

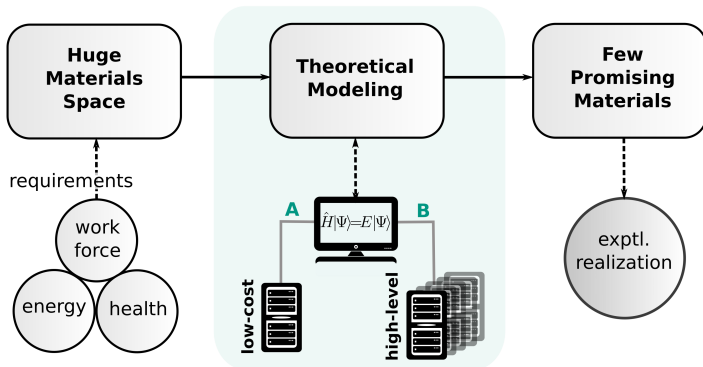
# Predicting properties of molecular crystals by multilevel strategies

**Gerit Brandenburg** <g.brandenburg@ucl.ac.uk> | 10<sup>th</sup> of November 2017

SFB 1249 COLLOQUIUM, HEIDELBERG UNIVERSITY, GERMANY

- 1 Introduction
- 2 Quantum Monte-Carlo for molecular materials
- 3 HSE-3c: A low-cost electronic structure method
- 4 Simulation based crystal structure prediction
- 5 Conclusions

# Materials discovery can employ computational models

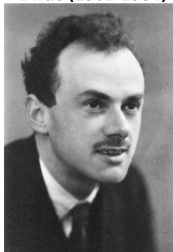


**A:** approximate models & local computer cluster

**B:** high-level models & world leading computational facility

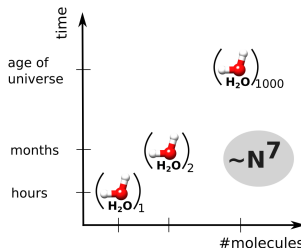
# Exact simulation of extended systems computationally very demanding

Paul Adrian Maurice  
Dirac (1902-1984)

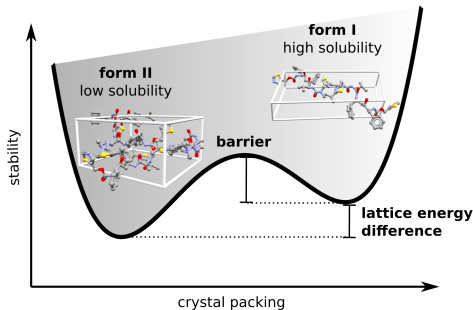


*"The underlying physical laws (...) of a large part of physics and the **whole of chemistry** are thus completely known,*

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



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

CN(C)C(=O)NC(=O)[C@H](Cc1ccc(O[C@@H](c2ccccc2)C(=O)NCC(c3ccccc3)O)c4ccccc4)C(=O)OCc5nc6ccccc6n5

- Currently no high-level method applicable

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

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# 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

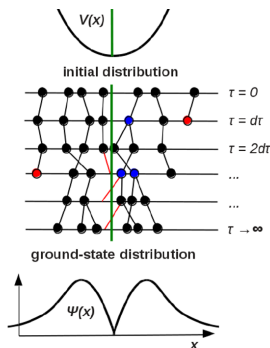
$$|\Psi_T(\mathbf{R}, \tau)\rangle = \text{hist} \left[ \sum \delta(\mathbf{R} - \mathbf{R}_i(\tau)) \right]$$

- 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

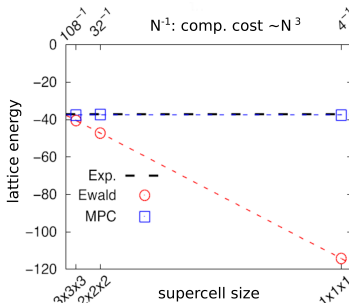
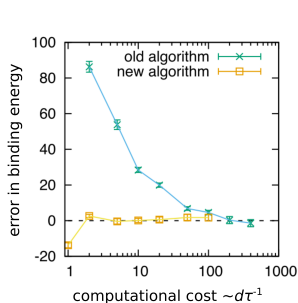
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau \rightarrow \infty} \exp[-\tau(\hat{H} - E_T)] |\Psi_T(\mathbf{R}, \tau)\rangle$$



- low-scaling ( $N^3$ ) with system size
- scalable to high-performance computing facilities

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

# New QMC algorithm leads to substantial speed up



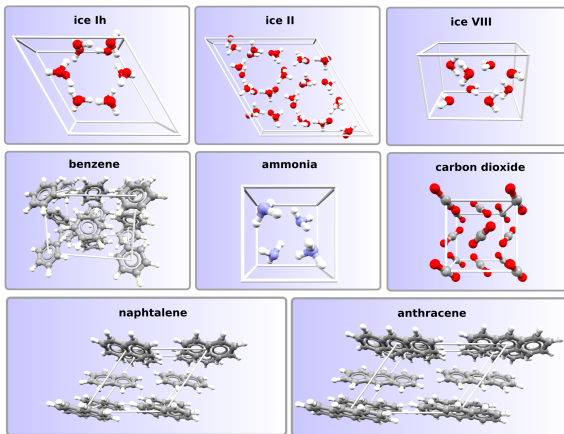
- new size-consistent implementation reduces  $\Delta\tau$  error drastically<sup>[5]</sup>
- Model periodic Coulomb for finite size correction<sup>[6]</sup>

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

[6] 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 cases



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

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



{non-published data}

- excellent agreement with experiment and CCSD(T)<sup>[7]</sup>
- uncertainty in  $H_{\text{sub}}^{\text{exp}}$  probably larger than DMC errors

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<sup>[7]</sup> 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 is feasible within one day on standard computer cluster

{non-published data}

- up to three orders of magnitude speed-up compared to best DMC practice two years ago<sup>[8]</sup>

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<sup>[8]</sup> A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *submitted*

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- realistic structures are key to many important physical and chemical properties
- Kohn-Sham density functional theory is method of choice for structures; wavefunction methods may take over for energies
- configurational sampling, entropy, and solvation issues are as important as good convergence in electronic energy

# Multilevel methodologies: Finding the right compromise

|                      | task/property                          | example method  |
|----------------------|--|---|
| <b>accurate QM</b>   | single-point energy                    | DLPNO-CCSD(T)<br>DMC, RPA+SE  |
| <b>cheap QM</b>      | optimization                           | metaGGA (SCAN-D3 <sup>[9]</sup> )<br>HSE-3c <sup>[10,11]</sup>        |
| <b>very cheap QM</b> | optimization/Hessians<br>conformations | semi-empirical<br>HF-3c <sup>[12,13]</sup> , DFTB3-D3 <sup>[14]</sup> |
| <b>force field</b>   | dynamics<br>conformational sampling    | transferable or molecule<br>specific (QM derived) FF                  |

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

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

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

[12] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013) [13] JGB, S. Grimme, *Top. Curr. Chem*, **345**, 1 (2014)

[14] JGB, S. Grimme, *J. Phys. Chem. Lett.* **5**, 1785 (2014)

# HSE-3c: Small basis DFT with semi-classical potentials

## Requirements

- $\sim 10 \times$  faster vs. standard DFA → small atomic orbital expansion
- reduce self-interaction error → use Fock exchange
- numerically robust → long-range screening of exchange

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

## Technical details:<sup>[10]</sup>

- modified HSE<sup>[15]</sup> in small def2-mSVP<sup>[11]</sup> basis set
- D3 and gCP semi-classical corrections (7 global parameters)

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<sup>[10]</sup> JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

<sup>[11]</sup> S. Grimme, JGB, C. Bannwarth, A. Hansen, *J. Chem. Phys.*, **143**, 054107 (2015)

<sup>[15]</sup> 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

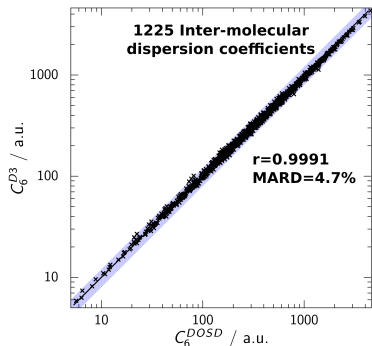
$$F_X^{\text{PBE}} = 1 + \frac{\mu s}{1 + \frac{\mu s^2}{\kappa}}, \quad s = |\nabla \rho / \rho^{4/3}|$$

- $\mu$  from PBEsol,  $\kappa$  averaged from PBE/revPBE
- $\beta = 0.03$  in  $F_C^{\text{PBE}}$  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<sup>[16-18]</sup>

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

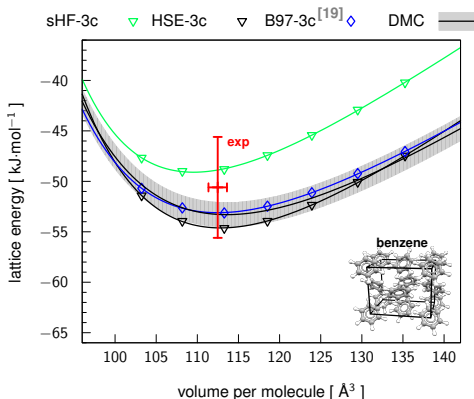
- Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error < 5%
- empiricism in short-range damping

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

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

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

# Close agreement with reference for equation of state of solid benzene

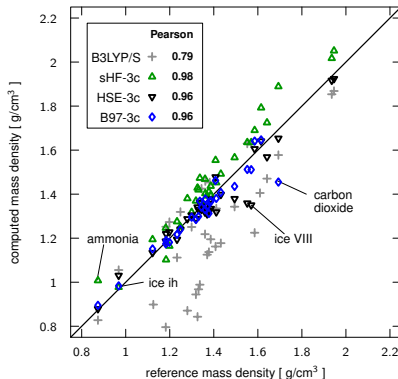
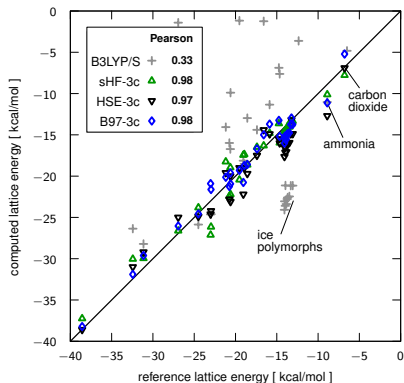


- zero-point and thermal effects crucial for comparing to measurement
- new references valuable for testing approximate methods

<sup>[19]</sup> JGB, C. Bannwarth, A. Hansen, S. Grimme, *submitted*.

# Good results on molecular crystals

X23<sup>[20,21]</sup> and ICE10<sup>[22]</sup> benchmark sets:



■ consistent structures and interaction energies by HSE-3c

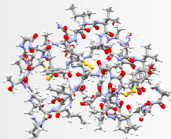
<sup>[20]</sup> E. Johnson, A. Otero-de-la-Roza, *J. Chem. Phys.* **137**, 054103 (2012), <sup>[21]</sup> A. Reilly, A. Tkatchenko, *JCP* **139**, 024705 (2013)

<sup>[22]</sup> JGB, T. Maas, S. Grimme, *J. Chem. Phys.* **142**, 124104 (2015)

# Fast electronic structure with ab-initio accuracy

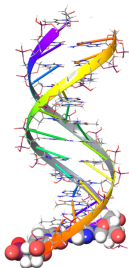
gas phase protein

dim: 0D  
#atoms/unit: 647 (647)  
wall time: 5h  
(HSE-3c on 16 cores)



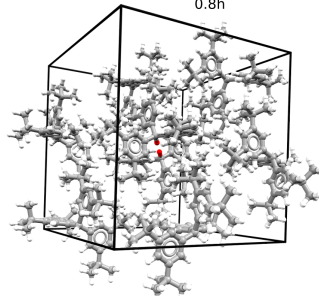
DNA helix

1D  
726 (66)  
0.5h



molecular crystal

3D  
856 (37)  
0.8h



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

[23] R. Dovesi, et al., *Int. J. Quantum Chem.*, **114**, 1287-1317 (2014), new release in 2017

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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.<sup>[24,25]</sup>

## Task

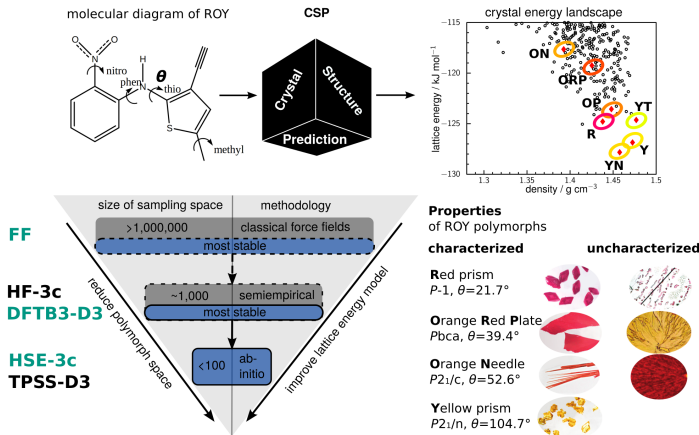
- molecule is chosen due to its chemical/physical/biological properties
- based on the molecular diagram only, the most stable crystal structures should be predicted
- predict properties of interest for the most promising candidates

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<sup>[24]</sup> A. Gavezzotti, *Acc. Chem. Res.* **27**, 309-314 (1994).

<sup>[25]</sup> J. Maddox, *Nature* **335**, 201-201 (1988).

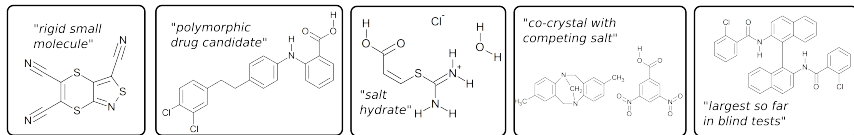
# Sampling and energetic ranking for crystal structure prediction



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

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

# Promising results in the 6<sup>th</sup> blind test



|         | 22       | 23         | 24       | 25       | 26       |
|---------|----------|------------|----------|----------|----------|
| PBE     | 2        | 1-9        | 6        | 3        | 1        |
| PBE-D3  | <b>1</b> | <b>1-9</b> | <b>1</b> | <b>1</b> | <b>1</b> |
| PBE-MBD | 1        | 1-7        | 1        | 2        | 1        |
| vdW-DF2 | 1        | 4-8        | 1        | 3        | 2        |
| M06L    | 1        | 4-13       | 1        | 1        | 7        |

lattice energy on fixed TPSS-D3 structures

- good lattice energy based ranking of PBE-D3<sup>[28,29]</sup>
- some structures lost in FF → DFT transition

<sup>[28]</sup> A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016)

<sup>[29]</sup> JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)





## Collaborators

- Andrea Zen (London)
- Jiří Klimeš (Prague)
- Alexander Tkatchenko (Luxenburg)
- Dario Alfè (London)
- Angelos Michaelides (London)
- Sally Price (London)
- Felix Fernandez-Alonso (Harwell Oxford)
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**Thanks**



## ■ QMC for molecular crystals:

A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *submitted*.

## ■ DFT development

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

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

## ■ DFA-DISP for crystal structure prediction:

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

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

## ■ website: [gerit-brandenburg.de](http://gerit-brandenburg.de)