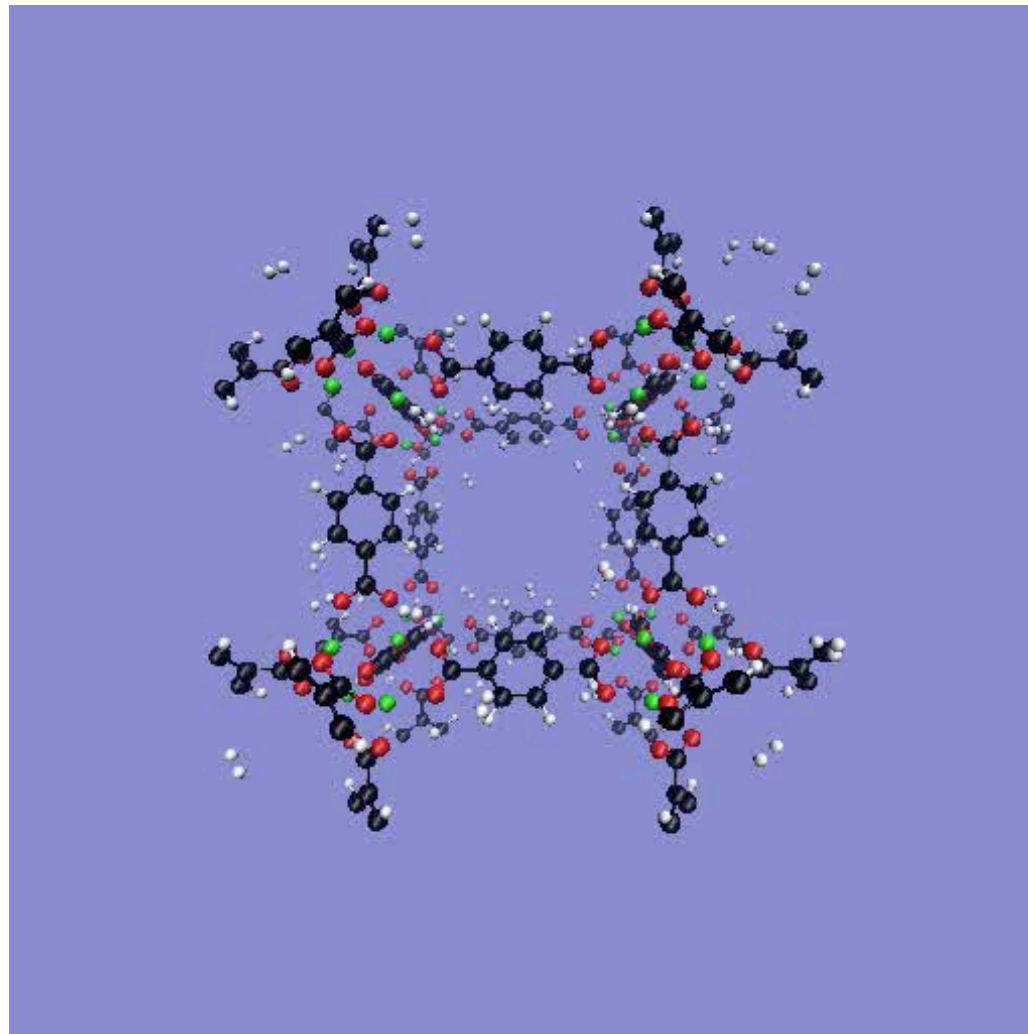


Understanding hydrogen storage in metal organic frameworks from first principles



Understanding hydrogen storage in metal organic frameworks from first principles

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<http://charm.cs.illinois.edu/OpenAtom>

Overview

- We plan to study metal organic frameworks (MOFS)
 - What is a MOF?
 - Why study hydrogen in MOFs?

- Software we run on Blue Waters: OpenAtom
 - What does it do?
 - How is it parallelized?
 - How does it perform?
 - Why do we need Blue Waters?

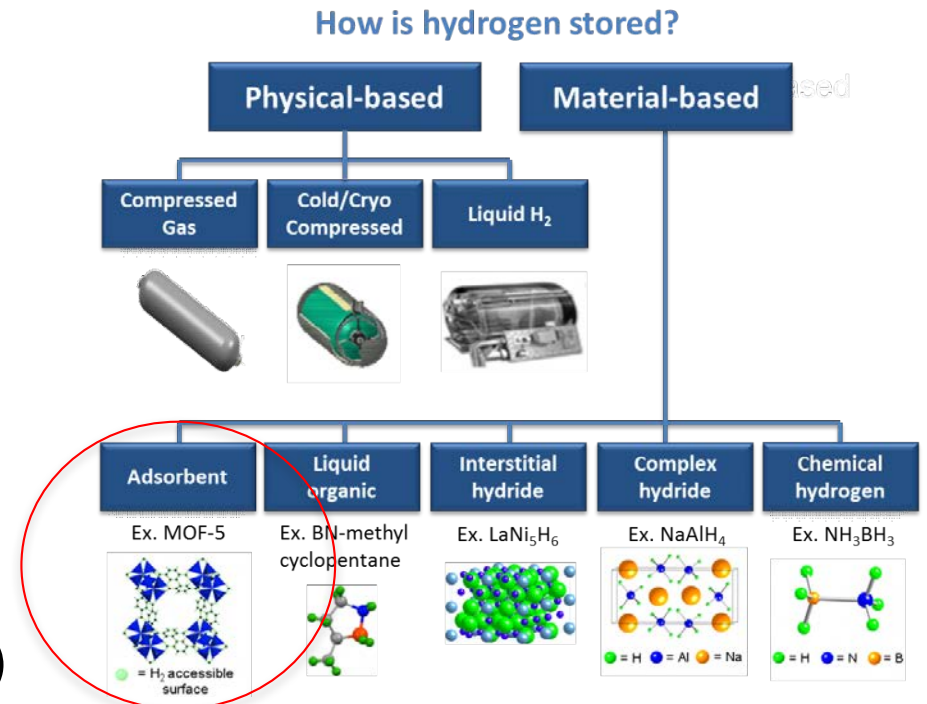
- What we learned so far

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Hydrogen storage for green energy

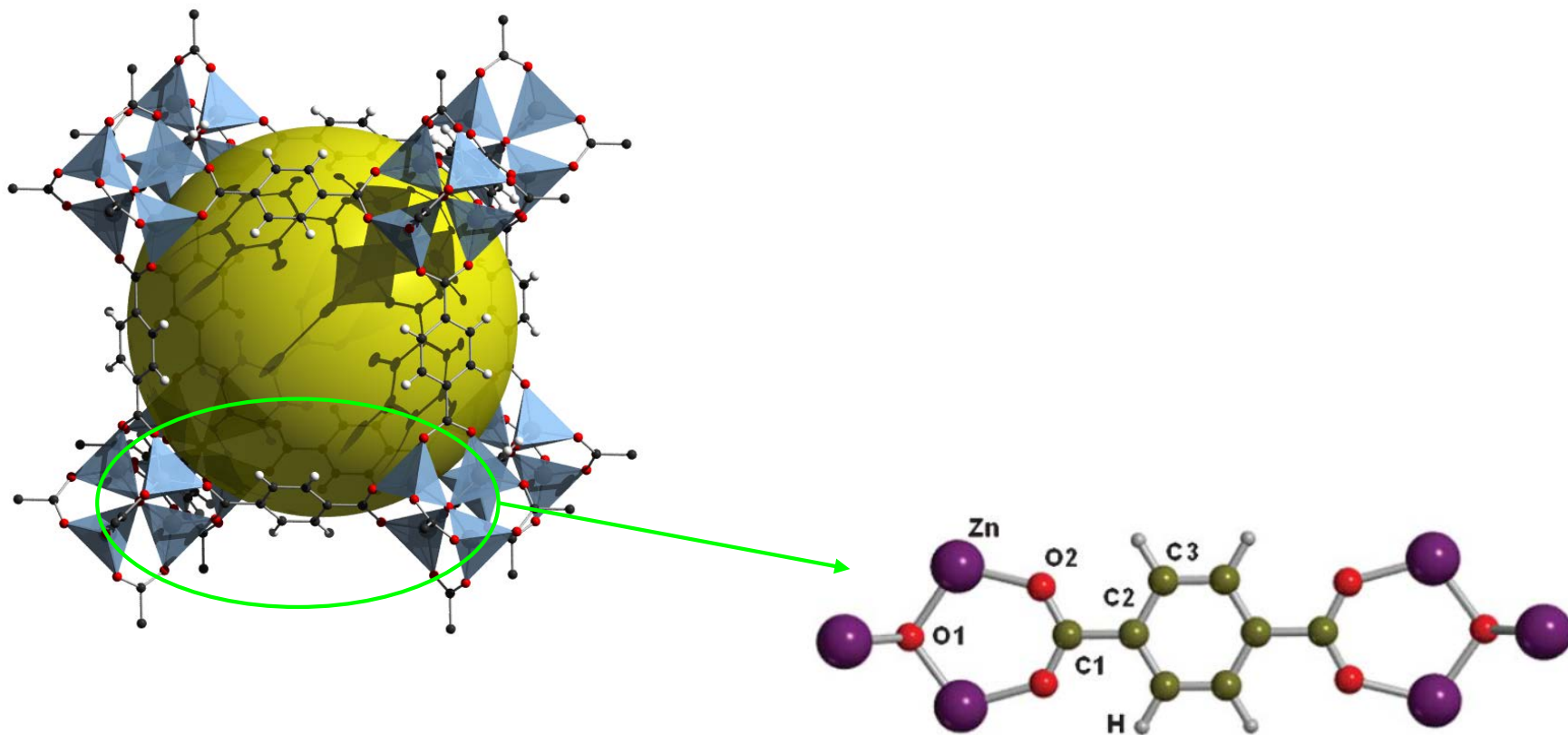
- Hydrogen as fuel
 - energy dense
 - with clean burn
 - hard to store
- Need lightweight material that can store and release a lot of H_2
- Metal organic frameworks (MOFs)
 - Porous
 - Large interior surface area
 - Can store reasonable amount of H_2
 - Complex material, details of process not known
 - Optimization of H_2 storage not great to date



<http://energy.gov/eere/fuelcells/hydrogen-storage>

DOE target for a H_2 storage system not yet been reached: e.g., capacity of 40 g H_2 per L.

Typical MOF structure



MOFs we study

- MOF-5 : $\text{Zn}_4\text{O}(\text{1,4 benzenedicarboxylate})_3$
- 424 atoms in a simulation cell
- Can change Zn to other metals

Questions to answer:

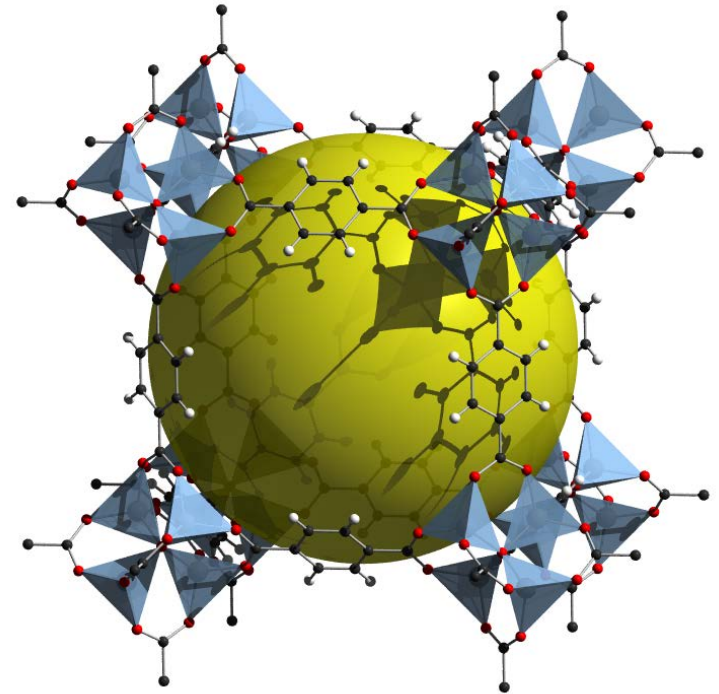
- How do H_2 bind / diffuse inside MOF?
- Temperature & loading dependence

Molecular dynamics (MD) needed

- Simulate motion of MOF + H_2 to see what happens in real time
- Dynamics & thermodynamics

Technical challenge: H_2 is very light

- Standard MD: point-like atoms move due to interatomic forces
- Hydrogen is *quantum mechanical*: not point-like but wavy...



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What is OpenAtom



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Glenn Martyna
Physical Chemistry
& Materials
IBM

NSF SI2-SSI: Scalable, Extensible, and
Open Framework for Ground and
Excited State Properties of Complex Systems

- OpenAtom software package : DFT (now) , GW (next)
- Plane waves and pseudopotentials
- charm++ parallel infrastructure

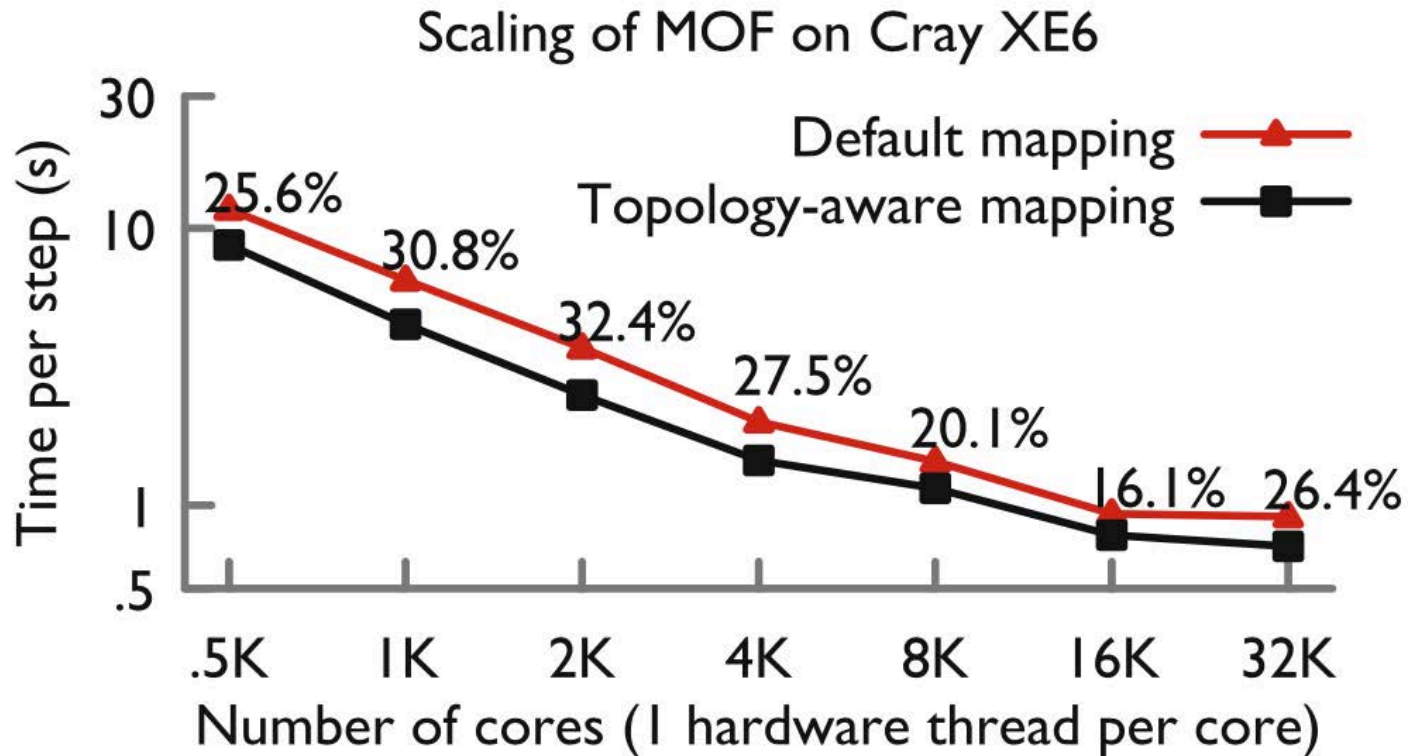
OpenAtom: what does it do?

- Massively parallel *ab initio* molecular dynamics (AIMD)
- Describes electrons quantum mechanically, i.e., bonding, *explicitly* using basic physics (no fudge parameters or fits)
- Uses general Fourier basis to represent electron waves
- Uses Charm-FFT *library*: 2D decomposed parallel FFT with spherical cutoff awareness

For the experts:

- Plane waves and pseudopotentials
- Car-Parrinello and Born-Oppenheimer MD

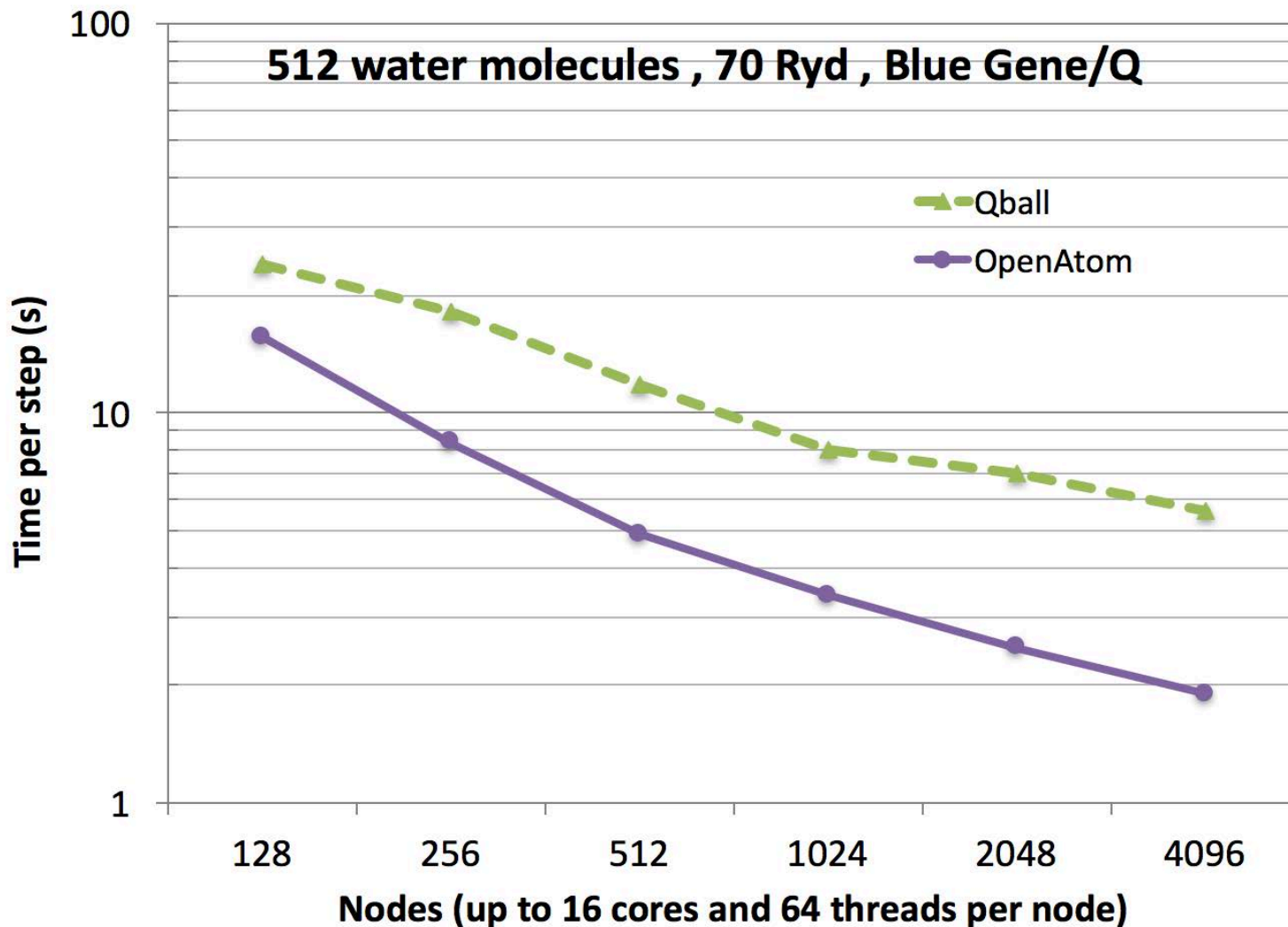
Strong scaling performance



- Few MD steps of AIMD with MOF
- Fixed problem size (strong scaling)
- Time to solution with increased of cores

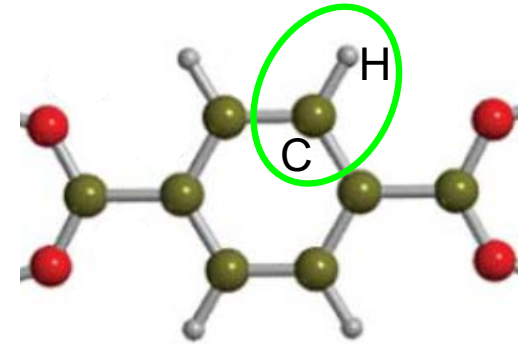
Is OpenAtom competitive?

- Few steps of AIMD
- Compared to Qball : a LANL fork of Qbox AIMD software



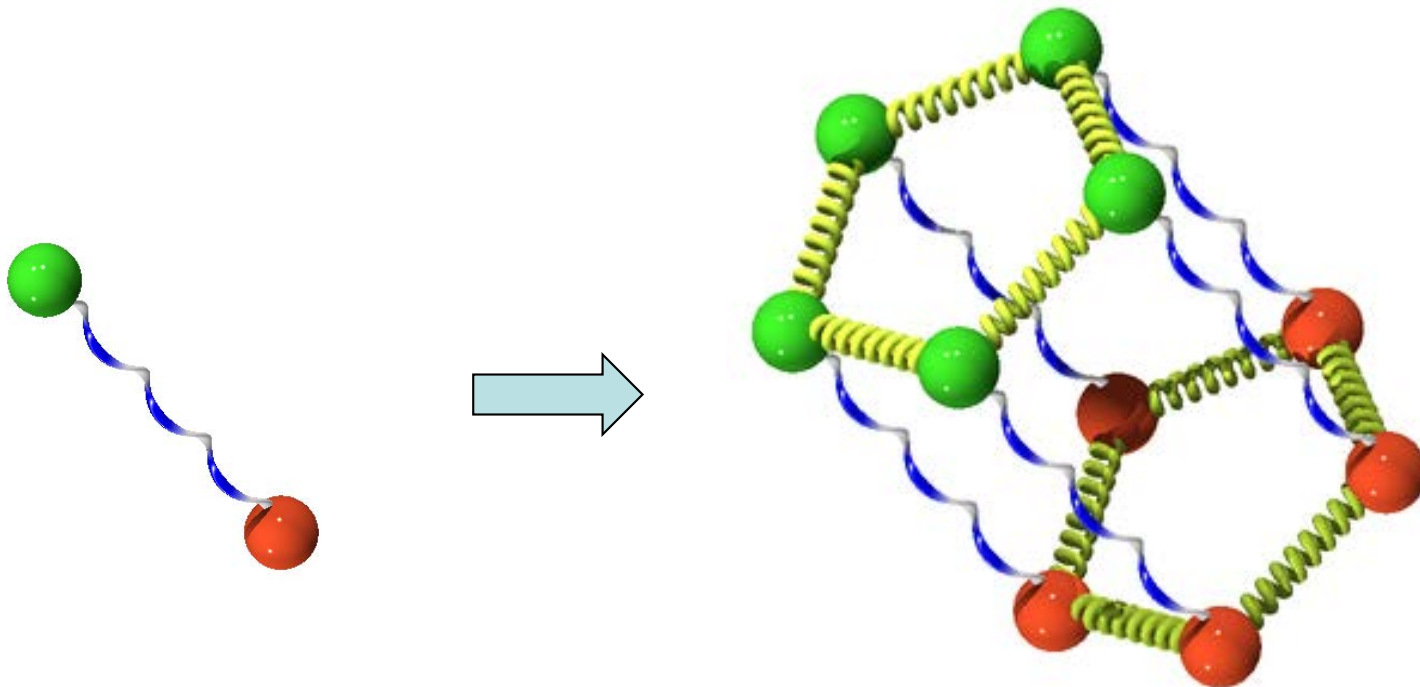
Why quantum hydrogen?

- Consider C-H bond in part of the MOF
- Vibration frequency $f \sim 9 \times 10^{13}$ Hz
- Classical (point-like atom) picture
 - C-H length vibrates at this frequency
 - Continuous vibrational energy
- Quantum systems: energy discrete
 - Einstein says $E = hf$
 - Convert to temperature : 4300 K !
- For any reasonable temperature, the C-H bond
 - does *not* vibrate at all (stuck in ground state)
 - no dynamics per se



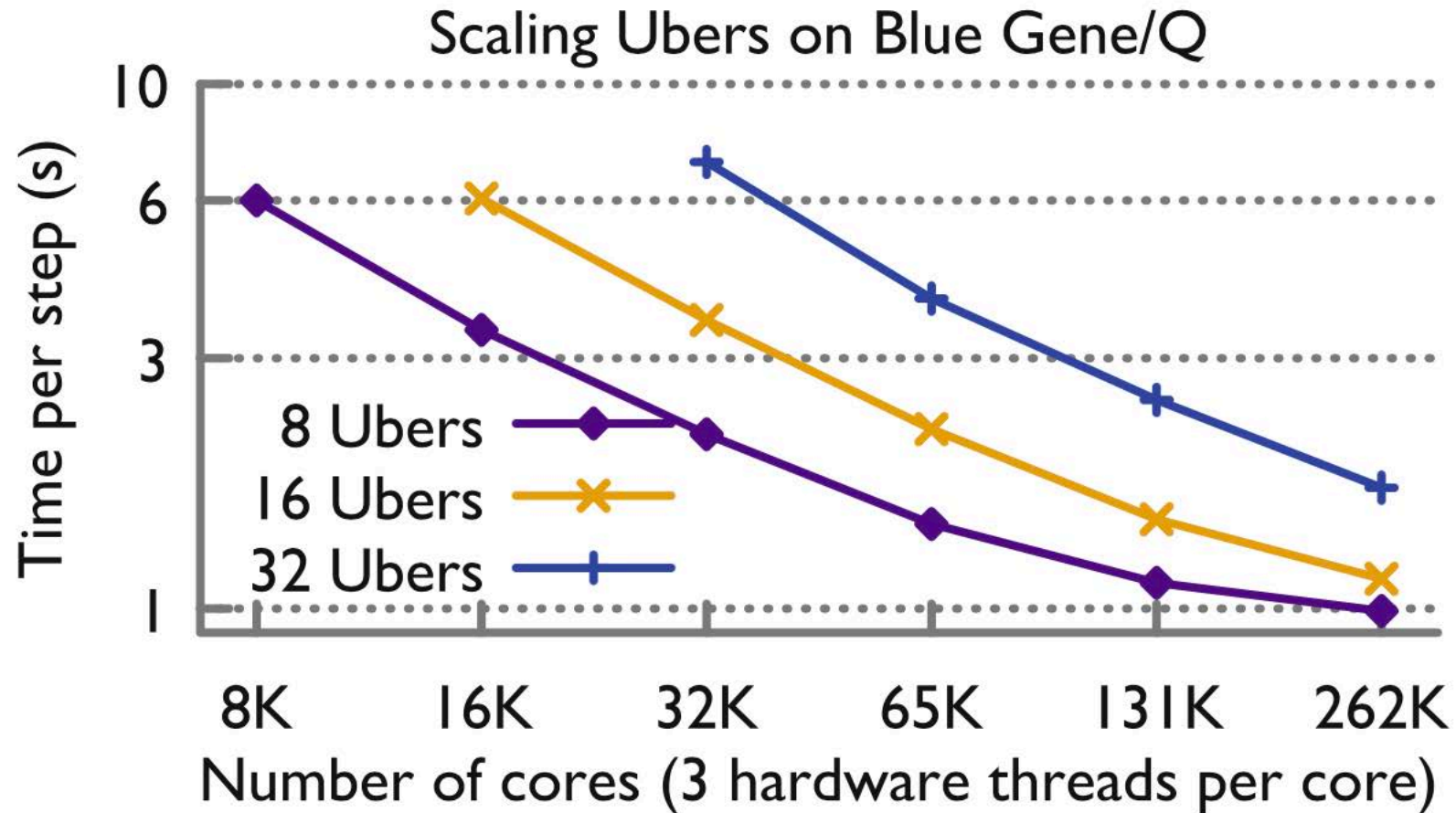
Path integral Monte Carlo

- A way to make atomic coordinates (nuclei) quantum
- Multiple images of MOF (“beads”)
- Beads connected by appropriate springs
- Entirety evolves as a giant MD



Path integral strong scaling

- Multiple beads of MOF (ubers)
- Entirety evolves as giant MD



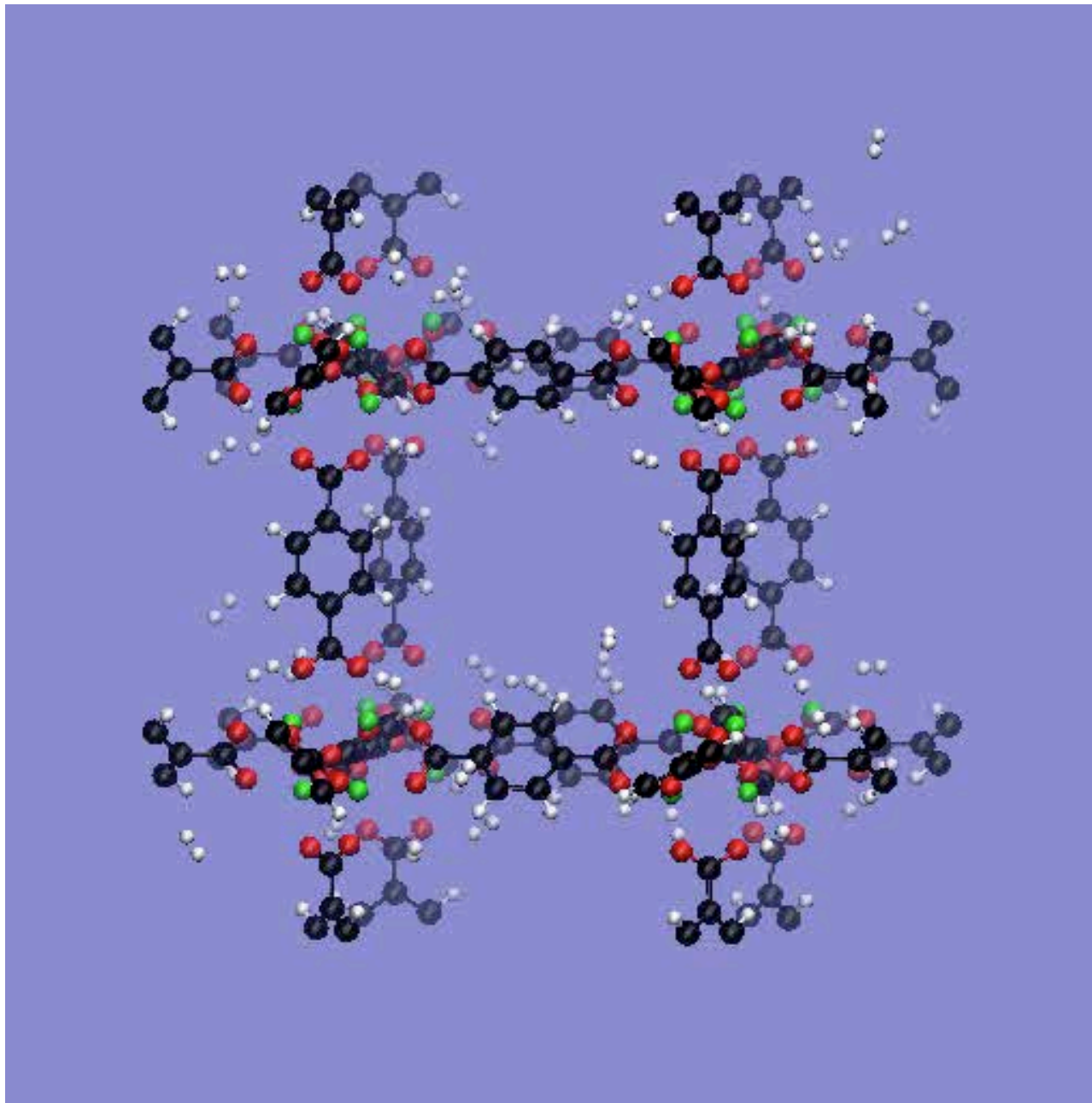
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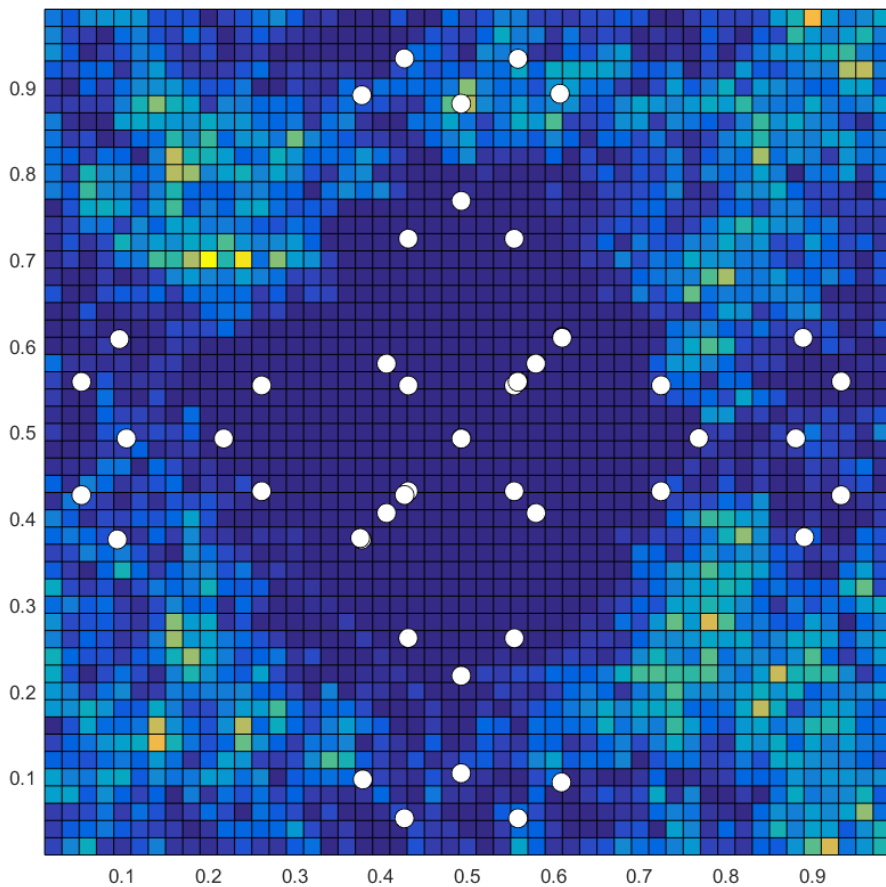
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Preliminary results: MD itself

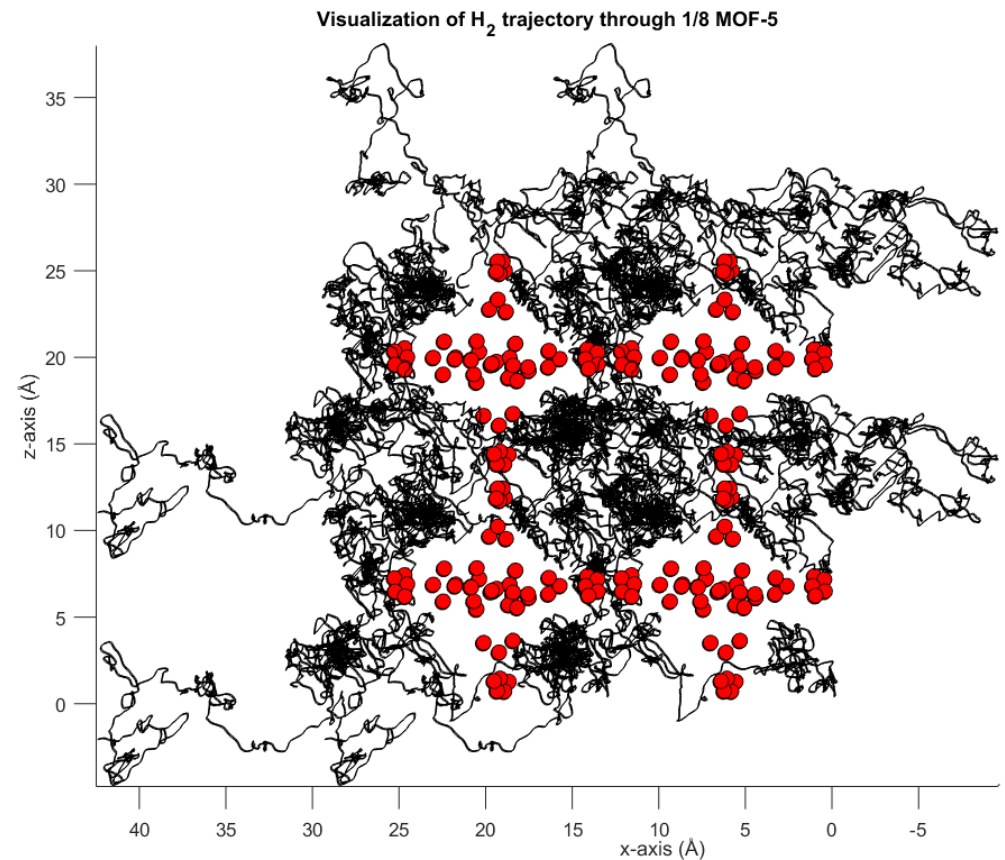


Preliminary results: diffusion

Heatmap: mean H_2 positions
in simulation cell



Diffusive paths followed by
 H_2 molecules over time



Preliminary results: diffusion

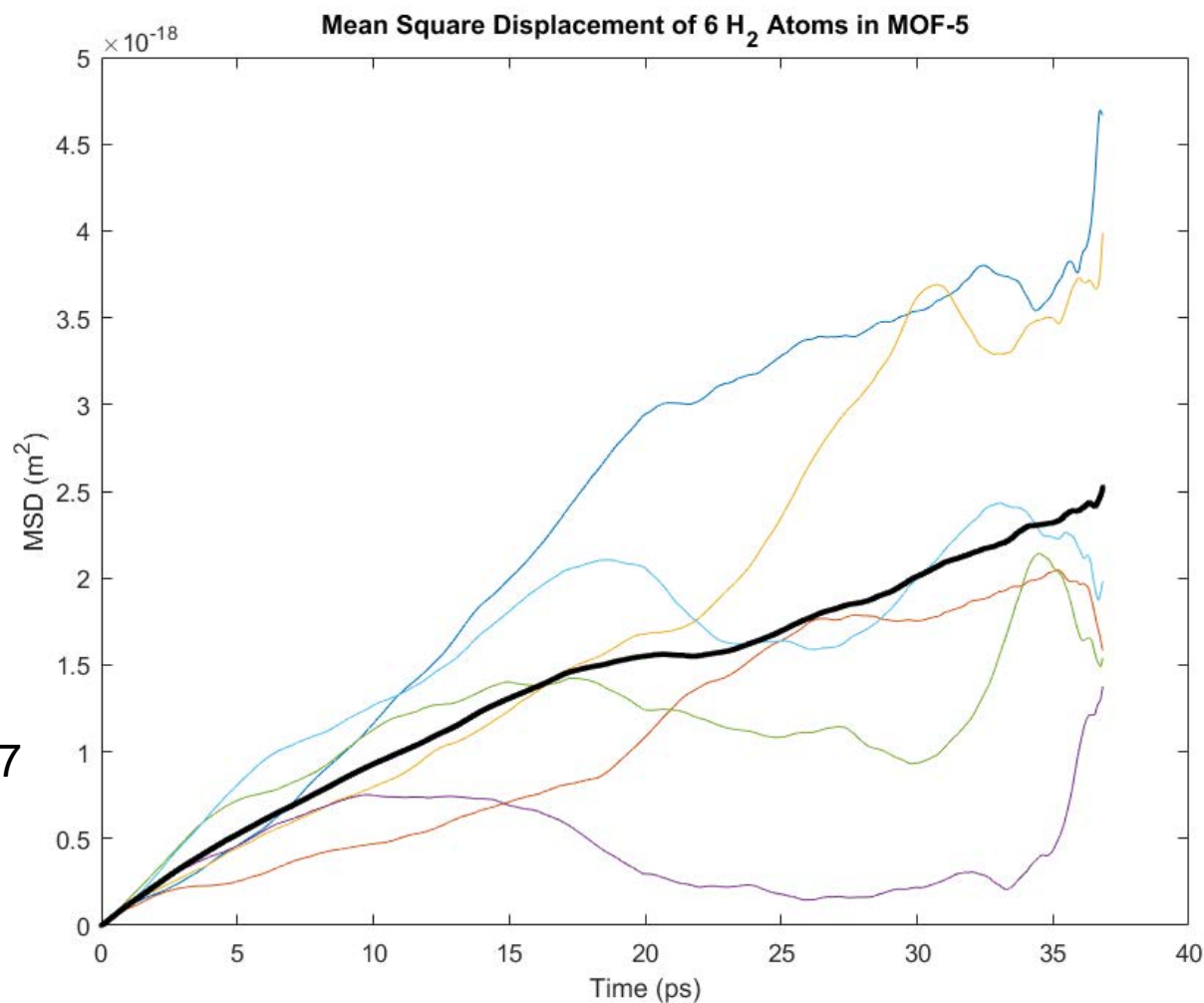
- Slope: $m = 7 \times 10^{-8} \text{ m}^2/\text{s}$

$$- \boxed{D \approx 10^{-8} \frac{\text{m}^2}{\text{s}}}$$

- Seems to agree with available literature

$$D \approx 7 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

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Summary

- Study metal organic frameworks (MOFS) for H₂ storage
- Use OpenAtom on Blue Waters: OpenAtom
 - Highly parallel
 - Scales well
 - Can simulate quantum nuclear effects
- Preliminary non-quantum simulations
 - Seem reasonable
 - Need longer simulations/more statistics
- Gear up for fully quantum simulations this year