Molecular and Electronic Dynamics Using the OpenAtom Software

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http://charm.cs.illinois.edu/OpenAtom
What is OpenAtom

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

- OpenAtom software package: DFT, GW
- Plane waves and pseudopotentials
- charm++ parallel infrastructure
**OpenAtom: what does it do?**

- Massively parallel *ab initio* molecular dynamics (AIMD)
- Excited electronic states (Green function methods)

- 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, pseudopotentials, LDA or GGA
- Car-Parrinello and Born-Oppenheimer MD of electronic ground state
- GW self-energy for electronic excitations
Overview

• What is OpenAtom?

• We are studying metal organic frameworks (MOFS)
  o What is a MOF?
  o Why study hydrogen in MOFs?

• What we learned so far on MOFs

• Improving large scale GW calculations
Hydrogen storage for green energy

- Hydrogen as fuel
  - energy dense
  - clean burn
  - hard to store

- Need lightweight material that stores and releases a lot of $\text{H}_2$

- Metal organic frameworks (MOFs)
  - Porous
  - Large interior surface area
  - Stores plenty of $\text{H}_2$
  - Complex material, details of process not known
  - Optimization of $\text{H}_2$ storage not great to date

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

DOE target for a $\text{H}_2$ storage system not yet been reached: e.g., capacity of 40 g $\text{H}_2$ per L.
Typical MOF structure
MOFs we study

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

Questions to answer:
- How do $\text{H}_2$ bind / diffuse inside MOF?
- Temperature & loading dependence

Molecular dynamics (MD) needed
- Simulate motion of MOF + $\text{H}_2$ to see what happens in real time
- Dynamics & thermodynamics

Technical challenge: $\text{H}_2$ is very light
- Standard MD: point-like atoms move due to interatomic forces
- Hydrogen is *quantum mechanical*: not point-like but wavy…
Difficulties: quantum nuclei

- Quantum nuclear module validated/tested in serial
- Quantum nuclear module validated/tested on small parallel calculations we can do locally

- Quantum nuclear for large MOF with many nodes and “beads” (quantum replicas) fails on BW at present (need to run ~1000 nodes for ~3 hours to reach failure)

- Some type of irreproducible parallel problem
- ~9 months of work and bug removal has narrowed it to a single module but not isolated yet

- **General problem**: how to validate/test parallel code when only possible on a computer as big as BW? How to know code is correct before BW allocation?
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Preliminary results: MD itself
Preliminary results: diffusion

Paths of H₂ molecules over simulation
Preliminary results: diffusion

Heatmap: mean H\textsubscript{2} positions in simulation cell
Preliminary results: diffusion

\[ 6Dt = \langle \| \vec{r}(t) - \vec{r}(0) \|^2 \rangle \quad \text{(for long times } t) \]

- Slope of black curve:
  \[ D \approx 8.5 \pm 0.5 \times 10^{-8} \frac{m^2}{s} \]

- Seems to agree with available literature
  \[ D \approx 7 \times 10^{-9} \frac{m^2}{s} \]

\[ \vec{r}_2 = \vec{r}_1 - \vec{r}_0 \] (for long times \( t \))

\[
\begin{align*}
\text{Full MOF-5 at 77 K: 43 H}_2 \text{ molecules}\\
\text{J. Phys. Chem. C} \ 2008, \ 112, 2911-2917
\end{align*}
\]
Preliminary results: diffusion

<table>
<thead>
<tr>
<th>$D$ (10^{-8} \text{ m}^2/\text{s})</th>
<th>Mini-MOF</th>
<th>Full MOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>77 K</td>
<td>1.1 ± 0.2</td>
<td>0.85 ± 0.05</td>
</tr>
<tr>
<td>300 K</td>
<td>6.9 ± 0.8</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>ratio</td>
<td>6.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>
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DFT: problems with excitations

Energy gaps (eV)

<table>
<thead>
<tr>
<th>Material</th>
<th>LDA</th>
<th>Expt. [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>3.9</td>
<td>5.48</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
<td>1.17</td>
</tr>
<tr>
<td>LiCl</td>
<td>6.0</td>
<td>9.4</td>
</tr>
</tbody>
</table>


Solar spectrum
$P(r, r') = \frac{\partial n(r)}{\partial V(r')} = -2 \sum_{v}^{\text{filled}} \sum_{c}^{\text{empty}} \frac{\psi_v(r) \psi_c(r) \psi_v(r') \psi_c(r')}{\varepsilon_v - \varepsilon_c}$
GW : scaling

\[ P(r, r') = \frac{\partial n(r)}{\partial V(r')} = -2 \sum_v^{\text{filled}} \sum_c^{\text{empty}} \frac{\psi_v(r)\psi_c(r)\psi_v(r')\psi_c(r')}{\varepsilon_v - \varepsilon_c} \]

Scaling on Mira

- 32 threads per node

Scaling on BlueWaters

- 32 cores per node
GW : scaling

\[ f_{vc} = \psi_v \times \psi_c \text{ for all } v, c \]
\[ P += f_{vc} \times f_{vc}^T \text{ for all } f \]

GW Scaling Results on Bluewaters
(Dataset Si108)
Summary

• Study metal organic frameworks (MOFS) for H₂ storage

• Used OpenAtom on Blue Waters

• Preliminary non-quantum simulations
  o Seem reasonable
  o Must be mined for more physical insight
  o Next 3 months: finalize analysis of MD results

• GW part in OpenAtom: scaling greatly improved on BW ready for public release