

Towards the design of molecular materials

Improved quantum mechanical methods for structure and stability prediction

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SEMINAR AT THE MAX PLANCK INSTITUTE FOR POLYMER RESEARCH, MAINZ, GERMANY

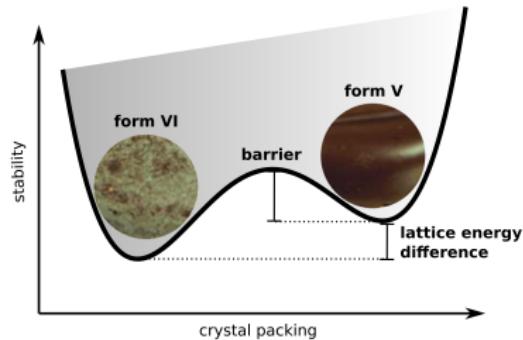
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Many properties depend on the polymorphic form of a crystal

Polymorphism

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

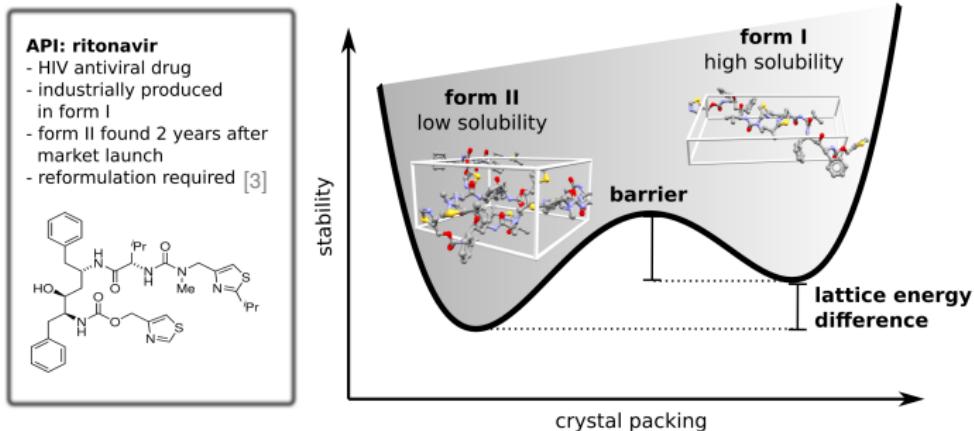


- cocoa butter (form VI) has a dull surface, soft texture, higher melting point
- metastable form V has glossy surface, crisp hardness, melts at 300 K^[2]

[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

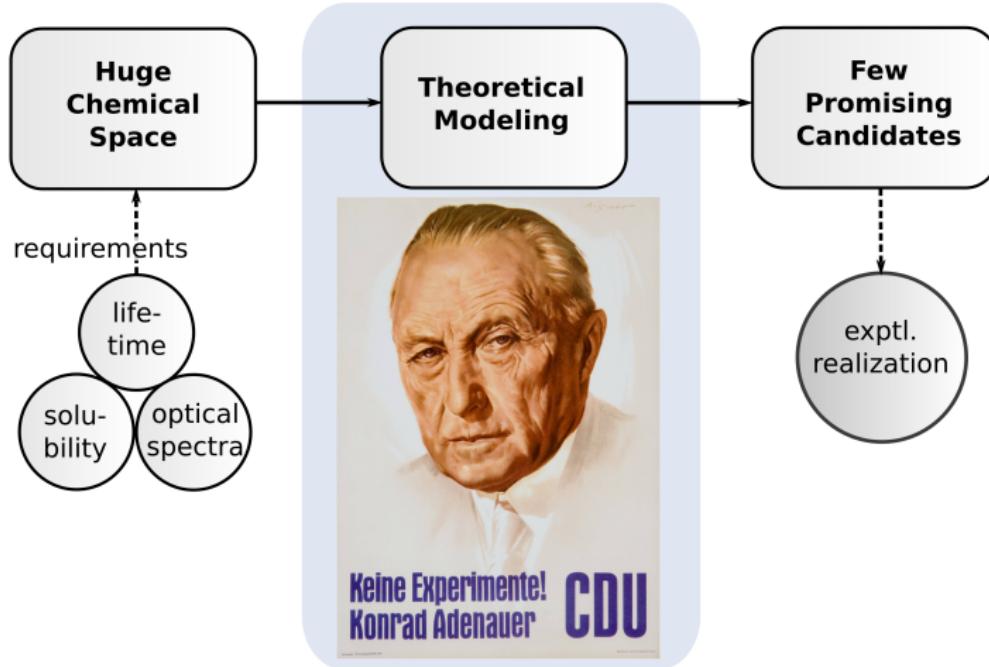


- tools to predict possible polymorphs would be valuable^[4]
→ Simulation methods aim at complementing experimental screening

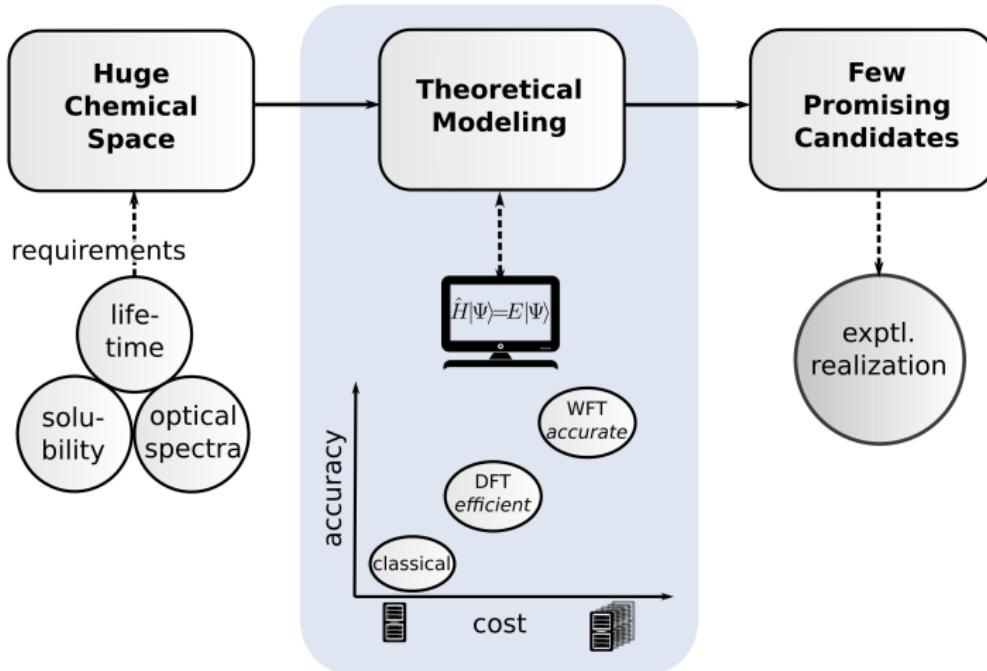
[3] J. Bauer, et al., *J. Pharm. Res.* 18, 859-866 (2001).

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

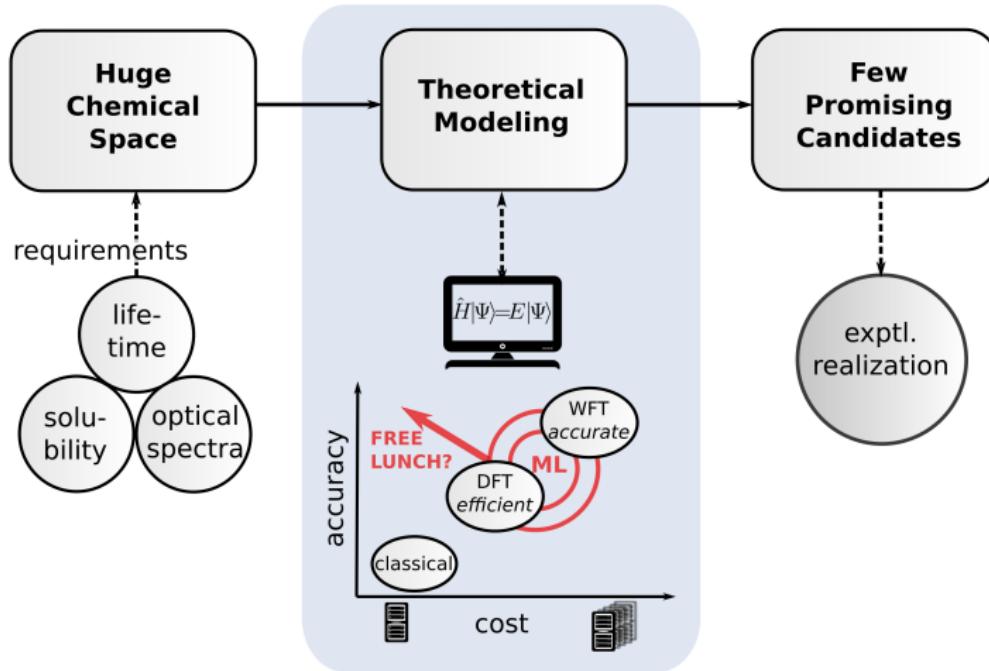
Material discovery can employ computational models



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

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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]

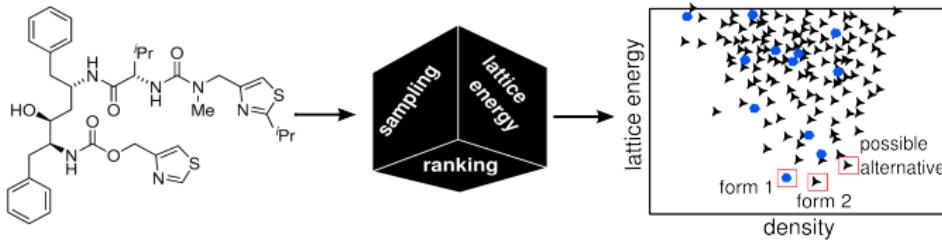
Task

- 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).

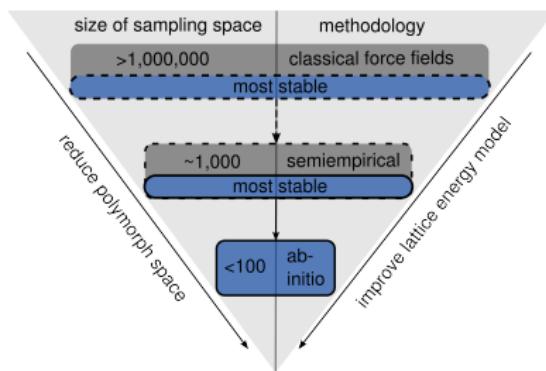
^[7] K. N. Houk, F. Liu, *Acc. Chem. Res.*, **50**, 539 (2017).

Sampling and energetic ranking for crystal structure prediction



Layers of complexity:

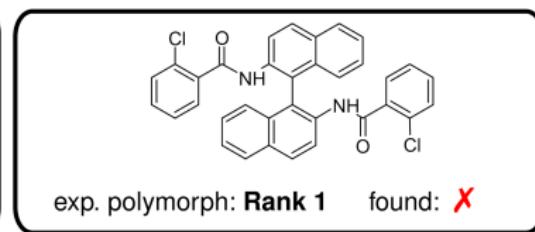
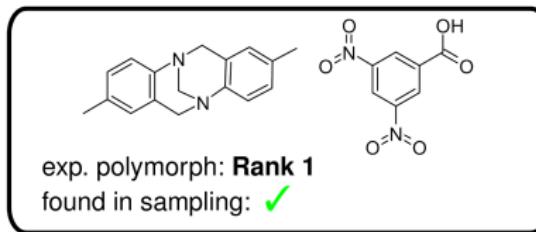
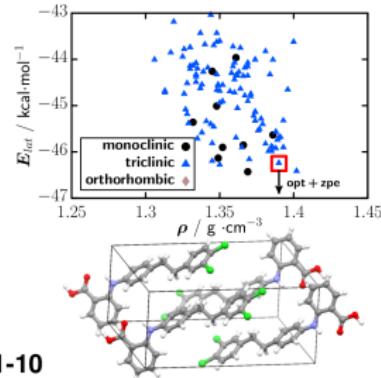
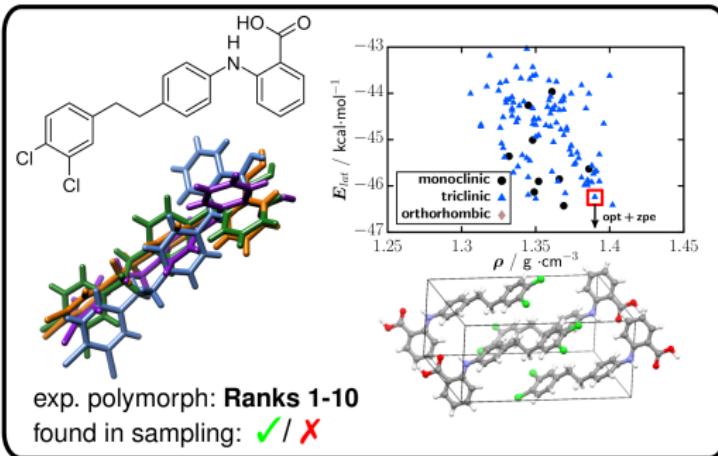
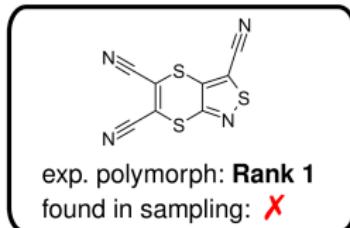
- molecular conformational space
- space groups (varying orientation, conformation, etc.)
- polymorph ranking according to free energy^[8,9]



^[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 6th blind test



[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).

⇒ **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.

⇒ **Can we improve modern DFAs?**

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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

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

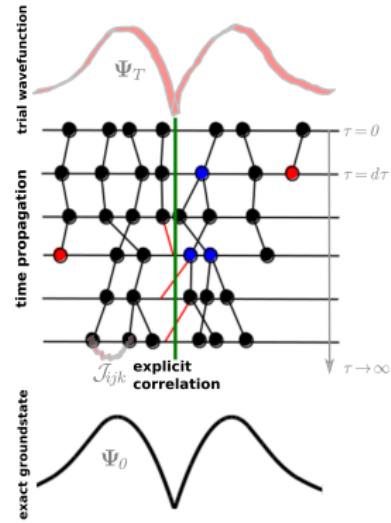
3) Diffusion in imaginary time

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

4) Projection to exact ground state

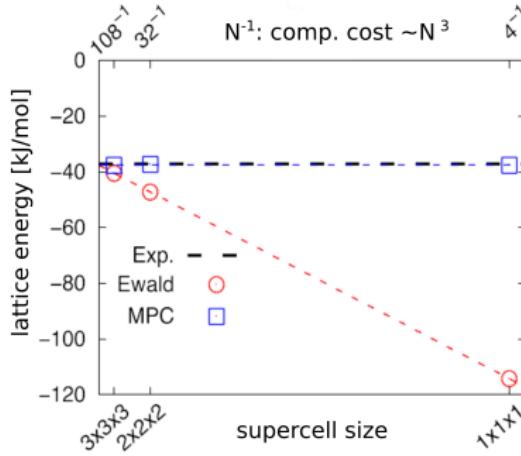
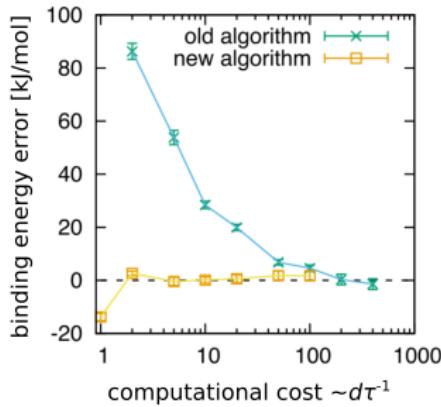
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau \rightarrow \infty} \exp[-\tau(\hat{H} - E_T)] |\Psi_T(\mathbf{R}, \tau)\rangle$$

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



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

New DMC algorithm leads to substantial speed up

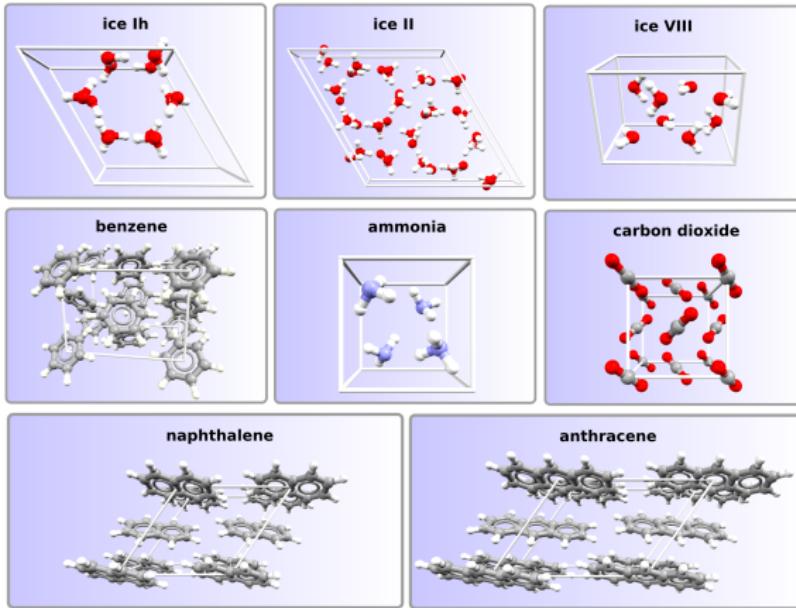


- new size-consistent implementation reduces $\Delta\tau$ error drastically^[13]
- Model periodic Coulomb for finite size correction^[14]

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

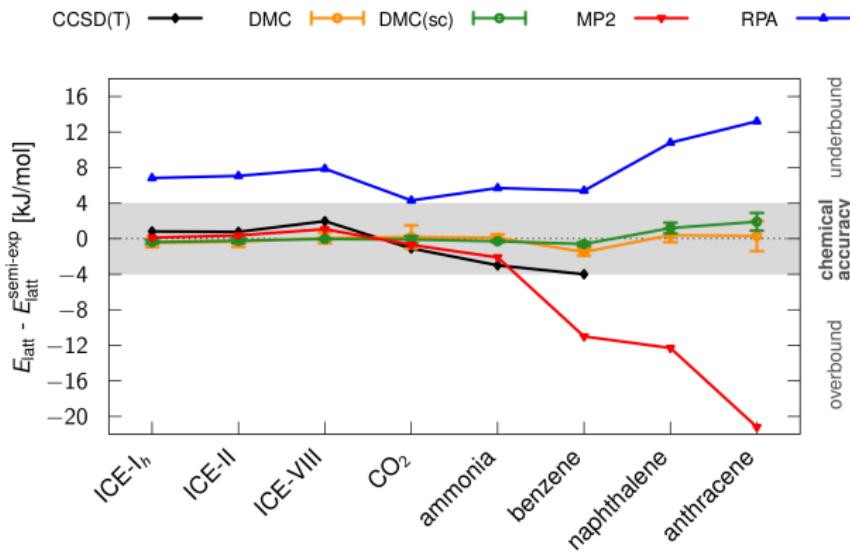
[14] L. M. Fraser, W. M. C. Foulkes, G. Rajagopal, R. J. Needs, S. D. Kenny, A. J. Williamson, *Phys. Rev. B* **53**, 1814 (1996).

Molecular crystals as challenging test



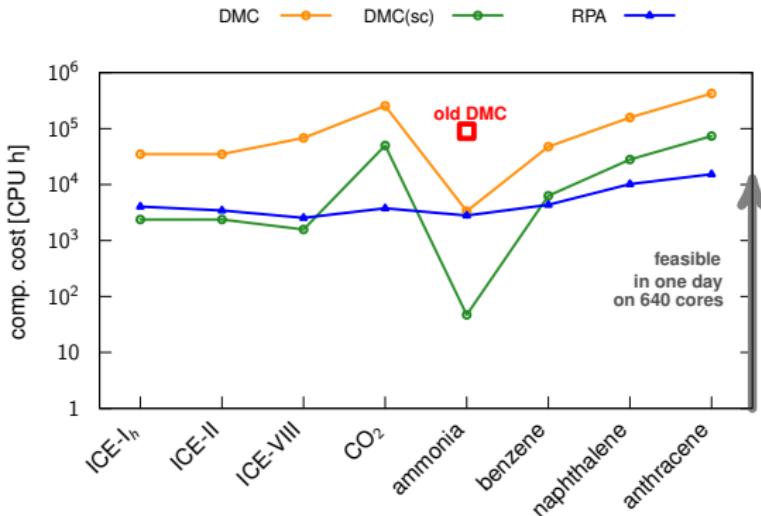
- strong H-bonds, vdW of saturated and unsaturated molecules
- problematic for all readily applicable methods (DFA-DISP, MP2)

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



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

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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
→ small atomic orbital expansion
- avoid most self-interaction error
→ use one-determinantal (Fock) exchange
- numerically robust including small gap solids
→ 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

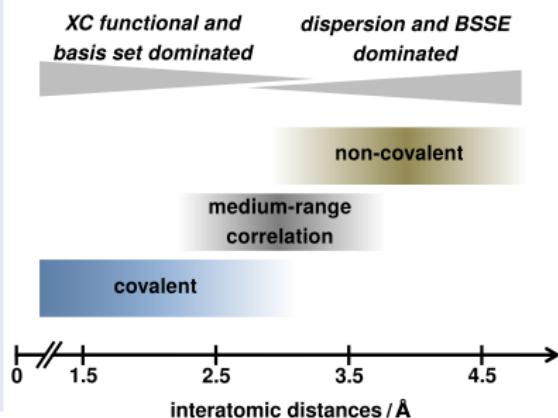
mod. HSE^[24] / def2-mSVP^[22]

(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

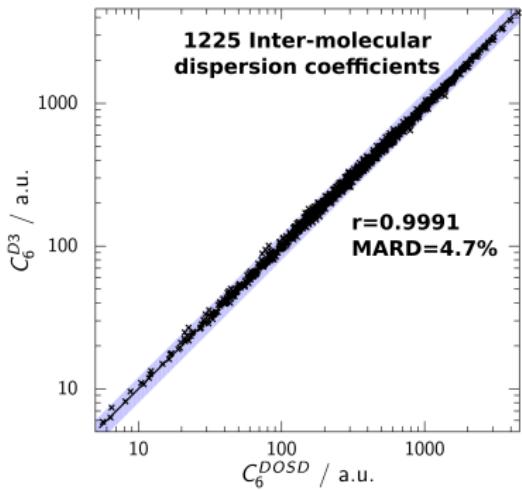
$$E_{xc}^{(\text{modHSE})} = a_x E_x^{(\text{HF,SR})}(\omega) + (1 - a_x) E_x^{(\text{HSE,SR})}(\omega) + E_x^{(\text{HSE,LR})}(\omega) + E_c^{(\text{modPBE})}$$

- modified HSE to reproduce modified PBE-XC

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

- μ from PBEsol, κ averaged from PBE/revPBE
 - $\beta = 0.03$ in F_C^{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
- only **seven** globally fitted parameters

Semi-classical correction yields highly accurate dispersion coefficients



D3 correction^[25-27]

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

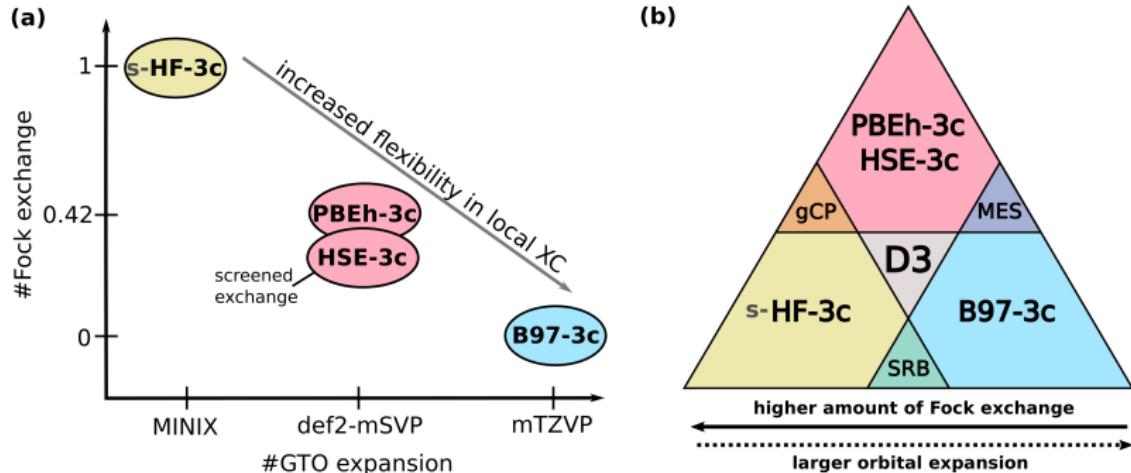
- Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error < 5%
- empiricism in short-range damping

[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

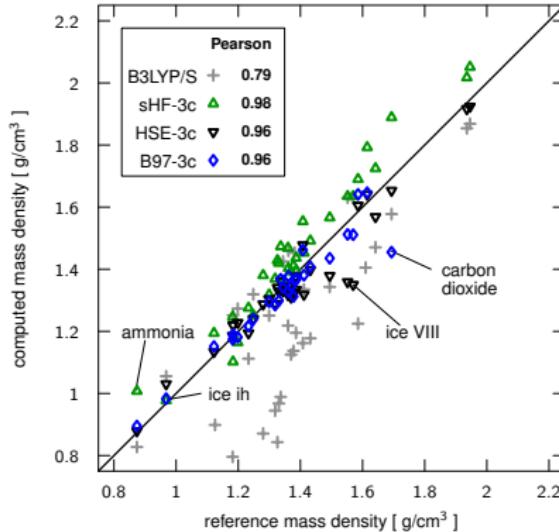
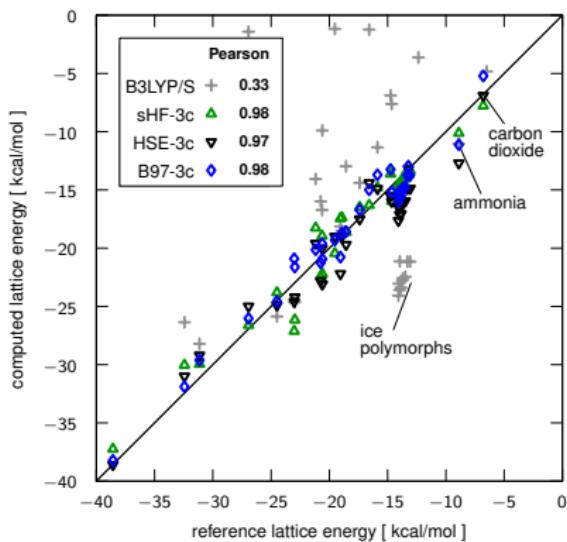


- HSE-3c/PBEh-3c: General purpose
- HF-3c: SIE dominated systems, nor MR character
- B97-3c: SIE unproblematic, possible MR character

[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:

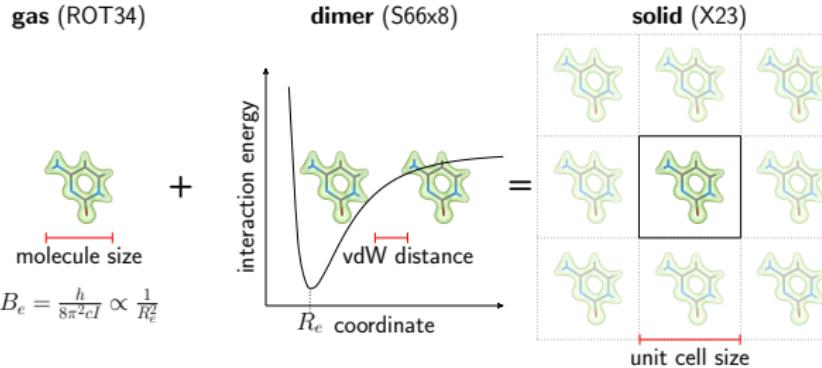


- consistent structures and interaction energies by HSE-3c

[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



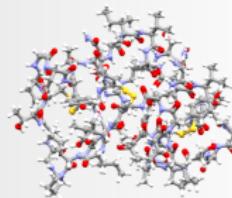
	ROT34 org. mol.	S66x8 non-covalent	X23 molecular crystal
TPSS/large basis	1.9	14.6	27.9
TPSS-D3/large basis	1.3	1.3	1.0
HF-3c (very cheap QM)	1.5	-1.2	-5.7
DFTB3-D3 (very cheap QM)	1.2	-2.9	-12.6
HSE-3c (cheap QM)	0.2	1.3	0.7

mean of relative deviation in %

Fast electronic structure with ab-initio accuracy

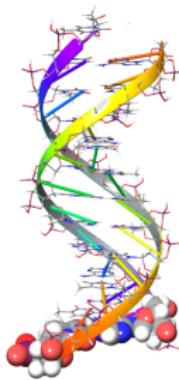
gas phase protein

dim:
#atoms/unit:
wall time:
(HSE-3c on 16 cores)



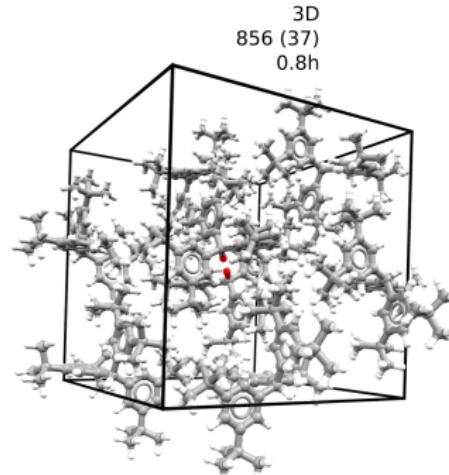
DNA helix

0D
647 (647)
5h



molecular crystal

1D
726 (66)
0.5h



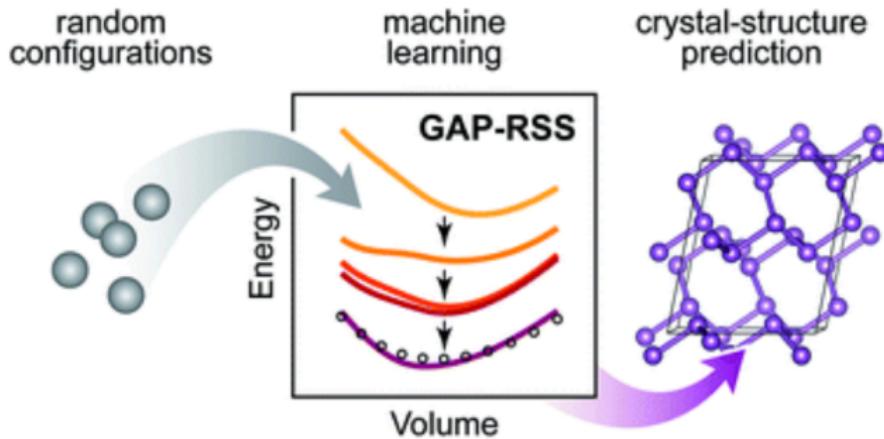
3D
856 (37)
0.8h

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

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Use of ML potentials within CSP workflow

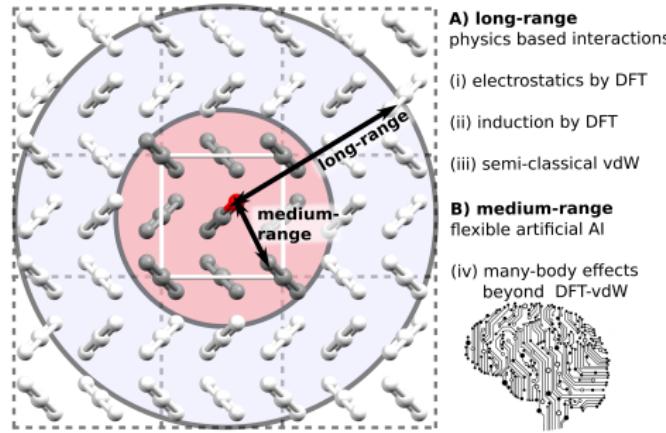


- use DFT data in crystal structure search to train ML
- ML to continue sampling configurations

"Stolen from"

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

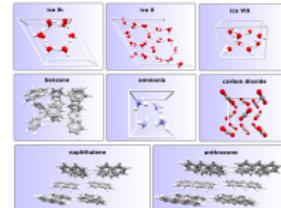
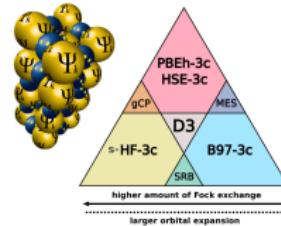
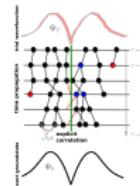
Learn many-body exchange-correlation to improve DFAs



- 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



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Principal investigator



Alfè (UCL)



Tkatchenko
(Luxembourg)



Klimes (Prague)



Benjamin
Ramberger



Theodoros
Tsatsoulis



Grimme (Bonn)



Perdew (Temple)



Kresse (Vienna)



Behler (Göttingen)



Rebecca Sure (BASF)



Eike Caldeweyher



Luca Iuzzolino



Price (UCL)



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Principal investigator



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Tkatchenko
(Luxembourg)



Klimes (Prague)



Benjamin
Ramberger



Theodoros
Tsatsoulis



Grimme (Bonn)



Perdew (Temple)



Kresse (Vienna)



Behler (Göttingen)



Rebecca Sure (BASF)



Eike Caldeweyher



Luca Iuzzolino



Price (UCL)



Grüneis (Vienna)



Civalleri (Turin)



Maschio (Turin)



Antreas Afantitis
(NovaMechanics)

Alexander von Humboldt
Stiftung/Foundation

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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)

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