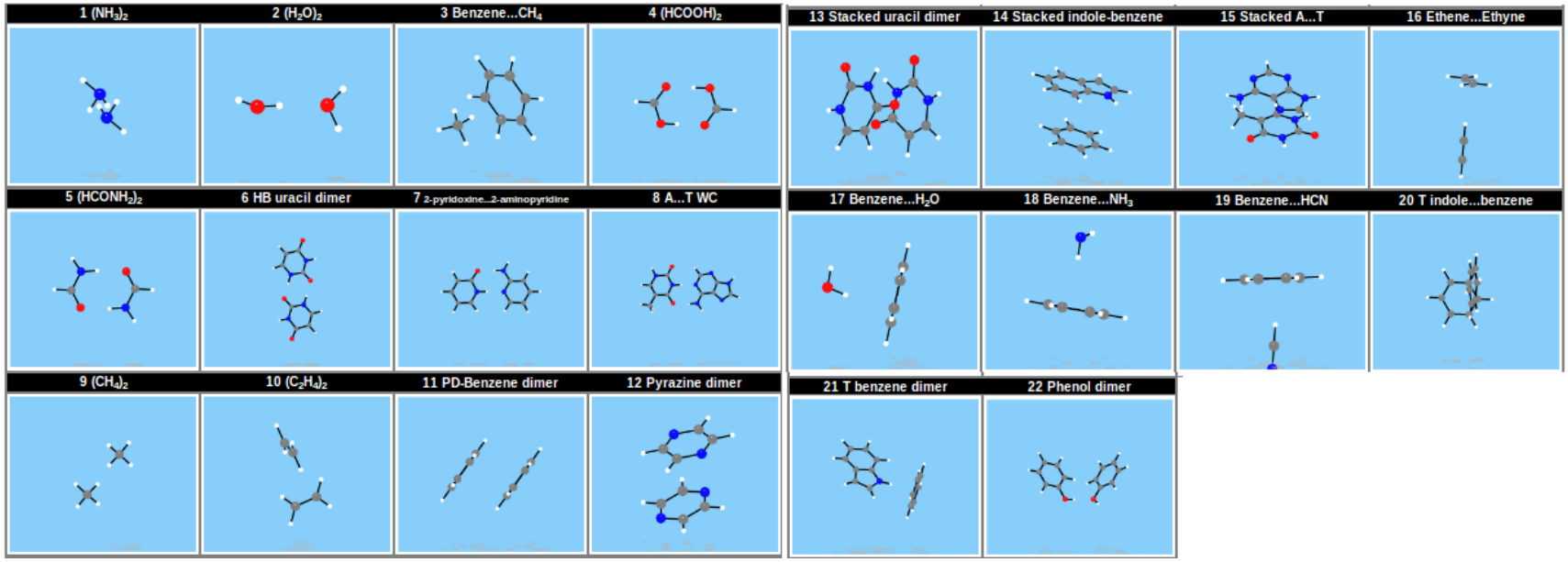




- binding solely from electron correlation effects

S22: Small molecular dimers

Molecular complexes with focus on DNA base pairs

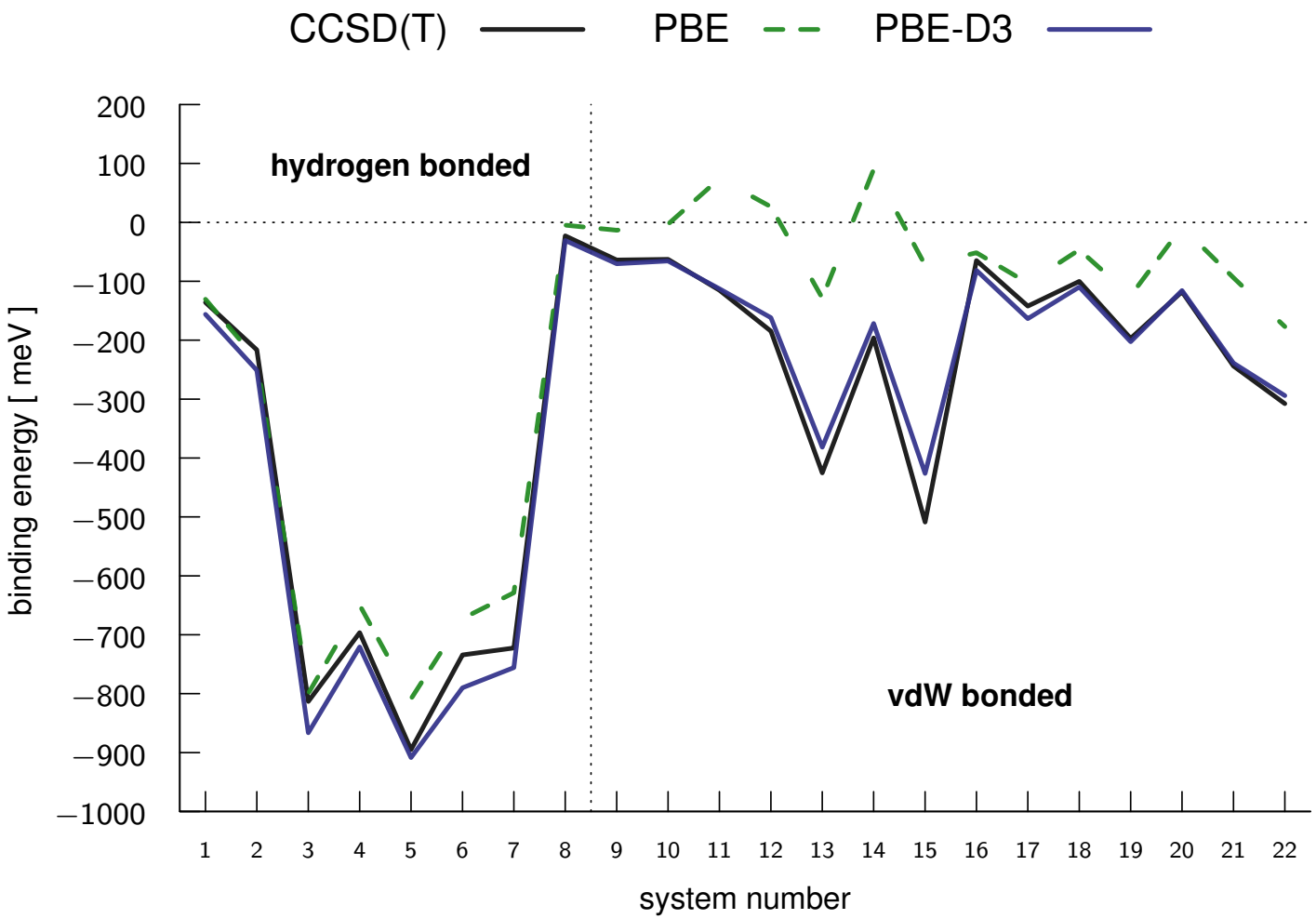


- reference method: CCSD(T) with estimated orbital basis limit (2x revised)
  $\longrightarrow$ error of about 1% $\equiv$ 5 meV

[1] P. Jurecka, J. Sponer, J. Cerny, P. Hobza, *Phys Chem Chem Phys*, **8**, 1985 (2006)

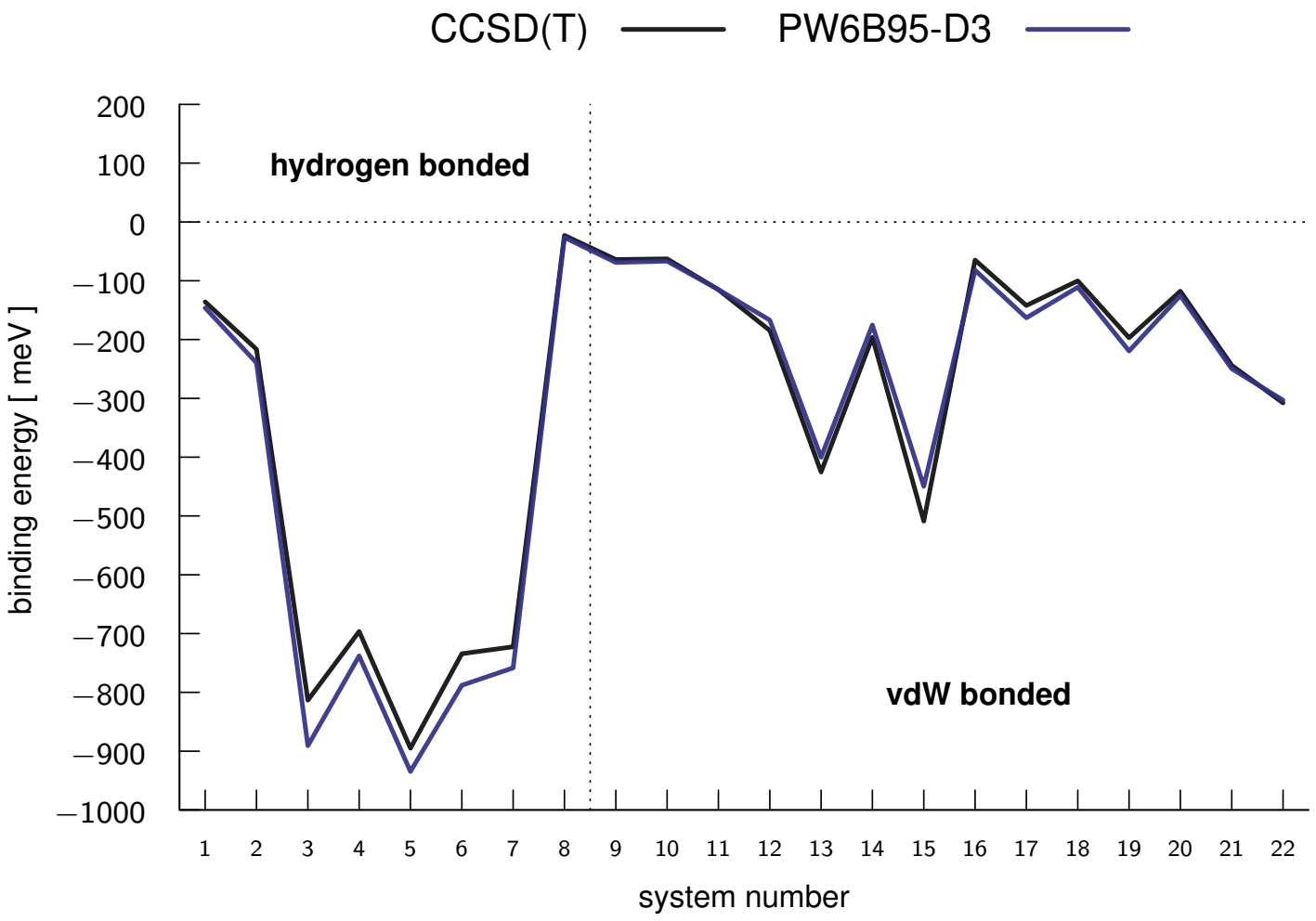
[2] T. Takatani, E. Hohenstein, M. Malagoli, M. Marshall, C. Sherrill, *J. Chem. Phys.*, **132**, 144104 (2010)

S22: Small molecular dimers



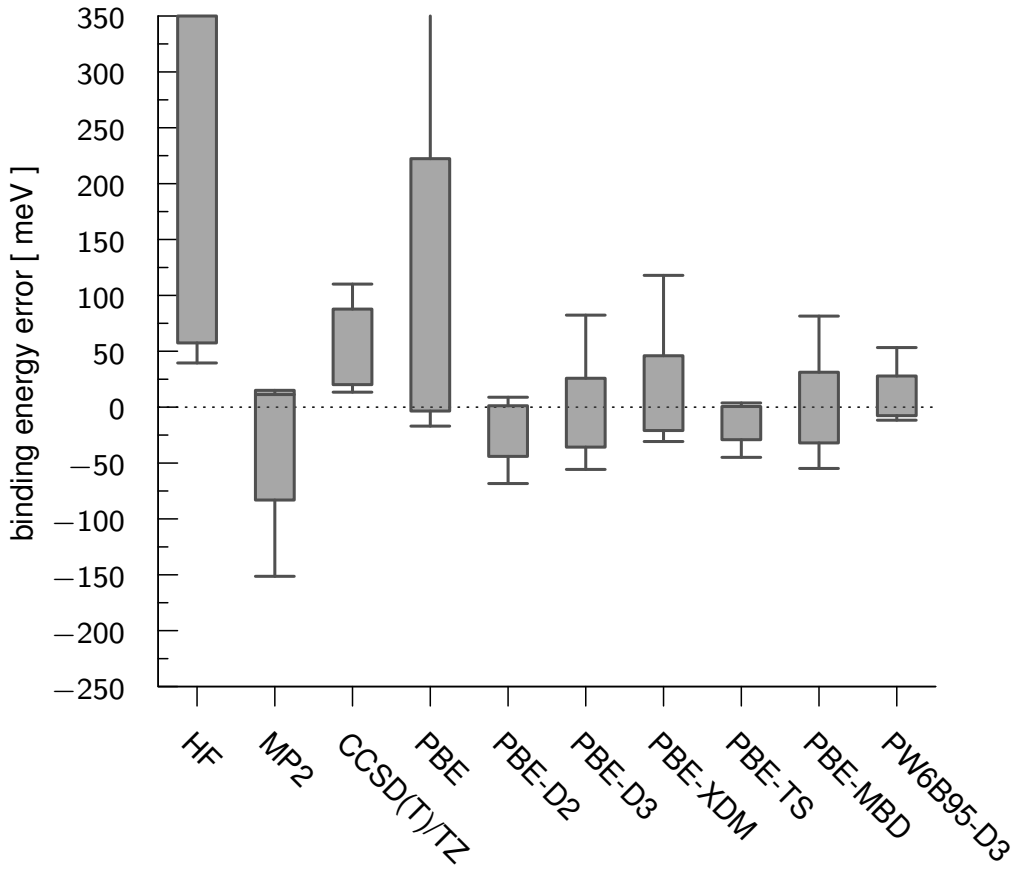
- vdW correction clearly improves plain PBE results
- PBE seem to overestimate hydrogen bondings

S22: Small molecular dimers



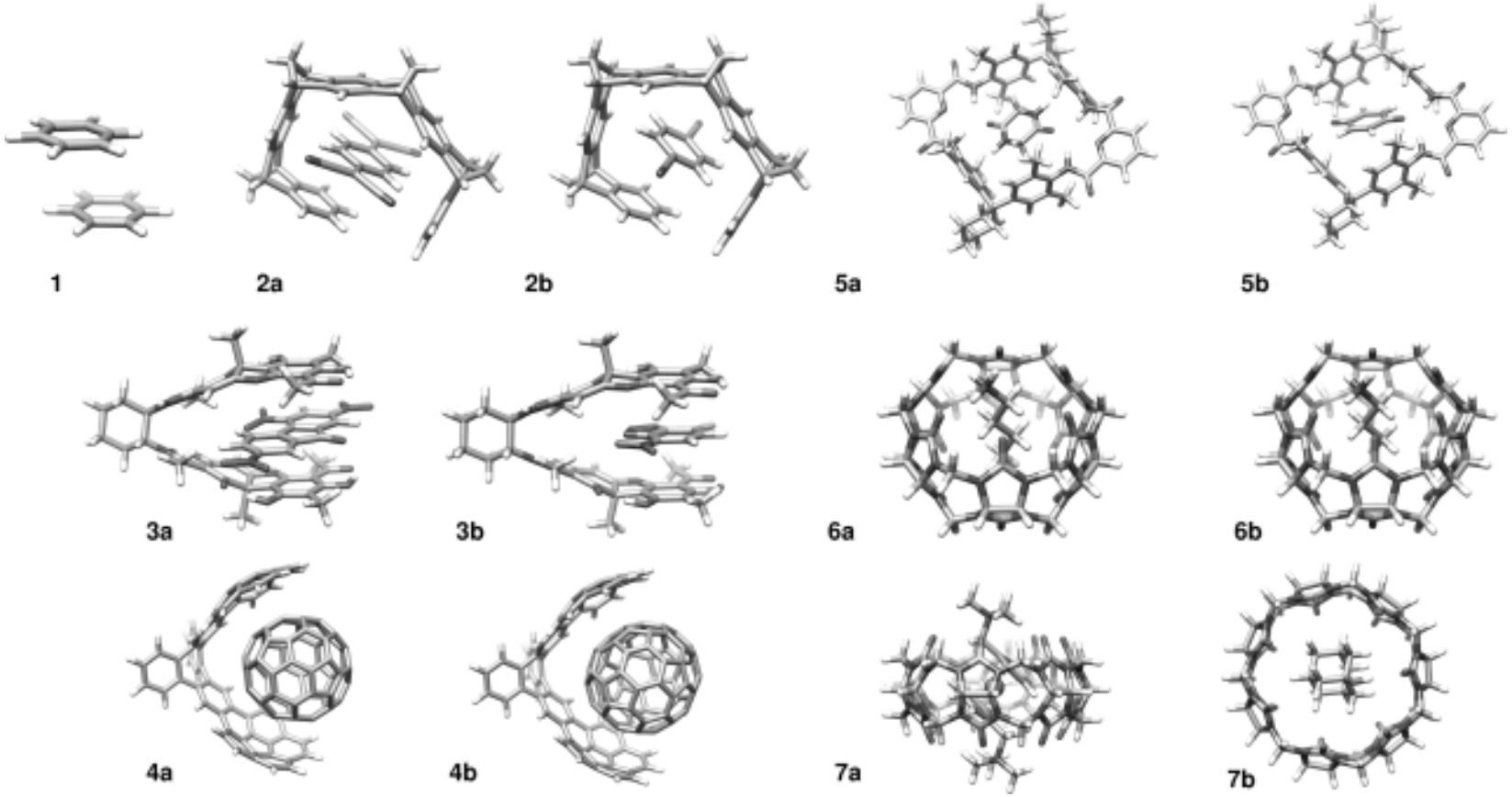
- semi-local functional can be as important as type of vdW correction

S22: Small molecular dimers



- HF, MP2, CC/TZ unreliable, DFT-DISP errors of 20-40 meV
- often used as fit set for damping function

S12L: Supramolecular complexes



- free energy of association measured in solution

S12L: Supramolecular complexes

- separate energy contributions

$$\Delta G_a = \Delta E + \Delta G_{\mathrm{RRHO}}(T) + \Delta\delta G_{\mathrm{solv}}$$

- estimate $G_{\mathrm{RRHO}}(T)$ from harmonic frequency estimate

$$\Delta G_{\mathrm{RRHO}}(T) = \sum_p \frac{\hbar\omega_p}{2} + k_B T \sum_p \left[\ln\left(1 - \mathrm{e}^{-\frac{\hbar\omega_p}{k_B T}}\right)\right],$$

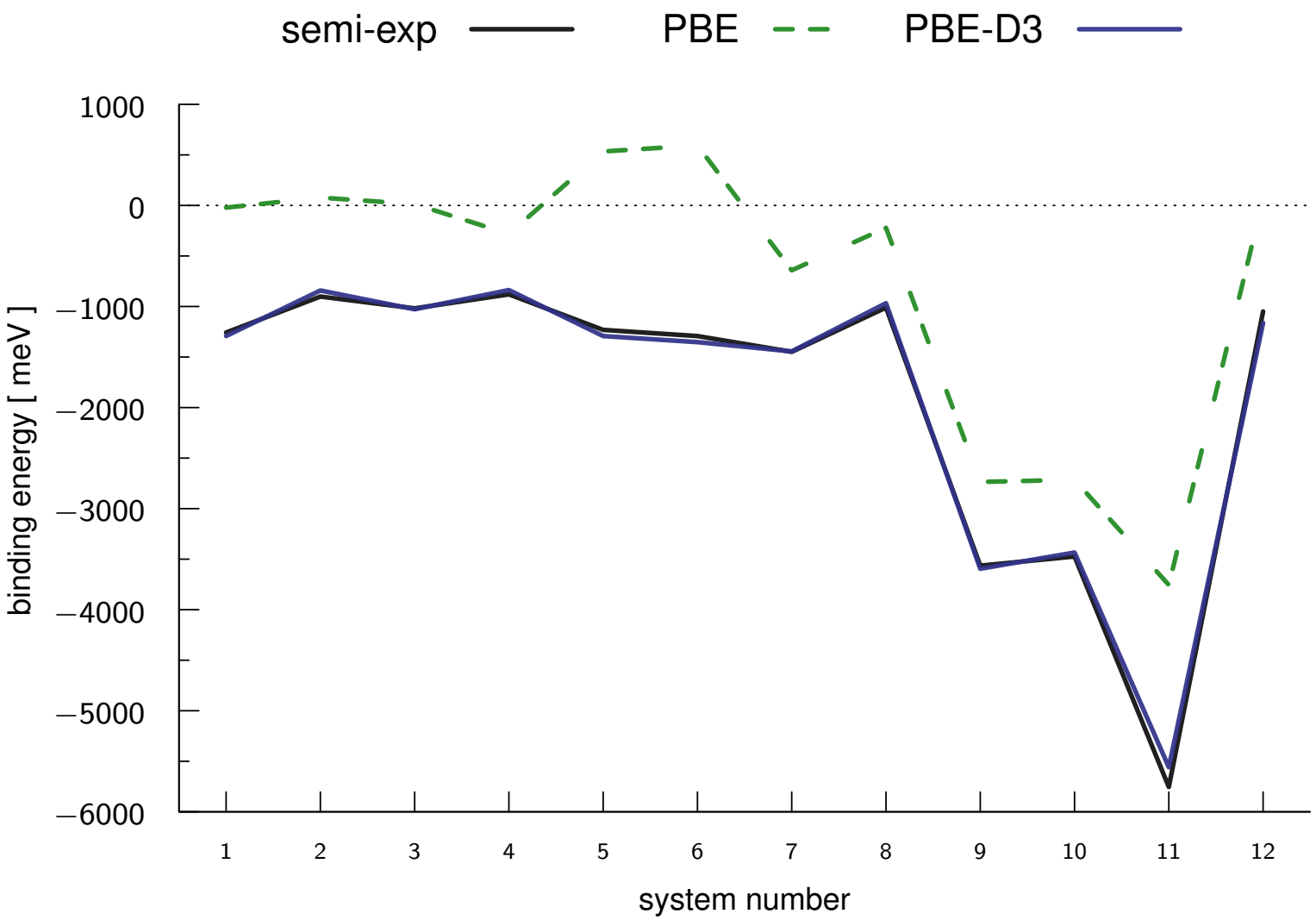
  $\longrightarrow$ error of about 3%

- estimate $\Delta\delta G_{\mathrm{solv}}$ from implicit solvation model
  $\longrightarrow$ error of about 5-10%

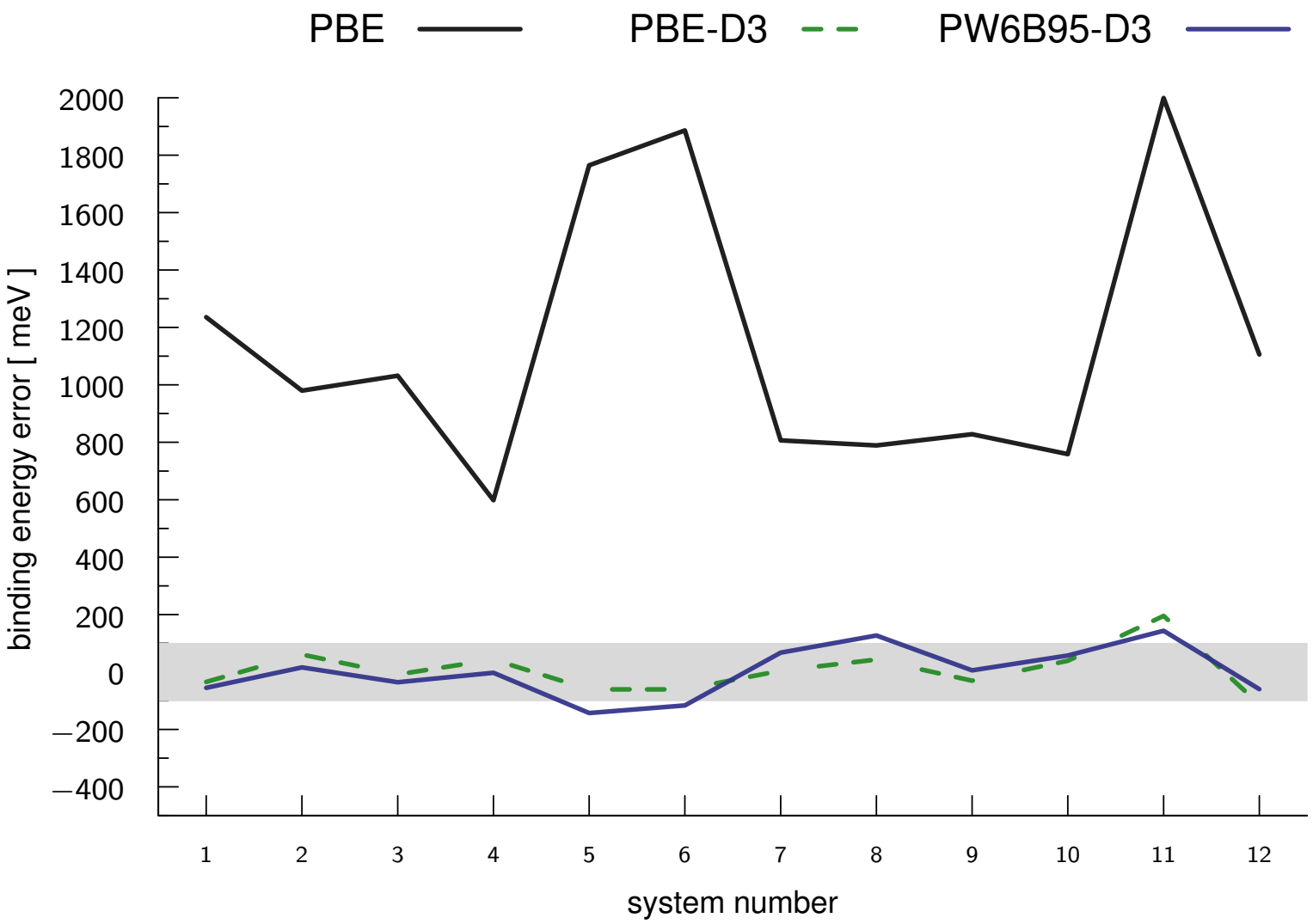
- remove contributions yielding semi-experimental ΔE
  $\longrightarrow$ error of about 5-10% $\equiv$ 100 meV

[3] S. Grimme, *Chem. Eur. J.*, **18**, 9955 (2012)

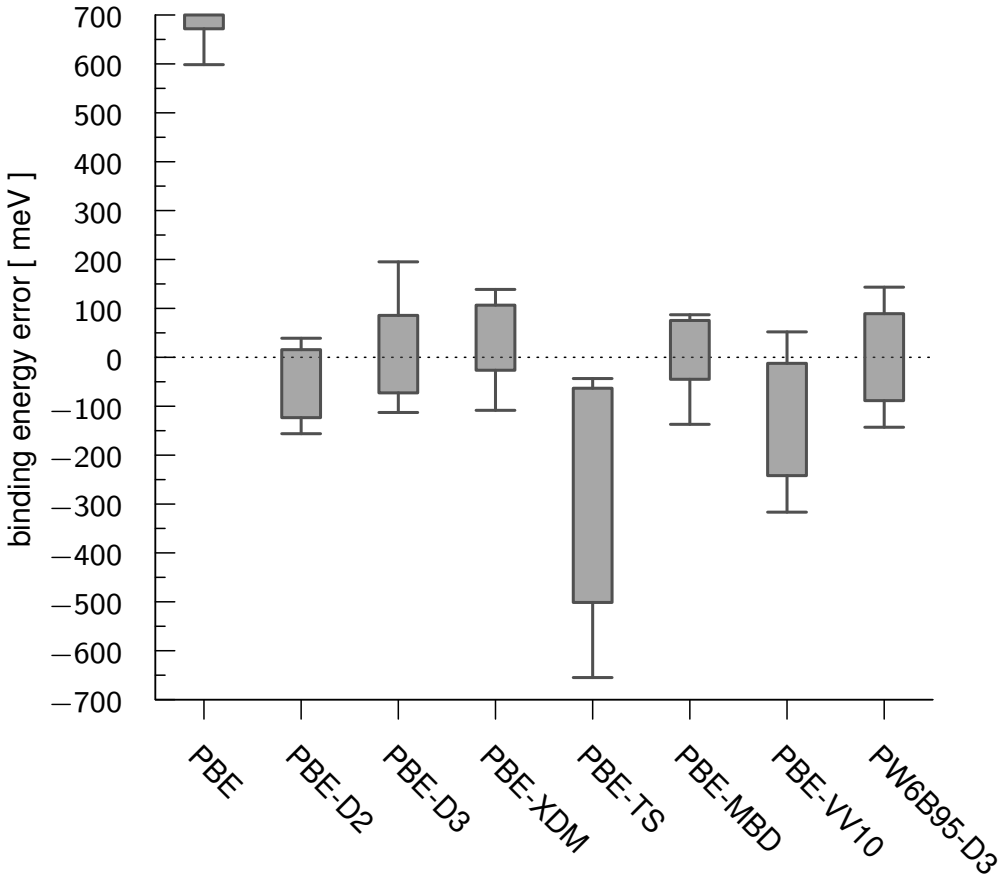
S12L: Supramolecular complexes



S12L: Supramolecular complexes

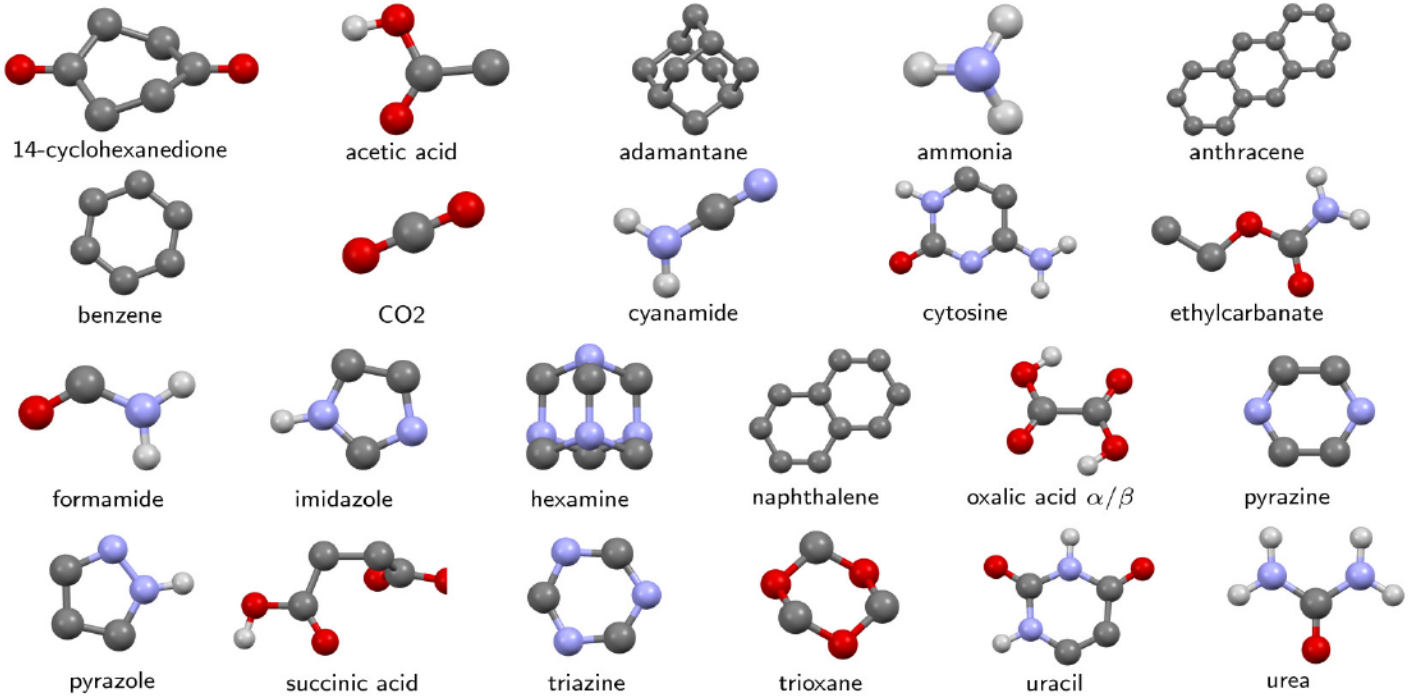


S12L: Supramolecular complexes



- some pair-wise methods are problematic

X23: molecular crystals

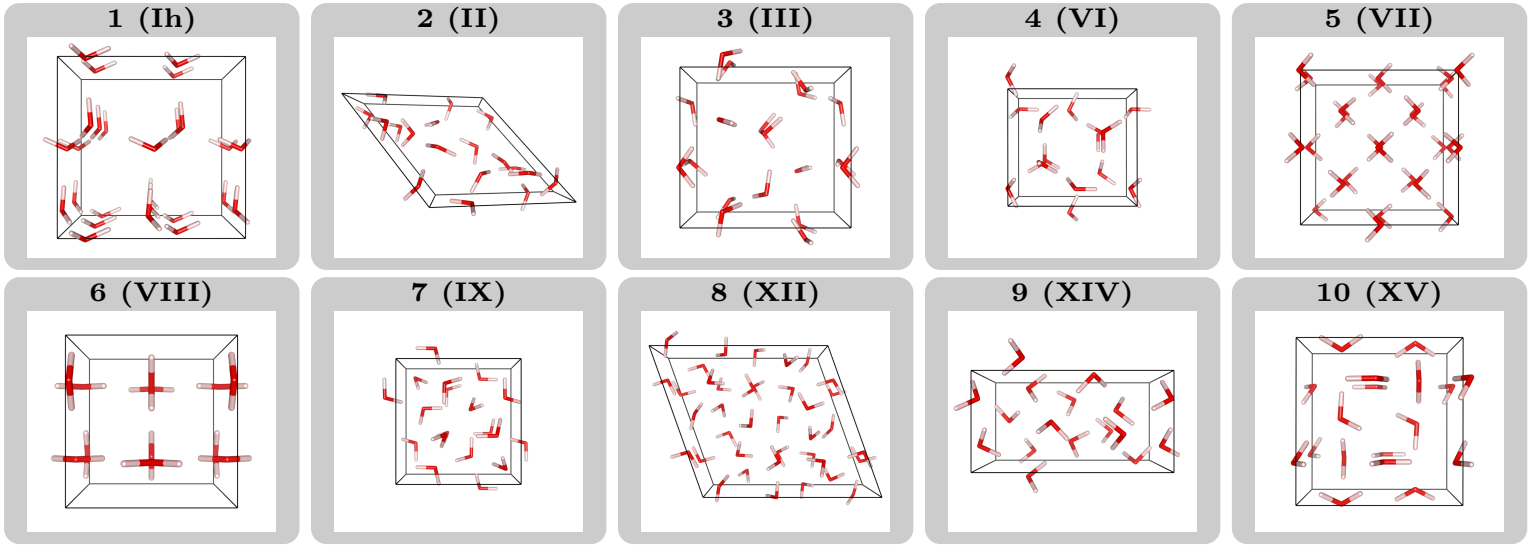


- molecular crystals of small molecules, emphasis on vdW bonding

[4] A. Otero-de-la-Roza, E. R. Johnson, *J. Chem. Phys.* **137**, 054103 (2012).

[5] A. M. Reilly, A. Tkatchenko, *J. Chem. Phys.* **139**, 024705 (2013)

ICE10: Ice polymorphs



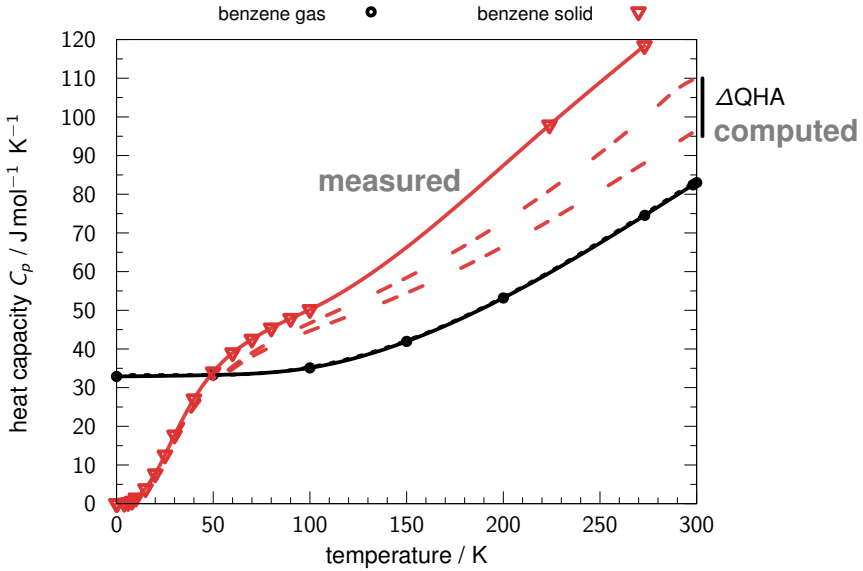
- ice polymorphs at varying density
- focus on strong hydrogen bonds, i.e. induction and exchange effects

[6] JGB, T. Maas, S. Grimme, *J. Chem. Phys.* **142**, 124104 (2015).

X23/ICE10: Molecular crystals

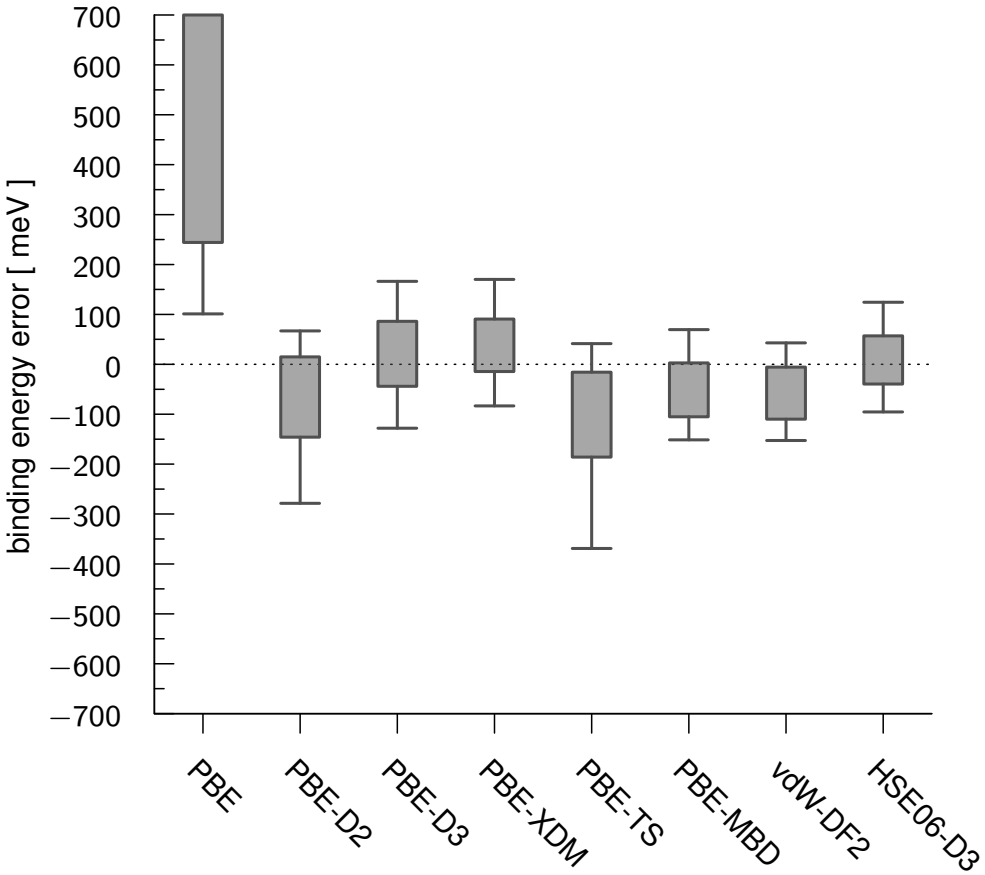
$$E_{\text{latt}} = -\Delta H_{\text{sub}}(T) + \Delta E_{\text{ZPVE}} + \int_0^T \Delta C_p(T')\,\mathrm{d}T'$$

- measured sublimation enthalpy H_{sub}
- zero-point energy from phonon modes
- thermal contribution from heat capacities (measured or computed)



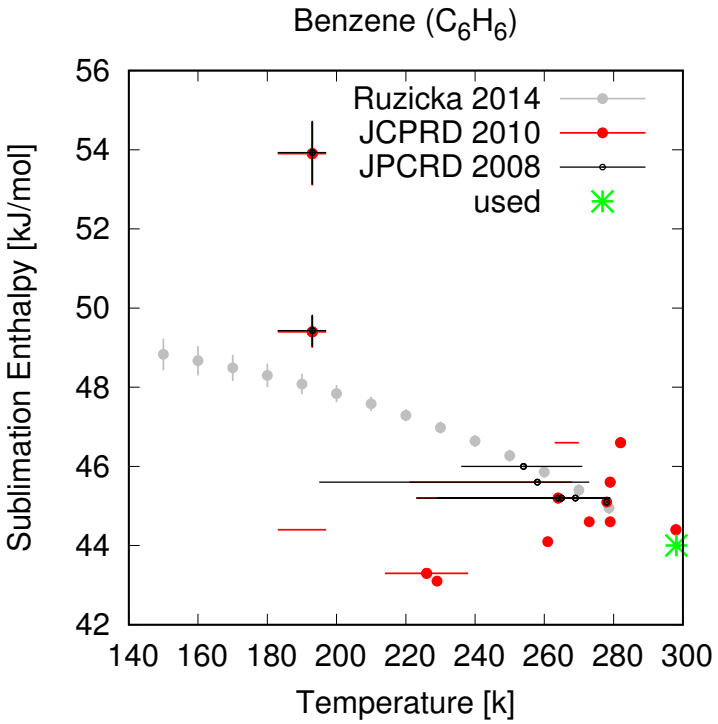
$\longrightarrow$ error of about 5% $\equiv$ 50 meV

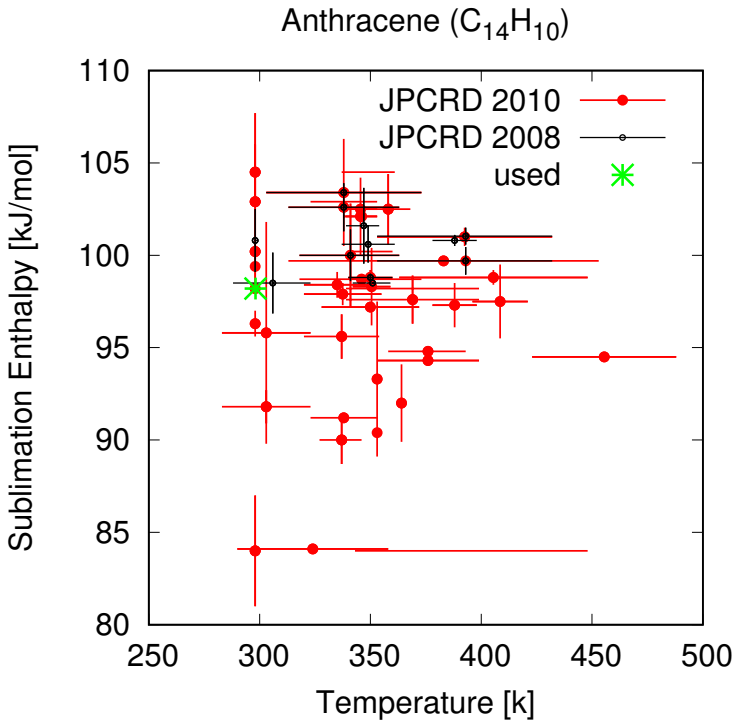
X23/ICE10: Molecular crystals



- older pair-wise methods (D2, TS) should be avoided
- other uncertainties within error margins of references

Significant uncertainties in lattice energy references



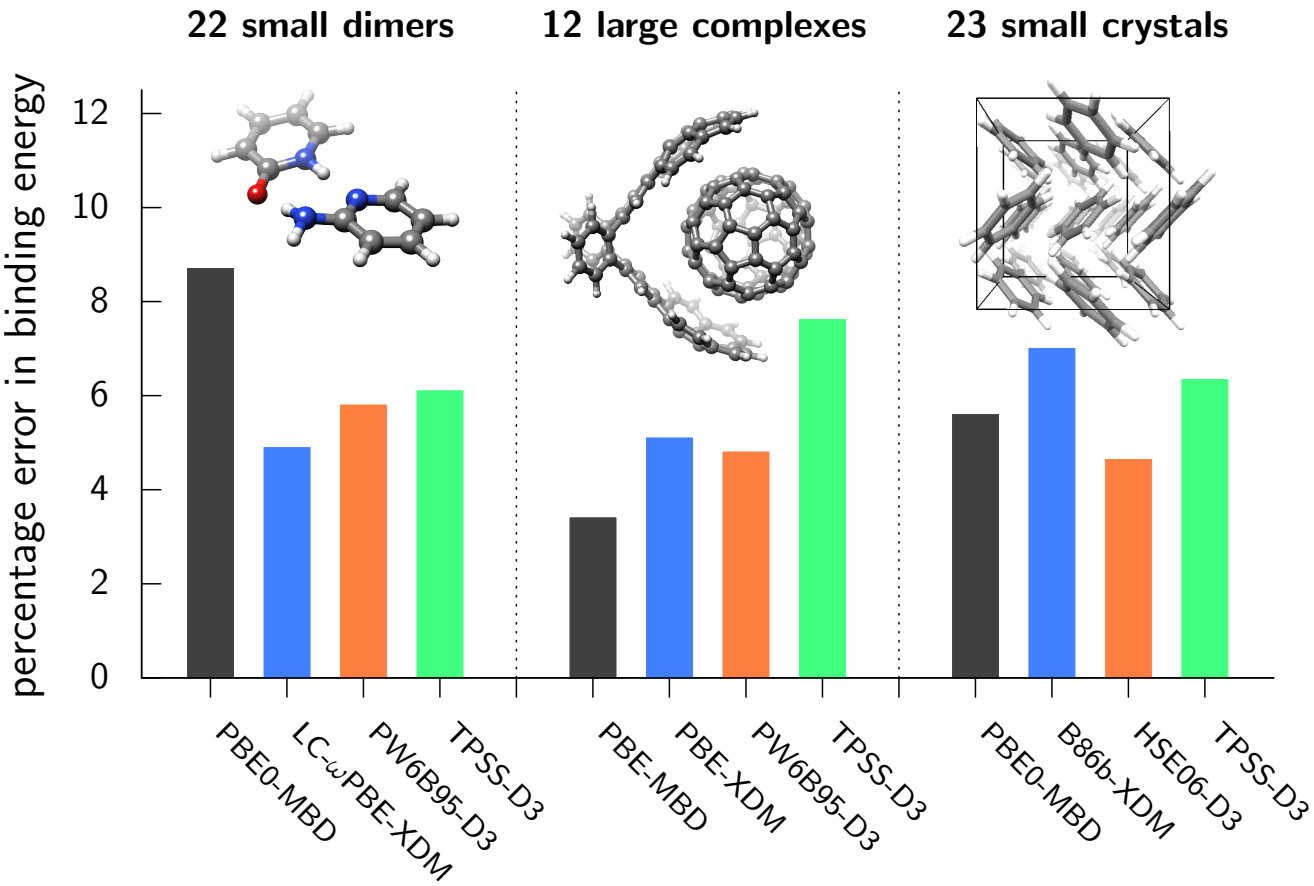


- measure H_{sub}, statistical survey yields error of $\sim 50\,\text{meV}$

  $\rightarrow$ High-level references needed

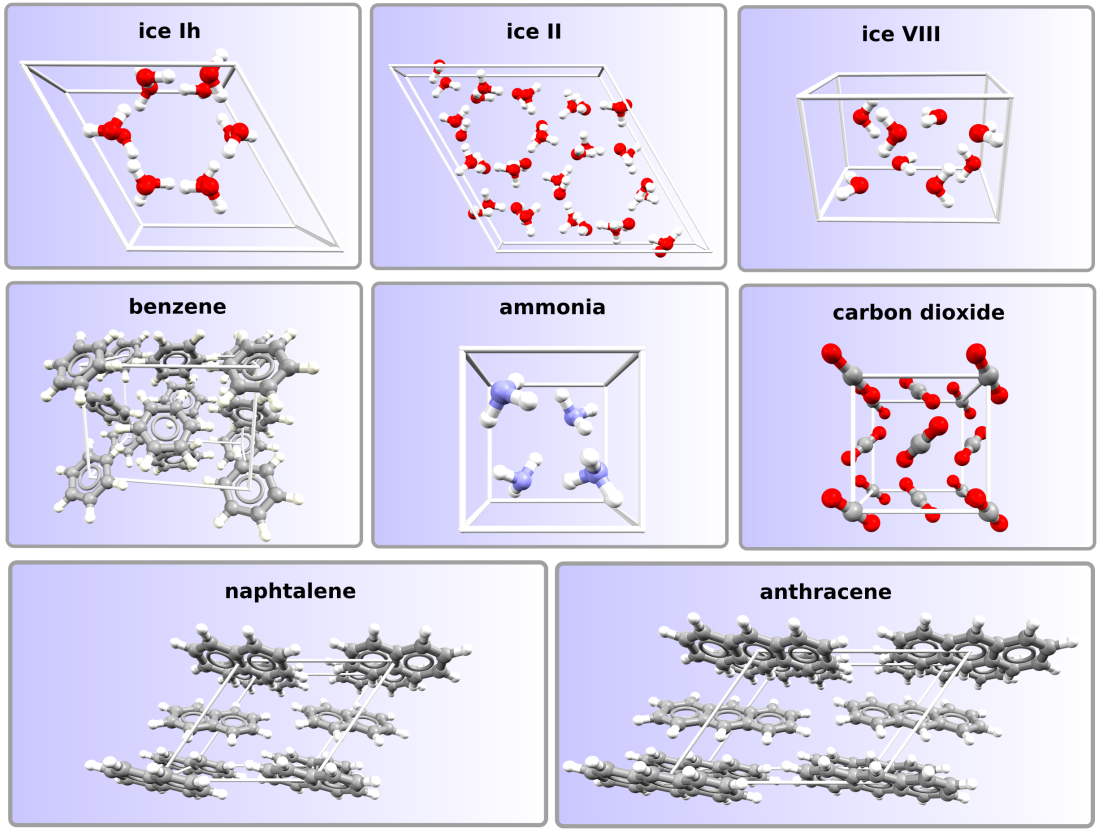
[7] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* **39**, 043101 (2010).

Summarized performance on NCI benchmark sets



- different dispersion corrected DFAs yield high quality results
- for S12L and X23 errors within reference uncertainties

DMC8: Molecular crystals

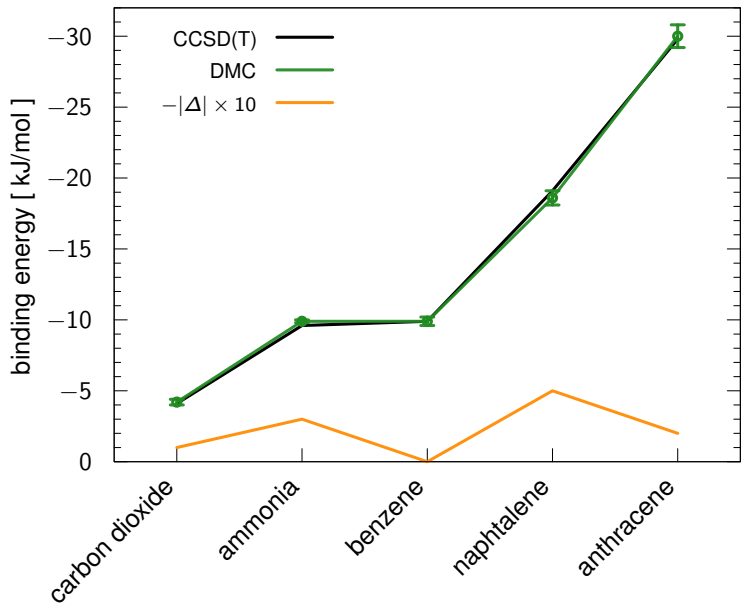


- diffusion Monte-Carlo to compute reference energies
- use subset of challenging X23/ICE10 crystals

[8] A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *Proc. Natl. Acad. Sci. U.S.A*, **115**, 1724 (2018).

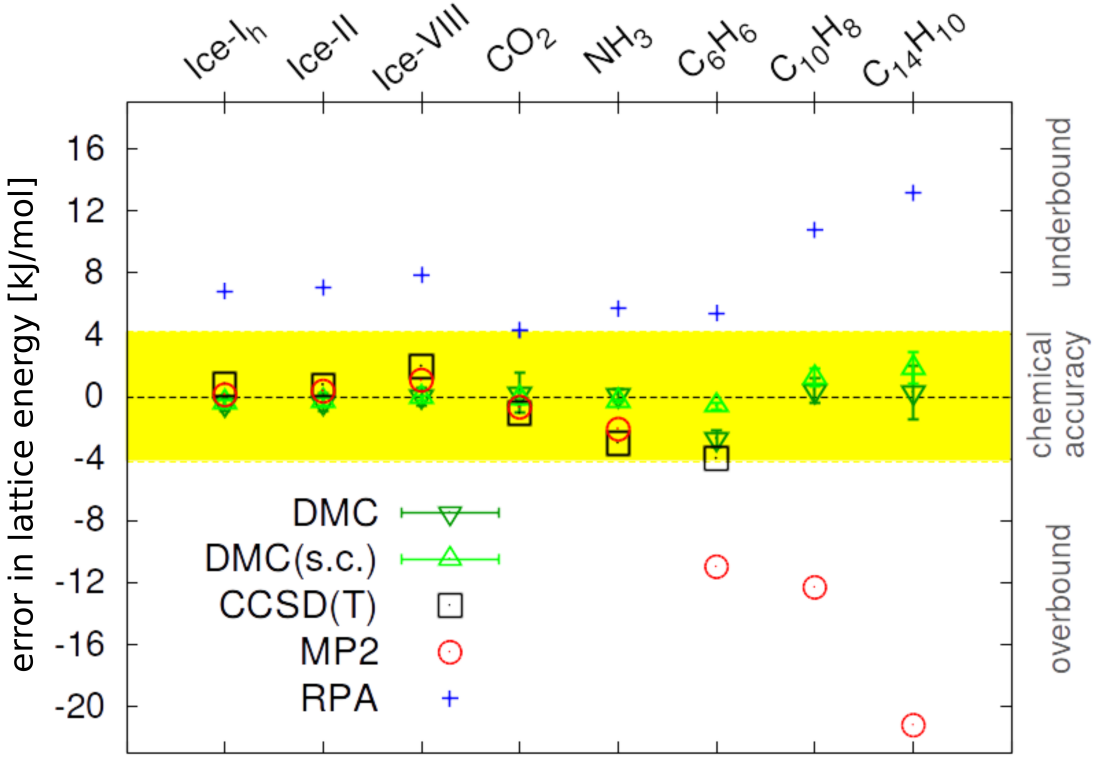
Close agreement between CCSD(T) and DMC on dimers

- dimers extracted from crystal structure
- CCSD(T)-F12 / cc-pV(T,Q)Z-F12 for CO_2 and NH_3
- L-DLPNO-CCSD(T) / cc-pV(T,Q)Z (tight settings)
- largest deviation of 0.5 kJ/mol $\equiv$ 5 meV



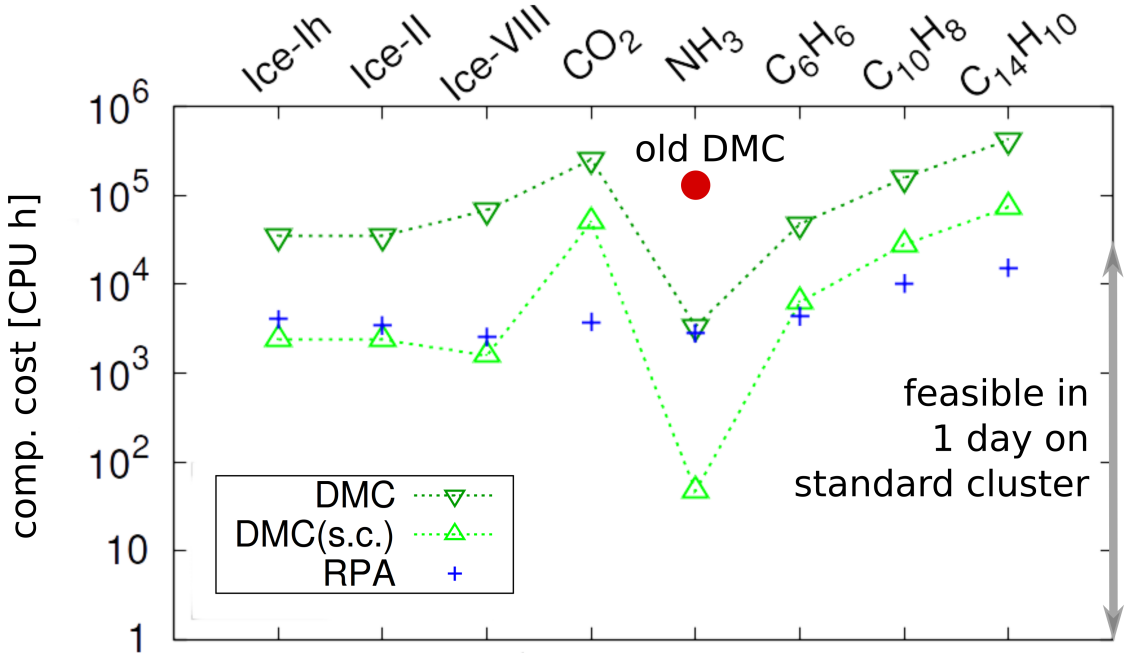
$\rightarrow$ good agreement between different high-level methods

QMC delivers (sub-) chemical accuracy for all tested systems



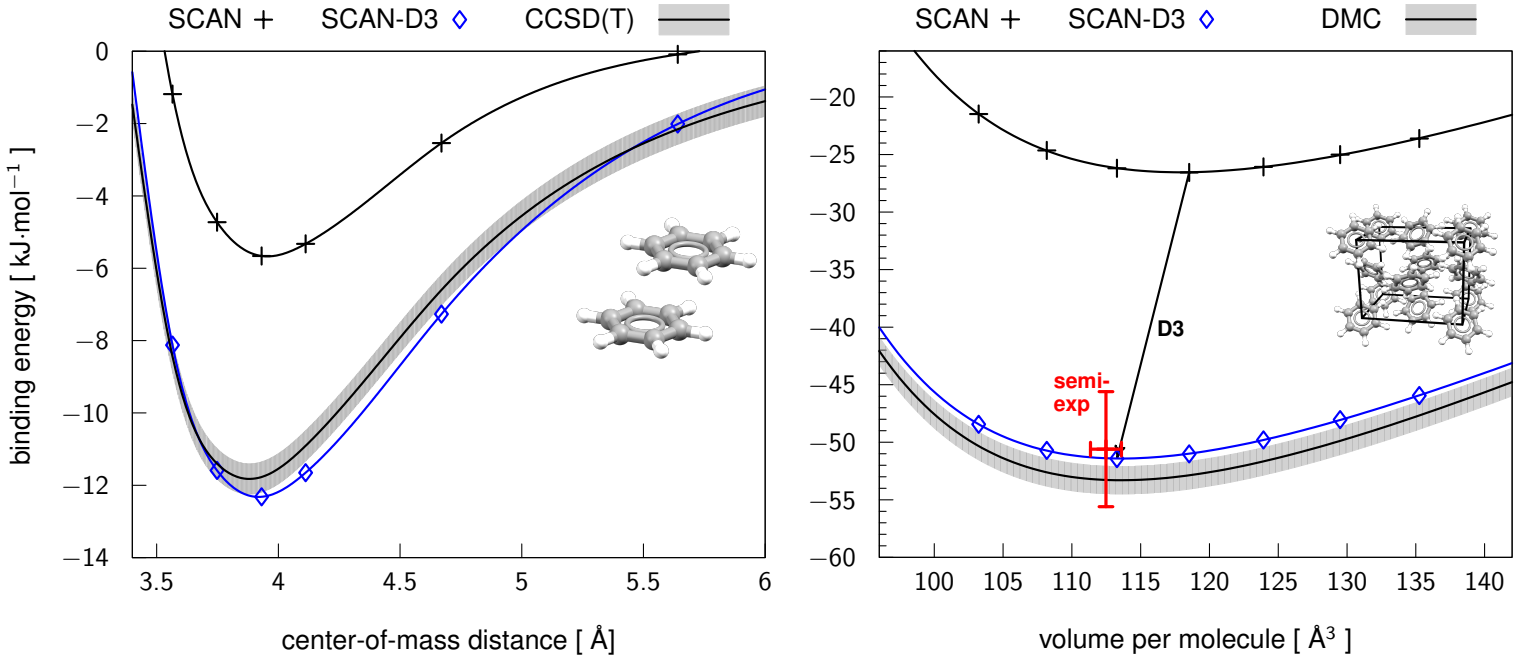
- excellent agreement with experiment and CCSD(T)
- uncertainty in $H_{\text{sub}}^{\text{exp}}$ larger than DMC errors

QMC is feasible within one day on standard computer cluster



- up to three orders of magnitude speed-up compared to best DMC practice two years ago

Testing modern density functionals with reference data



- zero-point and thermal effects crucial for comparing to measurement
- new references valuable for testing approximate methods

Outline of talk

DFT methods crucial for genration of reliable geometries

	task/property	example method
accurate QM	single-point energy	many-body WFT
cheap QM	optimization	DFT
very cheap QM	optimization/Hessians conformations	semi-empirical
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

Generation of reference data: Small molecules

Variant 1: Optimize using high-level method

- clear comparison with lower level theory
- CCSD(T)/CBS with at least triple-ζ quality basis
- only affordable for 2-4 atom molecules

Variant 2: Use experimentally measued geometries

- X-ray: small noise, but effect of temperature, zero-point motion, crystal packing effect unclear
- Jet-expansion: only rotational constants, effect of zero-point motion

Generation of reference data: Small to medium sized molecules

Semi-experimental structure:

- measure rotational constants at low temperature
- estimate zero-point effects to get equilibrium value

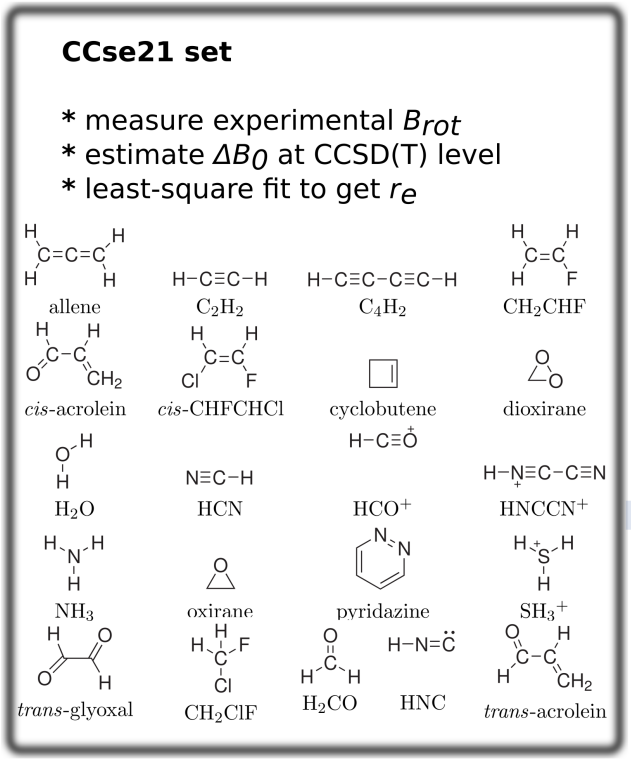
$$
\begin{aligned}
(B_e^\beta)^{\mathrm{SE}} &= (B_0^\beta)^{\mathrm{EXP}} - (\Delta B_0^\beta)^{\mathrm{QM}} \\
(\Delta B_0^\beta)^{\mathrm{QM}} &= \Delta B_{el}^\beta + \Delta B_{vib}^\beta \\
&= \frac{m_e}{m_P} g^{\beta\beta} B_e^\beta - \sum_i \frac{\alpha_i^\beta d_i}{2} \\
(B_e^\beta)^{\mathrm{QM}} &\propto 1/I^\beta
\end{aligned}
$$

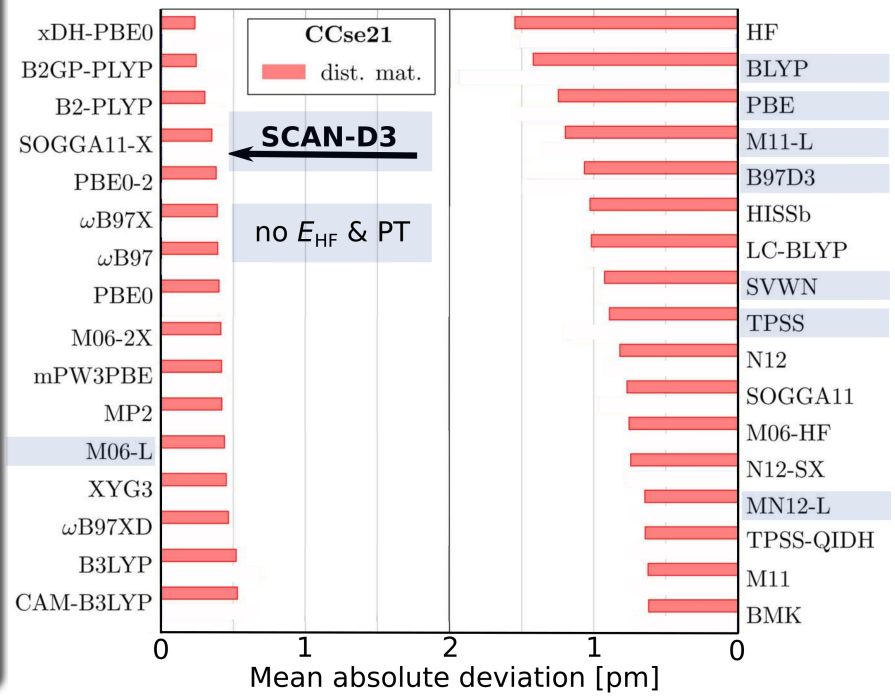
- directly compare $B^\beta \rightarrow$ just averaged structure
- fit coordinates to minimize $\Delta(B_e^\beta)^{\text{QM-SE}} \rightarrow$ full geometry model

[9] C. Puzzarini, M. Heckert, J. Gauss, *J. Chem. Phys.* **128**, 194108 (2008).

[10] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* **15**, 16031 (2013).

Benchmark set of Barone and coworkers



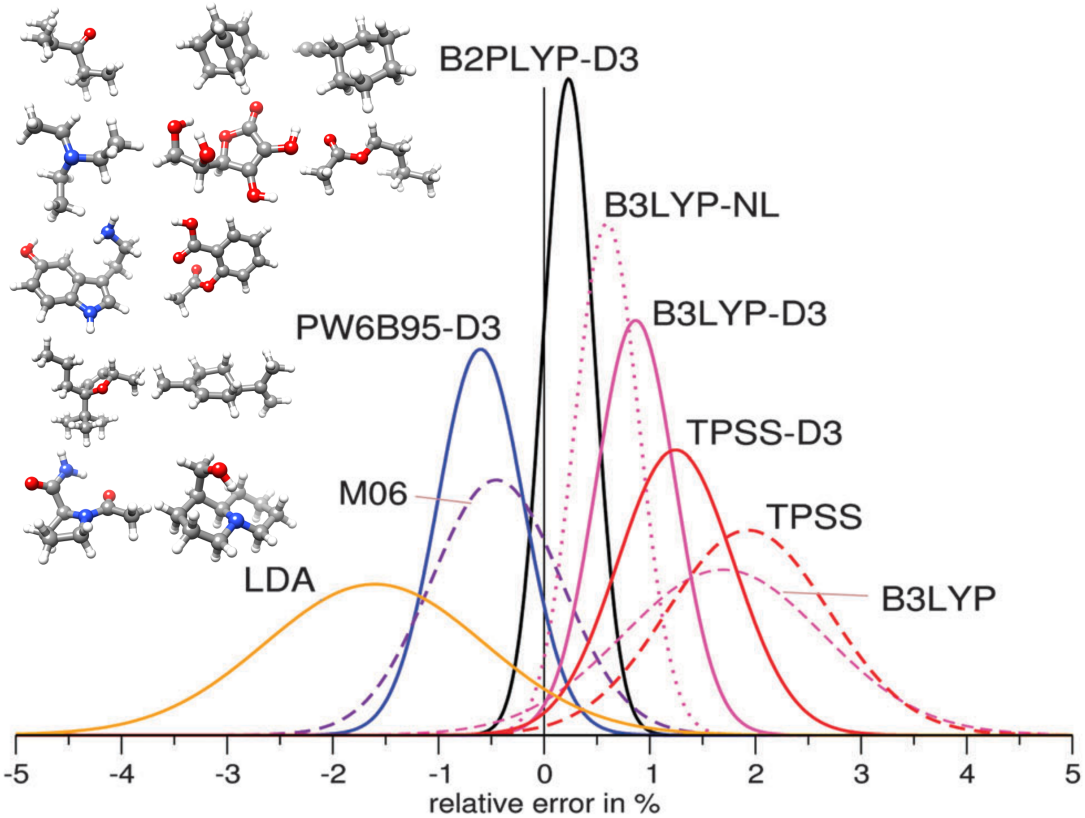


- errors vary from 1.5 to 0.2 pm
- DFAs including E_{HF} and E_{PT2} perform best
  $\rightarrow$ unfortunately those are unreliable for heavier elements

[11] M. Piccardo, E. Penocchio, C. Puzzarini, M. Biczysko, V. Barone, *J. Phys. Chem. A*, **19**, 2058 (2015).

[12] É. Brémond, M. Savarese, N. Q. Su, A. J. Pérez-Jiménez, X. Xu, J. C. Sancho-García, C. Adamo, *JCTC* **12**, 459 (2016).

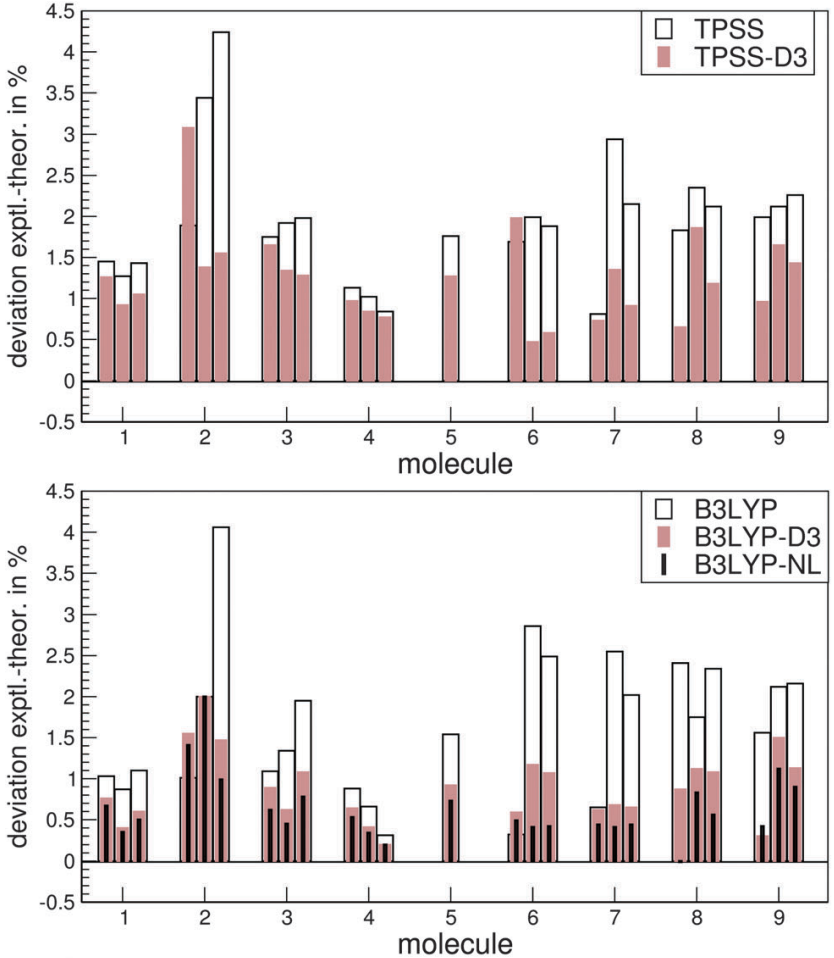
Benchmark set of Grimme and coworkers: ROT34



- hierarchy according to Jacobs ladder, once vdW corrections are included

[10] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* **15**, 16031 (2013).

Benchmark set of Grimme and coworkers: ROT34



- vdW corrections improve geometries by a factor of 2

[10] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.* **15**, 16031 (2013).

Generation of reference data: Intermolecular distances

Interpolate specific coordinate

- use fixed monomer geometries
- coordinate can be center-of-mass distance of dimers (S66x8 set)
  $\rightarrow$ interpolate with smooth cubic splines
- coordinate can be unit cell volume
  $\rightarrow$ interpolate with equation of state, e.g. third-order Birch-Murnaghan

$$E = E_0 + \frac{B_0 V}{B_0'(B_0' - 1)} \left(B_0' \left(1 - \frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^{B_0'} - 1 \right)$$

- extract binding energy E_0, unit cell volume V_0, bulk modulus B_0 and its derivative B_0'

Generation of reference data: Intermolecular distances

Extract from diffraction data

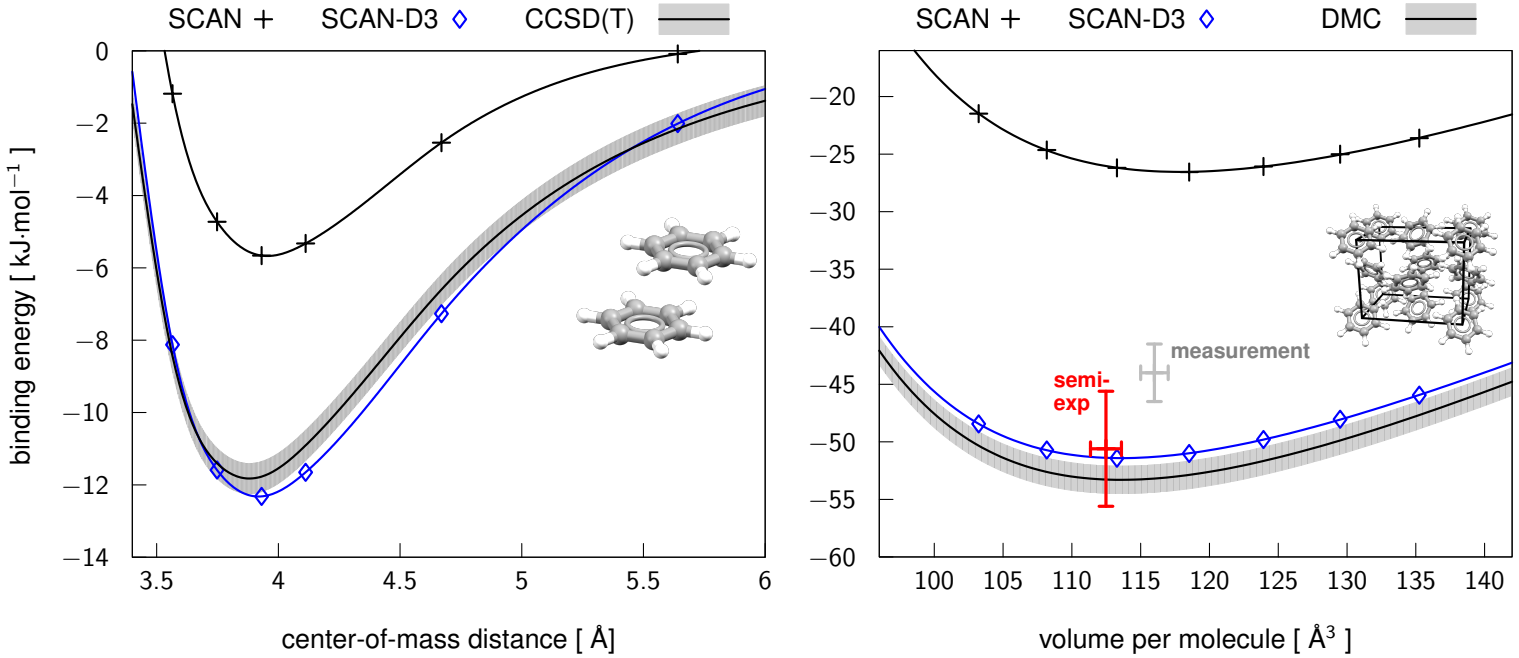
- use measured unit cells of molecular crystals
- estimate thermal expansion
  $\rightarrow$ experimental extrapolation to 0 K
- estimate nuclear quantum effects
  $\rightarrow$ path-integral molecular dynamics (potential surface accurate enough?)
  $\rightarrow$ quasi-harmonic model for free energy

$$F^{\mathrm{QHA}}(T,V) = E_{\mathrm{latt}}(V) + F^{\mathrm{QHA}}_{\mathrm{vib}}(T,V)$$

$$F^{\mathrm{QHA}}_{\mathrm{vib}}(T,V) = \sum_{\mathbf{k},p} \frac{\hbar\omega_{\mathbf{k},p}(V)}{2} + k_B T \sum_{\mathbf{k},p} \left[\ln\left(1 - \mathrm{e}^{-\frac{\hbar\omega_{\mathbf{k},p}(V)}{k_B T}}\right)\right],$$

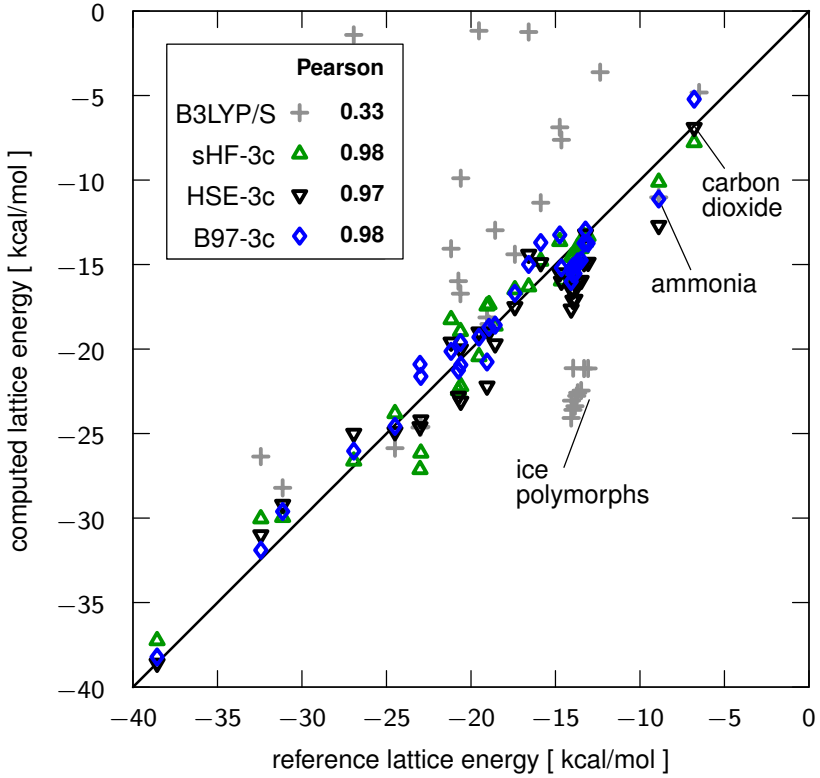
- minimize $F^{\mathrm{QHA}}(V)$ for given T yields free energy correction to unit cell volume

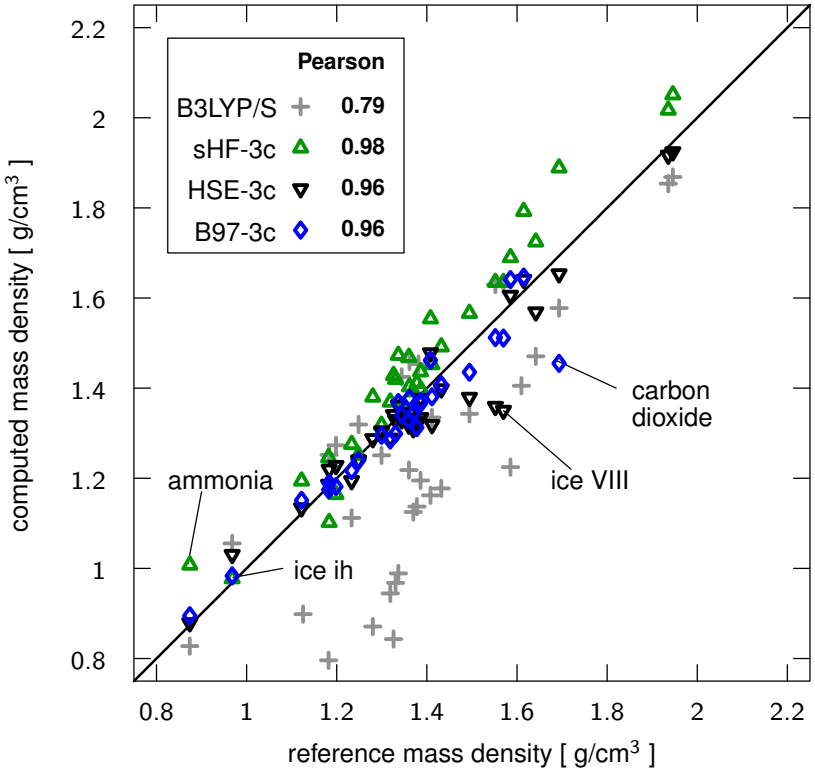
Intermolecular distances: Example of benzene



- zero-point and thermal effects crucial for comparing to measurement
- error in volume mainly from QHA back-correction (about 1%)

Lattice energy and mass density of 33 molecular crystals

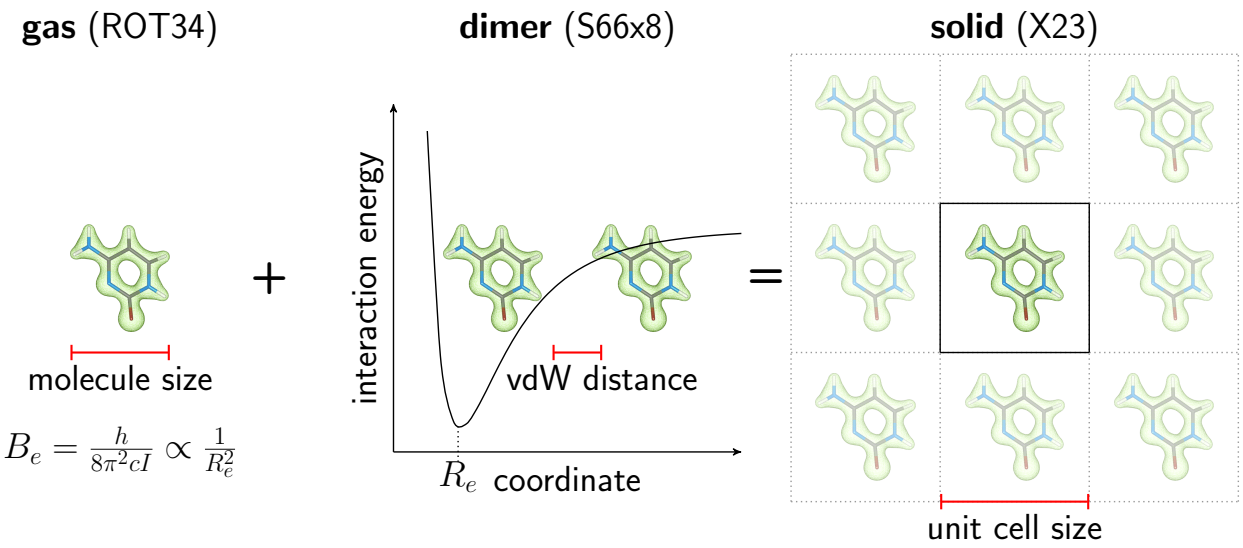




- vdW correction crucial for reasonable geometries
- few outliers due to problematic electrostatic/induction

[13] JGB, C. Bannwarth, A. Hansen, S. Grimme, *J. Chem. Phys.*, **148**, 64104 (2018).

Consistency from gas to solid phase



	ROT34 org. mol.	**S66x8** non-covalent	**X23** molecular crystal
TPSS/large basis	1.9	14.6	27.9
TPSS-D3/large basis	1.3	1.3	1.0
HF-3c (very cheap QM)	1.5	-1.2	-5.7
DFTB3-D3 (very cheap QM)	1.2	-2.9	-12.6
HSE-3c (cheap QM)	**0.2**	**1.3**	**0.7**

mean of relative deviation in %

Outline of talk

Numerical convergence & different functional approximations

- check literature if similar systems have been studied
- are high-level theory data available?
  $\rightarrow$ use those or generate your own
- are experimental references available?
  $\rightarrow$ be careful to compare the right observables
- converge all numerical thresholds
  (basis set, k-point sampling, SCF/geometry thresholds)
- different methods in terms of computational efficiency and accuracy
  $\rightarrow$ influence of XC treatment (PBE vs. BLYP vd. SCAN vs. PBE0)
  $\rightarrow$ vdW correction should always be included (D3, MBD, XDM, vdW-DF2)
- use affordable method with acceptable accuracy

  if none exist abandon project