Discontinuous methods for massively parallel quantum molecular dynamics:
Lithium ion interface dynamics from first principles

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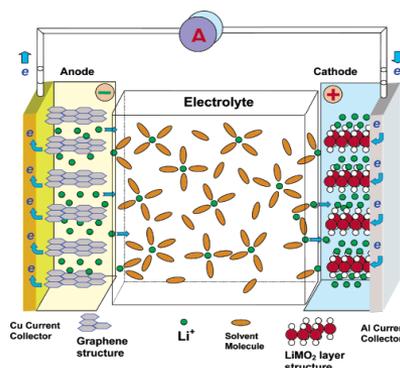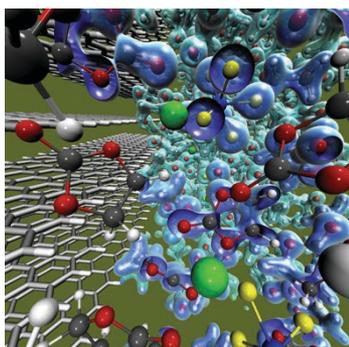
Erik Draeger, Timo Bremer, Harsh Bhatia**
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**SciDAC SDAV Institute

Overview

- Li-ion batteries have revolutionized consumer electronics and have the potential to do the same for transportation (e.g., plug-in hybrids, all-electrics, aircraft) and electrical distribution (e.g., load leveling, Tesla Powerwall)

- To do so, energy/power density, lifetime, safety must be increased

- Key issue: **solid-electrolyte interphase** (**SEI**) layer at anode-electrolyte interface, product of electrolyte decomposition

- Understanding has been hindered by need for both quantum mechanical description and sufficiently large length/time scales to capture necessary complexity

- In this work, we:

  – *Develop* new **Discontinuous Galerkin (DG)** based electronic structure method to accomplish quantum molecular dynamics (QMD) on an unprecedented scale

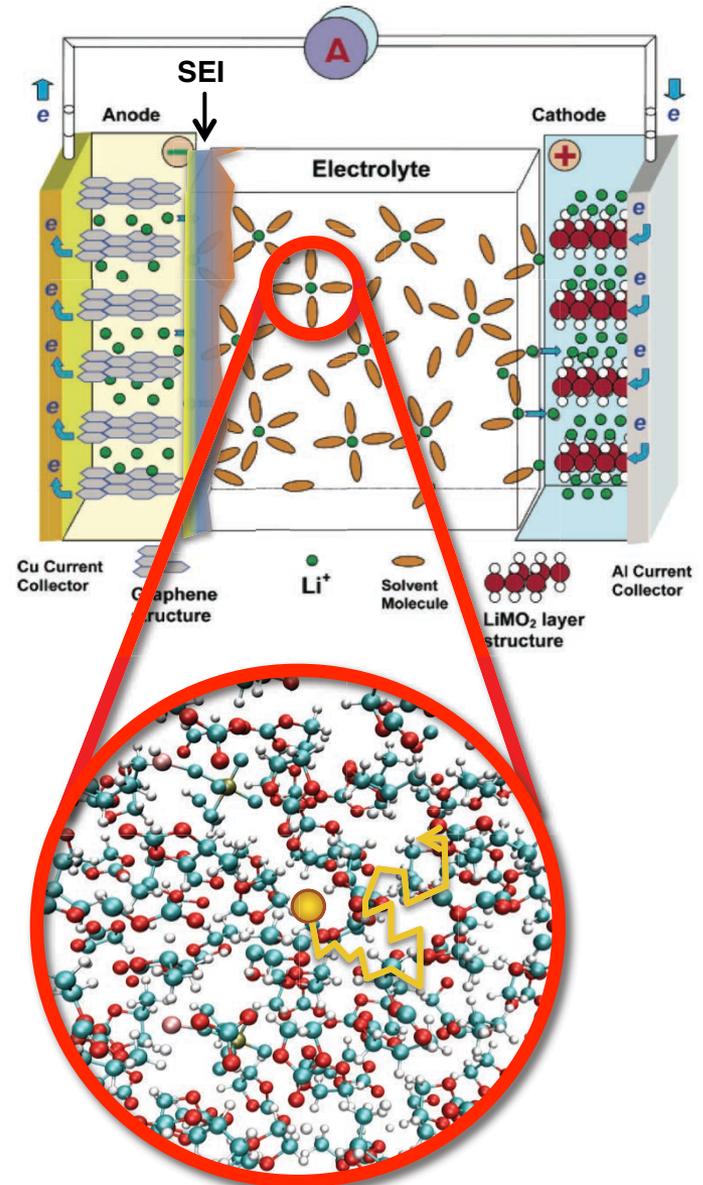 – *Apply* new method to advance understanding of the **chemistry & dynamics of electrolyte/SEI/anode systems**
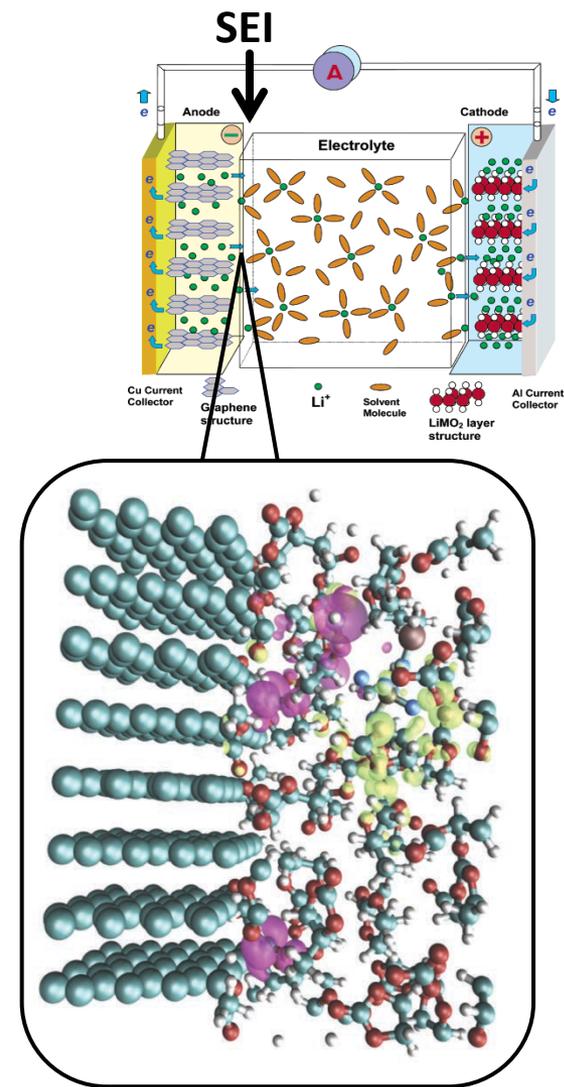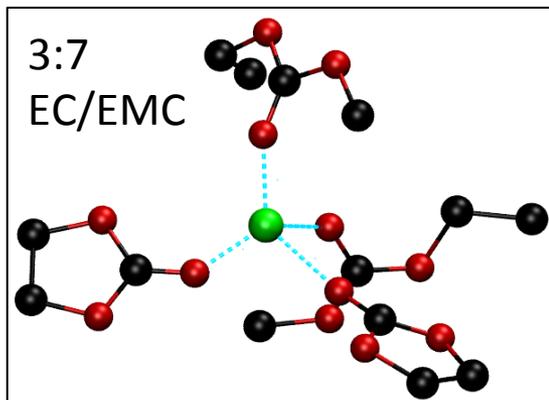

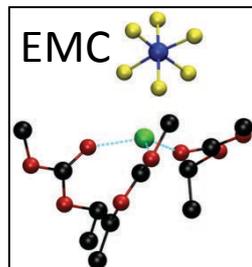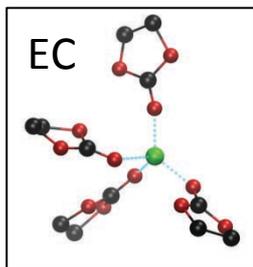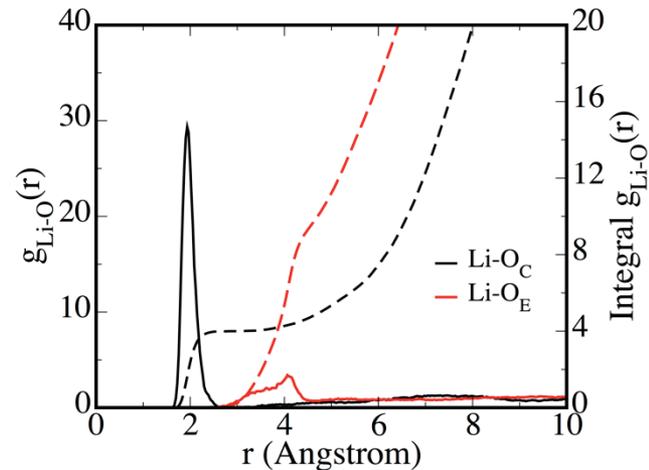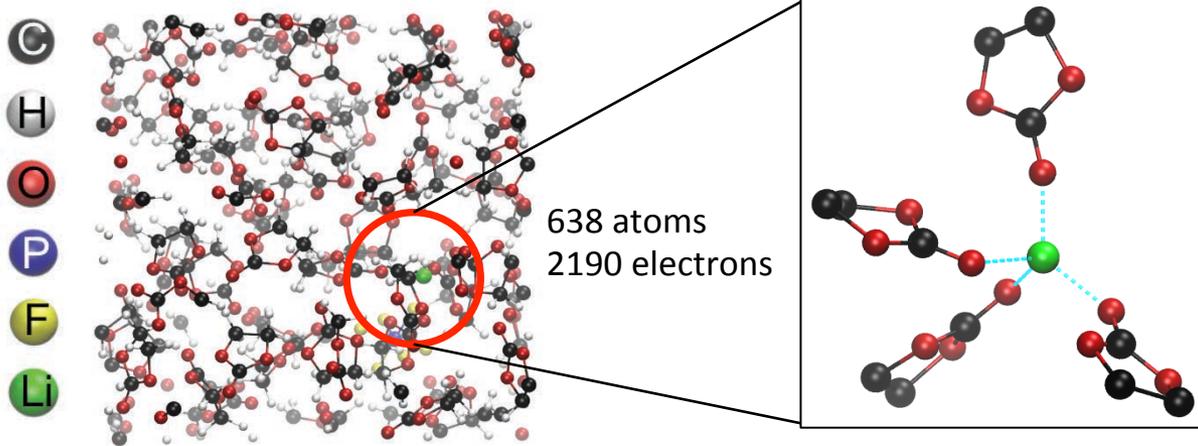QMD snapshot of SEI layer in Li-ion cell

Simulations

- Initial phase of project, while new DG/PEXSI code is developed and optimized: **Qbox** [1] for systems of < 2,000 atoms

- Li$^+$ solvation and diffusion: determine diffusion coefficients, effect of counter-ion, differences in bulk vs near interface

Molecular dynamics simulation of 50/50 ethylene carbonate/propylene carbonate electrolyte

[Adapted from K. Xu, *Chem. Rev.* **104**, 4303 (2004)]

[1] Gygi, Draeger, et al., Proc. ACM/IEEE Supercomputing '06; Gygi, IBM J. Res. Dev., 2008

Ion solvation

638 atoms
2190 electrons

C H O P F Li

EC

EMC

3:7
EC/EMC

- Li$^+$ prefers tetrahedrally-coordinated first solvation shell

- Stronger solvation for Li$^+$ than PF$_6^-$

- Mixture shows preference for Li$^+$ to be solvated by EC over EMC

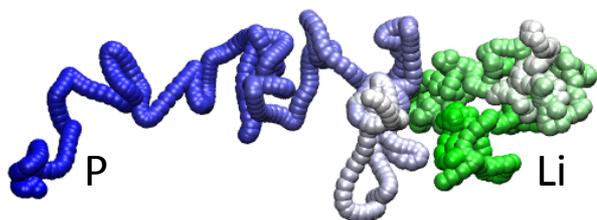- PF$_6^-$ more mobile than Li$^+$ due to weaker solvation

Ong, Verners, Draeger, van Duin, Lordi, Pask, J. Phys. Chem. B, 2015

Ion diffusion

Ethylene Carbonate (EC)

P   Li
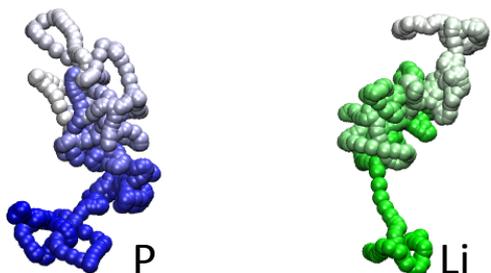
	D_{Li} (10^{-6} cm^2/s)	D_P (10^{-6} cm^2/s)
EC	5.2 ± 0.8	7.1 ± 0.9
EMC	**9.6 ± 1.6**	**30.8 ± 8.8**
3:7 EC/EMC	2.6 ± 1.3	5.7 ± 2.4

**Ethyl Methyl Carbonate (EMC)**

P   Li

3:7 EC/EMC Mixture

Li   P

- Smallest diffusion coefficients in systems with strongest ion solvation

- EC/EMC mixture shows similar behavior to pure EC due to preference for solvation by EC

- Faster diffusion for Li$^+$ seen in EMC than EC

- PF$_6^-$ has larger diffusion coefficient than Li$^+$ since Li$^+$ is more strongly solvated than PF$_6^-$

- **Size of coefficient tied to solvation structure**

Ong, Verners, Draeger, van Duin, Lordi, Pask, J. Phys. Chem. B, 2015

Anode/electrolyte interface
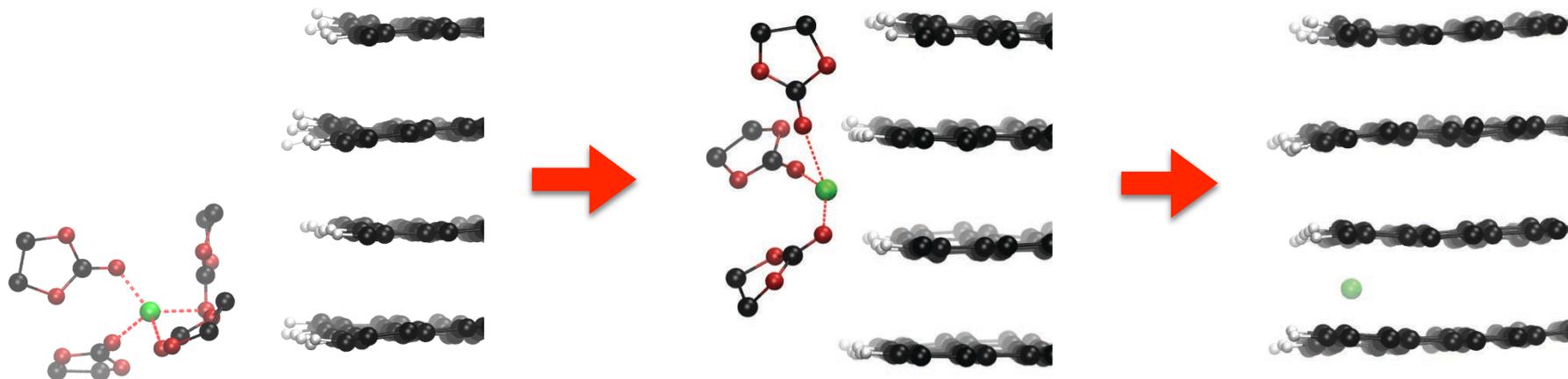
Li⁺ sheds first solvation shell to intercalate into graphite
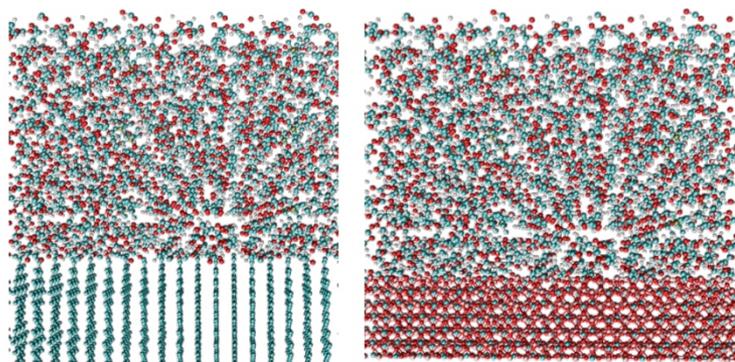
Example **anode/electrolyte (left)** and **SEI/ electrolyte (right)** systems of ~10,000 atoms to study initial SEI formation and growth

- Kinetics and solvation of Li⁺ intercalation into graphite with different edge terminations

- Use **Qbox** to study smaller interface systems (~1400-2000 atoms)

- Use new **DG-PEXSI** QMD code to study larger interface systems (~10,000 atoms)

- Apply constant bias potential using ESM method in Qbox and DG-PEXSI

Anode/electrolyte interface

- Graphite anode / ethylene carbonate (EC) electrolyte

  - 120 EC molecules + 8 $LiPF_6$ (1M)

  - 2,014 atoms (7,164 valence e^-)

  - Armchair graphite with H or H/OH surface termination; lithiated vs. delithiated

  - With electric field and without

- ReaxFF classical force field for up to 1ns, checked by Qbox DFT for few ps

- **Simulations show insertion barrier for Li into graphite, particularly when OH terminated**

graphite

1 M $LiPF_6$ in EC

graphite

H term.

OH/H term.

33 Å

13 Å

PF_6

EC
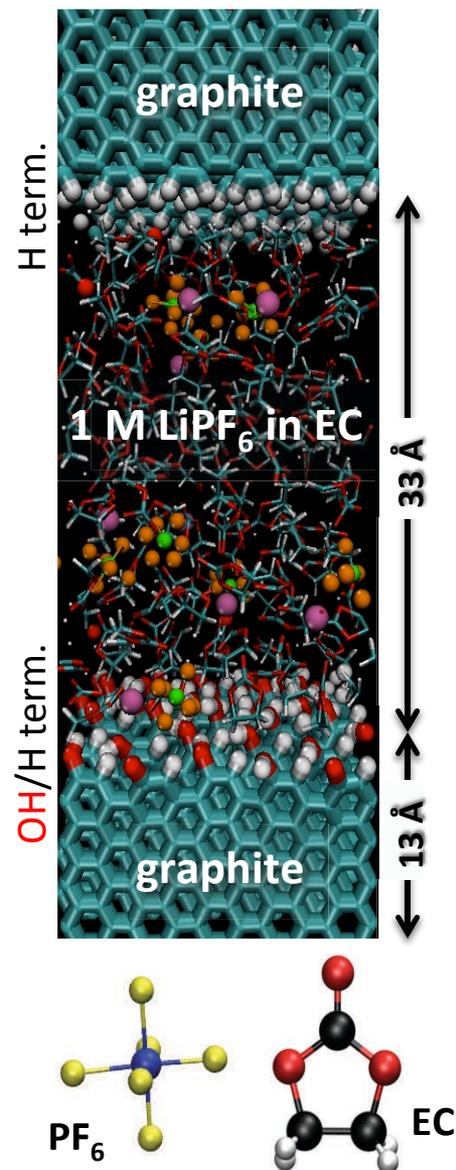
How to reach the needed length and time scales?

Throw off the shackles of continuity.

Rethink the need for eigenfunctions.

Quantum molecular dynamics (QMD)

- Solve Kohn-Sham equations for electronic structure, compute quantum mechanical forces, move atoms, repeat – thousands to hundreds of thousand of times

Kohn-Sham equations

$$-\tfrac{1}{2}\nabla^2 \psi_i(\mathbf{x}) + \hat{V}_{eff}\psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x}),$$

$$\hat{V}_{eff} = V_I^\ell + \hat{V}_I^{n\ell} + V_H + V_{xc}, \quad \text{(Schrödinger)}$$

$$V_I^\ell = \sum_a V_{I,a}(\mathbf{x}),$$

$$\hat{V}_I^{n\ell}\psi_i = \sum_a \int d\mathbf{x}' V_{I,a}^{n\ell}(\mathbf{x},\mathbf{x}')\psi_i(\mathbf{x}'),$$
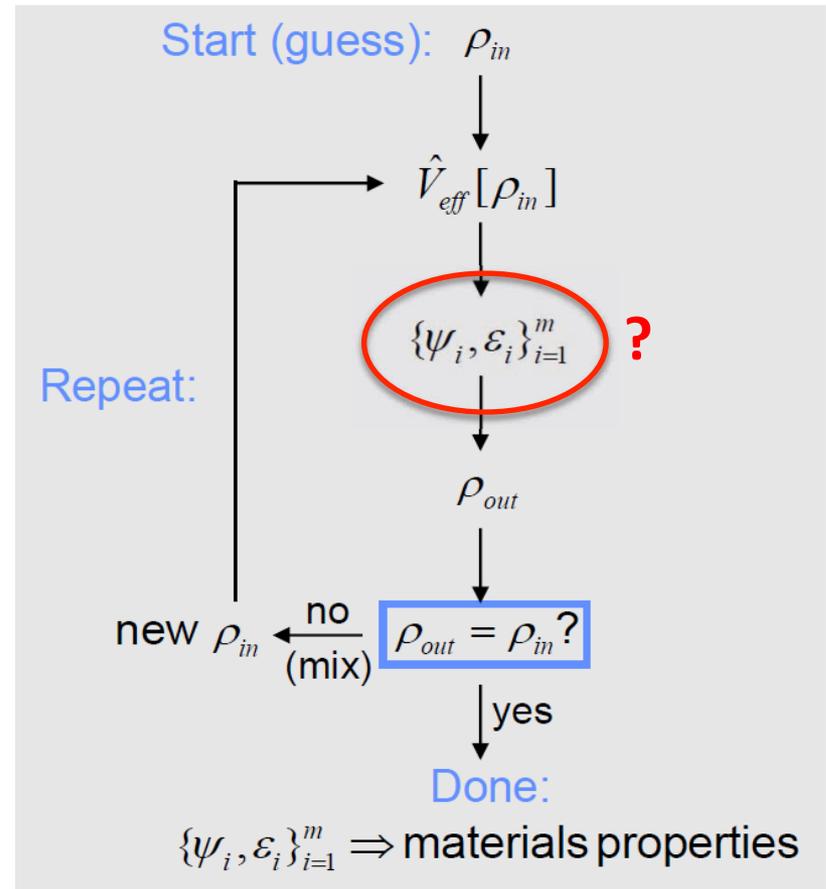
$$V_H = -\int d\mathbf{x}' \frac{\rho_e(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}, \quad \text{(Poisson)}$$

$$V_{xc} = V_{xc}(\mathbf{x};\rho_e),$$

$$\rho_e = -\sum_i f_i \psi_i^*(\mathbf{x})\psi_i(\mathbf{x}),$$

~ 10^4 atoms, more eigenfunctions

Self-consistent field (SCF) solution process

Start (guess): ρ_{in}

$\hat{V}_{eff}[\rho_{in}]$

$\{\psi_i,\varepsilon_i\}_{i=1}^m$ **?**

Repeat:

ρ_{out}

new ρ_{in} $\xleftarrow[\text{(mix)}]{\text{no}}$ $\rho_{out} = \rho_{in}$?

yes

Done:
$\{\psi_i,\varepsilon_i\}_{i=1}^m \Rightarrow$ materials properties

Pushing the current state of the art: Qbox application and development

- Strong scaling to **65,536 cores** on BG/Q

  - Uses hardware threading & SIMD registers on BG/Q

  - Optimized BLAS/ScaLAPACK kernels on BG/Q

  - Preconditioned steepest descent for occupied subspace

- **→ 1,700-atom anode-electrolyte system in 40 sec per QMD step**

- Up to 2,014-atom anode-electrolyte systems presently: 79 sec per MD step on 64k cores
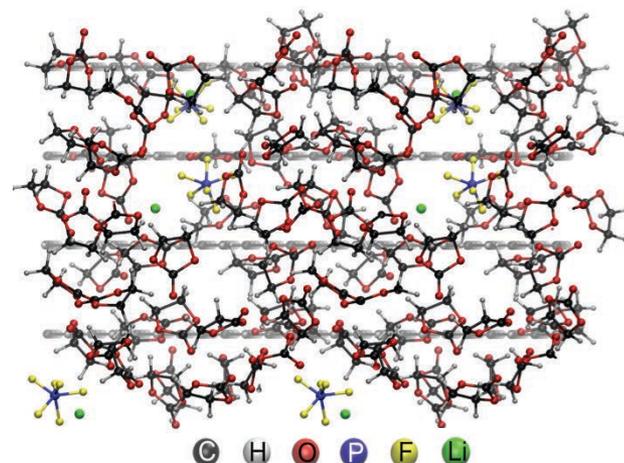

1700-atom anode-electrolyte cell
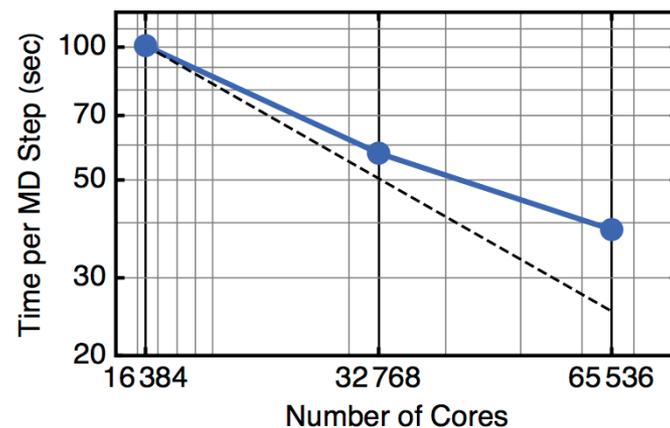
Qbox strong scaling on BG/Q

Current focus: Eigensolver

- Metallic calculations rely on diagonalization in the occupied subspace (Rayleigh-Ritz)

- Limits both efficiency (N^3) and parallel scaling

- In collaboration with **FASTMath**, we are investigating alternatives to minimize or eliminate Rayleigh-Ritz entirely

  - **Trace penalty minimization**: minimize trace of Rayleigh quotient and penalty term to enforce orthogonality [1]

  - **Projected Preconditioned Conjugate Gradient (PPCG)**: Replace $3m$ x $3m$ Rayleigh-Ritz with m 3x3 ones [2]

  - PPCG now implemented in Quantum Espresso (QE) and Qbox parallel planewave codes

  - **2x speedup** and potentially superior parallel scalability relative to current state-of-the-art Davidson solver in **QE**

  - **2x speedup** on metallic systems relative to current optimized PSDA solver in **Qbox**.

- **Goal: Metallic as fast as insulating, 2,000-atom metallic QMD**

1600 gold atoms (16384 orbitals)

SCF convergence of Al108 (120 cores on Edison)
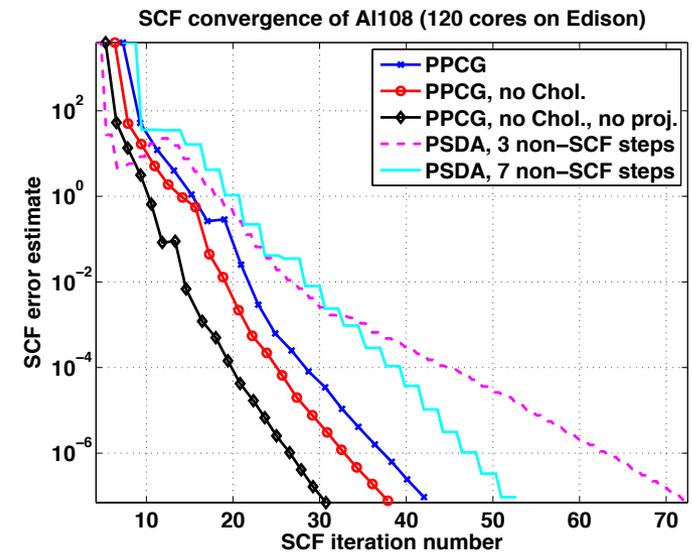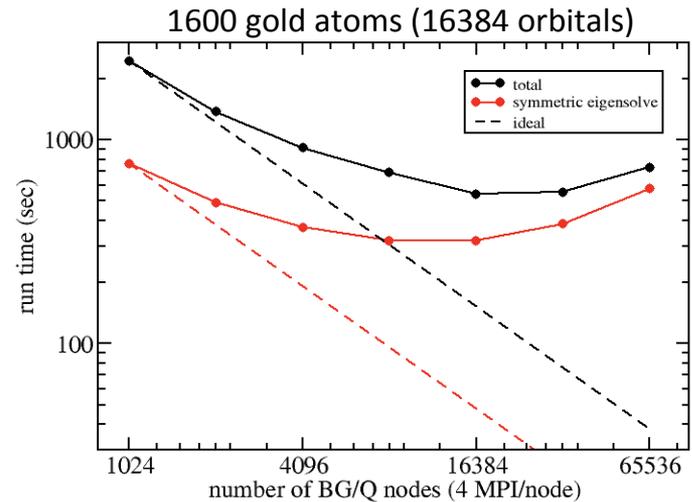
[1] Wen, Yang, Liu, Zhang, J. Sci. Comp., in press
[2] Vecharynski, Yang, Pask, J. Comp. Phys., 2015

Moving beyond the current state of the art: DGDFT

- DG framework allows solving the Kohn-Sham equations in a discontinuous basis

- Because basis can be discontinuous, can possess number of desirable properties simultaneously:

  - **Efficient** (few tens of DOF/atom)

  - **Systematically improvable**

  - **Strictly local:** identically zero outside prescribed subdomain, zero overlap across subdomains

  - **Orthonormal:** standard eigenproblem, well-cond.

- How?

  - Partition domain into subdomains (elements)

  - Solve Kohn-Sham equations in each (extended) element

  - Basis is union of local Kohn-Sham solutions
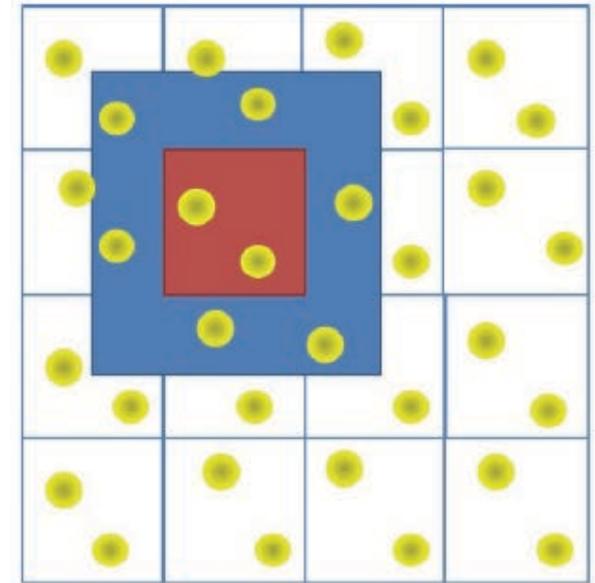
Solve large N-atom problem in highly efficient basis of O(N) local Kohn-Sham solutions

Lin, Lu, Ying, E, JCP **231**, 2140, 2012

DG method

- Discontinuity is accommodated by surface ("flux") terms [1 - 4]

- Kohn-Sham Hamiltonian becomes

$$H_{DG}(k', j'; k, j) = \frac{1}{2} \langle \nabla u_{k',j'}, \nabla u_{k,j} \rangle_{\mathcal{T}} + \alpha \langle [[u_{k',j'}]], [[u_{k,j}]] \rangle_{\mathcal{S}} - \frac{1}{2} \langle [[u_{k',j'}]], \{\{\nabla u_{k,j}\}\} \rangle_{\mathcal{S}}$$

$$- \frac{1}{2} \langle \{\{\nabla u_{k',j'}\}\}, [[u_{k,j}]] \rangle_{\mathcal{S}} + \langle u_{k',j'}, V_{\text{eff}} u_{k,j} \rangle_{\mathcal{T}} + \sum_{\ell} \gamma_\ell \langle u_{k',j'}, b_\ell \rangle_{\mathcal{T}} \langle b_\ell, u_{k,j} \rangle_{\mathcal{T}}$$

$\mathcal{T} = $ elements
$\mathcal{S} = $ element surfaces
$u_{k,j} = j$th basis function in kth element
$\{\{\cdot\}\}$ and $[[\cdot]] = $ average and jump operators across surfaces

- Kohn-Sham equations: $H_{DG} c_i = \varepsilon_i c_i$

- Wavefunctions: $\displaystyle \psi_i = \sum_{E_k \in \mathcal{T}} \sum_{j=1}^{J_k} c_{i;k,j} u_{k,j}$

- Density: $\displaystyle \rho = \sum_{E_k \in \mathcal{T}} \sum_{i=1}^{N} | \sum_{j=1}^{J_k} c_{i;k,j} u_{k,j} |^2$

- Energy: $\displaystyle E_{\text{tot}} = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} \, \mathrm{d}x \, \mathrm{d}y + \int \epsilon_{\text{xc}}[\rho(x)] \, \mathrm{d}x - \int \epsilon'_{\text{xc}}[\rho(x)]\rho(x) \, \mathrm{d}x$

[1] Lin, Lu, Ying, E, JCP 231, 2140, 2012; [2] Lin, Lu, Ying, E, JCP 231, 4515, 2012; [3] Lin, Ying, PRB 2012; [4] Lin, Stamm, submitted.
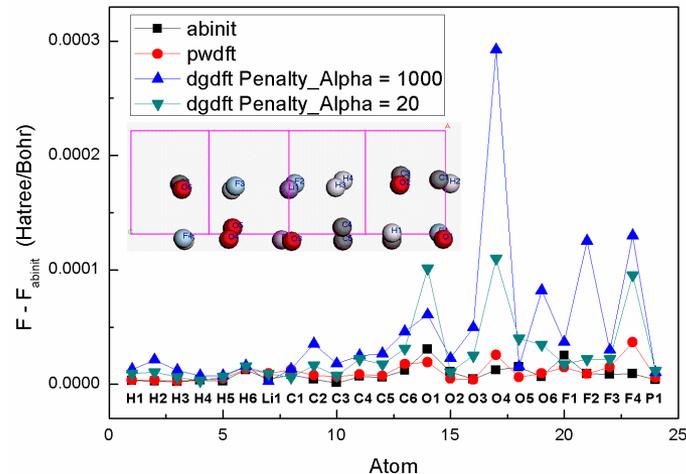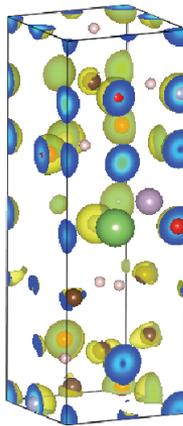
Energies, forces, degrees of freedom

- Energies to **< 1e-3 Ha/atom,** forces to **< 1e-3 Ha/au** *absolute* error with **~10 basis funcs/atom**

~40 DOF/atom
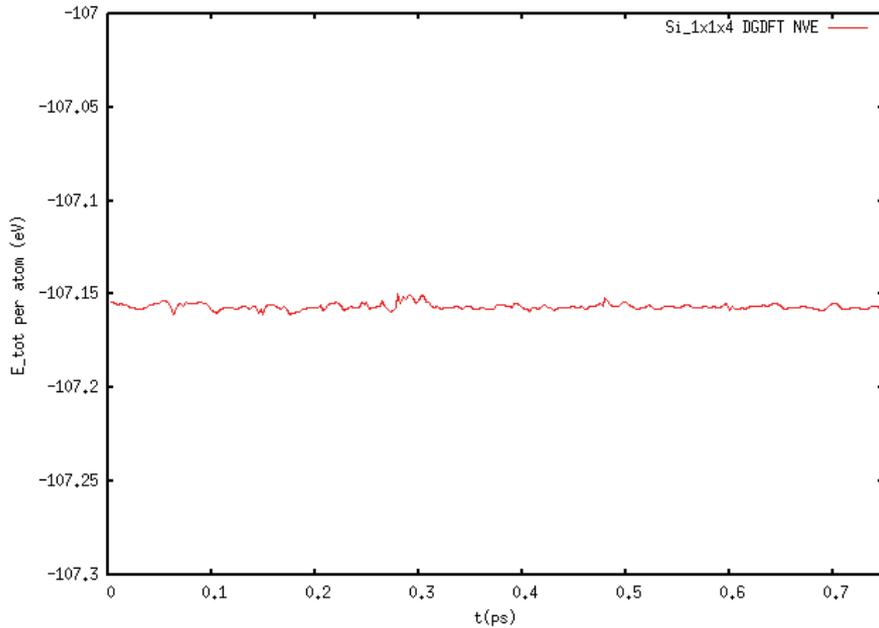for 3D

Si 1x1x4: random displacements
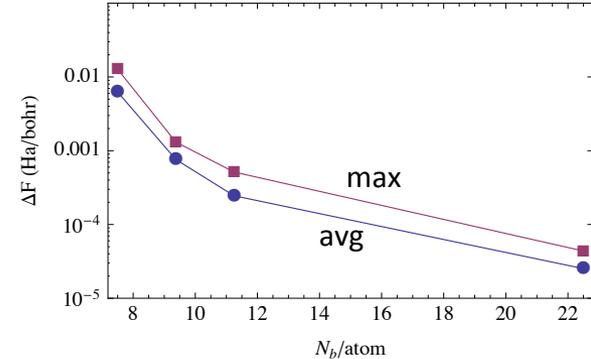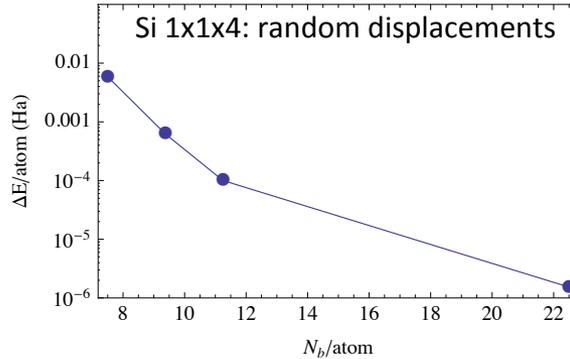
- Hard atoms: Li-ion system – Li, P, F, C, H, O

- Forces to **1e-4 Ha/au** absolute error with **15 basis funcs/atom**

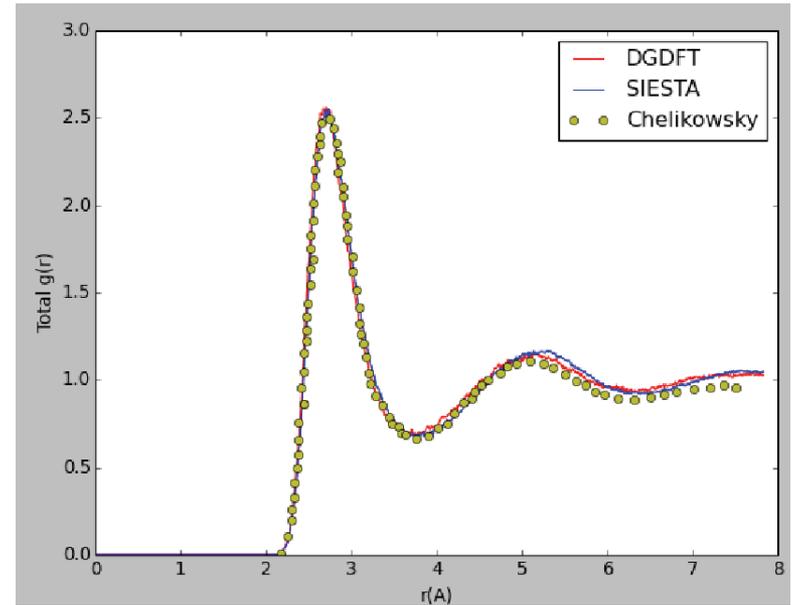- Largest system so far: **10,800 atoms** on 50,000 CPUs [1]

[1] Hu, Lin, Yang, PCCP, 2015

Molecular dynamics

NVE MD simulation of liquid Si at 3000K using DGDFT

Energy drift < 1.5 meV/atom/ps

Pair correlation for $Si_{0.12}Al_{0.88}$ alloy with 200 atoms

Agreement with previous literature and independent calculations

Zhang, Lin, Hu, Yang, Pask 2015 (in preparation)

Current focus: pseudopotentials, XC, eigensolver

- **Hartwigsen, Goedecker, Hutter (HGH) pseudopotentials** are robust and transferrable but hard, e.g., can require 2x planewave cutoff of corresponding Troullier-Martins (TM) → costly to compute ALBs

- However, HGH analytic form permits smooth, localized pseudocharge formulation [1] of local potential interaction whereas C^2-continuous TM does not

    - Construct smoother TM? Other form?

    - Separate ionic and electronic computations?

- **van der Waals density functional** to better model interface system, e.g., DFT-D2

- **ScaLAPACK eigensolver** limits system size and parallel scalability

- DG Hamiltonian matrices are sparse, well conditioned, and have limited spectral width; however, no efficient preconditioner available

- → Chebyshev filtered subspace iteration [2]

[1] Pask, Sterne, PRB 2005
[2] Zhou, Saad, Tiago, Chelikowsky, JCP 2006

For the largest systems: PEXSI

- Solving for Kohn-Sham wavefunctions of N atom system scales as O(N^3)

- Solve for density directly instead

$$\rho(x) = \text{diag}\left(f_\beta(\hat{H}[\rho(x)] - \mu\delta(x, x'))\right)$$

$\hat{H}$ = Hamiltonian, μ = chemical potential, $f_\beta(x) = 2/(1 + e^{\beta x})$
$\beta = 1/k_B T$, k_B = Boltzmann constant, T = temperature

- Need efficient approximation of Fermi function → **Pole expansion** [1]

$$f_\beta(\varepsilon - \mu) \approx \Im \sum_{l=1}^{P} \frac{\omega_l^\rho}{\varepsilon - (z_l + \mu)}$$

$z_l, \omega_l^\rho \in \mathbb{C}$ are complex shifts and weights

- Need efficient inversion

- Need only diagonal → **Selected Inversion** [2]

- → **Pole Expansion and Selected Inversion (PEXSI)**

- **No need to compute eigenfunctions or eigenvalues**

- Scaling O(N) for quasi-1D systems; **O(N^2) for metallic 3D**

[1] Lin, Lu, Ying, E, 2009; [2] Lin, Yang, Meza, Lu, Ying, E, 2011
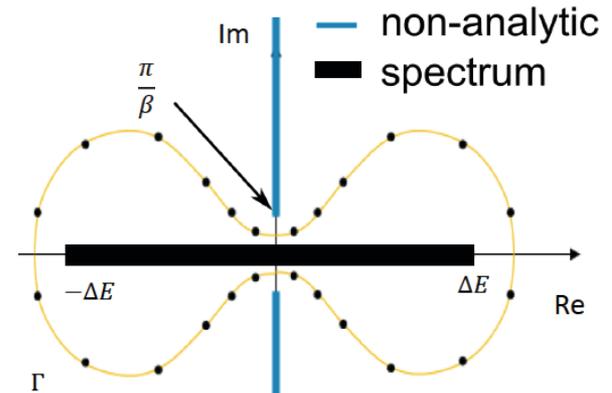
Energies, forces, poles

- Metallic carbon nanotube, CNT (8,8), 512 atoms, atomic orbital basis [1]
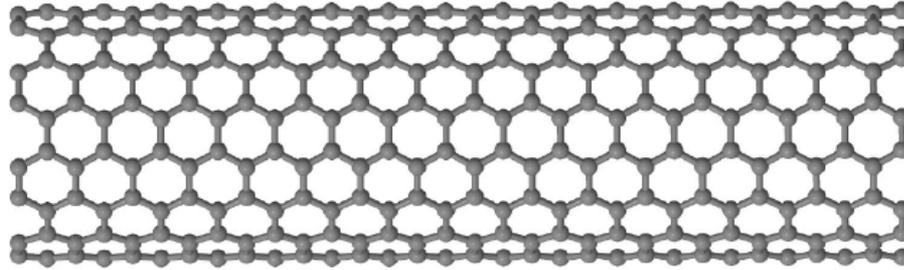
- Accuracy of expansion at T = 300K

# Poles	$E_{PEpSI} - E_{ref}$ (eV)	MAE Force (eV/Angstrom)
20	5.868351108	0.400431
40	0.007370583	0.001142
60	0.000110382	0.000026
80	0.000000360	0.000002

- Largest 3D system so far: **24,000-atom** water using SIESTA DZP basis [2]
  - **314 sec** SCF iteration on 10,240 cores
  - **30-fold speedup** relative to diagonalization

[1] Lin, Chen, Yang, He, J. Phys.: Cond. Mat., 2013
[2] Lin, Garcia, Huhs, Yang, J. Phys.: Cond. Mat., 2014

PEXSI released, integrated into standard codes

The PEXSI library is available online
http://pexsi.org/, BSD license

- Integrated with **SIESTA** and **CP2K** for accelerating atomic-orbital based calculations

- Massively parallel to **10,000 – 100,000 processors** on high performance computers

M. Jacquelin, L. Lin and C. Yang, ACM TOMS, in press 2015

DG+PEXSI: parallelization, scaling

- DG: 2-level parallelization
  - Elements → ~10,000
  - Intra-element → up to ~300 cores per element
- PEXSI: 2-level parallelization
  - Poles → 40--80
  - LU/SelInv → up to ~2000 cores per pole
- DG+PEXSI: over **100,000 cores**

- **Large-scale calculations: 2D Phosphorene**
- P3500, P14000: **3,500**- and **14,000**-atom layers
- T = 300K
- 40 x 40 and 80 x 80 element partition
- ~36 ALB/atom → Energy and force errors <1e-3 Ha/atom and <1e-3 Ha/bohr, resp.
- PEXSI: 50 poles
- P3500: **~45 sec/SCF on ~100,000 cpu** (LBL Edison)

Hu, Lin, Yang, 2015, arXiv:1506.08147
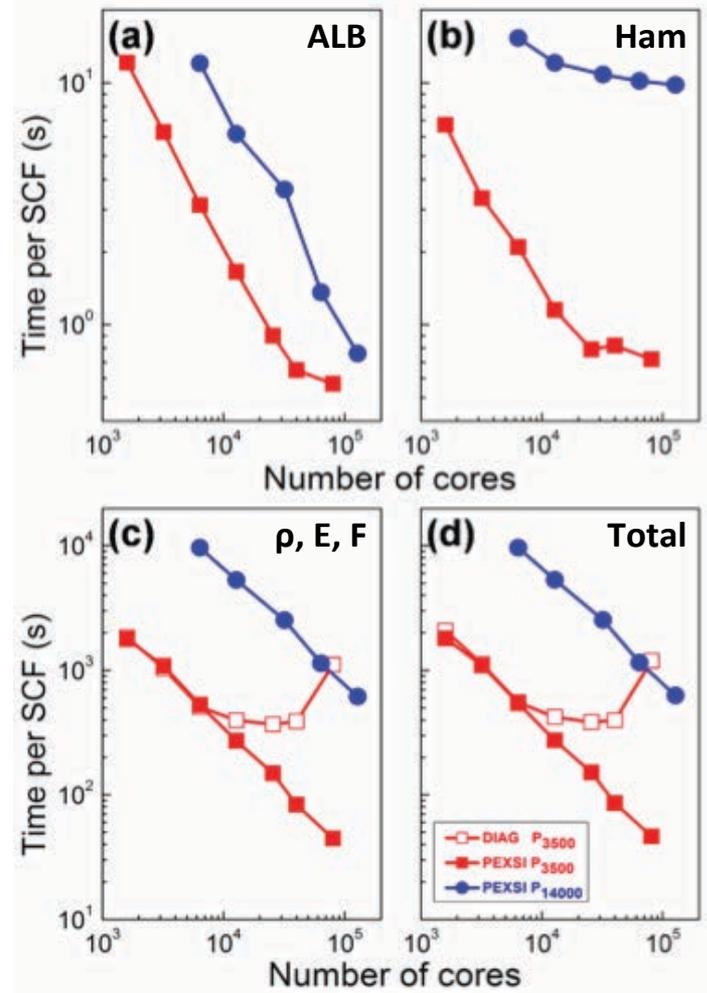
DG+PEXSI: Li-ion anode-electrolyte interface
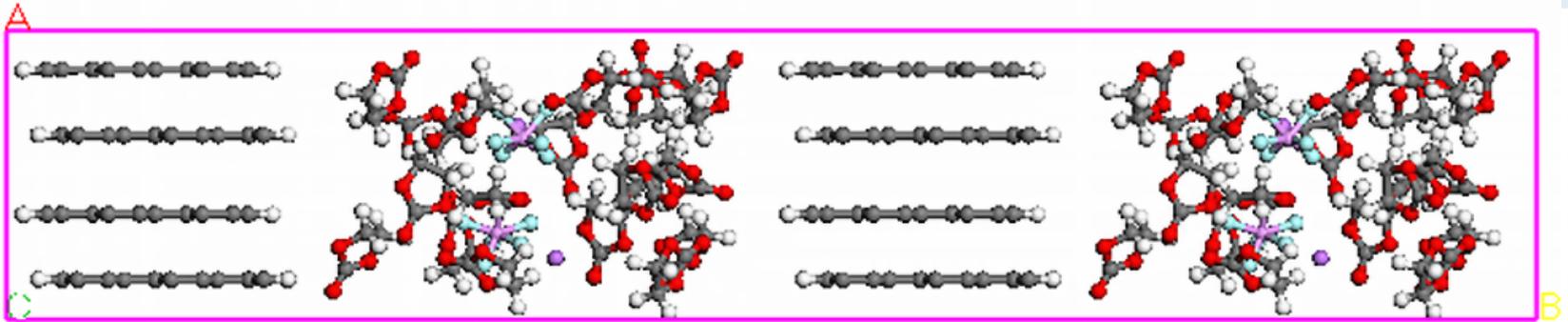
- **4,720-atom Li-ion anode-electrolyte interface** (graphite, EC, LiPF$_6$)

- T = 300K

- 1 x 30 x 30 2D element partition

- 60 Hartree energy cutoff for DG basis

  – 1e-4 Ha/atom energy error

  – 1e-3 Ha/Bohr force error

- 22 DG basis functions/atom

- PEXSI: 50 poles

- **~30 sec/SCF on 10,800 cpu** (LBL Edison)
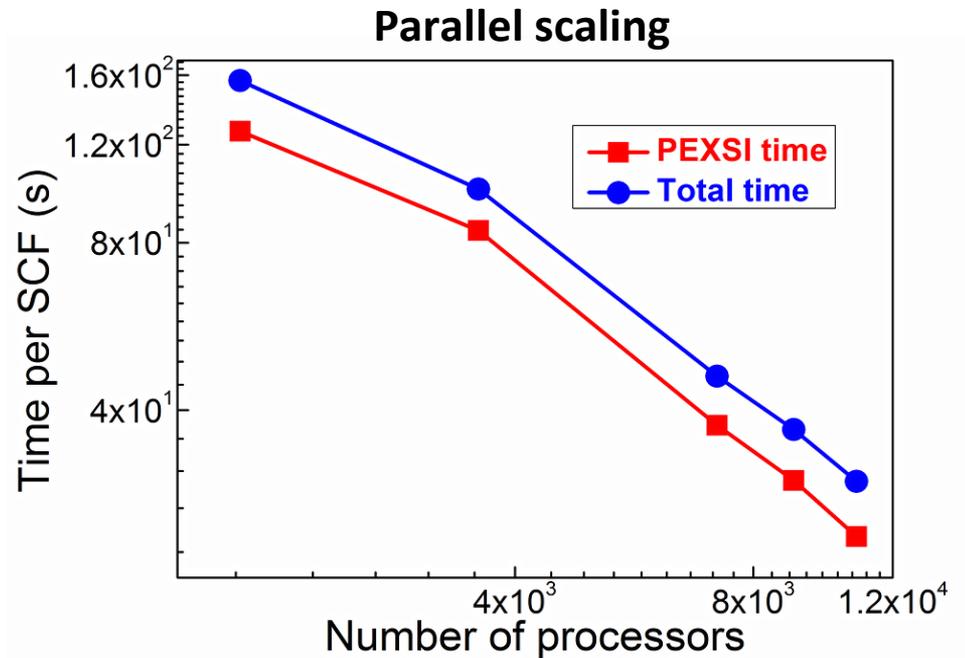
Parallel scaling

Current focus: factorization

- Parallel scaling of *LU* factorization

- By pipelining and overlapping communication with computation, SelInv now faster and better scaling than SuperLU_DIST

- SuperLU_DIST scales to only ~1000 CPU

- In collaboration with **FASTMath**, we are exploring alternatives for better scaling sparse direct factorization

  - More robust symbolic factorization

  - New symmetric factorization code under development: exploring block fan-both method and dynamic task scheduling for better parallel scaling

  - Leverage results of previous SCF iteration: previous *H*, *LU*?

- To get SCF step times down *further* for 3D systems may require *iterative methods* to fully leverage information from previous SCF/MD steps

SDAV collaboration: topological analysis of quantum mechanical data

- Systematic topological analysis of quantum mechanical data: density, potential, wavefunctions

- Compute Morse-Smale complex: minima, maxima, saddle points → mountains, voids, ridges, valleys, *connectivity*

- Evolution in space and time

- Bond formation and breaking

- Voids/tunnels for Li^+ transport

- On the fly → inform/accelerate MD?

Peer-Timo Bremer & Harsh Bhatia (LLNL), Valerio Pascucci & Attila Gyulassi (University of Utah)
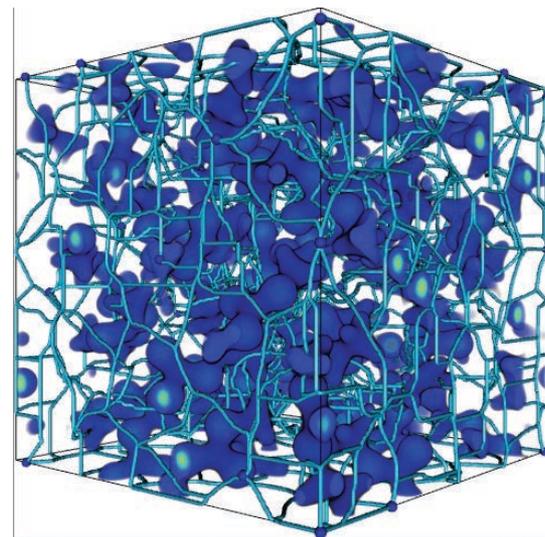
Valley lines connecting voids in QMD charge density
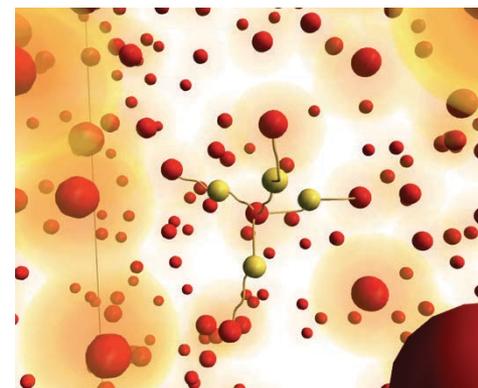
Saddle-max-saddle connections in distance field

SDAV collaboration: bond formation and breaking

- Detect Li-O bond breaking, formation, and strength from topological analysis of evolving QMD electronic charge density

- → Parameter-free bond detection, strength
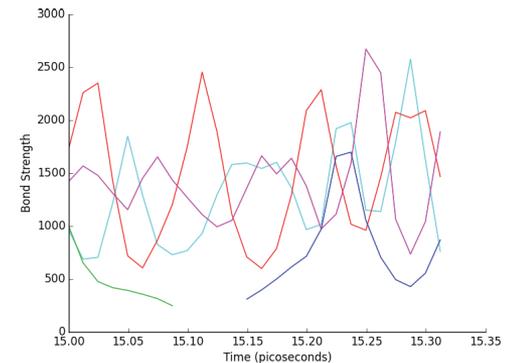

Contiguous regions of influence
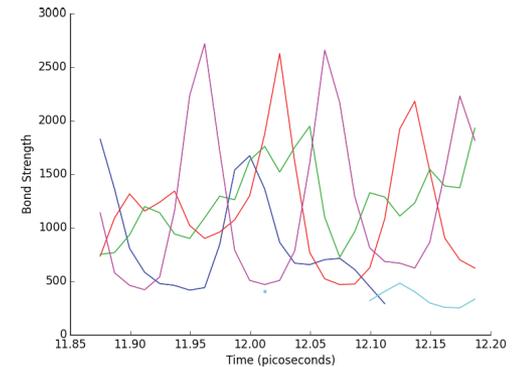

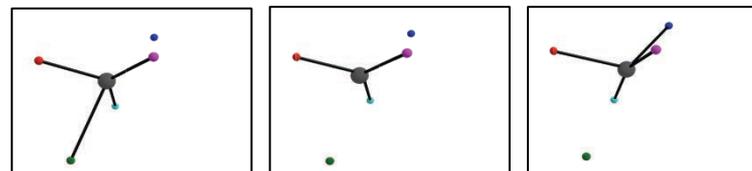QMD electronic charge density
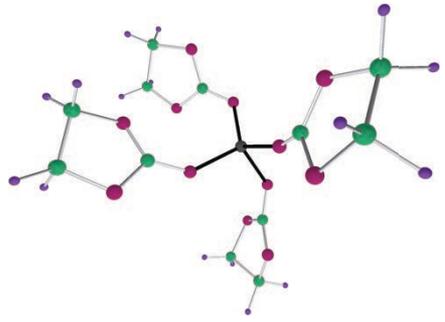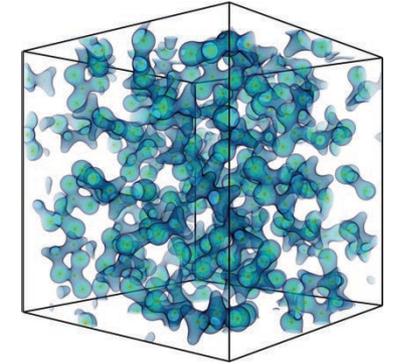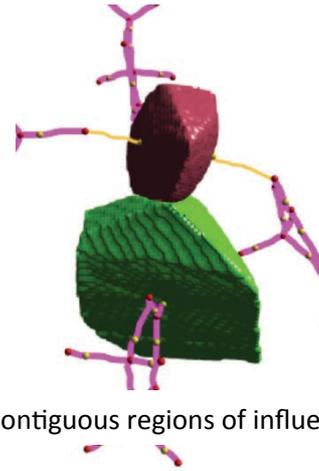
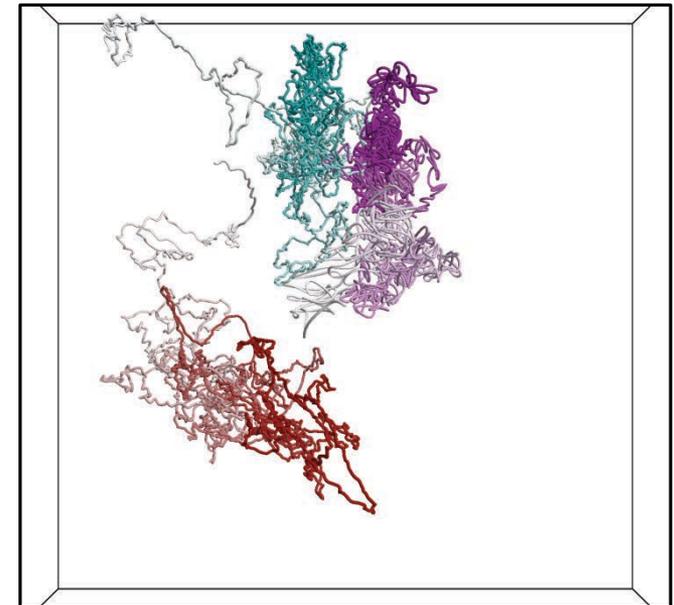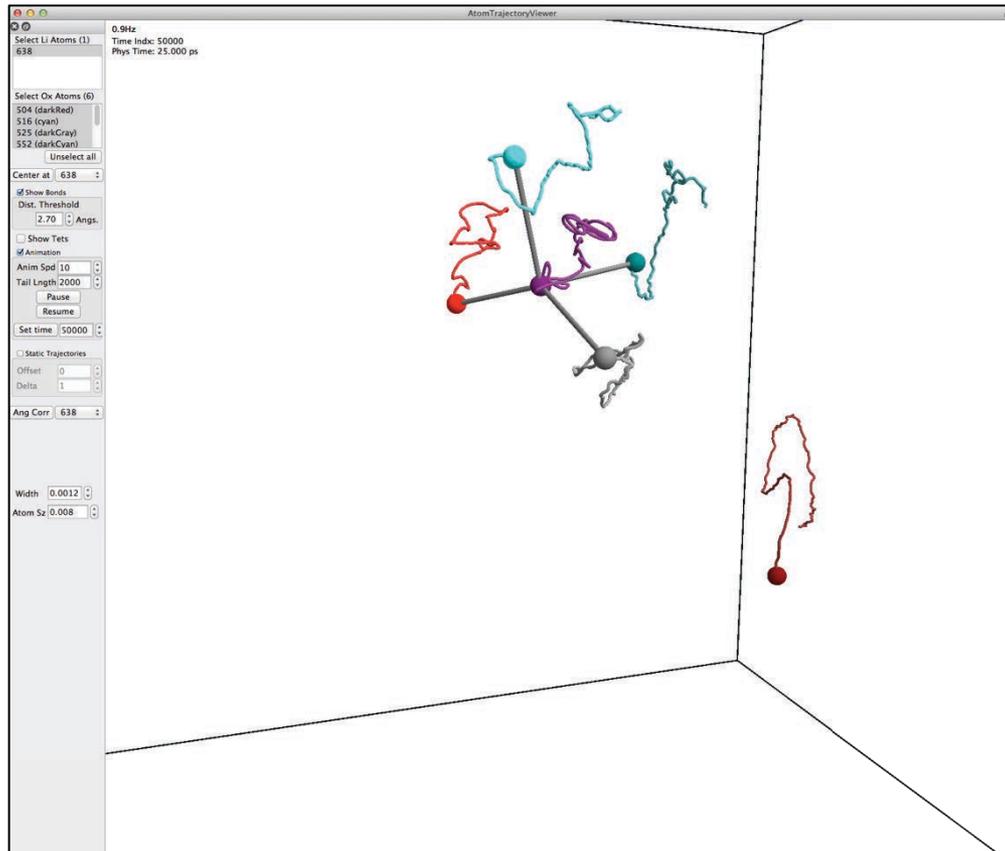Li+ bonded with 4 EC molecules

4-5-4 swap
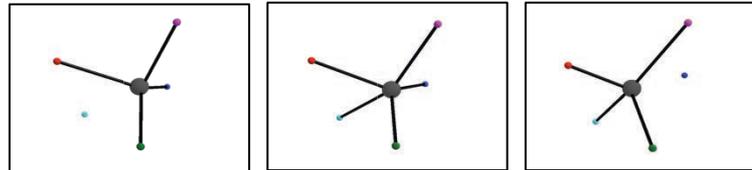
4-3-4 swap

SDAV collaboration: tools

- Building custom tools to interact with voluminous simulation data in space and time
  → see chemistry and dynamics

Trajectories of Li⁺ (magenta) and selected Oxygen atoms.

Thanks for your attention!

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