Control and Prediction of Molecular (&) Crystal Properties by Multilevel Strategies

Gerit Brandenburg <g.brandenburg@ucl.ac.uk> | 26th of Februrary 2018

VORTRAG IM RAHMEN DES BERUFUNGSVERFAHRENS 530, TECHNISCHE UNIVERSITÄT DARMSTADT, GERMANY

TECHNISCHE UNIVERSITÄT DARMSTADT

Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

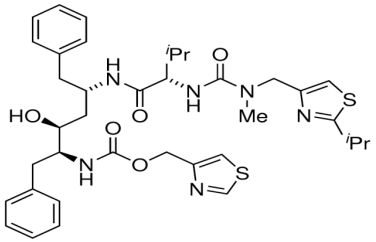
4 Quantum Monte-Carlo for molecular materials

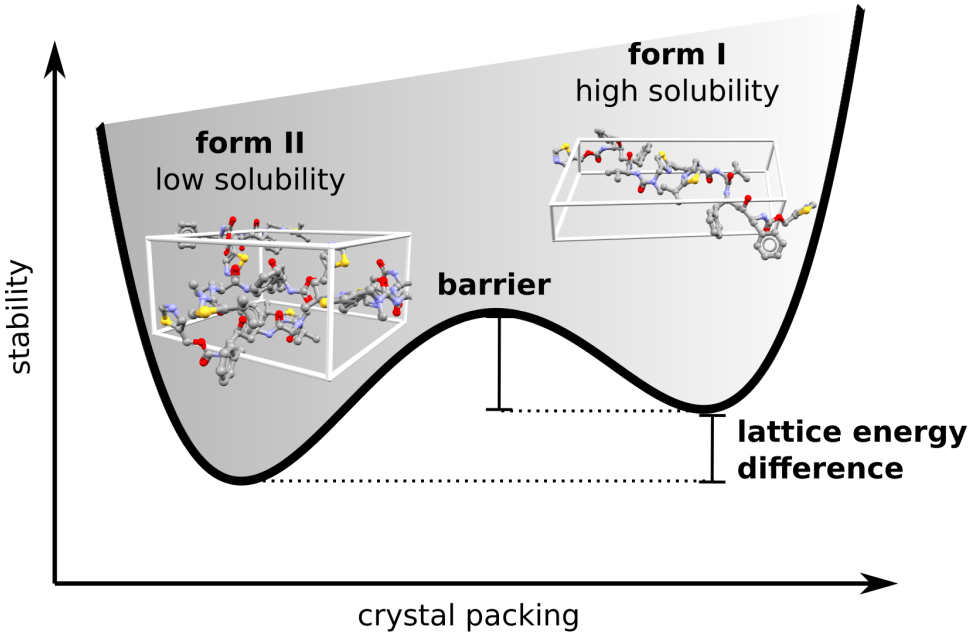
5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

Academic and industrial interest in molecular materials

API: ritonavir
- HIV antiviral drug
- industrially produced in form I
- form II found 2 years after market launch
- reformulation required [1]





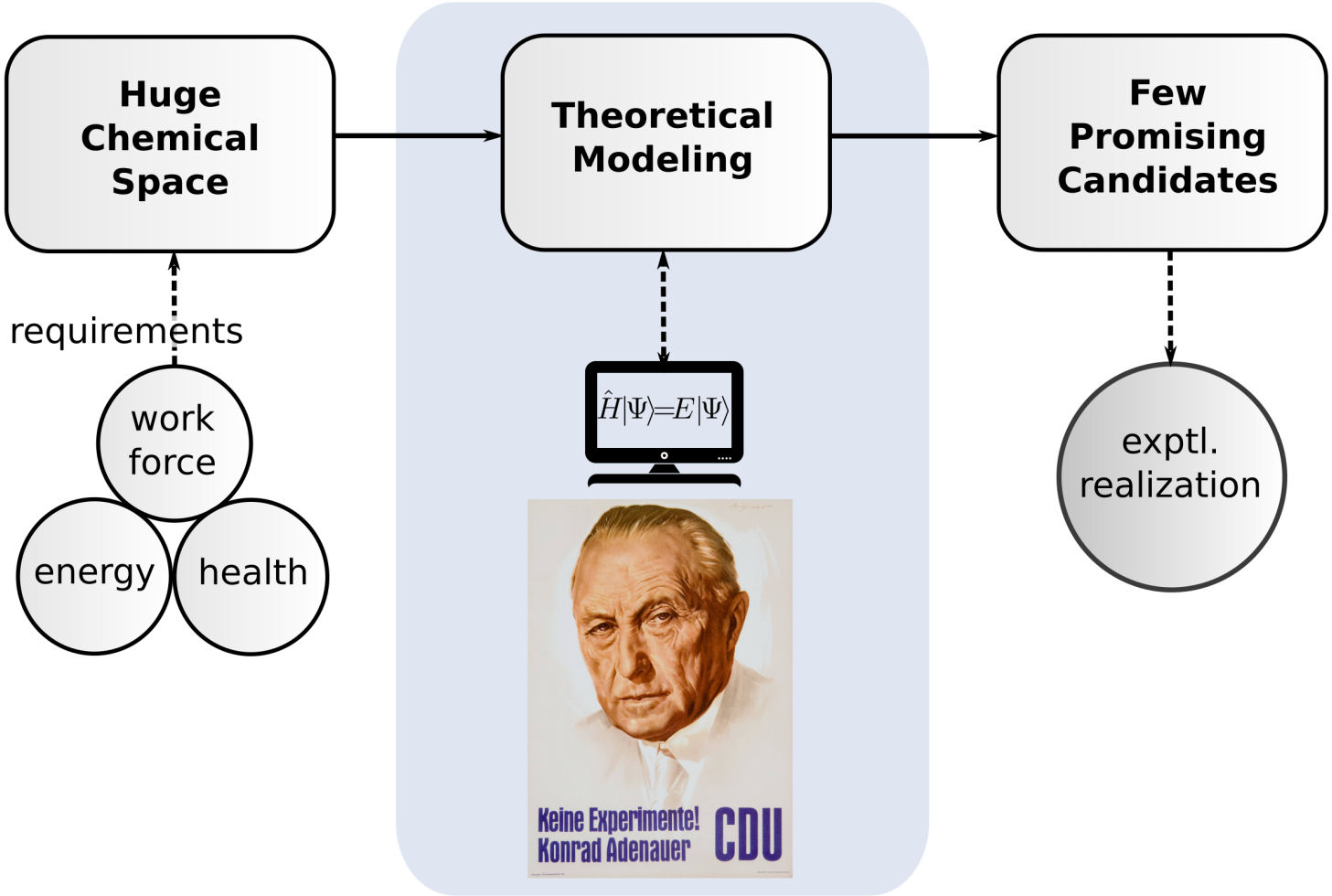
- tools to predict possible polymorphs would be valuable[2]

  → Simulation methods aim at complementing experimental screening

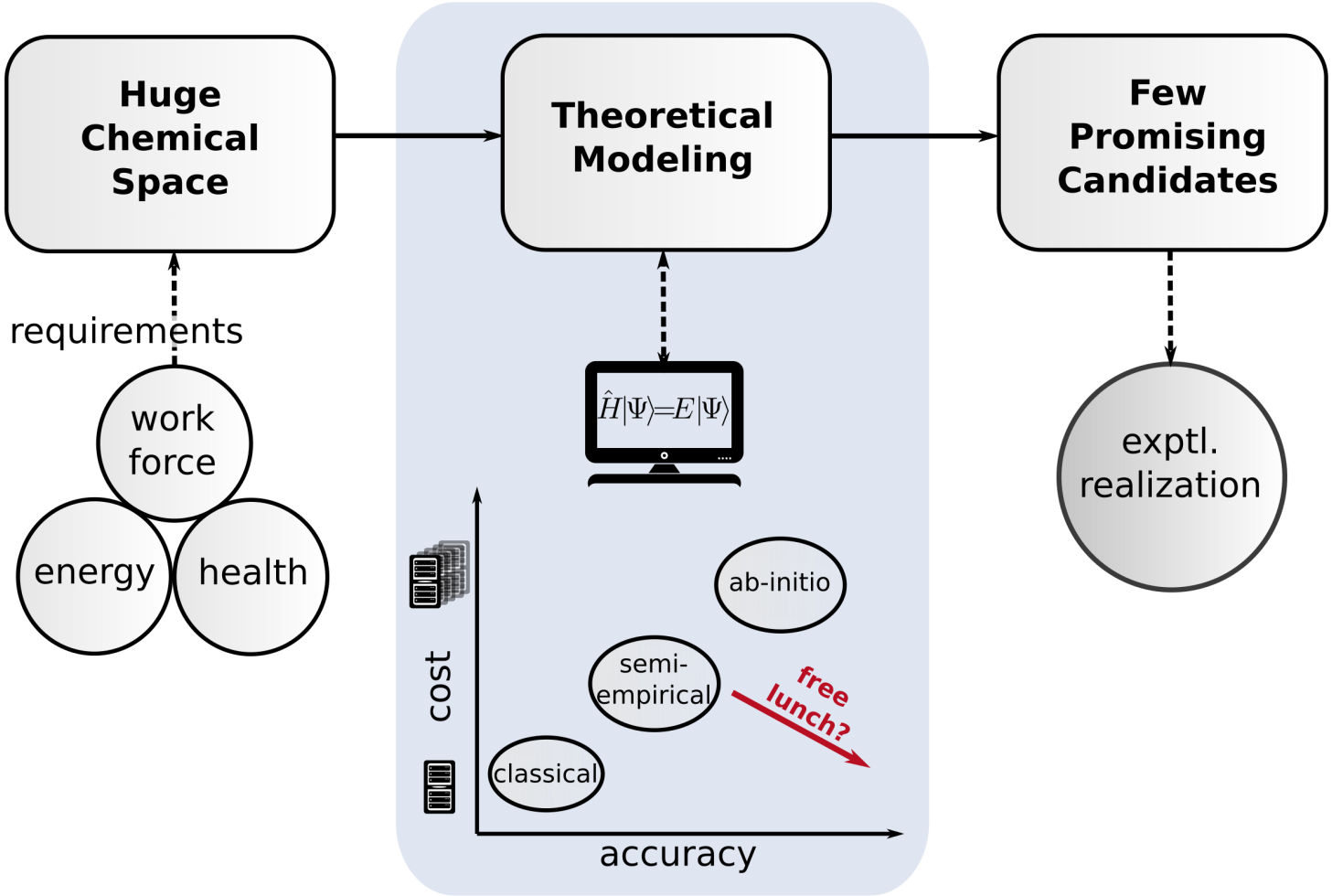
[1] J. Bauer, et al., *J. Pharm. Res.* **18**, 859-866 (2001).

[2] S. L. Price, JGB, *Molecular Crystal Structure Prediction*; Elsevier Australia ISBN: 9780128098356 (2017).

Chemical and material discovery can employ computational models

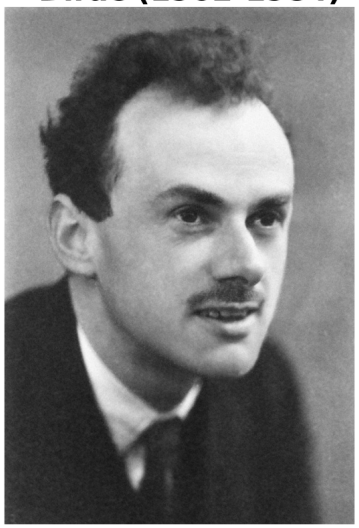


Chemical and material discovery can employ computational models



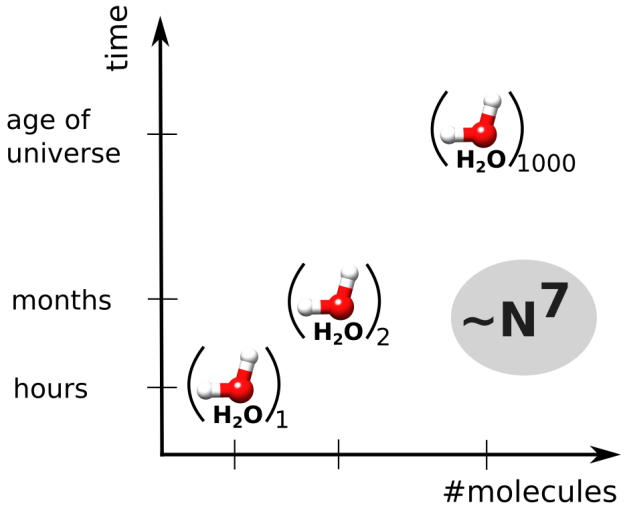
Exact simulation of extended systems computationally very demanding

Paul Adrian Maurice Dirac (1902-1984)



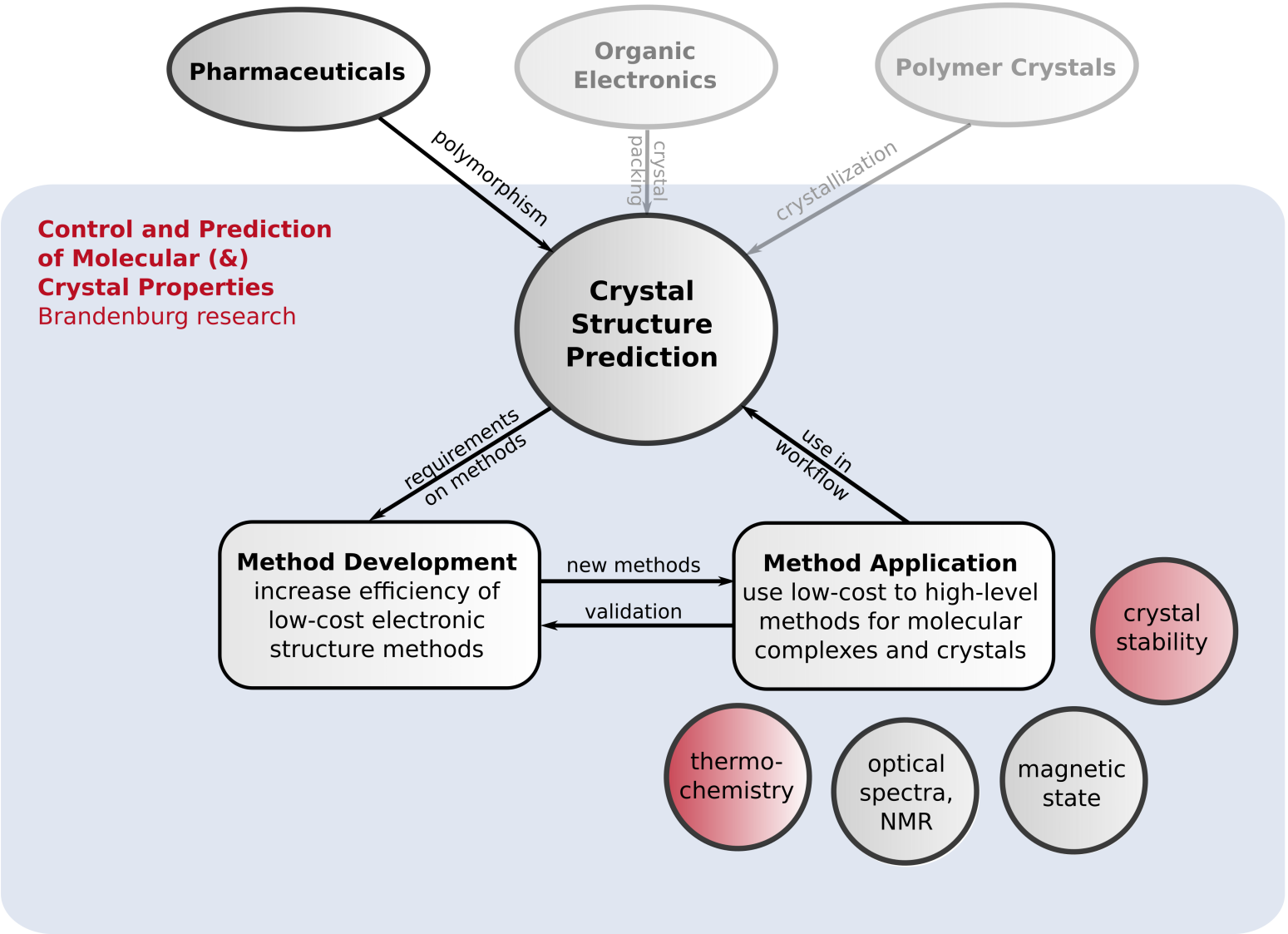
"The underlying physical laws (...) of a large part of physics and the ***whole of chemistry*** *are thus completely known,*

and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"[1]



[3] P. A. M. Dirac, *Proc. Roy. Soc.Ser. A* **123**, 714 (1929).

Brandenburg research concept



Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

4 Quantum Monte-Carlo for molecular materials

5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

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.[4–6]

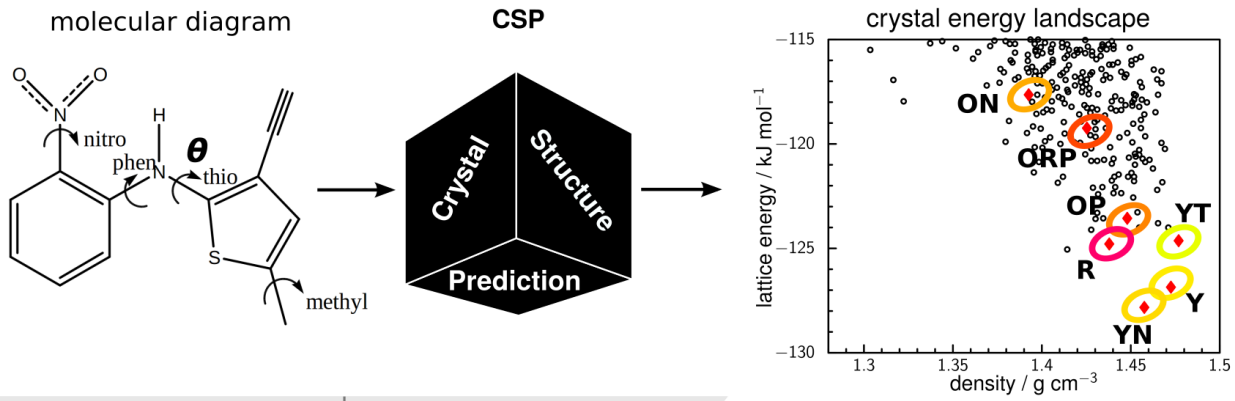
Task

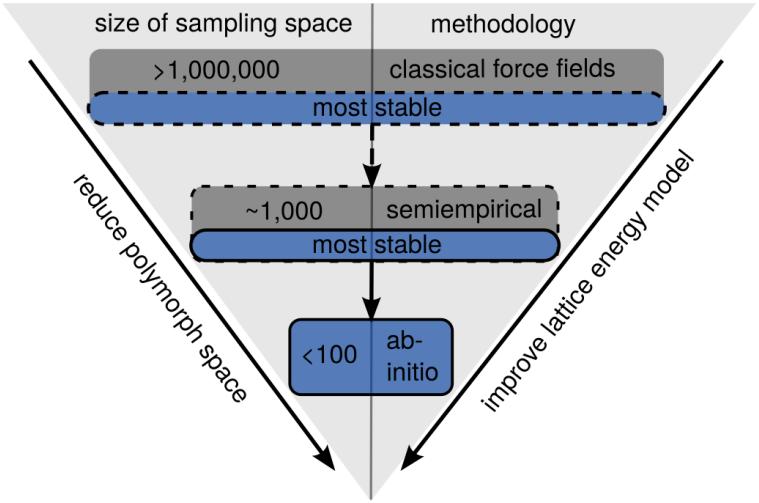
- molecule is chosen due to its chemical/physical/biological properties
- based on the molecular diagram only, the most stable crystal structures should be predicted
- predict properties of interest for the most promising candidates

[4] A. Gavezzotti, *Acc. Chem. Res.* **27**, 309-314 (1994). [5] J. Maddox, *Nature* **335**, 201-201 (1988).

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

Sampling and energetic ranking for crystal structure prediction



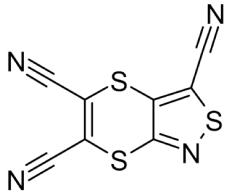


Properties
of ROY polymorphs

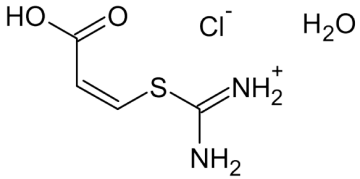
[7] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

[8] M. Vasileiadis, A. V. Kazantsev, P. G. Karamertzanis, C. S. Adjiman, C. C. Pantelides, *Acta Cryst. B* **68**, 677 (2012)

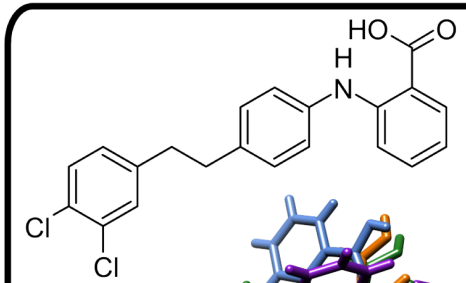
Promising results in the 6th blind test

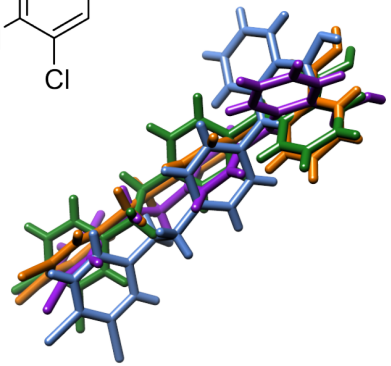


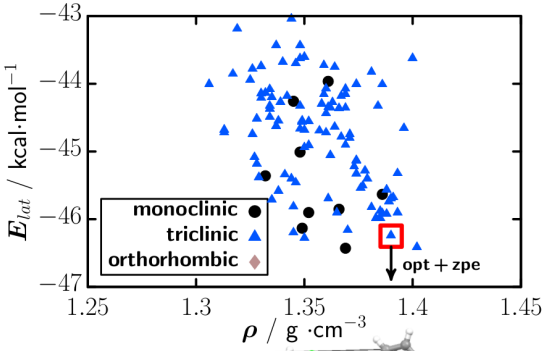
exp. polymorph: **Rank 1**
found in sampling: ✗

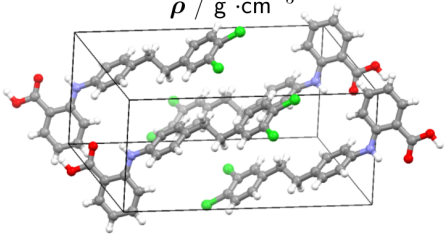


exp. polymorph: **Rank 1**
found in sampling: ✗

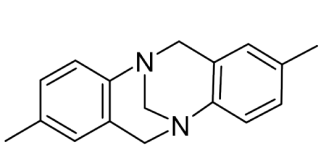


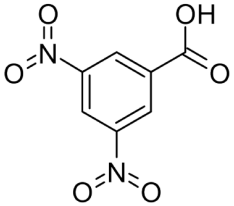




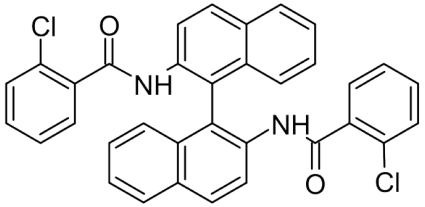


exp. polymorph: **Ranks 1-10**
found in sampling: ✓/ ✗





exp. polymorph: **Rank 1**
found in sampling: ✓



exp. polymorph: **Rank 1** found: ✗

[9] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016). [10] JGB, S. Grimme, *Acta Cryst. B*, **72**, 502 (2016).

Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

4 Quantum Monte-Carlo for molecular materials

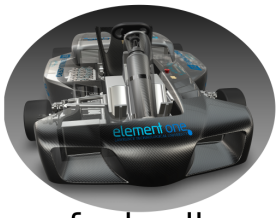
5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

Metal-free catalysis for H_2 activation

Hydrogen activation

fertilizer



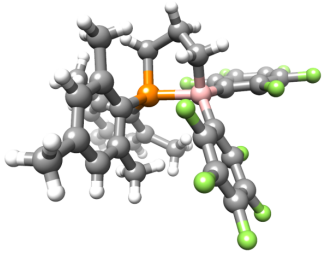
fuel cell

oil cracking

Frustrated Lewis acid and base Pair (FLP)

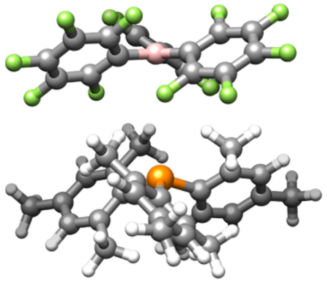
intra-molecular

$Mes_2{-}P{\cdots}B{-}(C_6F_5)_2$



inter-molecular

$Mes_3\text{-}P{\cdots}\,B\text{-}(C_6F_5)_3$



- 'frustration' by carbon bridges (intra) or steric hindrance
- activate small molecules in solution[11−13]

[11] G. Welch, R. Juan, J. Masuda, D. Stephan, *Science*, **314**, 1124 (2006).

[12] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **49**, 46 (2010).

[13] S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem. Int. Ed.* **49**, 1402 (2010).

FLP condensed phase thermochemistry

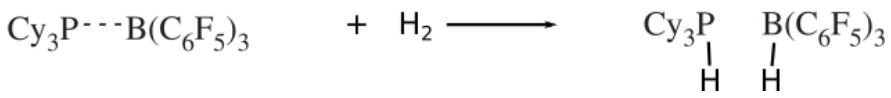
	ΔG^{gas}	ΔG^{solv}	ΔG^{solid}
$Mes_2-P\cdots B-(C_6F_5)_2 + H_2 \longrightarrow Mes_2-P(H)-B(H)-(C_6F_5)_2$	3.9	-5.0	-1.1
$Mes_2-P\cdots B-(C_6F_5)_2 + H_2 \longrightarrow Mes_2-P(H)-B(H)-(C_6F_5)_2$	10.4	1.6	9.7
$Mes_2-P\cdots B-(C_6F_5)_2 + H_2 \longrightarrow Mes_2-P(H)-B(H)-(C_6F_5)_2$	11.1	0.5	6.3
$Cy_3P\cdots B(C_6F_5)_3 + H_2 \longrightarrow Cy_3P(H)-B(H)(C_6F_5)_3$	-7.2	-18.2	-17.0

SCAN-D3//HF-3c, HF-3c RRHO energies [kcal/mol][14]
COSMO-RS(toluene) implicit solvation, normal conditions

- reaction reversible, H_2 and other small molecules (CO_2, SO_2)
- two promising candidates for the solid state

[14] L. Liu, JGB, S. Grimme, *Phil. Trans. R. Soc. A*, **375**, 20170006 (2017).

FLP chemistry can be transfered to the solid state



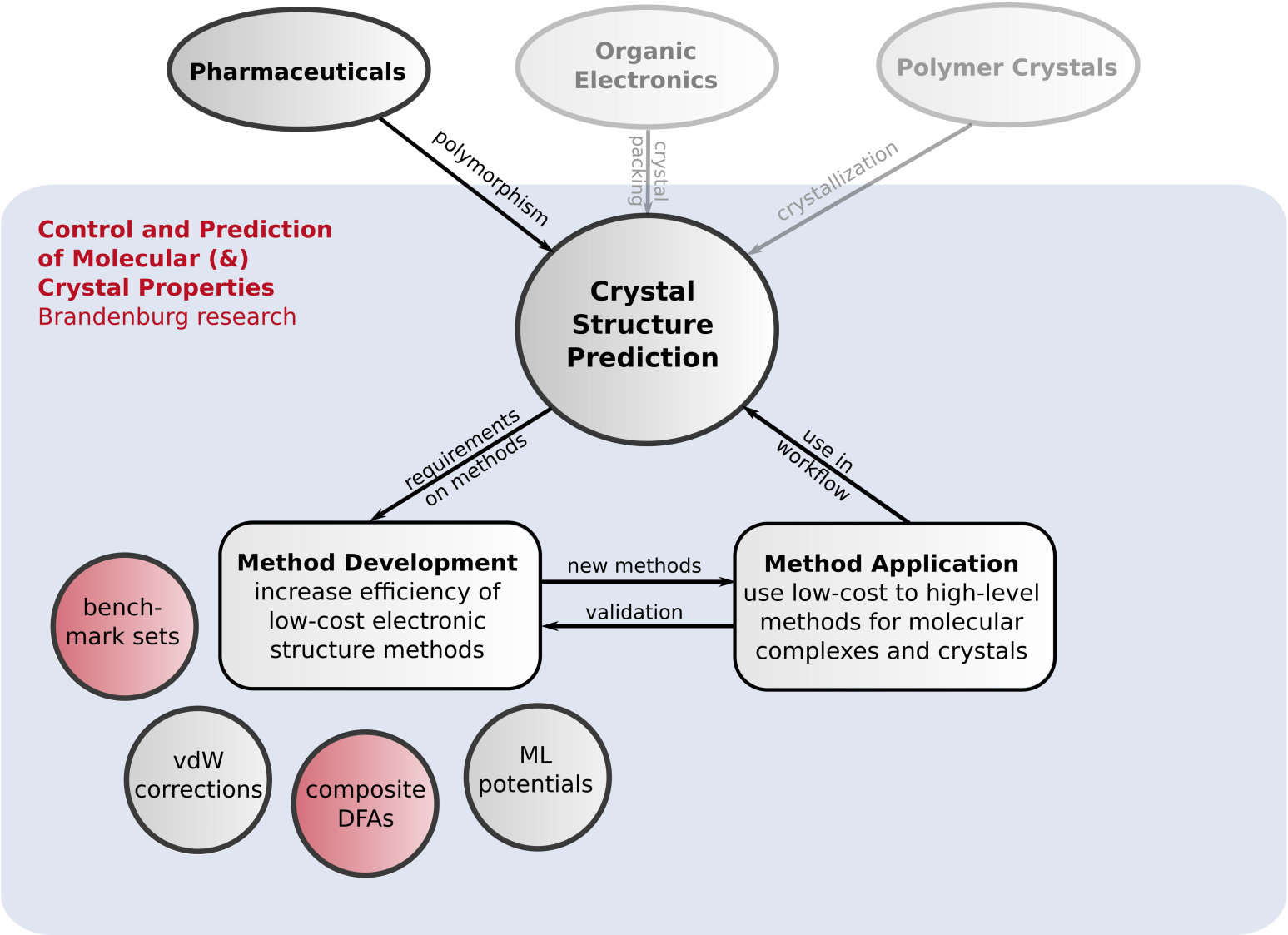
- solid state reactivities confirmed experimentally[15]
- crystal field stabilizes FLP products
- avoiding unesired products in solution, new FLP routes may be enabled

  $\longrightarrow$ screen for further candidates

  $\longrightarrow$ heterogeneous FLP-catalysis? (work in progress)

[15] L. Wang, G. Kehr, C. G. Daniliuc, M. Siedow, T. Wiegand, Anna-Lena Wübker, H. Eckert, L. Liu, JGB, S. Grimme, G. Erker *submitted* (2018).

Brandenburg research concept



Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

4 Quantum Monte-Carlo for molecular materials

5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

Multilevel methodologies: Finding the right compromise

	task/property	example method
accurate QM	single-point energy	many-body WFT (DMC[16])
cheap QM	optimization	DFT[17–19] (SCAN-D3[20])
very cheap QM	optimization/Hessians conformations	semi-empirical[21–22]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

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

[17] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016).

[18] JGB, C. Bannwarth, A. Hansen, S. Grimme, *JCP*, **148**, 064104 (2018). [19] M. Cutini, et al., *JCTC*, **12**, 3340 (2016).

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

[21] JGB, S. Grimme, *JPCL*, **5**, 1785 (2014). [22] M. Mortazavi, JGB, R. J. Maurer, A. Tkatchenko, *JPCL*, **9**, 399 (2018)

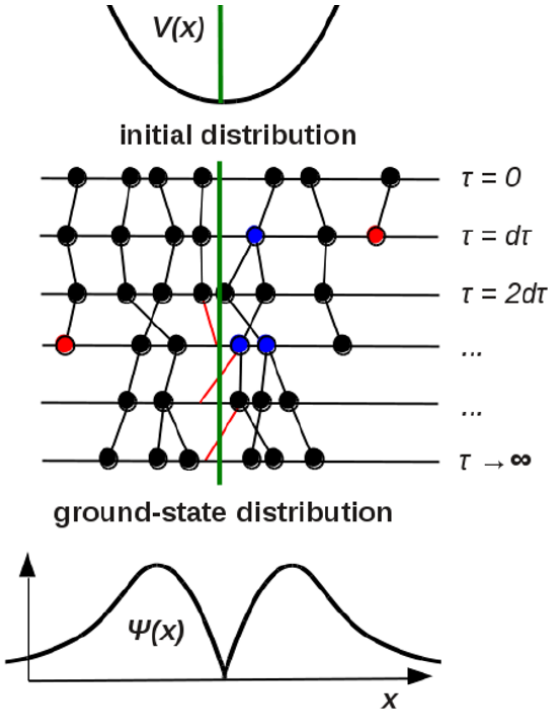
Quantum Monte-Carlo in a nutshell: A scalable high-level method

How to solve Schrödinger equation for large systems?

FN-diffusion Monte-Carlo

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

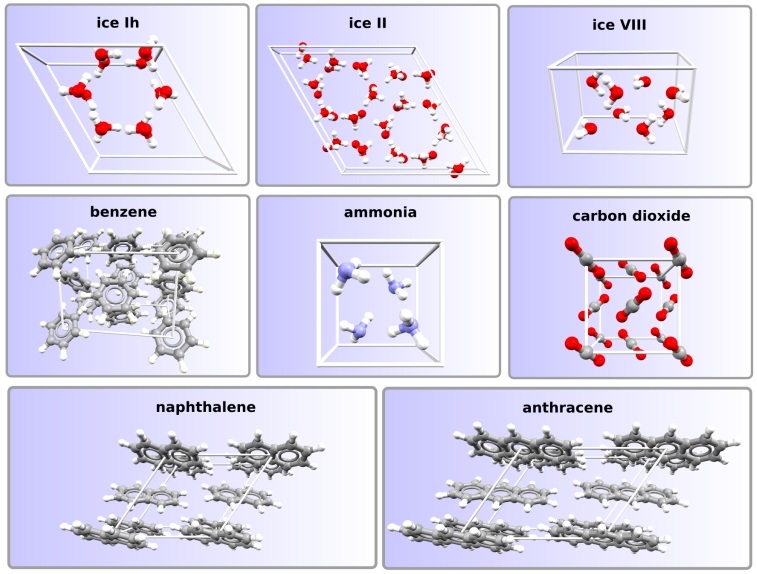
- low-scaling (N^3) with system size
- scaleable to HPCs[23]
- new size-consistent algorithm leads to substantial speed up[24]

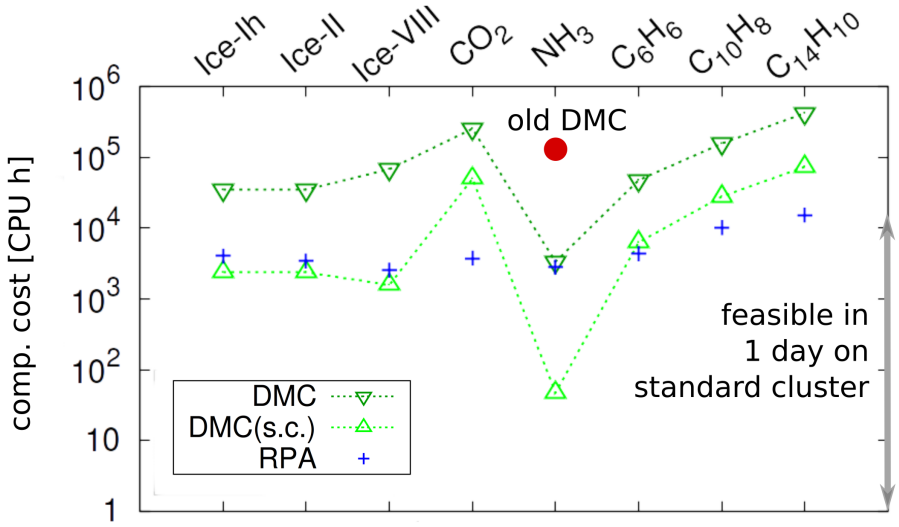


[23] M. Ďubecký, L. Mitas, P. Jurečka, *Chem. Rev.* **116**, 5188 (2016).

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

QMC delivers (sub-) chemical accuracy for molecular crystals





- up to three orders of magnitude speed-up compared to best DMC practice two years ago[25]
- significance will extend to all classes of systems[16]

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

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

Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

4 Quantum Monte-Carlo for molecular materials

5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

Multilevel methodologies: Finding the right compromise

	task/property	example method
accurate QM	single-point energy	many-body WFT (DMC[16])
cheap QM	optimization	DFT[17–19] (SCAN-D3[20])
very cheap QM	optimization/Hessians conformations	semi-empirical[21–22]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

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

[17] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016).

[18] JGB, C. Bannwarth, A. Hansen, S. Grimme, *JCP*, **148**, 064104 (2018). [19] M. Cutini, et al., *JCTC*, **12**, 3340 (2016).

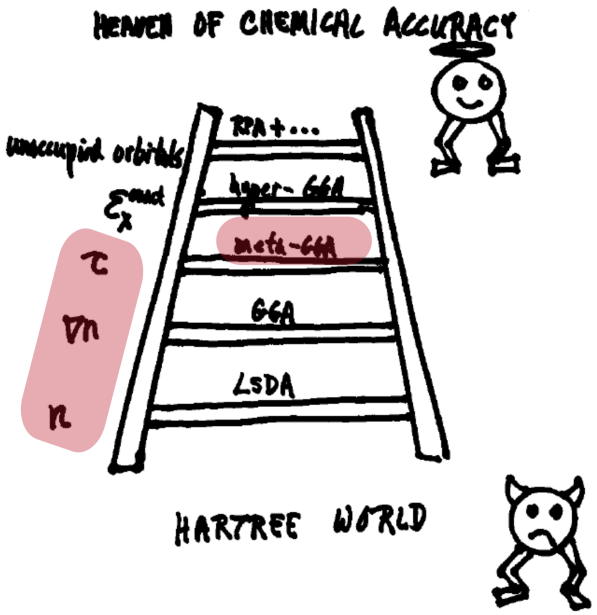
[20] JGB, J. E. Bates, J. Sun, J. P. Perdew *Phys. Rev. B*, **94**, 115144 (2016).

[21] JGB, S. Grimme, *JPCL*, **5**, 1785 (2014). [22] M. Mortazavi, JGB, R. J. Maurer, A. Tkatchenko, *JPCL*, **9**, 399 (2018)

Strongly constrained and appropriately normed semilocal functional (SCAN)

SCAN functional[26]

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



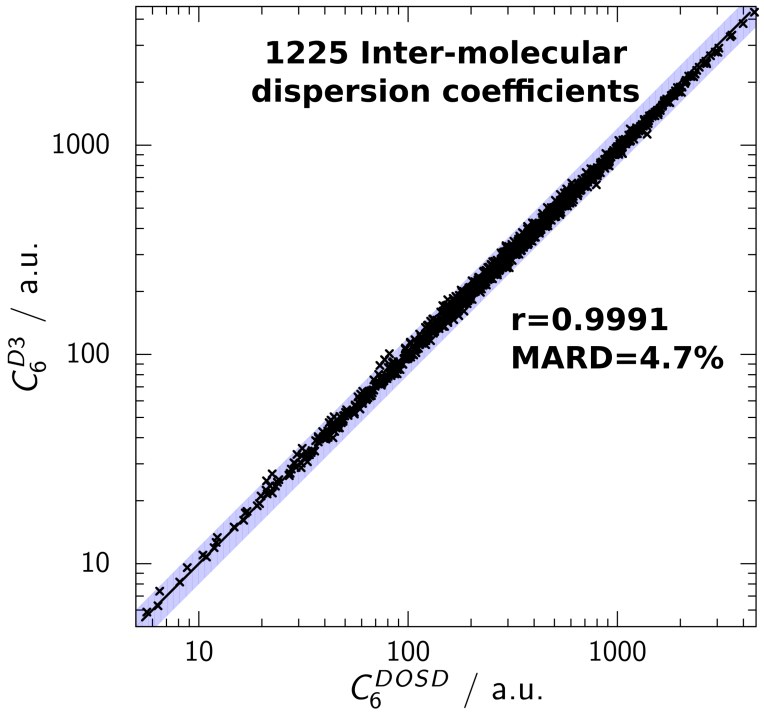
- add semi-classical correction for long-range correlation[5]

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

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

[17] 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[27-29]

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

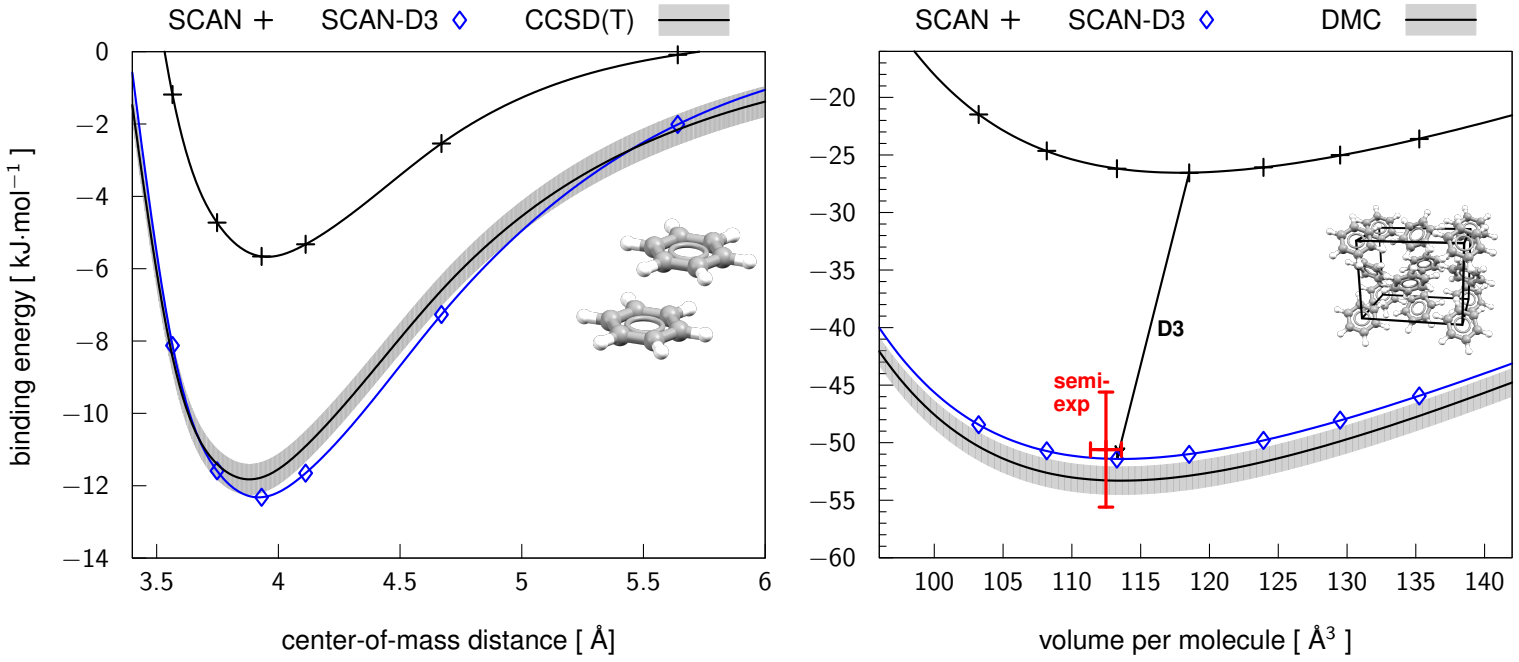
- Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error $< 5\%$
- empiricism in short-range damping

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

[28] S. Grimme, *WIREs Comput. Mol. Sci* **1**, 211 (2011)

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

Close agreement with reference for noncovalently bound systems

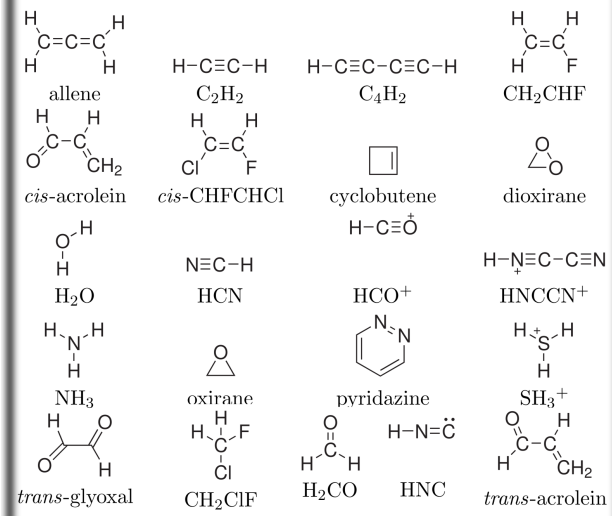


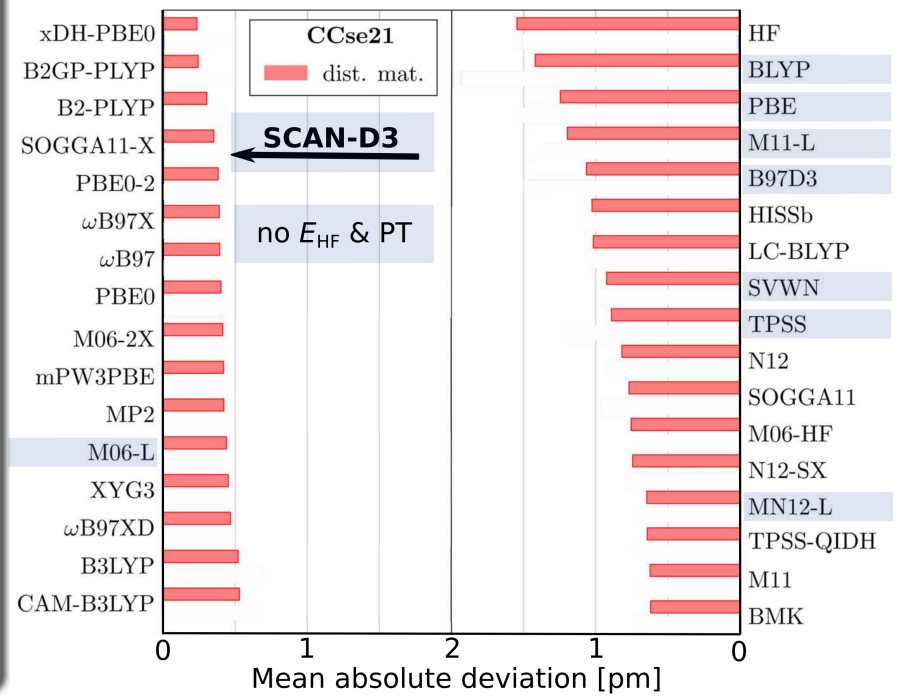
- zero-point and thermal effects crucial for comparing to measurement
- new references valuable for testing approximate methods
- strong hydrogen bonded systems bound to strongly by SCAN

Excellent geometries across the periodic table

CCse21 set

* measure experimental B_{rot}
* estimate ΔB_0 at CCSD(T) level
* least-square fit to get r_e



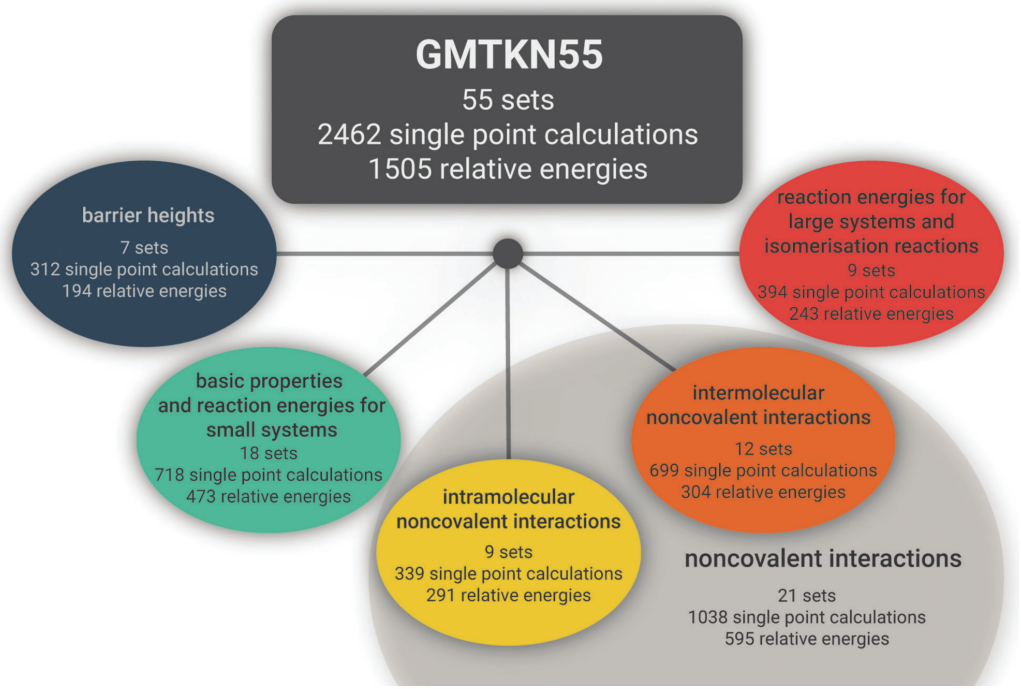


- structures better than all other tested (meta)GGAs
- extends to heavy main group bonds and transition metal complexes

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

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

Reliable main group thermochemistry, kinetics, and noncovalent interactions



- best metGGA functional for GMTKN55, WTMAD-1 of 4.7 kcal/mol
- good performance extends to metal-organic reactions (MOR set)

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

[32] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, S. Grimme, *Phys. Chem. Chem. Phys.*, **19**, 32184 (2017).

Outline of talk

1 Introduction

2 Simulation based crystal structure prediction

3 Frustrated Lewis pair chemistry in the solid state

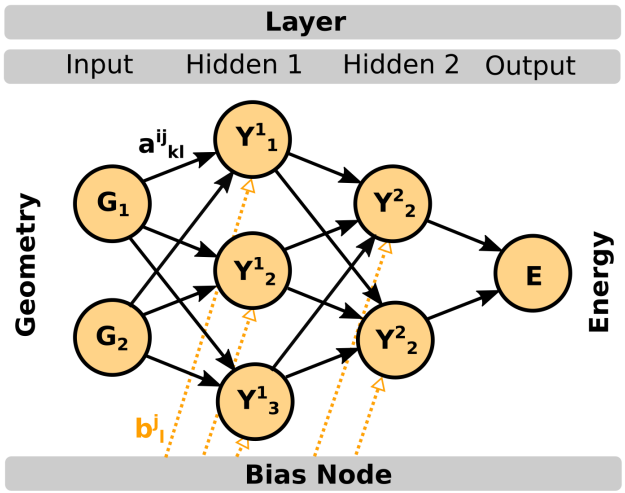
4 Quantum Monte-Carlo for molecular materials

5 SCAN-D3: Boosting the accuracy of meta-GGAs

6 Project outlook

Understanding dynamical properties of complex systems

- high dimensional neural networks for potential interpolation[33–34]
- reduce the number of required *ab initio* calculations within CSP
- enable molecular dynamics on approximate *ab initio* potential

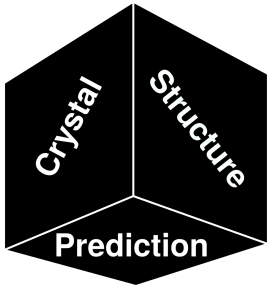


Collaborative Research Centre on
Multiscale Simulation Techniques for Soft Matter

[33] J. Behler, M. Parrinello, *Phys. Rev. Lett.*, **98**, 146401 (2007).
[34] J. Behler, *Angew. Chem. Int. Ed.*, **56**, 12828 (2017).

Building a bridge between molecular and solid state properties

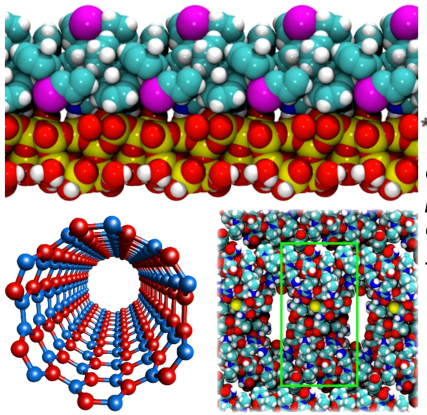
- relative stability of enantiopure and racemic crystal structures
- structure prediction of porous materials
- crystal structure prediction for organic electronics
  $\longrightarrow$ crystal packing effect?
  $\longrightarrow$ modified adsorption/emission?



Extend the collaboration through Merck Lab@TU Darmstadt?

Extend methodologies to inorganic materials

- major contributions to CRYTAL17
- combine efficient program handling with modern density functionals



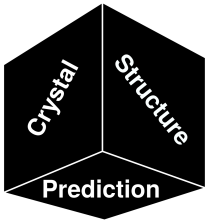
CRYSTAL17

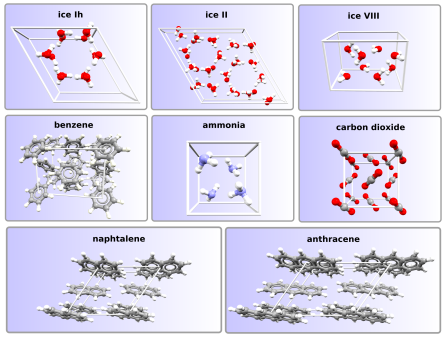
enables consistent studies of the physical and chemical properties of molecules, polymers, nanotubes, surfaces and crystalline solids

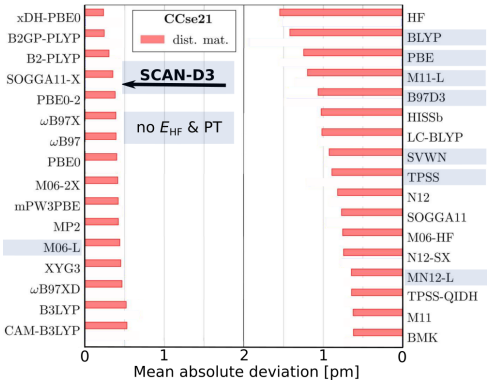
Organic-inorganic interfaces and nanomaterials?

Summary

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



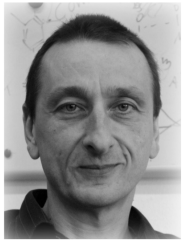




Acknowledgements

PhD / Postdocs

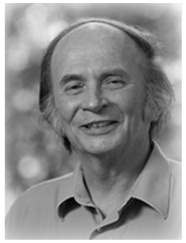

Eike Caldeweyer


Andrea Zen


Luca Iuzzolino

Principal investigator


Grimme (Bonn)


Perdew (Temple)


Civalleri (Turin)


Maschio (Turin)


Michaelides (UCL)

Alfé (UCL)

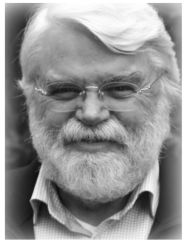

Tkatchenko (Luxembourg)


Behler (Göttingen)


Price (UCL)

Hall (Bristol)


Fernandez-Alonso (ISIS)


Erker (Münster)

Industry


Rebecca Sure (BASF)


Antreas Afantitis (NovaMechanics)

Alexander von Humboldt Stiftung/Foundation

THE THOMAS YOUNG CENTRE TYC

cposs

Acknowledgements

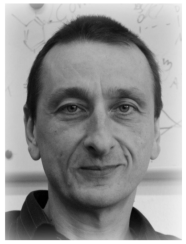
PhD / Postdocs

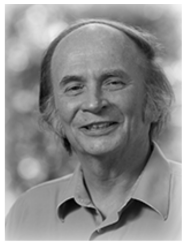

Eike Caldeweyer


Andrea Zen


Luca Iuzzolino

Principal investigator


Grimme (Bonn)


Perdew (Temple)


Civalleri (Turin)


Maschio (Turin)


Michaelides (UCL)


Alfé (UCL)

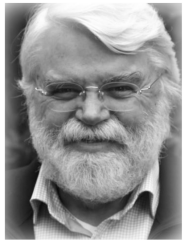

Tkatchenko (Luxembourg)


Behler (Göttingen)


Price (UCL)


Hall (Bristol)


Fernandez-Alonso (ISIS)


Erker (Münster)

Industry


Rebecca Sure (BASF)


Antreas Afantitis (NovaMechanics)

Alexander von Humboldt Stiftung/Foundation

Thanks

Key references

- Crystal structure prediction:

  S. L. Price, JGB, *Molecular Crystal Structure Prediction*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, *ISBN: 9780128098356* (2017).

- Solid state thermochemistry

  L. Liu, JGB, S. Grimme, *Phil. Trans. A*, **375**, 20170006 (2017).

- 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).

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