Excitation vs. projection techniques:
Towards sub-chemical accuracy for large noncovalent systems

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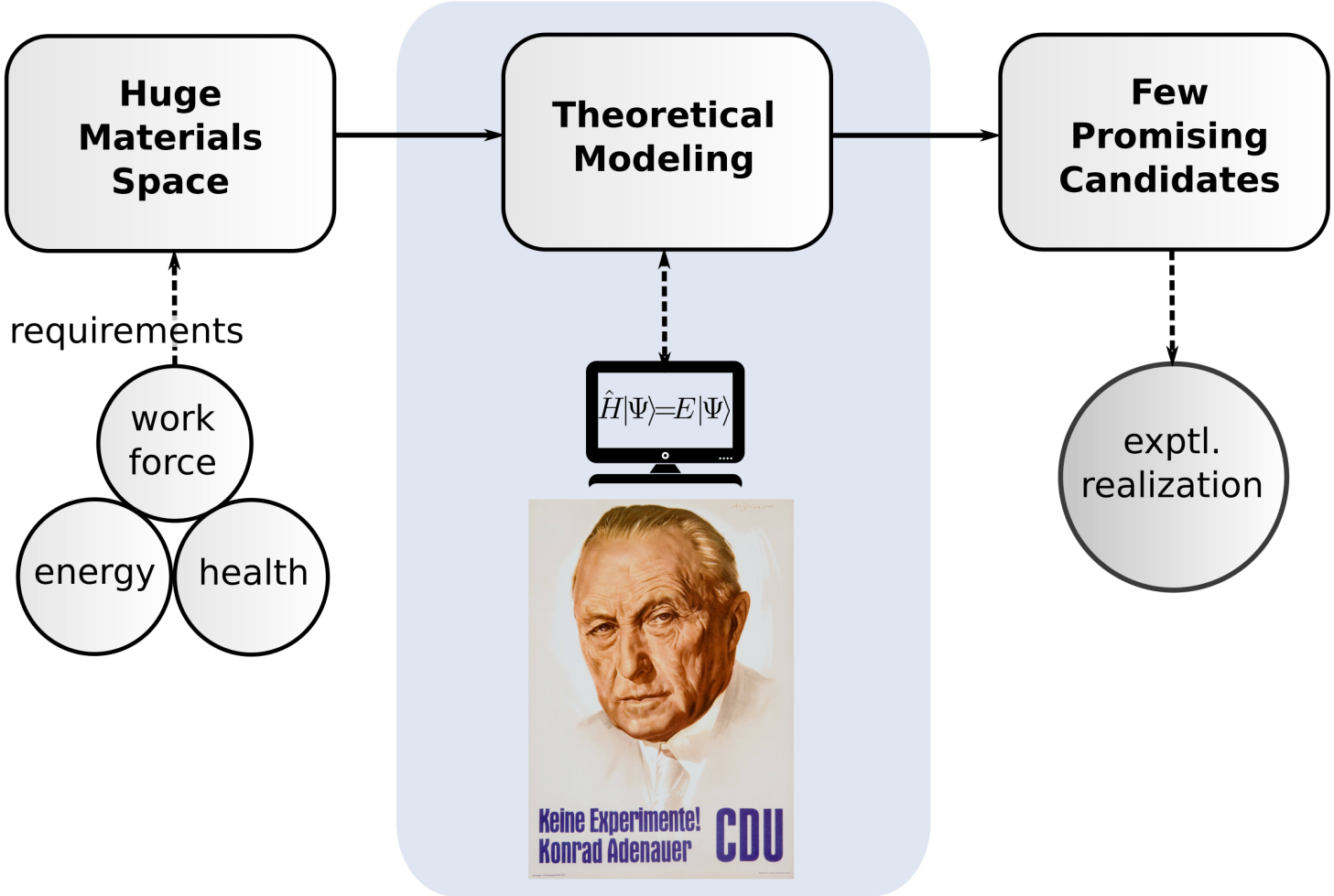
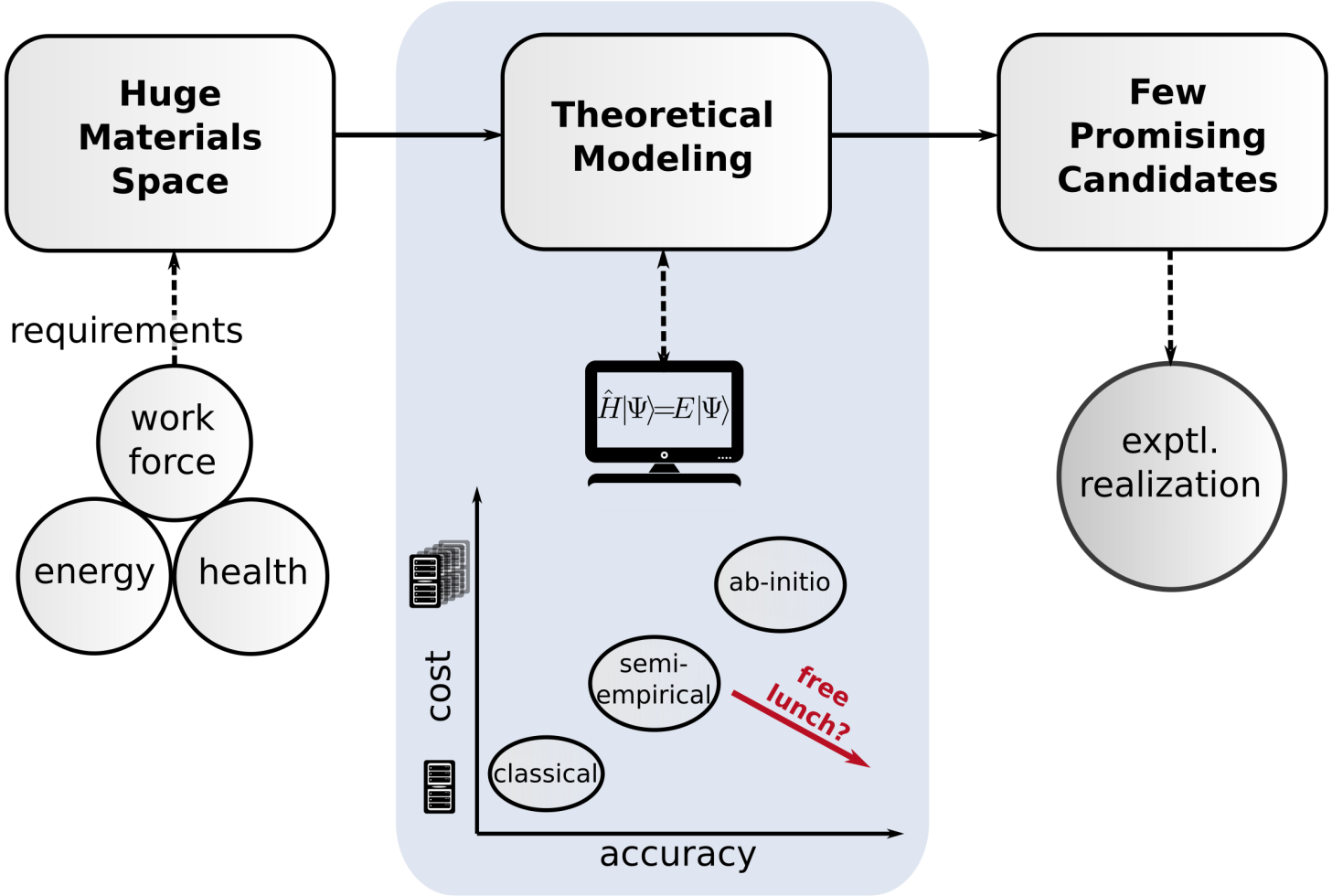
SPECIAL PROBLEMS IN QUANTUM CHEMISTRY, MULLIKEN CENTER FOR THEORETICAL CHEMISTRY, BONN, GERMANY

Outline of talk

Material discovery can employ computational models



Material discovery can employ computational models



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

Experimental vs. theoretical referencea

Experimental

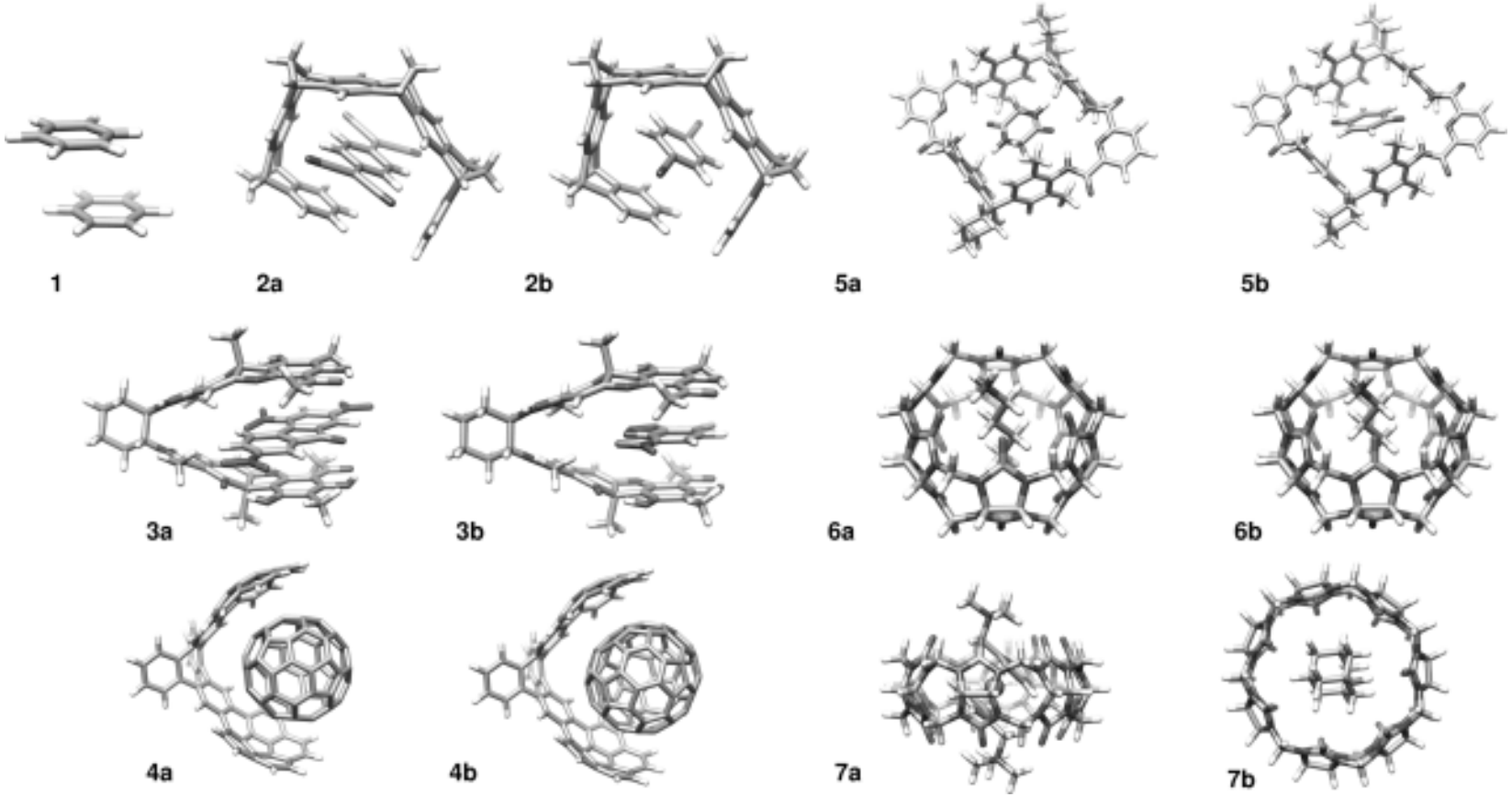
- final goal should be to describe experimental conditions
- possible for complex systems
- measurement uncertainty
- no separation of effects

Theoretical

- straight-forward comparison
- computational cost affordable?
- only possible for 'small enough' systems
- uncertainty of reference method

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

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

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

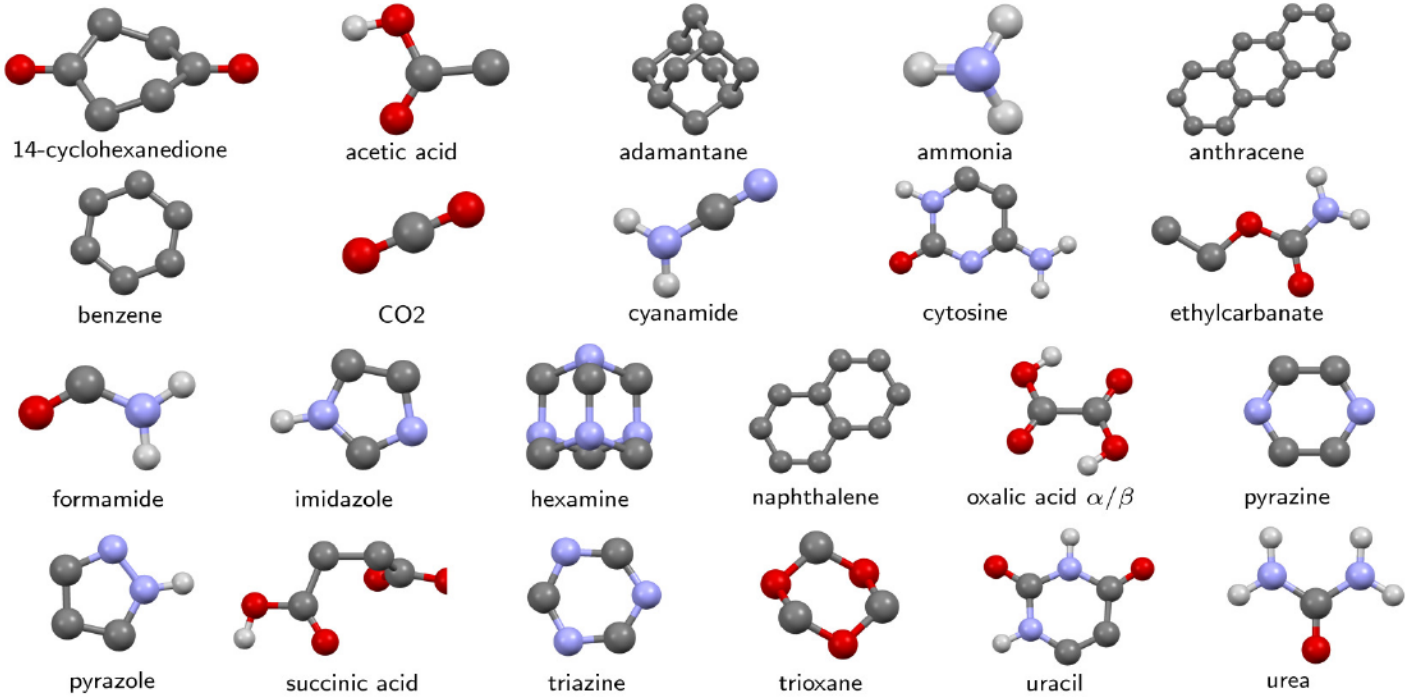
  $\longrightarrow$ error of about 3%

- 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**

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

X23: Molecular crystals

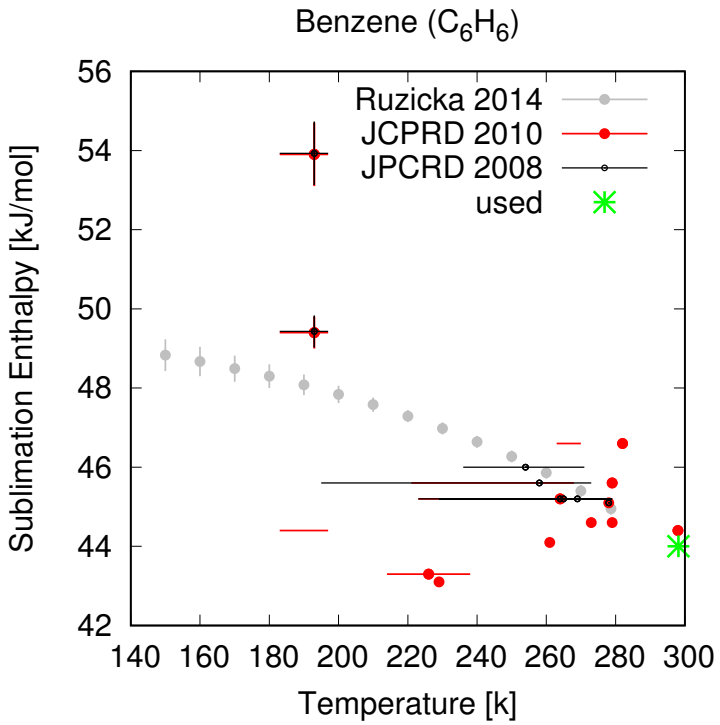


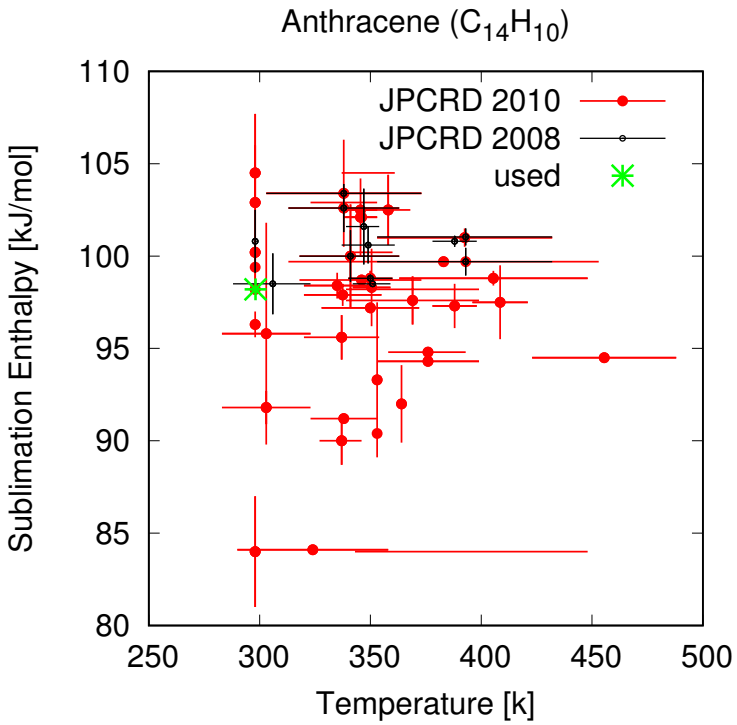
- molecular crystals of small molecules, emphasis on vdW bonding

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

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

Significant uncertainties in measured sublimation enthalpies





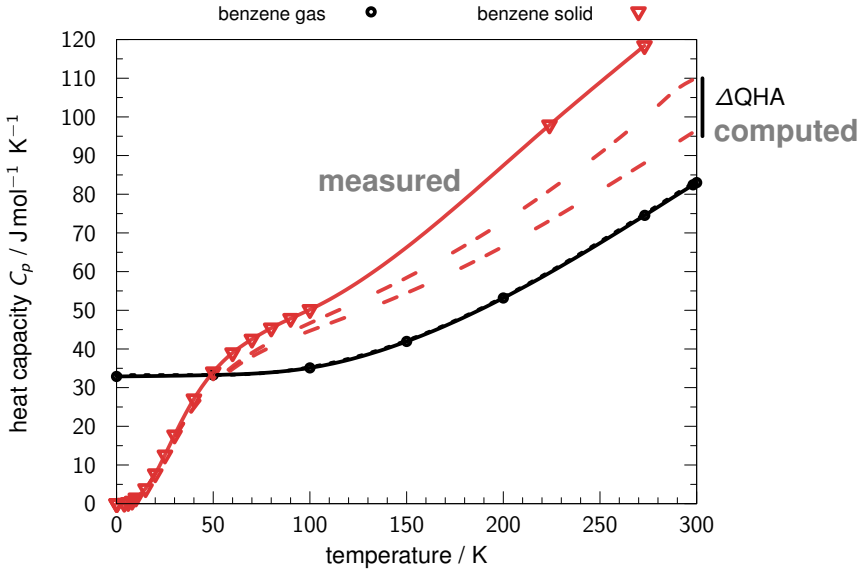
- measure H_{sub}, statistical survey yields error of $\sim 50\,\text{meV}$

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

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**

Quantum Monte-Carlo in a nutshell: A scalable high-level method

Fixed-node diffusion Monte-Carlo

1) Enforce nodal surface of Fermions

$$\Gamma = \{\mathbf{R}; |\Psi_T\rangle = 0\}$$

2) Walkers in configuration space

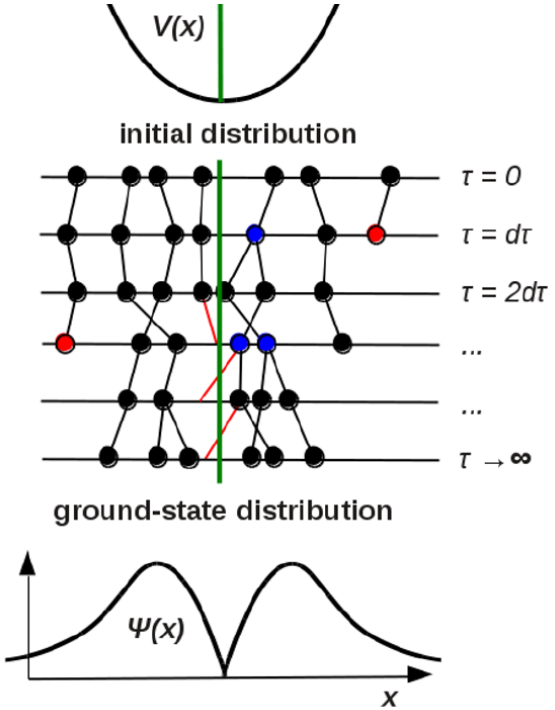
$$|\Psi_T(\mathbf{R},\tau)\rangle = \text{hist}\left[\sum \delta(\mathbf{R} - \mathbf{R_i}(\tau))\right]$$

3) Diffusion in imaginary time

$$\partial_\tau |\Psi_T(\mathbf{R},\tau)\rangle = \left[\frac{1}{2}\nabla^2_{\mathbf{R}} - (V - E_T)\right] |\Psi_T(\mathbf{R},\tau)\rangle$$

4) Projection to exact ground state

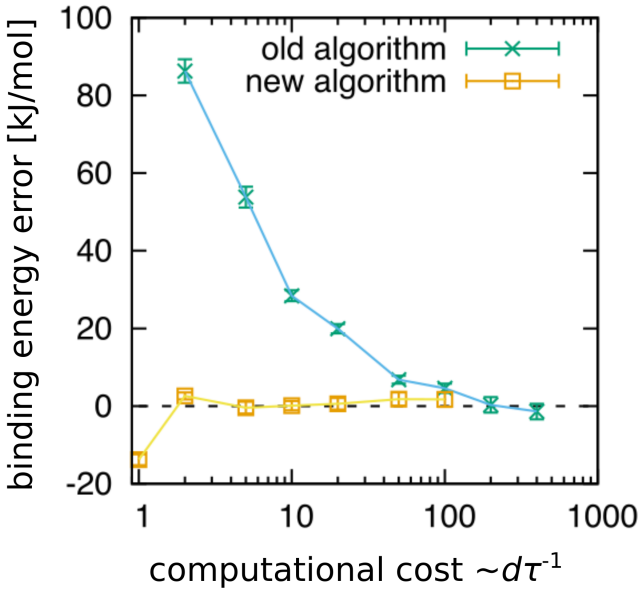
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau\to\infty} \exp\left[-\tau(\hat{H} - E_T)\right] |\Psi_T(\mathbf{R},\tau)\rangle$$

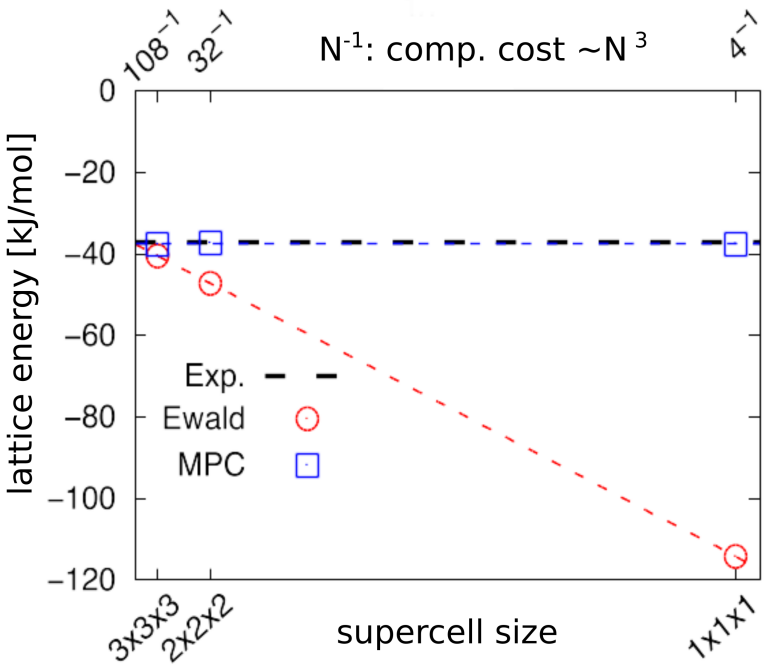


- exact within Γ and $d\tau \to 0$ and $\tau \to \infty$
- non-local part of pseudopotentials impact electron correlation

[5] M. Ďubecký, L. Mitas, P. Jurečkaâ , *Chem. Rev.* **116**, 5188 (2016)

New DMC algorithm leads to substantial speed up





- new size-consistent implementation reduces $\Delta\tau$ error drastically[6]
- Model periodic Coulomb for finite size correction[7]

[6] A. Zen, S. Sorella, M. J. Gillan, A. Michaelides, D. Alfé, *Phys. Rev. B* **93**, 241118(R) (2016).

[7] L. M. Fraser, W. M. C. Foulkes, G. Rajagopal, R. J. Needs, S. D. Kenny, A. J. Williamson, *Phys. Rev. B* **53**, 1814 (1996).

Methods with 'benchmark quality' for noncovalent interactions

UCL

CCSD(T)

- + 'gold standard' of quantum chemistry
- + linear scaling variants
- - pair-screening thresholds
- - slow basis set convergence
- - non-trivial to parallelize (shared memory: 100 GB/core)

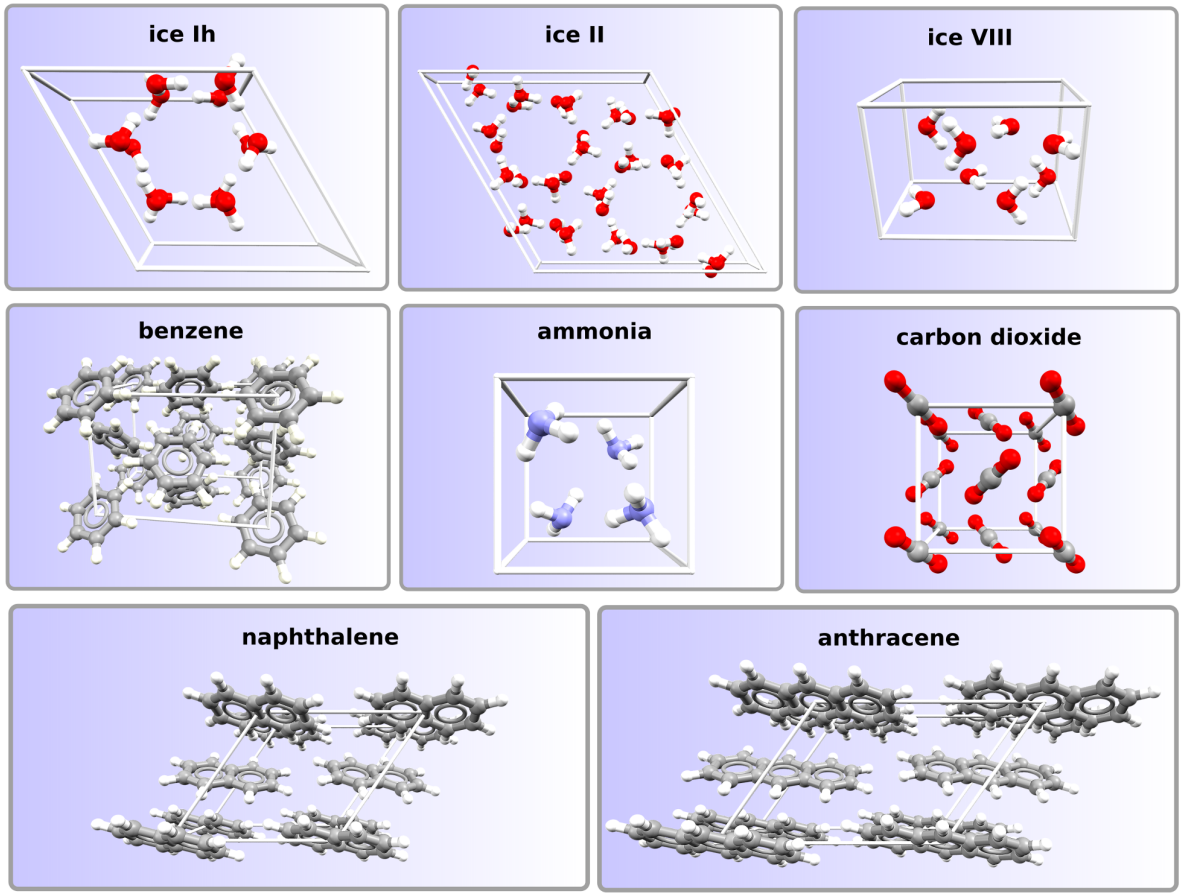
DMC

- + exact projection to ground state
- + N^3 scaling, [-] huge prefactor
- + fast basis set convergence
- + scaleable to HPCs
- - stochastic error
- - uncertainties from FN and non-local pseudopotentials

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

Outline of talk

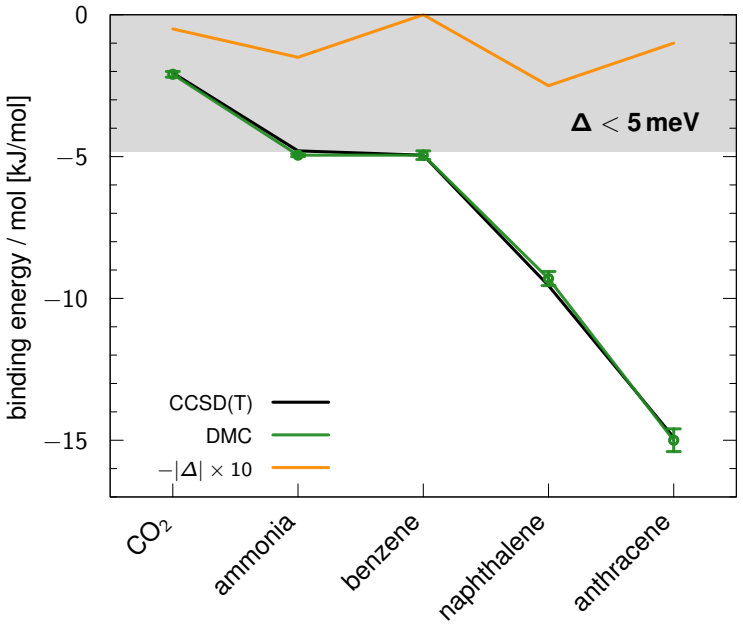
Diverse interactions in test crystals



- strong H-bonds, vdW of saturated and unsaturated molecules
- problematic for all readily applicable methods (DFA-DISP, MP2)

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 PNO settings)[8]
- largest deviation of 3 meV

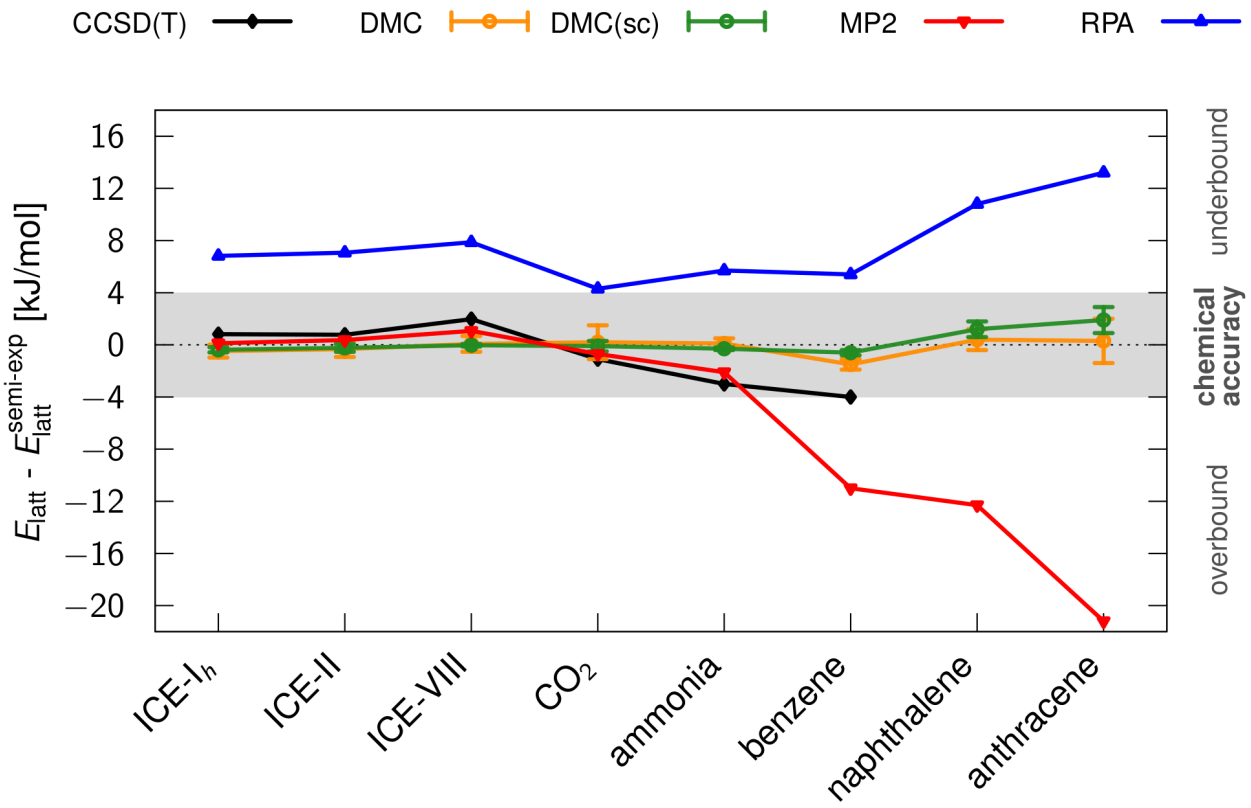


→ good agreement between different high-level methods[9]

[8] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.* **139**, 134101 (2013).

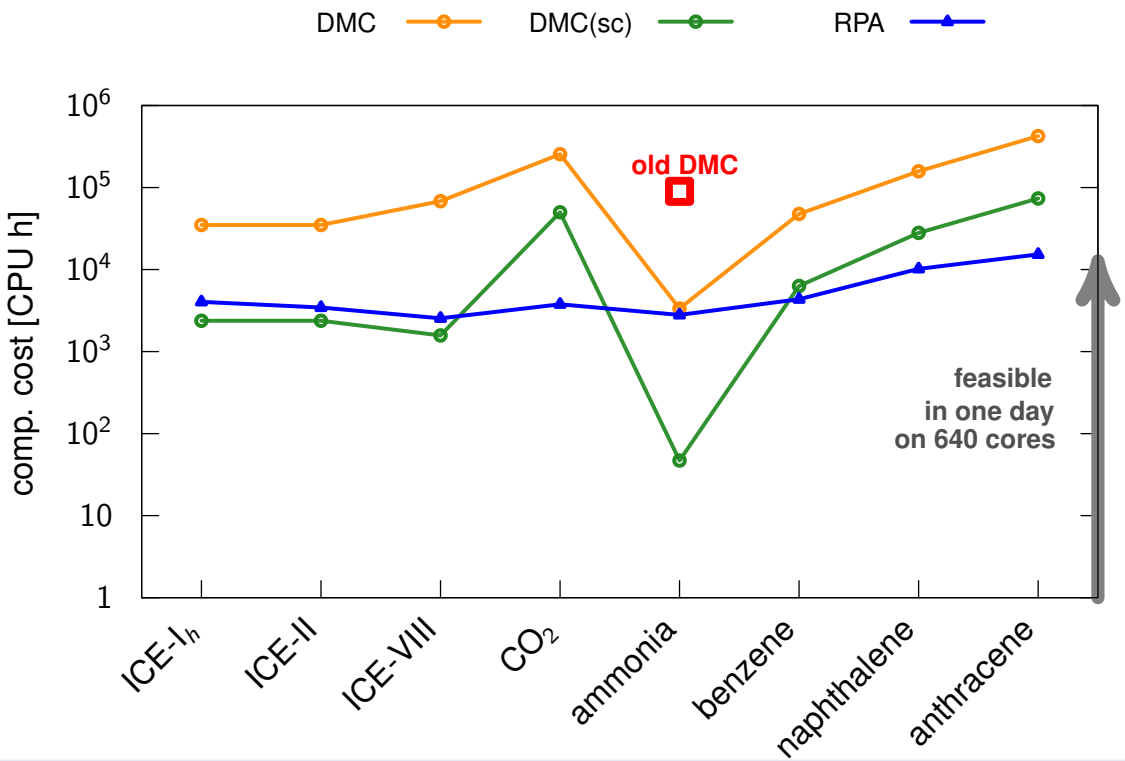
[9] Y. S. Al-Hamdani, M. Rossi, D. Alfè, T. Tsatsoulis, B. Ramberger, JGB, A. Zen, G. Kresse, A. Grüneis, A. Tkatchenko, A. Michaelides *J. Chem. Phys.* **147**, 044710 (2017).

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



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

QMC is feasible within one day on standard computer cluster

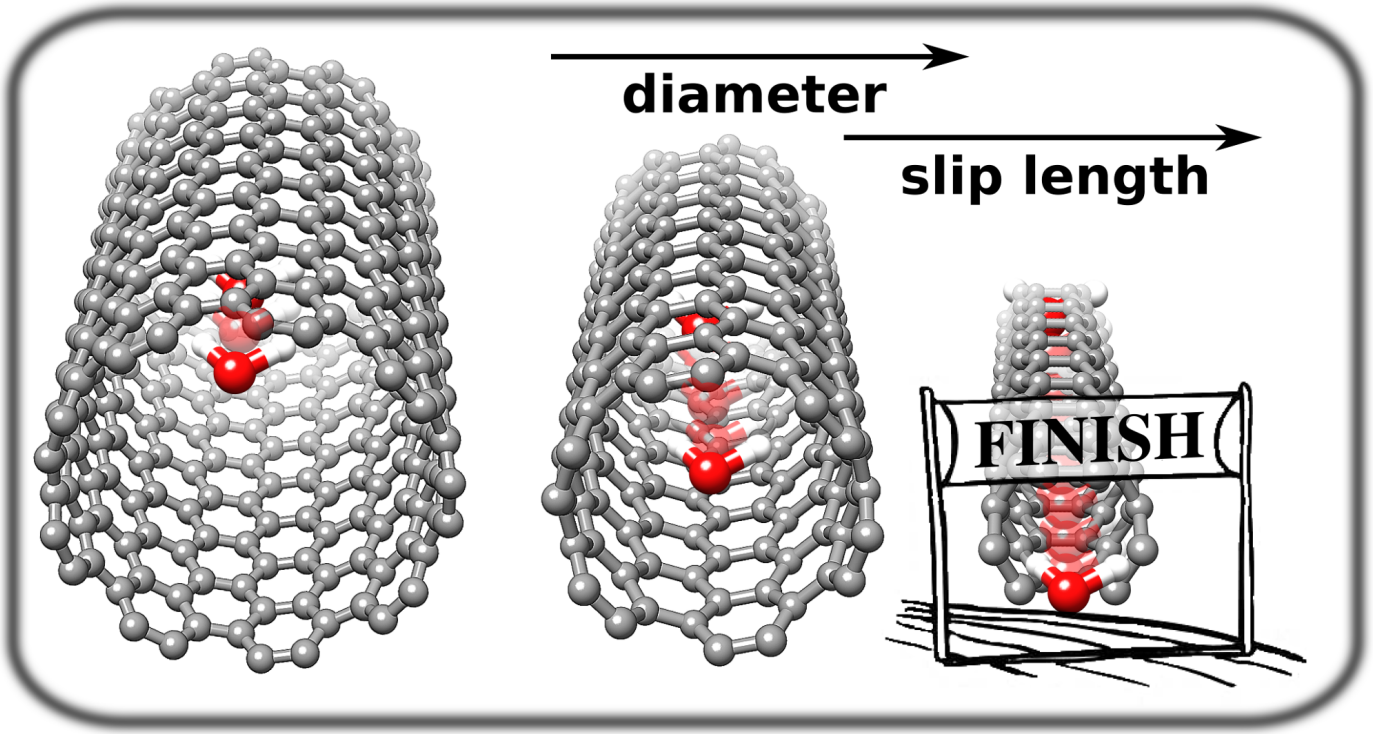


- up to three orders of magnitude speed-up compared to best DMC practice two years ago
- significance will extend to all classes of systems[10]

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

Outline of talk

Relevance of water graphene interaction?

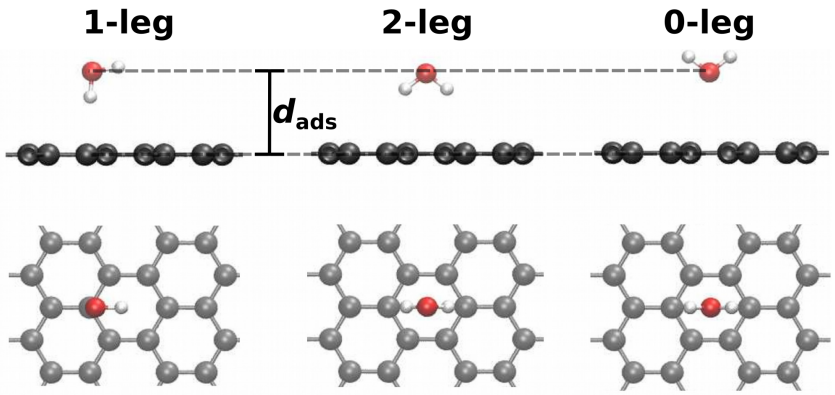


- graphite/graphene used as water filters
- water monomer adsorped on graphene as fundamental vdW system

[11] E. Secchi, S. Marbach, A. Niguelès, D. Stein, A. Siria, L. Bocquet, *Nature* **537**, 210 (2016).

[12] R. Joshi, P. Carbone, F. Wang, V. Kravets, Y. Su, I. Grigorieva, H. Wu, A. Geim, R. Nair, *Science* **343**, 752 (2014).

Severe discrepancy of literature values



DMC	i-CCSD(T)	SAPT, DFT/CC
-70 meV[13]	-135 meV[14]	-130 meV[15,16]

- differences of > 60 meV not acceptable

[13] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

[14] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

[15] G. R. Jenness, O. Karalti, K. D. Jordan, *PCCP* **12**, 6375 (2010), [16] M. Rubeš, *et al. JPC C* **113**, 8412 (2009).

L-CCSD(T) setup for molecular clusters

- tight pair-thresholds and non canonical triples (T0)
- BB-CP corrected binding energies and extrapolation

$$E_{\text{corr}}[\text{CC/CSB}] = E_{\text{corr}}(\text{CC/QZ}) \times \frac{E_{\text{corr}}(\text{RPA/CBS})}{E_{\text{corr}}(\text{RPA/QZ})}$$

{non-published data}

Water@graphene binding energies

{non-published data}

Extrapolation of substrate size

{non-published data}

- convergence with substrate size very slow
  $\longrightarrow$ extrapolations using benzene, coronene data unreliable

Redistribution of charge density strongly dependent on adsorption motif

{non-published data}

- convergence with substrate size very slow
  $\longrightarrow$ extrapolations using benzene, coronene data unreliable

Discrepancies of literature values resolved

UCL

DMC

-70 meV[13]

- stochastic error
- finite-size correction

i-CCSD(T)

-135 meV[14]

- unconverged basis set expansion

SAPT, DFT/CC

-130 meV[15,16]

- unreliable extrapolation

revised DMC

-99 ± 5 meV

[13] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

[14] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

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Benchmarking of density functional approximations

{non-published data}

Outline of talk

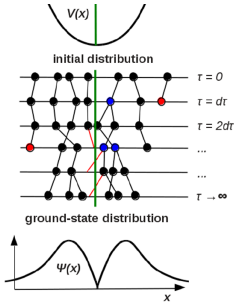
Summary

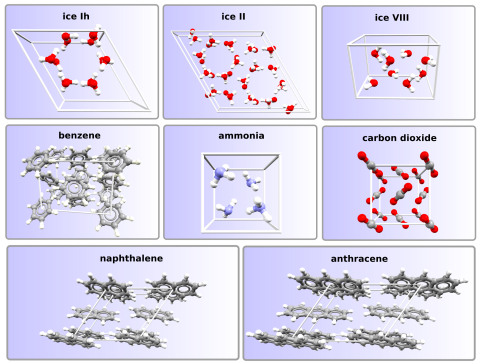
Conclusions

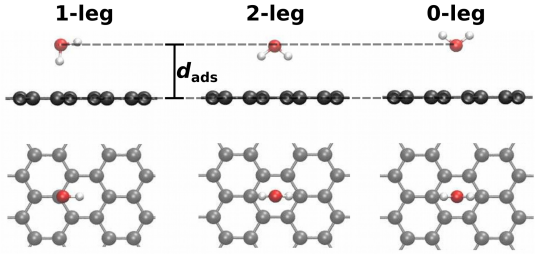
- DMC delivers (sub-) chemical accuracy with three orders of magnitude speed up
- chemically accurate lattice energies
- revised reference value for water@graphene

Outlook

- improved DMC for even larger systems
- use improved methodologies in CSP
- NNP training within CSP algorithms







Acknowledgements

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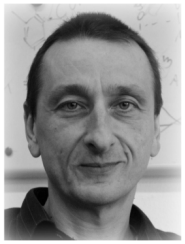
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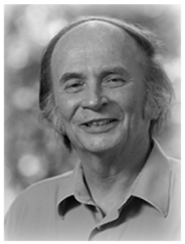
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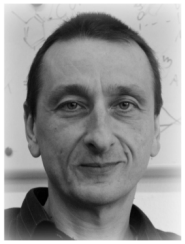
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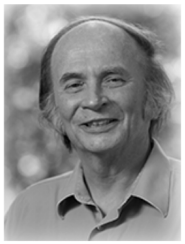
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Thanks

Key references

- QMC for molecular crystals:

  JGB, A. Zen, A. Michaelides, G. Kresse, and D. Alfè, in preparation

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

- DFT development

  JGB, J. E. Bates, J. Sun, J. P. Perdew, *Phys. Rev. B*, **94**, 115144 (2016).

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

- Crystal structure prediction:

  S. L. Price, JGB, *Molecular Crystal Structure Prediction*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, 336-363 (2017).

- website: **gerit-brandenburg.de**