Nailing down the **water-graphene** adsorption strength indicates a mild **hydrophilicity**

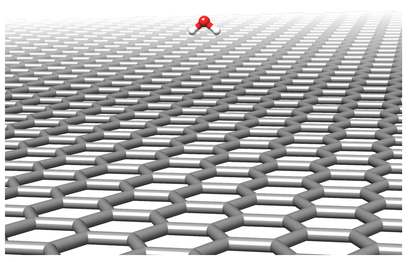
Physisorption of Water on Graphene: Subchemical Accuracy from Many-Body Electronic Structure Methods

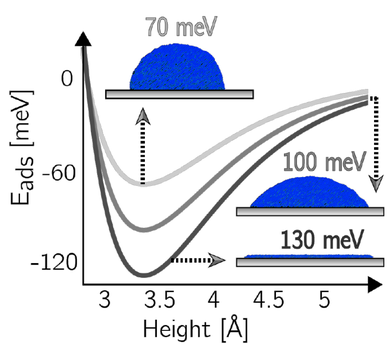
Jan Gerit Brandenburg, A. Zen, M. Fitzner, B. Ramberger, G. Kresse, T. Tsatsoulis, A. Grüneis, A. Michaelides, and D. Alfè

Background

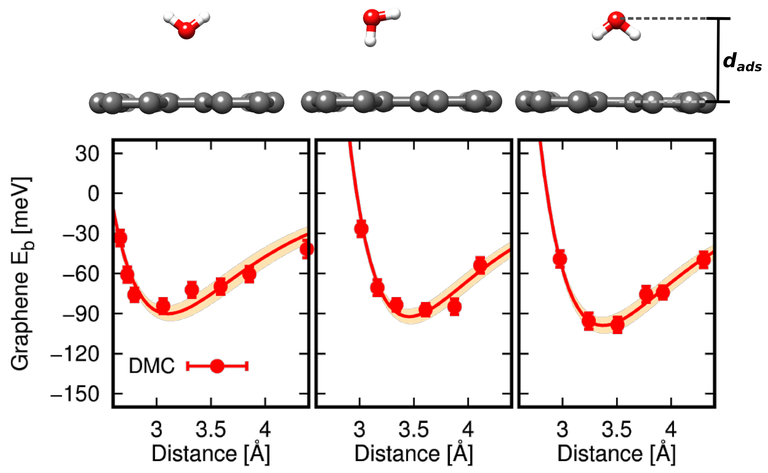
- Is graphene hydrophobic or hydrophilic?
- Directly related to adsorption.

Eb [meV]	Method	Comment
-70 ± 10	DMC	Finite-size errors
-135	i-CCSD(T)	Small basis set
-80 ± 100	DFT	Highly XC dependent
-87	p-CCSD(T)	Large basis set
-99 ± 6	**DMC**	**FSE corrected**





RESULTS



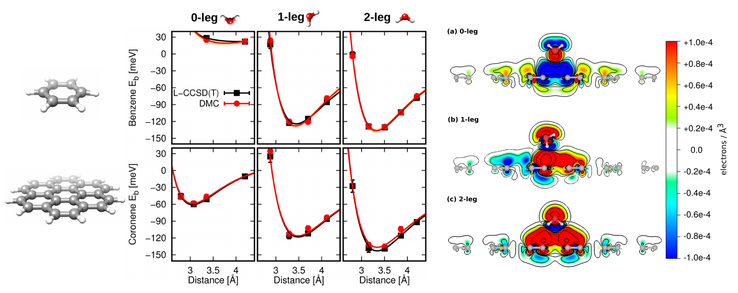
- Motif independence → low friction.
- Contact angle is ≦56°.

→ **Graphene is mildly hydrophilic.**[1]

METHODS

- Fixed-node Diffusion Monte-Carlo.[2]
- (Periodic) CCSD(T), RPA.
- 5x5 supercell of graphene, bias from finite coverage and size corrected.

AMMO BAR



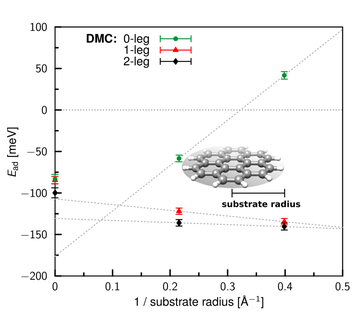
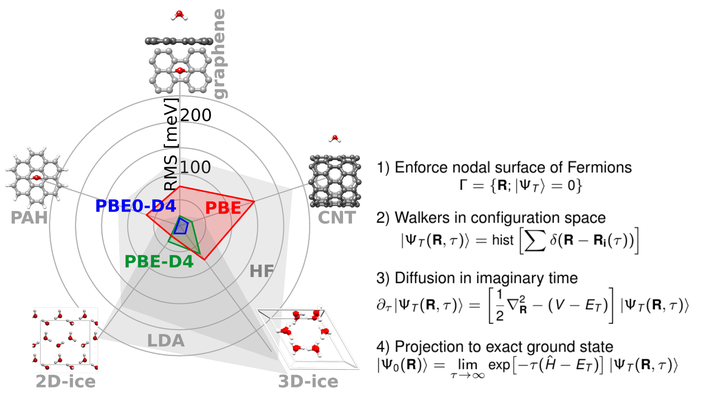


TABLE I. Reference interaction energies for considered systems given per water molecule in meV. The reported error represents the uncertainty on the evaluation.

w@graphene[55]		**w@benzene**[55]		**w@coronene**[55]	
0-leg	-90 ± 6	0-leg	$+43 \pm 1$	0-leg	-61 ± 3
1-leg	-92 ± 6	1-leg	-124 ± 3	1-leg	-118 ± 5
2-leg	-99 ± 6	2-leg	-136 ± 2	2-leg	-143 ± 4
w@CNT [a]					
external	-85 ± 18				
internal	-287 ± 16				
3D ice[42]		**2D ice**[47]			
Ih	-615 ± 5	hex.	-423 ± 3	pent	-419 ± 3
II	-613 ± 6	square	-404 ± 3	rhombic	-389 ± 3
VIII	-594 ± 6				

[a] Evaluation based on Ref. 52, but recomputed in this work. See details in Section II B.



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

DMC Details:
Fock pseudopotentials with the LA are used. The trial wavefunctions were of the Slater-Jastrow type with LDA determinant. The recently developed size-consistent DMC algorithm (ZSGMA) was used. Finite time-step errors are carefully minimised by performing simulations with different values of the time-step, till the bias appears safely smaller than the stochastic error. In periodic calculations, finite-size corrections are applied using the model periodic Coulomb interaction.

[1] *J. Phys. Chem. Lett.* **2019**, 10, 358
[2] *P.N.A.S. USA* **2018**, 115, 1724

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386
universität wien
UCL
TU WIEN TECHNISCHE UNIVERSITÄT WIEN

Take a picture to **download** the **full paper**