

## Numerical Solution of 3D Poisson-Nernst-Planck Equations Coupled with Classical Density Functional Theory for Modeling Ion and Electron Transport in a Confined Environment

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Received 4 September 2013; Accepted (in revised version) 12 May 2014

Available online 29 August 2014

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**Abstract.** We have developed efficient numerical algorithms for solving 3D steady-state Poisson-Nernst-Planck (PNP) equations with excess chemical potentials described by the classical density functional theory (cDFT). The coupled PNP equations are discretized by a finite difference scheme and solved iteratively using the Gummel method with relaxation. The Nernst-Planck equations are transformed into Laplace equations through the Slotboom transformation. Then, the algebraic multigrid method is applied to efficiently solve the Poisson equation and the transformed Nernst-Planck equations. A novel strategy for calculating excess chemical potentials through fast Fourier transforms is proposed, which reduces computational complexity from  $\mathcal{O}(N^2)$  to  $\mathcal{O}(N \log N)$ , where  $N$  is the number of grid points. Integrals involving the Dirac delta function are evaluated directly by coordinate transformation, which yields more accurate results compared to applying numerical quadrature to an approximated delta function. Numerical results for ion and electron transport in solid electrolyte for lithium-ion (Li-ion) batteries are shown to be in good agreement with the experimental data and the results from previous studies.

**AMS subject classifications:** 92C35, 35J47, 35J60, 35R09, 65M06, 65N55, 65T50

**Key words:** Poisson-Nernst-Planck equations, classical density functional theory, algebraic multigrid method, fast Fourier transform, Li-ion battery.

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## 1 Introduction

Poisson-Nernst-Planck (PNP) equations are widely used to describe the macroscopic properties of ion transport in electrochemical systems [1–5] (e.g., lithium-ion (Li-ion) batteries, fuel cells) and biological membrane channels [6–13]. PNP equations are also known as the drift-diffusion equations for the description of currents in semiconductor devices [14–17]. In these models, excess chemical potential of mobile ions drives their diffusion. However, a highly simplified description of the interactions limited to Coulomb interactions between all charged species, is often used. To overcome this oversimplification in the representation of collective interactions, classical density functional theory (cDFT) can be used. cDFT is a powerful analytical tool to describe mesoscopic interactions, such as excluded volume effects and electrostatic correlation interactions, and thermodynamic properties of inhomogeneous systems from first principles [18]. The PNP-cDFT model is a generalization of the PNP model often used to describe fluids of charged hard spheres in a confined environment. It has been applied to study the selectivity and ionic flux in biological ion channels [19–22] and shown to provide computational results in good agreement with experimental data and/or theoretical analysis.

In solid state ion and electron diffusion is also affected by the barriers for elementary transport processes: ion hopping between the adjacent equilibrium sites and electron hopping between the cations in the lattice. Similarly, in biological ion channels, short-range dispersion interactions between the ions and functional groups in the channel proteins would also affect their diffusion. These short-range interactions have a quantum mechanical nature, which makes it challenging to evaluate them analytically. To include these short-range interactions in cDFT model, quantum mechanical simulations can be used to evaluate the barriers for the elementary transport processes and represent the interactions with a square-well potential, featuring depth equal to the barrier and the width comparable to ionic diameters [23, 24].

To summarize, in our approach — apart from Coulomb interactions — electrostatic correlation and excluded volume effects are treated using cDFT with short-range interactions quantum mechanically evaluated. This approach is equally applicable to study ion and electron transport in nanostructured materials, ion transport through biological ion channels, and small molecule diffusion in mesoporous materials.

In this work, we use the solid electrolyte, lithium phosphorus oxynitride (LiPON), for Li-ion batteries as a test system and study temperature dependence of  $\text{Li}^+$  conductivity in LiPON films. This material has a complex  $\text{Li}^+$  diffusion pathway [25, 26], which requires a full 3D model for ion and electron transport. Our previous work showed the PNP-cDFT model's unique capability to capture the physics of nanostructured electrode materials for Li-ion batteries, providing insights into the origin of size effects of conductivity and temperature dependence. The model can be used to guide synthesis of new nanocomposite materials with significantly improved electrochemical properties [23, 26–30]. This research also revealed limitations in modeling realistic nanocomposites with complex structures, calling for optimization of the efficiency of the PNP-cDFT solvers.