Computational techniques for accelerating quantum molecular dynamics simulation of the solid electrolyte interface (SEI) in Li-ion batteries

DGDFT Collaboration

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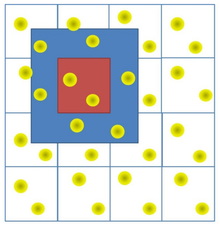
Discontinuous Galerkin Method: Overview



Idea for discretization:

- Solve basis functions adaptively in the local domain
- Solve the global problem using the Discontinuous Galerkin method
- Results in highly efficient, strictly local, systematically improvable, well conditioned basis

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

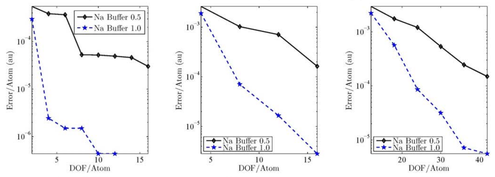
$$-\sum_{i=1}^{N}\langle\{\{\nabla\psi_i\}\},[\![\psi_i]\!]\rangle_{\mathcal{S}}+\frac{\alpha}{h}\sum_{i=1}^{N}\langle[\![\psi_i]\!],[\![\psi_i]\!]\rangle_{\mathcal{S}}. \quad \Leftarrow \text{New terms}$$

average and jump operators across surfaces S:

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

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

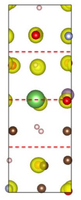
Previously established accuracy for energy calculation (for Na)



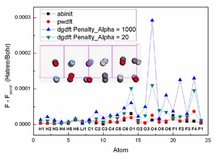
1e-3 Hartree/atom accuracy with < 15 basis functions/atom

Accuracy of Force; Pulay force

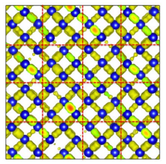
- Compare the accuracy of the Hellman-Feynman force to converged planewave reference (using ABINIT)
- Pulay force: force caused by the dependence of basis functions on the atomic positions



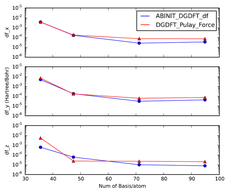
LiHCOFP-24



Accuracy of force,2e-4 Hartree/Bohr with 15 ALB per atom



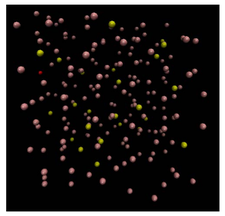
Disordered Si-216



Pulay force comparable to the total error of the force

1e-3 Hartree/Bohr accuracy with ~40 basis functions/atom

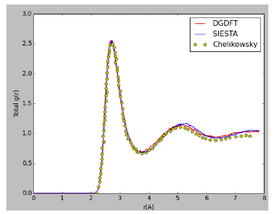
Molecular Dynamics



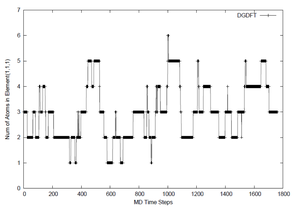
$Si_{0.12}Al_{0.88}$ alloy with 200 atoms

Parameters taken from [Ko-Chan-Kim-Chelikowsky, 2011]

- Temperature: 973K
- Nose-Hoover thermostat
- 51 basis per atom, 4x4x4 element partition
- $\Delta t = 2.4\ fs$
- $E_{cut} = 10\ au$
- Also compare with SIESTA.



Total pair correlation function



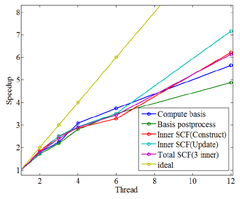
The number of atoms in the (1,1,1) element along the MD trajectory.

OpenMP/MPI Parallelization

The inter-element parallelization has been done using MPI, with a rather general data structure for data communication and converting matrices to different formats (DG native, ScaLAPACK, PEXSI, Fourier, etc.)

Intra-element parallelization: Reduce the computational time for generating the adaptive local basis functions in the local element, and the time for constructing the DG Hamiltonian matrix.

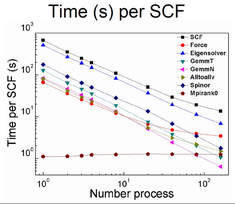
- OpenMP level (already used for MD simulation, etc.) Compatible with next generation architecture



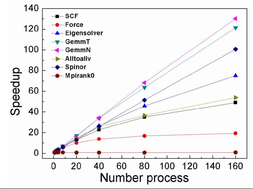
Total SCF time reduced from 180.2 sec (OMP=1) to 29.4 sec (OMP=12)

- MPI level: Initial work for PWDFT: Can use more than 160 cores with 70 fold speedup for generating the basis.

Time (s) per SCF



Speedup



A Posteriori Error Estimator

A posteriori error estimator:

- Measuring the accuracy of eigenvalues and densities without performing an expensive converged calculation, or benchmarking with another code.
- Optimal non-uniform allocation of basis functions for inhomogeneous systems.

$$\eta_{i,R_K}^2 = \gamma_1(J_K)\left\|\left(-\frac{1}{2}\Delta+V_{\text{eff}}-\varepsilon_{i,\mathcal{J}}\right)u_{i,\mathcal{J}}\right\|_K^2 \qquad \eta_{i,K}^2 = \eta_{i,R_K}^2+\eta_{i,G_K}^2+\eta_{i,V_K}^2$$

$$\eta_{i,G_K}^2 = \frac{1}{4}\sum_{F\subset\partial K}\gamma_2(J_F)\left\|[\![\nabla u_{i,\mathcal{J}}]\!]\right\|_F^2$$

$$\eta_{i,V_K}^2 = \frac{1}{4}\sum_{F\subset\partial K}\gamma_2(J_F)\alpha^2(J_F)\left\|[\![u_{i,\mathcal{J}}]\!]\right\|_F^2. \qquad \eta_i^2 = \sum_{K\in\mathcal{T}}\eta_{i,K}^2$$

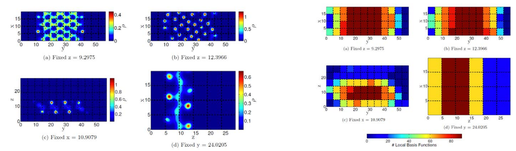
Measure the error in the energy norm

$$\|u\|_{E,\mathcal{T}}^2 := \sum_{K\in\mathcal{T}}\frac{1}{2}\|\nabla u_K\|^2+\sum_{F\in\mathcal{S}}\alpha(J_F)\left\|[\![u]\!]\right\|_F^2$$

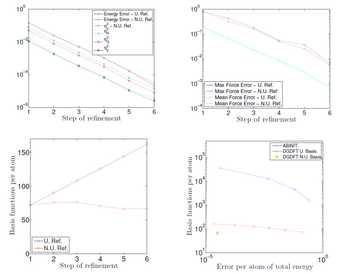
Under certain assumptions, we can show the reliability of the estimator (ξ_i, G_i are high order terms)

$$\left\|u_{i,\mathcal{J}}-u_i\right\|_{E,\mathcal{T}} \lesssim \eta_i+\left(1+\sqrt{\gamma_{1,\mathcal{J}}}\right)\xi_i \qquad \left|\lambda_i-\lambda_{i,\mathcal{J}}\right| \lesssim \eta_i^2+G_i$$

Example: Graphene oxide with 160 atoms



Non-uniform electron density



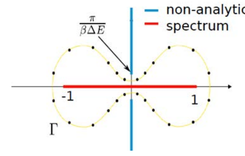
Adaptive refinement of basis

Non-uniform refinement improves the accuracy by orders of magnitude without increasing the number of basis functions.

PEXSI

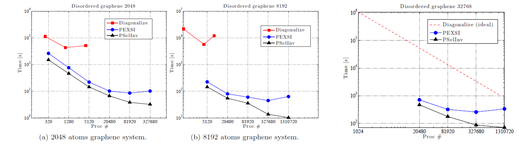
PEXSI: Pole EXpansion and Selected Inversion

Accurate evaluation of the electron density, energy, and atomic force with at most $O(N^2)$ scaling.



$$\rho \approx \text{diag}\sum_{i=1}^{Q}\frac{\omega_i}{H-z_i I}$$

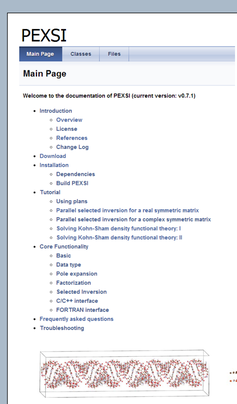
Two level parallelization



(a) 2048 atoms graphene system. (b) 8192 atoms graphene system.

PEXSI applied to DG-generated graphene matrices.

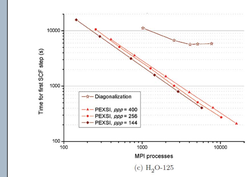
PEXSI



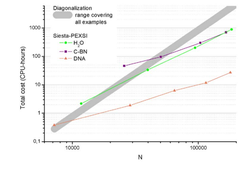
The PEXSI library:

- Available online http://pexsi.org/
- BSD license
- Integrated with SIESTA for accelerating atomic-orbital based calculation
- Being integrated into CP2K and other electronic structure packages.
- Massively parallel to 10,000 – 100,000 processors on high performance computers

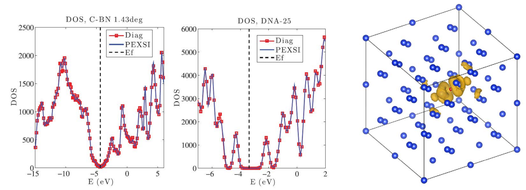
SIESTA-PEXSI for DNA (quasi-1D, 17k atoms), C-BN (quasi-2D, 12k atoms), Water (3D, 24k atoms).



Wall clock time for water with 24K atoms

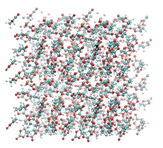


Total CPU work.

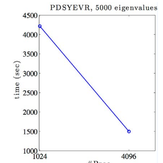


DOS generated from PEXSI is nearly identical to that obtained from diagonalization.

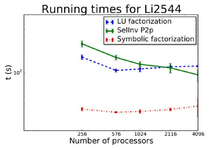
LDOS generated from PEXSI for SiH.



LiHCOFP-2544



Diagonalization time using pdsyevr



PEXSI time (per pole per μ iteration)

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