Control and Prediction of Molecular Crystal Properties by Multilevel Strategies

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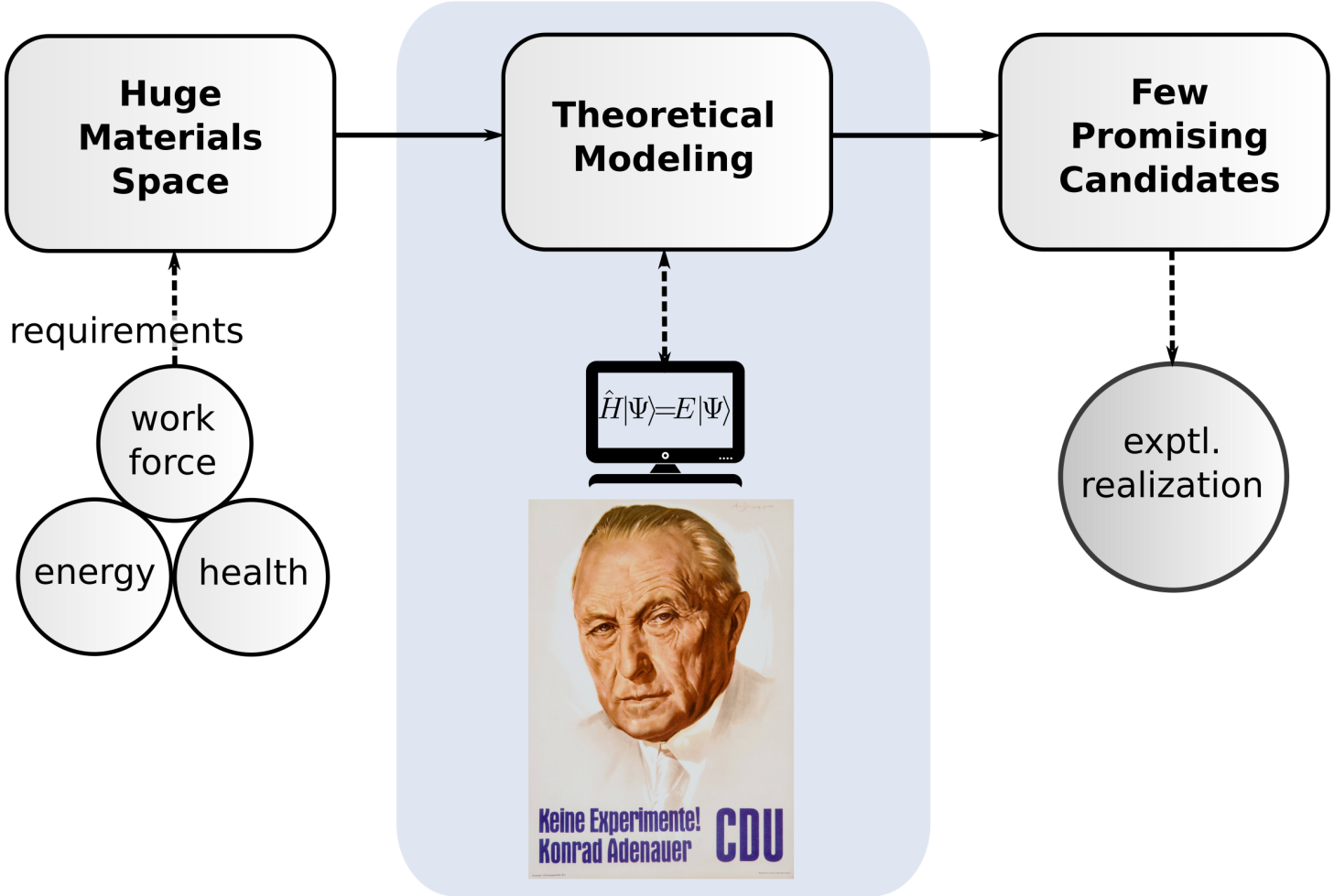
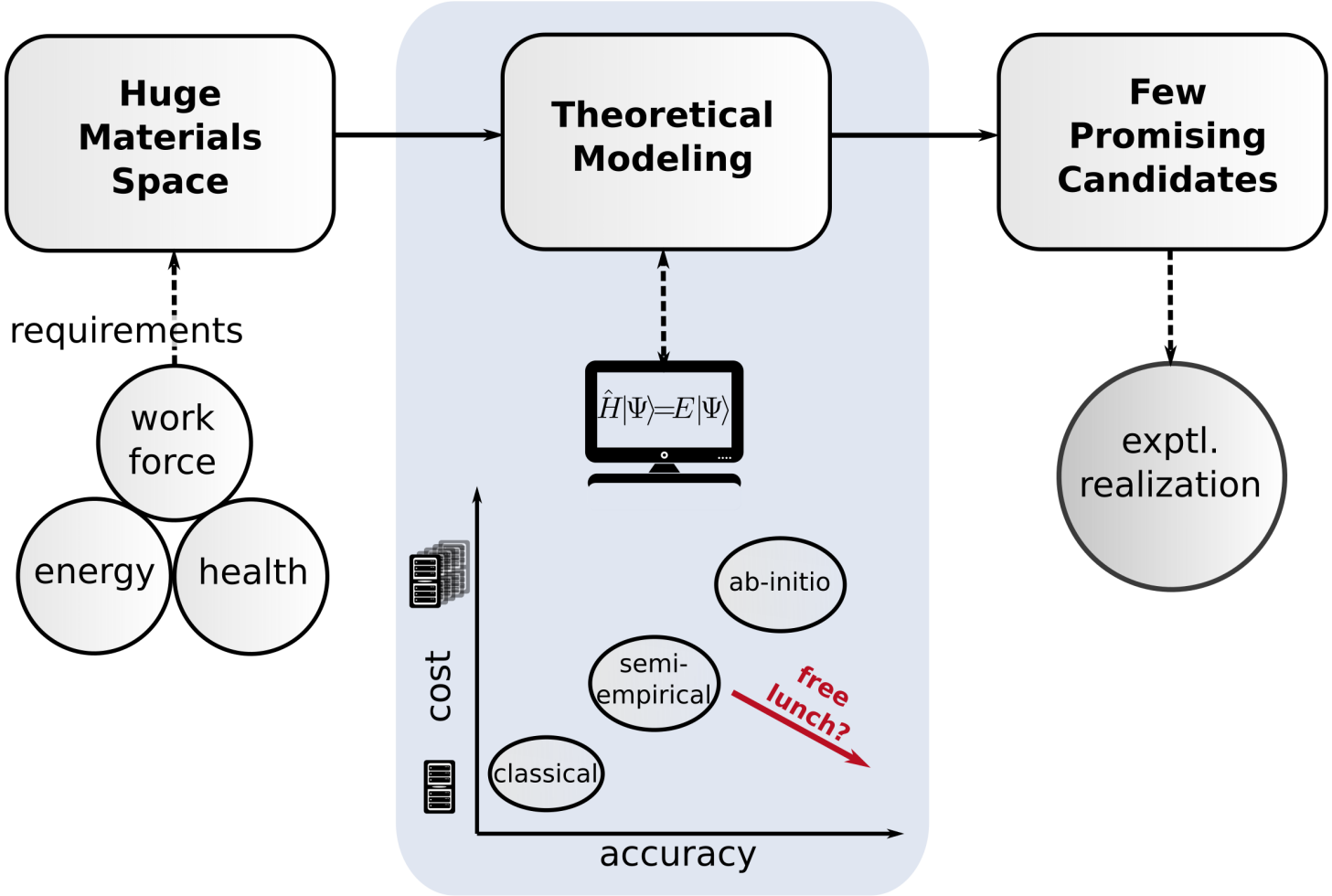
FOCUS SESSION: FRONTIERS OF ELECTRONIC-STRUCTURE THEORY, TECHNICAL UNIVERSITY BERLIN, GERMANY

Outline of talk

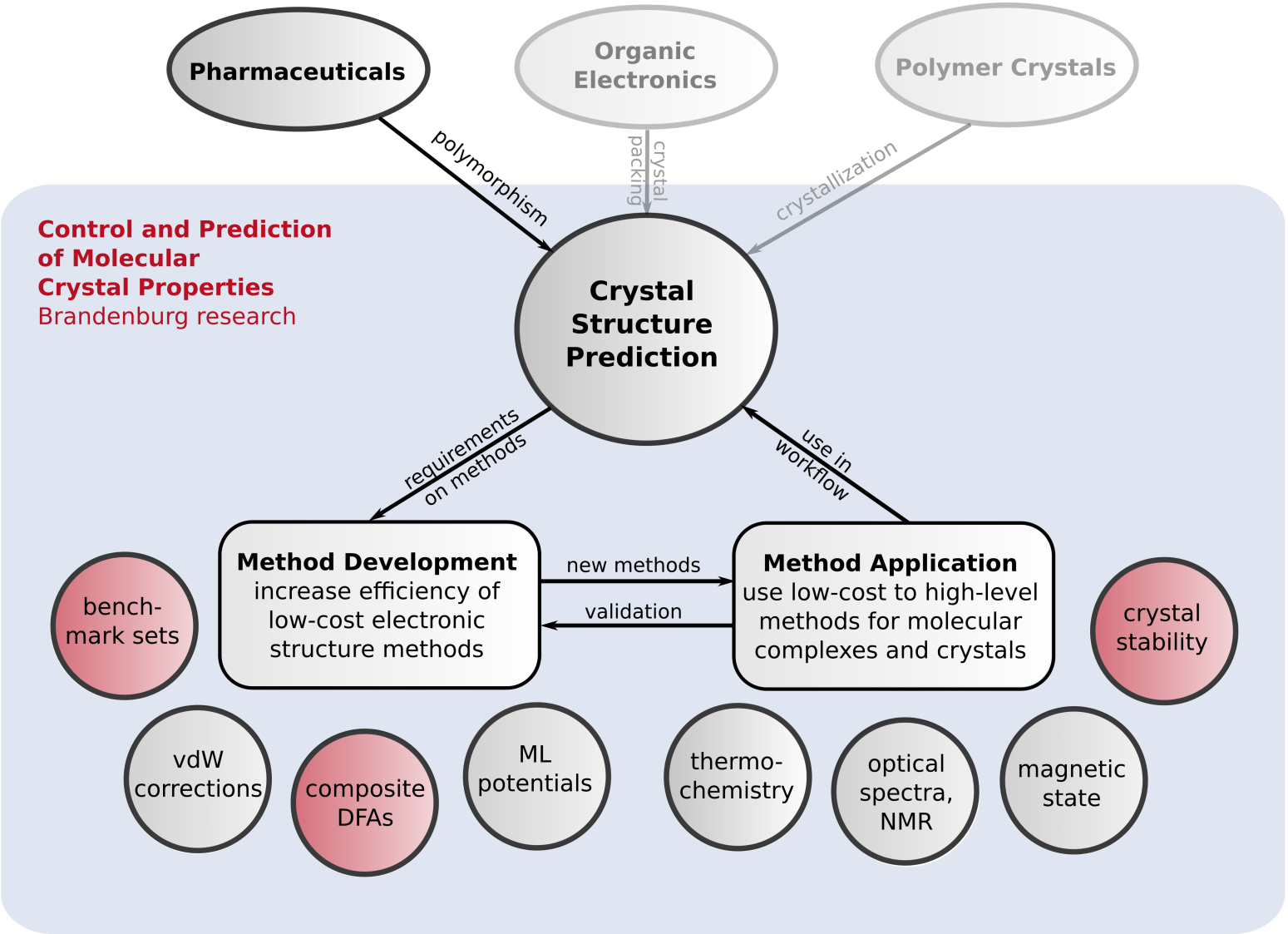
Material discovery can employ computational models



Material discovery can employ computational models



Brandenburg research concept



Outline of talk

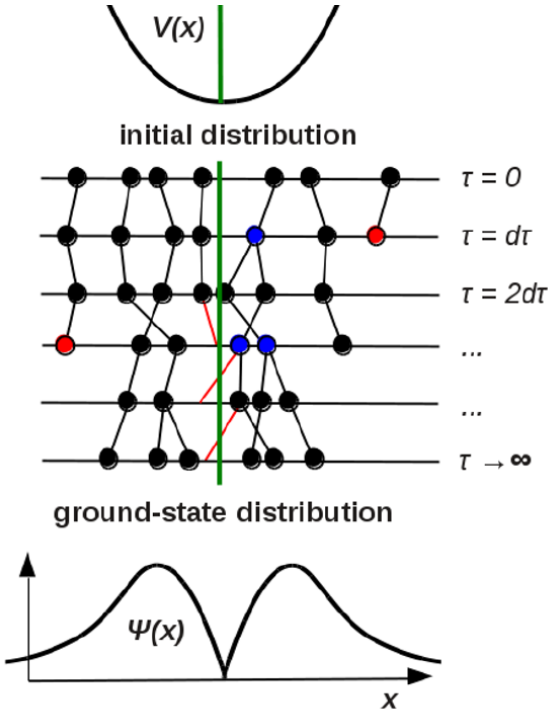
Quantum Monte-Carlo in a nutshell: A scalable high-level method

How to solve Schrödinger equation for large systems?

FN-diffusion Monte-Carlo

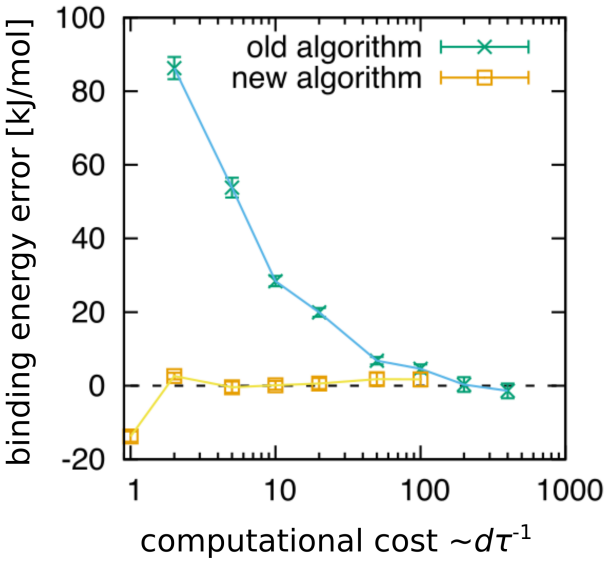
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau\to\infty} \exp\left[-\tau(\hat{H} - E_T)\right] |\Psi_T(\mathbf{R},\tau)\rangle$$

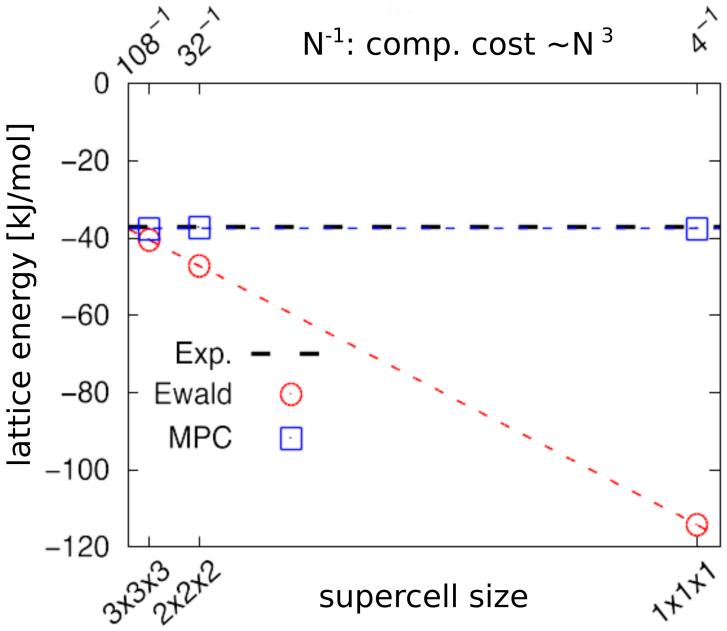
- well behaved convergence with single-particle basis set
- low-scaling (N^3) with system size
- scaleable to HPCs



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

New QMC algorithm leads to substantial speed up



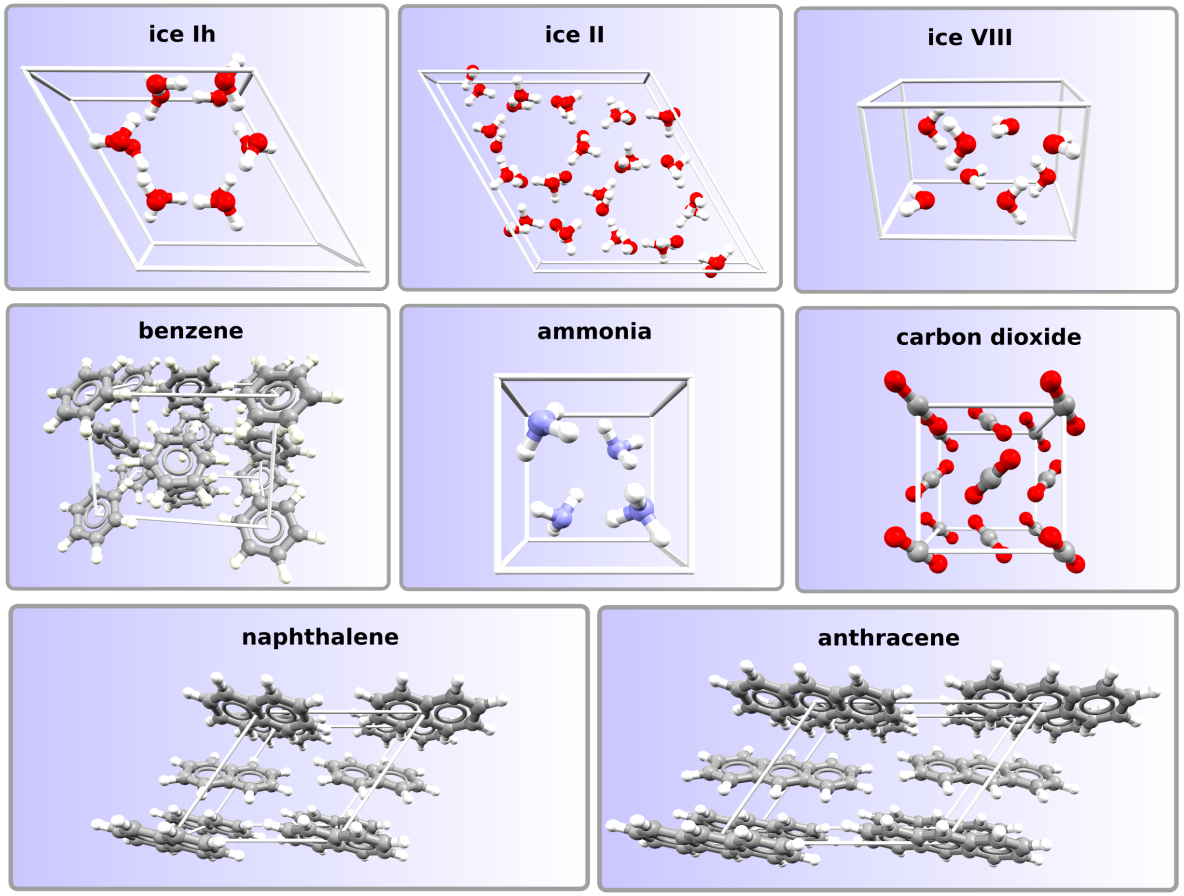


- new size-consistent implementation reduces $\Delta\tau$ error drastically[2]
- Model periodic Coulomb for finite size correction[3]

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

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

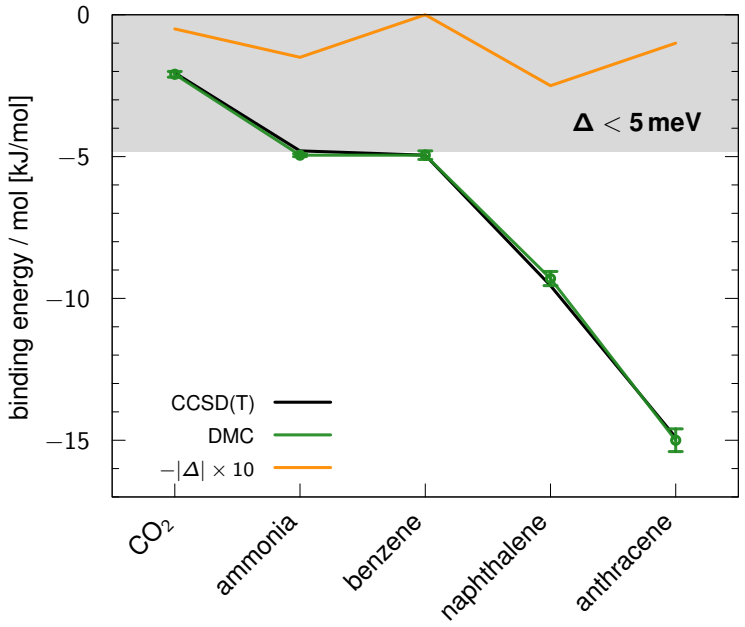
Diverse interactions in test crystals



- 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)[4]
- largest deviation of 3 meV

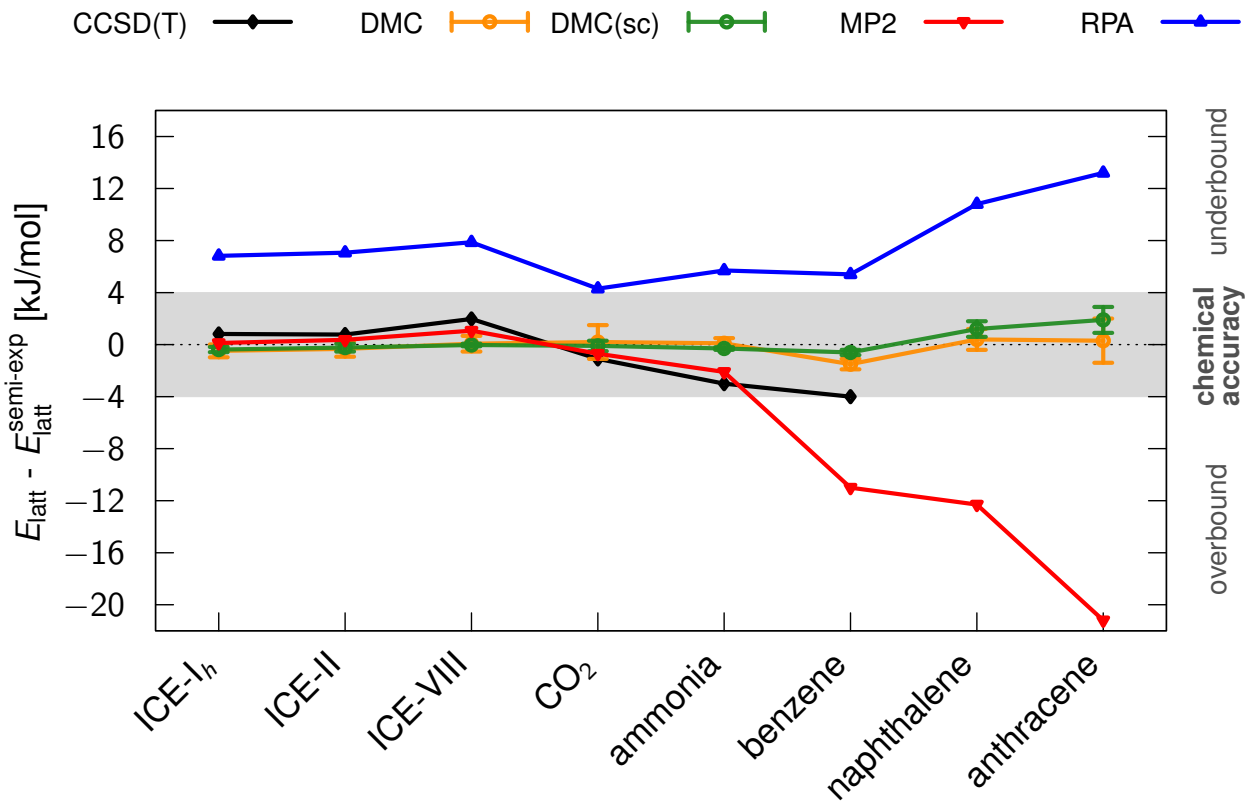


→ good agreement between different high-level methods[5]

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

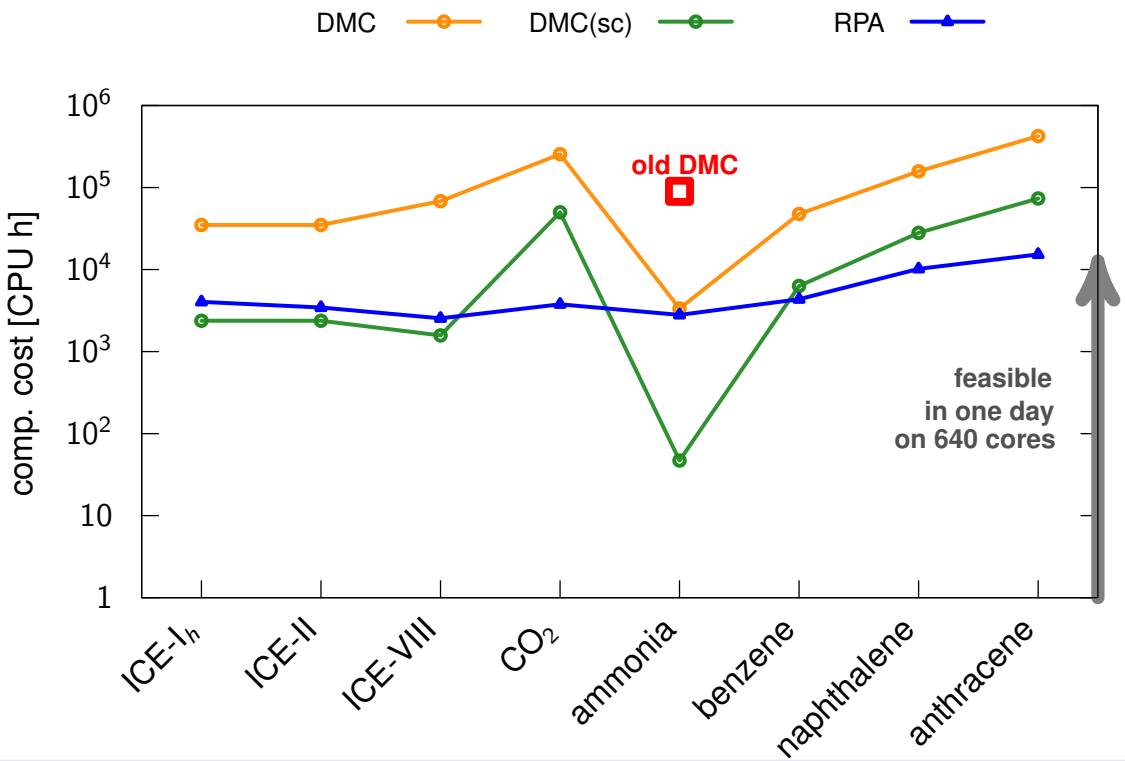
[5] Y. S. Al-Hamdani, M. Rossi, D. Alfè, T. Tsatsoulis, B. Ramberger, JGB, A. Zen, G. Kresse, A. Grüneis, A. Tkatchenko, A. Michaelides *J. Chem. Phys.* **147**, 044710 (2017).

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[6]

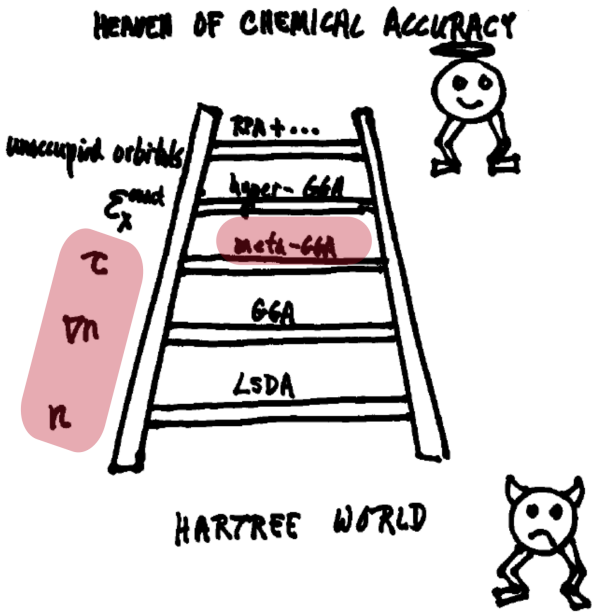
[6] A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *Proc. Natl. Acad. Sci. U.S.A* , **115**, 1724 (2018).

Outline of talk

Strongly constrained and appropriately normed semilocal functional (SCAN)

SCAN functional[7]

- metaGGA expansion dimensionless ∇n, τ
- 7 parameters in F_x and F_c
- obeys all 17 known exact constraints



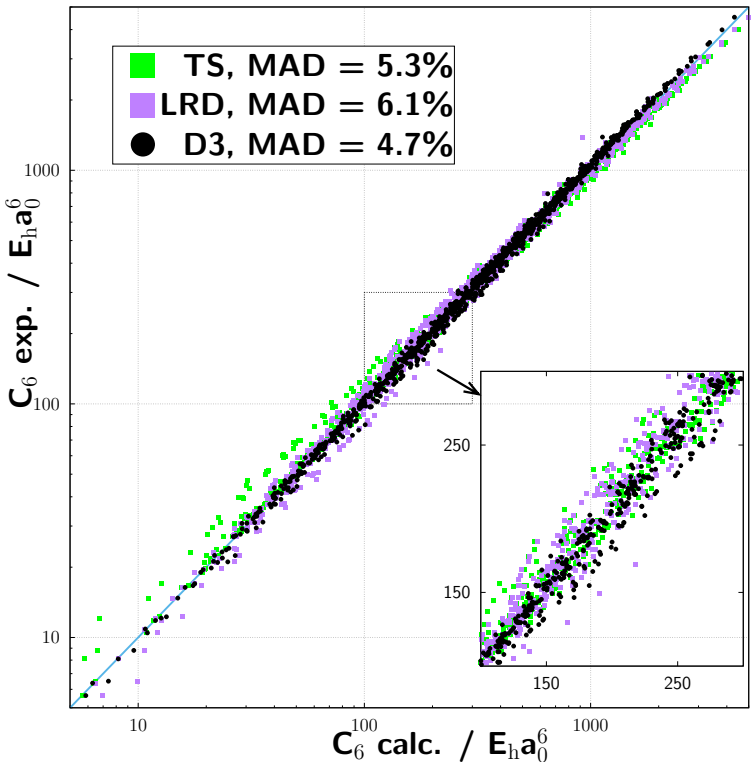
- add semi-classical correction for long-range correlation[8]

$$E_c^{(D3)} = -\frac{1}{2}\sum_{n=6,8}\sum_{A,B}^{\text{pairs}} \frac{C_n^{AB}}{r_{AB}^n} f_n^d(r_{AB}) - \frac{1}{6}\sum_{A,B,C}^{\text{triples}} \frac{C_9^{ABC}\left(1+3\cos\theta_A\cos\theta_B\cos\theta_C\right)}{r_{ABC}^9} f_9^d(r_{ABC})$$

[7] J. Sun, A. Ruzsinszky, J. P. Perdew, *Phys. Rev. Lett.* **115**, 036402 (2015).

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

Semi-classical correction yields highly accurate dispersion coefficients



D3 correction[9,10]

$$C_6^{\alpha\beta} = -\frac{3}{\pi}\int_0^\infty \alpha^\alpha(i\omega)\alpha^\beta(i\omega)\,\mathrm{d}\omega$$

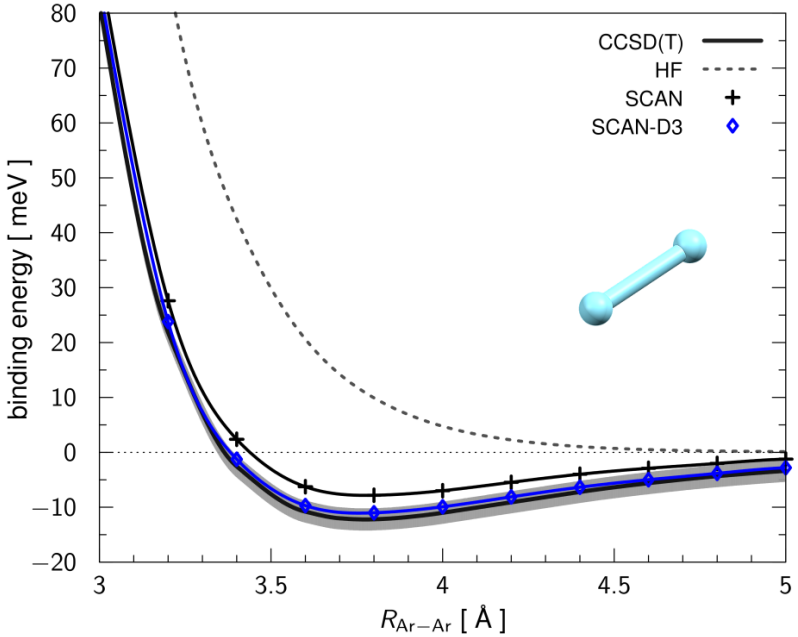
- Casimir-Polder integration of TD-DFT polarizabilities on model hydrides
- residual long-range error $< 5\%$
- empiricism in short-range damping

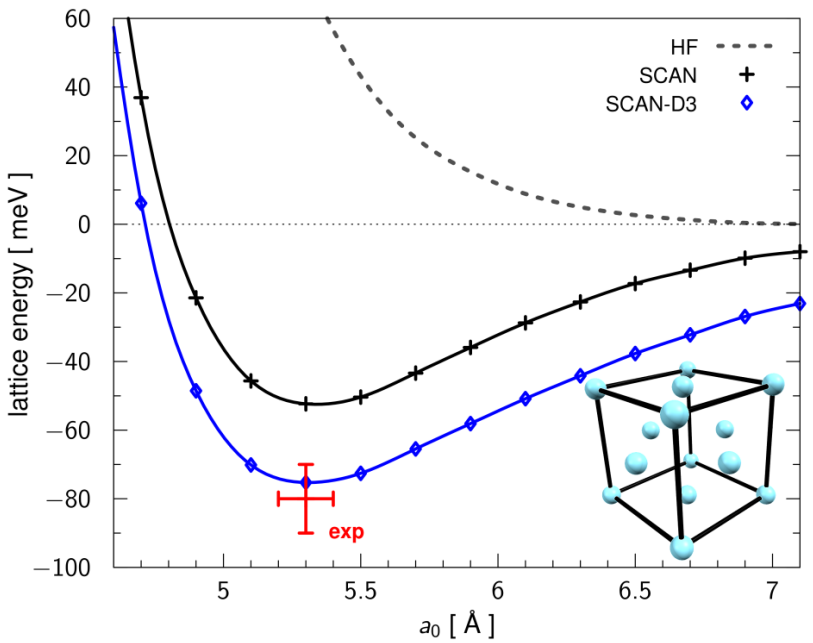
[9] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010).

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

Guinea pig for testing vdW interactions

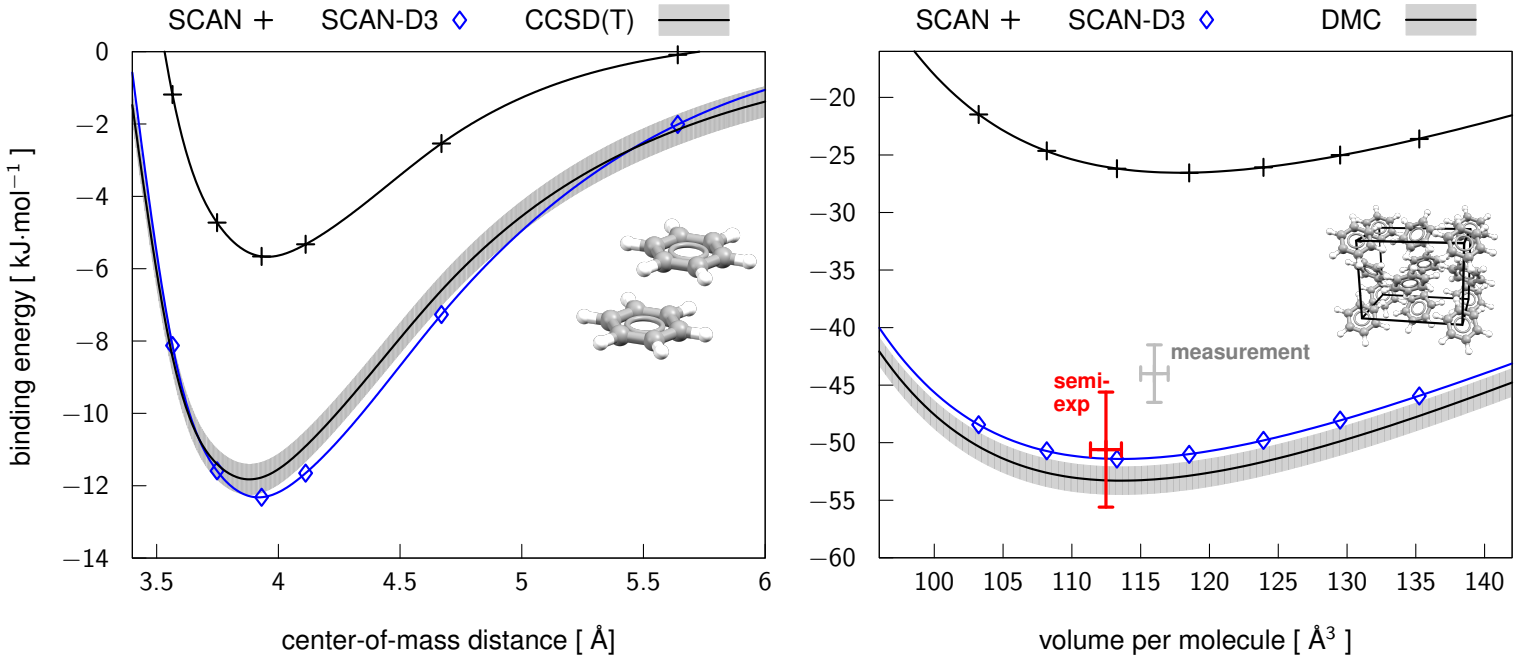
Noble gas assemblies





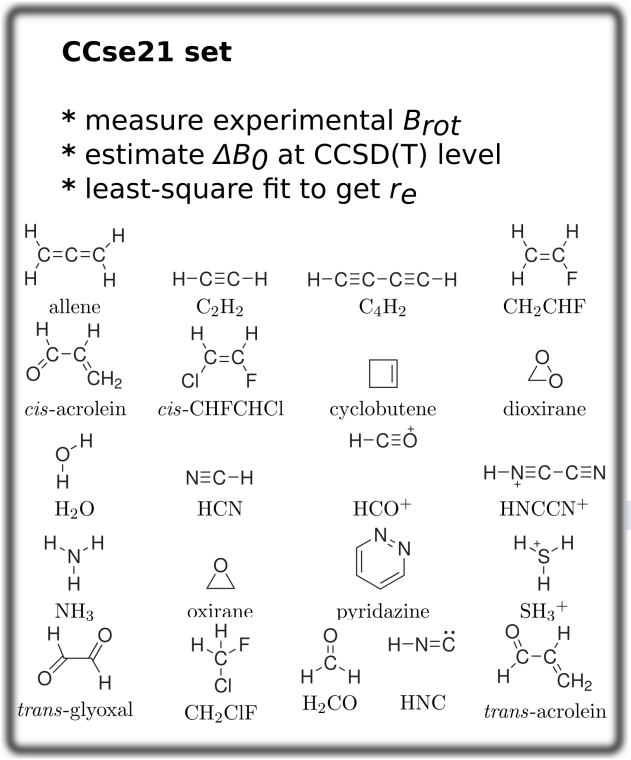
- binding solely from electron correlation effects
- SCAN-D3 mean unsigned error (MUE) on S22 set reduced to 17 meV

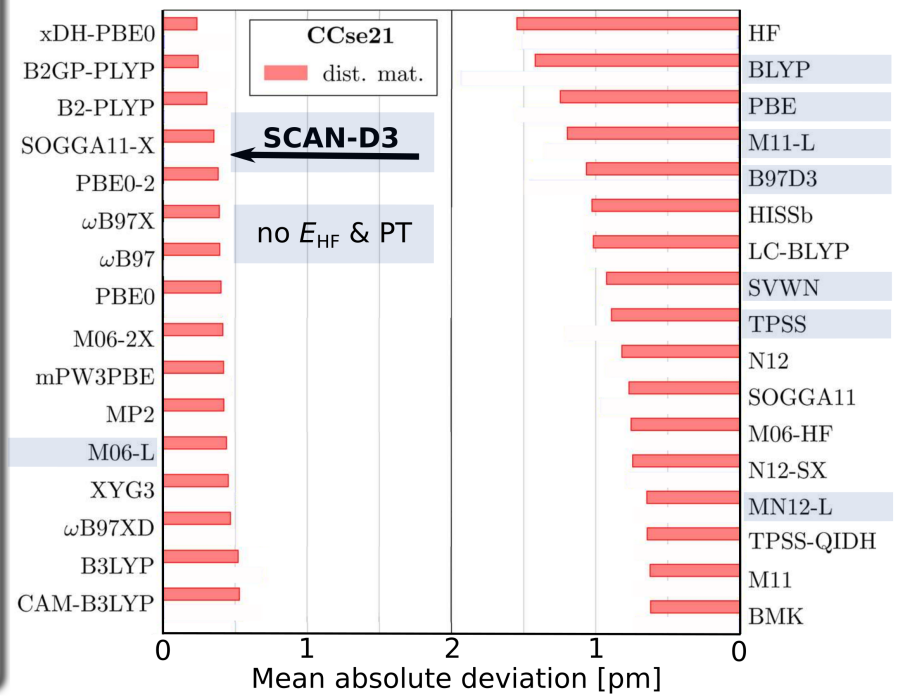
Close agreement with reference for noncovalently bound systems



- zero-point and thermal effects crucial for comparison to measurement
- new references valuable for testing approximate methods
- vdW correction crucial for accurate results

Excellent geometries across the periodic table





- structures better than all other tested (meta)GGAs
- extends to heavy main group bonds and transition metal complexes

[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).

Outline of talk

Predict most stable crystal polymorphs based on the molecular diagram

The inability to predict something as simple as how a molecule would crystallize is one of the continuing scandals in the physical sciences.[13–15]

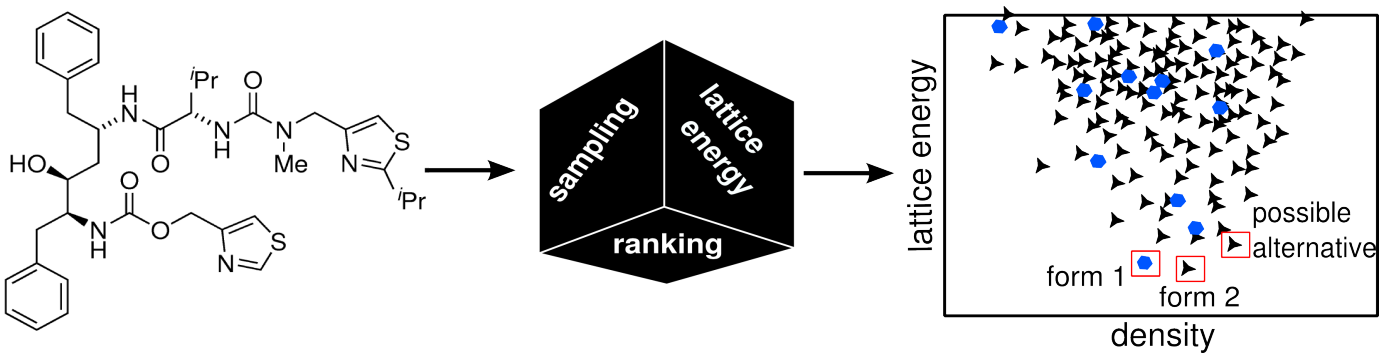
Task

- molecule is chosen due to its chemical/physical/biological properties
- based on the molecular diagram only, the most stable crystal structures should be predicted
- predict properties of interest for the most promising candidates

[13] A. Gavezzotti, *Acc. Chem. Res.* **27**, 309-314 (1994). [14] J. Maddox, *Nature* **335**, 201-201 (1988).

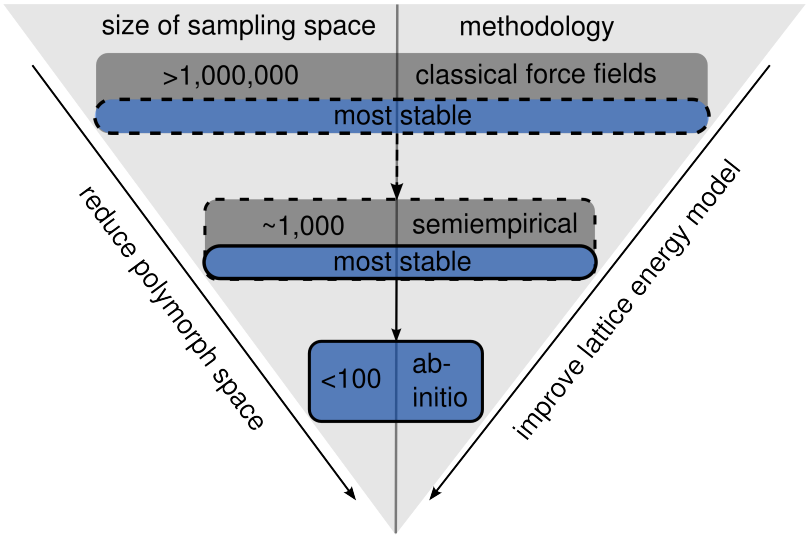
[15] K. N. Houk, F. Liu, *Acc. Chem. Res.*, **50**, 539 (2017).

Sampling and energetic ranking for crystal structure prediction



Layers of complexity:

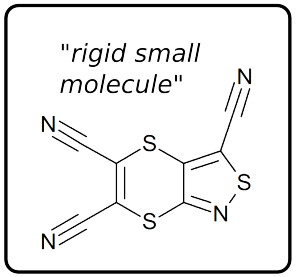
- molecular conformational space
- space groups (varying orientation, conformation, etc.)
- polymorph ranking according to free energy[16,17]

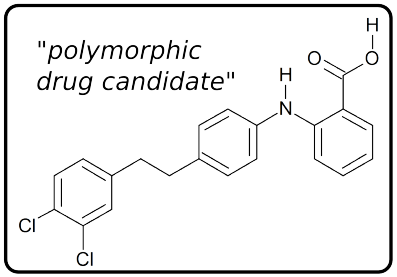


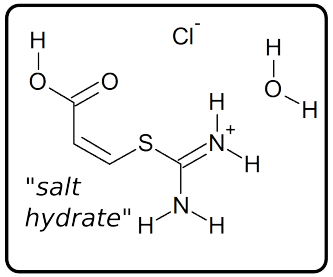
[16] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

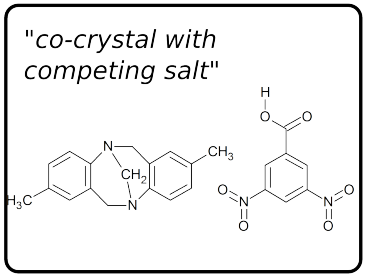
[17] S. L. Price, JGB, *Molecular Crystal Structure Prediction*; Elsevier Australia, 336-363 (2017).

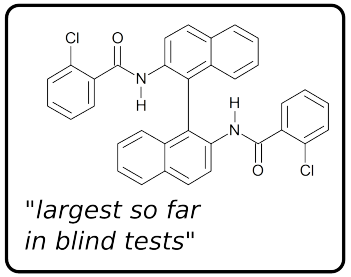
Promising results in the 6th blind test











	22	23	24	25	26
PBE	2	1-9	6	3	1
PBE-D3	1	1-9	1	1	1
PBE-MBD	1	1-7	1	2	1
M06L	1	4-13	1	1	7
SCAN-D3	**1**	**1-13**	**1**	**3**	**1**

ranking computed on fixed TPSS-D3 structures

- good lattice energy based ranking of modern DFA-DISP[18,19]
- energy differences too small to get conclusive results

[18] A. Reilly, R. Cooper, C. Adjiman, S. Bhattacharya, A. Boese, JGB, et al. *Acta Cryst. B*, **72**, 439 (2016).

[19] JGB, S. Grimme, *Acta Cryst. B*, **72**, 502 (2016).

Outline of talk

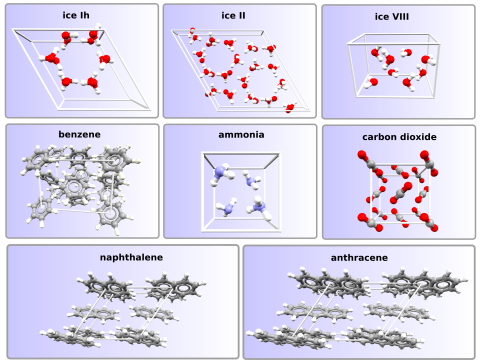
Summary

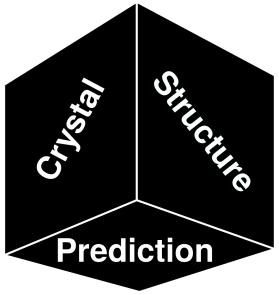
Conclusions

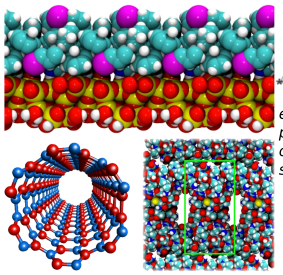
- DMC delivers (sub-) chemical accuracy with three orders of magnitude speed up
- approximate QM methods like SCAN-D3 useful for reliable electronic structures
- promising results of crystal energy rankings in CSP blind test

Outlook

- extending the merits of DMC (APIs, OLEDs, MOFs)
- free energy estimations for CSP







CRYSTAL17

enables consistent studies of the physical and chemical properties of molecules, polymers, nanotubes, surfaces and crystalline solids

Acknowledgements

PhD / Postdocs


Andrea Zen

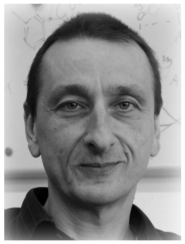

Michaelides (UCL)

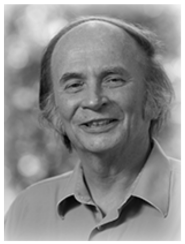

Alfé (UCL)


Tkatchenko (Luxembourg)


Klimes (Prague)


Eike Caldeweyer


Grimme (Bonn)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Antreas Afantitis (NovaMechanics)

Principal investigator

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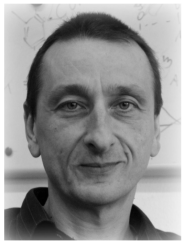
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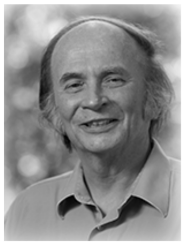
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Thanks

Key references

- QMC for molecular crystals:

  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).

  L. Iuzzolino, P. McCabeb, S. L. Price, JGB, *Faraday Discuss.*, in press DOI: 10.1039/C8FD00010G (2018).

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