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# Convergence Analysis on a Second-Order, Positive, and Unconditional Energy Dissipative Scheme for the Poisson-Nernst-Planck Equations

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**Abstract.** In this paper, we propose and analyze a second-order accurate numerical scheme for the Poisson-Nernst-Planck equations. The proposed scheme combines a novel second-order temporal discretization with the centered finite difference method in space. By using a Taylor expansion for the logarithmic term in the chemical potential, this second-order accurate numerical scheme is able to preserve original energy dissipation. Based on the gradient flow formulation, the resulting scheme guarantees several crucial physical properties: mass conservation, positivity of ionic concentration, preservation of original energy dissipation, and steady states preservation. Remarkably, these properties are ensured without any restriction on the time step size. Furthermore, an optimal rate convergence estimate is provided for the proposed numerical scheme. Due to the non-constant mobility and the nonlinear and singular properties of the logarithm terms, a higher-order asymptotic expansion and a combination of rough and refined error estimation techniques are introduced to accomplish this analysis. A few numerical tests are provided to validate our theoretical claims.

**AMS subject classifications**: 35K35, 35K61, 65M06, 65M12, 65Z05

**Key words**: Poisson-Nernst-Planck equation, second-order accurate, original energy dissipation, optimal rate convergence analysis.

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## 1. Introduction

The Poisson-Nernst-Planck (PNP) equations have been used to describe the diffusion and convection of charges in various contexts, including semiconductors [19, 25, 32], ion channels [17, 18, 42], electrochemical energy devices [2, 3] and others. Based on the mean-field approximation, the Nernst-Planck (NP) equations describe the diffusion of ions in the gradient of the electrostatic potential. The Poisson's equation

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determines the electrostatic potential with the charge density arising from diffusing ions. The dimensionless PNP equations can be formulated as

$$\begin{cases} \partial_t c^\ell = \nabla\cdot\left(\nabla c^\ell + q^\ell c^\ell \nabla\psi\right), \quad \ell = 1,\dots,M & \text{in } \Omega, \\ -\kappa\Delta\psi = \sum_{\ell=1}^M q^\ell c^\ell + \rho^f & \text{in } \Omega, \end{cases} \tag{1.1}$$

where $c^\ell = c^\ell(\boldsymbol{x},t)$ is the ionic concentration for the $\ell$-th species in a multi-dimensional bounded, connected open domain $\Omega$, $q^\ell$ is the valence of the $\ell$-th species, the coefficient $\kappa > 0$ arises from nondimensionalization, $\psi = \psi(\boldsymbol{x},t)$ is the electric potential, and $\rho^f = \rho^f(\boldsymbol{x})$ is the distribution of fixed charge density. For simplicity of presentation, we consider a cubic $\Omega$ with periodic boundary conditions. An extension to the model with homogeneous Neumann boundary conditions is straightforward. The PNP equations are supplemented with the initial condition for ionic concentrations

$$c^\ell(\boldsymbol{x},0) = c^\ell_{\text{in}}(\boldsymbol{x}), \quad \ell = 1,2,\dots,M,$$

where $c^\ell_{\text{in}}(\boldsymbol{x})$ is the initial data. With periodic boundary conditions for $c^\ell$, the analytical solution to (1.1) has four desired properties:

- Mass conservation: the total mass of ions is conservative in $\Omega$ for each species,

$$\int_\Omega c^\ell(\boldsymbol{x},t)d\boldsymbol{x} = \int_\Omega c^\ell(\boldsymbol{x},0)d\boldsymbol{x}, \quad \ell = 1,2,\dots,M, \quad \forall t > 0.$$

- Positivity of ionic concentration: the ionic concentration is positive, i.e.,

$$c^\ell(\boldsymbol{x},t) > 0, \quad \text{if} \quad c^\ell(\boldsymbol{x},0) \in (0,\infty), \quad \text{for} \quad \ell = 1,2,\dots,M, \quad \boldsymbol{x}\in\Omega, \quad \forall t > 0.$$

- Free-energy dissipation: the free-energy decays in time [14, 26, 28, 37]

$$\frac{dF}{dt} = \sum_{\ell=1}^M \int_\Omega \frac{\delta F}{\delta c^\ell}\frac{\partial c^\ell}{\partial t} dV = -\sum_{\ell=1}^M \int_\Omega \frac{1}{c^\ell}\left|\nabla c^\ell + q^\ell c^\ell \nabla\psi\right|^2 dV \le 0,$$

  where the corresponding free energy of PNP system (1.1) is

$$F = \int_\Omega \left[\sum_{\ell=1}^M c^\ell\left(\ln c^\ell - 1\right) + \frac{1}{2}\left(\sum_{\ell=1}^M q^\ell c^\ell + \rho^f\right)\psi\right] dV.$$

- Preservation of steady state: the solution to the PNP equations (1.1) converges to the corresponding Poisson-Boltzmann equation

$$-\kappa\Delta\psi^\infty = \sum_{\ell=1}^M q^\ell e^{-q^\ell\psi^\infty + \alpha_\ell} + \rho^f$$

  as $t \to +\infty$. Here $\alpha_\ell = \ln c^{\ell,\infty} + q^\ell\psi^\infty$.