Benchmarking the interaction strength between water and graphene

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Collaborators: Dario Alfè,[1] Angelos Michaelides,[1] Benjamin Ramberger,[3] Georg Kresse,[3] Theodoros Tsatsoulis,[4] Andreas Grüneis [4]

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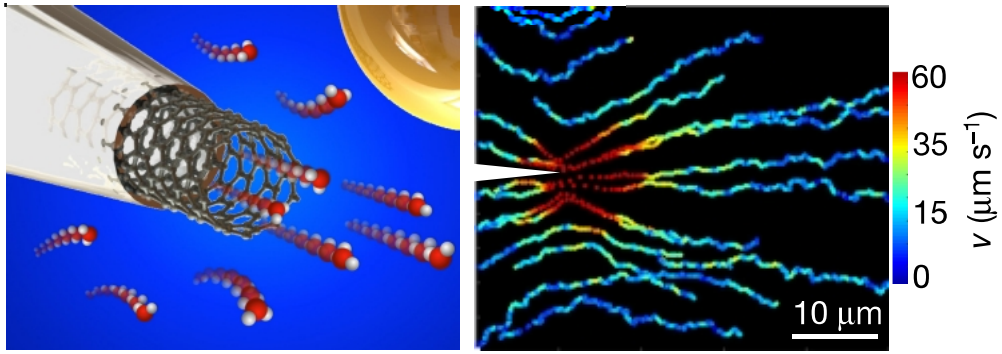
[3] *University of Vienna;* [4] *Vienna University of Technology*

`Properties of Water at Molecular Scale' Workshop, NGI, Manchester, UK July 3rd, 2018

Water-graphene is important

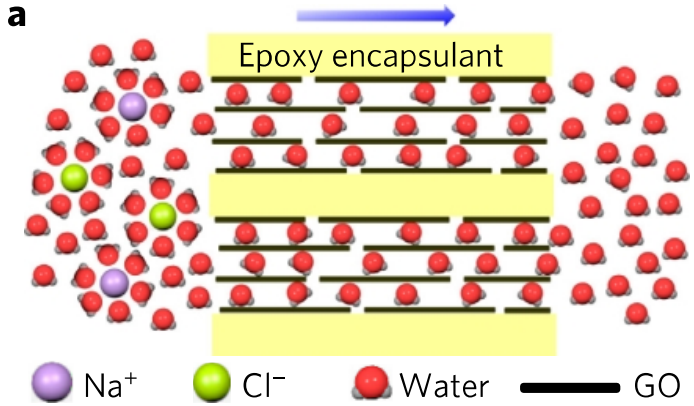
Important applications in:
Desalination, Nano-filtration and Energy harvesting.

- Experimental study of water flow through carbon nanotubes [Nature **537**, 210 (2016).]



Massive radius-dependent flow slippage in carbon nanotubes

- Applications for water filters [Nature Nanotech. **12**, 546–550 (2017)]



Tunable sieving of ions using graphene oxide membranes

Outline

❑ Molecular level understanding

- Binding energy of a single water molecule adsorbed on graphene
- Missing a reliable benchmark value (discrepancies among different methods)

❑ Diffusion quantum Monte Carlo

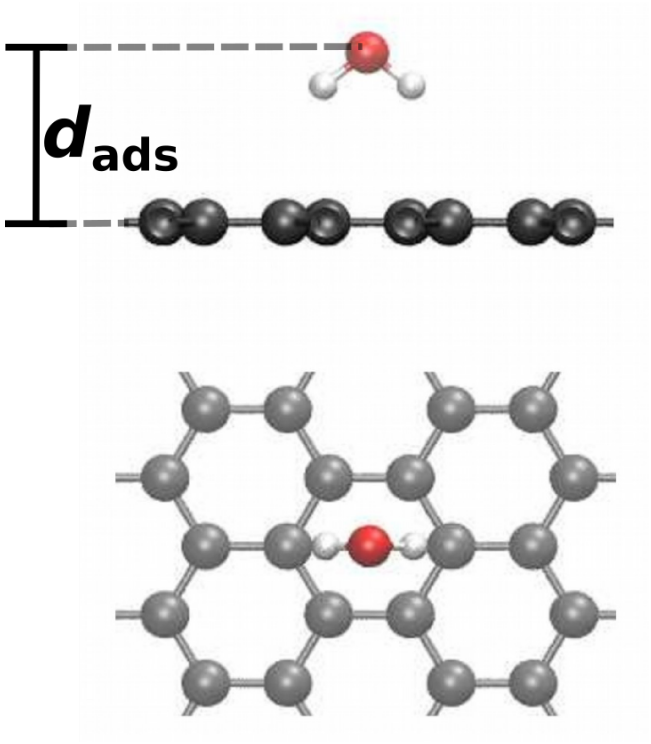
- Recent algorithmic developments, improved accuracy and efficiency
- Revised DMC value for the water-graphene binding energy

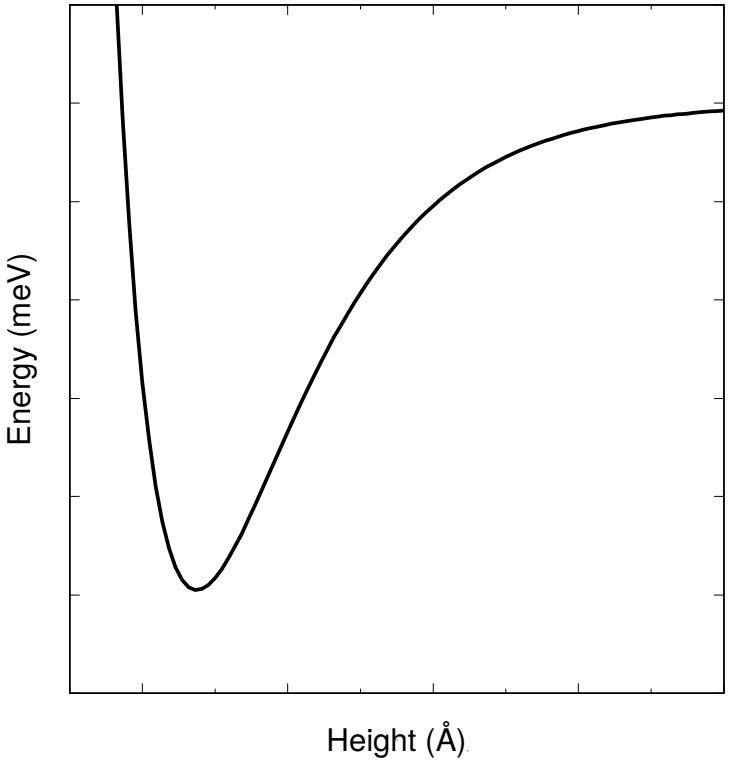
❑ Results and discussion

- Adsorption energies from many-body methods
- Analyzing contributions to adsorption motifs
- Convergence with substrate size
- Benchmarking density functional approximations

Adsorption of a single water

- The most important quantity to consider is the **Binding Energy** (**E_b**).

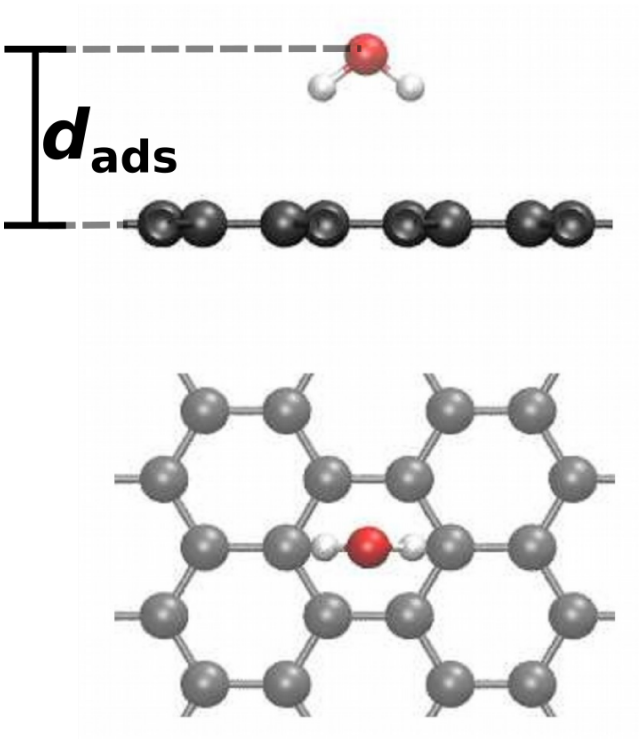


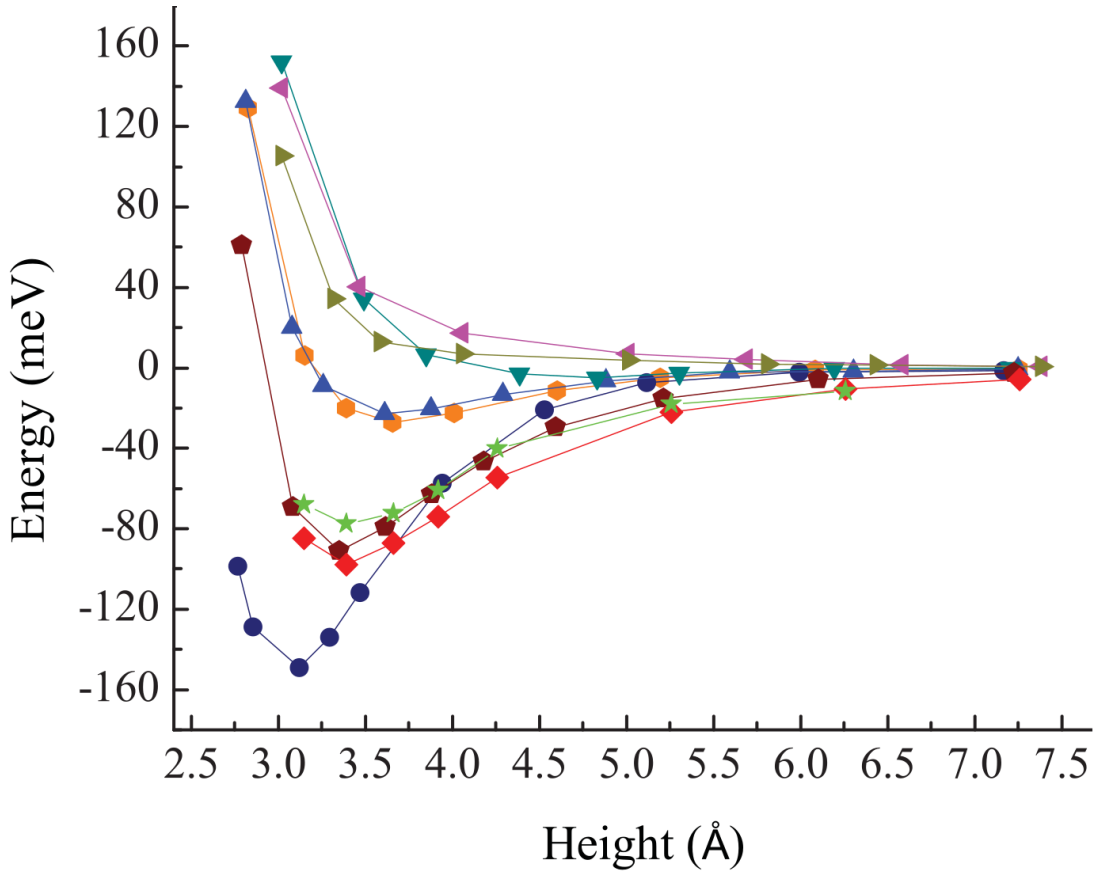


- E_b crucially related to the **contact angle** of a water droplet on graphene.

DFT is useless

- **Density functional theory** (**DFT**) can provide any value between 0 and -160 meV depending on the exchange-correlation functional and vdW-corrections [Phys. Rev. B, **84**, 033402 (2011)] .





Value of E_b is still unknown

Ref.	E_b	Method
1	**-130 meV**	**DFT/CC**
2	**-130 meV**	**DFT-SAPT**
3	**-70 ± 10 meV**	**Diffusion Monte Carlo (DMC)**
4	**-135 meV**	**i-CCSD(T)**

1. Miroslav Rubes *et al., JPC C* **2009**, 113, 8412
2. G.R. Jenness, O. Karalti and K.D. Jordan, *PCCP* **2010**, 12, 6375
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- All these approaches had weakness and possible issues.

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- The method of choice is DMC (accuracy and efficiency drastically improved in the last 7 years).

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A **propagation** according to the imaginary time Schrodinger equation is performed to **project out the exact ground state** from a trial wave function.

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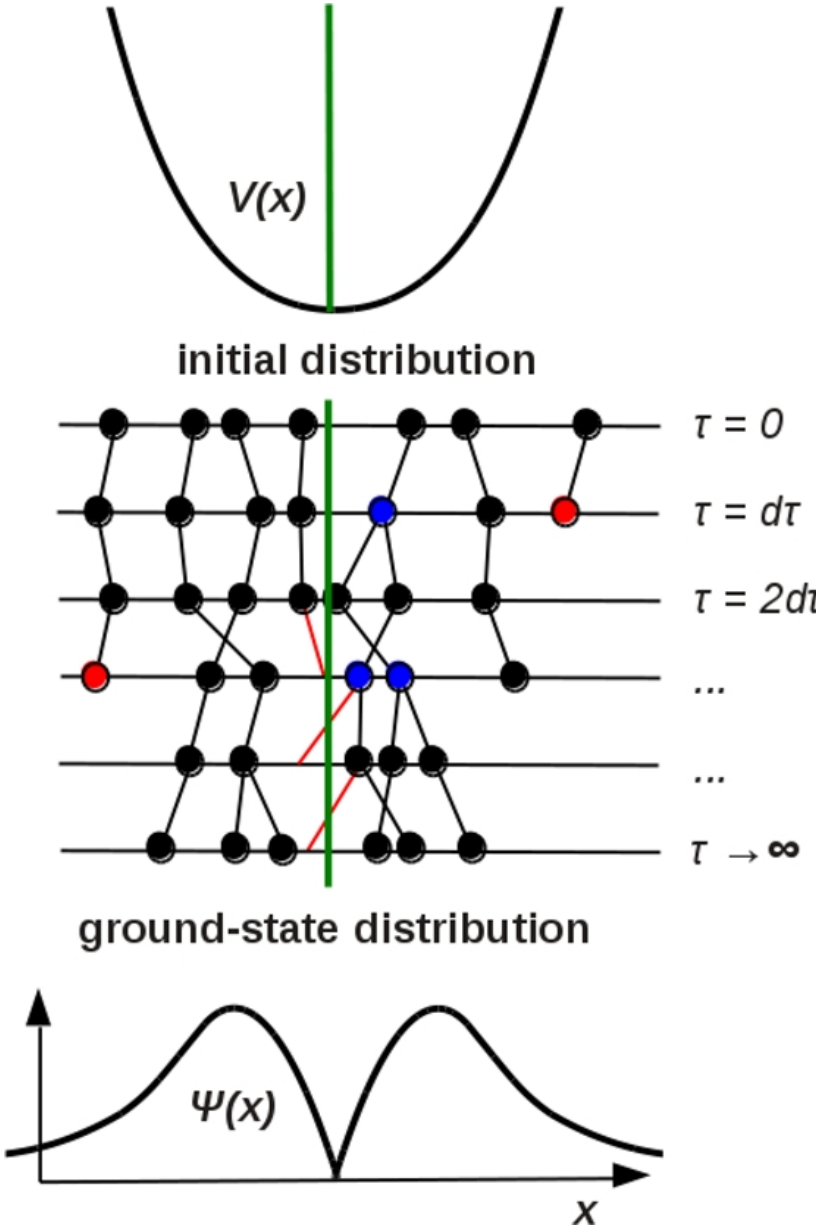
- Generate a set of configurations (**walkers**) according to a trial wave function
- Propagate in time, with finite **time-step** (*branching-drift-diffusion process*)
- **Equilibration** (project out the exact G.S.)
- **Statistical sampling** (stochastic method, autocorrelation time)



Chem. Rev., 116, 5188, (2016)

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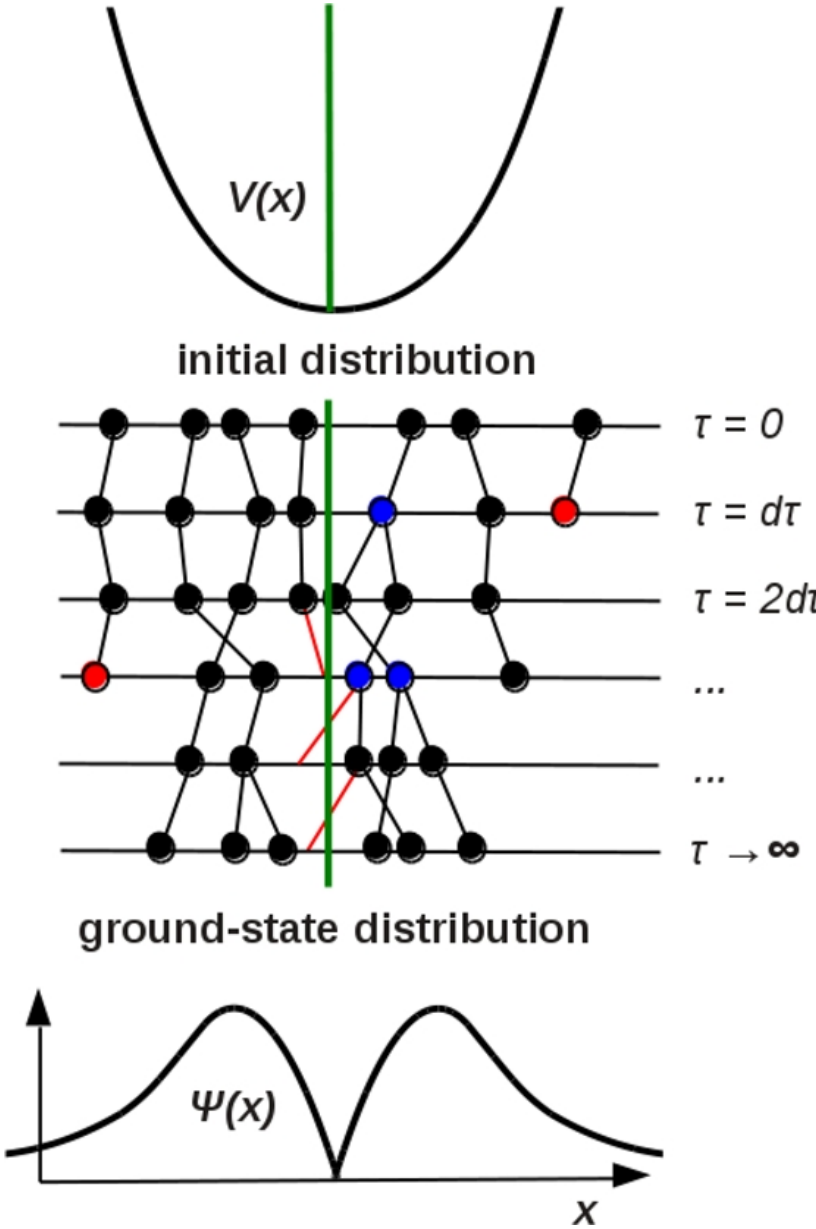
Value of time-step is crucial:
DMC exact for infinitesimal time-step;
DMC cost is proportional to time-step inverse.

Other approximations employed are not an issue in non-covalent interactions.



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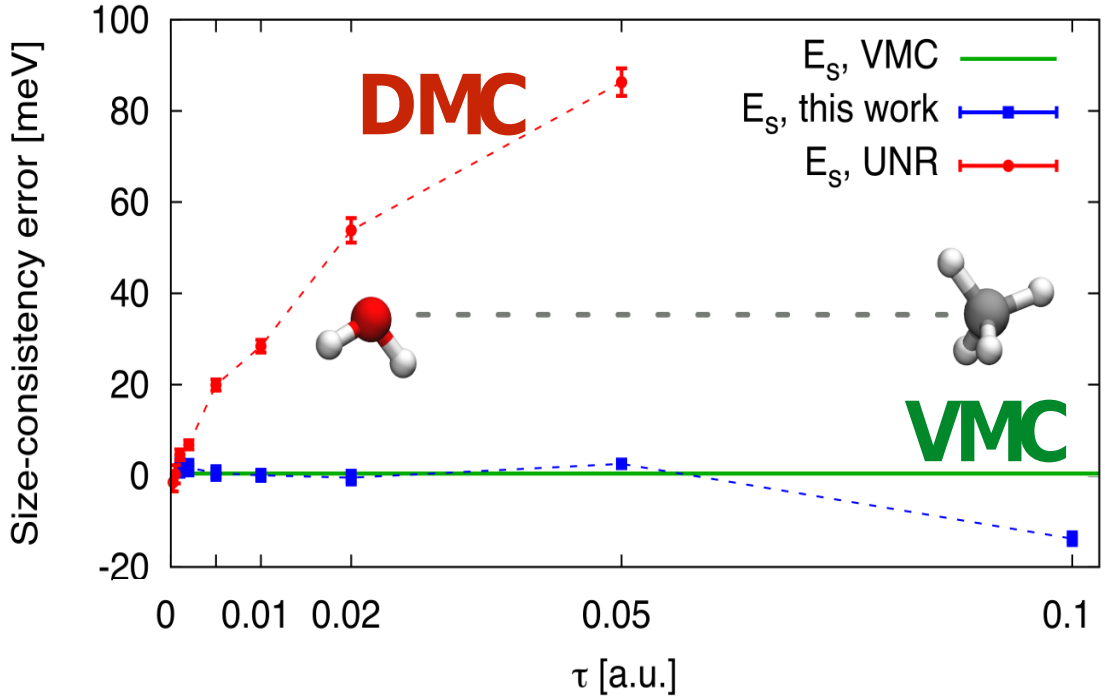
Recent developments in DMC



Discovered and solved a size-consistency issue for finite time-step
[Phys. Rev. B, **93**, 241118(R) (2016)]

- Old DMC algorithm => **UNR**
- New DMC algorithm => **ZSGMA**

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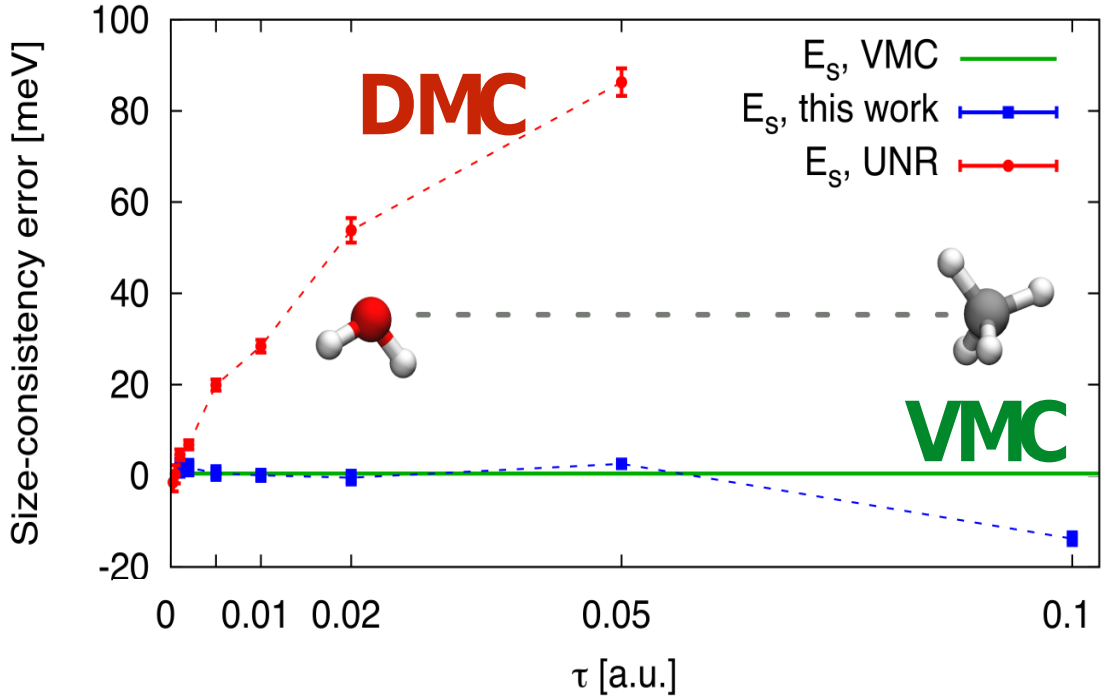

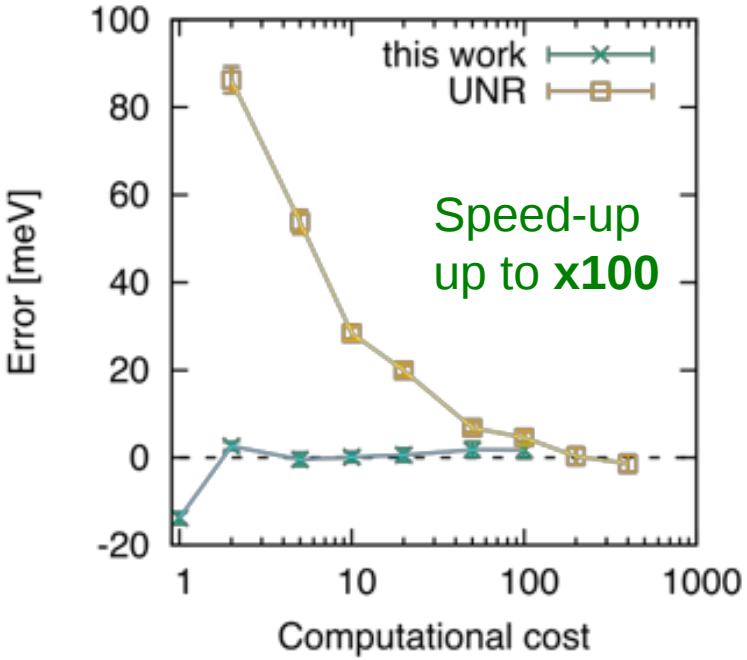

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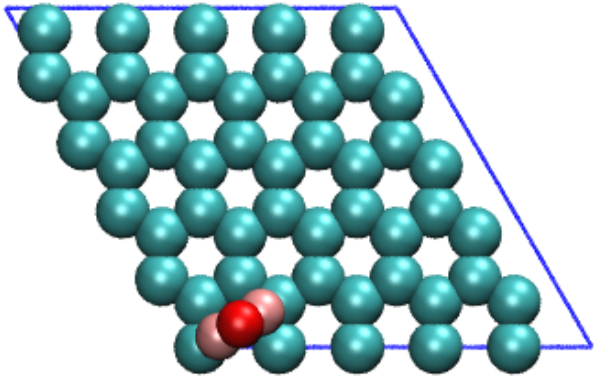
High precision and accuracy at (relatively) low computational cost

DMC in periodic systems

Simulation cell
water in 5x5 graphene



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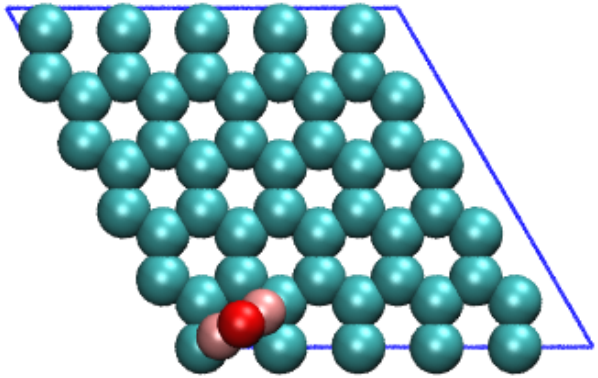
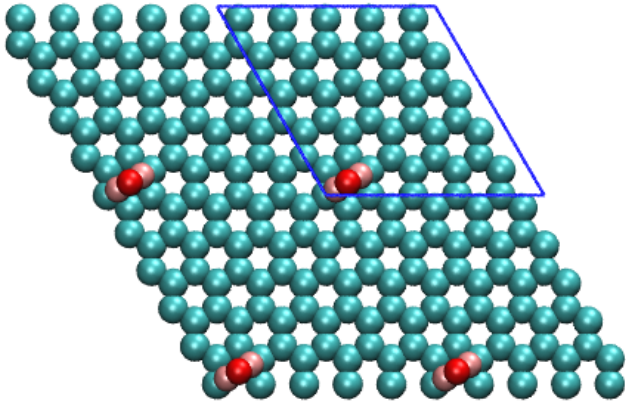
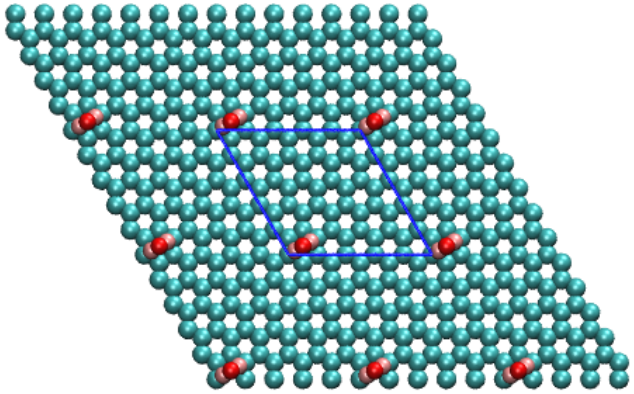


2 x 2 supercell



3 x 3 supercell



There are **finite-size effects (FSE)**!
Exact binding energy is the converged result for *n* x *n* supercell

DMC in periodic systems

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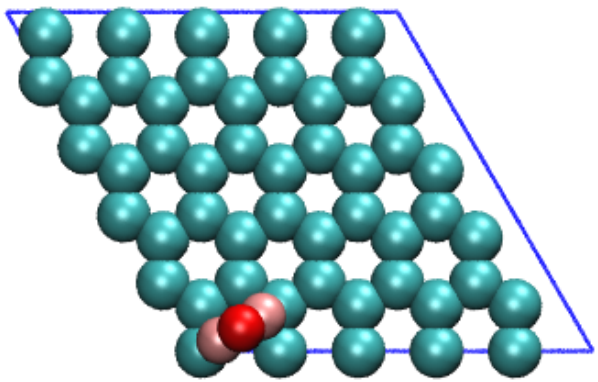

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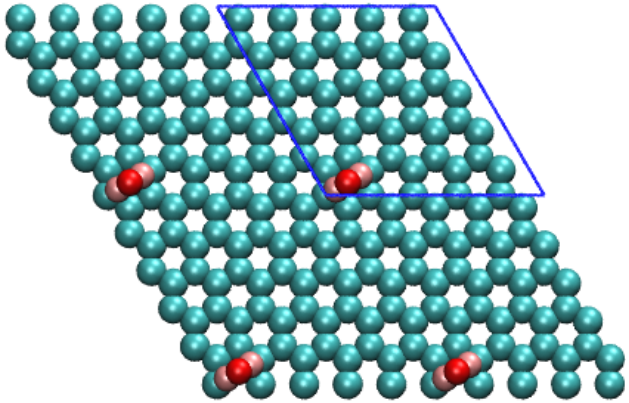

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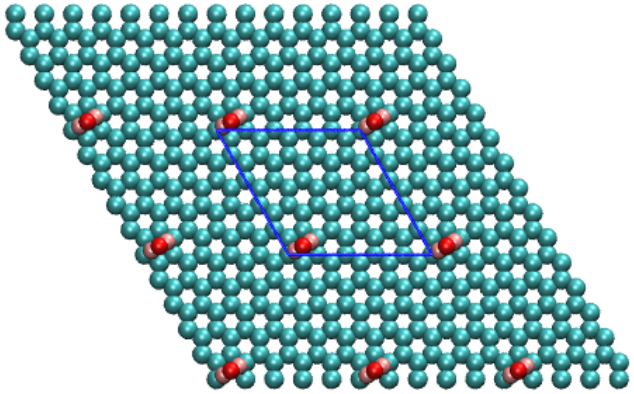

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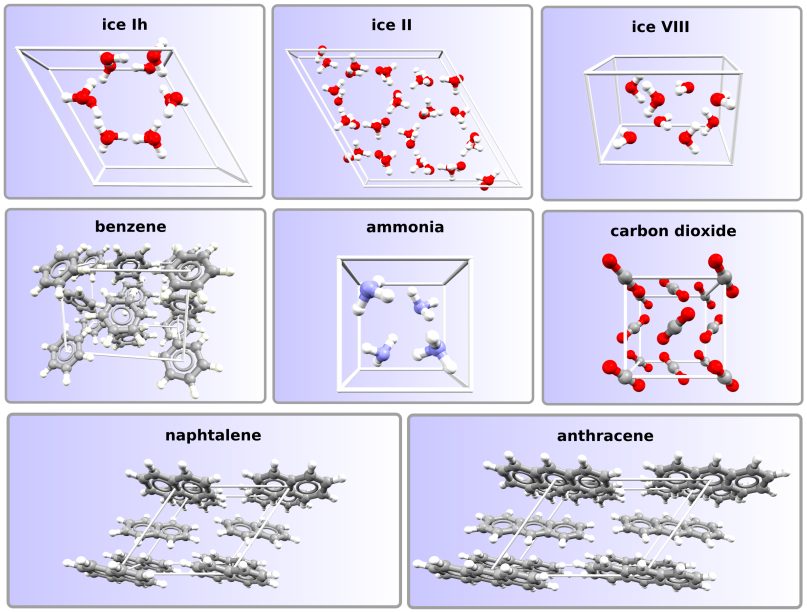
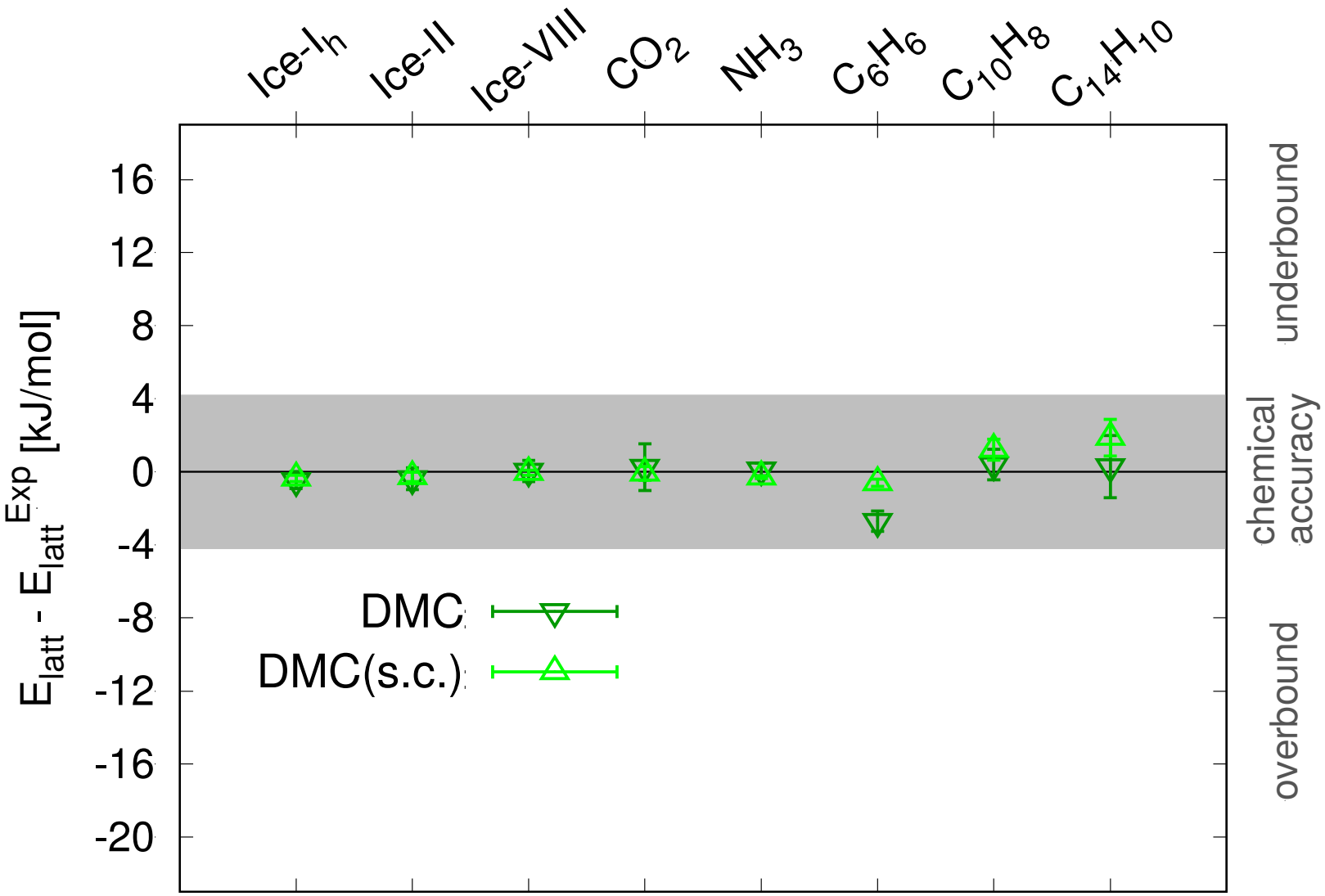
Proc. Natl. Acad. Sci. U.S.A.,**115**, 1724 (2018)

Tested all available schemes for **FSE correction** in **molecular crystals**, where can compare with experimental results



Accurate in periodic systems



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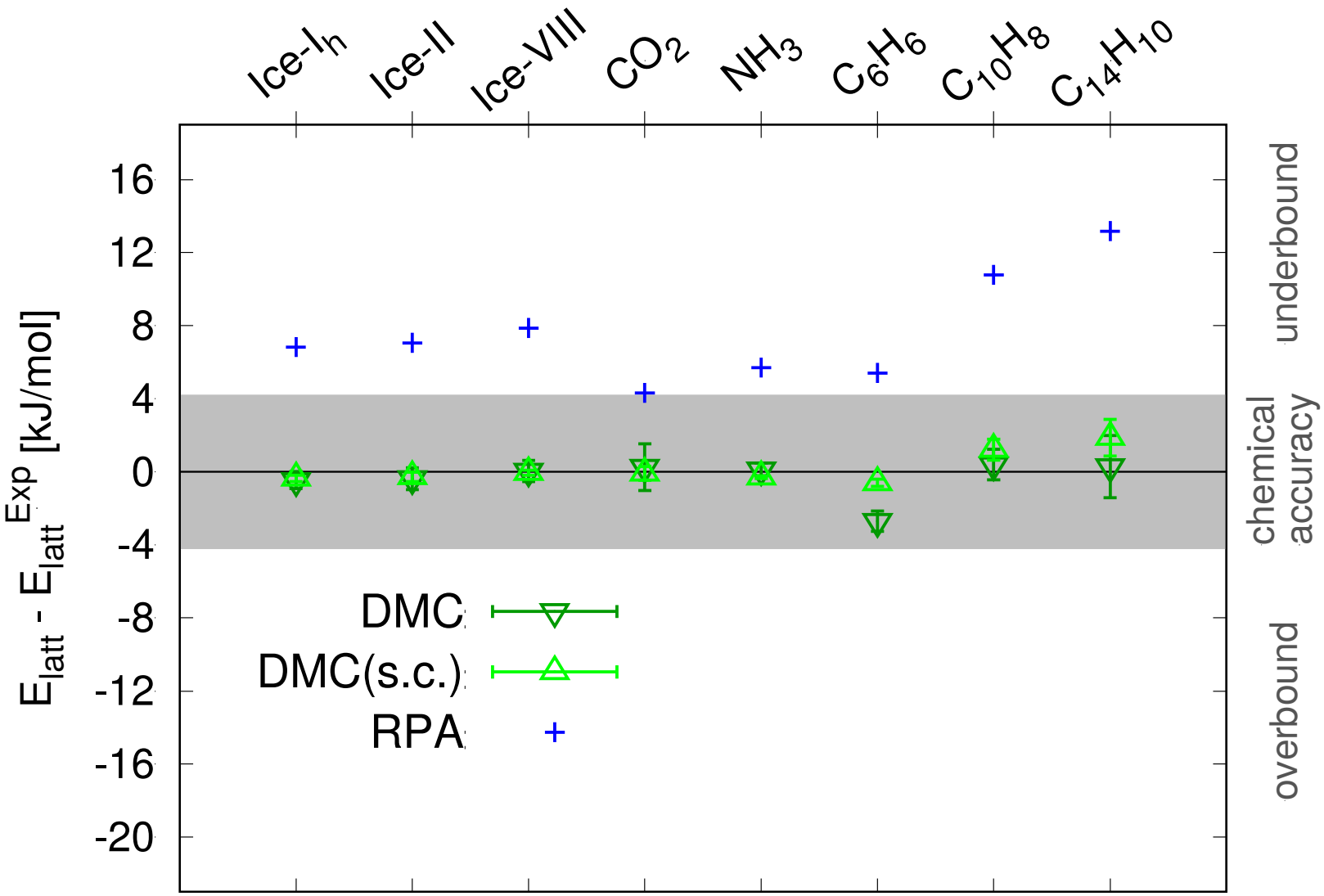

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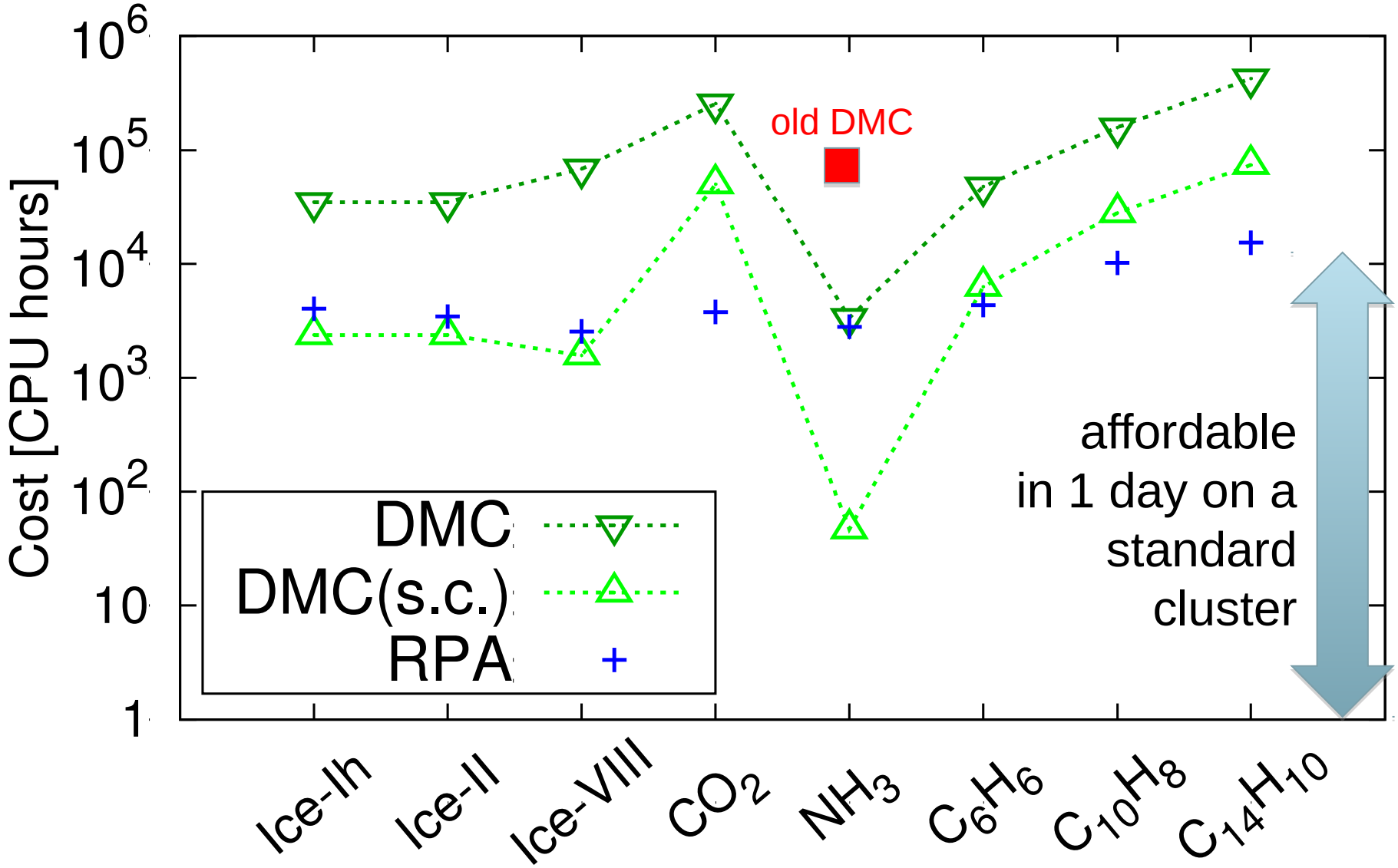
Much more efficient



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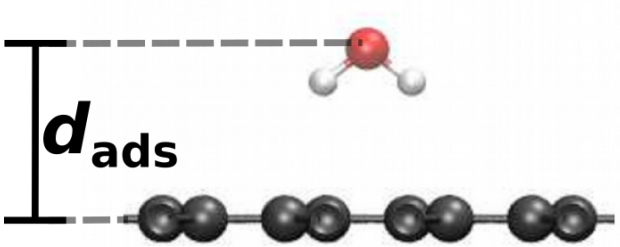
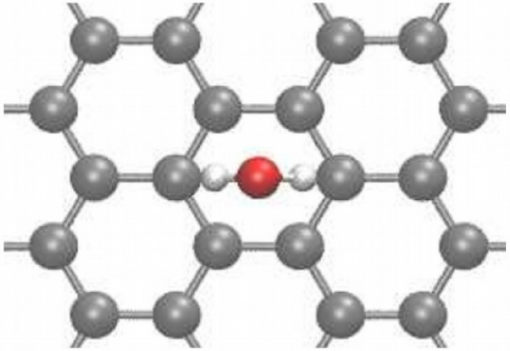
Revised E_b from DMC





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E_b = -99 ± 5 meV

Higher precision;
FSE correction

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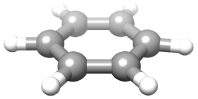
Adsorption on small substrates

0-leg 

1-leg 

2-leg 



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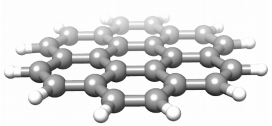
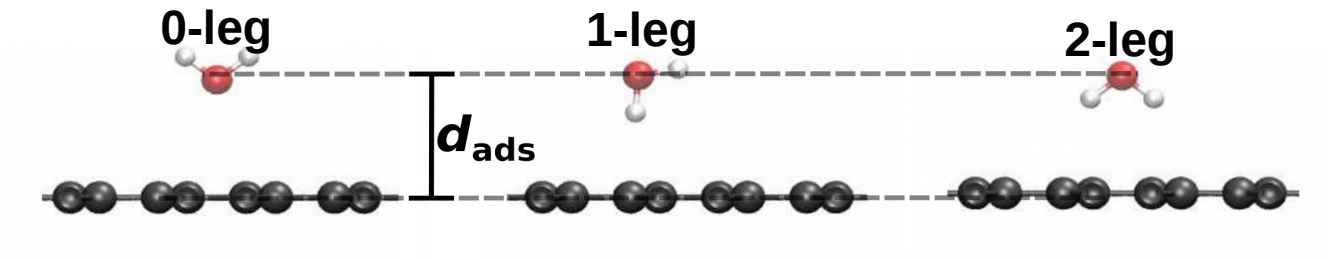


Adsorption on periodic graphene

- Very similar binding energies for different motifs
- In contrast to smaller substrates



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Slow convergence of QC

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Domain based **L**ocal **P**air **N**atural **O**rbital **C**oupled **C**luster with **S**ingles, **D**oubles and perturbative **T**riples *DLPNO-CCSD(T)*

- Needs to describe exited determinants
- Cubic convergence $\sim X^{-3}$

Local coupled cluster:
J. Chem. Phys. **2001**, 114, 661
J. Chem. Phys. **2013**, 139, 134101
J. Chem. Phys. **2018**, 148, 011101

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Extrapolation of substrate size

- Convergence with substrate size very slow
- Extrapolations using benzene and coronene data is unreliable

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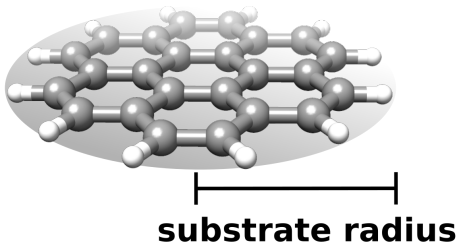

Charge redistribution

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$x\ 10^{-4}$

Density difference compared to separated fragments

- Distribution strongly dependent on motif
- 1&2-leg induce locally charge-rich areas
- 0-leg induces charge-loss

Discrepancies resolved

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2	**-130 meV**	**DFT-SAPT**	*Unreliable extrapolation, SAPT is not a reference method*
3	**-70 ± 10 meV**	**Diffusion Monte Carlo (DMC)**	*Large stochastic error, finite-size effects are neglected*
4	**-135 meV**	**i-CCSD(T)**	*Single particle basis set too small*
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Benchmarking DFT

High level references with small error margins

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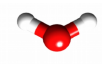

Benchmarking DFT

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Van der Waals interactions mandatory

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Benchmarking DFT

Large range of DFT results: Benchmark needed

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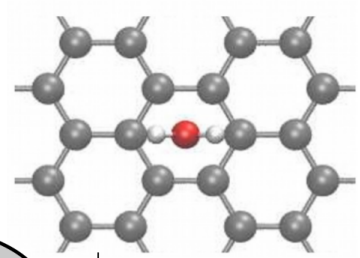
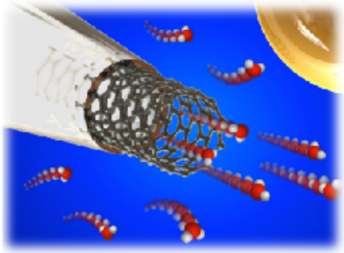
Route to larger scales

Large scale applications are accessible via machine learning (ML) techniques





Identify reasonable DFA *(correct limits)*

Calibrate DMC numerical settings

Experience of tracktable size

DFT sampling
smallish sytem

representative geometries

DFT energies and forces

DMC energy

require additional data

DFT+ML dynamics

dataset for AI optimization

ML energies and forces

ML potential
for Δ(DMC-DFT)

Method: AI improved DFT

Dataset: E_{int} for water adsorption

Insight on water dynamics on graphene

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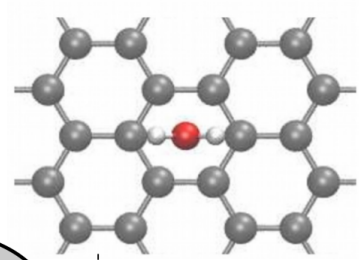

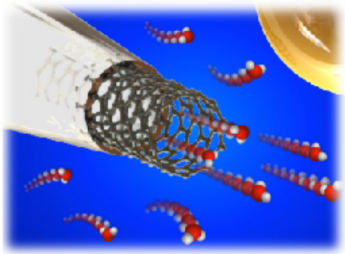

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Patrick Rowe

Method: AI improved DFT

Dataset: E_{int} for water adsorption

Insight on water dynamics on graphene

Conclusions

- Modeling to be used complimentary to experimental studies
- DMC is affordable method with controllable high accuracy
- Molecular level understanding of water-graphene interaction

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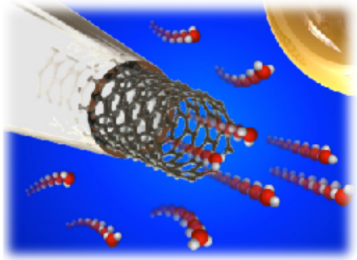
Outlook

- Algorithmic DMC improvements
- Study of water dynamics on graphene via DMC based ML

$$\langle \mathbf{R}|W|\mathbf{R}'\rangle = \sum_{l=1} \frac{2l+1}{4\pi} v_l(r_{iJ}) \frac{\delta(r_{iJ} - r'_{iJ})}{r_{iJ}^2} P_l(\hat{r}_{iJ} \cdot \hat{r}'_{iJ})$$

$$W_{\text{eff}} = \Psi_{\text{T}}^{-1}(\mathbf{R}) \int \langle \mathbf{R}|W|\mathbf{R}'\rangle \Psi_{\text{T}}(\mathbf{R}')\, \mathrm{d}\mathbf{R}'$$



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