HIGH-ORDER SPACE-TIME FINITE ELEMENT METHODS FOR THE POISSON-NERNST-PLANCK EQUATIONS: POSITIVITY AND UNCONDITIONAL ENERGY STABILITY

GUOSHENG FU AND ZHILIANG XU

Abstract. We present a novel class of high-order space-time finite element schemes for the Poisson-Nernst-Planck (PNP) equations. We prove that our schemes are mass conservative, positivity preserving, and unconditionally energy stable for any order of approximation. To the best of our knowledge, this is the first class of (arbitrarily) high-order accurate schemes for the PNP equations that simultaneously achieve all these three properties.

This is accomplished via (1) using finite elements to directly approximate the so-called entropy variable \( u := U'(c_i) = \log(c_i) \) instead of the density variable \( c_i \), where \( U'(c_i) = (\log(c_i) - 1)c_i \) is the corresponding entropy, and (2) using a discontinuous Galerkin (DG) discretization in time. The entropy variable formulation, which was originally developed by Metti et al. [17] under the name of a log-density formulation, guarantees both positivity of densities \( c_i = \exp(u_i) > 0 \) and a continuous-in-time energy stability result. The DG in time discretization further ensures an unconditional energy stability in the fully discrete level for any approximation order, where the lowest order case is exactly the backward Euler discretization and in this case we recover the method of Metti et al. [17].

1. Introduction

The Poisson-Nernst-Planck (PNP) equations describe the diffusion of charged particles under the effect of an electric field that is itself affected by these particles. This system of equations has been widely used in the modelling of semiconductors [11] and ion channels in biology [7].

Various numerical methods with different properties have been developed for the PNP equations [1, 4, 15, 16, 18, 23]. We particularly cite the very recent schemes [8, 9, 13, 14, 17, 20] that were provably positivity preserving for the particle densities and unconditionally energy dissipative for the free energy, among which the schemes in [8, 13, 14, 17, 20] are first-order accurate in time, while the scheme in [9] is high-order accurate in time but the associated energy dissipation law is only valid for a modified energy due to the use of the recent scalar auxiliary variable (SAV) technique [21]. To the best of our knowledge, no provable positivity preserving and unconditionally energy dissipative scheme for the original energy that is at least second-order accurate in time exists so far. We fill this gap by presenting a class of arbitrarily high-order accurate space-time finite element (STFEM) schemes satisfying these properties. Our spatial discretization is the same as the one developed in [17] which is based on a log-density formulation. We remark that this log-density based formulation is similar in spirit to the entropy-stable schemes based on the so-called entropy variables for hyperbolic conservation laws and compressible flow in the CFD literatures [2, 6, 10, 22]. Our temporal discretization is an upwinding discontinuous Galerkin (DG) scheme, which guarantees unconditional energy stability. We also discuss adaptive time stepping using the classical proportional integral (PI) step size controller [5].

2020 Mathematics Subject Classification. 65N30, 65N12, 76S05, 76D07.

Key words and phrases. Poisson-Nernst-Planck equation; energy stability; positivity preservation; entropy variable; space-time FEM.

G. Fu acknowledge the partial support of this work from U.S. National Science Foundation through grant DMS-2012031. Z. Xu was partially supported by the NSF CDS&E-MSS 1854779.
Since the PNP equations can be viewed as a Wasserstein gradient flow \[12\], we expect our STFEM scheme with *entropy variables* can be applied to construct high-order positivity preserving and unconditionally energy stable schemes for other Wasserstein gradient flow problems, like the Fokker-Planck equation and the porous medium equation.

The rest of the paper is organized as follows. In Section 2 we first introduce the PNP equations then present the spatial/temporal finite element discretizations and prove that they are mass conserv-ative, positivity preserving, and unconditionally energy dissipative. We further discuss about the nonlinear system solver via the Newton’s method and adaptive time step size control. Numerical results are presented in Section 3. We conclude in Section 4.

2. The PNP equations and the space-time finite element schemes

2.1. PNP equations. We consider the PNP equations with \(N\) species of charged particles \[3\] on a bounded domain \(\Omega \subset \mathbb{R}^d\), \(d = 1, 2, 3\), with boundary \(\partial \Omega\):

\[
\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i c_i \nabla \mu_i), \quad i = 1, 2, \cdots, N, \tag{1a}
\]

\[-\nabla \cdot (\epsilon \nabla \phi) = \rho_0 + \sum_{i=1}^{N} z_i e c_i, \tag{1b}\]

where \(c_i\) is the density of the \(i\)-th charged particle species, \(D_i\) is the diffusion constant,

\[\mu_i := \log(c_i) + \frac{z_i e k_B}{k_B T} \phi\]

is the chemical potential of the \(i\)-th species, \(z_i\) is the valence, \(e\) is the unit charge, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\epsilon\) is the electric permittivity, \(\phi\) is the electrostatic potential, \(\rho_0\) is the permanent (fixed) charge density of the system, and \(N\) is the number of charged particle species.

The PNP system (1a)–(1b) is closed with the following set of initial and boundary conditions:

\[
c_i(0, x) = c_i^0(x), \quad \text{in } \Omega \tag{1c}
\]

\[
c_i \frac{\partial \mu_i}{\partial n} = \frac{\partial \phi}{\partial n} = 0, \quad \text{on } \partial \Omega. \tag{1d}
\]

Here for simplicity, we use the homogeneous Neumann boundary condition for the charged particle densities. Other boundary conditions will be used in our numerical experiments. Note that the electrostatic potential \(\phi\) is determined up to a constant due to the pure Neumann boundary condition. Following the classical convention, we select a unique \(\phi\) by requiring

\[\int_{\Omega} \phi \, dx = 0.\]

The PNP system (1) satisfies the following three important properties:

(i) Mass conservation:

\[\int_{\Omega} c_i(t, x) \, dx = \int_{\Omega} c_i^0(x) \, dx. \tag{2a}\]

(ii) Positivity preservation:

If \(c_i^0(x) > 0\), then \(c_i(t, x) > 0\) for any \(t > 0\). \(\tag{2b}\)

(iii) Energy dissipation:

\[
\frac{d}{dt} E = -\sum_{i=1}^{N} \int_{\Omega} D_i c_i |\nabla \mu_i|^2 \, dx, \tag{2c}\]

\[E = \int_{\Omega} \rho_0 \phi \, dx + \frac{1}{2} \int_{\Omega} \sum_{i=1}^{N} D_i c_i |\nabla \mu_i|^2 \, dx.\]
where \( E(\{c_i\}, \phi) := \int_{\Omega} \left( \sum_{i=1}^{N} (c_i (\log(c_i) - 1)) + \frac{1}{2} k_B T |\nabla \phi|^2 \right) \, dx \) is the total free energy.

**Remark 2.1.** The above energy dissipation (2c) is obtained by a standard energy variational argument, where, in particular, one multiplies the equation (1a) with the test function \( \mu_i = \log(c_i) + \frac{z_i e}{k_B T} \phi \) and integrates over the domain \( \Omega \). An immediate consequence is that such energy dissipation would fail to hold in a standard finite element discretization where one only approximates the fields \( c_i \) and \( \phi \) using finite elements.

One approach to recover energy stability is to use a log-density formulation \cite{17}, where one directly discretizes the entropy variables

\[
u_i = U'(c_i) = \log(c_i),
\]

instead of the densities \( c_i \), where \( U(c_i) := c_i (\log(c_i) - 1) \) is the entropy of the \( i \)-th species. In this formulation, the species densities \( c_i(u_i) := \exp(u_i) \) are derived variables which are guaranteed to stay positive \( c_i = \exp(u_i) > 0 \) for any time \( t > 0 \). We point out that such entropy-variable based schemes are similar in spirit to the entropy stable schemes using entropy variables for hyperbolic conservation laws and compressible flow \cite{2, 6, 10, 22}.

To this end, we work with the following reformulated PNP equations (1a)–(1b):

\[
\frac{\partial \exp(u_i)}{\partial t} = \nabla \cdot \left( D_i \exp(u_i) \left( \nabla u_i + \frac{z_i e}{k_B T} \nabla \phi \right) \right),
\]

\[
-\nabla \cdot (\epsilon \nabla \phi) = \rho_0 + \sum_{i=1}^{N} z_i e \exp(u_i).
\]

### 2.2. Spatial discretization.

Let \( \mathcal{T}_h := \{ K \} \) be a conforming simplicial triangulation of the domain \( \Omega \). We shall use the following conforming finite element space

\[
V^k_h := \{ v \in H^1(\Omega) : v|_K \in P_k(K), \quad \forall K \in \mathcal{T}_h \},
\]

where \( P_k(K) \) is the space of polynomials of degree at most \( k \geq 1 \) on \( K \).

The spatial discretization of our finite element scheme for the equations (4) with initial and boundary conditions (1c)–(1d) reads as follows: Find \( u_{h,1}, \ldots, u_{h,N} \in V_h \) and \( \phi_h \in V_h \) with \( \int_{\Omega} \phi_h \, dx = 0 \) such that, for \( t > 0 \),

\[
\int_{\Omega} \frac{\partial \exp(u_{h,i})}{\partial t} v_i \, dx + \int_{\Omega} D_i \exp(u_{h,i}) \left( \nabla u_{h,i} + \frac{z_i e}{k_B T} \nabla \phi_h \right) \cdot \nabla v_i \, dx = 0, \quad \forall v_i \in V_h,
\]

\[
\int_{\Omega} \epsilon \nabla \phi_h \cdot \nabla \psi \, dx - \int_{\Omega} \left( \rho_0 + \sum_{i=1}^{N} z_i e \exp(u_{h,i}) \right) \psi \, dx = 0, \quad \forall \psi \in V_h,
\]

with initial conditions

\[
u_{h,i}(0, x) = \log(c_i^0(x)), \quad i = 1, 2, \ldots, N.
\]

The following results show that the semi-discrete scheme (6) satisfies the three properties (2).

**Theorem 2.1.** Assume \( c_i^0 > 0 \) for all \( i \). Then the three properties (2) are satisfied for the solution to the semi-discrete scheme (6), where the densities \( c_i \) in (2) are given explicitly as \( c_i = \exp(u_{h,i}) \).

**Proof.** Taking \( v_i = 1 \) in (6a), we get mass conservation property (2a). Positivity property (2b) following directly by the definition of \( c_i = \exp(u_{h,i}) > 0 \).

Let us prove the energy dissipation property (2c). Denoting \( \mu_{h,i} := u_{h,i} + \frac{z_i e}{k_B T} \phi_h \in V_h \), taking test function \( v_i = \mu_{h,i} \) in (6a) and adding, we get

\[
\sum_{i=1}^{N} \int_{\Omega} \frac{\partial \exp(u_{h,i})}{\partial t} \mu_{h,i} \, dx + \sum_{i=1}^{N} \int_{\Omega} D_i \exp(u_i) |\nabla \mu_{h,i}|^2 \, dx = 0.
\]
A simple calculation yields that
\[ \int_{\Omega} \frac{\partial \exp(u_{h,i})}{\partial t} u_{h,i} \, dx = \frac{d}{dt} \int_{\Omega} \exp(u_{h,i})(u_{h,i} - 1) \, dx. \]
Hence,
\[ \sum_{i=1}^{N} \frac{d}{dt} \int_{\Omega} U(u_{h,i}) \, dx + \int_{\Omega} \sum_{i=1}^{N} \frac{z_{i} e}{k_{B}T} \frac{\partial \exp(u_{h,i})}{\partial t} \phi_{h} \, dx + \sum_{i=1}^{N} \int_{\Omega} D_{i} \exp(u_{i})|\nabla \mu_{h,i}|^{2} \, dx = 0. \quad (7) \]
Taking \( \psi = \frac{\partial \phi}{\partial t} / (k_{B}T) \) in equation (6b) and subtract the resulting expression from (7), we get
\[ \frac{d}{dt} E_{h} + \sum_{i=1}^{N} \int_{\Omega} D_{i} \exp(u_{i})|\nabla \mu_{h,i}|^{2} \, dx = 0, \]
where the discrete free energy
\[ E_{h} := \int_{\Omega} \left( \sum_{i=1}^{N} U(u_{h,i}) + \sum_{i=1}^{N} \frac{z_{i} e}{k_{B}T} \exp(u_{h,i})\phi_{h} - \frac{\epsilon}{2k_{B}T}|\nabla \phi_{h}|^{2} + \frac{\rho_{0}}{k_{B}T}\phi_{h} \right) \, dx. \]
Taking \( \psi = \phi_{h} / (k_{B}T) \) in (6b), we get
\[ \int_{\Omega} \sum_{i=1}^{N} \frac{z_{i} e}{k_{B}T} \exp(u_{h,i})\phi_{h} \, dx = \int_{\Omega} \left( \frac{\epsilon}{k_{B}T}|\nabla \phi_{h}|^{2} - \frac{\rho_{0}}{k_{B}T}\phi_{h} \right) \, dx. \]
Combining the above two expressions, we get
\[ E_{h} = \int_{\Omega} \left( \sum_{i=1}^{N} U(u_{h,i}) + \frac{\epsilon}{2k_{B}T}|\nabla \phi_{h}|^{2} \right) \, dx. \]
This completes the proof of (2c). \( \square \)

2.3. Temporal discretization. In this subsection, we discretize the differential-algebraic system (6) using a discontinuous Galerkin (DG) time integrator of degree \( m \geq 0 \). The major advantage of using the DG integrator is that we can prove an unconditional energy stability result for the fully discrete scheme for any polynomial degree \( m \geq 0 \) in time. To the best of our knowledge, this is the first class of arbitrarily high-order accurate numerical schemes for the PNP equations that are provably positive and unconditionally energy stable.

At the \( n \)-th time level \( t^{n} \), we denote the time step size as \( \Delta t^{n} \) and the update time interval as \( I^{n} = [t^{n}, t^{n+1}) \). We denote the space-time finite element space on the space-time slab \( \Omega \times I^{n} \) as follows:
\[ V_{h}^{k,m,n} := \{ v \in H^{1}(\Omega \times I^{n}) : v|_{K \times I^{n}} \in \mathcal{P}_{k}(K) \otimes \mathcal{P}_{m}(I^{n}), \ \forall K \in \mathcal{T}_{h} \}, \quad (8) \]
The fully discrete scheme then reads as follows: for any \( n = 1, 2, \cdots \), find \( u^n_{h,i} \in V^{k,m,n}_h \) and \( \phi^n_h \in V^{k,m,n}_h \) with \( \int_{\Omega} \phi^n_{h,i} \, dx = 0 \) such that

\[
\int_{t^n} \int_{\Omega} \frac{\partial \exp(u^n_{h,i})}{\partial t} v_i \, dxdt + \int_{\Omega} \left( \exp(u^n_{h,i}) - \exp(u^{n-1}_{h,i}) \right) v^n_{i,+} \, dx
+ \int_{t^n} \int_{\Omega} D_i \exp(u^n_{h,i}) \left( \nabla u^n_{h,i} + \frac{z_i e}{k_B T} \nabla \phi^n_h \right) \cdot \nabla v_i \, dxdt = 0, \quad \forall v_i \in V^{k,m,n}_h, \quad (9a)
\]

\[
\int_{t^n} \int_{\Omega} \epsilon \nabla \phi^n_h \cdot \nabla \psi \, dxdt - \int_{t^n} \int_{\Omega} \left( \rho_0 + \sum_{i=1}^N z_i e \exp(u^n_{h,i}) \right) \psi \, dxdt = 0, \quad \forall \psi \in V^{k-1,m,n}_h, \quad (9b)
\]

\[
\int_{t^n} \int_{\Omega} \epsilon \nabla \phi^n_{h,i} \cdot \nabla \psi^n_{h,i} \, dxdt - \int_{t^n} \int_{\Omega} \left( \rho_0 + \sum_{i=1}^N z_i e \exp(u^n_{h,i}) \right) \psi^n_{h,i} \, dxdt = 0, \quad \forall \psi \in V^{k}_h, \quad (9c)
\]

where we denote \( \xi^{n,-} := \lim_{\tau \downarrow t^n} \xi^n(t, x) \) and \( \xi^{n,+} := \lim_{\tau \uparrow t^n} \xi^n(t, x) \).

**Remark 2.2.** We note that the classical upwinding DG time integrator is used in (9a), and a non-standard Gauss-Radau type quadrature rule is used in (9b)–(9c) for the temporal discretization of the Poisson equation. This Gauss-Radau type quadrature rule is necessary for us to prove the unconditional energy stability of the scheme (9), see the proof of Theorem 2.2 below. We further note that when \( m = 0 \), the temporal discretization is simply the backward Euler method.

The following results show that the fully-discrete scheme (9) satisfies a discrete version of three properties (2).

**Theorem 2.2.** Assume \( c^0_i > 0 \) for all \( i \). For any solution to the scheme (9), the following three properties holds

\[
\int_{\Omega} \exp(u^n_{h,i}) \, dx = \int_{\Omega} \exp(u^{n-1}_{h,i}) \, dx, \quad (10a)
\]

\[
c^n_{h,i} := \exp(u^n_{h,i}) > 0, \quad (10b)
\]

\[
E^n_h - E^{n-1}_h = - \text{Diss}^n_h - N^n_{h,1} - N^n_{h,2} \quad (10c)
\]

where the discrete energy is given by

\[
E^n_h := \int_{\Omega} \left( \sum_{i=1}^N U(u^n_{h,i}) + \frac{\epsilon}{2k_B T} |\nabla \phi^n_{h,i}|^2 \right) \, dx, \quad (10d)
\]

the (non-negative) physical dissipation term

\[
\text{Diss}^n_h := \int_{t^n} \int_{\Omega} \sum_{i=1}^N D_i c^n_{h,i} |\nabla h^n_{h,i}|^2 \, dxdt,
\]

and the (non-negative) numerical dissipation terms \( N^n_{h,1} \) and \( N^n_{h,2} \) for the temporal discretization are given as follows

\[
N^n_{1,h} := \int_{\Omega} \sum_{i=1}^N \frac{1}{2} \exp(\xi^n_{h,i}) (u^{n-1}_{h,i} - u^n_{h,i})^2 \, dx,
\]

\[
N^n_{2,h} := \int_{\Omega} \frac{\epsilon}{2k_B T} |\nabla (\phi^n_{h,i} - \phi^{n-1}_{h,i})|^2 \, dx,
\]

where \( \xi^n_{h,i} \) is a function between \( u^{n,+}_{h,i} \) and \( u^{n,-}_{h,i} \) for each \( i \).
Proof. Again, we only need to prove the energy stability result \([10c]\) as the other two properties are trivially satisfied.

We follow the same proof as the semi-discrete case in Theorem \([2.1]\). Denoting \(c^n_{h,i} := \exp(u^n_{h,i})\), \(\mu^n_{h,i} := u^n_{h,i} + \frac{z_i\epsilon}{k_BT}\phi^n_h \in \mathcal{V}^{k,m,n}\), and taking test function \(v_i = \mu^n_{h,i}\) in \((9a)\), we get

\[
\int_{I^n} \int_{\Omega} \frac{\partial c^n_{h,i}}{\partial t} \mu^n_{h,i} \, dxdt + \int_{I^n} \int_{\Omega} \left( c^n_{h,i}^+ - c^n_{h,i}^- \right) \mu^n_{h,i} \, dx + \int_{I^n} \int_{\Omega} D_i c^n_{h,i} \nabla \mu^n_{h,i} \, dxdt = 0. \tag{11a}
\]

A simple calculation yields that

\[
\int_{I^n} \int_{\Omega} \frac{\partial c^n_{h,i}}{\partial t} u^n_{h,i} \, dxdt = \int_{I^n} \frac{d}{dt} \int_{\Omega} U(u^n_{h,i}) \, dxdt = \int_{\Omega} U(u^n_{h,i}) \, dx - \int_{\Omega} U(u^n_{h,i}) \, dx,
\]

where \(U(\eta) := \exp(\eta)(\eta - 1)\). By Taylor expansion we have

\[
(exp(a) - exp(b))a = U(a) - U(b) + \frac{1}{2} \exp(\xi)(a - b)^2
\]

for some \(\xi\) between \(a\) and \(b\). Hence,

\[
\int_{\Omega} \left( c^n_{h,i}^+ - c^n_{h,i}^- \right) u^n_{h,i} \, dx = \int_{\Omega} \left( U(u^n_{h,i}) - U(u^n_{h,i}^-) + \frac{1}{2} \exp(\xi_{h,i})(u^n_{h,i}^+ - u^n_{h,i}^-)^2 \right) \, dx
\]

for some \(\xi_{h,i}\) between \(u^n_{h,i}^-\) and \(u^n_{h,i}^+\). Combining the above two equalities and summing the terms \((11a)\) over all the indices \(i\), we get

\[
\sum_{i=1}^{N} \left( \int_{\Omega} U(u^n_{h,i}^-) \, dx - \int_{\Omega} U(u^n_{h,i}^+) \, dx \right) + N^n_{1,h} + I_{c,\phi} + \int_{I^n} \sum_{i=1}^{N} D_i c^n_{h,i} \nabla \mu^n_{h,i} \, dxdt = 0, \tag{11b}
\]

where \(N^n_{1,h}\) is the following numerical dissipation term from upwinding

\[
N^n_{1,h} := \int_{\Omega} \sum_{i=1}^{N} \frac{1}{2} \exp(\xi_{h,i})(u^n_{h,i}^+ - u^n_{h,i}^-)^2 \, dx \geq 0,
\]

and the term \(I_{c,\phi}\) is given as follows:

\[
I_{c,\phi} := \int_{I^n} \int_{\Omega} \frac{\partial S^n_{h}}{\partial t} \phi^n_h \, dxdt + \int_{I^n} \int_{\Omega} \left( S^n_{h} + S^n_{h}^- \right) \phi^n_{h,i} \, dx,
\]

with \(S^n_{h} := \sum_{i=1}^{N} \frac{z_i\epsilon}{k_BT} c^n_{h,i} + \frac{\rho_0}{k_BT}\) being the source term in \((9b)\), where we used the fact that \(\rho_0, z_i, k_BT\) are independent of time. Next, taking \(\psi = \frac{\partial \phi^n_h}{(k_BT)} \in \mathcal{V}^{k,m,n}\) in equation \((9b)\) and combining with the above term, we get

\[
I_{c,\phi} = -\int_{I^n} \int_{\Omega} \frac{\partial}{\partial t} \left( \frac{\epsilon}{2k_BT} |\nabla \phi^n_h|^2 \right) dxdt + \int_{I^n} \int_{\Omega} \frac{\partial}{\partial t} (S^n_{h} \phi^n_h) dxdt + \int_{I^n} \int_{\Omega} \left( S^n_{h} + S^n_{h}^- \right) \phi^n_{h,i} dxdt,
\]

\[
= \int_{\Omega} \left( -\frac{\epsilon}{2k_BT} |\nabla \phi^n_h|^2 + \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^+|^2 + S^n_{h} - S^n_{h}^- \phi^n_{h,i} \right) dxdt,
\]

\[
= \int_{\Omega} \left( S^n_{h} - \phi^n_{h,i} - \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^-|^2 + \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^+|^2 - S^n_{h}^- \phi^n_{h,i} + S^n_{h} \phi^n_{h,i} + \phi^n_{h,i} \phi^n_{h,i} \right) dxdt,
\]

\[
= \int_{\Omega} \left( \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^-|^2 + \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^+|^2 - \frac{\epsilon}{2k_BT} |\nabla \phi^n_{h,i}^-|^2 \right) dxdt,
\]

\[
= 0 \text{ by } \langle \partial \phi \rangle.
\]
where the last step is again due to (9c) by taking the test function \( \psi = \phi^n_h / (k_B T) \). Combining the above expression with the equality (11b), we finally get

\[
E^n_h + N^n_{1,h} + N^n_{2,h} + \text{Diss}^n_h = E_{h}^{n-1},
\]

where we used the definition of the energy \( E^n_h \) and the numerical dissipation term \( N^n_{2,h} \) from Theorem 2.2. This completes the proof. \( \square \)

**Remark 2.3.** Our proposed scheme (9) can be also applied to the variable coefficient case to achieve all the three properties in Theorem 2.2. For example, by multiplying all the spatial integrals in (2.2) with a coefficient \( A(x) > 0 \), we immediately get a positive and unconditionally energy stable scheme for the following PNP system with a variable (possibly discontinuous) \( A(x) \):

\[
A \frac{\partial c_i}{\partial t} = \nabla \cdot (AD_i c_i \nabla \mu_i), \quad i = 1, 2, \cdots, N, \quad (12a)
\]

\[-\nabla \cdot (A\epsilon \nabla \phi) = A(\rho_0 + \sum_{i=1}^{N} z_i e c_i). \quad (12b)\]

In this case, all the integrals in (10) shall be weighted by the cross-section \( A(x) \).

### 2.4. Nonlinear system solver and adaptive time stepping.

We use Newton’s method to solve the fully discrete nonlinear system (9). A sparse direct solver is used for the linear algebraic systems in each Newton’s iteration. The Newton’s iteration is stopped when the relative error of the energy (10d) is reduced by a factor of \( 10^{-8} \).

One main advantage of unconditionally energy stable schemes with arbitrary order is that they can be easily implemented with an adaptive time stepping strategy so that the time step is dictated only by accuracy rather than by stability as with conditionally stable schemes. Here we use the classical PI step size control algorithm [5]: given a previous time step size \( \Delta t^{n-1} \), the next time step size \( \Delta t^n \) is proposed as

\[
\Delta t_{\text{temp}} = \left( \frac{tol}{e_n} \right)^{K_t} \left( \frac{e_{n-1}}{e_n} \right)^{K_P} \Delta t^{n-1}, \quad \Delta t^n = \min\{\Delta t_{\text{temp}}, \theta_{\text{max}} \Delta t^{n-1}, \Delta t_{\text{max}}\},
\]

where \( tol \) is a prescribed error tolerance, \( \Delta t_{\text{max}} \) is a user defined maximum allowed time step size, and

\[
e^n := \left| \frac{E^n_h - E^{n,lo}_h}{E^n_h} \right|
\]

is the error estimator based on the relative error in energy between the scheme (9) (with temporal order \( m \geq 1 \)) and a companion (temporal) low-order scheme (with \( m = 0 \)) with the same spatial discretization, and we use the following parameters suggested in [5]:

\[
K_P = 0.13, \quad K_I = 1/15, \quad \theta_{\text{max}} = 2, \quad \rho = 1.2.
\]

We reject the proposed \( \Delta t^n \) in (13) if either the Newton iteration did not converge or the target tolerance is violated \( (e^n > \rho tol) \). In this case, we halve the time step size by setting \( \Delta t^n := 0.5 \Delta t^{n-1} \) and redo the computation.

### 3. Numerics

In this section, we present several numerical examples to validate our theoretical results in the previous section. Our numerical simulations are performed using the open-source finite-element software NGsolve [19], [https://ngsolve.org/](https://ngsolve.org/). In particular, NGsolve’s add-on library ngxfem, [https://github.com/ngsxfem/ngsxfem](https://github.com/ngsxfem/ngsxfem), is used in the implementation of the space-time finite element scheme (9).
Example 1. (Accuracy test) We first use a manufactured solution example to test the accuracy of the scheme (9). We consider the PNP equations (1) with $N = 2$, $z_1 = 1$, $z_2 = -1$, $e = k_B = T = D_1 = D_2 = \epsilon = 1$. The computational domain is a unit square, and we take source terms such that the smooth exact solution is

$$
c_1(t, x, y) = 1 + 0.5 \sin(t) \sin(\pi x) \sin(\pi y),$$
$$c_2(t, x, y) = 1 - 0.5 \sin(t) \sin(\pi x) \sin(\pi y),$$
$$\phi(t, x, y) = \sin(t) \sin(\pi x) \sin(\pi y).$$

We use homogeneous Dirichlet boundary conditions on $u_1$, $u_2$ and $\phi$.

We apply the space-time finite element scheme (9) with $k = m = 1$, $k = m = 2$, and $k = m = 3$ on a sequence of uniformly refined triangular meshes. We take uniform time step size $\Delta t = 2h$, where $h$ is the mesh size. The Newton’s method converges within 3–4 iterations for all the cases. The $L^2$-errors at time $t = 1$ are recorded in Table 1. Clearly, we observe the expected $(k + 1)$-th order of convergence for all the variables for the scheme (9) using polynomials of degree $k = m$.

| $k = m$ | $1/h$ | $L^2$-err in $u_1^h$ | rate | $L^2$-err in $u_2^h$ | rate | $L^2$-err in $\phi^h_2$ | rate |
|--------|------|----------------------|------|----------------------|------|----------------------|------|
| 1      | 8    | 5.228e-03            | –    | 1.362e-02            | –    | 2.140e-02            | –    |
|        | 16   | 1.473e-03            | 1.828| 3.821e-03            | 1.834| 5.461e-03            | 1.970|
|        | 32   | 3.923e-04            | 1.908| 1.000e-03            | 1.934| 1.374e-03            | 1.991|
|        | 64   | 1.016e-04            | 1.950| 2.552e-04            | 1.970| 3.442e-04            | 1.997|
| 2      | 8    | 1.218e-04            | –    | 2.615e-04            | –    | 1.999e-04            | –    |
|        | 16   | 1.407e-05            | 3.113| 1.928e-05            | 3.762| 1.762e-05            | 3.504|
|        | 32   | 1.702e-06            | 3.048| 1.782e-06            | 3.435| 1.869e-06            | 3.237|
|        | 64   | 2.106e-07            | 3.014| 1.992e-07            | 3.162| 2.215e-07            | 3.077|
| 3      | 8    | 9.026e-06            | –    | 1.980e-05            | –    | 1.809e-05            | –    |
|        | 16   | 4.813e-07            | 4.220| 1.115e-06            | 4.151| 1.083e-06            | 4.062|
|        | 32   | 2.768e-08            | 4.120| 6.665e-08            | 4.064| 6.651e-08            | 4.025|
|        | 64   | 1.675e-09            | 4.047| 3.990e-09            | 4.062| 4.122e-09            | 4.012|

Table 1. Example 1. $L^2$-errors at time $t = 1$ for the methods (9) with $k = m$ on a sequence of uniformly refined meshes. Time step size $\Delta t = 2h$.

Example 2. (One-dimensional problem with discontinuous coefficients) Here we solve a two-component ($N = 2$) one-dimensional system (12) with variable discontinuous coefficients. The domain is $\Omega = [-28, 25]$, and we use the homogeneous Dirichlet boundary conditions

$$
\phi(x) = u_1(x) = u_2(x) = 0 \quad \forall x \in \partial \Omega
$$

and initial condition

$$
u_1(0, x) = u_2(0, x) = 0.$$
We use the following set of parameters:

\[ k_B = T = e = 1, z_1 = 1, z_2 = -1, D_1 = 1, D_2 = 1.0383, \]

\[ A = \pi r^2, \text{ with } r(x) = \begin{cases} 
-0.5x - 7 & \text{if } -28 < x < -18, \\
2 & \text{if } -18 < x < -5, \\
0.5 & \text{if } -5 < x < 10, \\
0.9x - 8.5 & \text{if } 10 < x < 25,
\end{cases} \]

\[ \epsilon(x) = \begin{cases} 
4.7448 & \text{if } -5 < x < -10, \\
189.79 & \text{elsewhere},
\end{cases} \]

\[ \rho_0(x) = \begin{cases} 
-300 & \text{if } x \in (-2, -1) \cap (0, 1) \cup (2, 3) \cup (4, 5) \cup (6, 7), \\
0 & \text{elsewhere}.
\end{cases} \]

We apply the second-order scheme (9) with polynomial degree \( k = m = 1 \), and take the initial time stepsize as \( \Delta t_1 = 10^{-4} \). The adaptive time stepping algorithm (13) is used where the companion low order scheme takes \( k = 1 \) and \( m = 0 \) on the same mesh. For the two user defined parameters in (13), we take \( \text{tol} = 10^{-3} \), and \( \Delta t_{\text{max}} = \begin{cases} 
2 & \text{if } t < 250, \\
200 & \text{if } t > 250.
\end{cases} \) The simulation is terminated when relative error in the energy in two consecutive time steps is less than \( 10^{-13} \),

\[ \frac{|E^n_h - E^{n-1}_h|}{E^n_h} < 10^{-13}, \]

which indicates a steady state is reached. We find the steady state is reached around time \( t = 1400 \).

This problem is very challenging to solve as \( c_2 = \exp(u_2) \) stays near zero for \( x \in (-5, 10) \) for an extended period of time. Typical solutions at different times are shown in Figure 1–3, which is obtained by the scheme (9) on a very fine uniform mesh with mesh size \( h = 1/128 \). It is clear from Figure 3 that \( c_2 = \exp(u_2) \) stays positive and below \( \exp(-50) \approx 2 \times 10^{-22} \) for \( x \in (-5, 10) \) and \( t \in (20, 240) \), which can be as small as \( \exp(-150) \approx 7 \times 10^{-66} \) at around time \( t = 100 \). A non positivity preserving scheme may easily lead to a negative density \( c_2 \), hence an early termination of the code using such scheme due to the need to evaluate \( \log(c_2) \).

The initial and final energy, along with the total number of time steps to reach the steady state is recorded in Table 2 for four consecutively refined (uniform) meshes. We clearly observe a convergence in the energies as the mesh is refined. Moreover, the total number of time steps to reach the steady state is similar on all four meshes.

| mesh size \( h \) | 1/16 | 1/32 | 1/64 | 1/128 |
|-------------------|------|------|------|-------|
| initial energy    | 387788.75 | 387798.52 | 387800.97 | 387801.58 |
| final energy      | -3023.3435 | -3022.3990 | -3022.1619 | -3022.1025 |
| total time steps  | 206  | 208  | 210  | 210   |

Table 2. Example 2. Initial and final energy, and total number of time steps to reach the steady state for the scheme (9) with \( k = m = 1 \) and adaptive time stepping (13) on different meshes.

We plot in Figure 4 the energy evolution over time on the four meshes, along with the evolution of the dissipation rates

\[ -\frac{E^n_h - E^{n-1}_h}{\Delta t^n}, \text{ and } \frac{\text{Diss}^n_h}{\Delta t^n}, \]

The results in Figure 4 numerically confirmed the energy stability result in Theorem 2.2. Moreover, the energy and dissipation rate evolution are very similar on the four meshes, and we also observe
that the computed dissipation rate \((E_h^{n-1} - E_h^n)/\Delta t^n\) is very close to and slightly larger than the...
Figure 3. Example 2. Logarithmic density $u_2 = \log(c_2)$ at different times obtained with the scheme (9) with $k = m = 1$ on a uniform mesh with mesh size $h = 1/128$.

physical dissipation rate $\text{Diss}_h^n/\Delta t^n$, which is again consistent with the equality (10c) in Theorem 2.2.

Figure 4. Example 2. The evolution of energy and dissipation rates over time on the four meshes.

Finally we plot in Figure 5 the evolution of the time step size, the error estimator $e^n = \left| (E^n_h - E_h^{n,lo})/E_h^n \right|$, and the number of Newton iterations. Again, the results on the four meshes are very similar to each other, and the average number of Newton iterations is about 3 – 4. In particular, we observe that the time step size gradually increases from $\Delta t = 10^{-4}$ to $\Delta t = \Delta t_{\text{max}} = 2$ till time $t = 14$, then it stays at $\Delta t_{\text{max}} = 2$ for a period of time till around $t = 235$, where a few drops in time step size occur from $t = 235$ to $t = 243$ due to a relative large error $e^n$. Afterwards, $\Delta t$ gradually increases to $\Delta t_{\text{max}} = 200$. The advantage of adaptive time stepping is also clearly illustrated in Figure 5 as a scheme with a uniform time step size $\Delta t = \Delta t^1 = 10^{-4}$ would need
about \(1.4 \times 10^7\) time steps to converge to steady state, while our adaptive time stepping scheme only needs about 200 time steps as shown in Table 2.

**Example 3.** (Two-dimensional problem with discontinuous coefficients) Here we solve a problem similar to Example 2 on a two-dimensional geometry. The computational domain is shown in Figure 6. We solve the variable-coefficient PNP equations (12) on the domain \(\Omega\) using the same set of parameters as in Example 2, with the only exception that the cross-section term is taken to be \(A(x) = \pi r(x)\) to take into account the 2D geometry. Homogeneous Dirichlet boundary conditions are imposed on the left and right boundaries segments \(OA\) and \(PF\), and homogeneous Neumann boundary conditions are imposed on the rest of the domain boundary.

The same second-order scheme (9) with polynomial degree \(k = m = 1\) and adaptive time stepping (13) is used here on three uniform unstructured meshes. The coarse mesh with mesh size \(h = 1/16\) has \(1.10 \times 10^5\) elements which leads to a total of \(3.37 \times 10^5\) degrees of freedom (DOFs). The medium mesh with mesh size \(h = 1/32\) has \(4.43 \times 10^5\) elements which leads to a total of \(1.34 \times 10^6\) DOFs. The fine mesh with mesh size \(h = 1/64\) has \(1.77 \times 10^6\) elements which leads to a total of \(5.34 \times 10^6\) DOFs. We use this example to show the performance of our method in a challenging two-dimensional problem with variable coefficient and complex geometry.

The computational results are very similar to the 1D case in Example 2. Hence, we only present in Figure 7 the evolution of \(u_2 = \log(c_2)\) at different times along the center cut line \(y = 0\). In
particular, we still observe that $c_2 = \exp(u_2)$ stays near zero for $x \in (-5, 10)$ for an extended period of time.

![Graph](image)

**Figure 7.** Example 3. Logarithmic density $u_2 = \log(c_2)$ along cut line $y = 0$ at different times obtained with the scheme (9) with $k = m = 1$ on a uniform unstructured mesh with mesh size $h = 1/32$ ($4.43 \times 10^5$ triangular elements).

We present in Table 3 the initial and final energy and the total number of time steps to reach the steady state, in Figure 8 the energy evolution and the evolution of the dissipation rates, and in Figure 9 the evolution of the time step size, the error estimator and the number of Newton iterations. Again, all the results are very similar to the 1D case in Example 2.

| mesh size $h$ | 1/16   | 1/32   | 1/64   |
|---------------|--------|--------|--------|
| initial energy| 402624.10 | 395346.31 | 391737.06 |
| final energy  | -2918.1776 | -2969.7288 | -2995.4971 |
| total time steps | 216 | 213 | 212 |

**Table 3.** Example 3. Initial and final energy, and total number of time steps to reach the steady state for the scheme (9) with $k = m = 1$ and adaptive time stepping (13) on different meshes.

4. Conclusion

We presented a novel class of high-order accurate, positivity preserving, and unconditionally energy stable space-time finite element schemes for the PNP equations based on discretizing the entropy variables associated to the densities. To the best of our knowledge, this is the first class of arbitrarily high-order accurate schemes for PNP equations that is both positivity preserving and unconditionally energy stable.

Our ongoing work consists of extending the STFEM framework to design positivity preserving and unconditionally energy stable schemes for other Wasserstein gradient flow problems, and their
coupling with incompressible flows like electrokinetic problems. We are also planning to investigate on alternative finite element discretizations, efficient linear system solvers, and more computationally efficient temporal discretizations for the PNP equations in the future.

Acknowledgement: We would like to thank Christoph Lehrenfeld for suggesting using the space-time framework in the ngSxFem software.

REFERENCES

[1] R. E. Bank, D. J. Rose, and W. Fichtner, Numerical methods for semiconductor device simulation, SIAM J. Sci. Statist. Comput., 4 (1983), pp. 416–435.
[2] T. J. Barth, Numerical methods for gas-dynamics systems on unstructured meshes, Lecture Notes in Computational Science and Engineering VOL 5, Springer, 1999.
[3] R. S. Eisenberg, ed., Ion channels in biological membranes: Electrostatic analysis of a natural nanotube, vol. 39, 1998.
[4] A. Flavell, M. Machen, B. Eisenberg, J. Kabre, C. Liu, and X. Li, A conservative finite difference scheme for Poisson-Nernst-Planck equations, Journal of Computational Electronics, 13 (2014), pp. 235–249.
[5] K. Gustafsson, M. Lundh, and G. Söderlind, A PI stepsize control for the numerical solution of ordinary differential equations, BIT, 28 (1988), pp. 270–287.
[6] A. Harten, On the symmetric form of systems of conservation laws with entropy, J. Comput. Phys., 49 (1983), pp. 151–164.
[7] B. Hille, ed., Ion Channels and Excitable Membranes, 3rd ed., Sinauer Associates, Inc., Sunderland, MA, 2001.
[8] J. Hu and X. Huang, A fully discrete positivity-preserving and energy-dissipative finite difference scheme for Poisson-Nernst-Planck equations, Numer. Math., 145 (2020), pp. 77–115.
[9] F. Huang and J. Shen, *Bound/Positivity preserving and energy stable SAV schemes for dissipative systems: Applications to Keller-Segel and Poisson-Nernst-Planck equations*, SIAM J. Sci. Comput. To appear, 2021.

[10] T. J. R. Hughes, L. P. Franca, and M. Balestra, *A new finite element formulation for computational fluid dynamics. V. Circumventing the Babuška-Brezzi condition: a stable Petrov-Galerkin formulation of the Stokes problem accommodating equal-order interpolations*, Comput. Methods Appl. Mech. Engrg., 59 (1986), pp. 85–99.

[11] J. W. Jerome, *Analysis of charge transport: A mathematical study of semiconductor devices*, Springer-Verlag, Berlin, 1996.

[12] D. Kinderlehrer, L. Monsaingeon, and X. Xu, *A Wasserstein gradient flow approach to Poisson-Nernst-Planck equations*, ESAIM Control Optim. Calc. Var., 23 (2017), pp. 137–164.

[13] C. Liu, C. Wang, S. M. Wise, X. Yue, and S. Zhou, *A positivity-preserving, energy stable and convergent numerical scheme for the Poisson-Nernst-Planck system*, [arXiv:2009.08076](https://arxiv.org/pdf/2009.08076.pdf) [math.NA].

[14] H. Liu and W. Maimaitiyiming, *Efficient, positive, and energy stable schemes for multi-D Poisson-Nernst-Planck systems*, [arXiv:2001.08350](https://arxiv.org/pdf/2001.08350.pdf) [math.NA].

[15] B. Lu, M. J. Holst, J. A. McCammon, and Y. C. Zhou, *Poisson-Nernst-Planck equations for simulating biomolecular diffusion-reaction processes I: finite element solutions*, J. Comput. Phys., 229 (2010), pp. 6979–6994.

[16] D. Meng, B. Zheng, G. Lin, and M. L. Sushko, *Numerical solution of 3D Poisson-Nernst-Planck equations coupled with classical density functional theory for modeling ion and electron transport in a confined environment*, Commun. Comput. Phys., 16 (2014), pp. 1298–1322.

[17] M. S. Metti, J. Xu, and C. Liu, *Energetically stable discretizations for charge transport and electrokinetic models*, J. Comput. Phys., 306 (2016), pp. 1–18.

[18] A. Prohl and M. Schmuck, *Convergent discretizations for the Nernst-Planck-Poisson system*, Numer. Math., 111 (2009), pp. 591–630.

[19] J. Schöberl, *C++11 Implementation of Finite Elements in NGSolve*, 2014. ASC Report 30/2014, Institute for Analysis and Scientific Computing, Vienna University of Technology.

[20] J. Shen and X. Jie, *Unconditionally positivity preserving and energy dissipative schemes for Poisson–Nernst–Planck equations*, [arXiv:2007.06132](https://arxiv.org/pdf/2007.06132.pdf) [math.NA].

[21] J. Shen, J. Xu, and J. Yang, *A new class of efficient and robust energy stable schemes for gradient flows*, SIAM Rev., 61 (2019), pp. 474–506.

[22] E. Tadmor, *Skew-selfadjoint form for systems of conservation laws*, J. Math. Anal. Appl., 103 (1984), pp. 428–442.

[23] Q. Zheng, D. Chen, and G.-W. Wei, *Second-order Poisson-Nernst-Planck solver for ion transport*, J. Comput. Phys., 230 (2011), pp. 5239–5262.

Department of Applied and Computational Mathematics and Statistics, University of Notre Dame, USA.

*Email address: gfu@nd.edu*

Department of Applied and Computational Mathematics and Statistics, University of Notre Dame, USA.

*Email address: zhiliangxu@nd.edu*