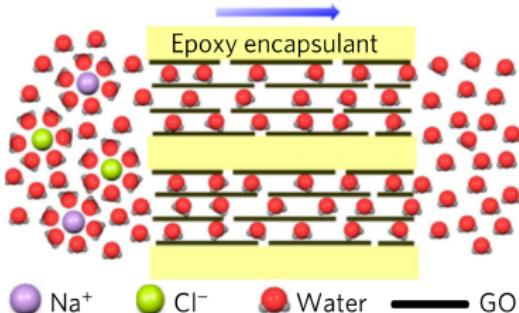
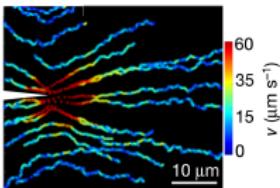
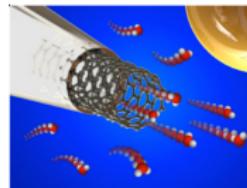


Physisorption of Water on Graphene: Subchemical Accuracy from Many-Body Electronic Structure Methods

Gerit Brandenburg <g.brandenburg@ucl.ac.uk> | 18th of January 2019

CHEMISTRY DEPARTMENT, UNIVERSITY OF ZURICH, SWITZERLAND

Water-carbon interaction important for emerging technologies



- Experimental study of water flow through carbon nanotubes
- Massive radius-dependent flow slippage^[1,2]
- sp^2 -bonded carbon materials for water filtration
- Tunable sieving of ions using graphene oxide membranes^[3]

[1] E. Secchi, S. Marbach, A. Niguëls, D. Stein, A. Siria, L. Bocquet, *Nature* **537**, 210 (2016).

[2] R. Joshi, P. Carbone, F. Wang, V. Kravets, Y. Su, I. Grigorieva, H. Wu, A. Geim, R. Nair, *Science* **343**, 752 (2014).

[3] J. Abraham, K. Vasu, C. D. Williams, K. Gopinadhan, Y. Su, C. T. Cherian, J. Dix, E. Prestat, S. J. Haigh, T. V. Grigorieva, et al., *Nat. Nanotechnol.* **12**, 546 (2017).

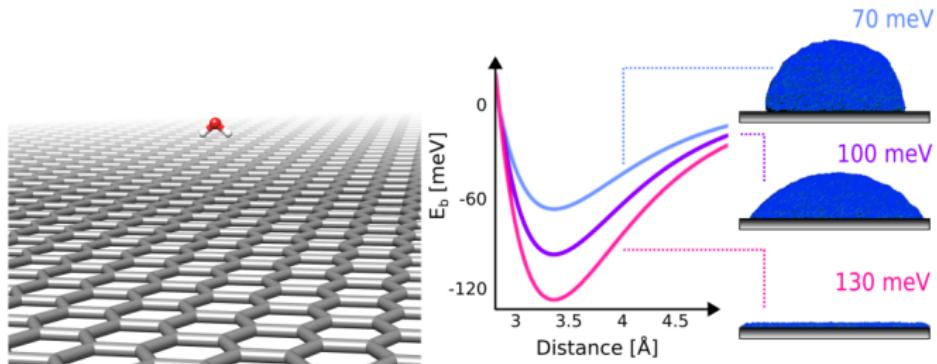
Outline of talk

- 1 Molecular Level Understanding of Water-Graphene
- 2 Benchmark Quality Methods: New DMC Developments
- 3 Results on the Water-Graphene Interaction
- 4 Conclusions and Future Perspective

Outline of talk

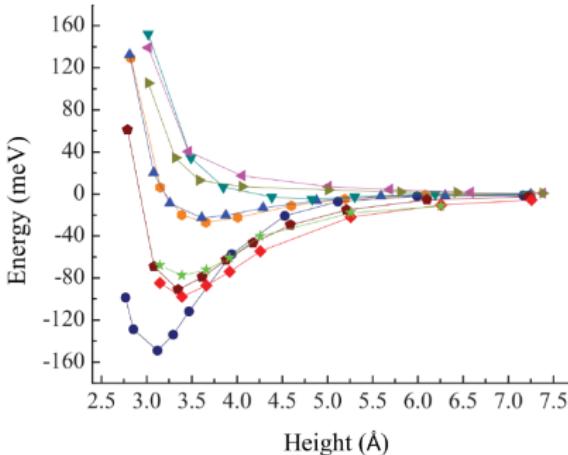
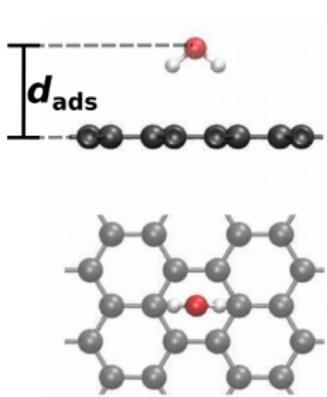
- 1 Molecular Level Understanding of Water-Graphene
- 2 Benchmark Quality Methods: New DMC Developments
- 3 Results on the Water-Graphene Interaction
- 4 Conclusions and Future Perspective

Fundamental quantity: Adsorption of a single water molecule



- The most important quantity to consider is the binding energy (E_b)
- E_b is related to the contact angle of a water droplet on graphene
- Is graphene hydrophobic to hydrophilic?
Currently no clear answer; neither from experiment nor theory

DFT lacks the needed accuracy



- Prediction of E_b have to be well below chemical accuracy
- DFT can provide any value between 0 and -160 meV depending on the exchange-correlation functional and vdW-corrections^[4,5]

[4] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

[5] I. Hamada, *Phys. Rev. B* **86**, 195436 (2012).

Contradicting results from 'reference quality' methodologies

E_b [meV]	Method	Comment
-130	DFT/CC	Corrects DFT based on differences on small cluster ^[6]
-130	DFT-SAPT	Extrapolation from cluster ^[7]
-70 ± 10	DMC	Periodic system, large stochastic error, finite-size effects ^[4]
-135	i-CCSD(T)	Incremental expansion, correlation from cluster, small basis set ^[8]

- differences of > 60 meV not acceptable

→ revised reference value needed

^[4] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

^[6] M. Rubeš, P. Nachtigall, J. Vondrášek, O. Bludský *J. Phys. Chem. C* **113**, 8412 (2009).

^[7] G. R. Jenness, O. Karalti, K. D. Jordan, *Phys. Chem. Chem. Phys.* **12**, 6375 (2010).

^[8] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

Outline of talk

- 1 Molecular Level Understanding of Water-Graphene
- 2 Benchmark Quality Methods: New DMC Developments
- 3 Results on the Water-Graphene Interaction
- 4 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

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

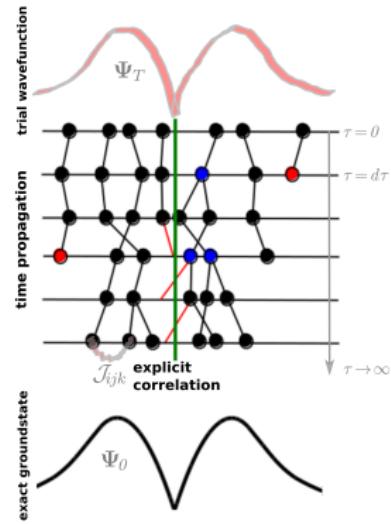
3) Diffusion in imaginary time

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

4) Projection to exact ground state

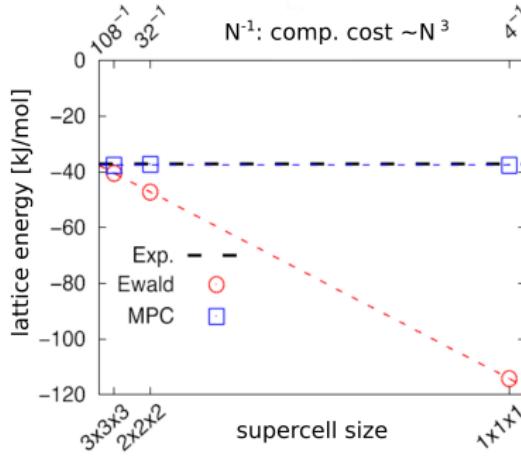
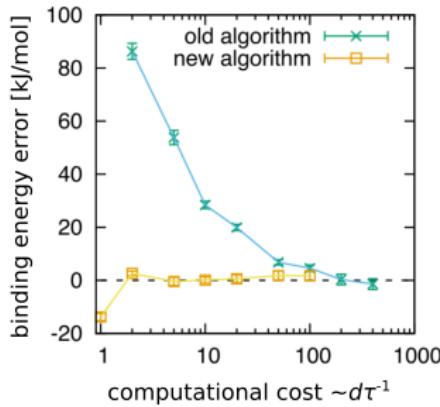
$$|\Psi_0(\mathbf{R})\rangle = \lim_{\tau \rightarrow \infty} \exp[-\tau(\hat{H} - E_T)] |\Psi_T(\mathbf{R}, \tau)\rangle$$

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



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

New DMC algorithm leads to substantial speed up

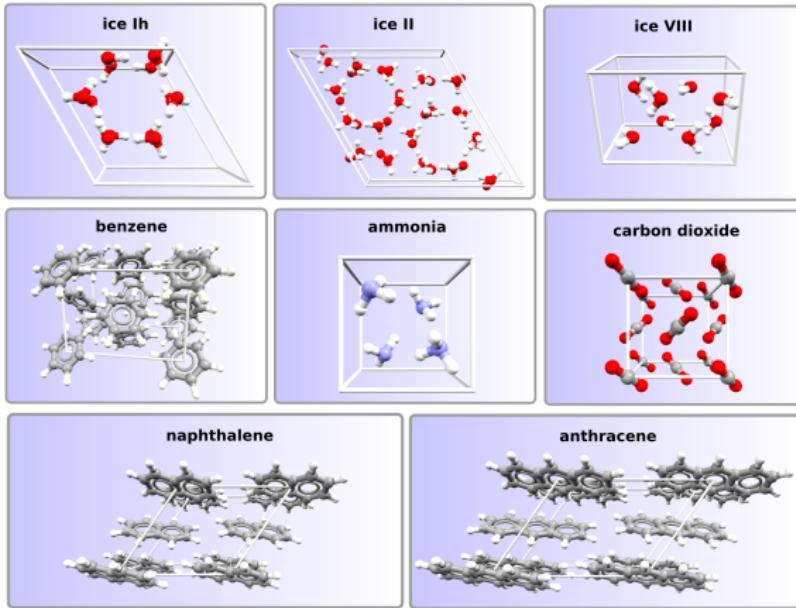


- new size-consistent implementation reduces $\Delta\tau$ error drastically^[10]
- Model periodic Coulomb for finite size correction^[11]

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

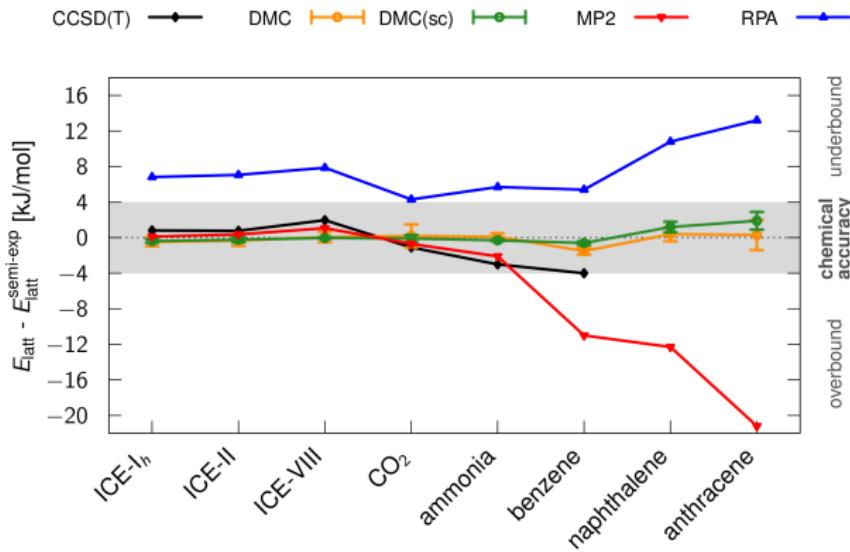
[11] L. M. Fraser, W. M. C. Foulkes, G. Rajagopal, R. J. Needs, S. D. Kenny, A. J. Williamson, *Phys. Rev. B* **53**, 1814 (1996).

Molecular crystals as challenging test



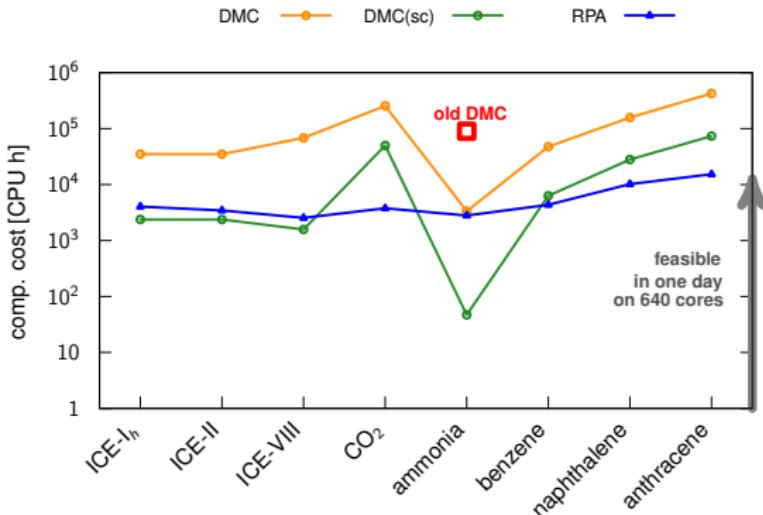
- strong H-bonds, vdW of saturated and unsaturated molecules
- problematic for all readily applicable methods (DFA-DISP, MP2)

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



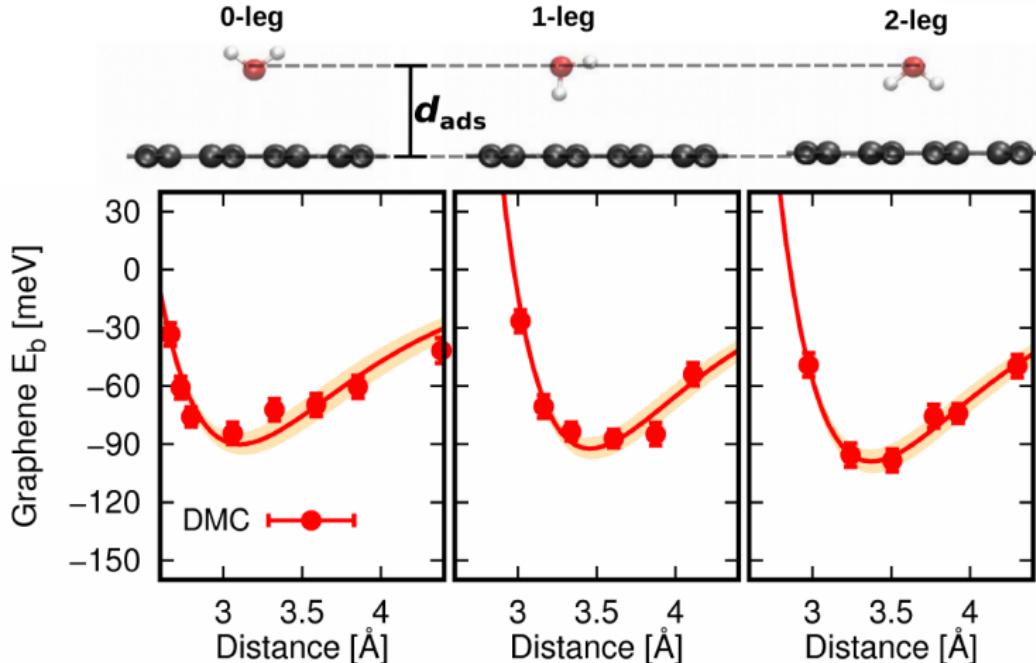
- up to three orders of magnitude speed-up compared to best DMC practice two years ago
- significance will extend to all classes of systems^[10]

[10] 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 Molecular Level Understanding of Water-Graphene
- 2 Benchmark Quality Methods: New DMC Developments
- 3 Results on the Water-Graphene Interaction
- 4 Conclusions and Future Perspective

Revised water adsorption on graphene



- Binding energy in minimum configuration: -99 ± 6 meV
- Very similar binding energies for different motifs

Contradicting results from 'reference quality' methodologies

E_b [meV]	Method	Comment
-130	DFT/CC	Corrects DFT based on differences on small cluster ^[6]
-130	DFT-SAPT	Extrapolation from cluster ^[7]
-70 ± 10	DMC	Periodic system, large stochastic error, finite-size effects ^[4]
-135	i-CCSD(T)	Incremental expansion, correlation from cluster, small basis set ^[8]
-87	p-CCSD(T)	Periodic system, FSE corrected ^[11]
-99 ± 6	DMC	Periodic system, FSE corrected^[11]

^[4] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

^[6] M. Rubeš, P. Nachtigall, J. Vondrásek, O. Bludský *J. Phys. Chem. C* **113**, 8412 (2009).

^[7] G. R. Jenness, O. Karaltı, K. D. Jordan, *Phys. Chem. Chem. Phys.* **12**, 6375 (2010).

^[8] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

^[11] JGB, A. Zen, M. Fitzner, B. Ramberger, G. Kresse, T. Tsatsoulis, A. Grüneis, A. Michaelides, D. Alfè, *J. Phys. Chem. Lett.* **10**, 358 (2019).

Contradicting results from 'reference quality' methodologies

E_b [meV]	Method	Issues
–130	DFT/CC	Small cluster? ^[6]
–130	DFT-SAPT	Small cluster? ^[7]
-70 ± 10	DMC	Large stochastic error, finite-size effects are neglected ^[4]
–135	i-CCSD(T)	Single particle basis set too small? ^[8]
–87	p-CCSD(T)	— ^[11]
-99 ± 6	DMC	— ^[11]

^[4] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

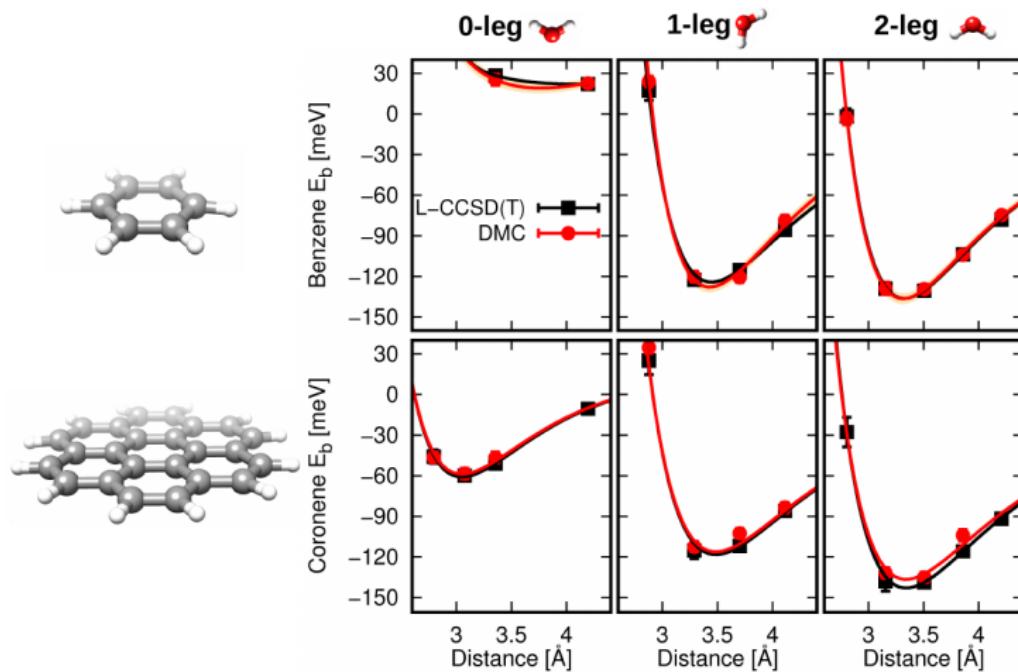
^[6] M. Rubeš, P. Nachtigall, J. Vondrásek, O. Bludský *J. Phys. Chem. C* **113**, 8412 (2009).

^[7] G. R. Jenness, O. Karaltı, K. D. Jordan, *Phys. Chem. Chem. Phys.* **12**, 6375 (2010).

^[8] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

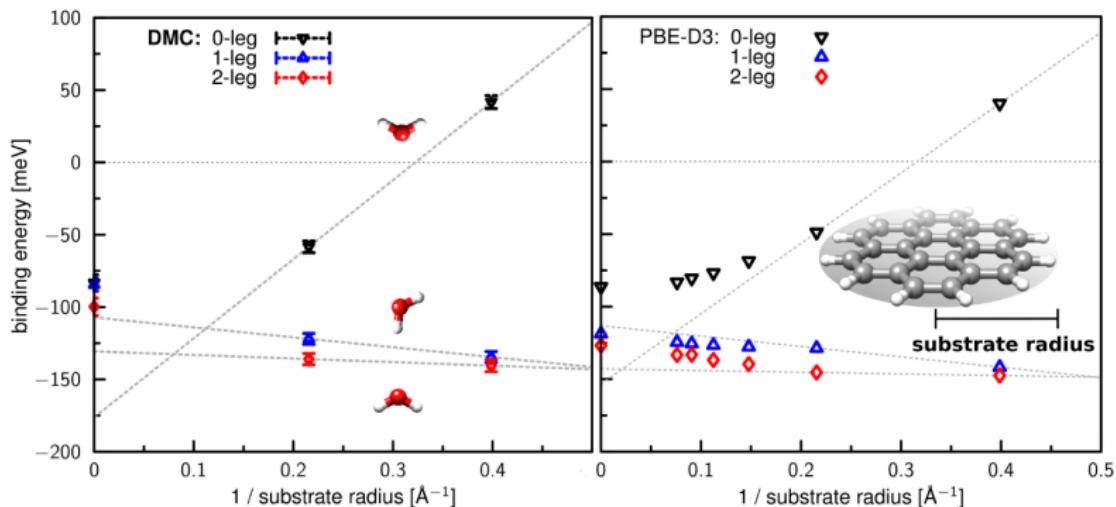
^[11] JGB, A. Zen, M. Fitzner, B. Ramberger, G. Kresse, T. Tsatsoulis, A. Grüneis, A. Michaelides, D. Alfè, *J. Phys. Chem. Lett.* **10**, 358 (2019).

Water adsorption on benzene and coronene as substrate model



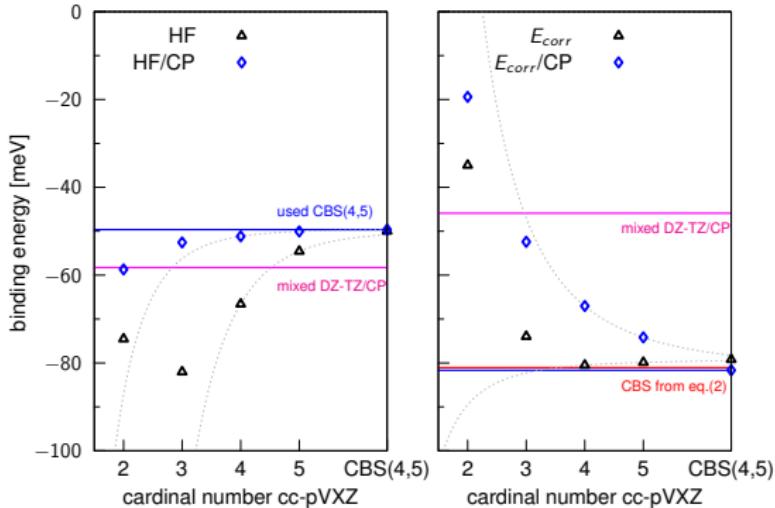
- Stark differences between adsorption motifs on small substrate models

Substrate size extrapolation problematic



- Behaviour strongly dependent on water orientation
- Convergence with substrate size very slow
→ extrapolations using benzene, coronene data unreliable

L-CCSD(T) setup for molecular clusters



- DLPNO-CCSD(T0) energies: counterpoise corrected extrapolation using large basis sets in current study
- Slow convergence, older study employed non-converged values

[¹²] C. Ripplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.* **139**, 134101 (2013).

[¹³] C. Ripplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **144**, 024109 (2016).

Discrepancies of literature values resolved



E _b [meV]	Method	Issues
-130	DFT/CC	Unreliable extrapolation [6]
-130	DFT-SAPT	Unreliable extrapol., SAPT2 inaccuracies [7]
-70 ± 10	DMC	Large stochastic error, finite-size effects are neglected [4]
-135	i-CCSD(T)	Single particle basis set too small [8]
-87	p-CCSD(T)	— [11]
-99 ± 6	DMC	— [11]

[4] J. Ma, A. Michaelides, D. Alfè, L. Schimka, G. Kresse, E. Wang, *Phys. Rev. B* **84**, 033402 (2011).

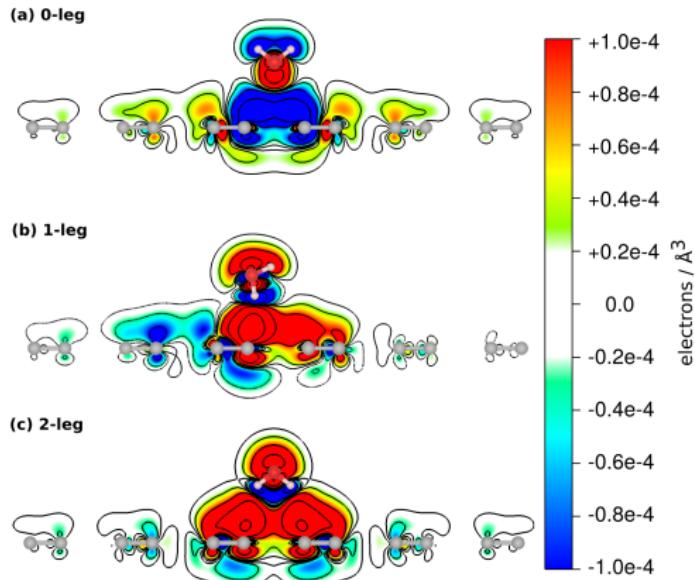
[6] M. Rubeš, P. Nachtigall, J. Vondrášek, O. Bludský *J. Phys. Chem. C* **113**, 8412 (2009).

[7] G. R. Jenness, O. Karaltı, K. D. Jordan, *Phys. Chem. Chem. Phys.* **12**, 6375 (2010).

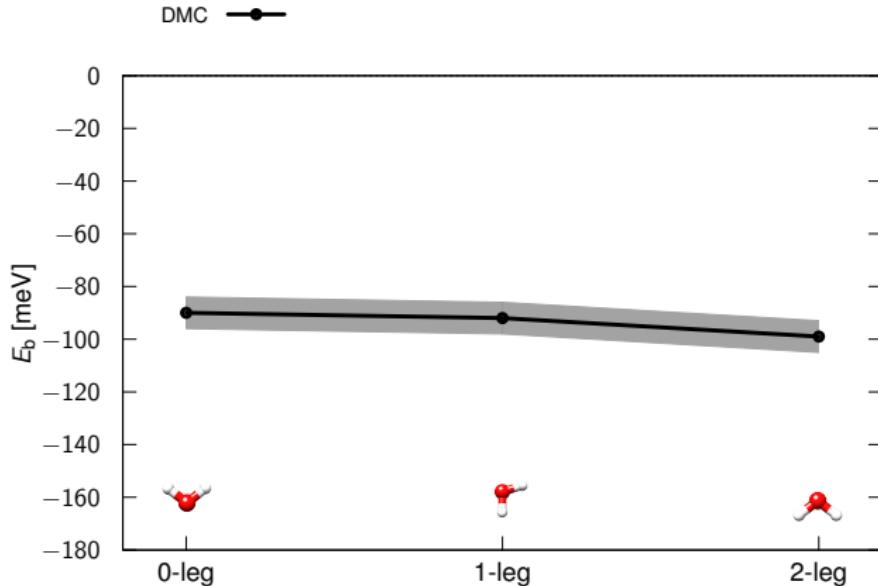
[8] E. Voloshina, D. Usvyat, M. Schütz, Y. Dedkov, B. Paulus, *Phys. Chem. Chem. Phys.* **13**, 12041 (2011).

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

Redistribution of charge density strongly dependent on adsorption motif

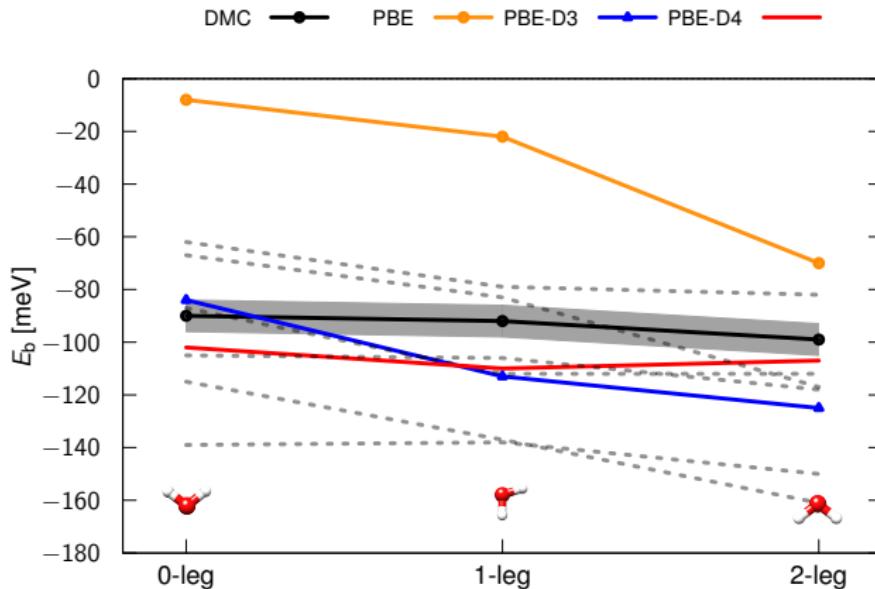


Benchmarking density functional approximations



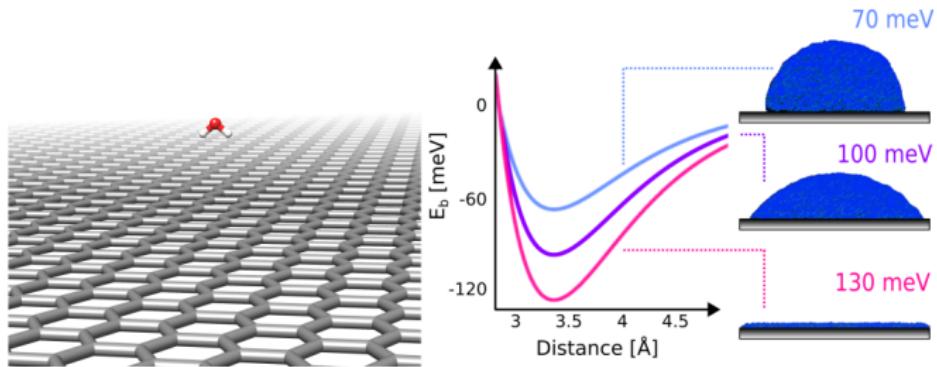
- High-level references with small error margins

Benchmarking density functional approximations



- Van der Waals interactions mandatory for reasonable descriptions
- Recent vdw developments (D4, MBD) improve agreement with references

Implications of revised water-graphene interaction



- Lack of orientational dependence might explain low friction
- Contact angle is $\leq 56^\circ$,
in agreement with recent experimental estimate ($42 \pm 3^\circ$ ^[14])
- Graphene is mildly hydrophilic

^[14] A. V. Prydatko, L. A. Belyaeva, L. Jiang, L. M. C. Lima, G. F. Schneider, *Nat. Commun.* **9**, 4185 (2018).

Outline of talk

- 1 Molecular Level Understanding of Water-Graphene
- 2 Benchmark Quality Methods: New DMC Developments
- 3 Results on the Water-Graphene Interaction
- 4 Conclusions and Future Perspective

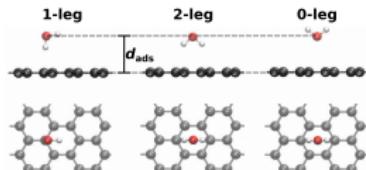
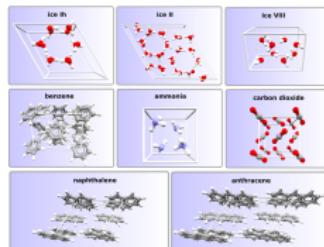
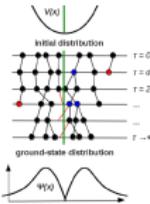
Summary

Conclusions

- DMC delivers (sub-) chemical accuracy with three orders of magnitude speed up
- revised water-graphene interaction
- resolved literature discrepancies

Outlook

- ML techniques as a route to large-scale water-carbon dynamics
- Employ improved DMC for molecular crystal polymorphs



Acknowledgements



PhD / Postdocs



Andrea Zen



Martin Fitzner



Michaelides (UCL)

Principal investigator



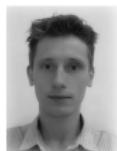
Alfè (UCL)



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)



Grüneis (Vienna)



Civalleri (Turin)



Maschio (Turin)



Anreas Afantitis
(NovaMechanics)



Alexander von Humboldt
Stiftung/Foundation



Acknowledgements



PhD / Postdocs



Andrea Zen



Martin Fitzner



Michaelides (UCL)

Principal investigator



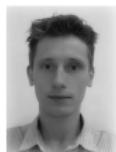
Alfè (UCL)



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)



Grüneis (Vienna)



Civalleri (Turin)



Maschio (Turin)



Antreas Afantitis
(NovaMechanics)

Alexander von Humboldt
Stiftung/Foundation

THOMAS YOUNG
CENTRE THE
GRAPHENE
AND
WATER
INTERACTIONS

cROSS

Key references

■ QMC for molecular crystals and water-graphene:

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

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

JGB, C. Bannwarth, A. Hansen, S. Grimme *J. Chem. Phys.*, **148**, 64104 (2018).

■ Crystal structure prediction:

S. L. Price, JGB, *Molecular Crystal Structure Prediction*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, 336-363 (2017).

■ website: **gerit-brandenburg.de**