Highly accurate stability prediction at surprisingly modest cost: Capabilities of quantum Monte-Carlo for molecular crystals

Gerit Brandenburg <g.brandenburg@ucl.ac.uk> | 19th of October 2017

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London Centre for Nanotechnology
Department of Physics and Astronomy – University College London

gerit-brandenburg.de

Outline of talk

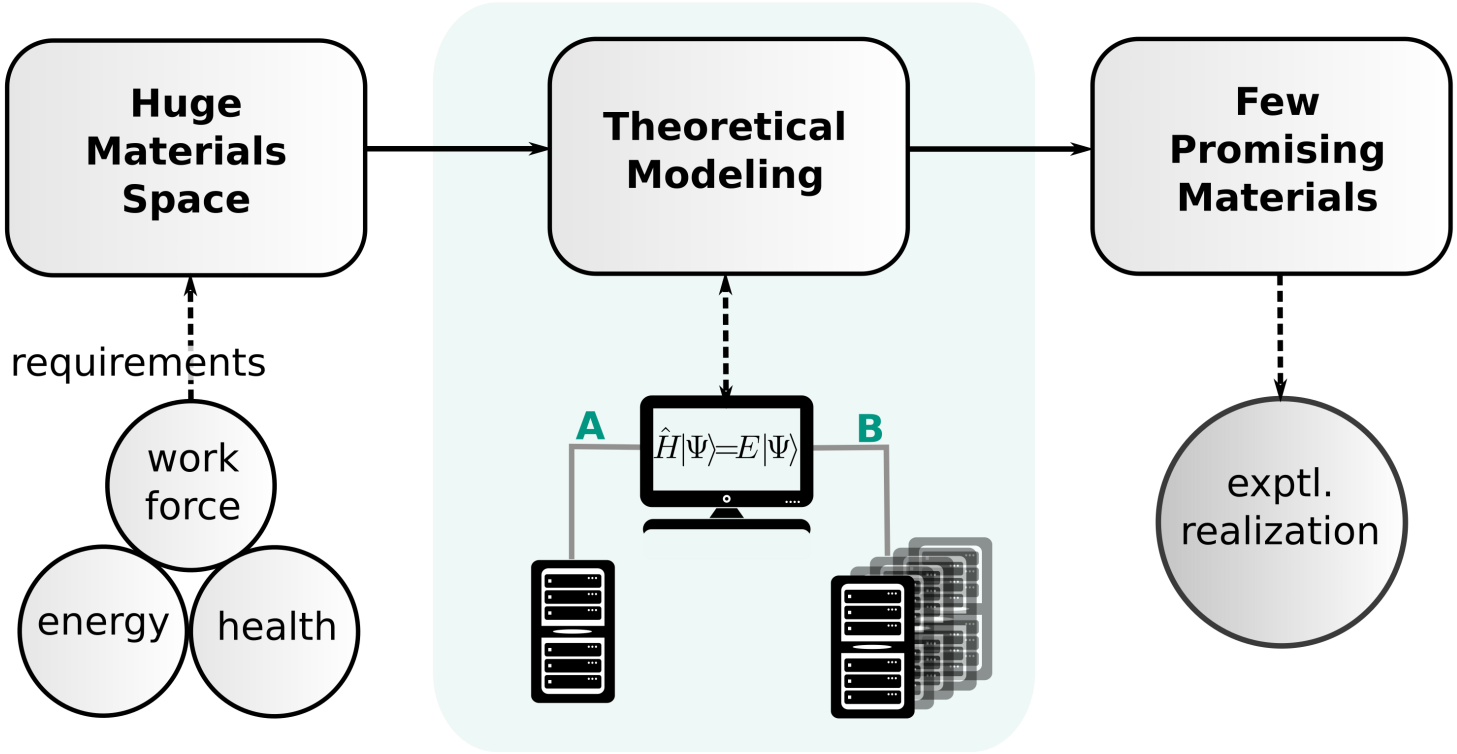
1 Introduction

2 Quantum Monte-Carlo: Basics and New Developments

3 Quantum Monte-Carlo for Molecular Materials

4 Conclusions

Materials discovery relies on computational models

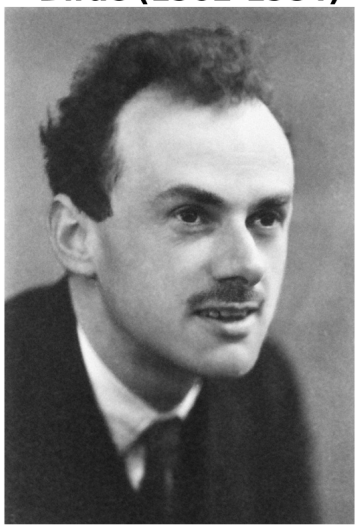


A: approximate models & local computer cluster

B: high-level models & world leading computational facility

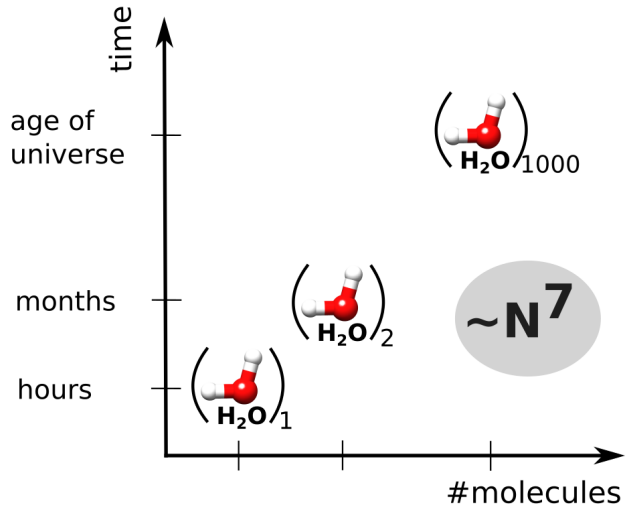
Exact simulation of extended systems computationally very demanding

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,*

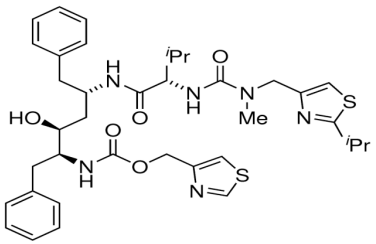
and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"[1]

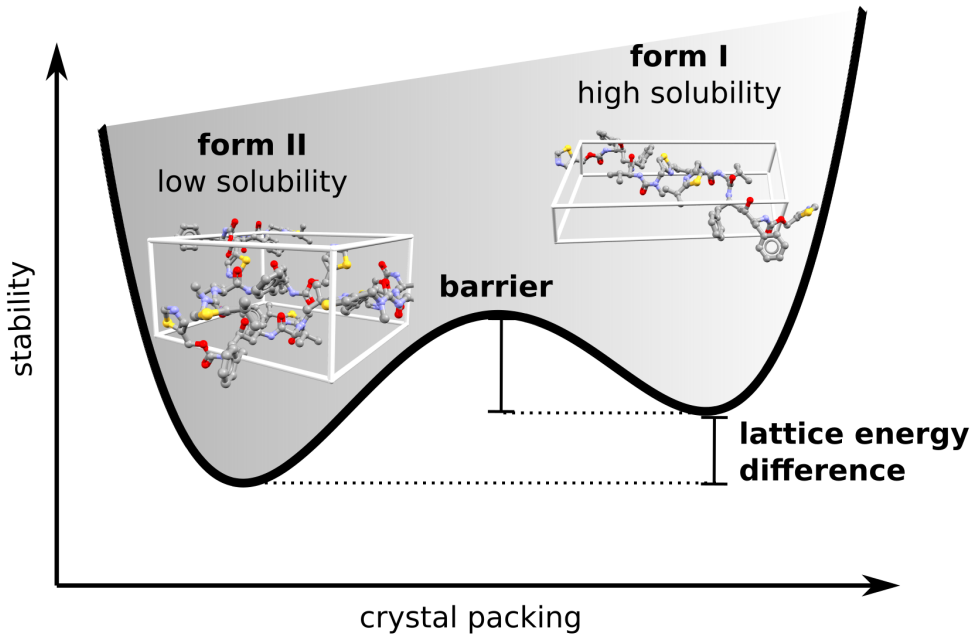


[1] P. A. M. Dirac, *Proc. Roy. Soc.Ser. A* **123**, 714 (1929)

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 [2]





- tools to predict possible polymorphs would be valuable[3]

  → Currently no high-level method applicable

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

[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

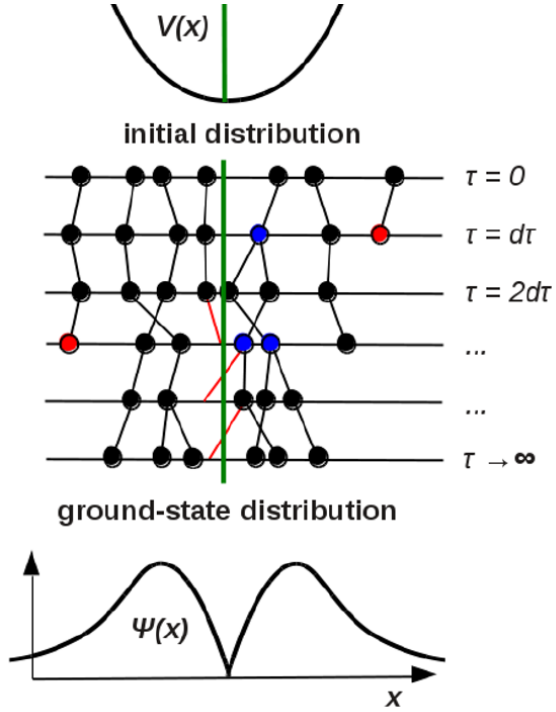
$$|\Psi_T(\mathbf{R},\tau)\rangle = \text{hist}\left[\sum \delta(\mathbf{R} - \mathbf{R_i}(\tau))\right]$$

3) Diffusion in imaginary time

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

4) Projection to exact ground state

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



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

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

New QMC algorithm leads to substantial speed up

{non-published data}

- size-consistent implementation (ZSGMA) reduces $\Delta\tau$ error drastically[5]
- Model periodic Coulomb for finite size correction [6]

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[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).

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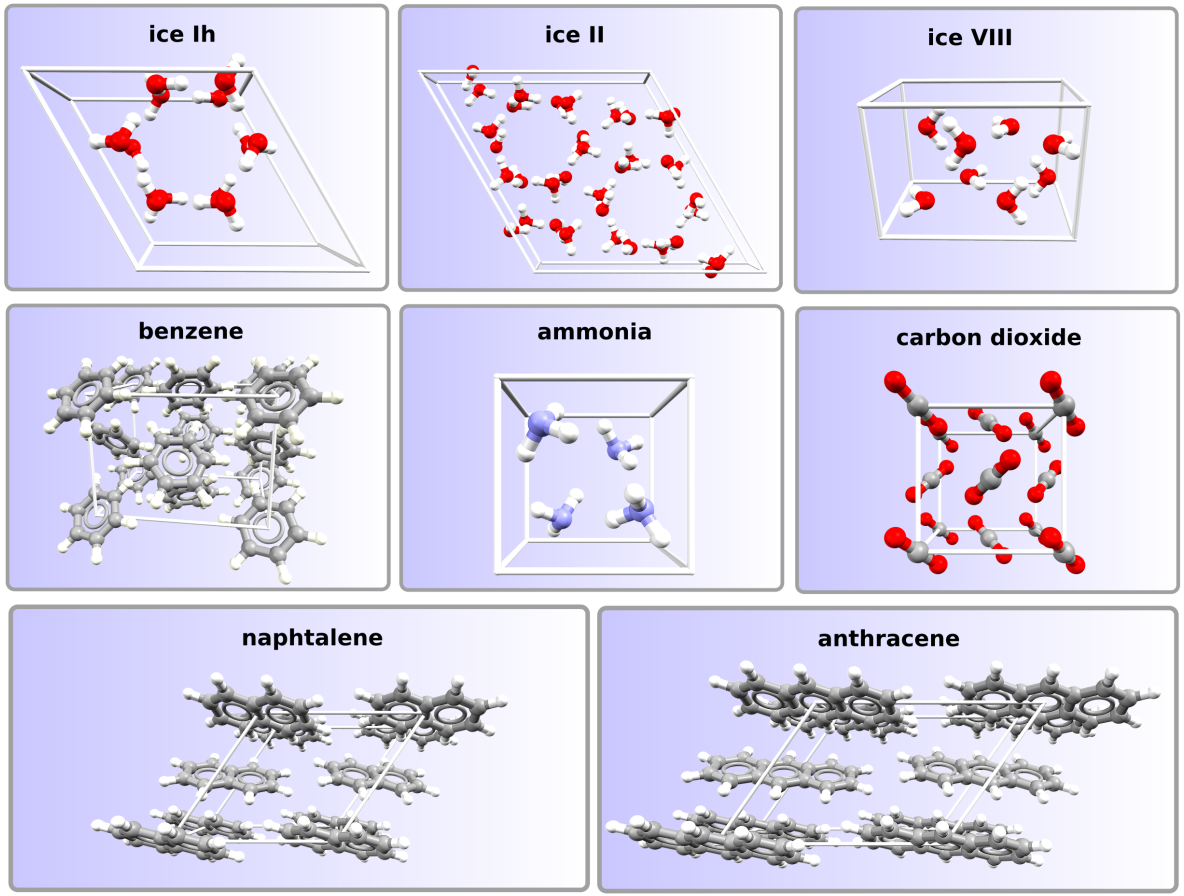
Diverse interactions in test cases



- strong H-bonds, vdW of saturated and unsaturated molecules
- problematic for all readily applicable methods (DFT-D, 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 settings for rest)[7]
- largest deviation of 0.5 kJ/mol

{non-published data}

$\rightarrow$ good agreement between different high-level methods[8]

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

[8] 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).

DMC agrees with 'experiment' within chemical accuracy

- 'brute force' DMC in a large supercell (lc)
- DMC in a small supercell (sc) relying on FSE corrections
- uncertainty in $E_{\text{lat}}^{\text{exp}}$ probably larger than DMC errors
- DMC quite affordable:
  10 000 CPU h for benzene
  100 000 CPU h for anthracene

{non-published data}

[9] J. Yang, W. Hu, D. Usvyat, D. Matthews, M. Schütz, G. K. L. Chan, *Science* **345**, 640 (2014).

[10] P. J. Bygrave, N. L. Allan, F. R. Manby, *J. Chem. Phys.* **137**, 164102 (2012).

[11] S. Wen, K. Nanda, Y. Huang, G. J. O. Beran, *Phys. Chem. Chem. Phys.* **14**, 7578 (2012).

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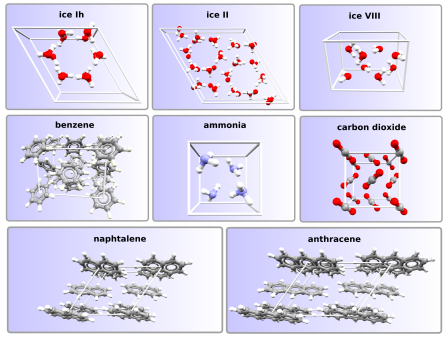
{non-published data}

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

Summary

Conclusions

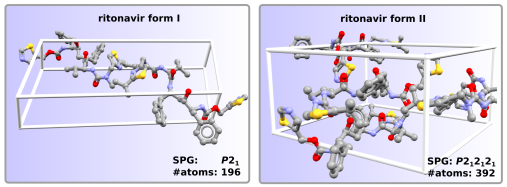
- DMC delivers (sub-) chemical accuracy for molecular crystals
- three orders of magnitude speed up
- high-level modeling on local computer cluster feasible



Outlook

- explore systems like APIs, OLEDs, MOFs, where high-level accuracy is needed

  $\rightarrow$ ritonavir polymorphs running



Acknowledgements

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Thanks

Key references

- 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:

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  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**