Many-body electronic structure theory:
Is Quantum Monte-Carlo affordable for molecular crystals?

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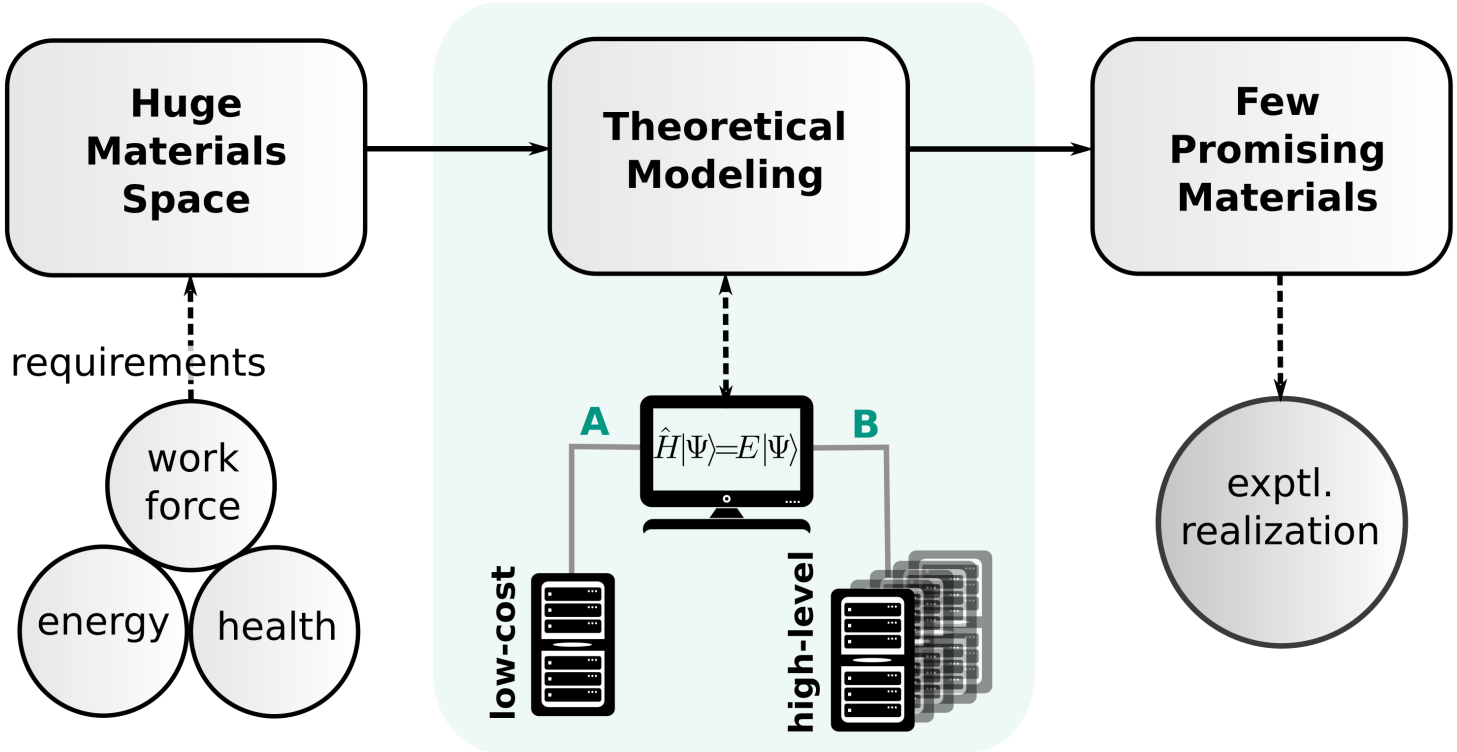
Outline of talk

Materials discovery can employ computational models

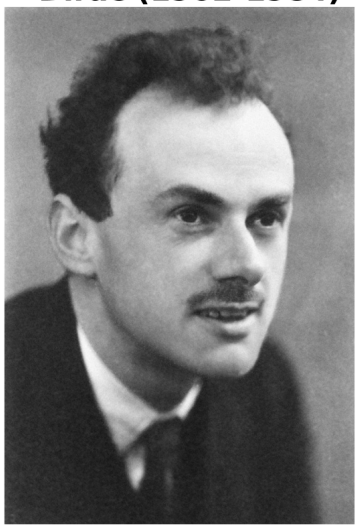


A: approximate models & local computer cluster

B: high-level models & world leading computational facility

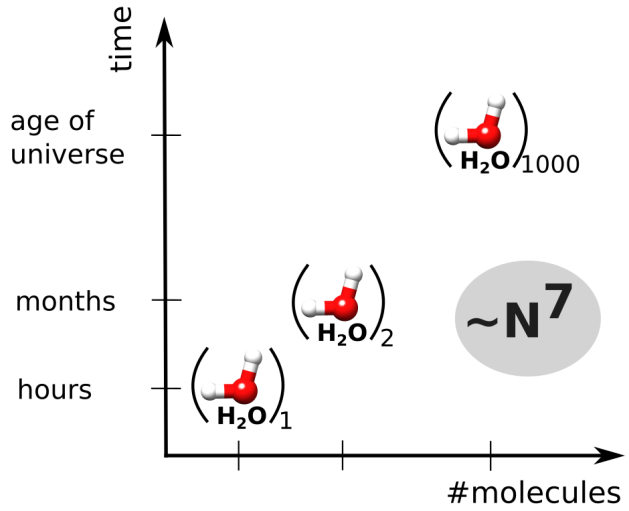
Exact simulation of extended systems computationally very demanding

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,*

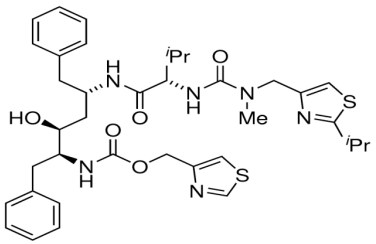
and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"[1]

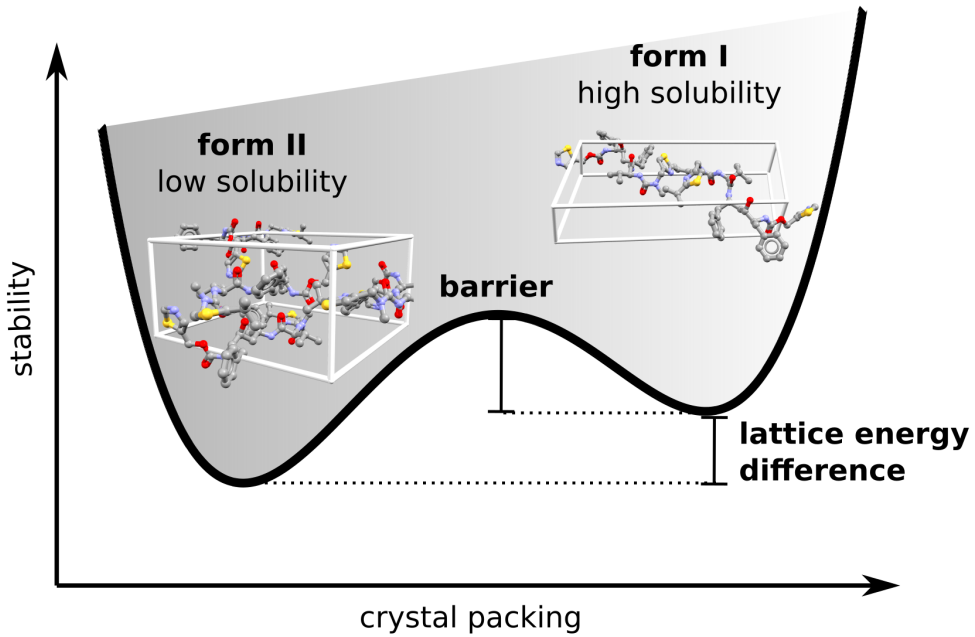


[1] P. A. M. Dirac, *Proc. Roy. Soc.Ser. A* **123**, 714 (1929)

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).

Multilevel methodologies: Finding the right compromise

	task/property	example method
accurate QM	single-point energy	DLPNO-CCSD(T) DMC, RPA+SE
cheap QM	optimization	metaGGA (SCAN-D3[4]) HSE-3c[5,6]
very cheap QM	optimization/Hessians conformations	semi-empirical HF-3c[7,8], DFTB3-D3[9]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

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

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

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

[7] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013) [8] JGB, S. Grimme, *Top. Curr. Chem*, **345**, 1 (2014)

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

Outline of talk

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

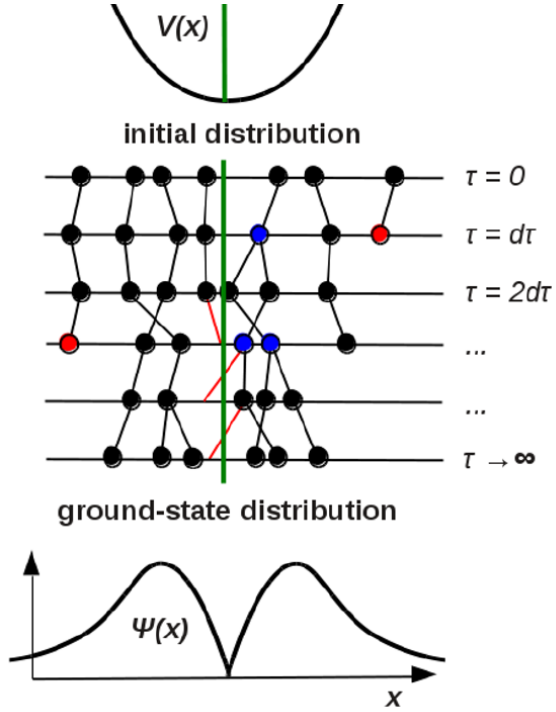
$$|\Psi_T(\mathbf{R},\tau)\rangle = \text{hist}\left[\sum \delta(\mathbf{R} - \mathbf{R_i}(\tau))\right]$$

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

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

New QMC algorithm leads to substantial speed up

{non-published data}

- new size-consistent implementation reduces $\Delta\tau$ error drastically[11]
- Model periodic Coulomb for finite size correction [12]

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

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

Scheme for performing DMC calculations

5 step procedure to assess lattice energy of a molecular crystal

(i) *Geometries*
DFT-D geometries at experimental density

(ii) *Independent particle finite size error (IPFSE)*
For a *l*x*m*x*n* MP grid: $\mathrm{IPFSE}^{DFT}_{lmn} = E^{DFT,lmn}_{\mathrm{crys}} - E^{DFT,\infty}_{\mathrm{crys}}$

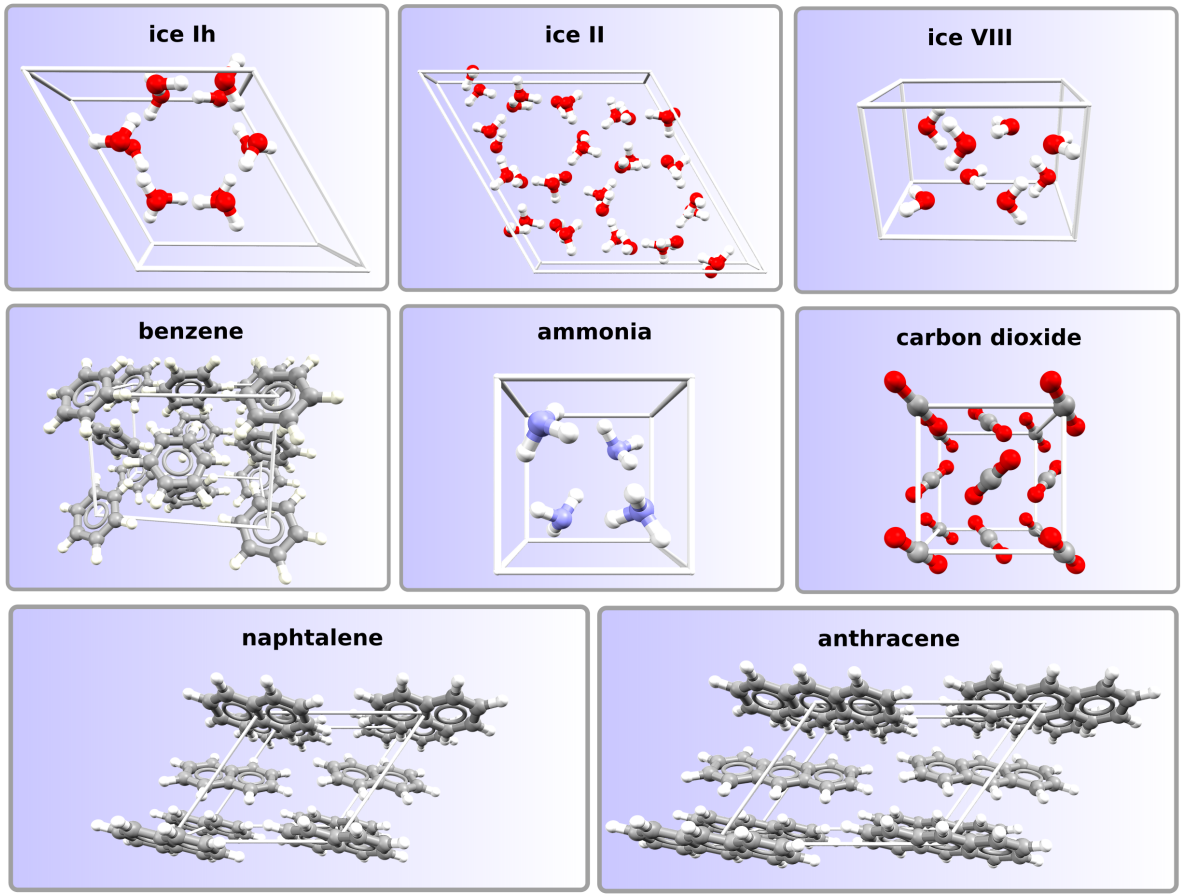
(iii) *Jastrow optimization*
Optimize Jastrow factor of the QMC wavefunction on a small cell, test its reliability on molecular dimers.

(iv) *DMC time step*
Check the time step dependence either on the cell used in step (iii) or on the molecular dimer.

(v) *Final DMC calculation of E_{latt}*
Use cell with $\mathrm{IPFSE}^{DFT}_{lmn} < 10\,\mathrm{kJ/mol}$, perform DMC simulation for this crystal using MPC, add IPFSE to result.

Outline of talk

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)[13]
- largest deviation of 0.5 kJ/mol

{non-published data}

$\rightarrow$ good agreement between different high-level methods

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

[14] 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 delivers (sub-) chemical accuracy for all tested systems

{non-published data}

- excellent agreement with experiment and CCSD(T)[14]
- uncertainty in $H_{\text{sub}}^{\text{exp}}$ probably larger than DMC errors

[14] 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).

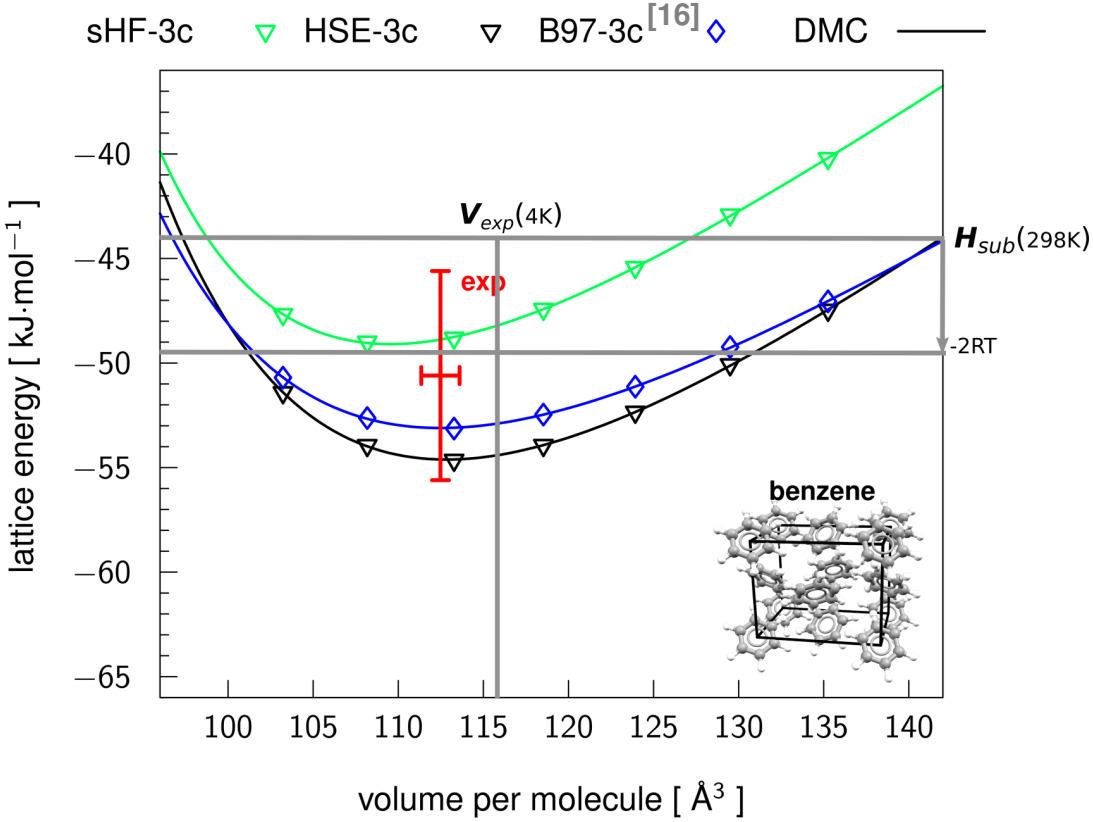
QMC is feasible within one day on standard computer cluster

{non-published data}

- up to three orders of magnitude speed-up compared to best DMC practice two years ago[15]

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

Substantial uncertainty in measured sublimation enthalpies



- zero-point and thermal effects crucial for comparing to measurement
- uncertainty of $\propto$ 4 kJ/mol for semi-experimental lattice energy

[16] JGB, C. Bannwarth, A. Hansen, S. Grimme, *submitted*.

Close agreement with reference for equation of state of solid benzene

{non-published data}

- new references valuable for testing approximate methods
- find hierarchy sHF-3c $\rightarrow$ HSE-3c $\rightarrow$ B97-3c

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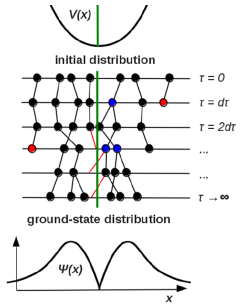
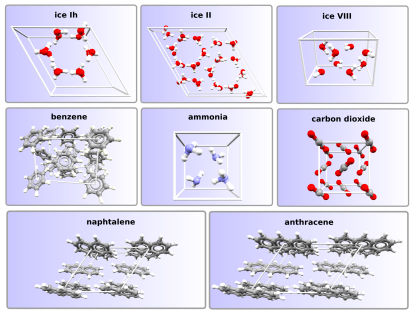
[16] JGB, C. Bannwarth, A. Hansen, S. Grimme, *submitted*.

Summary

Conclusions

- DMC delivers (sub-) chemical accuracy
- DMC for molecular crystals is feasible on standard computer cluster
- references valuable for approximate QM methods





Outlook

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

  → ritonavir polymorphs running

Acknowledgements

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- Andrea Zen (London)
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- Angelos Michaelides (London)
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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:

  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**