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

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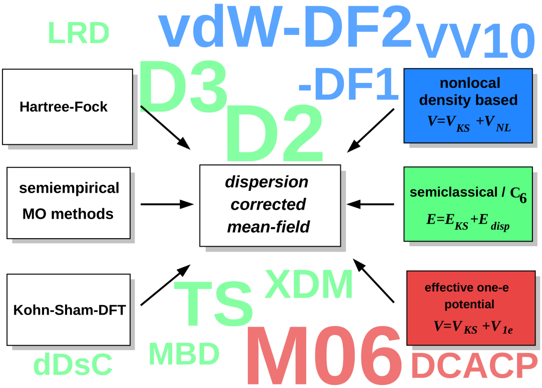
PHASG473 - UCL - ELECTRONIC STRUCTURE METHODS FOR MATERIALS MODELLING

London Centre for Nanotechnology
Department of Physics and Astronomy – University College London

Outline of talk

1. Benchmarking in the electronic structure community
2. Test sets for noncovalent interactions
3. Test sets for molecular and crystal geometries
4. Decision on method choice

Many good dispersion corrections exist



LRD
vdW-DF2
VV10
-DF1
D3
D2

Hartree-Fock

semiempirical MO methods

Kohn-Sham-DFT

dispersion corrected mean-field

nonlocal density based
$V = V_{KS} + V_{NL}$

semiclassical / C_6
$E = E_{KS} + E_{disp}$

effective one-e potential
$V = V_{KS} + V_{1e}$

TS
XDM
MBD
dDsC
M06
DCACP

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

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

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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

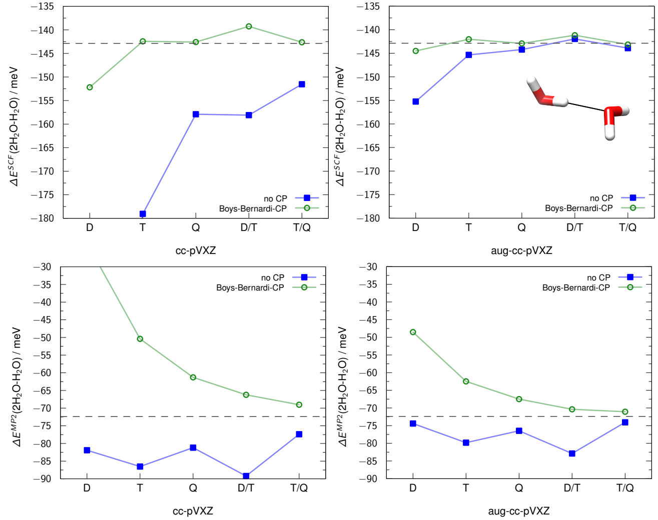
- established gold standard in quantum chemistry
- tight convergence of orbital basis set ⟶ aug-cc-pVQZ or better
- N^7 scaling with system size ⟶ linear-scaling variant for large systems

(2) Diffusion Monte-Carlo

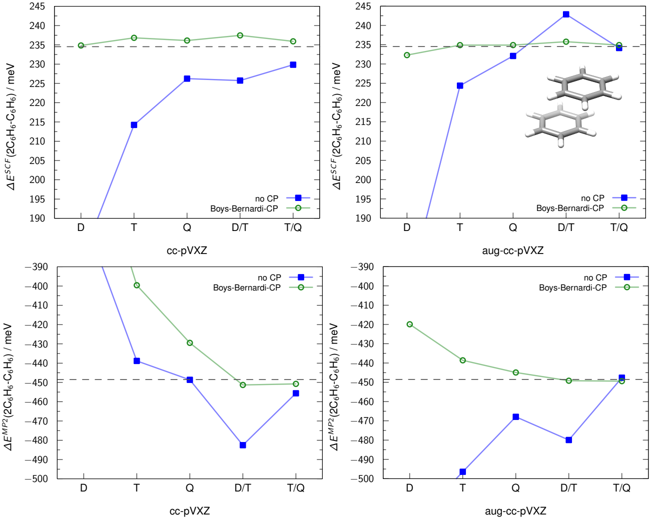
- capable of yielding CCSD(T) accuracy
- projection technique ⟶ basis set less crucial
- N^3 scaling with system size, scaleable to HPCs
- possible problems from fixed-node error and Jastrow optimization

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): $MAX = \max \{|x_i - r_i|\}$

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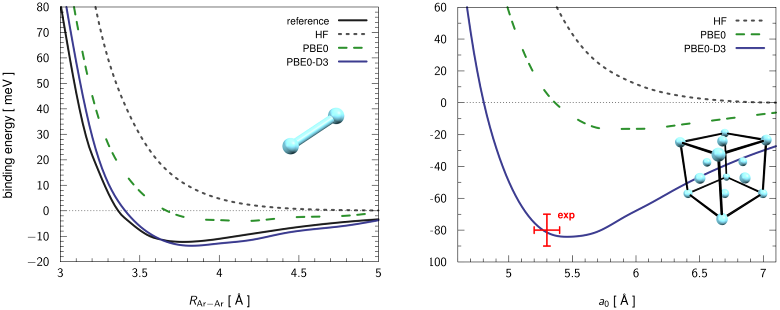
Guinea pig for testing vdW interactions

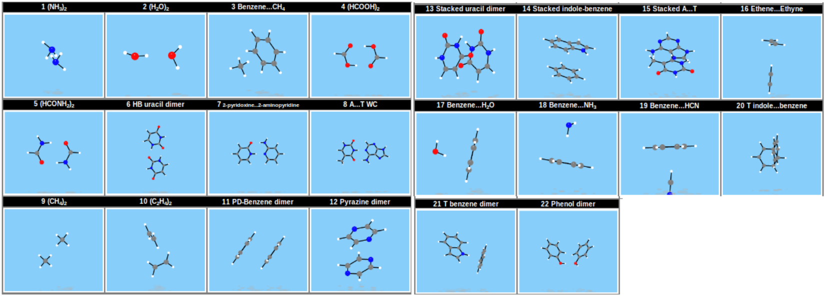
Noble gas assemblies



- 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

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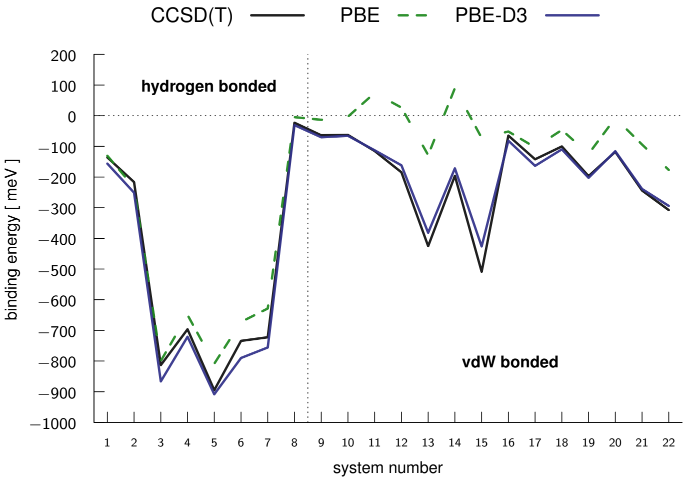
[1] P. Jurecka, J. Sponer, J. Cerny, P. Hobza, *Phys Chem Chem Phys*, **8**, 1985 (2006)

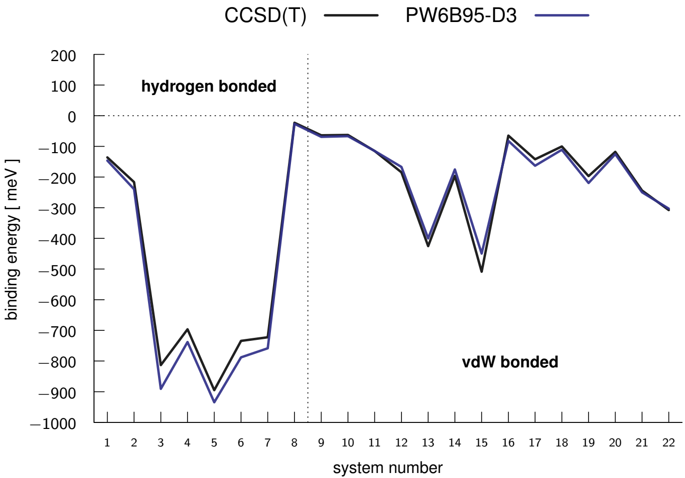
[2] T. Takatani, E. Hohenstein, M. Malagoli, M. Marshall, C. Sherrill, *J. Chem. Phys.*, **132**, 144104 (2010)

S22: Small molecular dimers



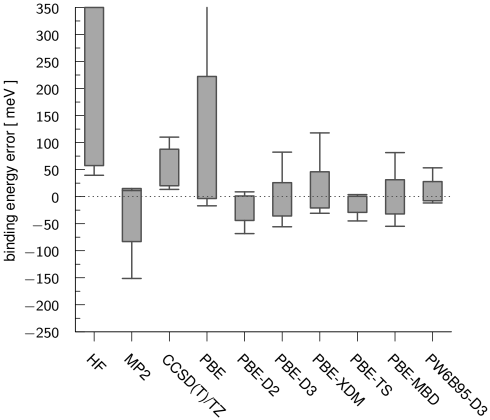
- vdW correction clearly improves plain PBE results
- PBE seem to overestimate hydrogen bondings

S22: Small molecular dimers



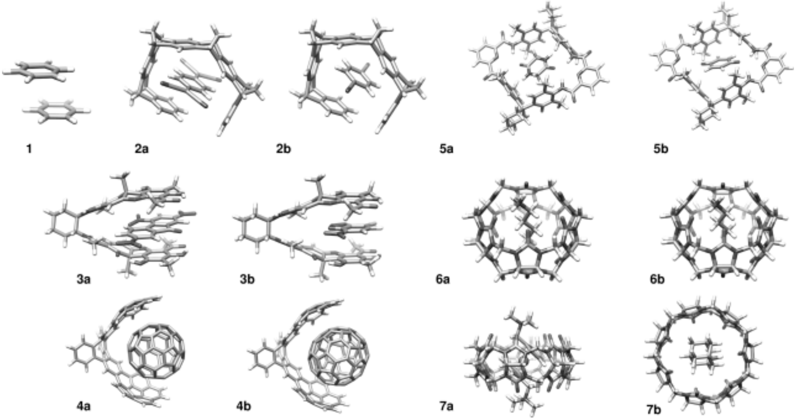
- semi-local functional can be as important as type of vdW correction

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

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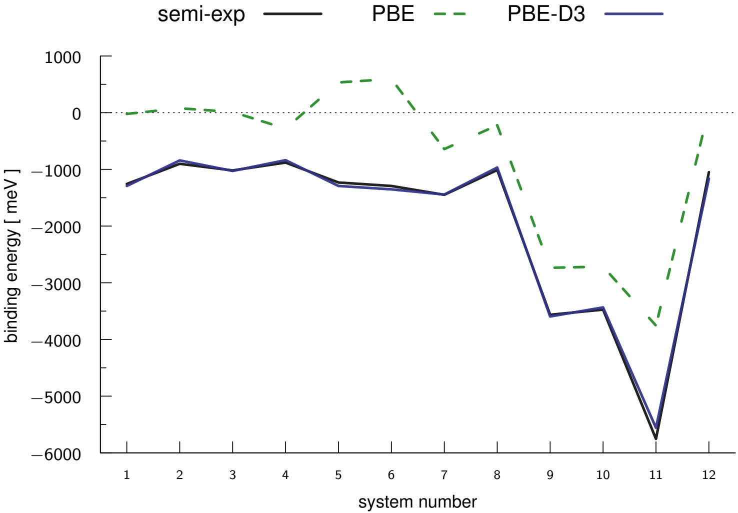
[3] S. Grimme, *Chem. Eur. J.*, **18**, 9955 (2012)

S12L: Supramolecular complexes



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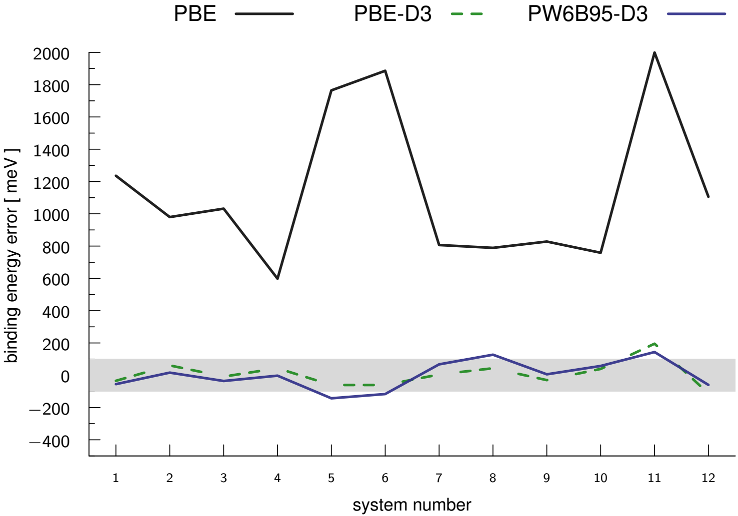
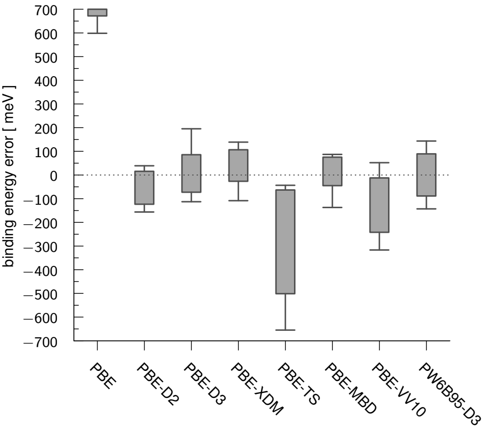
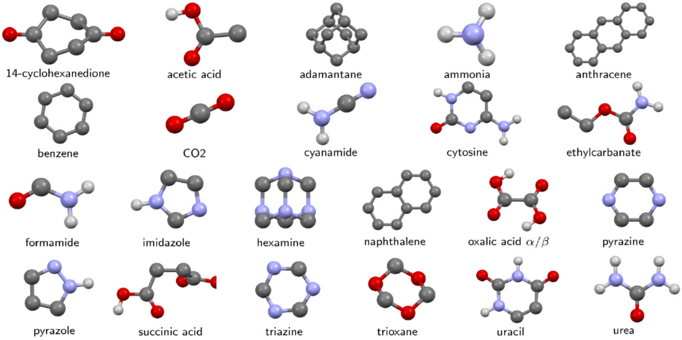


S12L: Supramolecular complexes



- some pair-wise methods are problematic

X23: molecular crystals



- molecular crystals of small molecules, emphasis on vdW bonding

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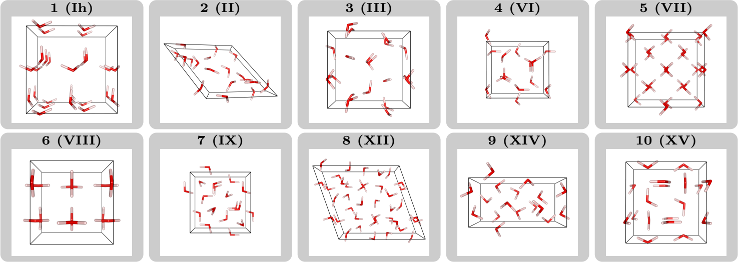
[4] A. Otero-de-la-Roza, E. R. Johnson, *J. Chem. Phys.* **137**, 054103 (2012).

[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

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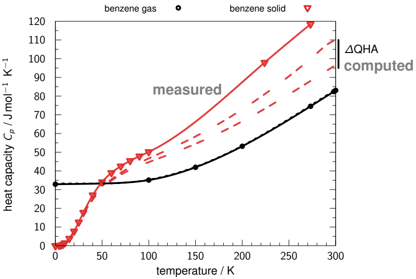
[6] JGB, T. Maas, S. Grimme, *J. Chem. Phys.* **142**, 124104 (2015).

X23/ICE10: Molecular crystals

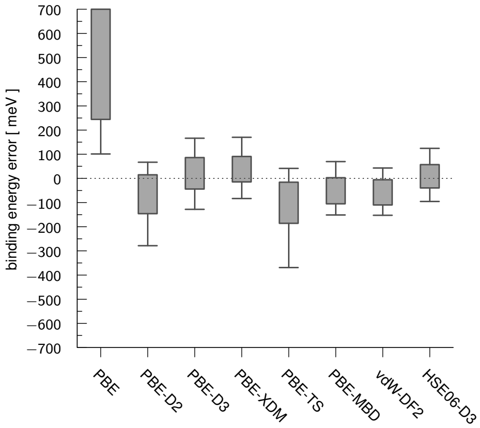
$$E_{\text{latt}} = -\Delta H_{\text{sub}}(T) + \Delta E_{\text{ZPVE}} + \int_0^T \Delta C_p(T')\,\mathrm{d}T'$$

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



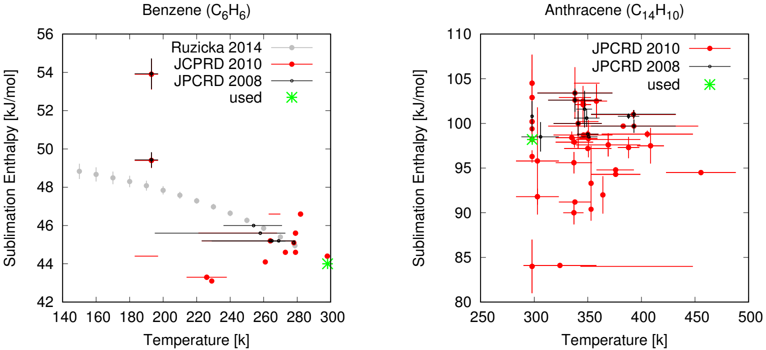
⟶ error of about 5% ≡ 50 meV

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 $\sim 50\,\text{meV}$

  → High-level references needed

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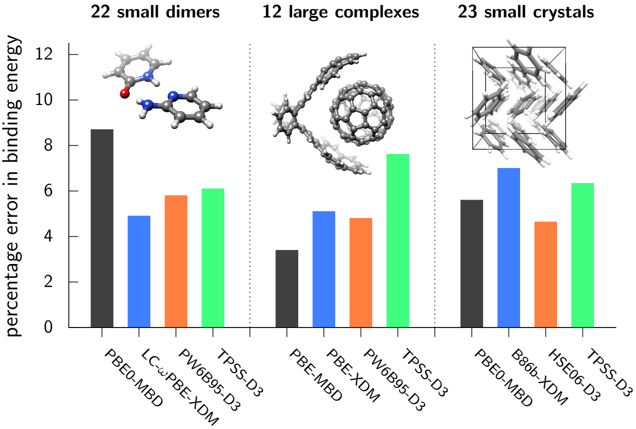
[7] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* **39**, 043101 (2010).

Summarized performance on NCI benchmark sets

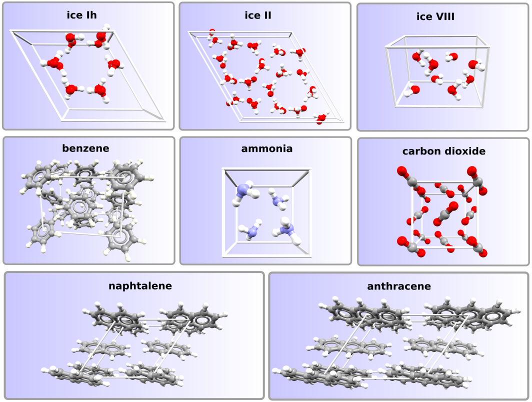

22 small dimers

12 large complexes

23 small crystals

- 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

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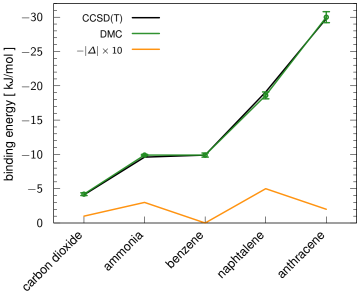
[8] A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *Proc. Natl. Acad. Sci. U.S.A*, **115**, 1724 (2018).

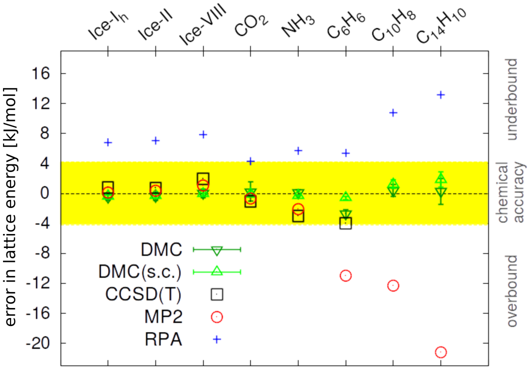
Close agreement between CCSD(T) and DMC on dimers

- 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 ≡ 5 meV



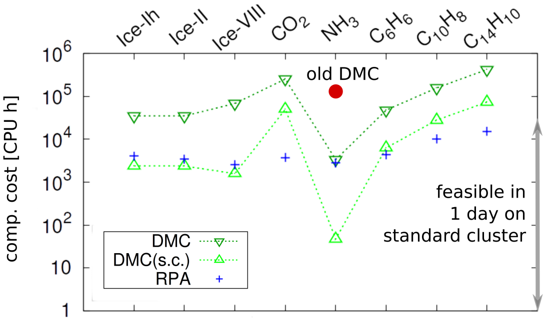
→ good agreement between different high-level methods

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



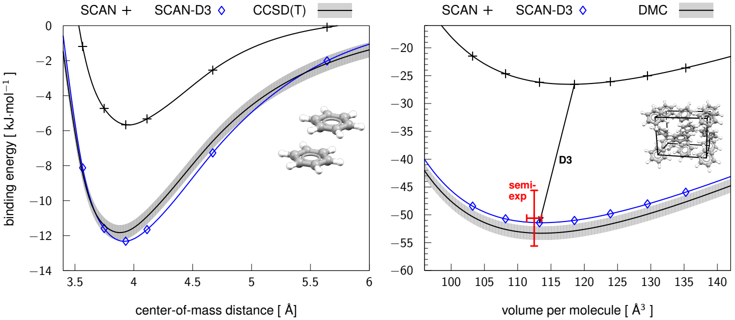
- excellent agreement with experiment and CCSD(T)
- uncertainty in $H_{\text{sub}}^{\text{exp}}$ larger than DMC errors

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

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