Title: The challenge to deliver high accuracy on large computer simulations

Speakers: Andrea Zen

Collection: Machine Learning for Quantum Design

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Abstract: Computer simulations are extremely useful in providing insight on the physical and chemical processes taking places in nature. Very often simulations are complementary to experimental investigations, providing the interpretations and the molecular level understanding that experiments struggle to deliver. Yet, simulations are useful only when their results may be relied upon, that is, when they can accurately model the physical system and the forces therein.
Thriving nanotechnologies and exciting experiments pose a big challenge to computational approaches, especially when dealing with solid-liquid interfaces. On the one hand, the systems to be simulated are large and often long molecular dynamics simulations are needed. On the other hand, extremely high accuracy is required.
We discuss here an approach to deliver high accuracy at low computational cost using quantum Monte Carlo and Machine Learning.

The challenge to deliver high accuracy on large computer simulations

Andrea Zen

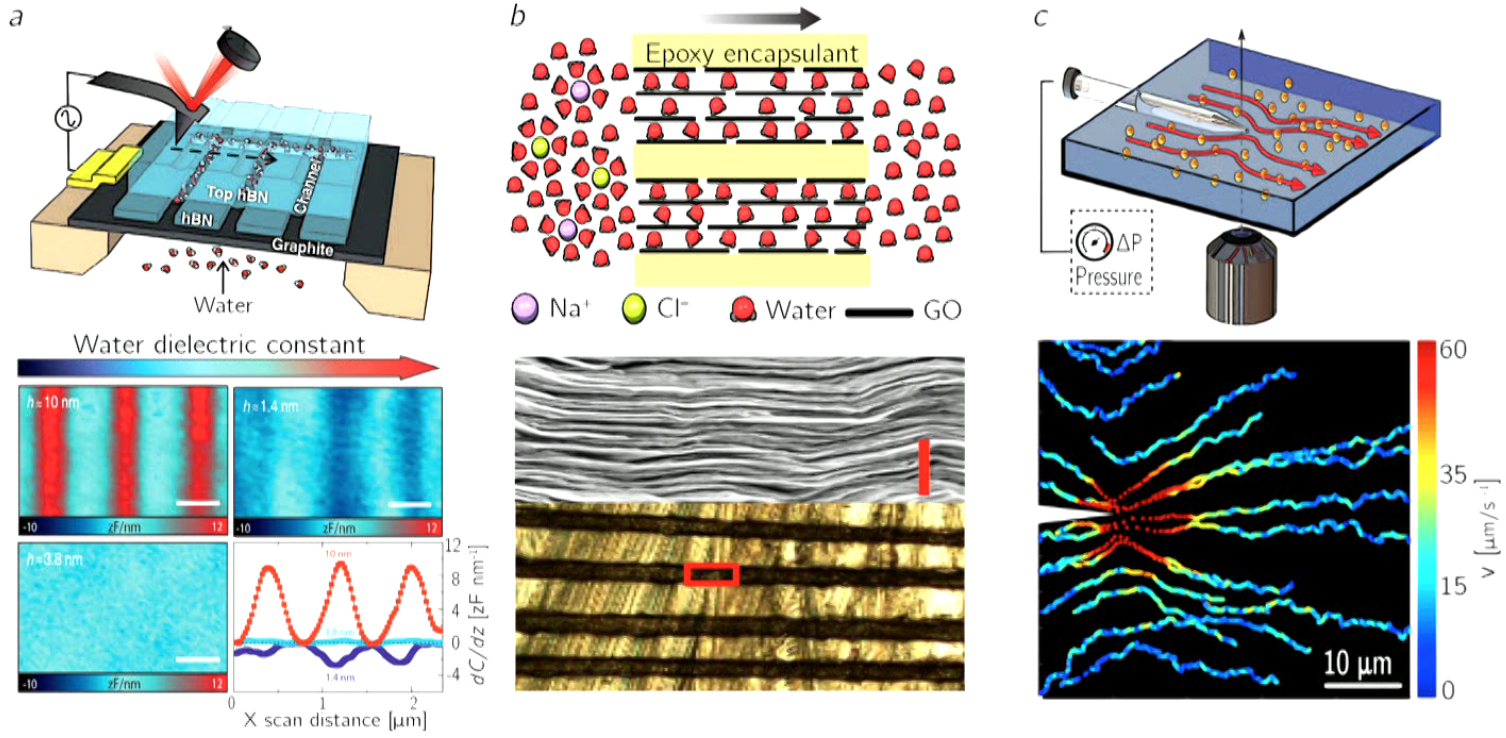
University College London

Main Collaborators: Dario Alfè, Angelos Michaelides

University College London

MACHINE LEARNING FOR QUANTUM DESIGN
Perimeter Institute, Waterloo, Canada July 10th , 2019

Computer simulations shall provide the molecular level insight

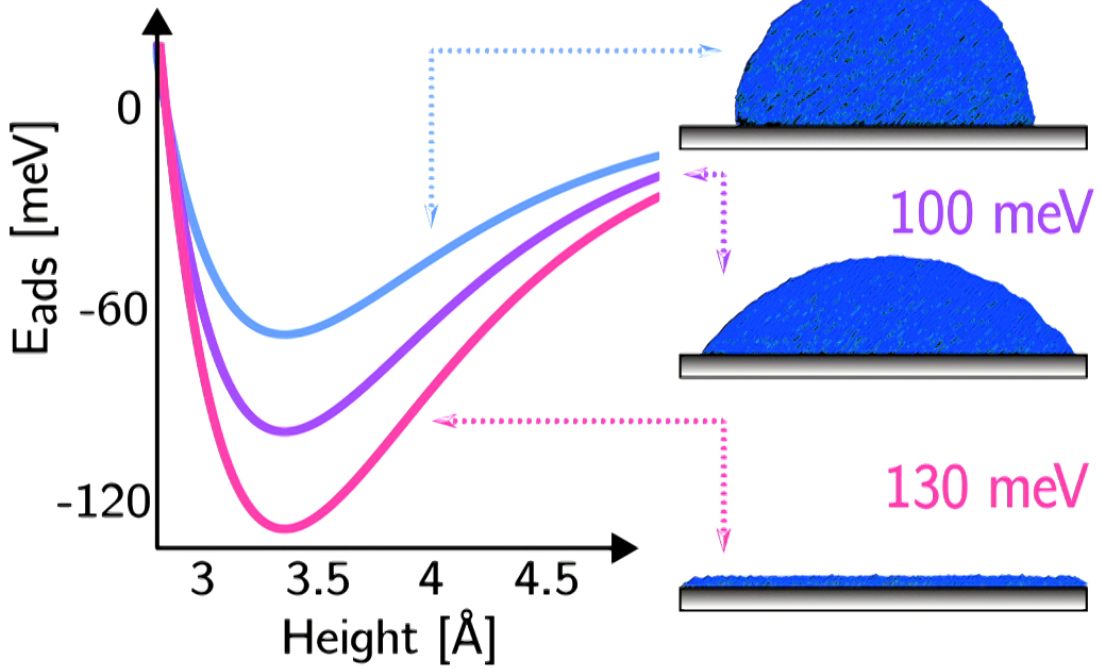


a. L. Fumagalli *et al.*, Anomalously low dielectric constant of confined water, *Science*, **360**, 1339 (2018)
b. J. Abraham *et* al., Tunable sieving of ions using graphene oxide membranes, *Nature Nanotechnology* **12**, 546 (2017)
c. E. Secchi *et al.*, Massive radius-dependent flow slippage in carbonnanotubes, *Nature* **537**, 210 (2016)

Accuracy is a big challenge

UCL

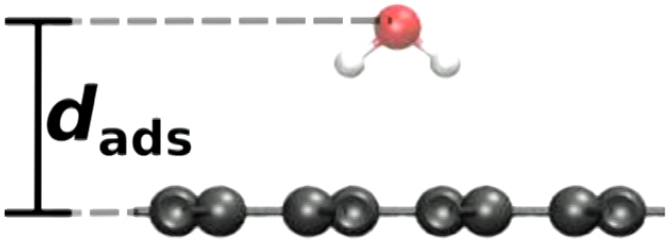
Example:
What is the contact angle of a water droplet on graphene?

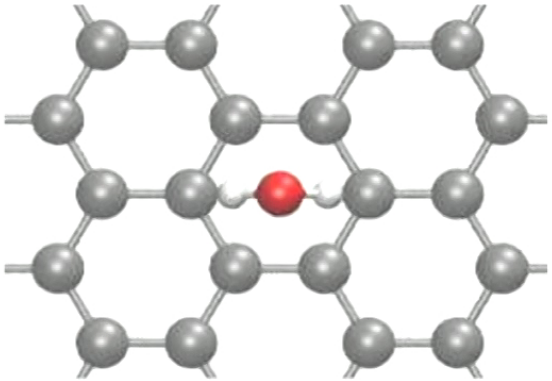


We need **subchemical accuracy!**

Accuracy is a big challenge

How challenging is to obtain subchemical accuracy?





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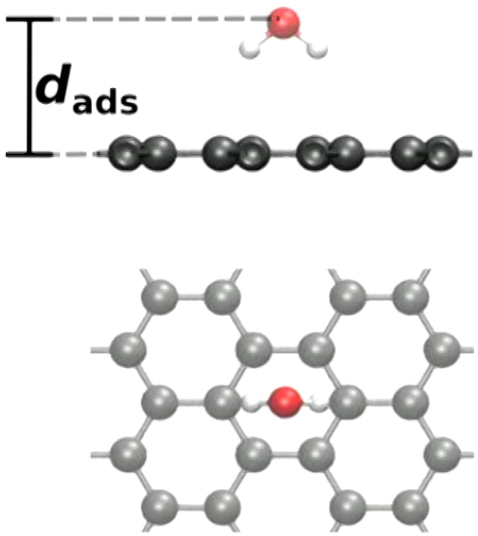
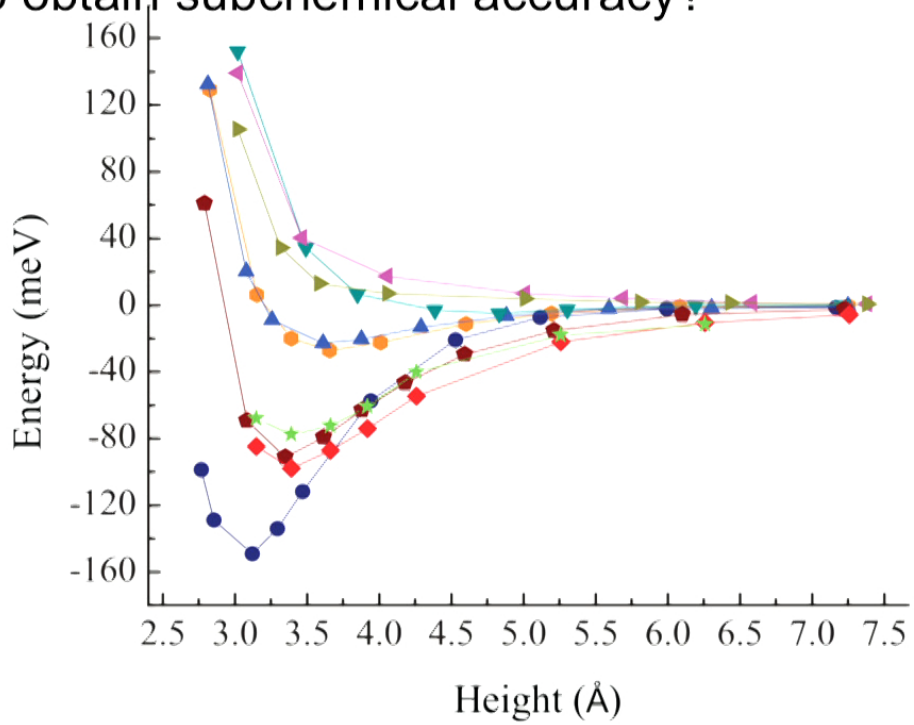
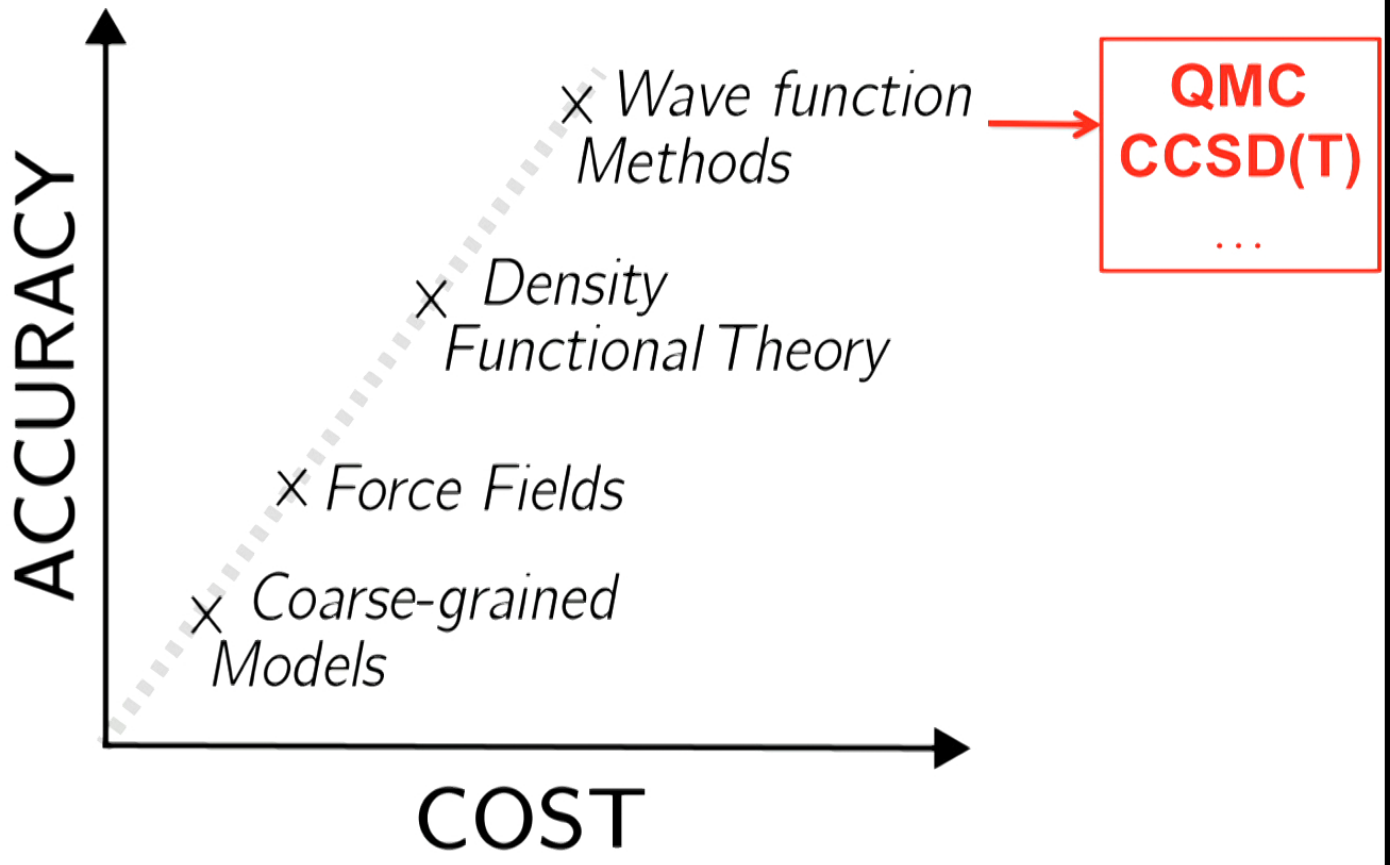




Density functional theory (grey curves) can provide any value between 0 and -160 meV depending on the exchange-correlation functional and vdW-corrections [PRB, 84, 033402 (2011)].

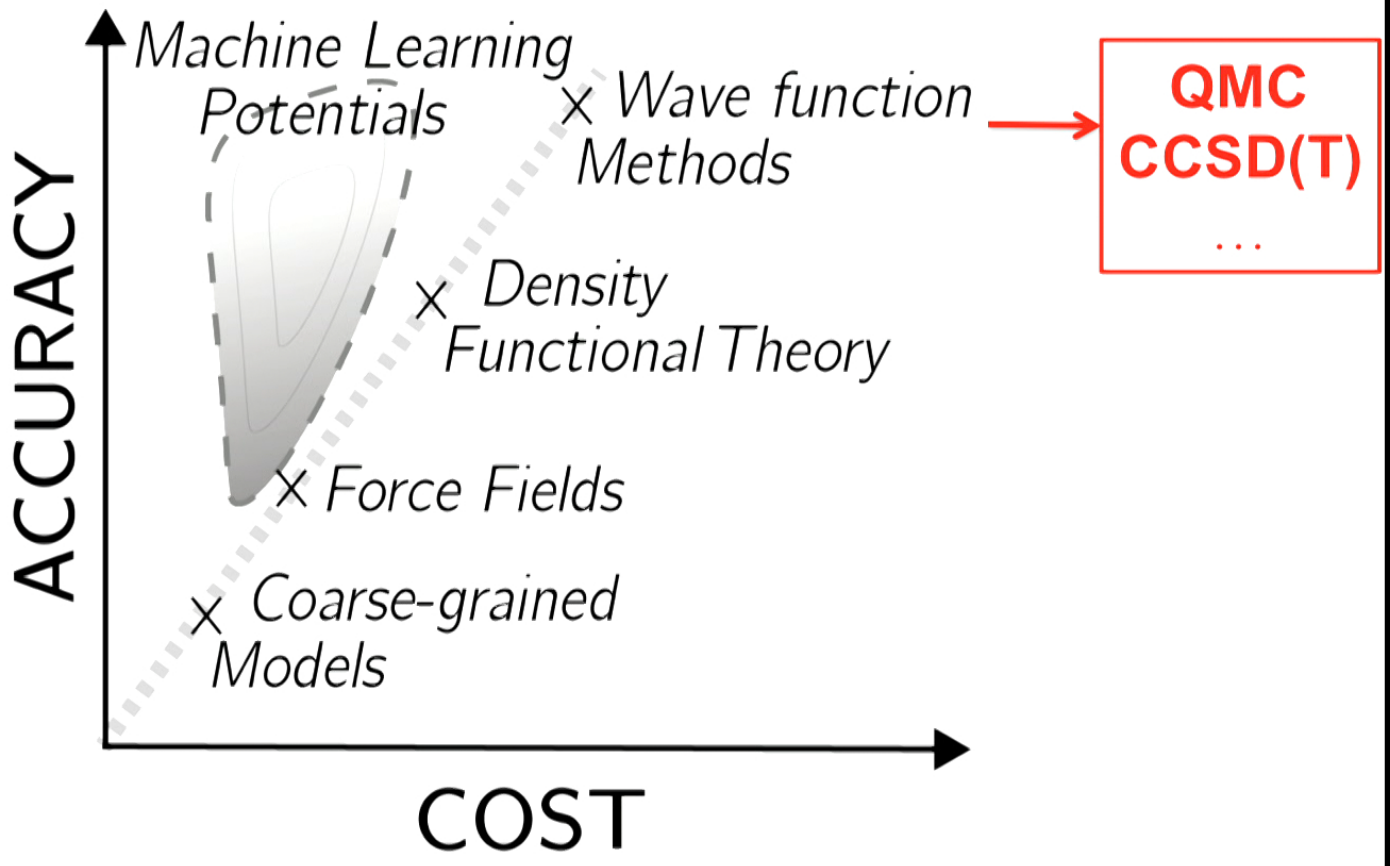
More accurate approaches are needed!

Accuracy Vs Cost



High accuracy comes with a big computational cost!

Accuracy Vs Cost



High accuracy comes with a big computational cost!

Outline

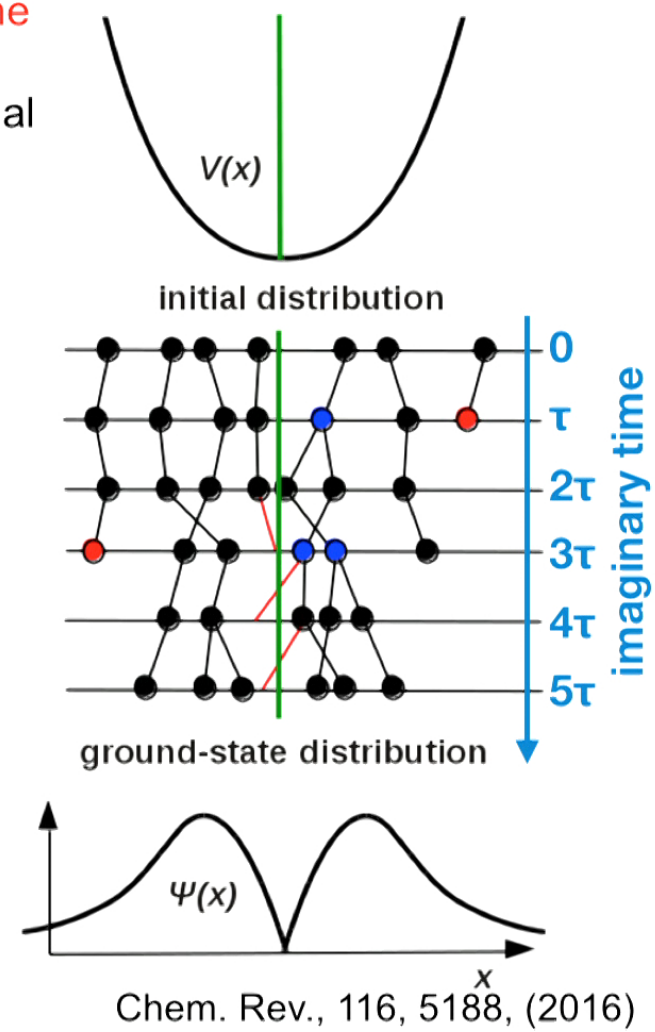
UCL

- Diffusion quantum Monte Carlo
  - DMC in a nutshell
  - Recent algorithmic developments, improved accuracy and efficiency
  - DMC in periodic systems
- Application: molecular crystals
  - MC are important and challenging systems, subchemical accuracy needed
  - A representative set of 8 molecular crystals
  - Lattice energy, experimental evaluation
  - DMC results versus experimental evaluations and other computational approaches
- Application: water on graphene
  - The system
  - Previous results
  - DMC results
  - Conundrum resolved

DMC in a nutshell

A **propagation** according to the imaginary time Schrodinger equation is performed to **project out the "exact" ground state** $\Phi(\mathbf{R})$ from a trial wave function $\Psi_T(\mathbf{R})$.

- Generate a set of configurations (**walkers**) according to a trial wave function $\Psi_T(\mathbf{R})$
- Propagate in time, with finite **time-step** τ, according to the Green's function (*branching-drift-diffusion process*)
- The set of walkers determines $f(\mathbf{R},t)$, converging to $\Phi(\mathbf{R})\Psi_T(\mathbf{R})$ for large time.



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

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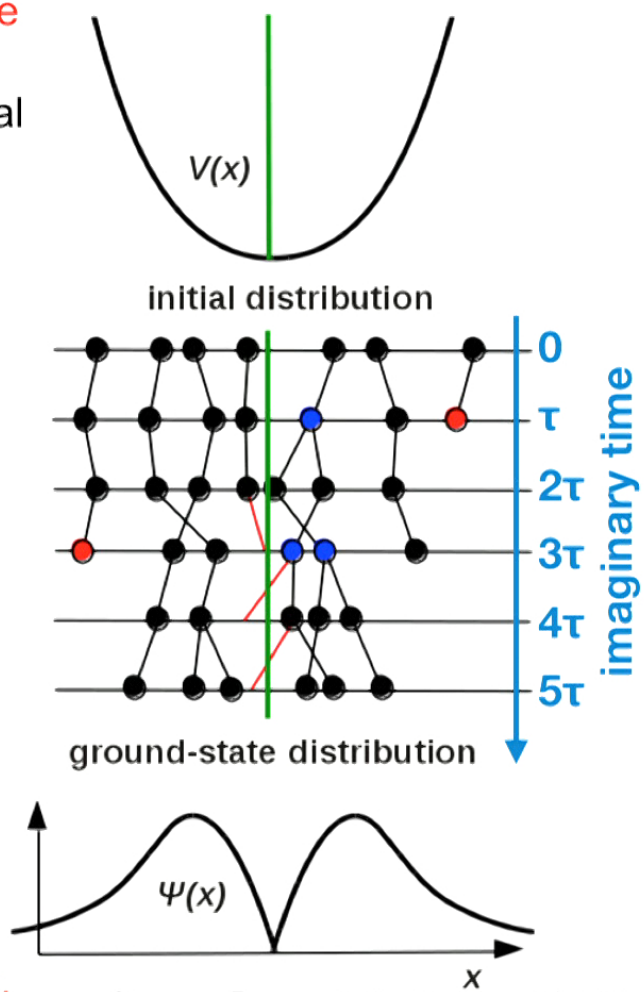
Two phases in DMC simulation:

- **Equilibration** (project out the exact G.S.)
- **Statistical sampling** (stochastic method, autocorrelation time)

Notice:
DMC computational **cost** is proportional to **1/τ**.



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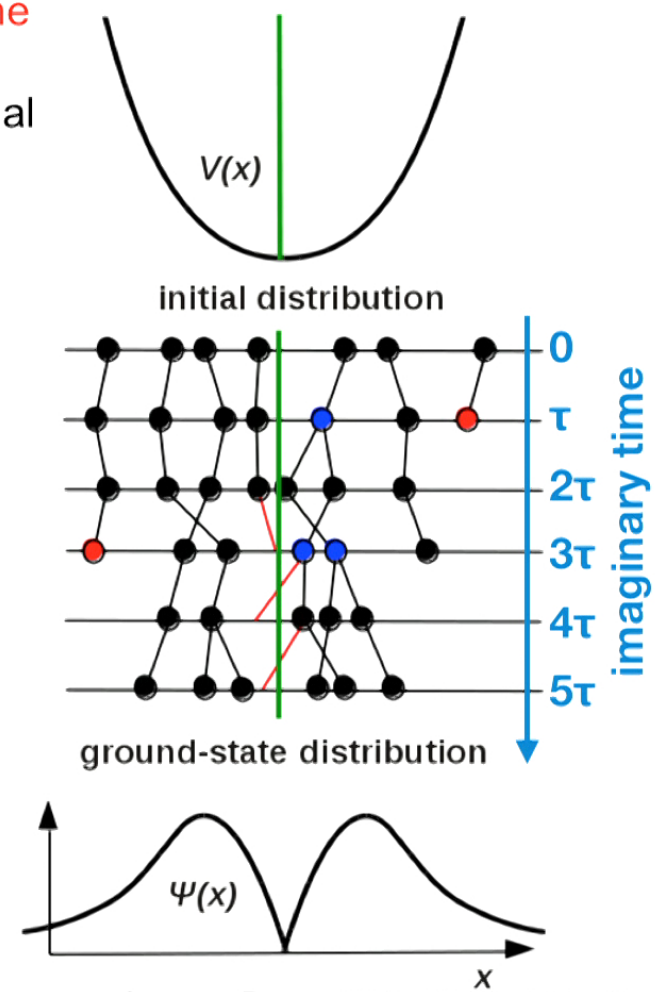
Approximations in DMC

A **propagation** according to the imaginary time Schrodinger equation is performed to **project out the "exact" ground state** $\Phi(\mathbf{R})$ from a trial wave function $\Psi_T(\mathbf{R})$.

Some **approximations** involved:

- **Fixed-node/phase** (fermionic systems)
- **Pseudo-potentials** (non-local terms)
- **Finite time-step τ** (Green's function is known exactly for infinitesimal **τ**)
- **Modified Green's function** (stability)



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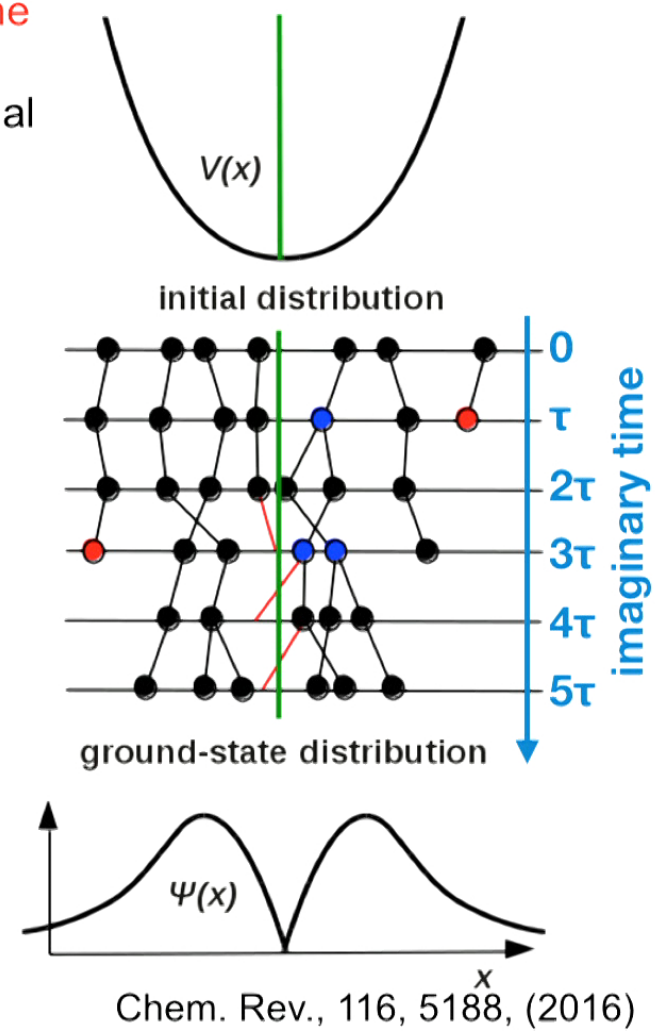

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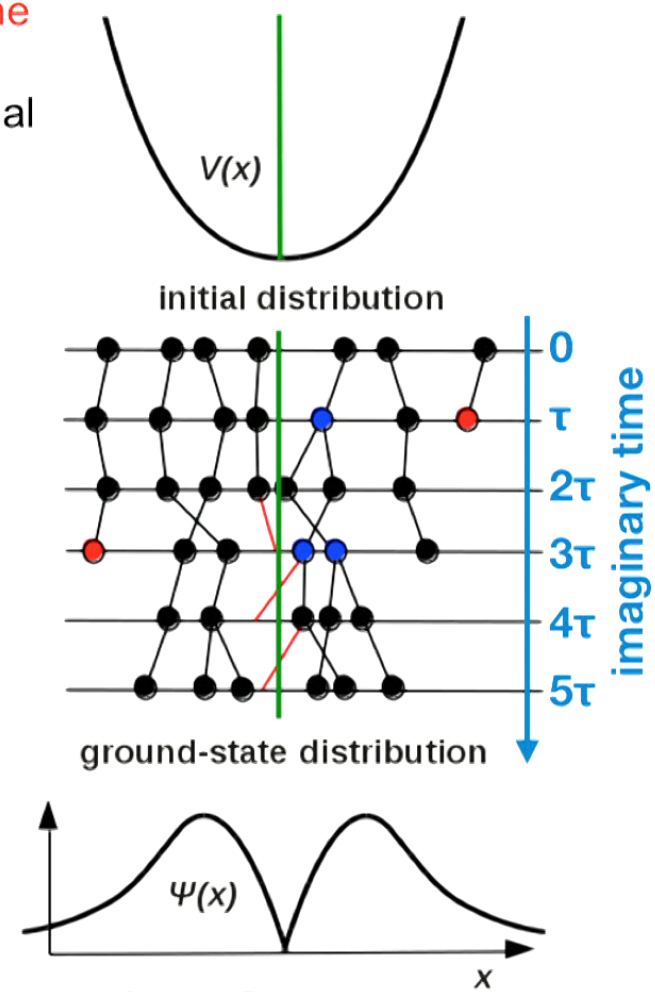
Value of time-step τ is crucial:
Trade-off between accuracy and efficiency

- **Modified Green's function** (stability)

Was at the source of a recently discovered size-consistency issue!



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Size-consistency

Size-consistent method: describes the **fragmentation limit**.
i.e.

--- far away ---

$$E_{\mathrm{AB}}\left(R_{\mathrm{AB}} \to \infty\right) = E_{\mathrm{A}} + E_{\mathrm{B}}$$

Size-consistency issue in DMC

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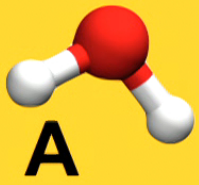

--- far away ---

$$E_{\mathrm{AB}}\left(R_{\mathrm{AB}} \to \infty\right) = E_{\mathrm{A}} + E_{\mathrm{B}}$$

Discovered ~3 years ago that the algorithm typically used DMC is **size-inconsistent for finite time-steps**, although size-consistency is recovered in the infinitesimal time-step limit.
Issue arising from the modification to the Green's function to enhance stability! [Phys. Rev. B, **93**, 241118(R) (2016)]

Size-consistency issue in DMC

importance sampling DMC

$$\tilde{G}_d(\mathbf{R} \leftarrow \mathbf{R}'; \tau) = (2\pi\tau)^{-\frac{3}{2}N} \exp\left[-\frac{(\mathbf{R} - \mathbf{R}' - \tau \mathbf{V}(\mathbf{R}'))^2}{2\tau}\right]$$

$$\tilde{G}_b(\mathbf{R} \leftarrow \mathbf{R}'; \tau) = \exp\left[\tau \frac{S(\mathbf{R}) + S(\mathbf{R}')}{2}\right]$$

Region	Local energy	Velocity
Nodes	$E_L \sim \pm\frac{1}{R_\perp}$ for ψ_T $E_L = E_0$ for ψ_0	$v \sim \frac{1}{R_\perp}$
Electron/ nucleus/electron	$E_L \sim \frac{1}{x}$ for some ψ_T $E_L = E_0$ for ψ_0	v has a discontinuity for both ψ_T and ψ_0

Umrigar *et al*, JCP 1993

$$\bar{\mathbf{v}}_i = \frac{-1 + \sqrt{1 + 2av_i^2\tau}}{av_i^2\tau}\mathbf{v}_i; \quad \mathbf{v}_i = \nabla_i \log|\psi_G(\mathbf{R})|$$

$$\bar{S}(\mathbf{R}) = [E_T - E_{\text{best}}] + [E_{\text{best}} - E_L(\mathbf{R})]\frac{\bar{V}}{V}$$

Size-consistency issue in DMC

UCL

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newDMC

$$\bar{S}(\mathbf{R}) = E_T - \bar{E}_L(\mathbf{R});$$

$$\bar{E}_L(\mathbf{R}) = E_{\text{best}} + \text{sign}[E_L(\mathbf{R}) - E_{\text{best}}] \times \min\{E_{\text{cut}}, |E_L(\mathbf{R}) - E_{\text{best}}|\};$$

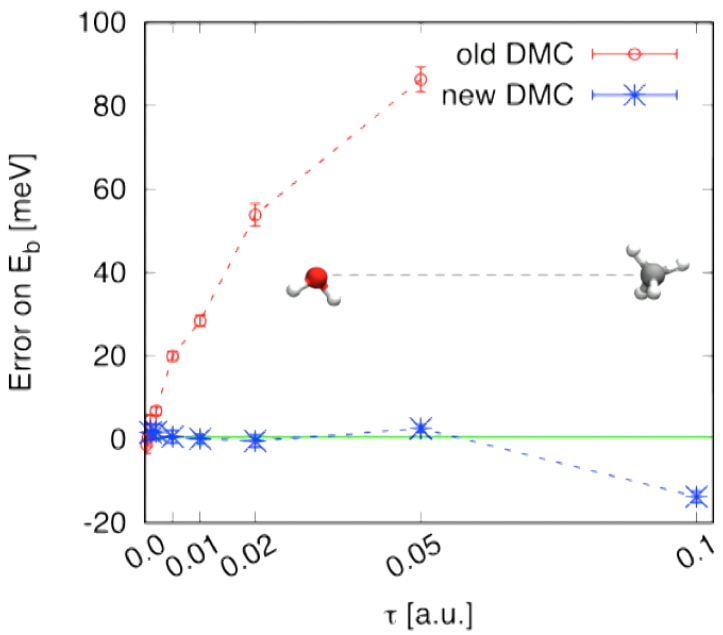
$$E_{\text{cut}} = \alpha\sqrt{N/\tau}$$

Size-consistent DMC

We developed a new DMC algorithm

Old DMC algorithm => **UNR**
- Size-inconsistent for finite τ
- Size-consistent only for infinitesimal τ

New DMC algorithm => **ZSGMA**
- Size-consistent for (almost) every τ



A Zen, S. Sorella, MJ Gillan, A Michaelides, D Alfè, Phys. Rev. B, **93**, 241118(R) (2016)]

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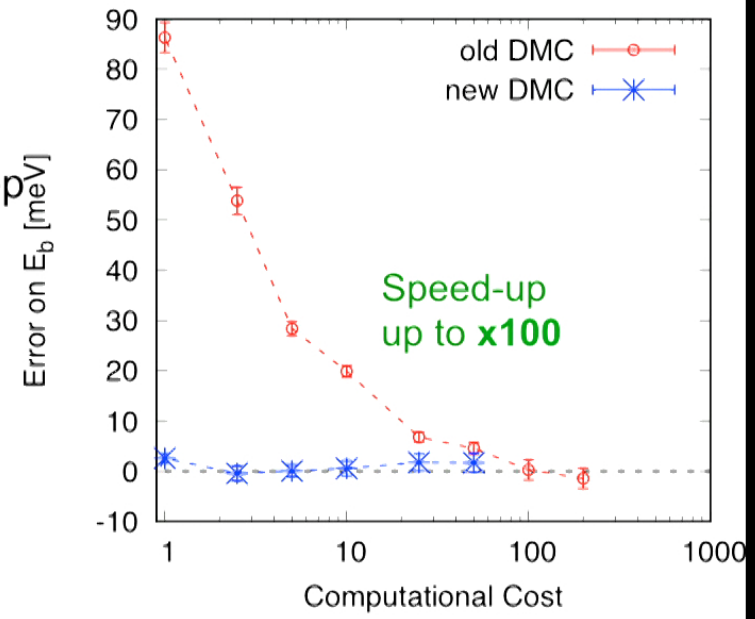
Observed also that most of the time-step error was due to size-inconsistency.

High precision and accuracy at (relatively) low computational cost



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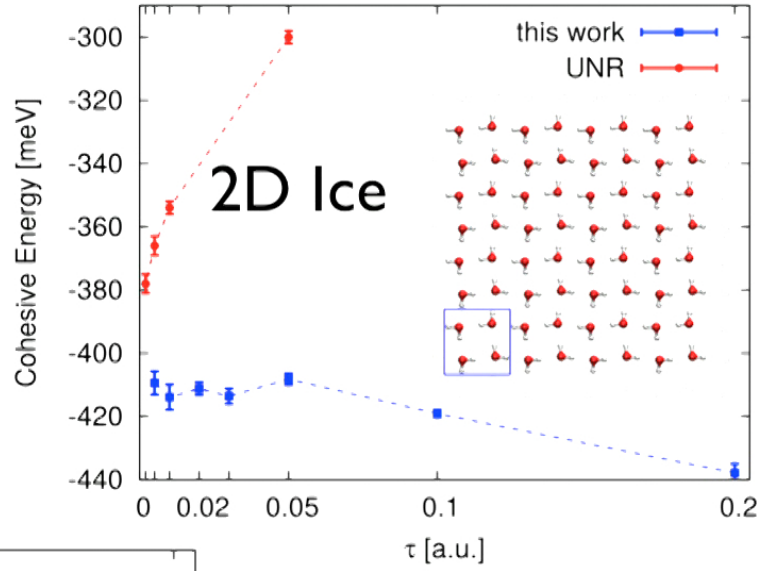
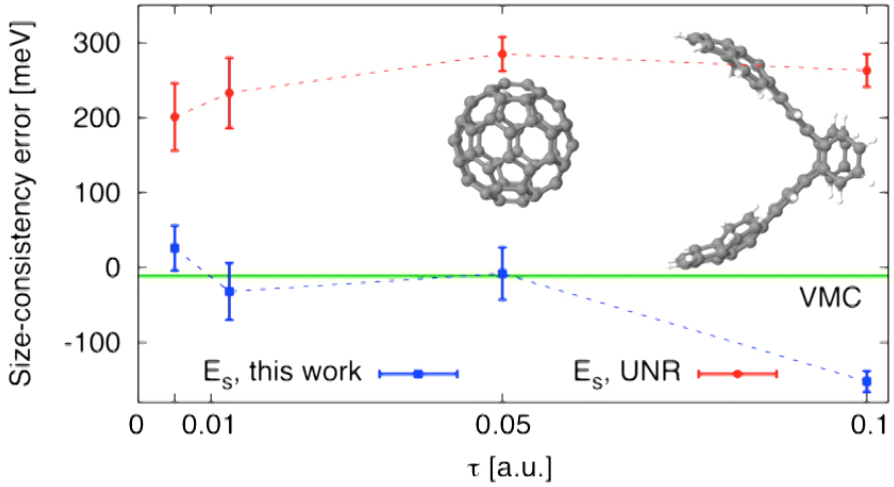
Important in large systems

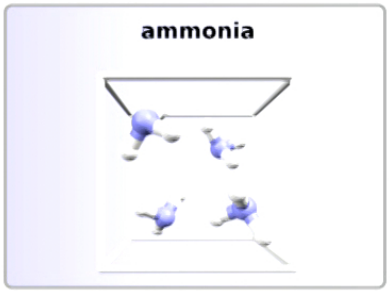
Worse in large systems!
Not possible a meaningful extrapolation (unfeasible)





DMC in periodic systems

- Molecular crystals are **periodic systems.**
- DMC simulations with periodic boundary conditions are affected by **finite-size errors.**
- By simulating the primitive cell and sampling the Brillouin zone (*twist averaging boundary condition*) we eliminate the **independent particle finite-size error.**
- But, there are beyond-1-body finite-size errors, that can be **very large**!



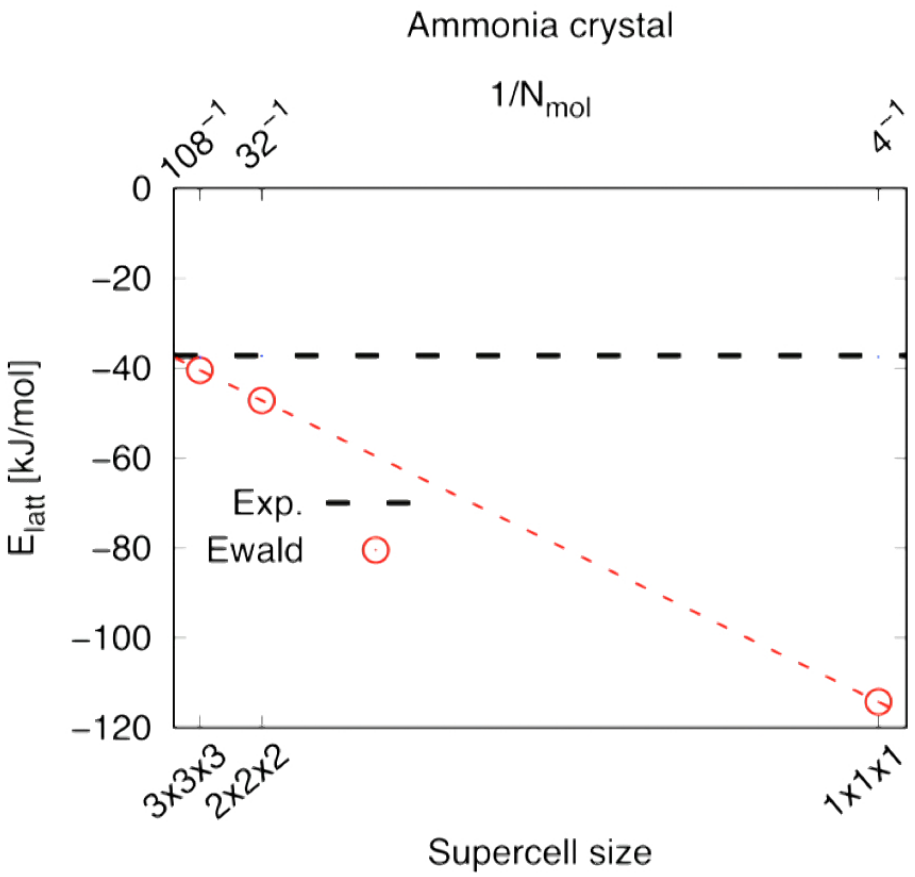
$$E_{\mathrm{latt}} = E_{\mathrm{crys}} - E_{\mathrm{gas}}$$

Experiment
-37.2 kJ/mol

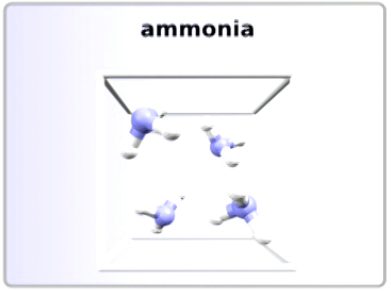
DMC Ewald, 1x1x1 cell,
@ Baldereschi point
-115 kJ/mol

Finite-size errors:

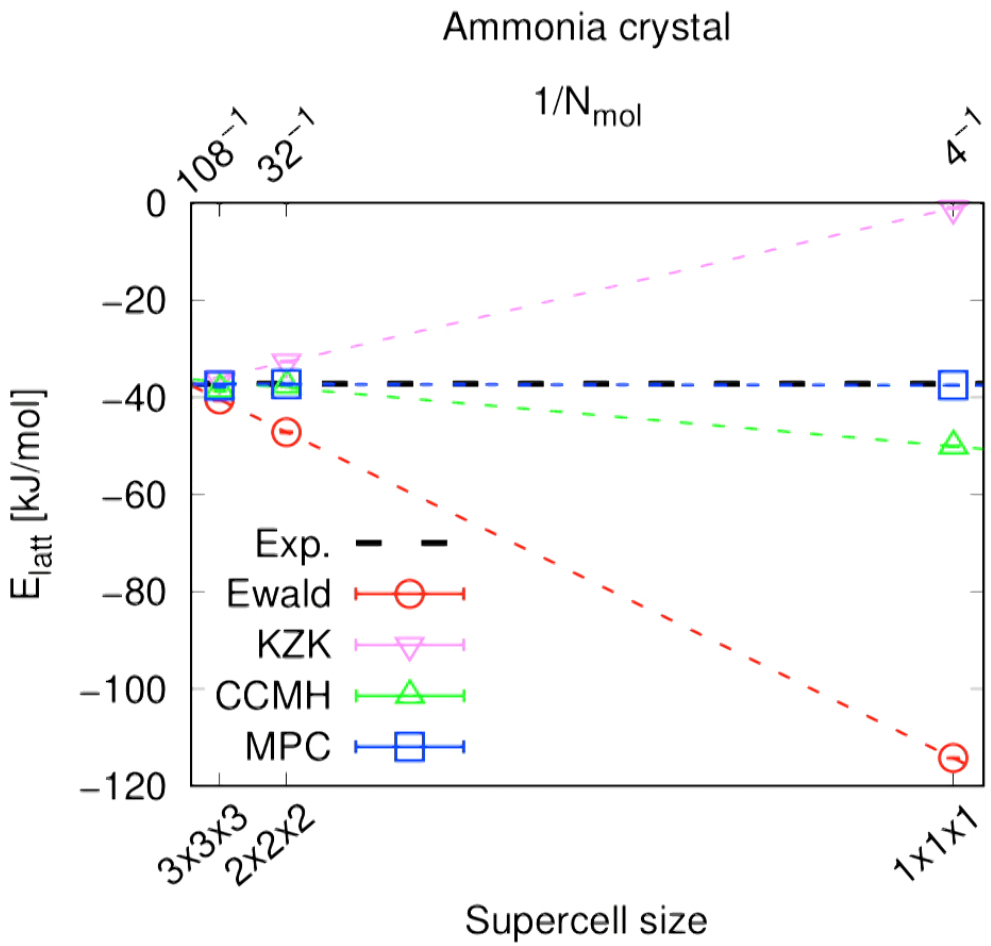
brute force solution: supercells



- Large supercells are computationally expensive
- Not a feasible approach for molecular crystals of large molecules
- FSE corrections?

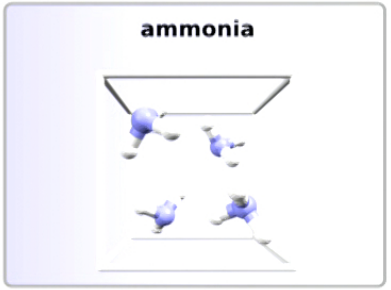


Finite-size errors corrections

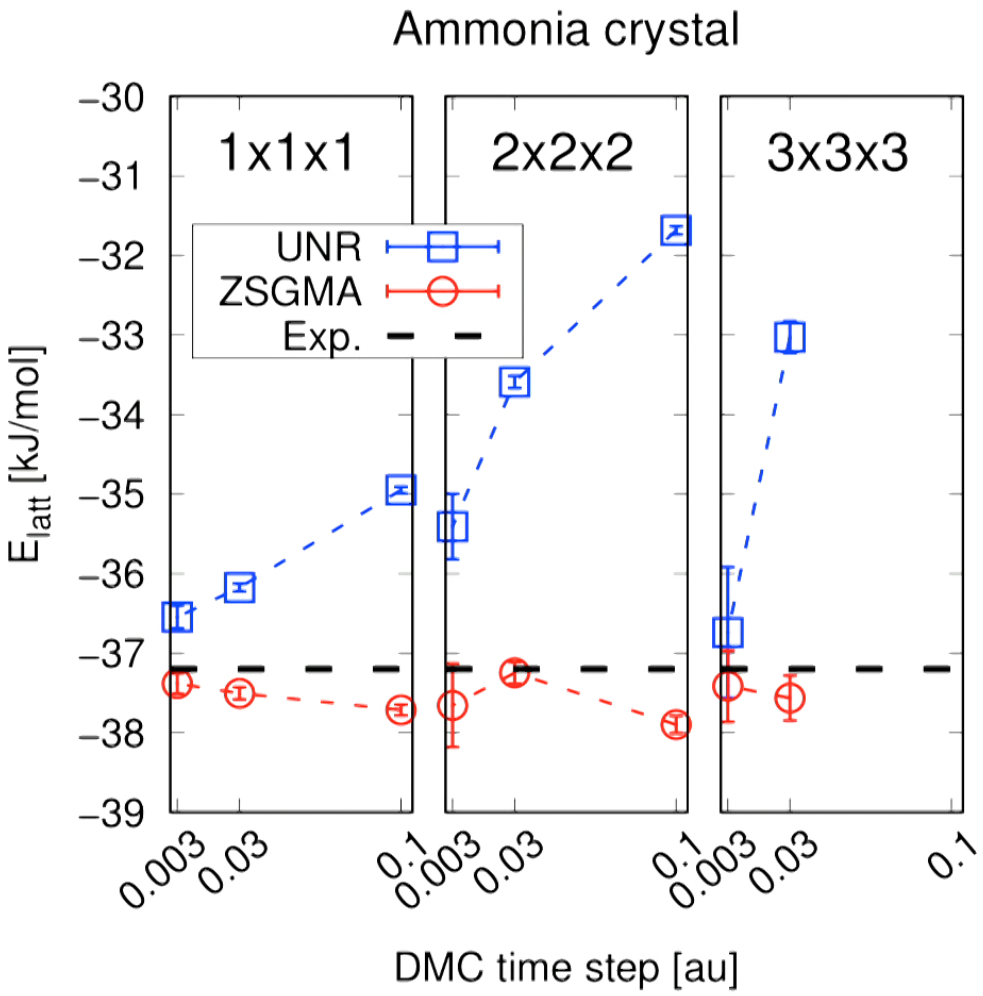


Check of available correction schemes

Model periodic Coulomb (MPC) interaction appears an extremely reliable correction!



Use the size-consistent DMC!



If old **size-inconsistent** DMC (UNR) were used, and the τ=0 **extrapolation** is not performed **for each supercell**, obtained inaccurate results!

With new DMC (ZSGMA) the τ dependence is the same for each supercell.

Perspective for DMC

UCL

DMC

Cumbersome setup
Pseudo potentials?
Jastrow?
Time step?
Finite size errors?

→ Automatic & validated setup

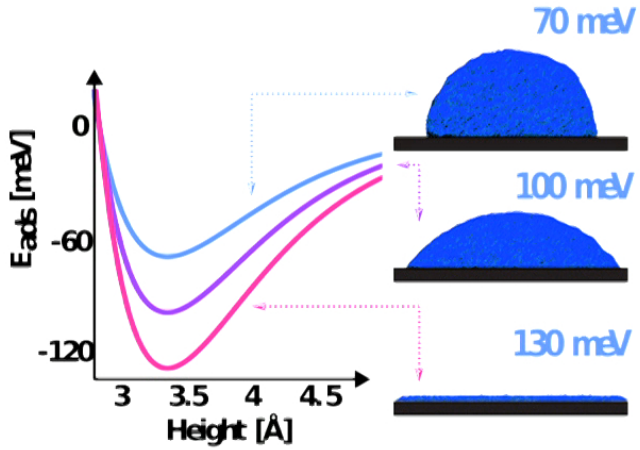
Intrinsic Potential
High accuracy
Large Systems
Suited for HPC

Issues
Stability
Cost
Forces

→ Algorithm development

Generate **accurate reference data:**

- benchmark other electronic structure theories,
- train machine learning (ML) potentials.



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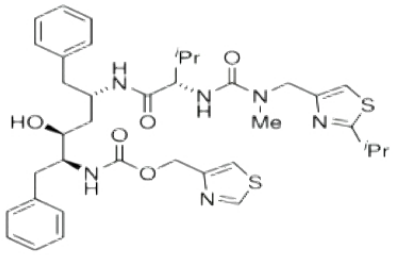
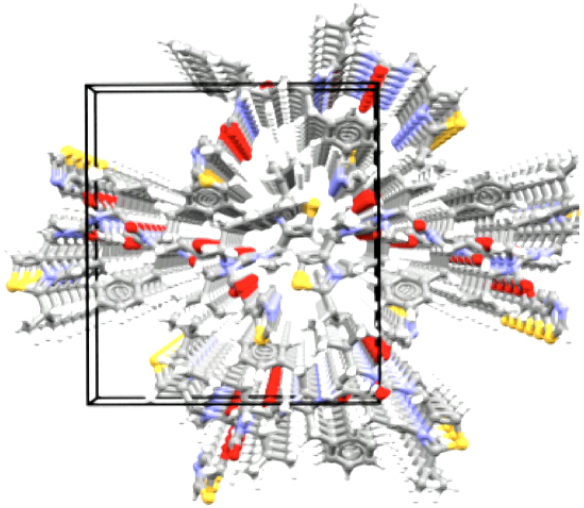
The case of Ritonavir

- They constitute the majority of **marketed pharmaceuticals**
- A molecule can have many different **polymorphs** with competing energy
- Arrangement of molecules in the crystal determines the physical properties, including key drug properties such as **dissolution rate** and **stability**
- The lack of knowledge of some polymorphs can lead to drastic consequences

API: ritonavir
- HIV antiviral drug
- industrially produced in form I
- form II found 2 years after market launch



form II



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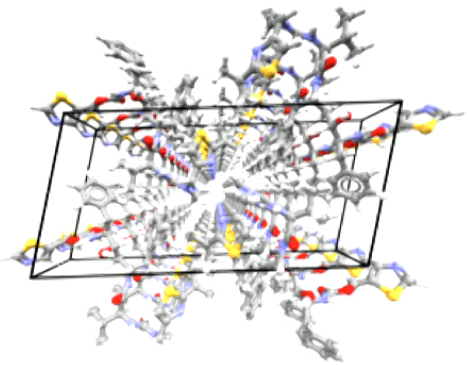

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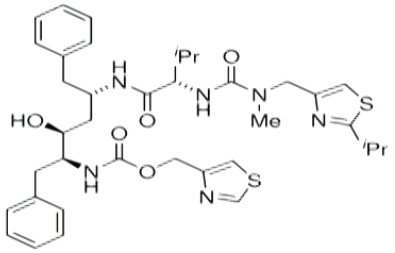

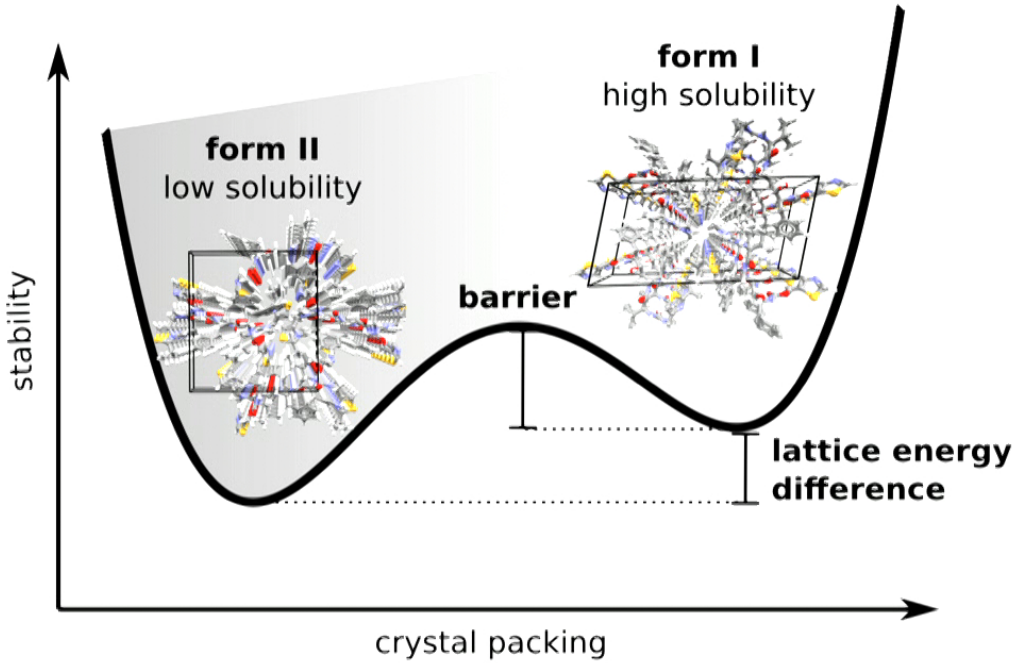

A challenge for theoretical methods

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- A **challenge for theoretical approaches:** to **predict** and **rank** polymorphs, **subchemical accuracy** (i.e., **< 1 kcal/mol**) in evaluating energy (and enthalpy) per molecule is required

A challenge for theoretical methods

- They constitute the majority of **marketed pharmaceuticals**
- A molecule can have many different **polymorphs** with competing energy
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	Accuracy	Affordability
DFT		
DFT+vdW		
CCSD(T)		
QMC	?	?

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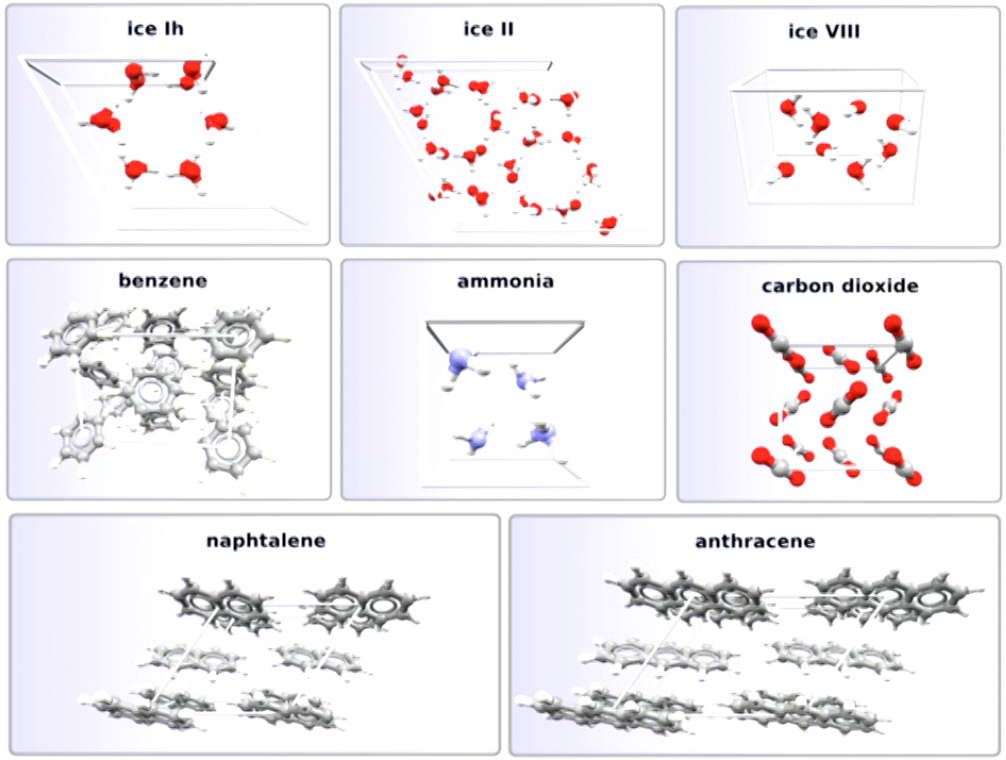
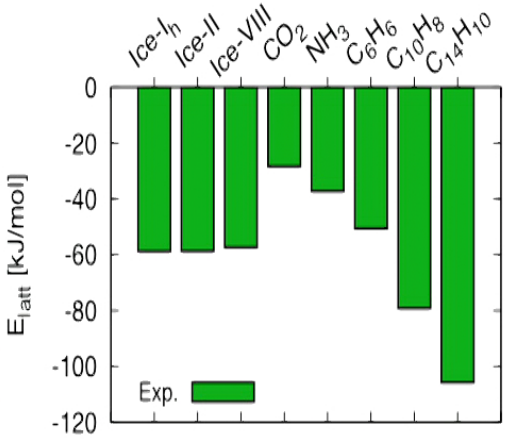
	Accuracy	Affordability
DFT		
DFT+vdW		
CCSD(T)		
QMC: DMC		

A representative set of 8 molecular crystals



comprises a diversity in intermolecular interactions, from strong **hydrogen bonds** to **London dispersion**



three polymorphs of ice and five crystals from the C21 test set of Otero-de-la-Roza and Johnson [JCP137:054103]

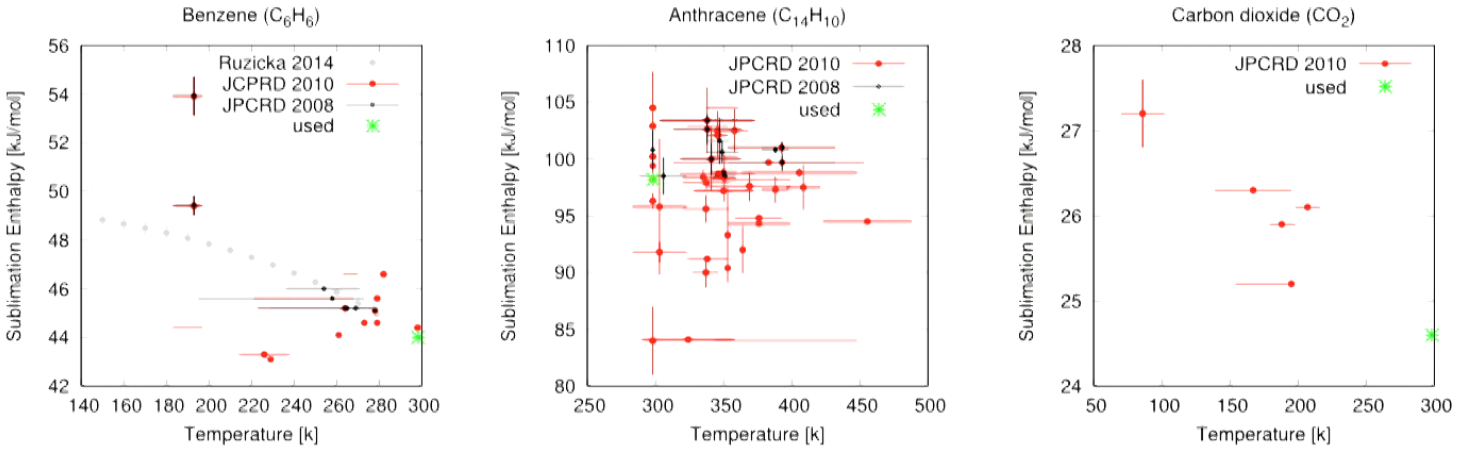
E_{latt} from experiments

$$E_{\mathrm{latt}} = E_{\mathrm{crys}} - E_{\mathrm{gas}}$$

Lattice energy $\mathbf{E_{latt}}$ can be indirectly obtained from measures of the Sublimation Enthalpy

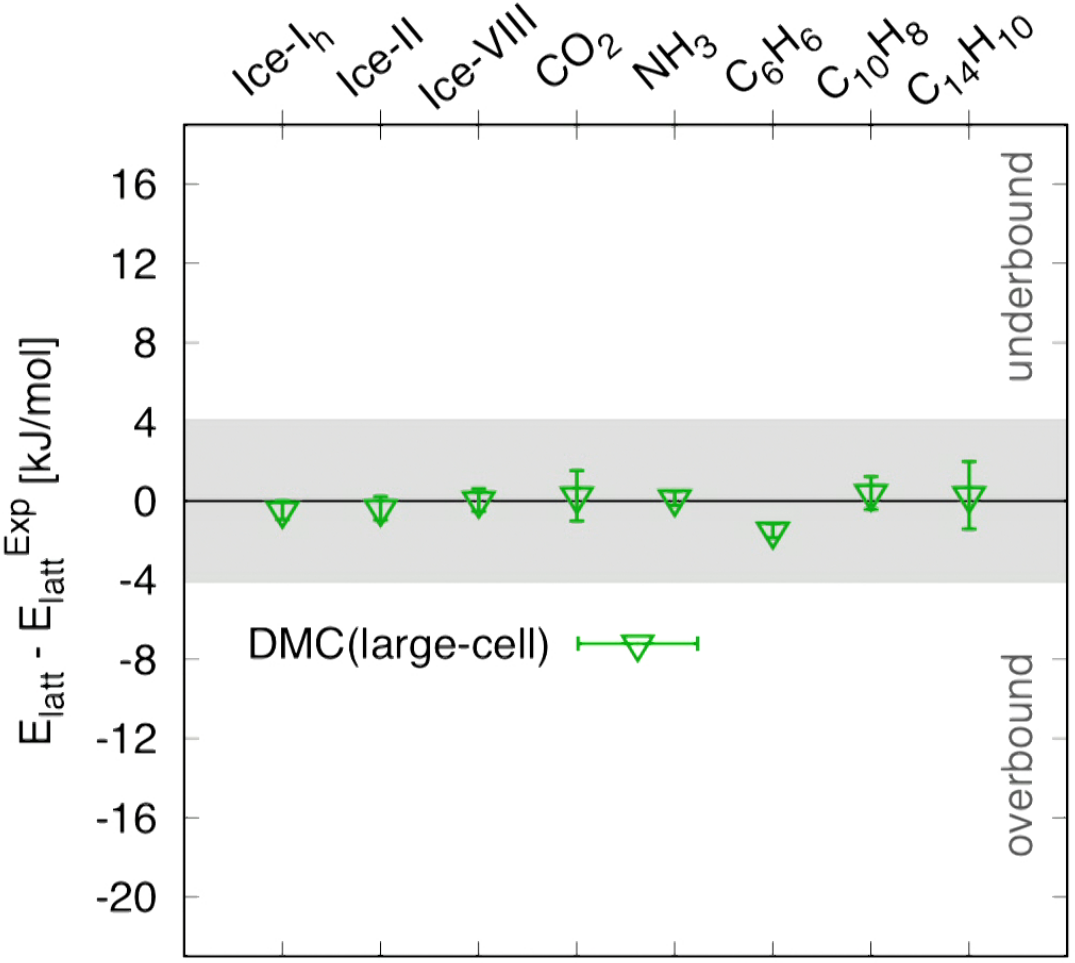
$$\Delta_{\mathrm{sub}} H(T) = -E_{\mathrm{latt}} + \Delta_{\mathrm{T\&QN}}(T)$$

$$\Delta_{\mathrm{T\&QN}}(T) = \Delta E_{\mathrm{ZPE}} + \int_0^T \Delta C_p(\tilde{T})\,\mathrm{d}\tilde{T}$$



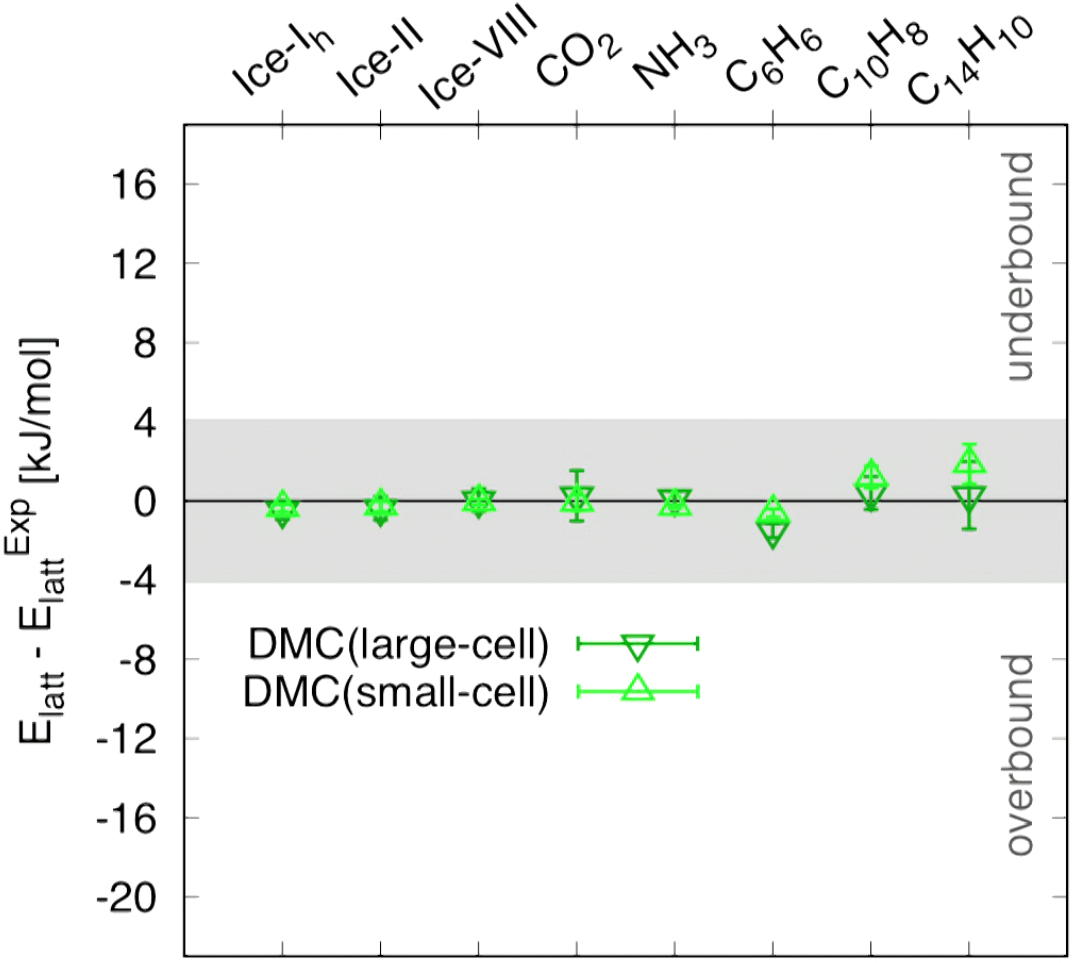
On average, experimental error on the sublimation energy of ~1 kcal/mol

Accuracy of DMC



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

DMC with small cell



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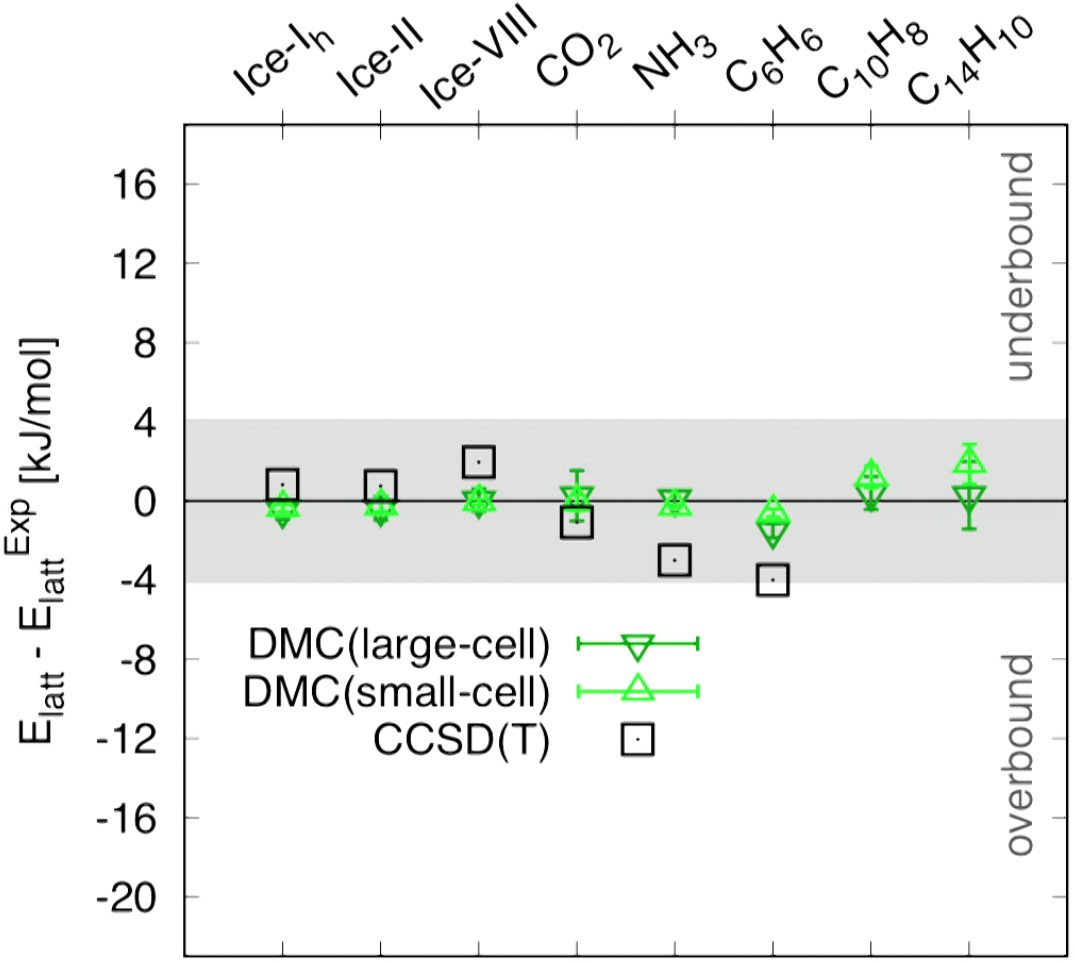
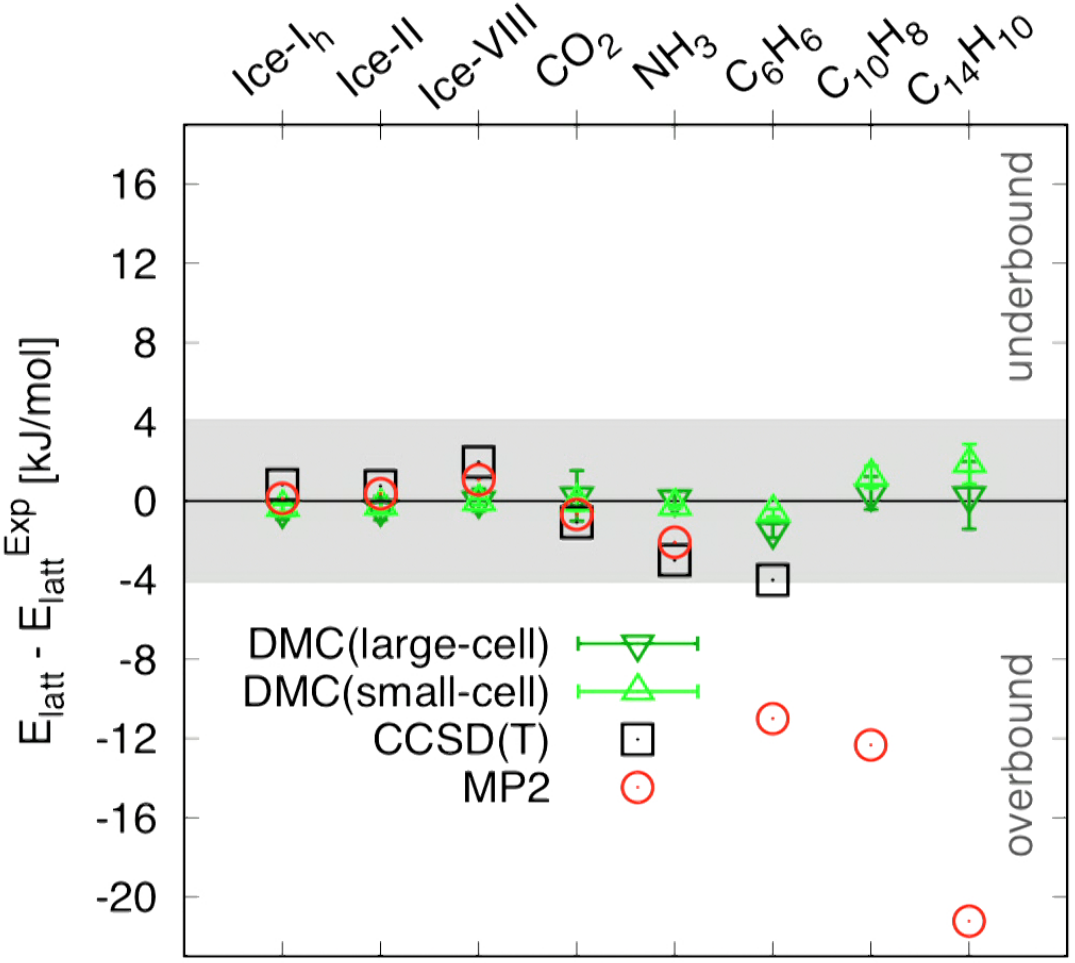
CCSD(T)



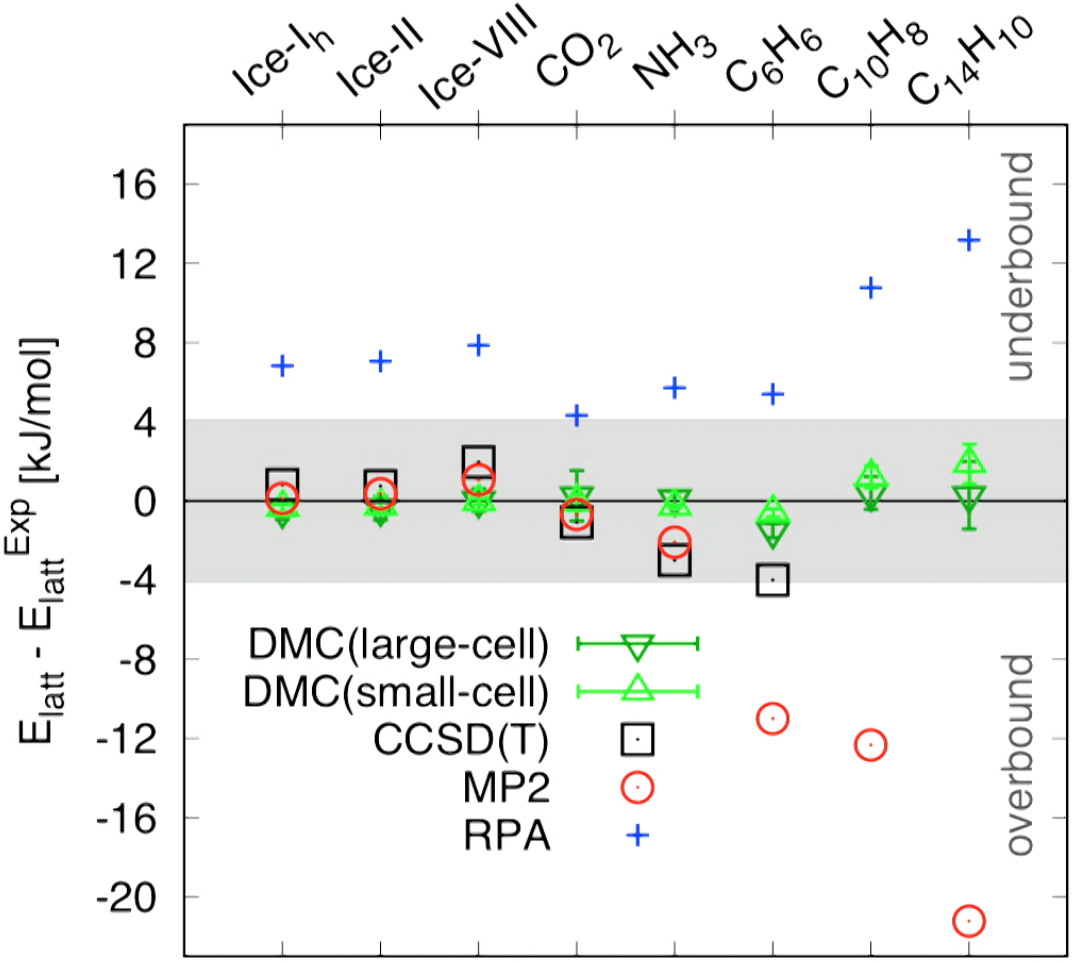
A Zen *et al.*, Proc. Natl. Acad. Sci. U.S.A.,115, 1724 (2018)

MP2



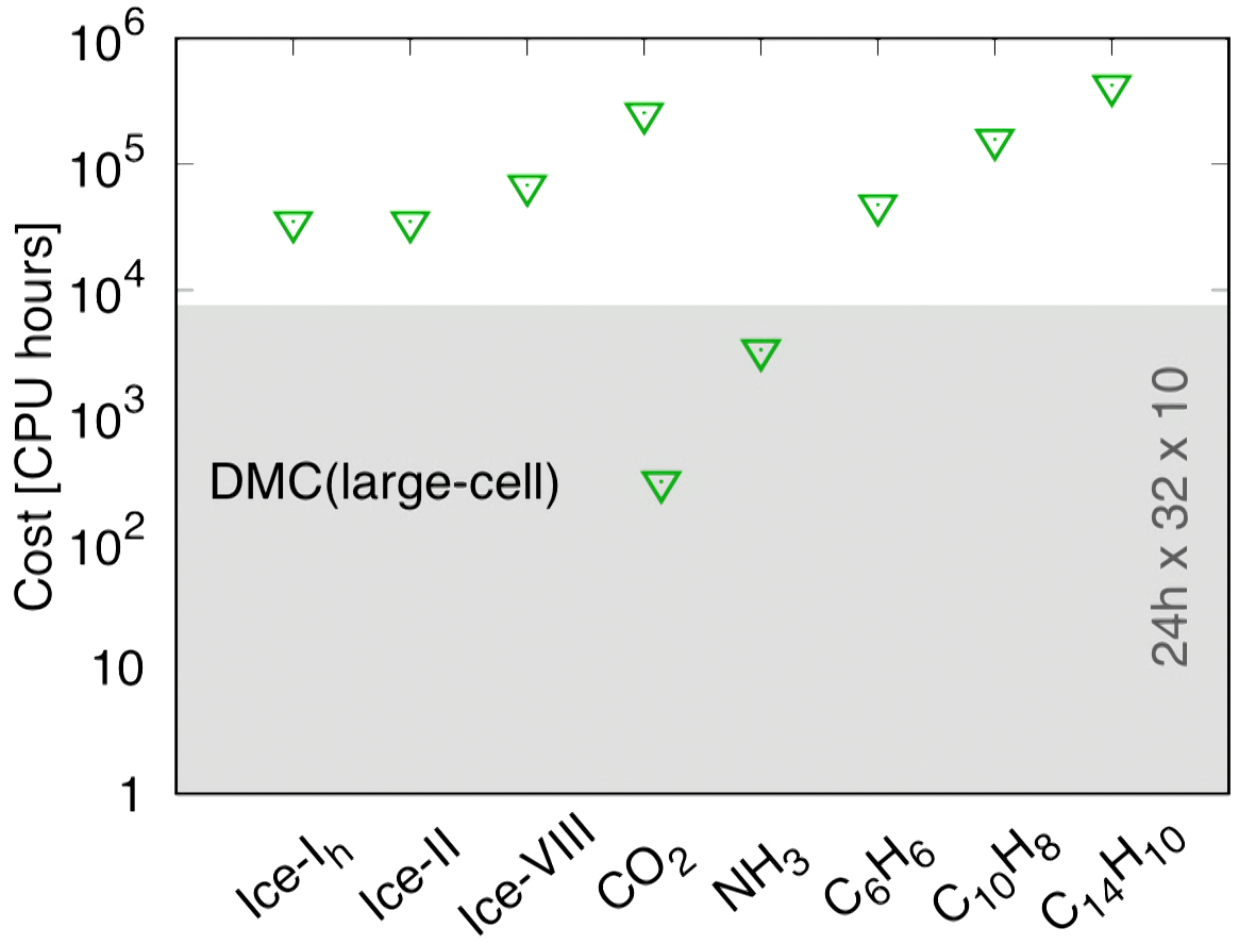
A Zen *et al.*, Proc. Natl. Acad. Sci. U.S.A.,115, 1724 (2018)

RPA



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

Affordability of DMC?



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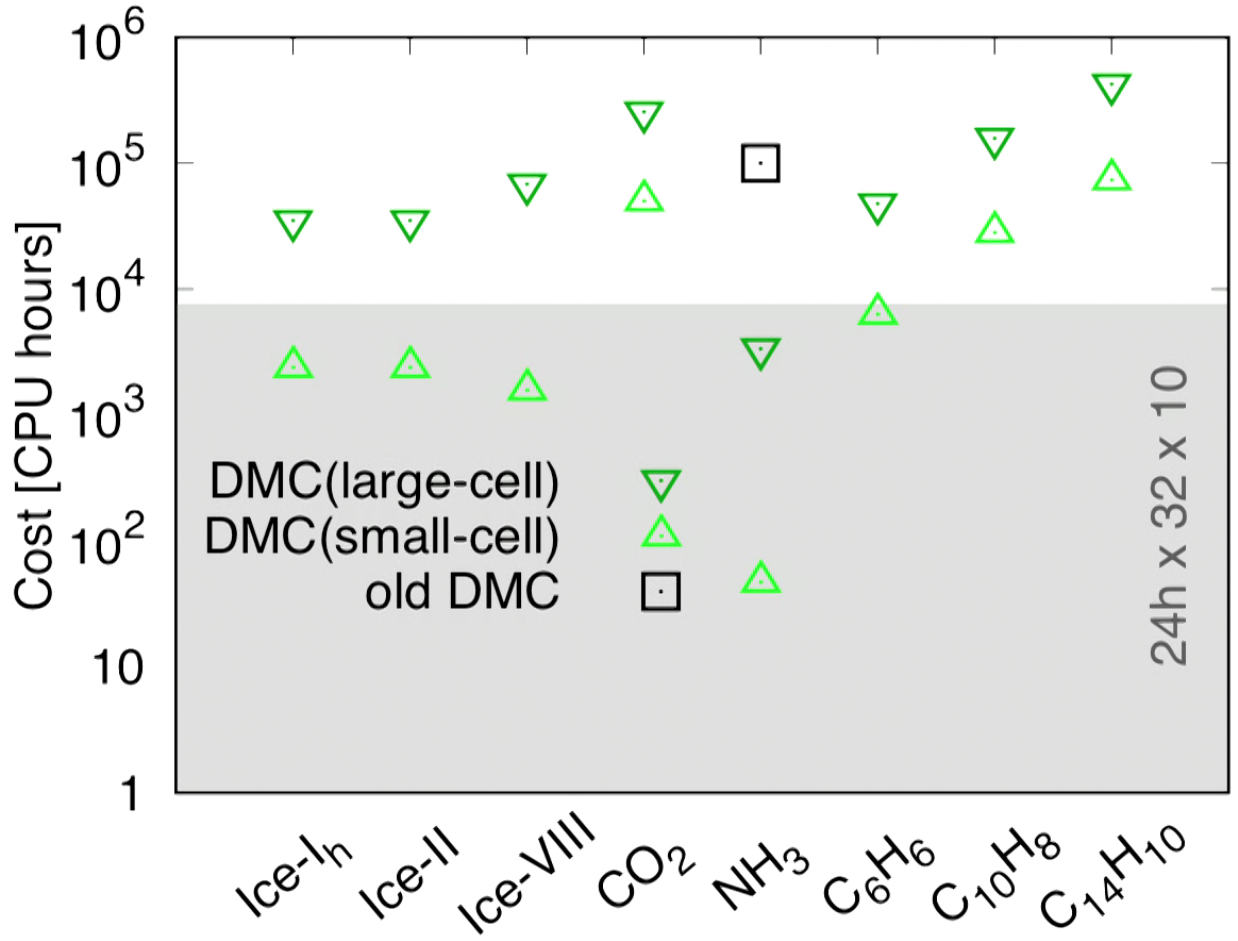

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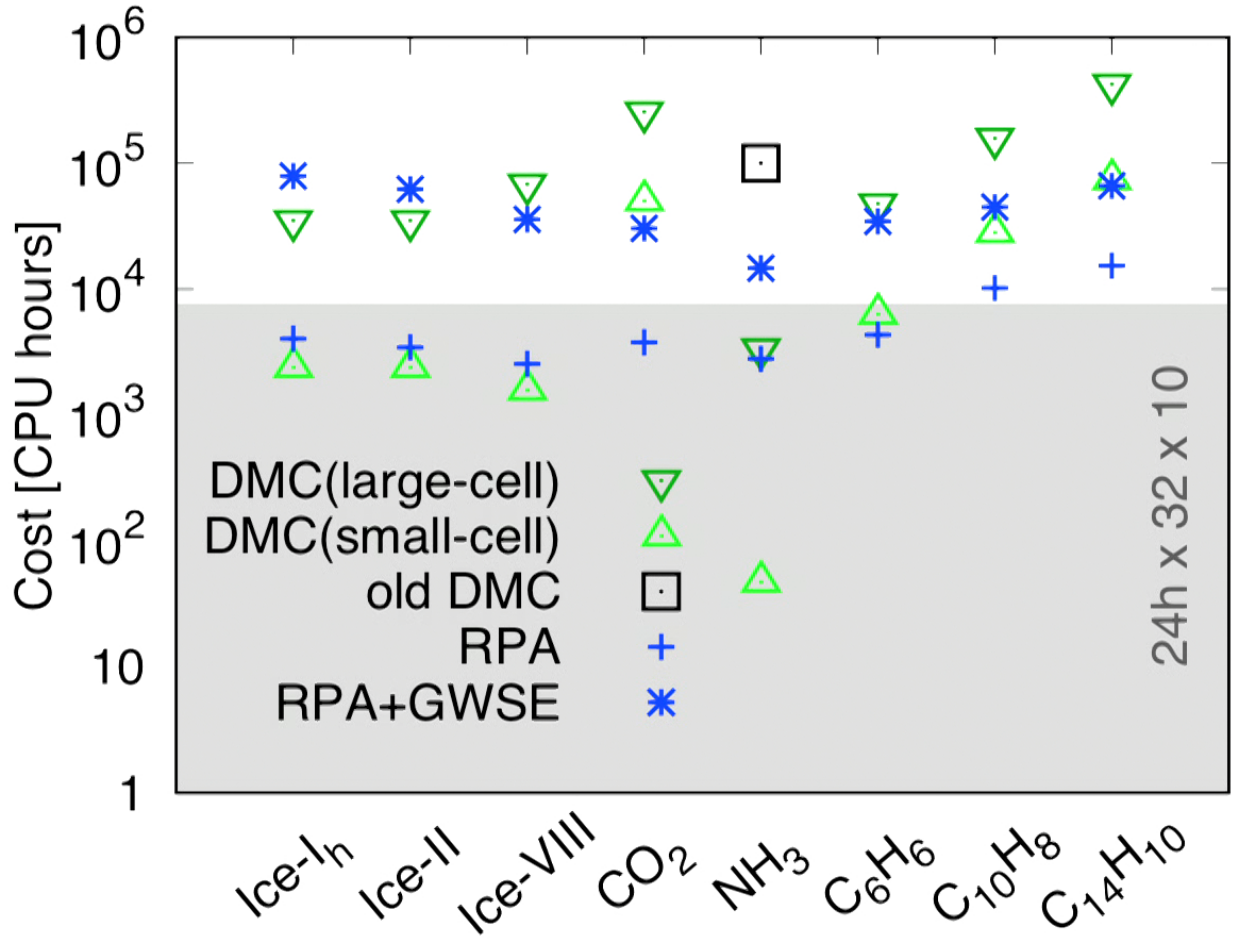
Affordability of DMC and RPA



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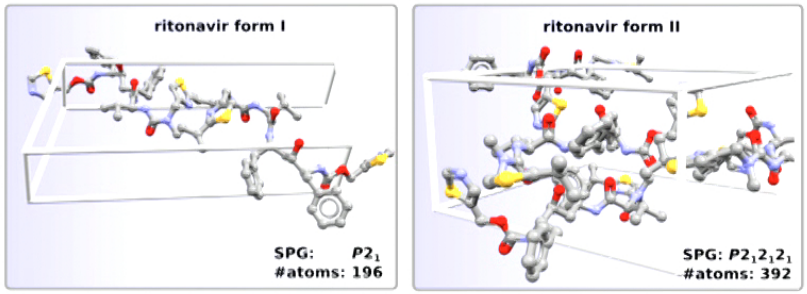
Perspectives

- QMC is a reference method able to tackle molecular crystal of actual pharmaceutical interest;



Deploy QMC for:

- understanding, screening and predicting the properties of complex molecular crystals;
- validating cheaper approaches (providing benchmarks) ;
- assessing the relative stability of different polymorphs;
- furthering crystal engineering to design novel pharmaceutical compounds.

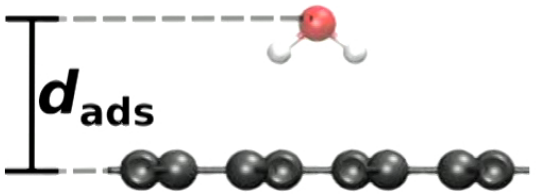
Outline

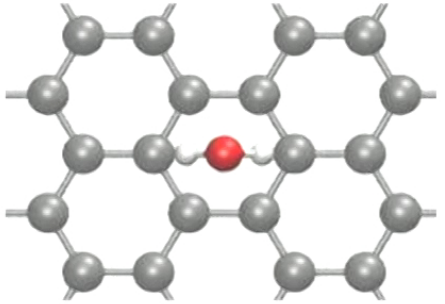
UCL

- Diffusion quantum Monte Carlo
  - DMC in a nutshell
  - Recent algorithmic developments, improved accuracy and efficiency
  - DMC in periodic systems
- Application: molecular crystals
  - MC are important and challenging systems, subchemical accuracy needed
  - A representative set of 8 molecular crystals
  - Lattice energy, experimental evaluation
  - DMC results versus experimental evaluations and other computational approaches
- Application: water on graphene
  - The system
  - Previous results
  - DMC results
  - Conundrum resolved

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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Value of E_b is still unknown

Ref.	E_b	Method	
1	**-130 meV**	**DFT/CC**	Corrects DFT based on differences at small **cluster** level
2	**-130 meV**	**DFT-SAPT**	Extrapolations on **clusters**
3	**-70 ± 10 meV**	**Diffusion Monte Carlo (DMC)**	**Periodic** system, ~ 50 Million Hours, large stochastic error, finite-size effects
4	**-135 meV**	**i-CCSD(T)**	Incremental expansion, correlation from **cluster**, small basis set

- All these approaches had weaknesses and possible issues.

1. Miroslav Rubes *et al., JPC C* **2009**, 113, 8412
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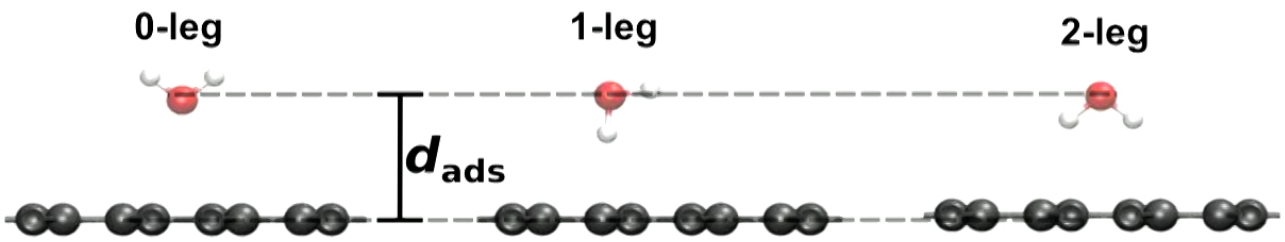
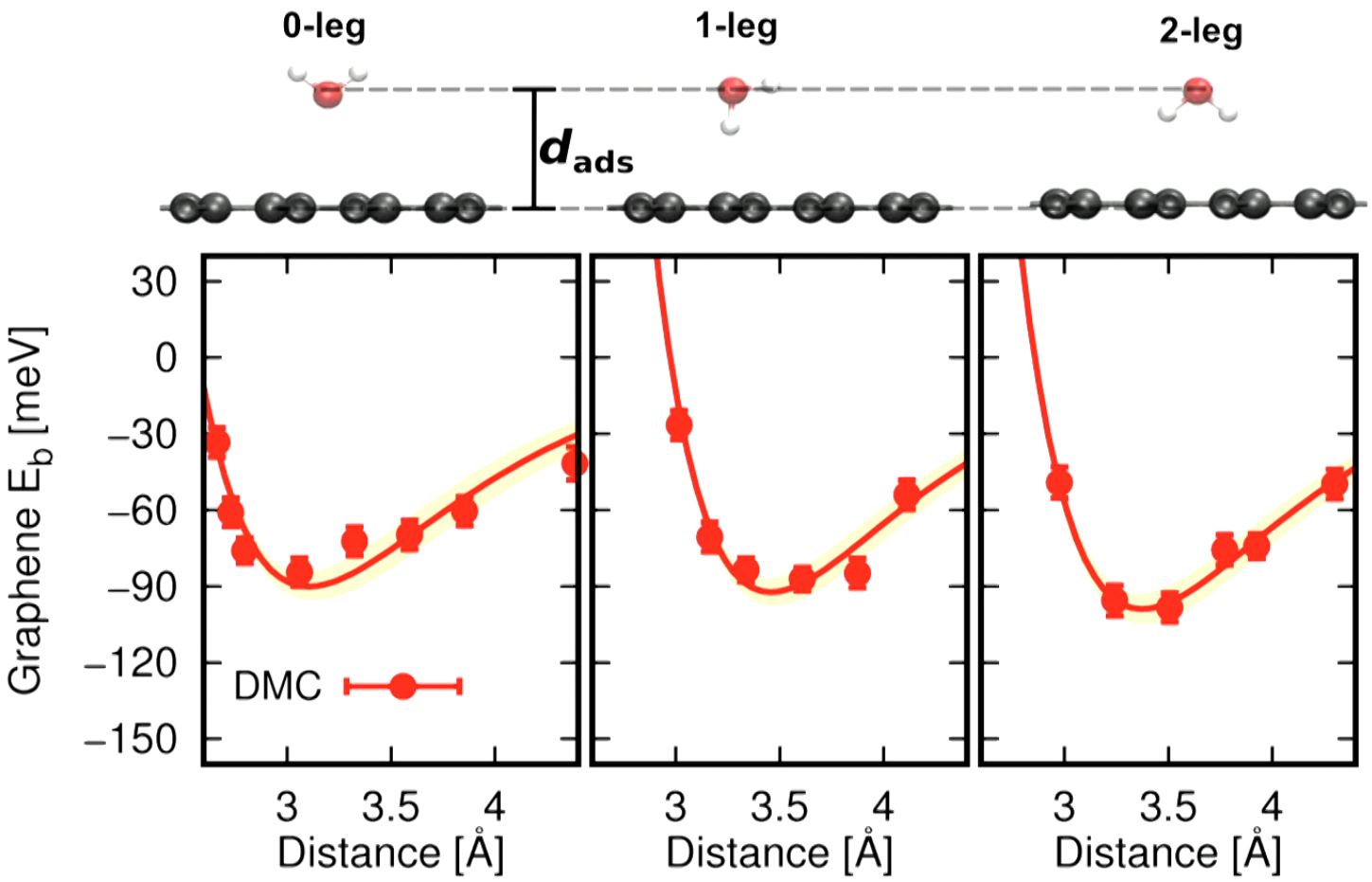
Adsorption on graphene



Adsorption on graphene



- Very similar binding energies for different motifs

New DMC, why discrepancies?

Ref.	E_b	Method	Issues
1	-130 meV	DFT/CC	?
2	-130 meV	DFT-SAPT	?
3	-70 ± 10 meV	Diffusion Monte Carlo (DMC)	Large stochastic error, finite-size effects are neglected
4	-135 meV	i-CCSD(T)	?
5	-99 ± 6 meV	Diffusion Monte Carlo (DMC)	

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New DMC, why discrepancies?

Ref.	E_b	Method	Issues
1	-130 meV	DFT/CC	*Small clusters?*
2	-130 meV	DFT-SAPT	*Small clusters?*
3	-70 ± 10 meV	Diffusion Monte Carlo (DMC)	Large stochastic error, finite-size effects are neglected
4	-135 meV	i-CCSD(T)	?
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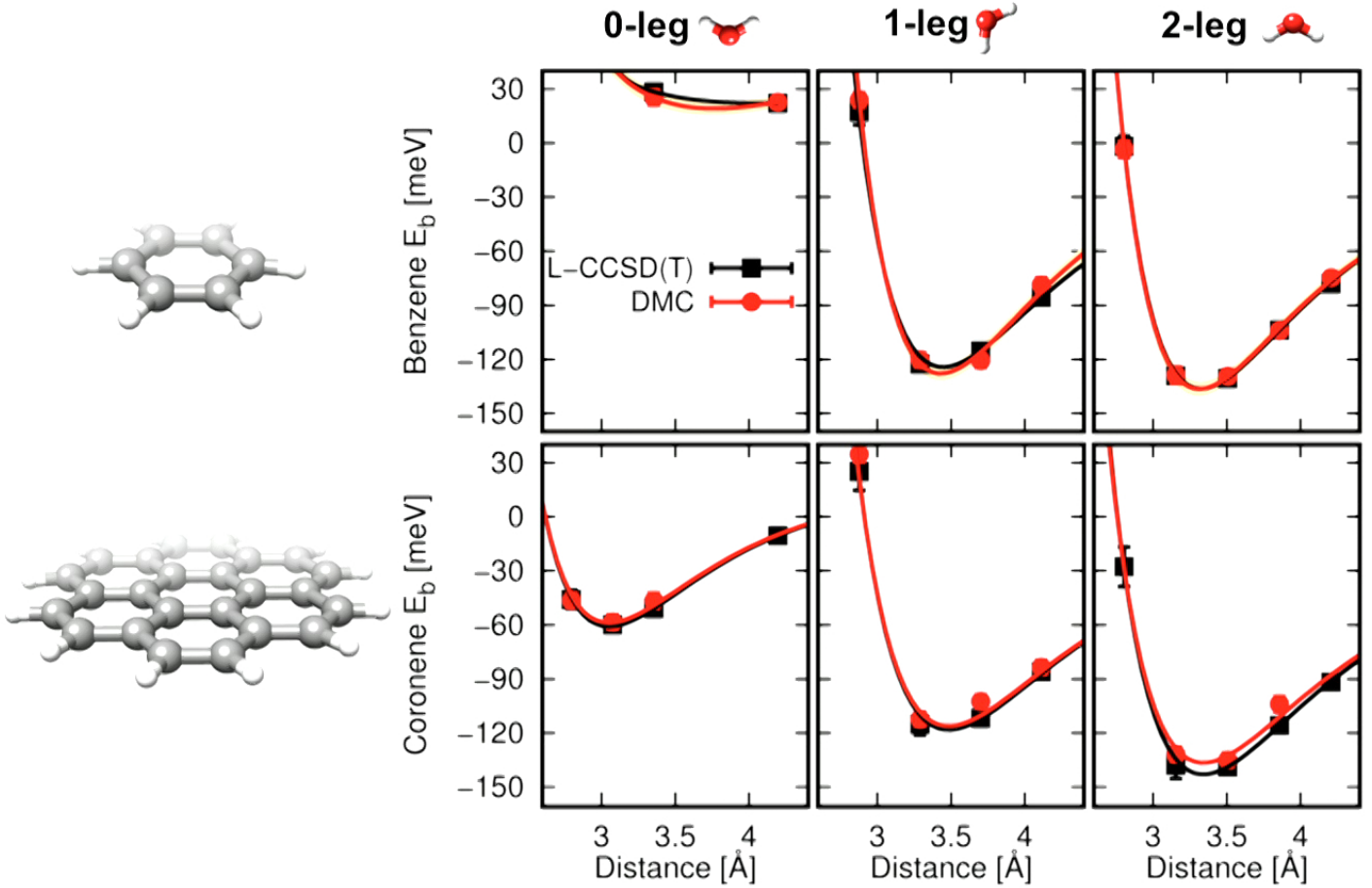
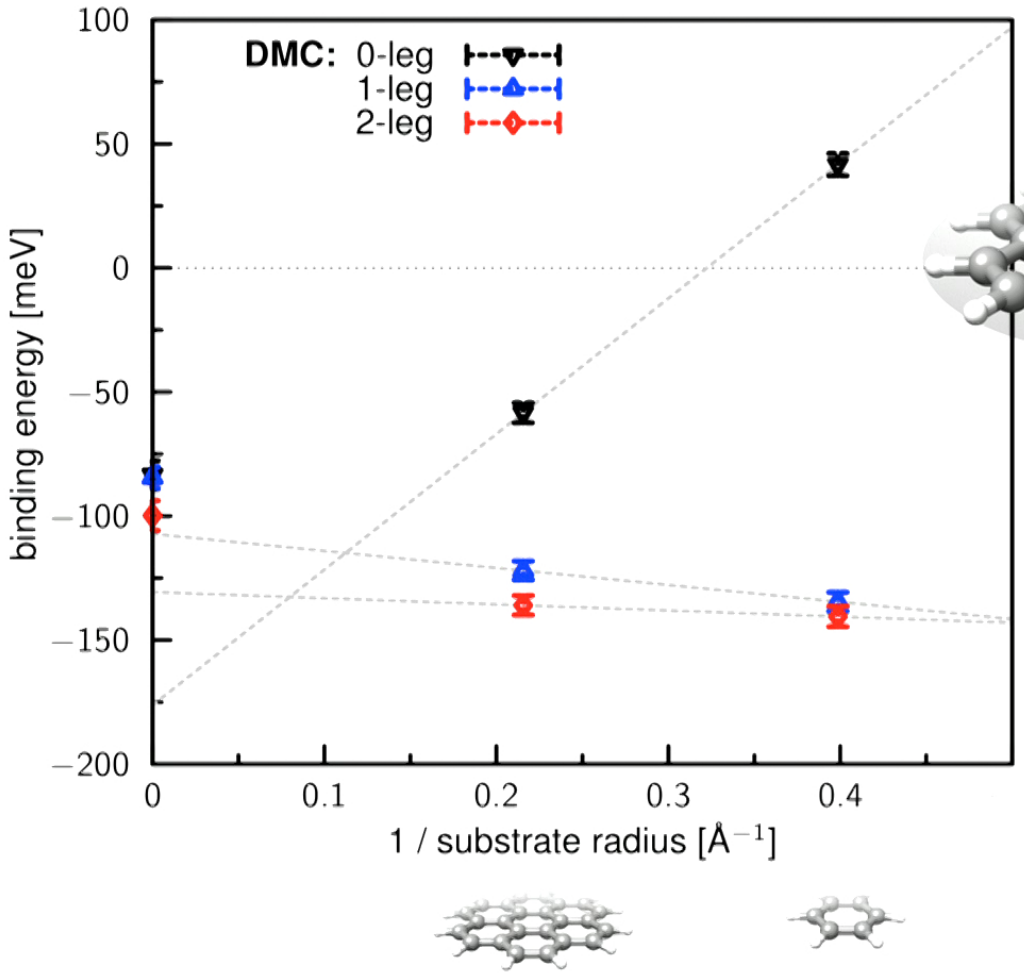
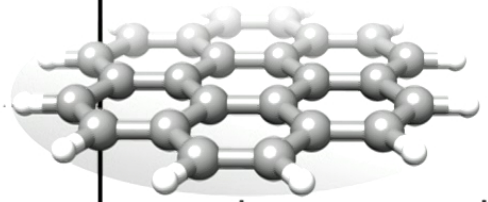
Adsorption on small substrates



L-CCSD(T): *JCP* **2001**, 114, 661; *JCP* **2013**, 139, 134101; *JCP* **2018**, 148, 011101

Extrapolation of substrate size





substrate radius

Extrapolations using benzene and coronene data are unreliable.

Slow convergence

Why discrepancies?

Ref.	E_b	Method	Issues
1	**-130 meV**	**DFT/CC**	Unreliable extrapolation
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?*
5	**-99 ± 6 meV**	**Diffusion Monte Carlo (DMC)**	

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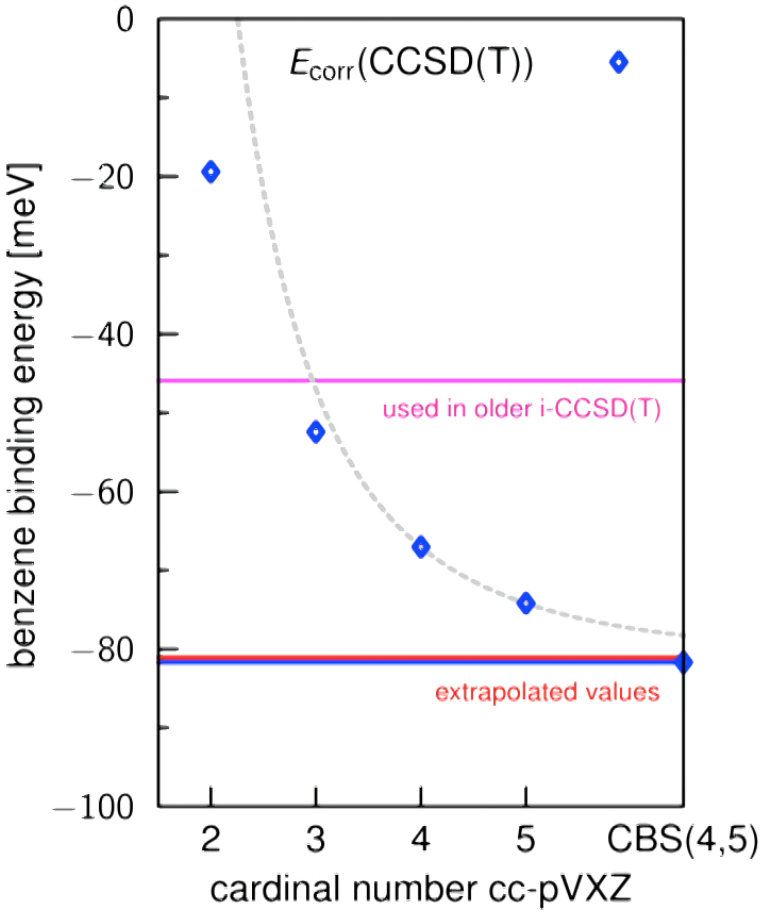
Slow convergence of QC



Coupled **C**luster with **S**ingles, **D**oubles and perturbative **T**riples

- Boys-Bernardi counter poise correction
- Needs to describe exited determinants
- Cubic convergence ~X^{-3}

Need for the complete basis set extrapolation (CBS).

Discrepancies resolved

UCL

Ref.	E_b	Method	Issues
1	**-130 meV**	**DFT/CC**	Unreliable extrapolation
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
5	**-99 ± 6 meV**	**Diffusion Monte Carlo (DMC)**	Value in agreement results from periodic CCSD(T) (-87 meV) and RPA+GWSE (-98 meV)

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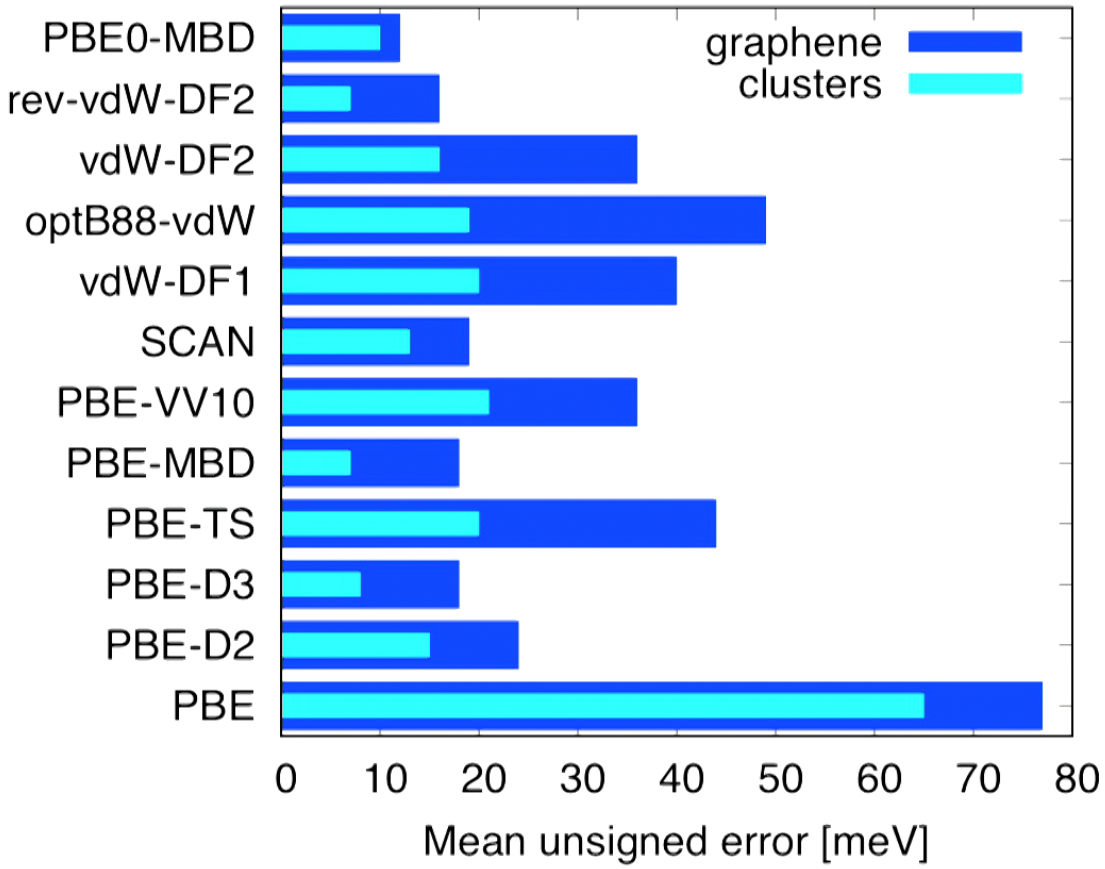
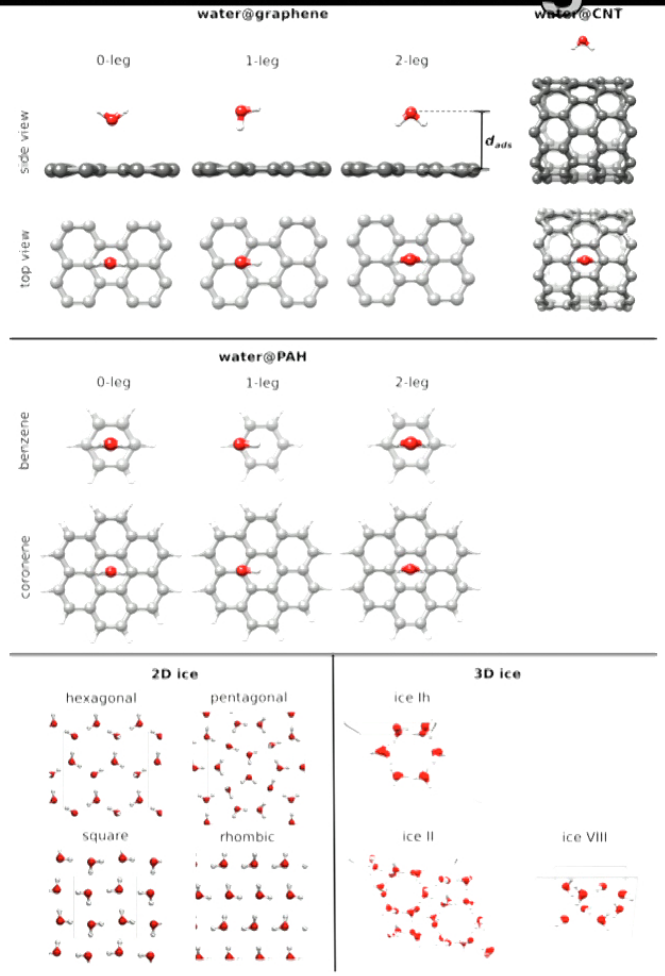
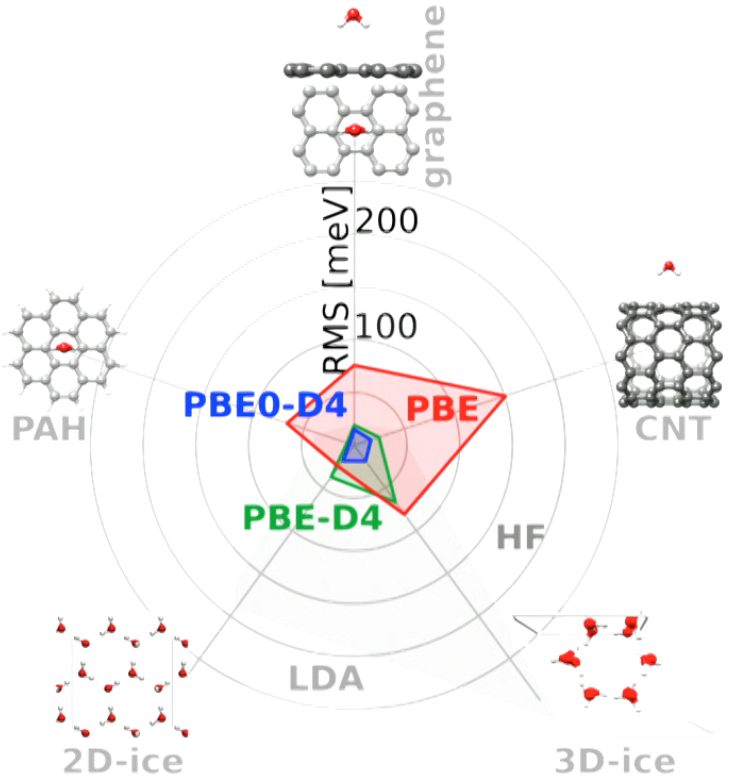
Benchmarking DFT



J.G. Brandenburg, A. Zen, D Alfè, A. Michaelides, Interaction between water and carbon nanostructures: How good are current density functional approximations?, *in preparation*

Benchmarking DFT





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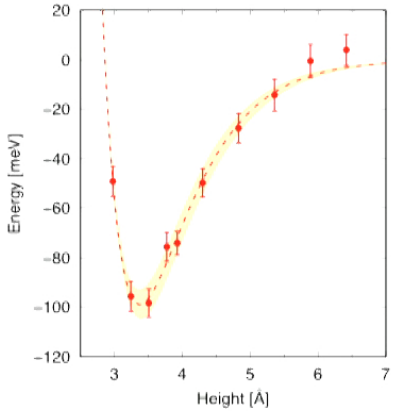
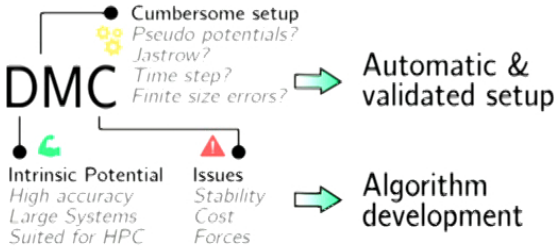
Conclusions

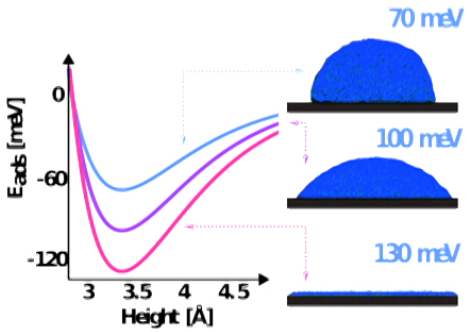
- Modeling to be used complementary to experimental studies
- DMC is affordable method with controllable high accuracy
- Molecular level understanding of water-graphene interaction





Outlook

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



Thanks

UCL

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Andrea Zen


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Dario Alfè

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Benjamin Ramberger


Georg Kresse


Theodoros Tsatsoulis


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Other collaborators


Sandro Sorella (Trieste)


Ji Chen (Stuttgart)


Jiri Klimes (Prague)


Alexandre Tkatchenko (Luxembourg)

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THE THOMAS YOUNG CENTRE TyC

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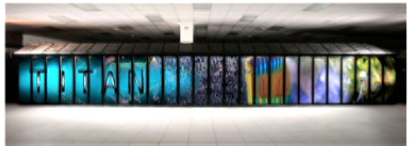

Fundraising for WaterAid

UCL

Swim, Run, Bike for WaterAid
because clean water is worth fighting for.

We're taking part in this year's **Castle Howard triathlon** (21July) in aid of **WaterAid**.

WaterAid is an international charity working to provide clean water and decent toilets to everyone, everywhere.

www.justgiving.com/fundraising/ice-group-at-ucl2

Please offer us whatever support you can.