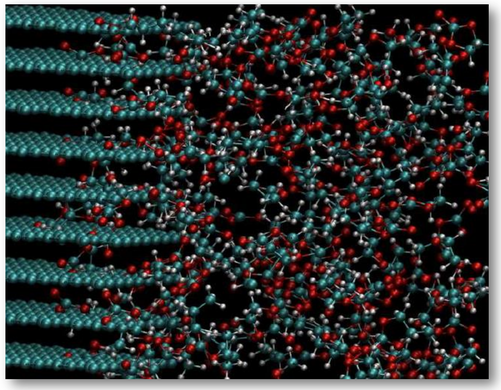
Computational techniques for accelerating quantum molecular dynamics simulations of the solid-electrolyte interface in Li-ion batteries

Chao Yang, Lin Lin, Mathias Jacquelin (LBNL) John Pask, Erik Draeger, Vince Lordi, Mitchell Ong (LLNL)

Objective

Develop fast quantum molecular dynamics (QMD) simulation tools for studying the formation and evolution of solid electrolyte interface in Li-ion battery cells



Anode-electrolyte interface in Li-ion cell

Born-Oppenheimer framework: compute electronic structure at each step to obtain energy and force required for time evolution.

Kohn-Sham Density Functional Theory

$$\left(-\frac{1}{2}\Delta + V_{ext}\left[\{R_j\}_{j=1}^{M}\right] + \int dx' \frac{\rho(x')}{|x-x'|} + V_{xc}[\rho]\right)\psi_i(x) = \varepsilon_i\psi_i(x)$$

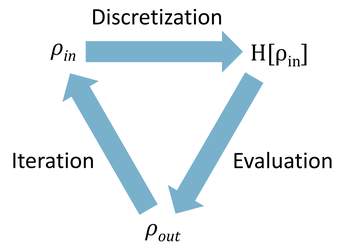
$$\rho(x) = 2\sum_{i=1}^{N/2}|\psi_i(x)|^2, \quad \int dx\, \psi_i^*(x)\psi_j(x) = \delta_{ij}$$

Energy and force

$$E_{tot}\left[\{R_j\}_{j=1}^{M}\right] = \sum_{i=1}^{N/2}\varepsilon_i - \frac{1}{2}\iint dx\, dy\, \frac{\rho(x)\rho(y)}{|x-y|} + E_{xc}[\rho(x)] - \int dx\, V_{xc}[\rho(x)]\rho(x)$$

$$F_i = -\frac{\partial E_{tot}}{\partial R_i}$$

Critical computation components

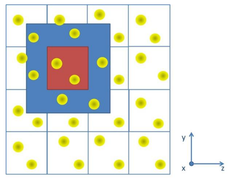


Discretization

Small to medium sized problem (up to 1000 atoms); planewave expansion (e.g. Qbox)

Large problem (10,000 atoms): Adaptive Local Basis functions in a Discontinuous Galerkin Framework (ALB-DG) to systematically reduce the number of basis functions, starting from a complete basis set such as planewaves

How to obtain the basis functions adaptively in local domains



Solve the global problem using the discontinuous Galerkin method

$$E_{DG}(\{\psi_i\}) = \frac{1}{2}\sum_{i=1}^{N}\langle\nabla\psi_i, \nabla\psi_i\rangle_{\mathcal{T}} + \langle V_{\text{eff}}, \rho\rangle_{\mathcal{T}} + \sum_{\ell}\gamma_\ell\sum_{i=1}^{N}|\langle b_\ell, \psi_i\rangle_{\mathcal{T}}|^2 \quad \leftarrow \text{Kohn-Sham}$$

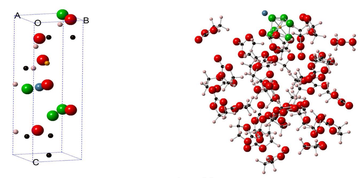
$$-\sum_{i=1}^{N}\langle\{\{\nabla\psi_i\}\}, [\![\psi_i]\!]\rangle_S + \frac{\alpha}{h}\sum_{i=1}^{N}\langle[\![\psi_i]\!], [\![\psi_i]\!]\rangle_S. \quad \leftarrow \text{New terms}$$

average and jump operators across surfaces S:

$$[\![u]\!] = u_1 n_1 + u_2 n_2 \quad \text{on } S.$$

$$\{\{q\}\} = \frac{1}{2}(q_1 + q_2) \quad \text{on } S.$$

Li test cells



Accuracy and efficiency

DOF/Element	30	60	90	120
DOF/Atom	5.6	11.3	16.9	22.5
Error (mev/atom) compared to ABINIT	2.3	4.7×10^{-3}	-0.014	-0.014
Max error (au) of force compared to ABINIT	$\mathbf{4.6 \times 10^{-4}}$	6.9×10^{-5}	6.3×10^{-5}	7.4×10^{-5}

The accuracy of energy and force for a 32-atom randomly displaced, orthorhombic LiH test cell, benchmarked with converged ABINIT result.

A new, efficient massively parallel C++ code is in development. The new code is designed to be compatible with various density evaluation solvers in the global domain (see below) and in the local domain (integration with Qbox).

Largest system so far: 4,392 atoms

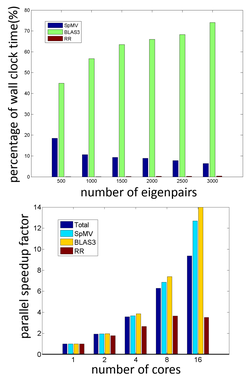
Density evaluation

Standard approach: compute Kohn-Sham eigenvalues and eigenvectors

- Qbox algorithm: block steepest descent (Davidson-Liu method)
- The Rayleigh-Ritz procedure (i.e., computing eigenvalues of a projected problem) becomes a bottleneck

Penalty trace minimization: reduce the number of Rayleigh-Ritz calculations

$$\min_X X^T AX + \mu(X^T X - I)$$



Pole expansion and selected inversion (PEXSI)

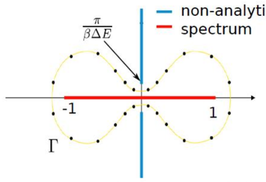
- Computing the density without diagonalizing the Hamiltonian.
- Based on a special Fermi Operator Expansion (pole expansion)

complexity

Quasi-1D $O(N)$

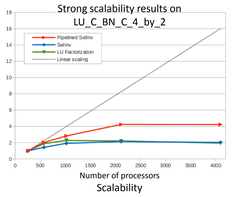
Quasi-2D $O(N^{1.5})$

3D bulk $O(N^2)$



Number of poles $\sim \log \beta\Delta E$

- Massively Parallel PEXSI can scale to tens of thousands of processors.



Parallel PEXSI (for a single pole) applied to 3-layer C-BN-C system with 20,256 atoms. The code scales to 2048 processors. With 40 poles it can scale to 81,920 cores.

# Poles	$E_{\text{PEXSI}} - E_{\text{ref}}$ (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

Accuracy of the pole expansion for a metallic CNT system at 300K, compared to the exact result obtained from LAPACK diagonalization.

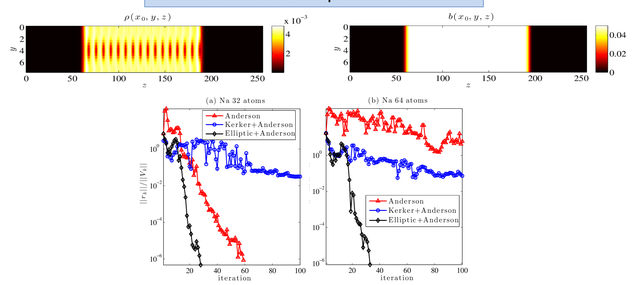
Elliptic preconditioner

- Efficient preconditioner for SCF iteration for large scale inhomogeneous systems with mixed metallic and insulating nature at low temperature.
- Simple mixing / Anderson mixing / Pulay mixing: good for insulators; exhibit "charge sloshing" for metallic systems.
- Kerker preconditioner: only applicable to homogeneous metallic systems close to uniform electron gas.
- Elliptic preconditioner:

$$A\tilde{r}_k = \left(-\nabla\cdot(a(x)\nabla) + 4\pi b(x)\right)\tilde{r}_k = -\Delta r_k$$

- $a(x)$, $b(x)$ can be spatially dependent for metal + insulator. Standard method to achieve $O(N)$ scaling for elliptic preconditioner: Multigrid, FMM, H-matrix, HSS etc.
- Applicable to DGDFT and Qbox to reduce SCF iterations.

32-atom sodium bar placed in vacuum



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