# Towards the design of molecular materials:

## From many-body methods to enhanced density functional approximations

**Gerit Brandenburg** <gerit.brandenburg@thch.uni-bonn.de> | 24th of January 2019

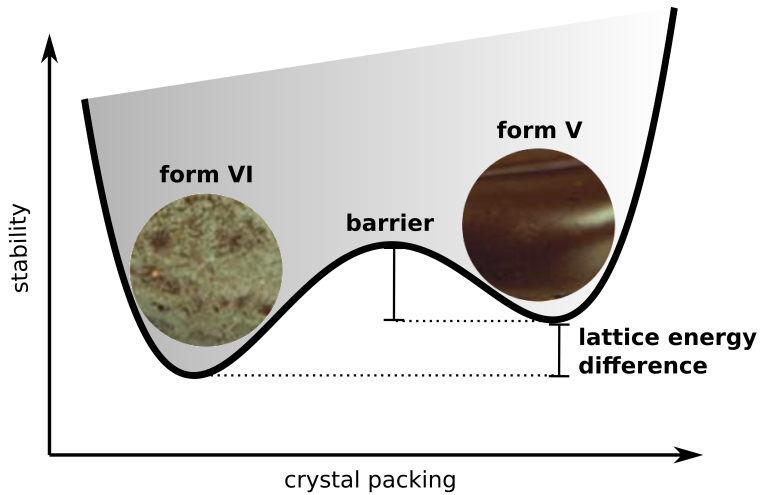
MARVEL MINI-SERIES, ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, SWITZERLAND

London Center for Nanotechnology – University College London
Institut for Physical Chemistry – University of Goettingen

# Many properties depend on the polymorphic form of a crystal

## Polymorphism

- ability of a molecule to crystallize in more than one structure
- properties change with crystal packing, e.g. solubility, color, etc.[1]



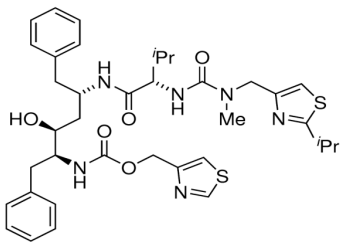

- cocoa butter (form VI) has a dull surface, soft texture, higher melting point
- metastable form V has glossy surface, crisp hardness, melts at 300 K[2]

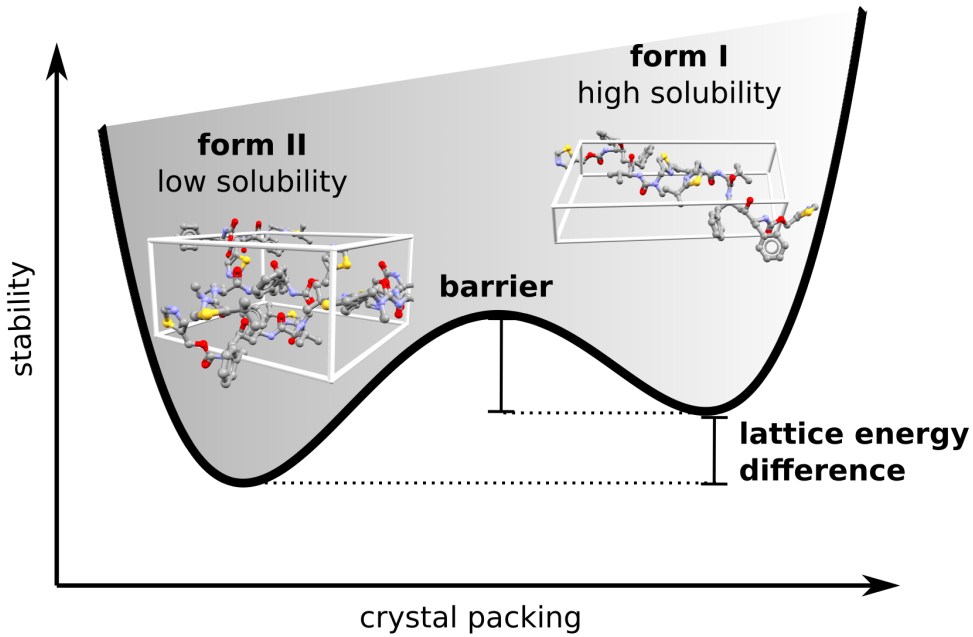
[1] A. J. Cruz-Cabeza, S. M. Reutzel-Edens, J. Bernstein, *Chem. Soc. Rev.* **44**, 8619-8635 (2015).

[2] S. T. Beckett, *Science of Chocolate*; RSC Paperbacks (2000).

# 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 [3]





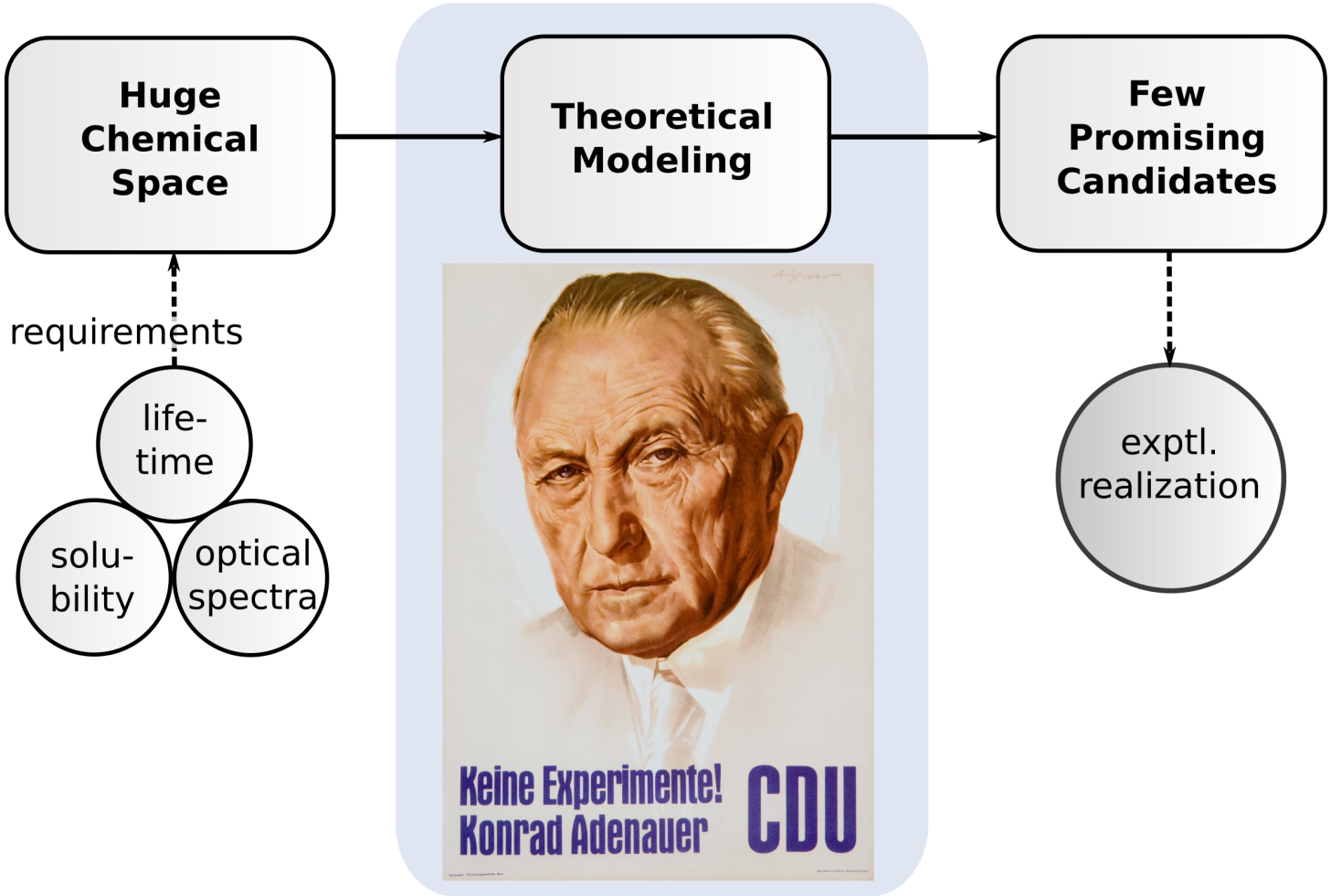

- tools to predict possible polymorphs would be valuable[4]

  → Simulation methods aim at complementing experimental screening

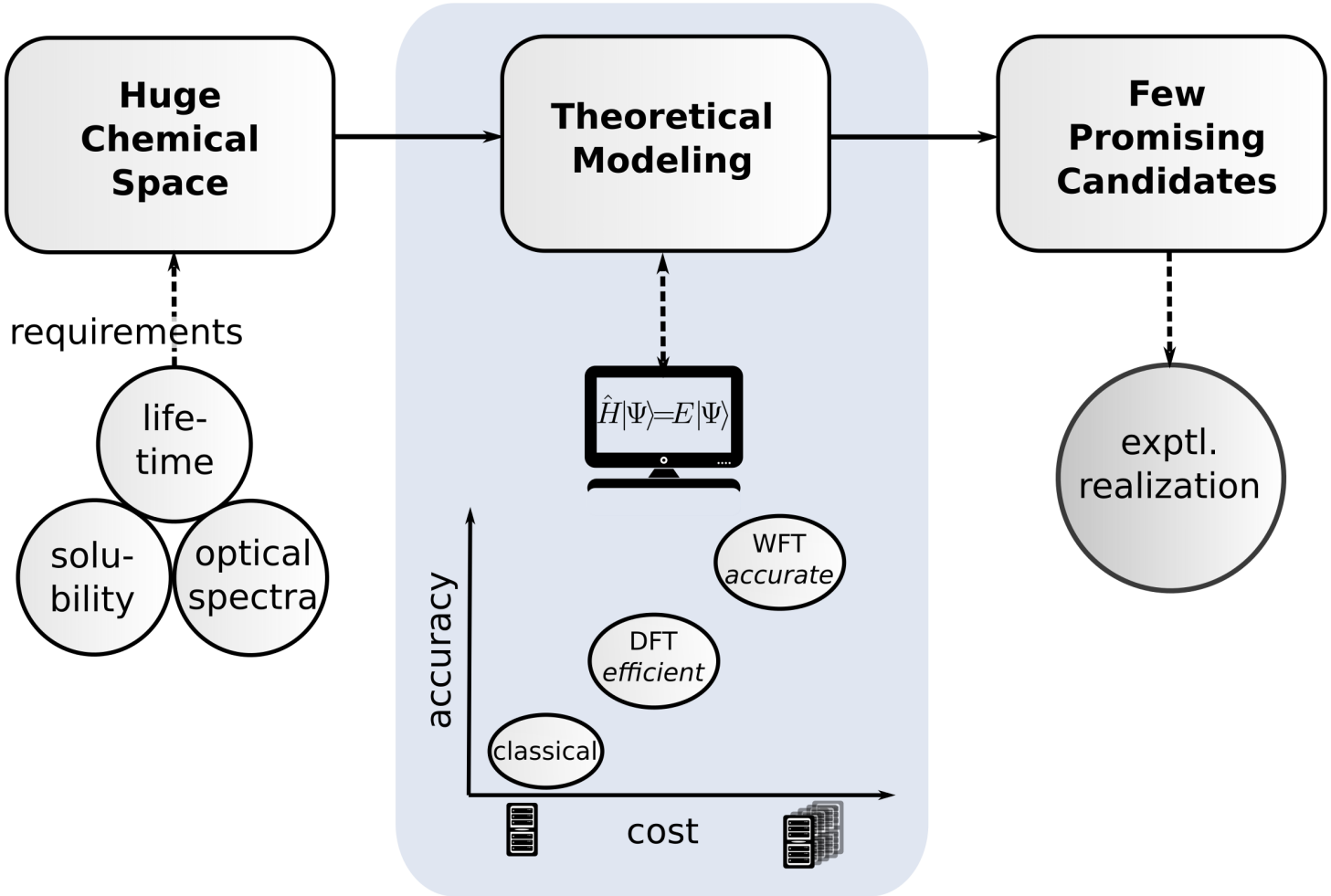
[3] J. Bauer, et al., *J. Pharm. Res.* **18**, 859-866 (2001).

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

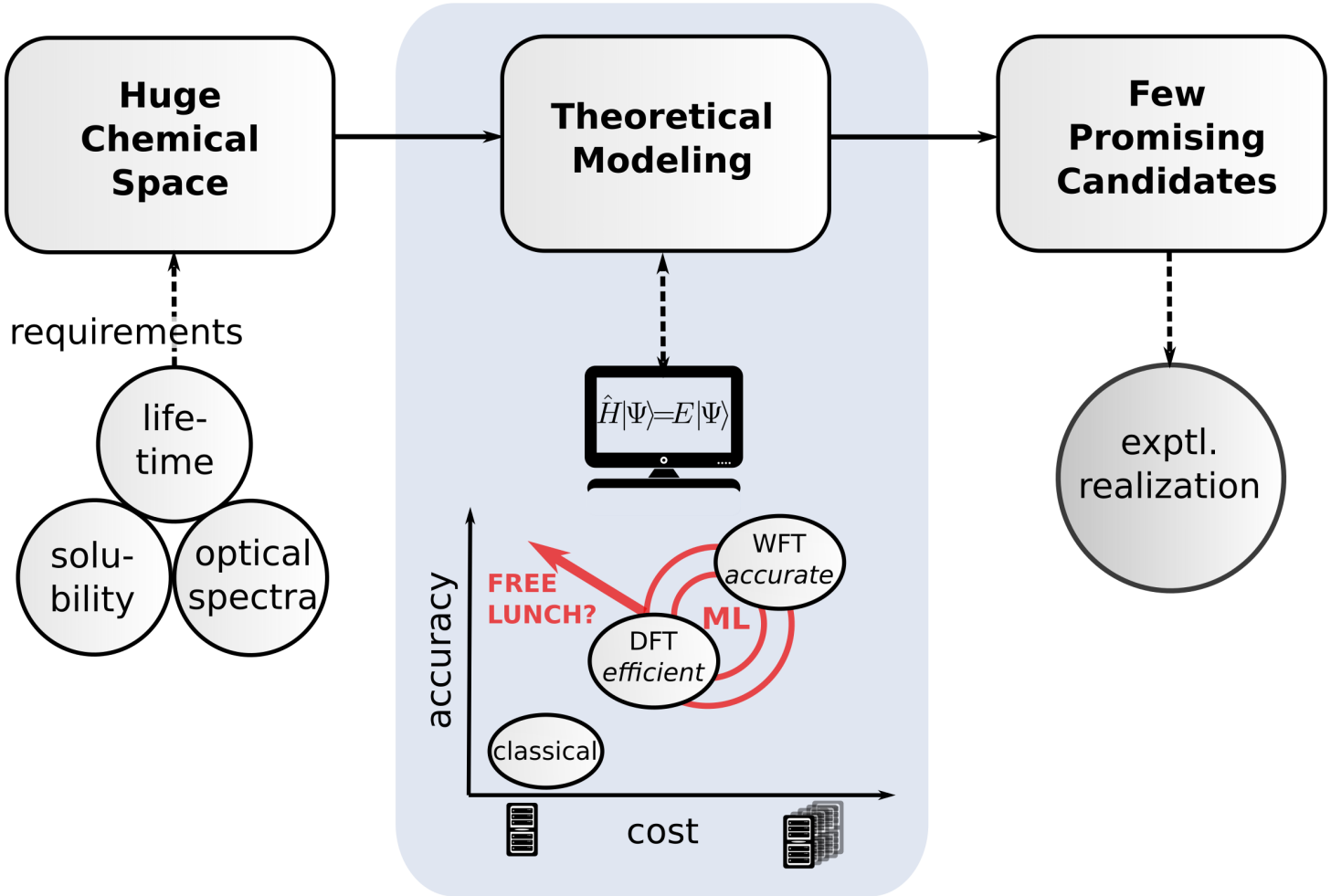
# Material discovery can employ computational models



# Material discovery can employ computational models



# Material discovery can employ computational models



# Outline of talk


1 Introduction

2 Simulation based crystal structure prediction

3 Quantum Monte-Carlo for molecular crystals

4 Simplified density functional approximations

5 Conclusions and Future Perspective

# Outline of talk


1 Introduction

2 Simulation based crystal structure prediction

3 Quantum Monte-Carlo for molecular crystals

4 Simplified density functional approximations

5 Conclusions and Future Perspective

# 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.[5–7]

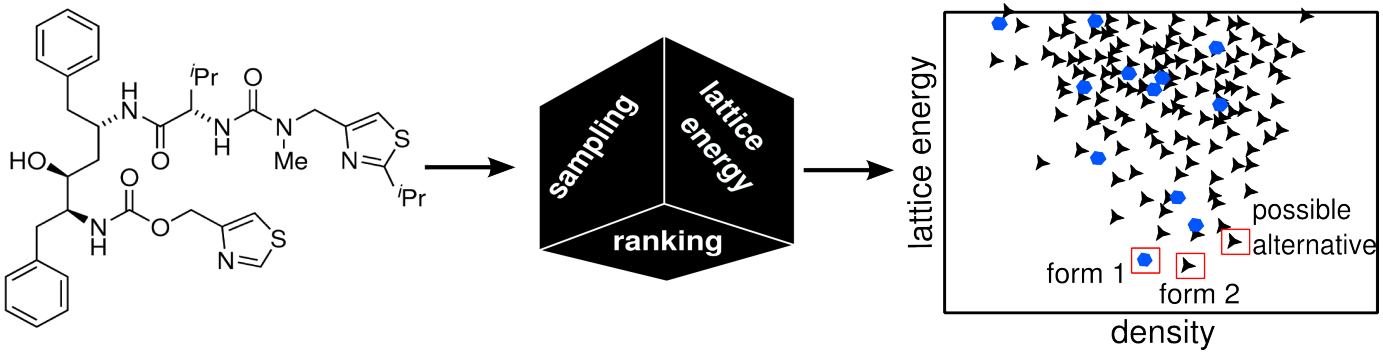
**Task**

- 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

[5] A. Gavezzotti, *Acc. Chem. Res.* **27**, 309-314 (1994). [6] J. Maddox, *Nature* **335**, 201-201 (1988).

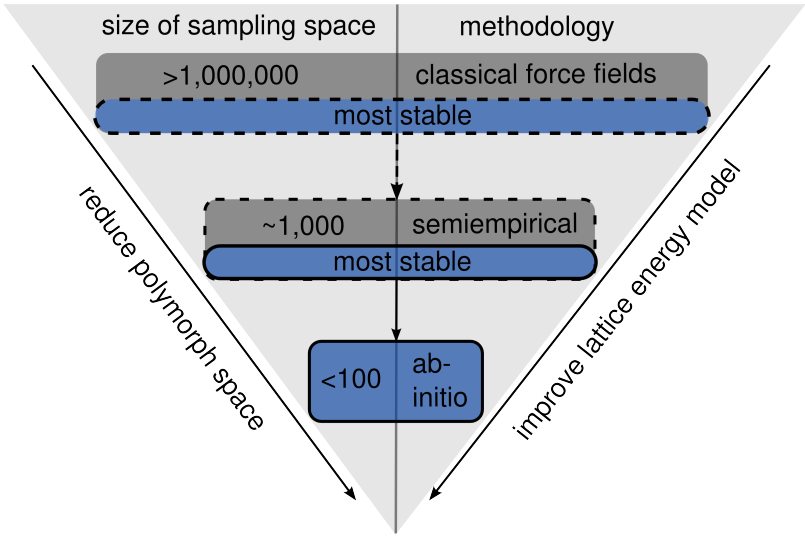
[7] K. N. Houk, F. Liu, *Acc. Chem. Res.*, **50**, 539 (2017).

# Sampling and energetic ranking for crystal structure prediction




## Layers of complexity:

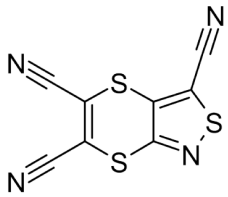
- molecular conformational space
- space groups (varying orientation, conformation, etc.)
- polymorph ranking according to free energy[8,9]



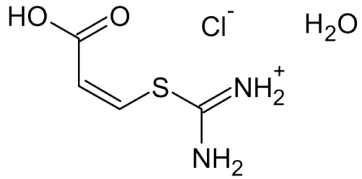

[8] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

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

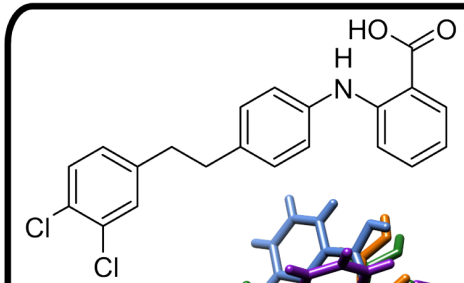
# Promising results in the 6$^{th}$ blind test

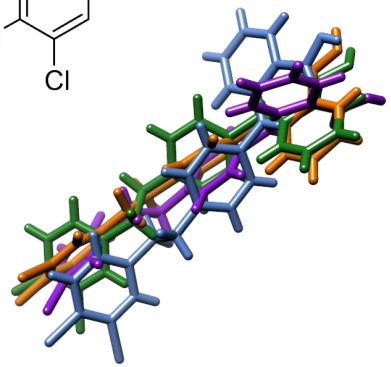


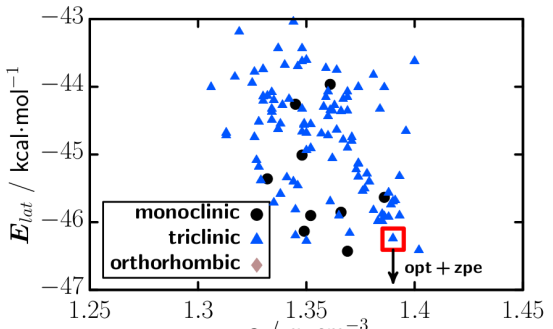
exp. polymorph: **Rank 1**
found in sampling: ✗

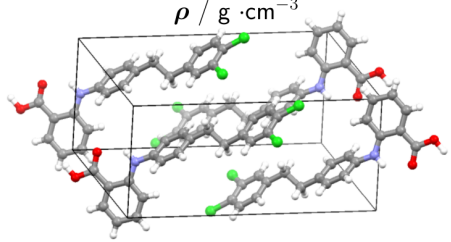


exp. polymorph: **Rank 1**
found in sampling: ✗

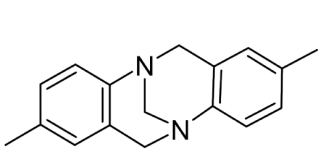


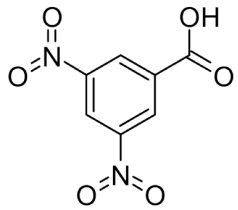




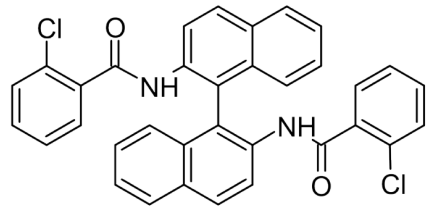



exp. polymorph: **Ranks 1-10**
found in sampling: ✓/ ✗





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



exp. polymorph: **Rank 1** found: ✗

[10] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016). [11] JGB, S. Grimme, *Acta Cryst. B*, **72**, 502 (2016).

# CSP bind test highlights two remaining challenges

## 1. Ranking stage

Crystal polymorphs are often separated by just a few kJ/mol, exceeding the accuracy of standard density functional approximations (DFAs).
$\Longrightarrow$ **Are many-body methods feasible?**

## 2. Sampling stage

Dealing with a vast search space, in particular for molecules with increased flexibility, one has to cover too many structures at DFT accuracy.
$\Longrightarrow$ **Can we improve modern DFAs?**

# Outline of talk


1 Introduction

2 Simulation based crystal structure prediction

3 Quantum Monte-Carlo for molecular crystals

4 Simplified density functional approximations

5 Conclusions and Future Perspective

# Methods with 'benchmark quality' for noncovalent interactions

## 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, RPA, CCSD, CCSD(T)/cc-pVTZ, VMC

# 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

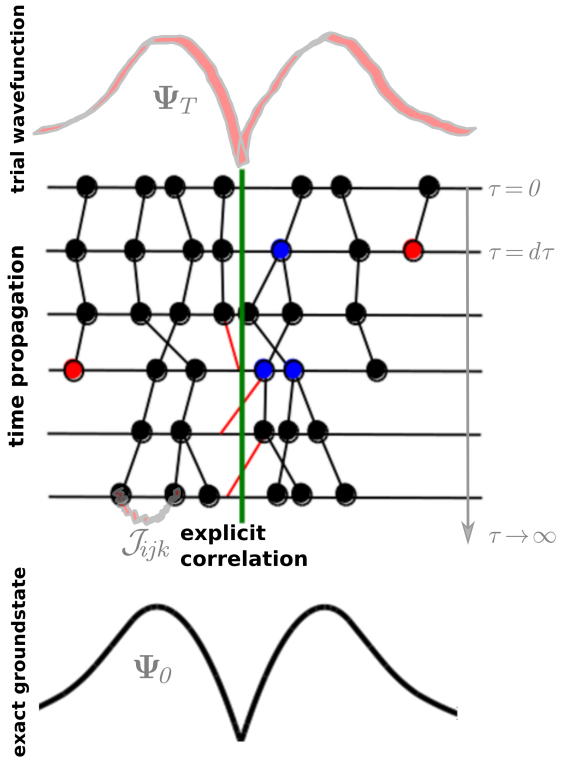
$$|\Psi_T(\mathbf{R}, \tau)\rangle = \text{hist}\left[\sum \delta(\mathbf{R} - \mathbf{R_i}(\tau))\right]$$

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

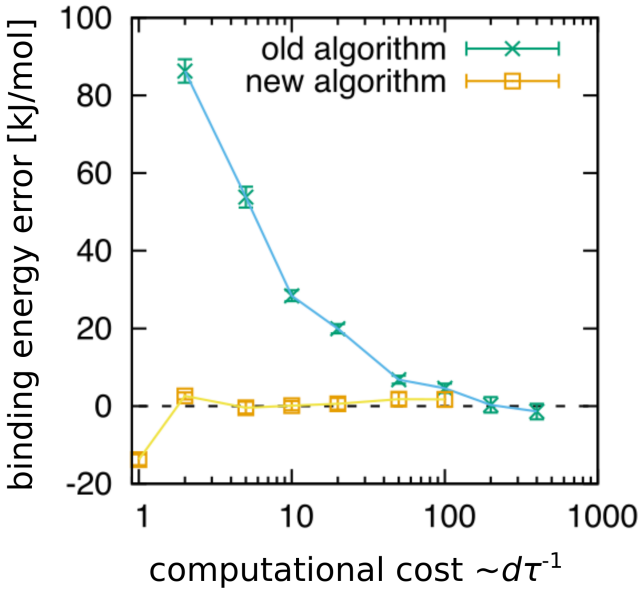
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau\to\infty} \exp\left[-\tau(\hat{H} - E_T)\right] |\Psi_T(\mathbf{R}, \tau)\rangle$$

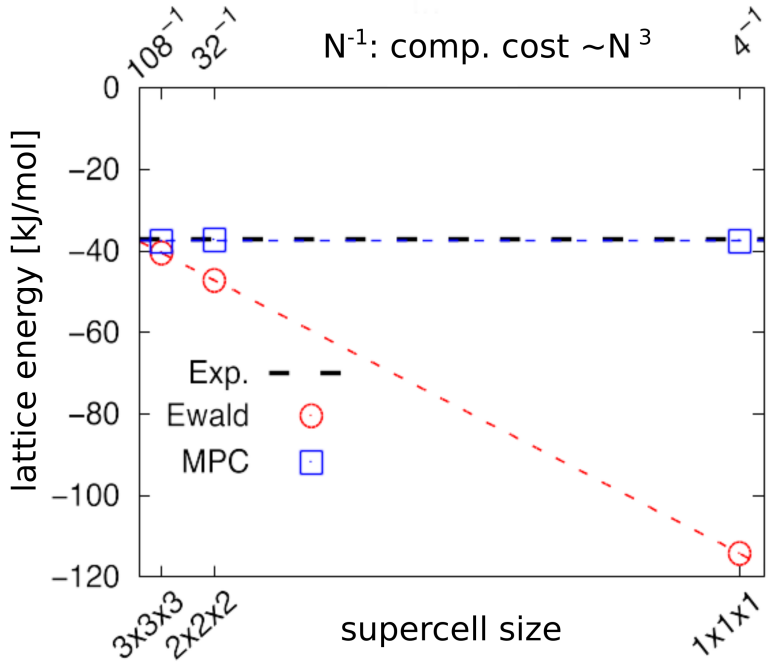



- exact within $\Gamma$ and $d\tau \to 0$ and $\tau \to \infty$
- non-local part of pseudopotentials impact electron correlation

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

# New DMC algorithm leads to substantial speed up



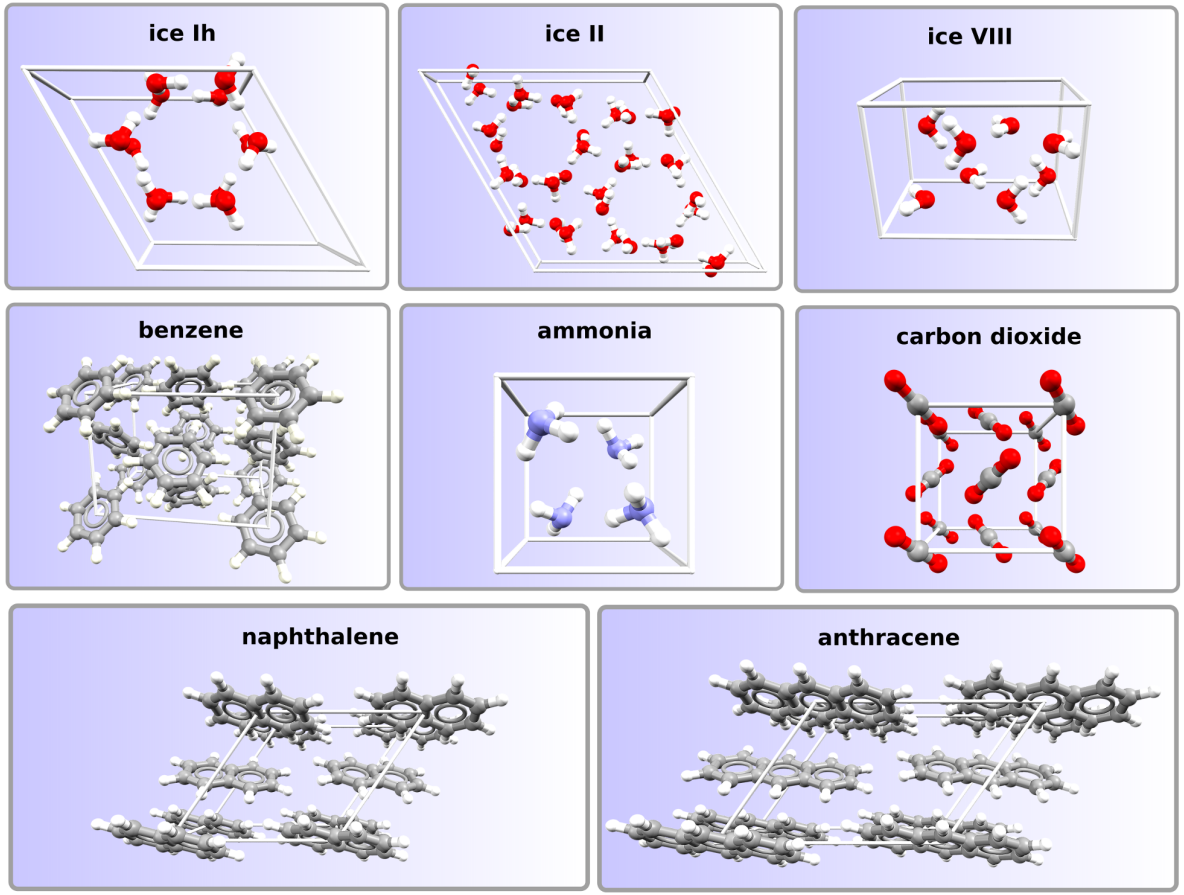




- new size-consistent implementation reduces $\Delta\tau$ error drastically[13]
- Model periodic Coulomb for finite size correction[14]

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

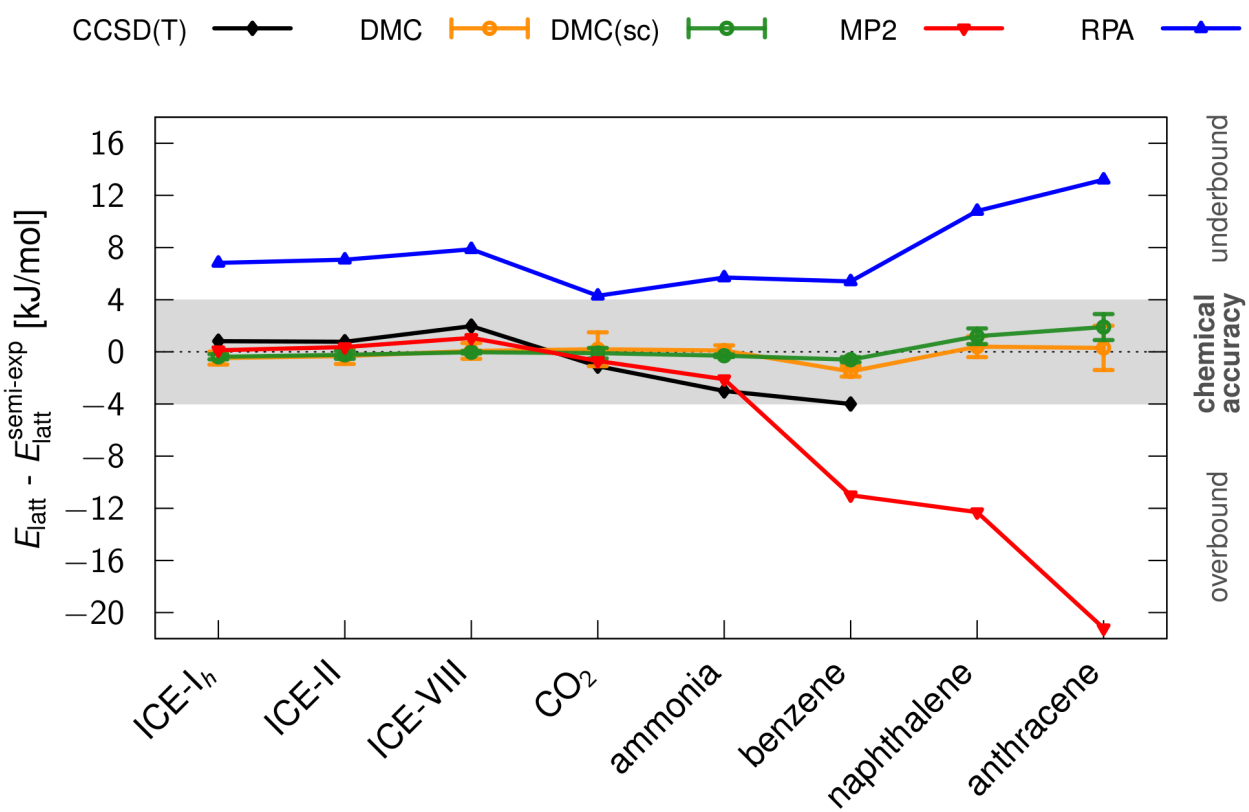
[14] L. M. Fraser, W. M. C. Foulkes, G. Rajagopal, R. J. Needs, S. D. Kenny, A. J. Williamson, *Phys. Rev. B* **53**, 1814 (1996).

# Molecular crystals as challenging test



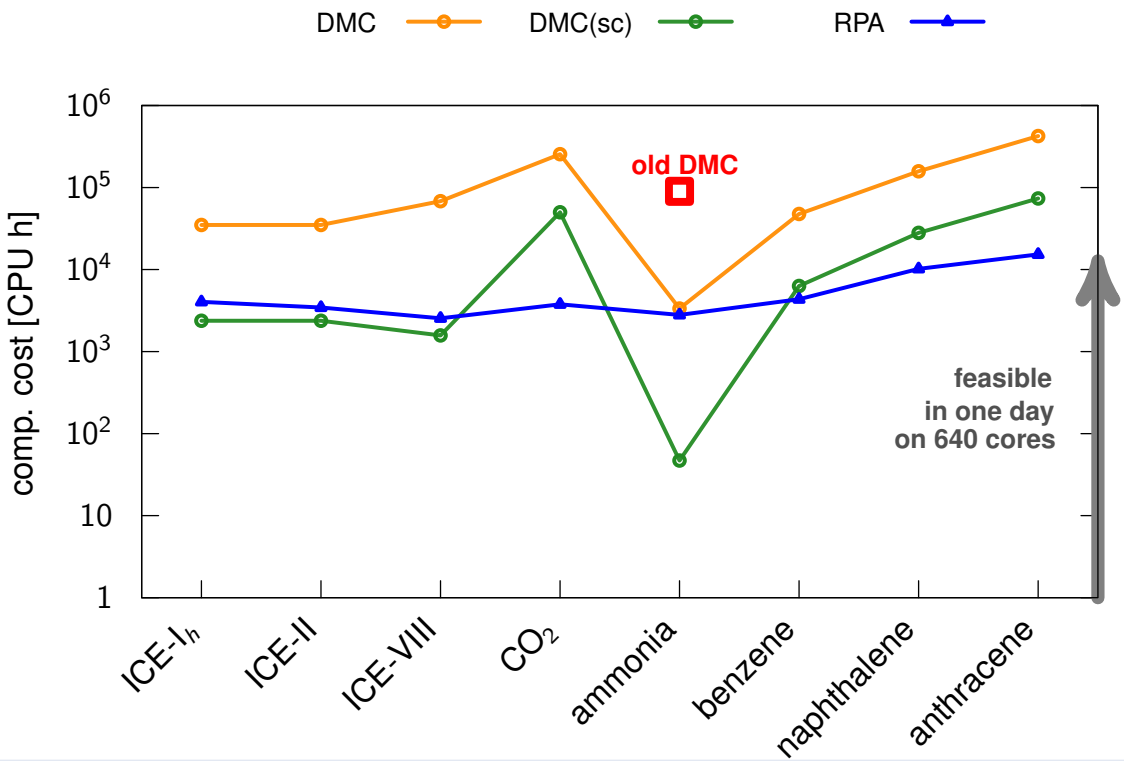

- strong H-bonds, vdW of saturated and unsaturated molecules
- problematic for all readily applicable methods (DFA-DISP, MP2)

# 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[15]

[15] 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 Quantum Monte-Carlo for molecular crystals

4 Simplified density functional approximations

5 Conclusions and Future Perspective

# Multilevel methodologies: Finding the right compromise

| | task/property | example method |
|---|---|---|
| **accurate QM** | single-point energy | many-body WFT (DMC[15]) |
| **cheap QM** | optimization | DFT[16–17] (HSE-3c[19]) |
| **very cheap QM** | optimization/Hessians conformations | semi-empirical[20,21] |
| **force field** | dynamics conformational sampling | transferable or molecule specific (QM derived) FF |

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

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

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

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

# Requirements on the new density functional method

- reasonably fast for optimizations and frequencies
  $\rightarrow$ small atomic orbital expansion
- avoid most self-interaction error
  $\rightarrow$ use one-determinantal (Fock) exchange
- numerically robust including small gap solids
  $\rightarrow$ long-range screening of Fock exchange
- good, globally accurate PES
- accurate non-covalent interactions
- consistency for isolated molecules and the condensed phase

# Three ingredients target different interaction regimes

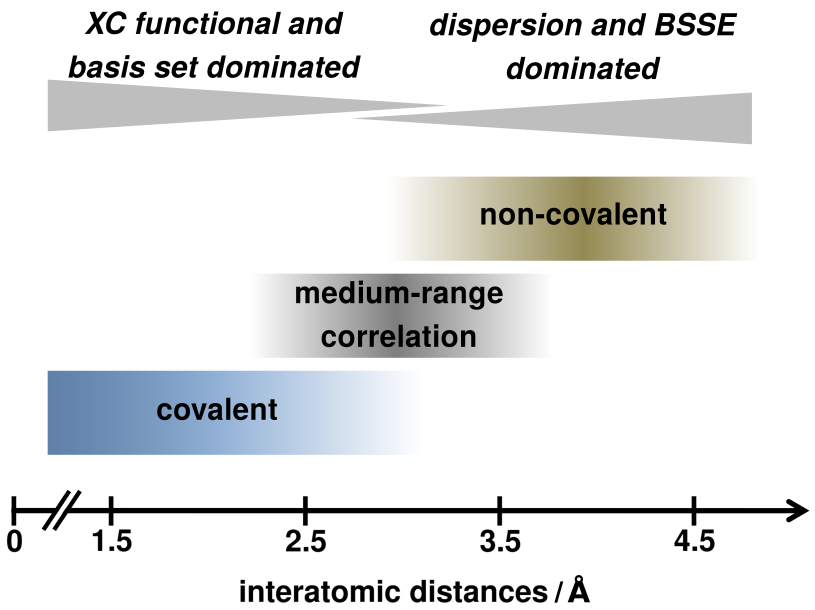
## HSE-3c contributions[23]

$$E_{\text{tot}}^{\text{HSE-3c}} = E_{\text{xc}}^{(\text{modHSE})} + E_{\text{DISP}}^{(\text{D3})} + E_{\text{BSSE}}^{\text{gCP}}$$

**(A)** DFA/basis set
mod. HSE[24] / def2-mSVP[22]

**(B)** London DISP interaction
**D3 correction**

**(C)** BSSE counterpoise correction
**gCP scheme**





[22] S. Grimme, JGB, C. Bannwarth, A. Hansen, *J. Chem. Phys.* **143**, 054107 (2015)

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

[24] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006)

# Compromise of known functionals for exchange correlation functional

$$E_{\mathrm{xc}}^{(\mathrm{modHSE})} = \mathbf{a_x}\, E_{\mathrm{x}}^{(\mathrm{HF,SR})}(\omega) + (1 - a_x)\, E_{\mathrm{x}}^{(\mathrm{HSE,SR})}(\omega) + E_{\mathrm{x}}^{(\mathrm{HSE,LR})}(\omega) + E_{\mathrm{c}}^{(\mathrm{modPBE})}$$

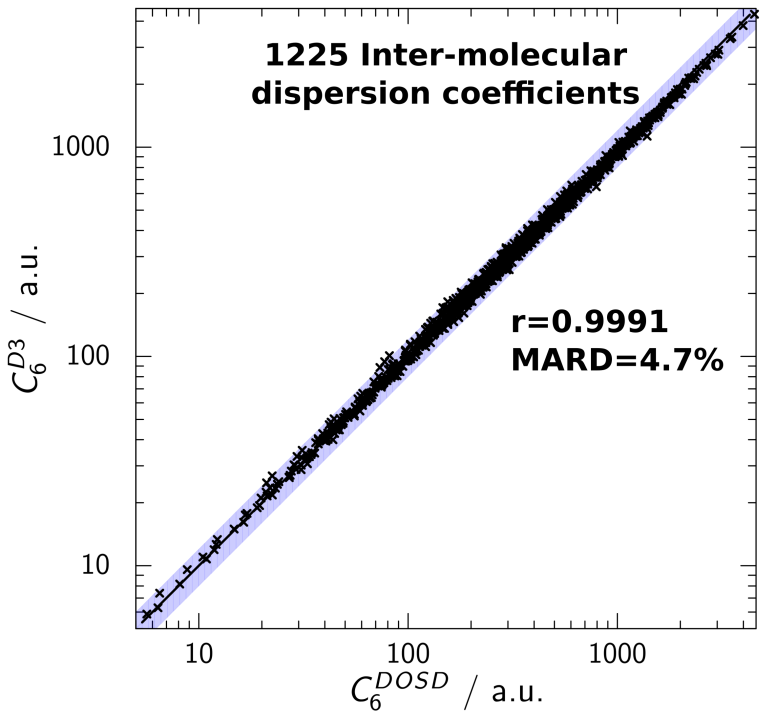
- modified HSE to reproduce modified PBE-XC

$$F_X^{\mathrm{PBE}} = 1 + \frac{\mu s}{1 + \frac{\mu s^2}{\kappa}}, \qquad s = |\nabla\rho/\rho^{4/3}|$$

- $\mu$ from PBEsol, $\kappa$ averaged from PBE/revPBE
- $\beta = 0.03$ in $F_C^{\mathrm{PBE}}$ fitted to atomization energies
- $a_x = 0.42$: getting bond length right (standard range-separation $\omega = 0.11$)
- mSVP atomic orbitals fixed and available for whole PES

$\rightarrow$ only **seven** globally fitted parameters

# Semi-classical correction yields highly accurate dispersion coefficients




## D3 correction[25-27]

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

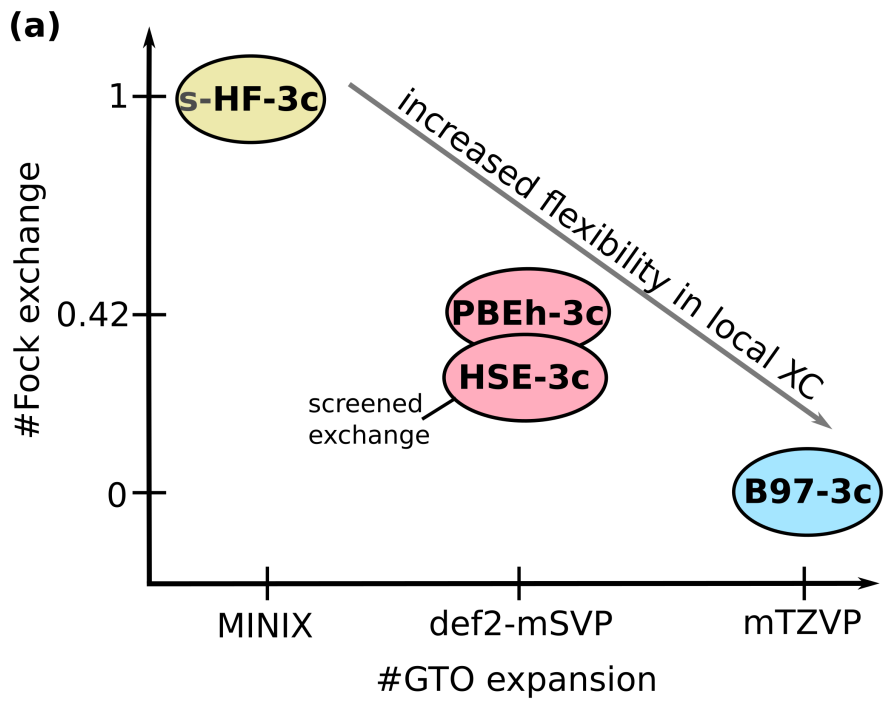
- Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error $< 5\%$
- empiricism in short-range damping

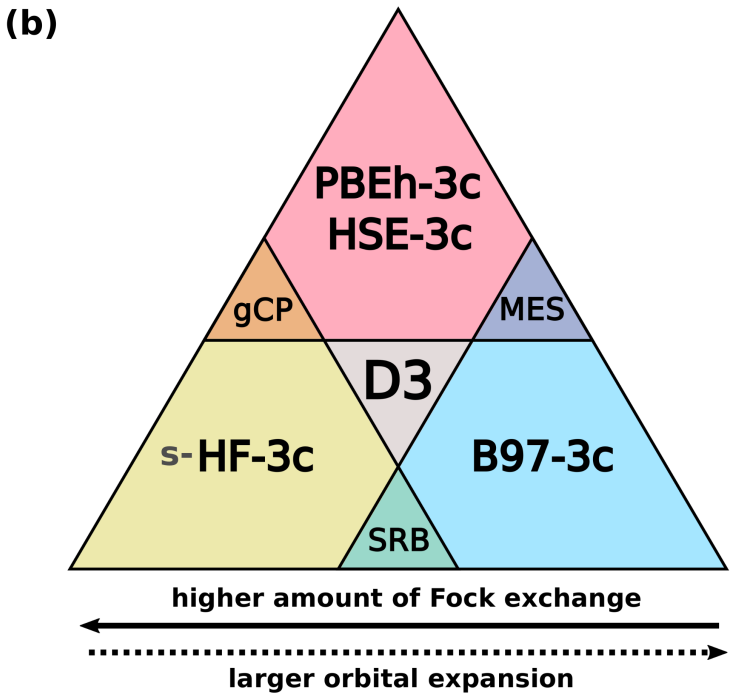

[25] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010)

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

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

# Full hierarchy of 'low-cost' methods



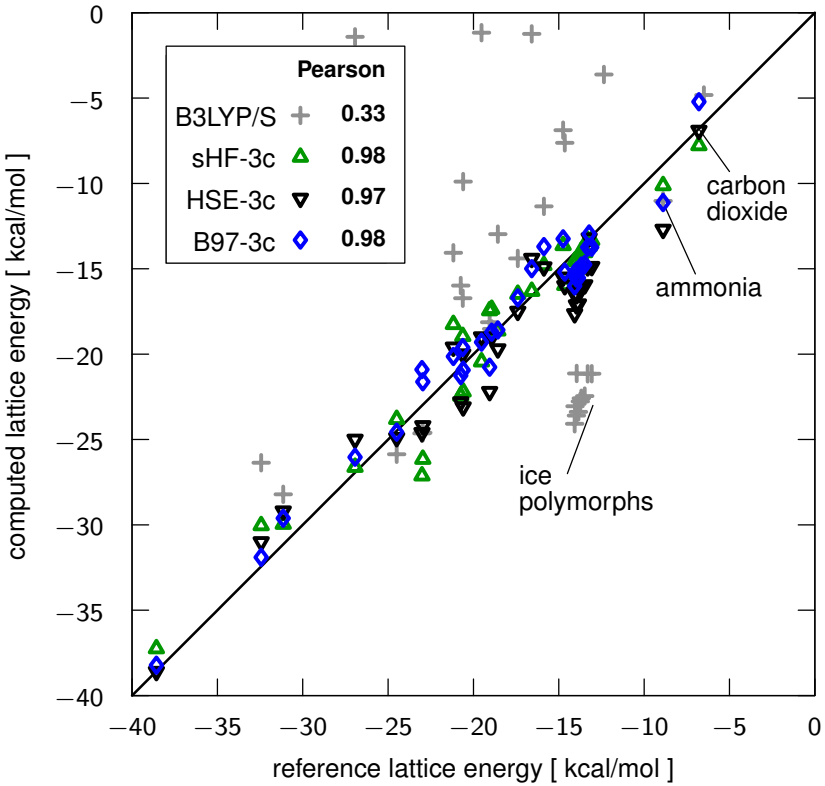



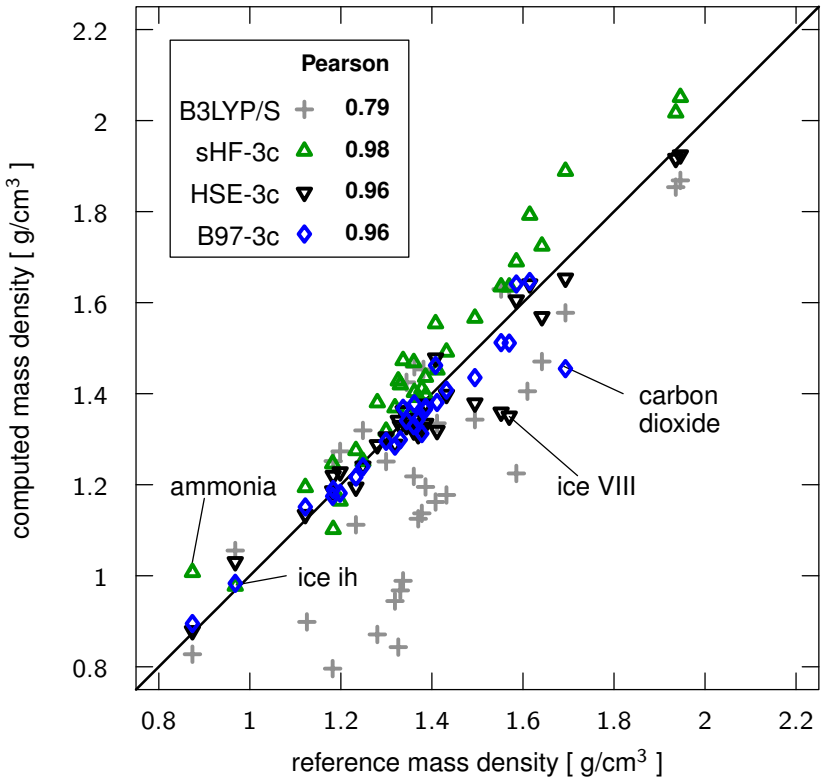

- HSE-3c/PBEh-3c: General purpose
- HF-3c: SIE dominated systems, nor MR character
- B97-3c: SIE unproblematic, possible MR character

[28] E. Caldeweyher, JGB, *J. Phys.: Condens. Matter* **30**, 213001 (2018) *[Psi-k Highlight Jan. 2019]*

# Good results on molecular crystals

X23[29,30] and ICE10[31] benchmark sets:



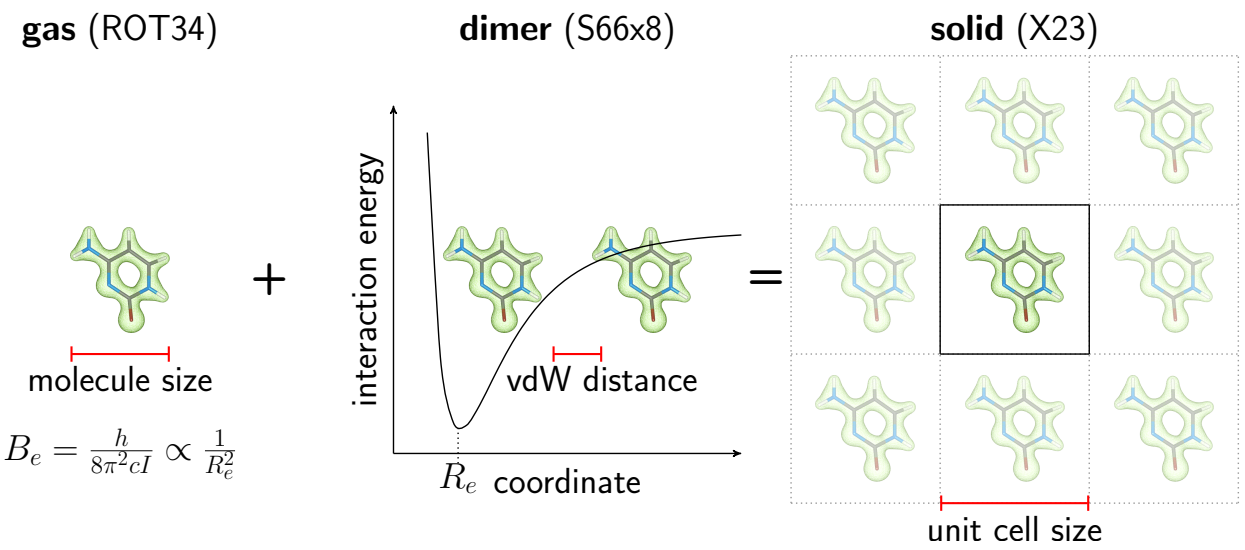




- consistent structures and interaction energies by HSE-3c

[29] E. Johnson, A. Otero-de-la-Roza, *J. Chem. Phys.* **137**, 054103 (2012), [30] A. Reilly, A. Tkatchenko, *JCP* **139**, 024705 (2013)

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

# Consistency for structures achieved



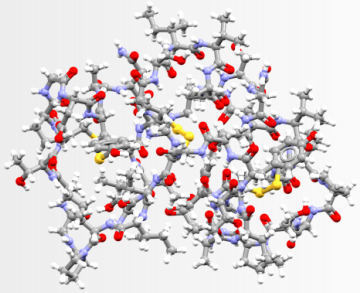

| | **ROT34** org. mol. | **S66x8** non-covalent | **X23** molecular crystal |
|---|---|---|---|
| TPSS/large basis | 1.9 | 14.6 | 27.9 |
| TPSS-D3/large basis | 1.3 | 1.3 | 1.0 |
| HF-3c (very cheap QM) | 1.5 | -1.2 | -5.7 |
| DFTB3-D3 (very cheap QM) | 1.2 | -2.9 | -12.6 |
| **HSE-3c** (cheap QM) |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

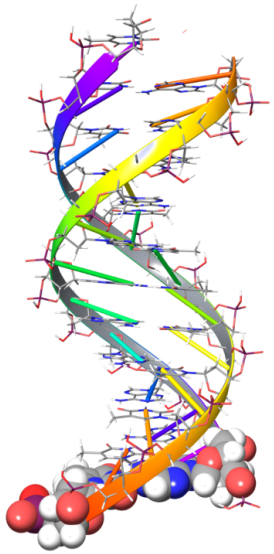
mean of relative deviation in %

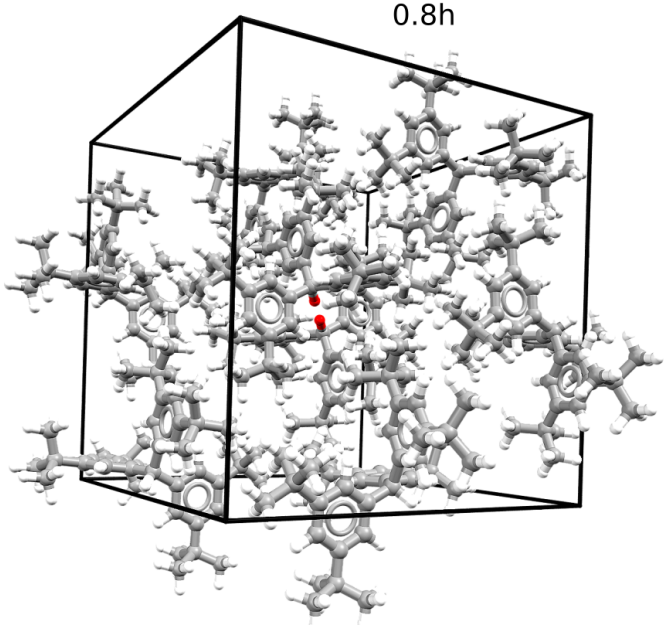
# Fast electronic structure with ab-initio accuracy

| | gas phase protein | DNA helix | molecular crystal |
|---|---|---|---|
| **dim:** | 0D | 1D | 3D |
| **#atoms/unit:** | 647 (647) | 726 (66) | 856 (37) |
| **wall time:** | 5h | 0.5h | 0.8h |

(**HSE-3c** on 16 cores)







- fast computer code CRYSTAL17[23] with cost-efficient methods
- enabling routine electronic structure calculation of large systems

# Outline of talk


1 Introduction

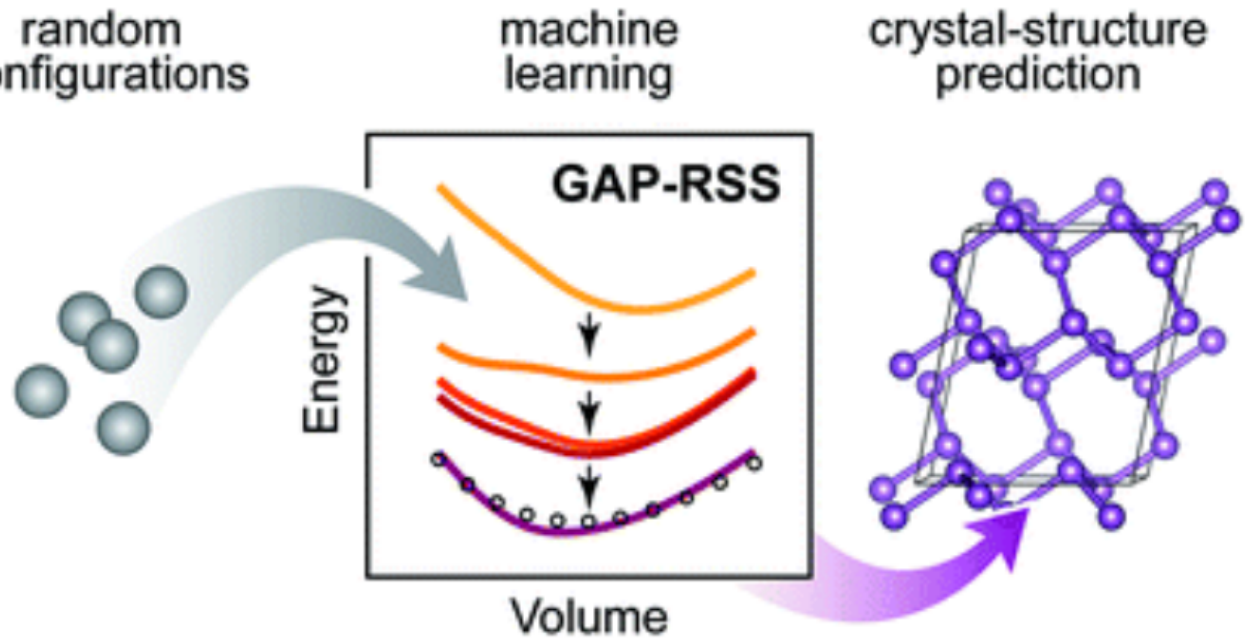
2 Simulation based crystal structure prediction

3 Quantum Monte-Carlo for molecular crystals

4 Simplified density functional approximations

5 Conclusions and Future Perspective

# Use of ML potentials within CSP workflow

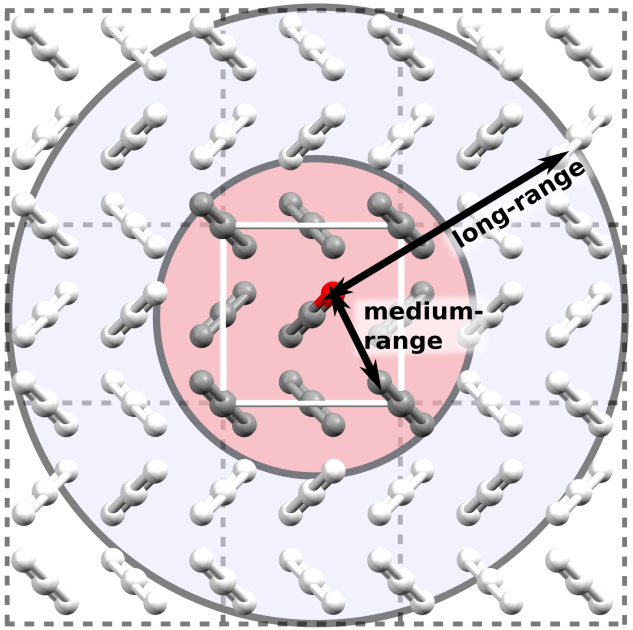



- use DFT data in crystal structure search to train ML
- ML to continue sampling configurations

"Stolen from"

[31] V. L. Deringer, D. M. Proserpio, G. Csányi, C. J. Pickard, *Faraday Discuss.* **211**, 45-59 (2018)

# Learn many-body exchange-correlation to improve DFAs




**A) long-range**
physics based interactions

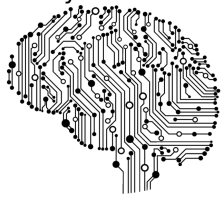
(i) electrostatics by DFT

(ii) induction by DFT

(iii) semi-classical vdW

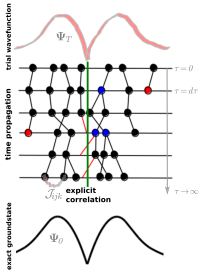
**B) medium-range**
flexible artificial AI

(iv) many-body effects
beyond DFT-vdW

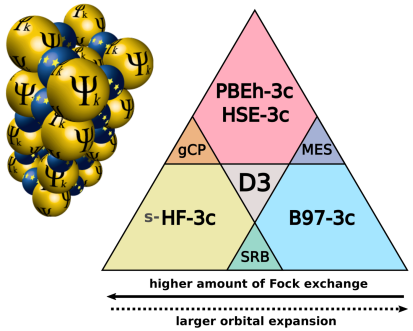


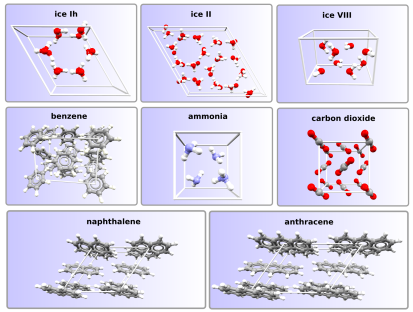
- DFT-vdW is capable to describe long-range interactions very accurately
- ML with local descriptor to learn medium-range many-body effects

# Summary




- DMC delivers (sub-) chemical accuracy with three orders of magnitude speed up
- hierarchy of simplified DFAs has been developed
- DMC and new DFAs applicable to molecular crystals with potential use in CSP



# Acknowledgements


**PhD / Postdocs**

Andrea Zen

Martin Fitzner

Benjamin Ramberger

Theodoros Tsatsoulis

Eike Caldeweyher

Luca Iuzzolino

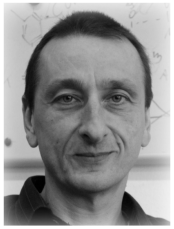
**Principal investigator**

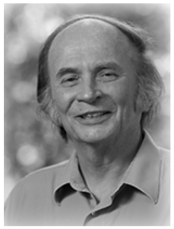
Michaelides (UCL)

Alfè (UCL)

Tkatchenko (Luxembourg)

Klimes (Prague)


Grimme (Bonn)


Perdew (Temple)

Kresse (Vienna)

Behler (Göttingen)

Price (UCL)

Grüneis (Vienna)

Civalleri (Turin)

Maschio (Turin)

**Industry**

Rebecca Sure (BASF)

Antreas Afantitis (NovaMechanics)

Alexander von Humboldt Stiftung/Foundation

THE THOMAS YOUNG CENTRE TyC

erc

cposs

# Acknowledgements

**PhD / Postdocs**

Andrea Zen

Martin Fitzner

Benjamin Ramberger

Theodoros Tsatsoulis

Eike Caldeweyher

Luca Iuzzolino

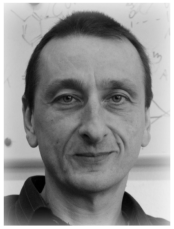
**Principal investigator**

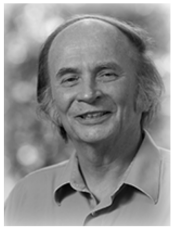
Michaelides (UCL)

Alfè (UCL)

Tkatchenko (Luxembourg)

Klimes (Prague)


Grimme (Bonn)


Perdew (Temple)

Kresse (Vienna)

Behler (Göttingen)

Price (UCL)

Grüneis (Vienna)

Civalleri (Turin)

Maschio (Turin)

**Industry**

Rebecca Sure (BASF)

Antreas Afantitis (NovaMechanics)

Alexander von Humboldt Stiftung/Foundation

# Thanks

erc

cposs

# Key references

- Crystal structure prediction:

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

  JGB, A. Zen, M. Fitzner, B. Ramberger, G. Kresse, T. Tsatsoulis, A. Grüneis, A. Michaelides, D. Alfè, *J. Phys. Chem. Lett.*, **10**, 358 (2019).

- DFT development

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

  E. Caldeweyher, JGB, *J. Phys.: Condens. Matter* **30**, 213001 (2018)

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