

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

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Objectives

Transformational changes in energy storage technologies are critically needed to enable the effective use of renewable resources such as solar and wind, and to make possible the transition from hybrid-electric vehicles to plug-in hybrids to all-electric vehicles, eliminating dependence on fossil fuels. Lithium ion cells have played a key role in the wireless revolution and have the potential to do the same for transportation and electrical distribution. To realize this potential, however, substantial increases in performance, lifetime, and safety will be required.

In this project, we address this critical need by bringing to fruition a breakthrough in quantum mechanical simulations, discontinuous Galerkin (**DG**) quantum molecular dynamics (**QMD**), and applying it to accomplish detailed simulations and analysis on an unprecedented scale.

Key limitations of current Li-ion technologies center on the formation and evolution of the solid-electrolyte interphase (**SEI**) layer between anode and electrolyte, a product of electrochemical electrolyte decomposition. Particularly, long-term reliability is affected as the flow of Li^+ into and out of the anode is hindered during charge cycling, and also the electrical characteristics of the battery degrade as the SEI layer forms. However, the passivating property of the SEI layer is critical for performance, since it helps prevent further decomposition of the electrolyte at the anode interface. In practice, a thin, stable SEI layer with high Li^+ ion conductivity and low electrical conductivity is required. Any dynamic and inhomogeneous build-up or modification of the SEI film during operation must be avoided.

A comprehensive theoretical understanding of the details of SEI layer formation and evolution is currently lacking, which has hindered progress in the design of optimal electrolyte/anode systems. Detailed atomistic understanding is needed of the electrochemical processes and interface charge transfer reactions that occur associated with the SEI layer. This includes obtaining detailed knowledge of the mechanism, energetics, and kinetics of Li^+ solvation, diffusion, and intercalation into the anode, as well as the decomposition reactions and rates that lead to SEI formation for different electrolyte/anode combinations.

Progress in understanding has been limited by the need for both a fully quantum mechanical description and sufficient length and time scales to capture the essential complexity of these dynamic mixed-phase systems. With the combination of new DG quantum mechanical methods and leadership-class massively parallel computational resources, however, we are now in a position to reach the required length and time scales; and so are poised for a genuine breakthrough in the understanding of these ubiquitous and mission-critical systems.

Our main objectives are thus two-fold:

1. To develop and implement the new Discontinuous Galerkin electronic structure method, to make possible quantum molecular dynamics simulations on an unprecedented scale.
2. To apply the new method to address fundamental questions on the formation and evolution of the solid-electrolyte interphase layer in Li-ion cells, completely from first principles.

Upon completion, we will make the resulting codes available to the broader research community to enable such large-scale *ab initio* calculations, both static and dynamic, in the gamut of other applications areas.

Approach

To accomplish the above objectives, we will carry out QMD simulations of an extensive series of systems, beginning with bulk pure-electrolyte systems, proceeding to mixed electrolytes with various salts, and finally to complete liquid-on-anode simulations. The initial simulations, requiring configurations of up to 1,000 atoms, will be carried out using the massively parallel **Qbox** planewave code at LLNL, while the new DG methodology is developed and verified. Larger simulations, requiring 10,000 atoms or more, will then be carried out using the new DG methodology.

The key advance making the present work possible is the new DG electronic structure method, recently pioneered by one of the PIs; a significant departure from previous methods, releasing the constraint of continuity in the electronic structure representation. In essence, the DG method solves the required N -atom Kohn-Sham problem in a basis of N independent, local Kohn-Sham solutions. By virtue of the DG mathematical framework, the resulting basis is free to be discontinuous. Hence, the basis is highly efficient, incorporating all local physics, systematically improvable, orthonormal, and strictly local—with zero overlap across subdomains. By virtue of these properties, the method achieves planewave accuracy in both energies and forces with one to two orders of magnitude fewer basis functions than required by conventional planewave methods—while retaining strict locality and thus natural, efficient parallelizability. Our initial DG implementation has accomplished self-consistent calculations with over 4,000 atoms. In the present work, we undertake the developments necessary to carry out QMD for complex systems of 10,000 atoms or more.

Applied Mathematics and Computer Science Challenges

To reach the required length and time scales, substantial mathematical and computational developments will be undertaken in close collaboration with the SciDAC **FASTMath** Institute. The larger of these include:

- Implementation of Fermi-operator expansion formulation (Pole Expansion plus Selected Inversion, **PEpSI**), developed by two of the PIs, to eliminate the need for diagonalization, thus reducing substantially memory requirements, interprocessor communications, and overall algorithmic scaling with the number of atoms. Unlike previous Fermi-operator formulations, PEpSI is applicable to the full range of temperatures of interest, above room temperature and below; while retaining strict equivalence to cubically scaling, diagonalization based approaches.
- Basis optimization: Recent work by two of the PIs has shown multiple paths toward reducing Pulay terms in forces further, and via optimized linear combinations across neighboring elements, reducing total degrees of freedom further, in higher-dimensional systems in particular.
- Multi-level parallelism: parallelization over k -points, poles, across elements (subdomains), and within; MPI and thread level. By exploiting the multiple levels available, scaling to in excess of 100,000 processors will be obtained.
- Numerical quadrature: Efficient numerical quadratures for integrands involving DG basis functions will be developed to reduce prefactors.
- Parallel eigensolver: A large-scale eigensolver, capable of returning large numbers of eigenpairs, and fully exploiting both the structure of the DG Hamiltonian and excellent initial approximations available will be developed.
- Parallel selected inversion: An efficient parallel LDL^T factorization will be developed, exploiting the symmetry of the Hamiltonian, as a basis for selected inversion employed in PEpSI.