

# On the physisorption of water on graphene: Sub-chemical accuracy from quantum Monte-Carlo

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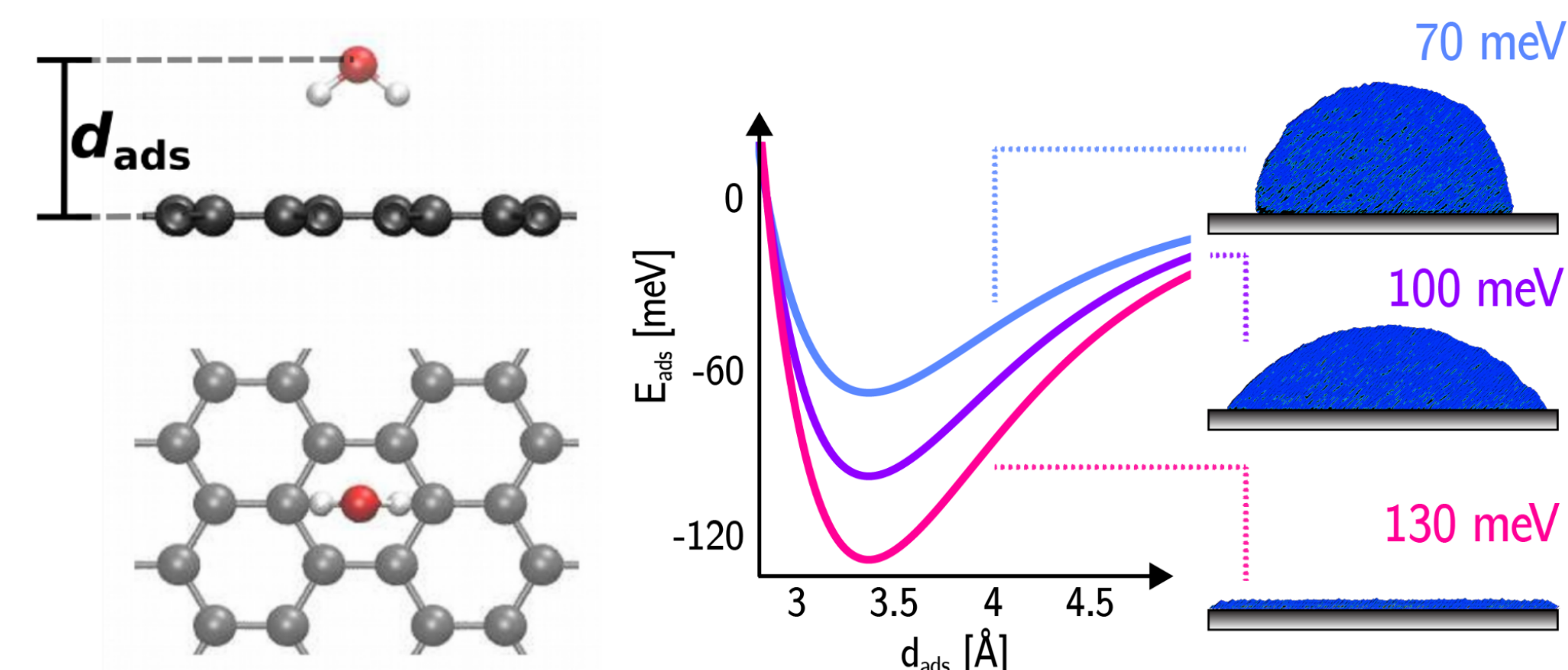
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## Abstract

Molecular adsorption on surfaces plays an important part in catalysis, corrosion, desalination, and various other processes that are relevant to industry and in nature. The most fundamental property determining the wetting of surfaces is the water adsorption energy. The adsorption on graphene is particularly interesting as it calls for an accurate treatment of electron correlation effects. Combined with the vanishing band gap, this poses practical challenges to experiments and simulation methods and the current literature values are in severe disagreement. Here, we employ DMC for calculating adsorption energies of water on graphene as well as on benzene and coronene. Different water orientations have a very similar binding energies though the contributions to the interaction are quite distinct. The high-level references are used to identify suitable approximated methods.



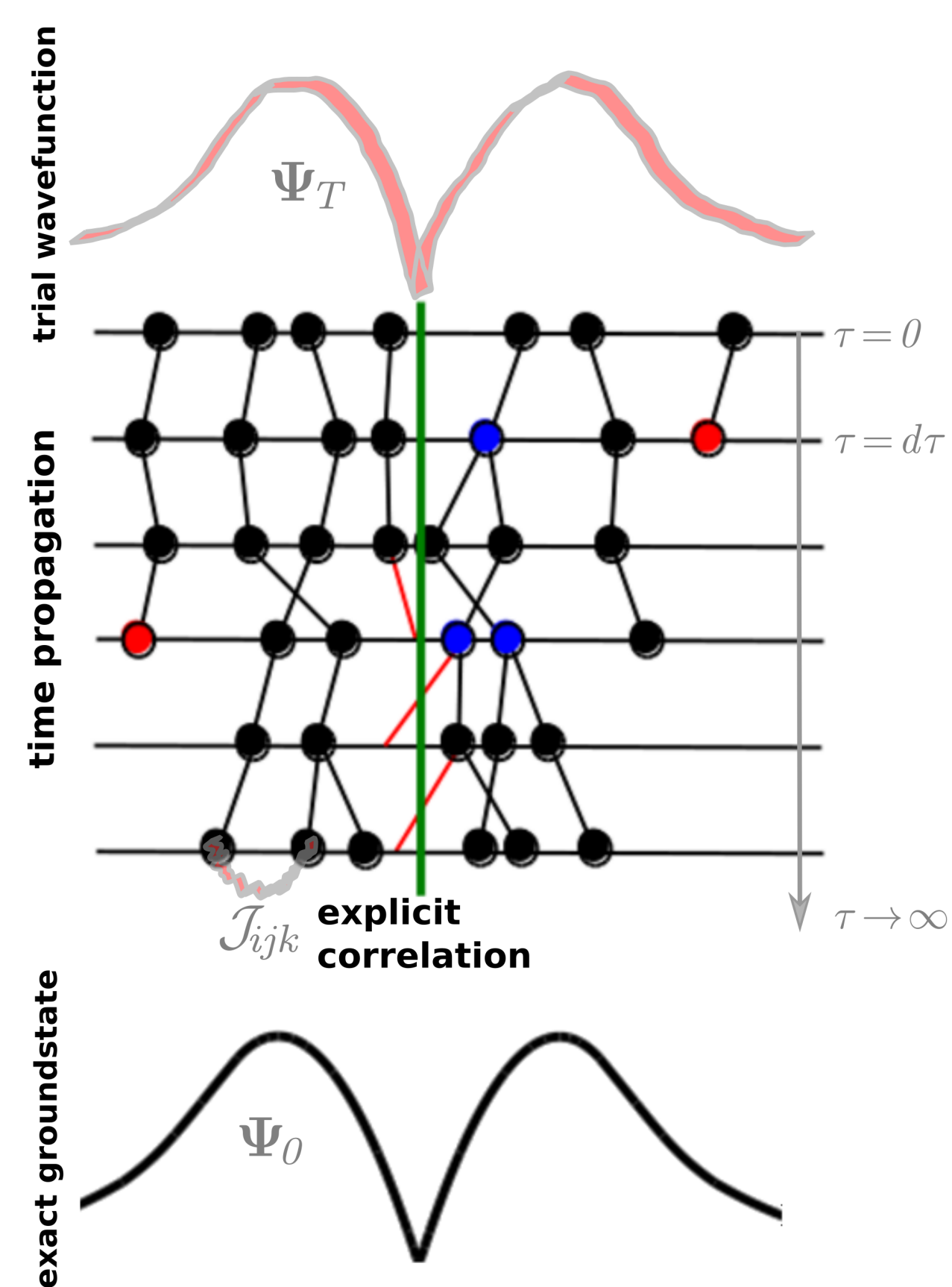
## Water binding strength on graphene is still unknown

**Goal:** Binding energy  $E_b$  of single water monomer adsorbed on graphene.  
Binding computed with frozen geometries from bound configuration.

### Literature values

Ref.	$E_b$ [meV]	method	issues
[1]	-130	DFT/CC	unreliable extrapolation of cluster
[2]	-130	DFT-SAPT	unreliable extrapolation, SAPT2 is not a reference method
[3]	-70±10	DMC	large stochastic error (~50 Mio CPU h used), finite-size effects are neglected
[4]	-135	i-CCSD(T)	single particle basis set too small
[5]	<b>-99±6</b>	DMC	this work (~1 Mio CPU h used)

## Diffusion Monte-Carlo in a nutshell



**Trial function:**  $\Psi_T = \mathcal{J} \times \Psi_{\text{DFT}}$   
with Slater-Determinant from DFT and explicit correlation factors  $\mathcal{J}$

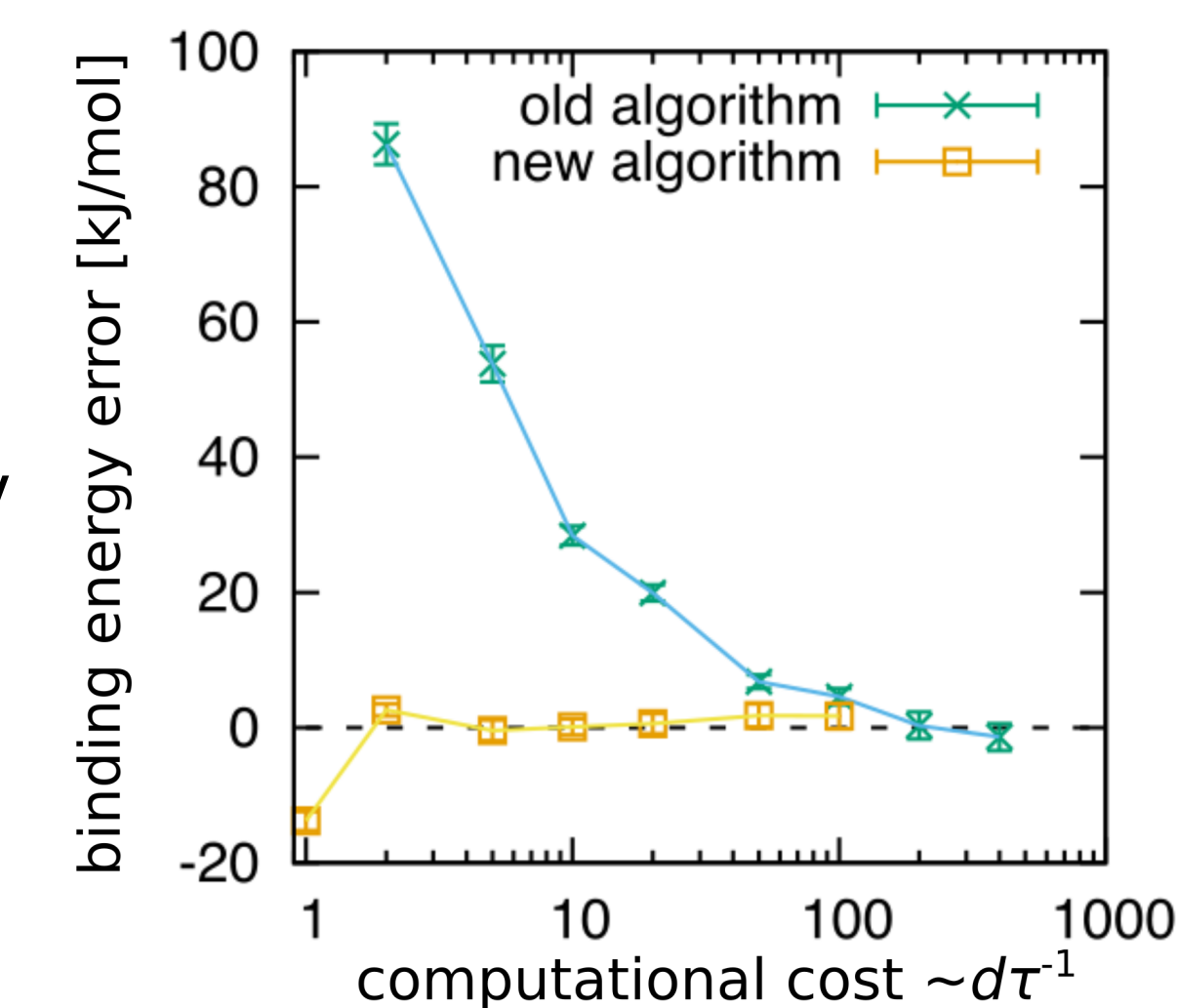
### Time propagation:

Diffusion-branching-drift with finite  $d\tau$  restricted within nodal surface of  $\Psi_T$  and guided by  $|\Psi_T|^2$ .

### Exact ground state:

Time propagation projects out all excited state components

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



### Recent DMC development

1. Energy size consistency with finite  $d\tau$  [6]
2. Finite-size correction for periodic systems by model periodic coulomb (MPC)
3. Established workflow for chemically accurate NCIs [7]

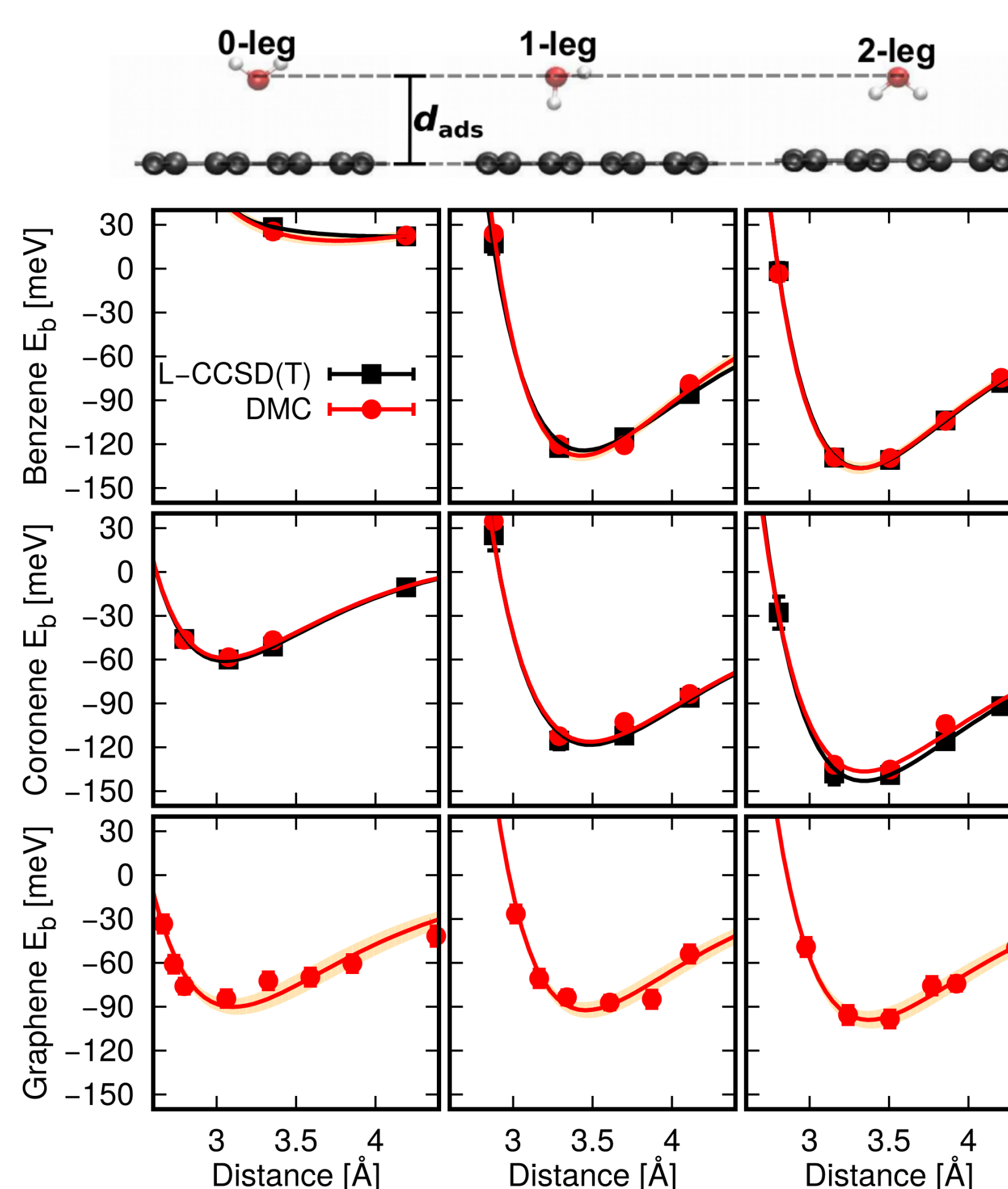
### CCSD(T)

- + linear scaling variants
- slow basis convergence
- non-trivial to parallelize

### DMC

- +  $N^3$  scaling, [-] huge prefactor
- + fast basis convergence
- + scaleable to HPCs
- stochastic error, uncertainties from FN and non-local pseudopotentials

## Revised high-level adsorption energies



### Technical aspects

- reference methods agree within sub-chemical accuracy (10 meV)
- CBS(QZ,5Z) needed for CC
- 5x5 cell & MPC for graphene
- convergence of substrate size depends strongly on orientation

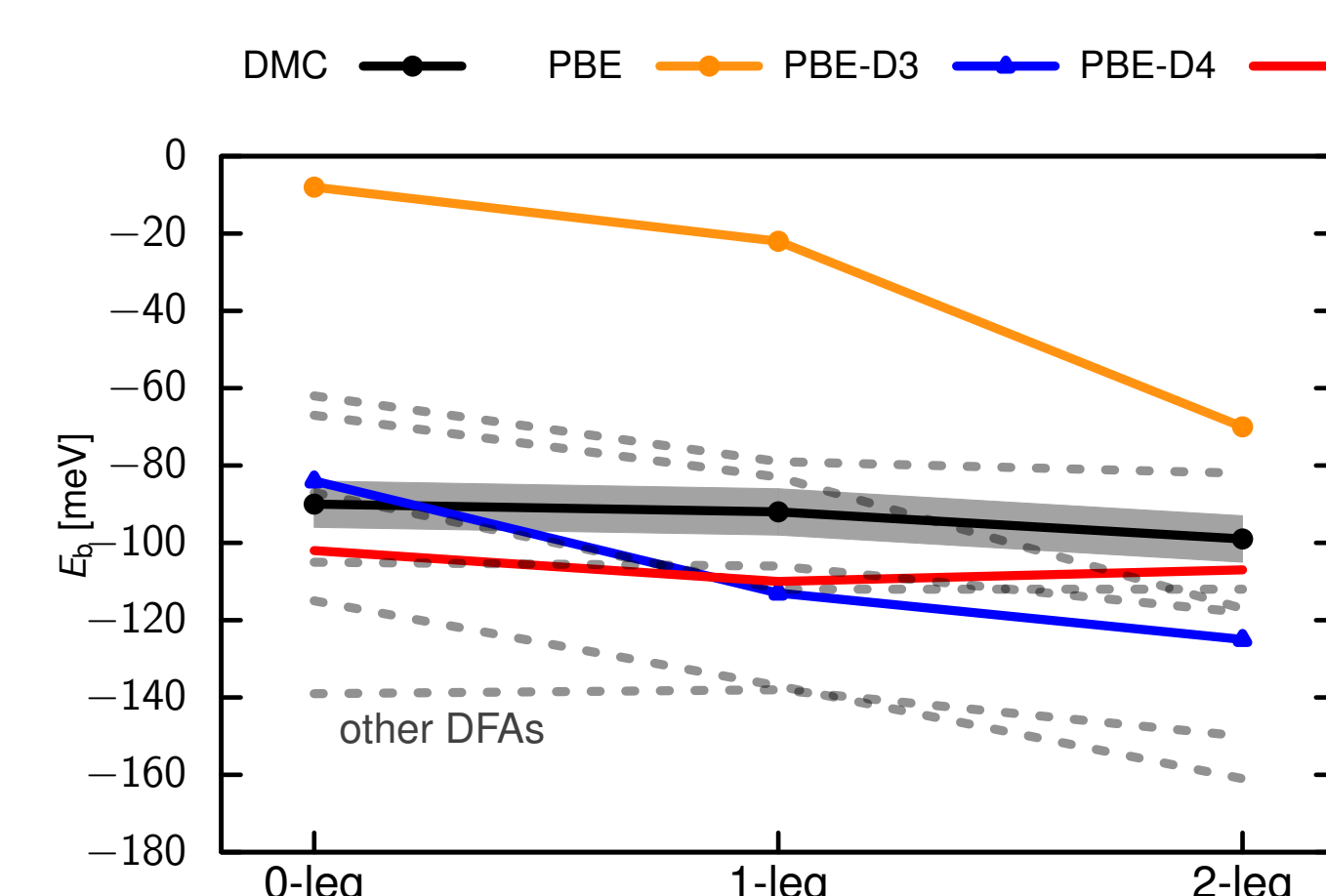
### Implications

- energies from cluster extrapolations are not reliable
- orientation dependency impossible to describe with coarse-grained water
- weak dependency of water orientation might reduce friction

→ revised water on graphene adsorption energy: **-99±6 meV**

## Benchmarking approximate methods

- large variation for graphene adsorption (all vdW corrected DFAs get adsorption on benzene correct)
- vdW correction crucial, beyond atom-pairwise terms important
- nonlocal Fock exchange improves description



→ impossible to choose DFA without high-level references

## London-Vienna collaboration

### UCL team

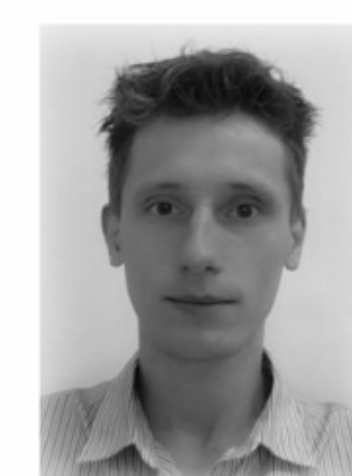


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