

THE FINITE ELEMENT APPROXIMATION OF THE NONLINEAR POISSON–BOLTZMANN EQUATION

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ABSTRACT. A widely used electrostatics model in the biomolecular modeling community, the nonlinear Poisson–Boltzmann equation, along with its finite element approximation, are analyzed in this paper. A regularized Poisson–Boltzmann equation is introduced as an auxiliary problem, making it possible to study the original nonlinear equation with delta distribution sources. A priori error estimates for the finite element approximation are obtained for the regularized Poisson–Boltzmann equation based on certain quasi-uniform grids in two and three dimensions. Adaptive finite element approximation through local refinement driven by an a posteriori error estimate is shown to converge. The Poisson–Boltzmann equation does not appear to have been previously studied in detail theoretically, and it is hoped that this paper will help provide molecular modelers with a better foundation for their analytical and computational work with the Poisson–Boltzmann equation. Note that this article apparently gives the first rigorous convergence result for a numerical discretization technique for the nonlinear Poisson–Boltzmann equation with delta distribution sources, and it also introduces the first provably convergent adaptive method for the equation. This last result is currently one of only a handful of existing convergence results of this type for nonlinear problems.

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1. INTRODUCTION

In this paper, we shall design and analyze finite element approximations of a widely used electrostatics model in the biomolecular modeling community, the nonlinear Poisson–Boltzmann equation (PBE):

$$-\nabla \cdot (\varepsilon \nabla \tilde{u}) + \bar{\kappa}^2 \sinh(\tilde{u}) = \sum_{i=1}^{N_m} q_i \delta_i \quad \text{in } \mathbb{R}^d, \quad d = 2, 3, \quad (1.1)$$

where the dielectric ε and the modified Debye–Hückel parameter $\bar{\kappa}$ are piecewise constants in domains Ω_m (the domain for the biomolecule of interest) and Ω_s (the domain for a solvent surrounding the biomolecule), and $\delta_i := \delta(x - x_i)$ is a Dirac distribution at point x_i . The importance of (1.1) in biomolecular modeling is well-established; cf. [14, 43] for thorough discussions. Some analytical solutions are known, but only for unrealistic structure geometries, and usually only for linearizations of the equation; cf. [29] for a collection of these solutions and for references to the large amount of literature on analytical solutions to the PBE and similar equations. The current technological advances are more demanding and require the solution of highly nonlinear problems in complicated geometries. To this end, numerical methods, including the finite element method, are widely used to solve the nonlinear PBE [29, 30, 5, 6, 44, 19, 56].

The main difficulties for the rigorous analysis and provably good numerical approximation of solutions to the nonlinear Poisson–Boltzmann equation include: (1) Dirac distribution sources, (2) exponential rapid nonlinearities, and (3) discontinuous coefficients. We shall address these difficulties in this paper. To deal with the δ distribution sources, we decompose \tilde{u} as an unknown function in H^1 and a known singular function, namely,

$$\tilde{u} = u + G, \quad \text{with } G = \sum_{i=1}^{N_m} G_i,$$

where G_i is the fundamental solution of $-\varepsilon_m \Delta G_i = q_i \delta_i$ in \mathbb{R}^d . Substituting this decomposition into the PBE, we then obtain the so-called regularized Poisson–Boltzmann equation (RPBE):

$$-\nabla \cdot (\varepsilon \nabla u) + \bar{\kappa}^2 \sinh(u + G) = \nabla \cdot ((\varepsilon - \varepsilon_m) \nabla G) \quad \text{in } \mathbb{R}^d, \quad d = 2, 3.$$

The singularities of the δ distributions are transferred to G , which then exhibits degenerate behavior at each $\{x_i\} \subset \Omega_m$. At those points, both $\sinh G(x_i)$ and $\nabla G(x_i)$ exhibit blowup. However, since G is known analytically, one avoids having to build numerical approximations to G . Moreover, both of the coefficients $\bar{\kappa}$ and $\varepsilon - \varepsilon_m$ are zero inside Ω_m where the blowup behavior arises. Due to this cutoff nature of coefficients, we obtain a well-defined nonlinear second-order elliptic equation for the regularized solution u with a source term in H^{-1} . We will show that it also admits a unique solution $u \in H^1$, even though the original solution $\tilde{u} \notin H^1$ due to the singularities present in G .

Singular function expansions are a common technique in applied and computational mathematics for this type of singularity; this type of expansion has been previously proposed for the Poisson–Boltzmann equation in [58] and was shown (empirically) to allow for more accurate finite difference approximations. In their work, the motivation for the technique was the poor discrete approximation of arbitrarily placed delta distributions using only the fixed corners of uniform finite difference meshes. In the present work, our interest is in developing finite element methods using completely unstructured meshes, so we are able to place the delta distributions precisely where they should be and do not have

this problem with approximate delta function placement. Our motivation here for considering a singular function expansion is rather that the solution to the Poisson–Boltzmann equation is simply not smooth enough to either analyze or approximate using standard methods without using some sort of two-scale or multiscale expansion that represents the nonsmooth part of the solution analytically. In fact, it will turn out that expanding the solution into the sum of three functions, namely, a known singular function, an unknown solution to a linear auxiliary problem, and an unknown solution to a second nonlinear auxiliary problem, is the key to establishing some fundamental results and estimates for the continuous problem and is also the key to developing a complete approximation theory for the discrete problem as well as provably convergent nonadaptive and adaptive numerical methods.

Starting with some basic results on existence, uniqueness, and a priori estimates for the continuous problem, we analyze the finite element discretization and derive discrete analogues of the continuous results to show that discretization leads to a well-posed discrete problem. Using maximum principles for the continuous and discrete problems, we derive a priori L^∞ -estimates for the continuous and discrete solutions to control the nonlinearity, allowing us to obtain a priori error estimates for our finite element approximation of the form

$$\|u - u_h\|_1 \lesssim \inf_{v_h \in V_D^h} \|u - v_h\|_1,$$

where V_D^h is the linear finite element subspace defined over quasi-uniform triangulations with a certain boundary condition, and u_h is the finite element approximation of u in V_D^h . The result is *quasi-optimal* in the sense it implies that the finite element approximation to the RPBE is within a constant of being the best approximation from the subspace V_D^h . After establishing these results for finite element approximations, we describe an adaptive approximation algorithm that uses mesh adaptation through local refinement driven by a posteriori error estimates. The adaptive algorithm can be viewed as a mechanism for dealing with the primary remaining difficulty in the RPBE, namely, the discontinuities of the coefficients across the interface between the solvent and the molecular regions. Finally, we shall prove that our adaptive finite element method will produce a sequence of approximations that converges to the solution of the continuous nonlinear PBE. This last result is one of only a handful of existing results of this type for nonlinear elliptic equations (the others being [24, 48, 15]).

The outline of this paper is as follows. In section 2, we give a brief derivation and overview of the Poisson–Boltzmann equation. In section 3, we derive a regularized form of the Poisson–Boltzmann equation by using a singular function expansion. In section 4, we give some basic existence and uniqueness results for the RPBE. In section 5, we derive an a priori L^∞ -estimate for the continuous problem. After introducing finite element methods for the RPBE, in section 6 we derive an analogous a priori L^∞ -estimate for the discrete problem, and based on this we obtain a quasi-optimal a priori error estimate for the finite element approximation. In section 7, we describe the adaptive algorithm, present an a posteriori error estimate, and prove a general convergence result for the algorithm. In the last section, we summarize our work and give further remarks on the practical aspects using results in the present paper.

2. THE POISSON–BOLTZMANN EQUATION

In this section we shall give a brief introduction to the nonlinear Poisson–Boltzmann equation. A detailed derivation can be found in [47, 29].

The nonlinear PBE, a second-order nonlinear partial differential equation, is fundamental to Debye–Hückel continuum electrostatic theory [22]. It determines a dimensionless potential around a charged biological structure immersed in a salt solution. The PBE arises from the Gauss law, represented mathematically by the Poisson equation, which relates the electrostatic potential Φ in a dielectric to the charge density ρ :

$$-\nabla \cdot (\varepsilon \nabla \Phi) = \rho,$$

where ε is the dielectric constant of the medium and here is typically piecewise constant. Usually it jumps by one or two orders of magnitude at the interface between the charged structure (a biological molecular or membrane) and the solvent (a salt solution). The charge density ρ consist of two components: $\rho = \rho_{\text{macro}} + \rho_{\text{ion}}$. For the macromolecule, the charge density is a summation of δ distributions at N_m point charges in the point charge behavior, i.e.,

$$\rho_{\text{macro}}(x) = \sum_{i=1}^{N_m} q_i \delta(x - x_i), \quad q_i = \frac{4\pi e_c^2}{\kappa_B T} z_i,$$

where $\kappa_B > 0$ is the Boltzmann constant, T is the temperature, e_c is the unit of charge, and z_i is the amount of charge.

For the mobile ions in the solvent, the charge density ρ_{ion} cannot be given in a deterministic way. Instead it will be given by the Boltzmann distribution. If the solvent contains N types of ions, of valence Z_i and of bulk concentration c_i , then a Boltzmann assumption about the equilibrium distribution of the ions leads to

$$\rho_{\text{ion}} = \sum_{i=1}^N c_i Z_i e_c \exp\left(-Z_i \frac{e_c \Phi}{\kappa_B T}\right).$$

For a symmetric 1 : 1 electrolyte, $N = 2$, $c_i = c_0$, and $Z_i = (-1)^i$, which yields

$$\rho_{\text{ion}} = -2c_0 e_c \sinh\left(\frac{e_c \Phi}{\kappa_B T}\right).$$

We can now write the PBE for modeling the electrostatic potential of a solvated biological structure. Let us denote the molecule region by $\Omega_m \subset \mathbb{R}^d$ and consider the solvent region $\Omega_s = \mathbb{R}^d \setminus \bar{\Omega}_m$. We use \tilde{u} to denote the dimensionless potential and $\bar{\kappa}^2$ to denote the modified Debye–Hückel parameter (which is a function of the ionic strength of the solvent). The nonlinear Poisson–Boltzmann equation is then

$$-\nabla \cdot (\varepsilon \nabla \tilde{u}) + \bar{\kappa}^2 \sinh(\tilde{u}) = \sum_{i=1}^{N_m} q_i \delta_i \quad \text{in } \mathbb{R}^d, \quad (2.1)$$

$$\tilde{u}(\infty) = 0, \quad (2.2)$$

where

$$\varepsilon = \begin{cases} \varepsilon_m & \text{if } x \in \Omega_m, \\ \varepsilon_s & \text{if } x \in \Omega_s, \end{cases} \quad \text{and} \quad \bar{\kappa} = \begin{cases} 0 & \text{if } x \in \Omega_m, \\ \sqrt{\varepsilon_s} \kappa > 0 & \text{if } x \in \Omega_s. \end{cases}$$

It has been determined empirically that $\varepsilon_m \approx 2$ and $\varepsilon_s \approx 80$. The structure itself (e.g., a biological molecule or a membrane) is represented implicitly by ε and $\bar{\kappa}$, as well as explicitly by the N_m point charges $q_i = z_i e_c$ at the positions x_i . The charge positions are located in the strict interior of the molecular region Ω_m . A physically reasonable

mathematical assumption is that all charge locations obey the following lower bound on their distance to the solvent region Ω_s for some $\sigma > 0$:

$$|x - x_i| \geq \sigma \quad \forall x \in \Omega_s, \quad i = 1, \dots, N_m. \quad (2.3)$$

In some models employing the PBE, there is a third region Ω_l (the Stern layer [11]), a layer between Ω_m and Ω_s . In the presence of a Stern layer, the parameter σ in (2.3) increases in value. Our analysis and results can be easily generalized to this case as well.

Some analytical solutions of the nonlinear PBE are known, but only for unrealistic structure geometries and usually only for linearizations of the equation; cf. [29] for a collection of these solutions and for references to the large amount of literature on analytical solutions to the PBE and similar equations. However, the problem is highly nonlinear. Surface potentials of the linear and the nonlinear PBE differ by over an order of magnitude [44]. Hence, using the nonlinear version of the PBE model is fundamentally important to accurately describe physical effects, and access to reliable and accurate numerical approximation techniques for the nonlinear PBE is critically important in this research area.

We finish this section by making some remarks about an alternative equivalent formulation of the PBE. It is well known (cf. [47, 29]) that the PBE is formally equivalent to a coupling of two equations for the electrostatic potential in different regions Ω_m and Ω_s through the boundary interface. This equivalence can be rigorously justified. Inside Ω_m , there are no ions. Thus the equation is simply the Poisson equation

$$-\nabla \cdot (\varepsilon_m \nabla \tilde{u}) = \sum_{i=1}^{N_m} q_i \delta_i \quad \text{in } \Omega_m.$$

In the solvent region Ω_s , there are no atoms. Thus the density is given purely by the Boltzmann distribution

$$-\nabla \cdot (\varepsilon_s \nabla \tilde{u}) + \bar{\kappa}^2 \sinh(\tilde{u}) = 0 \quad \text{in } \Omega_s.$$

These two equations are coupled together through the boundary conditions on the interface $\Gamma := \partial\Omega_m = \partial\Omega_s \cap \Omega_m$:

$$[\tilde{u}]_\Gamma = 0, \quad \text{and} \quad \left[\varepsilon \frac{\partial \tilde{u}}{\partial n_\Gamma} \right]_\Gamma = 0,$$

where $[f]_\Gamma = \lim_{t \rightarrow 0} f(x + tn_\Gamma) - f(x - tn_\Gamma)$, with n_Γ being the unit outward normal direction of interface Γ . We will assume Γ to be sufficiently smooth, say, of class C^2 .

Solving the individual subdomain systems and coupling them through the boundary, in the spirit of a nonoverlapping domain decomposition method, is nontrivial due to the complicated boundary conditions and subdomain shapes. Approaches such as mortar-based finite element methods to solve the coupled equations for linear or nonlinear PBE can be found in [19, 51].

3. REGULARIZATION OF THE CONTINUOUS PROBLEM

In this section, we shall introduce a regularized version of the nonlinear PBE for both analysis and discretization purposes. We first transfer the original equation posed on the whole space to a truncated domain using an artificial boundary condition taken from an approximate analytical solution. Then we use the fundamental solution in the whole space to get rid of the singularities caused by δ distributions. We shall mainly focus on more difficult problems in three dimensions. Formulation and results in two dimensions are similar and relatively easy.

Let $\Omega \subset \mathbb{R}^3$ with a convex and Lipschitz-continuous boundary $\partial\Omega$, and $\Omega_m \subset \Omega$. In the numerical simulation, for simplicity, we usually choose Ω to be a ball or cube containing a molecule region. The solvent region is chosen as $\Omega_s \cap \Omega$ and will be still denoted by Ω_s . On $\partial\Omega$ we choose the boundary condition $\tilde{u} = g$, with

$$g = \left(\frac{e_c^2}{k_B T} \right) \sum_{i=1}^{N_i} \frac{e^{-\kappa|x-x_i|}}{\varepsilon_s |x-x_i|}. \quad (3.1)$$

The boundary condition is usually taken to be induced by a known analytical solution to one of several possible simplifications of the linearized PBE. Far from the molecule, such analytical solutions provide a highly accurate boundary condition approximation for the general nonlinear PBE on a truncation of \mathbb{R}^3 . For example, (3.1) arises from the use of the Green's function for the Helmholtz operator arising from linearizations of the Poisson–Boltzmann operator, where a single constant global dielectric value of ε_s is used to generate the approximate boundary condition. (This is the case of a rod-like molecule approximation; cf. [29].) Another approach to handling the boundary condition more accurately is to solve the PBE with boundary conditions such as (3.1) on a large Ω (with a coarse mesh) and then solve it in a smaller Ω (with a fine mesh) with the boundary condition provided by the earlier coarse mesh solution. The theoretical justification of this approach can be found at [28] using the two-grid theory [53]. We are not going to discuss more on the choice of the boundary condition in this paper.

Employing (3.1) we obtain the nonlinear PBE on a truncated domain:

$$-\nabla \cdot (\varepsilon \nabla \tilde{u}) + \bar{\kappa}^2 \sinh(\tilde{u}) = \sum_{i=1}^{N_m} q_i \delta_i \quad \text{in } \Omega, \quad (3.2)$$

$$\tilde{u} = g \quad \text{on } \partial\Omega. \quad (3.3)$$

This is, in most respects, a standard boundary-value problem for a nonlinear second-order elliptic partial differential equation. However, the right side contains a linear combination of δ distributions, which individually and together are not in $H^{-1}(\Omega)$; thus we cannot apply standard techniques such as classical potential theory. This has at times been the source of some confusion in the molecular modeling community, especially with respect to the design of convergent numerical methods. More precisely, we will see shortly that the solution to the nonlinear Poisson–Boltzmann equation is simply not globally smooth enough to expect standard numerical methods (currently used by most PBE simulators) to produce approximations that converge to the solution to the PBE in the limit of mesh refinement.

In order to gain a better understanding of the properties of solutions to the nonlinear PBE, primarily so that we can design new provably convergent numerical methods, we shall propose a decomposition of the solution to separate out the singularity caused by the δ distributions. This decomposition will turn out to be the key idea that will allow us to design discretization techniques for the nonlinear PBE which have provably good approximation properties and, based on this, also design a new type of adaptive algorithm which is provably convergent for the nonlinear PBE.

We now give this decomposition. It is well known that the function

$$G_i = \frac{q_i}{\varepsilon_m} \frac{1}{|x-x_i|}$$

solves the equation

$$-\nabla \cdot (\varepsilon_m \nabla G_i) = q_i \delta_i \quad \text{in } \mathbb{R}^3.$$

We thus decompose the unknown \tilde{u} as an unknown smooth function u and a known singular function G :

$$\tilde{u} = u + G,$$

with

$$G = \sum_{i=1}^{N_m} G_i. \quad (3.4)$$

Substituting the decomposition into (3.2), we then obtain

$$-\nabla \cdot (\varepsilon \nabla u) + \bar{\kappa}^2 \sinh(u + G) = \nabla \cdot ((\varepsilon - \varepsilon_m) \nabla G) \quad \text{in } \Omega, \quad (3.5)$$

$$u = g - G \quad \text{on } \partial\Omega, \quad (3.6)$$

and call it the RPBE. The singularities of the δ distributions are transferred to G , which then exhibits degenerate behavior at each $\{x_i\} \subset \Omega_m$. At those points, both $\sinh G(x_i)$ and $\nabla G(x_i)$ exhibit blowup. However, since G is known analytically, one avoids having to build numerical approximations to G . Moreover, both of the coefficients $\bar{\kappa}$ and $\varepsilon - \varepsilon_m$ are zero inside Ω_m , where the blowup behavior arises. Due to this cutoff nature of coefficients, the RPBE is a mathematically well defined nonlinear second-order elliptic equation for the regularized solution u with the source term in H^{-1} . We give a fairly standard argument in the next section to show that it also admits a unique solution $u \in H^1$, even though the original solution $\tilde{u} \notin H^1$ due to the singularities present in G . In the remainder of the paper we shift our focus to establishing additional estimates and developing an approximation theory to guide the design of convergent methods, both nonadaptive and adaptive.

Before moving on, it is useful to note that, away from $\{x_i\}$, the function G is smooth. In particular, we shall make use of the fact that $G \in C^\infty(\Omega_s) \cap C^\infty(\Gamma) \cap C^\infty(\partial\Omega)$ in the later analysis. Also, a key technical tool will be a further decomposition of the regularized solution u into linear and nonlinear parts, $u = u^l + u^n$, where u^l satisfies

$$-\nabla \cdot (\varepsilon \nabla u^l) = \nabla \cdot ((\varepsilon - \varepsilon_m) \nabla G) \quad \text{in } \Omega, \quad (3.7)$$

$$u^l = 0 \quad \text{on } \partial\Omega, \quad (3.8)$$

and where u^n satisfies

$$-\nabla \cdot (\varepsilon \nabla u^n) + \bar{\kappa}^2 \sinh(u^n + u^l + G) = 0 \quad \text{in } \Omega, \quad (3.9)$$

$$u^n = g - G \quad \text{on } \partial\Omega. \quad (3.10)$$

4. EXISTENCE AND UNIQUENESS

In this section we shall discuss the existence and uniqueness of the solution of the continuous RPBE. The arguments we use in this section appear essentially in [29], except there the PBE was artificially regularized by replacing the delta distributions with H^{-1} -approximations directly rather than being regularized through a singular function expansion.

We first write out the weak formulation. Since $\Delta G = 0$ away from $\{x_i\}$, through integration by parts we get the weak formulation of RPBE: Find

$$u \in M := \{v \in H^1(\Omega) \mid e^v, e^{-v} \in L^2(\Omega_s), \text{ and } v = g - G \text{ on } \partial\Omega\}$$

such that

$$A(u, v) + (B(u), v) + \langle f_G, v \rangle = 0 \quad \forall v \in H_0^1(\Omega), \quad (4.1)$$

where

- $A(u, v) = (\varepsilon \nabla u, \nabla v),$

- $(B(u), v) = (\bar{\kappa}^2 \sinh(u + G), v)$, and
- $\langle f_G, v \rangle = \int_{\Omega} (\varepsilon - \varepsilon_m) \nabla G \cdot \nabla v$.

Let us define the energy on M :

$$E(w) = \int_{\Omega} \frac{\varepsilon}{2} |\nabla w|^2 + \bar{\kappa}^2 \cosh(w + G) + \langle f_G, w \rangle.$$

It is easy to characterize the solution of (4.1) as the minimizer of the energy.

Lemma 4.1. *If u is the solution of the optimization problem, i.e.,*

$$E(u) = \inf_{w \in M} E(w),$$

then u is the solution of (4.1).

Proof. For any $v \in H_0^1(\Omega)$ and any $t \in \mathbb{R}$, the function $F(t) = E(u + tv)$ attains the minimal point at $t = 0$, and thus $F'(0) = 0$, which gives the desired result. \square

We now recall some standard variational analysis on the existences of the minimizer. In what follows we suppose S is a set in some Banach space V with norm $\|\cdot\|$, and $J(u)$ is a functional defined on S . S is called *weakly sequential compact* if, for any sequence $\{u_k\} \subset S$, there exists a subsequence $\{u_{k_i}\}$ such that $u_{k_i} \rightharpoonup u \in S$, where \rightharpoonup stands for the convergence in the weak topology. For any $u_k \rightharpoonup u$, if $J(u_k) \rightarrow J(u)$, we say J is *weakly continuous* at u ; if

$$J(u) \leq \liminf_{k \rightarrow \infty} J(u_k),$$

we say J is *weakly lower semicontinuous* (w.l.s.c.) at u . The following theorem can be proved by the definition easily.

Theorem 4.2. *If*

1. S is weakly sequential compact, and
2. J is weakly lower semicontinuous on S ,

then there exists $u \in S$ such that

$$J(u) = \inf_{w \in S} J(w).$$

We shall give conditions for the weakly sequential compactness and weakly lower semicontinuity. First we use the fact that a bounded set in a reflexive Banach space is weakly sequential compact.

Lemma 4.3. *One has the following results:*

1. *The closed unit ball in a reflexive Banach space V is weakly sequential compact.*
2. *If $\lim_{\|v\| \rightarrow \infty} J(v) = \infty$, then*

$$\inf_{w \in V} J(w) = \inf_{w \in S} J(w).$$

The next lemma concerns when the functional is w.l.s.c. The proof can be found at [57].

Lemma 4.4. *If J is a convex functional on a convex set S and J is Gâteaux differentiable, then J is w.l.s.c. on S .*

Now we are in the position to establish the existence and uniqueness of solutions to the RPBE.

Theorem 4.5. *There exists a unique $u \in M \subset H^1(\Omega)$ such that*

$$E(u) = \inf_{w \in M} E(w).$$

Proof. It is easy to see $E(w)$ is differentiable in M with

$$\langle DE(u), v \rangle = A(u, v) + (B(u), v) + \langle f_G, v \rangle.$$

To prove the existence of the minimizer, we need only to verify that

- (1) M is a convex set,
- (2) E is convex on M , and
- (3) $\lim_{\|v\|_1 \rightarrow \infty} E(v) = \infty$.

The verification of (1) is easy and thus skipped here. (2) comes from the convexity of functions x^2 and $\cosh(x)$. Indeed E is *strictly* convex. (3) is a consequence of the inequality

$$E(v) \geq C(\varepsilon, \bar{\kappa})\|v\|_1^2 + C(G, g), \quad (4.2)$$

which can be proved as following. First, by Young's inequality we have for any $\delta > 0$

$$\langle f_G, v \rangle \leq \varepsilon_s \|\nabla G\|_{\Omega_s} \|\nabla v\|_{\Omega_s} \leq \frac{1}{\delta} \|\nabla G\|_{\Omega_s}^2 + \delta \varepsilon_s^2 \|\nabla v\|_{\Omega_s}^2.$$

Since $\cosh(x) \geq 0$, we have then $E(v) \geq C(\varepsilon, \bar{\kappa})\|\nabla v\|^2 - (1/\delta)\|\nabla G\|_{\Omega_s}^2$, where we can ensure $C(\varepsilon, \bar{\kappa}) > 0$ if δ is chosen to be sufficiently small. Then using norm equivalence on M , we get (4.2). The uniqueness of the minimizer comes from the strict convexity of E . \square

5. CONTINUOUS A PRIORI L^∞ -ESTIMATES

In this section, we shall derive a priori L^∞ -estimates of the solution of the RPBE. The main result of this section is the following theorem.

Theorem 5.1. *Let u be the weak solution of RPBE in $H^1(\Omega)$. Then u is also in $L^\infty(\Omega)$.*

Note that we cannot apply the analysis of [31, 32] directly to the RPBE, since the right side $f_G \in H^{-1}(\Omega)$ and does not lie in $L^\infty(\Omega)$ as required for use of these results. We shall overcome this difficulty through further decomposition of u into linear and nonlinear parts.

Let $u = u^l + u^n$, where $u^l \in H_0^1(\Omega)$ satisfies the linear elliptic equation (the weak form of (3.7)–(3.8))

$$A(u^l, v) + \langle f_G, v \rangle = 0 \quad \forall v \in H_0^1(\Omega) \quad (5.1)$$

and where $u^n \in M$ satisfies the nonlinear elliptic equation (the weak form of (3.9)–(3.10))

$$A(u^n, v) + (B(u^n + u^l), v) = 0 \quad \forall v \in H_0^1(\Omega). \quad (5.2)$$

Theorem 5.1 then follows from the estimates of u^l and u^n in Lemmas 5.2 and 5.3; cf. (5.3) and (5.4).

Lemma 5.2. *Let u^l be the weak solution of (5.1). Then*

$$u^l \in L^\infty(\Omega). \quad (5.3)$$

Proof. Since $\Delta G = 0$ in Ω_s , using integral by parts we can rewrite the functional f_G as

$$\langle f_G, v \rangle = ((\varepsilon - \varepsilon_m) \nabla G, \nabla v) = \left([\varepsilon] \frac{\partial G}{\partial n_\Gamma}, v \right)_\Gamma,$$

where $[\varepsilon] = \varepsilon_s - \varepsilon_m$ is the jump of ε at the interface. We shall still use f_G to denote the smooth function $[\varepsilon] \frac{\partial G}{\partial n_\Gamma}$ on Γ .

It is easy to see that the linear equation (5.1) is the weak formulation of the elliptic interface problem

$$-\nabla \cdot (\varepsilon \nabla u^l) = 0 \text{ in } \Omega \quad [u^l] = 0, \quad \left[\varepsilon \frac{\partial u^l}{\partial n} \right] = f_G \text{ on } \Gamma, \quad \text{and } u = 0 \text{ on } \partial\Omega.$$

Since $f_G \in C^\infty(\Gamma)$ and $\Gamma \in C^2$, by the regularity result of the elliptic interface problem [4, 12, 20, 41], we have $u^l \in H^2(\Omega_m) \cap H^2(\Omega_s) \cap H_0^1(\Omega)$. In particular by the embedding theorem we conclude that $u^l \in L^\infty(\Omega)$. \square

To derive a similar estimate for the nonlinear part u^n , we define

$$\begin{aligned} \alpha' &= \arg \max_c \left(\bar{\kappa}^2 \sinh(c + \sup_{x \in \Omega_s} (u^l + G)) \leq 0 \right), & \alpha &= \min \left(\alpha', \inf_{\partial\Omega} (g - G) \right), \\ \beta' &= \arg \min_c \left(\bar{\kappa}^2 \sinh(c + \inf_{x \in \Omega_s} (u^l + G)) \geq 0 \right), & \beta &= \max \left(\beta', \sup_{\partial\Omega} (g - G) \right). \end{aligned}$$

The next lemma gives the a priori L^∞ -estimate of u^n .

Lemma 5.3. *Let u^n be the weak solution of (5.2). Then $\alpha \leq u^n \leq \beta$, and thus*

$$u^n \in L^\infty(\Omega). \quad (5.4)$$

Proof. We use a cutoff-function argument similar to that used in [31]. Since the boundary condition $g - G \in C^\infty(\partial\Omega)$, we can find a $u_D \in H^1(\Omega)$ such that $u_D = g - G$ on $\partial\Omega$ in the trace sense, or more precisely

$$Tu_D = g - G,$$

where $T : \Omega \mapsto \partial\Omega$ is the trace operator. Then the solution can be written $u^n = u_D + u_0$, with $u_0 \in H_0^1(\Omega)$. Let $\bar{\phi} = (u^n - \beta)^+ = \max(u^n - \beta, 0)$ and $\underline{\phi} = (u^n - \alpha)^- = \min(u^n - \alpha, 0)$. Then from

$$\begin{aligned} 0 &\leq \bar{\phi} = (u^n - \beta)^+ = (u_D + u_0 - \beta)^+ \leq (u_D - \beta)^+ + u_0^+, \\ 0 &\geq \underline{\phi} = (u^n - \alpha)^- = (u_D + u_0 - \alpha)^- \geq (u_D - \alpha)^- + u_0^-, \end{aligned}$$

and

$$\begin{aligned} 0 &\leq T\bar{\phi} \leq T(u_D - \beta)^+ + Tu_0^+ = 0, \\ 0 &\geq T\underline{\phi} \geq T(u_D - \alpha)^- + Tu_0^- = 0, \end{aligned}$$

we conclude that both $\bar{\phi}, \underline{\phi} \in H_0^1(\Omega)$. Thus for either $\phi = \bar{\phi}$ or $\phi = \underline{\phi}$, we have

$$(\varepsilon \nabla u^n, \nabla \phi) + (\bar{\kappa}^2 \sinh(u^n + u^l + G), \phi) = 0.$$

Note that $\bar{\phi} \geq 0$ in Ω and its support is the set $\bar{\mathcal{Y}} = \{x \in \bar{\Omega} \mid u^n(x) \geq \beta\}$. On $\bar{\mathcal{Y}}$, we have

$$\bar{\kappa}^2 \sinh(u^n + u^l + G) \geq \bar{\kappa}^2 \sinh \left(\beta' + \inf_{x \in \Omega_s} (u^l + G) \right) \geq 0.$$

Similarly, $\underline{\phi} \leq 0$ in Ω with support set $\underline{\mathcal{Y}} = \{x \in \bar{\Omega} \mid u^n(x) \leq \alpha\}$. On $\underline{\mathcal{Y}}$, we now have

$$\bar{\kappa}^2 \sinh(u^n + u^l + G) \leq \bar{\kappa}^2 \sinh \left(\alpha' + \inf_{x \in \Omega_s} (u^l + G) \right) \leq 0.$$

Together this implies

$$0 \geq (\varepsilon \nabla u^n, \nabla \phi) = (\varepsilon \nabla (u^n - \beta), \nabla \phi) = \varepsilon \|\nabla \phi\|^2 \geq 0$$

for either $\phi = \bar{\phi}$ or $\phi = \underline{\phi}$. Using the Poincare inequality we have finally

$$0 \leq \|\phi\| \lesssim \|\nabla \phi\| \leq 0,$$

giving $\phi = 0$, again for either $\phi = \bar{\phi}$ or $\phi = \underline{\phi}$. Thus $\alpha \leq u^n \leq \beta$ in Ω . \square

6. FINITE ELEMENT METHODS FOR THE REGULARIZED POISSON–BOLTZMANN EQUATION

In this section we shall discuss the finite element discretization of RPBE using linear finite element spaces V_D^h and prove the existence and uniqueness of the finite element approximation u_h . Furthermore, under some assumptions on the grids we shall derive a priori L^∞ -estimates for u_h and use these to prove that u_h is a quasi-optimal approximation of u in the H^1 norm in the sense that

$$\|u - u_h\|_1 \lesssim \inf_{v_h \in V_D^h} \|u - v_h\|_1. \quad (6.1)$$

While the term on the left in (6.1) is in general difficult to analyze, the term on the right represents the fundamental question addressed by classical approximation theory in normed spaces, of which much is known. To bound the term on the right from above, one picks a function in V_D^h which is particularly easy to work with, namely, a nodal or generalized interpolant of u , and then one employs standard techniques in interpolation theory. Therefore, it is clear that the importance of approximation results such as (6.1) are that they completely separate the details of the Poisson–Boltzmann equation from the approximation theory, making available all known results on finite element interpolation of functions in Sobolev spaces (cf. [21]).

Now we assume Ω can be triangulated exactly (e.g., Ω is a cube) with a shape regular and conforming (in the sense of [21]) triangulation \mathcal{T}_h . Here $h = h_{\max}$ represents the mesh size which is the maximum diameter of elements in the triangulation. We further assume in the triangulation that the discrete interface Γ_h approximates the known interface Γ to the second order, i.e., $d(\Gamma, \Gamma_h) \leq Ch^2$.

Given such a triangulation \mathcal{T}_h of Ω , we construct the linear finite element space $V^h := \{v \in H^1(\Omega), v|_\tau \in \mathcal{P}_1(\tau) \forall \tau \in \mathcal{T}_h\}$. Since the boundary condition $g - G \in C^\infty(\partial\Omega)$, we can find a $u_D \in H^1(\Omega)$ such that $u_D = g - G$ on $\partial\Omega$ in the trace sense. Then the solution can be uniquely written as $u = u_D + u_0$, with $u_0 \in H_0^1$. Thus we will use $H_D^1(\Omega) := H_0^1(\Omega) + u_D$ to denote the affine space with a specified boundary condition and $V_D^h = V^h \cap H_D^1(\Omega)$ to denote the finite element affine space of $H_D^1(\Omega)$. Similarly $V_0^h = V^h \cap H_0^1(\Omega)$. Here to simplify the analysis the boundary condition is assumed to be represented exactly.

Recall that the weak form of RPBE is

$$\text{Find } u \in H_D^1(\Omega) \text{ such that (s.t.) } A(u, v) + (B(u), v) + \langle f_G, v \rangle = 0 \forall v \in H_0^1(\Omega). \quad (6.2)$$

We are interested in the quality of the finite element approximation:

$$\text{Find } u_h \in V_D^h \text{ s.t. } A(u_h, v_h) + (B(u_h), v_h) + \langle f_G, v \rangle = 0 \forall v_h \in V_0^h. \quad (6.3)$$

It is easy to show that the finite element approximation u_h is the minimizer of E in V_D^h , i.e., $E(u_h) = \inf_{v_h \in V_D^h} E(v_h)$. Then the existence and uniqueness follows from section 3 since V_D^h is convex. As in the continuous setting, it will be convenient to split the discrete solution to the RPBE into linear and nonlinear parts $u_h = u_h^l + u_h^n$, where u_h^l and u_h^n satisfy, respectively,

$$\text{Find } u_h^l \in V_0^h \text{ s.t. } A(u_h^l, v_h) + \langle f_G, v \rangle = 0 \forall v_h \in V_0^h, \quad (6.4)$$

$$\text{Find } u_h^n \in V_D^h \text{ s.t. } A(u_h^n, v_h) + \langle B(u_h^n + u_h^l), v_h \rangle = 0 \forall v_h \in V_0^h. \quad (6.5)$$

6.1. Quasi-optimal a priori error estimate. We begin with the following properties of the bilinear form A and operator B .

Lemma 6.1. 1. *The bilinear form $A(u, v)$ satisfies the coercivity and continuity conditions. That is, for $u, v \in H^1(\Omega)$*

$$\|u\|_1^2 \lesssim A(u, u), \quad \text{and} \quad A(u, v) \lesssim \|u\|_1 \|v\|_1.$$

2. *The operator B is monotone in the sense that*

$$(B(u) - B(v), u - v) \geq \bar{\kappa}^2 \|u - v\|^2 \geq 0.$$

3. *The operator B is bounded in the sense that for $u, v \in L^\infty(\Omega), w \in L^2(\Omega)$,*

$$(B(u) - B(v), w) \leq C \|u - v\| \|w\|.$$

Proof. The proof of (1) and (2) is straightforward. We now prove (3). By the mean value theorem, there exists $\theta \in (0, 1)$ such that

$$B(u) - B(v) = \bar{\kappa}^2 \cosh(\theta u + (1 - \theta)v + G)(u - v).$$

Then by the convexity of \cosh and the fact that $u, v \in L^\infty(\Omega), G \in C^\infty(\Omega_s)$, we get

$$\|\cosh(\theta u + (1 - \theta)v + G)\|_{\infty, \Omega_s} \leq \|\cosh(u + G)\|_{\infty, \Omega_s} + \|\cosh(v + G)\|_{\infty, \Omega_s} \leq C.$$

The desired result then follows since $B(\cdot)$ is nonzero only in Ω_s . \square

Theorem 6.2. *Let u and u_h be the solution of RPBE and its finite element approximation, respectively. When u_h is uniformly bounded, we have*

$$\|u - u_h\|_1 \lesssim \inf_{v_h \in V^h} \|u - v_h\|_1.$$

Proof. By the definition, the error $u - u_h$ satisfies

$$A(u - u_h, w_h) + (B(u) - B(u_h), w_h) = 0 \quad \forall w_h \in V_0^h.$$

We then have, for any $v_h \in V_D^h$,

$$\begin{aligned} \|u - u_h\|_1^2 &\lesssim A(u - u_h, u - u_h) = A(u - u_h, u - v_h) + A(u - u_h, v_h - u_h) \\ &\lesssim \|u - u_h\|_1 \|u - v_h\|_1 - (B(u) - B(u_h), v_h - u_h). \end{aligned}$$

The second term on the right side is estimated by

$$\begin{aligned} -(B(u) - B(u_h), v_h - u_h) &= -(B(u) - B(u_h), u - u_h) + (B(u) - B(u_h), u - v_h) \\ &\leq (B(u) - B(u_h), u - v_h) \\ &\lesssim \|u - u_h\|_1 \|u - v_h\|_1. \end{aligned}$$

Here we make use of the monotonicity of B in the second step and the boundness of B in the third step. In summary we obtain for any $v_h \in V_D^h$

$$\|u - u_h\|_1 \lesssim \|u - v_h\|_1,$$

which leads to the desired result by taking the infimum. \square

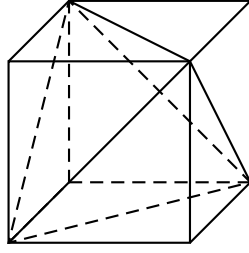


FIGURE 1. Divide a cube into 5 tetrahedra.

6.2. Discrete a priori L^∞ -estimates. We now derive L^∞ -estimates of the finite element approximation u_h . To this end, we have to put assumptions on the grid. Let (a_{ij}) denote the matrix of the elliptic operator $(\varepsilon \nabla u, \nabla v)$, i.e., $a_{i,j} = A(\varphi_i, \varphi_j)$. Two nodes i and j are adjacent if there is an edge connecting them.

(A1) The off-diagonal term $a_{i,j}$, i, j are adjacent, satisfies

$$a_{i,j} \leq -\frac{\rho}{h^2} \sum_{e_{i,j} \subset T} |T|, \quad \text{with } \rho > 0.$$

We now give example grids satisfying (A1). In three dimensions, to simplify the generation of the grid, we choose Ω as a cube and divide into small cubes with length h . For each small cube, we divide it into 5 tetrahedra; see Figure 1 for a prototype of the triangulation of one cube. Neighbor cubes are triangulated in the same fashion (with different reflection to make the triangulation conforming). By the formula of the local stiffness matrix in [32, 54], it is easy to verify that the grids will satisfy assumption (A1). We comment that the uniform grid obtained by dividing each cube into 6 tetrahedra will not satisfy the assumption (A1), since in this case if i, j are vertices of diagonal of some cube, then $a_{ij} = 0$.

Theorem 6.3. *In general dimension \mathbb{R}^d , $d \geq 2$, with assumption (A1) and h sufficiently small, the finite element approximation u_h of RPBE satisfies*

$$\|u_h\|_\infty \leq C,$$

where C is independent of h .

Proof. We shall use the decomposition $u_h = u_h^n + u_h^l$. By the regularity result [41], we know $u^l \in B_{2,\infty}^{3/2}(\Omega)$ and thus obtain a priori estimate on quasi-uniform grids

$$\|u^l - u_h^l\|_\infty \leq Ch_{\max}^s \leq C \text{diam}(\Omega)^s \quad \text{for some } s \in (0, 3/2).$$

This implies that $\|u_h^l\|_\infty \leq \|u^l\|_\infty + \|u^l - u_h^l\|_\infty \leq C$ is uniformly bounded with respect to h_{\max} . The estimate of u_h^n follows from Theorem 3.3 in [32], where the grid assumption (A1) is used. \square

In two dimensions, we can relax the assumption on the grid and obtain a similar result. Later we will see that, due to this relaxation, the local refinement in two dimensions is pretty simple.

(A1') The off-diagonal terms $a_{i,j} \leq 0$, $j \neq i$; i.e., the stiffness matrix corresponding to $A(\cdot, \cdot)$ is an M-matrix.

Theorem 6.4. *For a two-dimensional triangulation satisfying (A1'), the finite element approximation u_h of RPBE is bounded, i.e.,*

$$\|u_h\|_\infty \leq C.$$

Proof. Similarly $\|u_h^l\|_\infty \leq C$ is uniformly bounded. In two dimensions the estimate of u_h^n follows from Theorem 3.1 in [32], where the grid assumption (A1) is used. \square

7. CONVERGENCE OF ADAPTIVE FINITE ELEMENT APPROXIMATION

In this section, we shall follow the framework presented in [49, 50] to derive an a posteriori error estimate. Furthermore we shall present an adaptive method through local refinement based on this error estimator and prove that it will converge. The a priori L^∞ -estimates of the continuous and discrete problems derived in the previous sections play an important role here.

7.1. A posteriori error estimate. There are several approaches to adaptive error control, among which the one based on a posteriori error estimation is usually the most effective and most general. Although most existing work on a posteriori estimates has been for linear problems, extensions to the nonlinear case can be made through linearization. For example, consider the nonlinear problem

$$F(u) = 0, \quad F \in C^1(\mathcal{B}_1, \mathcal{B}_2^*), \quad (7.1)$$

where the Banach spaces \mathcal{B}_1 and \mathcal{B}_2 are, e.g., Sobolev spaces and where \mathcal{B}^* denotes the dual space of \mathcal{B} . Consider now also a discretization of (7.1)

$$F_h(u_h) = 0, \quad F_h \in C^0(U_h, V_h^*), \quad (7.2)$$

where $U_h \subset \mathcal{B}_1$ and $V_h \subset \mathcal{B}_2$. For the RPBE and a finite element discretization, the function spaces would be taken to be $\mathcal{B}_1 = \mathcal{B}_2 = H_0^1(\Omega)$. The nonlinear residual $F(u_h)$ can be used to estimate the error through the use of a linearization inequality

$$C_1 \|F(u_h)\|_{\mathcal{B}_2^*} \leq \|u - u_h\|_{\mathcal{B}_1} \leq C_2 \|F(u_h)\|_{\mathcal{B}_2^*}. \quad (7.3)$$

See, for example, [49] for a proof of this linearization result under weak assumptions on F . The estimator is then based on an upper bound on the dual norm of the nonlinear residual on the right in (7.3).

In this section, to show the main idea, we will assume $F_h(u_h) = F(u_h)$ by making the following assumption on the grid.

(A2) The smooth interface Γ is replaced by its discrete approximation Γ_h such that ε and $\bar{\kappa}$ are piecewise constants on each element of the triangulation \mathcal{T}_h .

In our setting of the weak formulation, we need to estimate $\|F(u_h)\|_{-1,\Omega}$. To this end, we first introduce quite a bit of notation. We assume that the d -dimensional domain Ω has been exactly triangulated with a set \mathcal{T}_h of shape-regular d -simplices (the finite dimension d is arbitrary, not restricted to $d \leq 3$, throughout this discussion). A family of simplices will be referred to here as shape-regular in the sense of [21].

It will be convenient to introduce the following notation:

$$\begin{aligned} \mathcal{T}_h &= \text{the set of shape-regular simplices triangulating the domain } \Omega. \\ \mathcal{N}(\tau) &= \text{the union of faces contained in simplex set } \tau \text{ lying on } \partial\Omega. \\ \mathcal{I}(\tau) &= \text{the union of faces contained in simplex set } \tau \text{ not in } \mathcal{N}(\tau). \\ \mathcal{F}(\tau) &= \mathcal{N}(\tau) \cup \mathcal{I}(\tau). \\ \mathcal{F} &= \cup_{\tau \in \mathcal{T}_h} \mathcal{F}(\tau). \\ \omega_\tau &= \bigcup \{ \tilde{\tau} \in \mathcal{T}_h \mid \tau \cap \tilde{\tau} \neq \emptyset, \text{ where } \tau \in \mathcal{T}_h \}. \\ \omega_S &= \bigcup \{ \tilde{\tau} \in \mathcal{T}_h \mid S \cap \tilde{\tau} \neq \emptyset, \text{ where } S \in \mathcal{F} \}. \\ h_\tau &= \text{the diameter of the simplex } \tau. \\ h_S &= \text{the diameter of the face } S. \end{aligned}$$

When the argument to one of the face set functions \mathcal{N} , \mathcal{I} , or \mathcal{F} is in fact the entire set of simplices, we will leave off the explicit dependence on \mathcal{S} without danger of confusion. Finally, we will also need some notation to represent discontinuous jumps in function values across faces interior to the triangulation. For any face $S \in \mathcal{N}$, let n_S denote the unit outward normal; for any face $S \in \mathcal{I}$, take n_S to be an arbitrary (but fixed) choice of one of the two possible face normal orientations. Now, for any $v \in L^2(\Omega)$ such that $v \in C^0(\tau) \forall \tau \in \mathcal{T}_h$, define the *jump function*:

$$[v]_S(x) = \lim_{t \rightarrow 0^+} v(x + tn_S) - \lim_{t \rightarrow 0^-} v(x - tn_S).$$

We now define our a posteriori error estimator

$$\eta_\tau^2(u_h) = h_\tau^2 \|B(u_h)\|_{0,\tau}^2 + \frac{1}{2} \sum_{S \in \mathcal{I}(\tau)} h_S \| [n_S \cdot (\varepsilon \nabla u_h + (\varepsilon - \varepsilon_m) \nabla G)]_S \|_{0,S}^2, \quad (7.4)$$

and the oscillation

$$\text{osc}_\tau^2(u_h) = h_\tau^4 (\|\nabla u_h\|_{0,\tau}^2 + \|\nabla G\|_{0,\tau}^2). \quad (7.5)$$

Theorem 7.1. *Let $u \in H^1(\Omega)$ be a weak solution of the RPBE and u_h be the finite element approximation with a grid satisfying assumptions (A1) and (A2). There exist two constants depending only on the shape regularity of \mathcal{T}_h such that*

$$\|u - u_h\|_1^2 \leq C_1 \eta_h^2 + C_2 \text{osc}_h^2, \quad (7.6)$$

where

$$\eta_h^2 := \sum_{\tau \in \mathcal{T}_h} \eta_\tau^2(u_h), \quad \text{and} \quad \text{osc}_h^2 := \sum_{\tau \in \mathcal{T}_h \cap \Omega_s} \text{osc}_\tau^2(u_h).$$

Proof. We shall apply the general estimate in [50, Chapter 2] (see also [49]) to

$$\underline{a}(x, u, \nabla u) = \varepsilon \nabla u + (\varepsilon - \varepsilon_m) \nabla G, \quad \text{and} \quad b(x, u, \nabla u) = -\bar{\kappa}^2 \sinh(u + G).$$

We then use the following facts to get the desired result:

- $\nabla \cdot (\varepsilon \nabla u_h) |_\tau = 0 \forall \tau \in \mathcal{T}_h$ by the assumption (A2) of the grid;
- $\nabla \cdot ((\varepsilon - \varepsilon_m) \nabla G) |_\tau = 0 \forall \tau \in \mathcal{T}_h$ since $\Delta G(x) = 0$ if $x \notin \{x_i\}$.
- For $\tau \in \mathcal{T}_h \cap \Omega_s$, let \bar{u}_h and \bar{G} denote the average of u_h and G over τ , respectively.

We then have

$$\begin{aligned} \|\sinh(u_h + G) - \sinh(\bar{u}_h + \bar{G})\|_{0,\tau} &\leq |\cosh(\xi)| \|u_h - \bar{u}_h + G - \bar{G}\|_{0,\tau} \\ &\leq Ch_\tau^2 (\|\nabla u_h\|_{0,\tau} + \|\nabla G\|_{0,\tau}). \end{aligned}$$

Here we use the L^∞ -estimates of u and u_h to conclude that $|\cosh(\xi)| \leq C$ and the standard error estimate for $\|u_h - \bar{u}_h\|_{0,\tau}$ and $\|G - \bar{G}\|_{0,\tau}$.

We give some remarks on our error estimator and the oscillation term. First, using (4.2) one can easily show that $\|\nabla u_h\|_{0,\Omega} \leq C$ uniformly with respect to h and thus $\text{osc}_\tau = O(h_\tau^2)$. Comparing to the order of $\eta_\tau = O(h_\tau)$, the error estimator η_τ will dominate in the upper bound. Second, in (7.4) the jump of $[n_S \cdot (\varepsilon - \varepsilon_m) \nabla G]_S \neq 0$ only if $S \in \Gamma_h$. This additional term with order $O([\varepsilon])$ will emphasize the elements around the interface where the refinement most occurs.

Although it is clear that the upper bound is the key to bounding the error, the lower bound can also be quite useful; it can help to ensure that the adaptive procedure does not do too much work by overrefining an area where it is unnecessary. Again using the general framework for the a posteriori error estimate in [49, 50], we have the following lower bound result.

Theorem 7.2. *There exists two constants C_3, C_4 depending only on the shape regularity of \mathcal{T}_h such that*

$$\eta_\tau^2(u_h) \leq C_3 \|u - u_h\|_{1, \omega_\tau}^2 + C_4 \sum_{\tilde{\tau} \in \omega_\tau \cap \Omega_s} \text{osc}_{\tilde{\tau}}^2(u_h) \quad \forall \tau \in \mathcal{T}_h.$$

7.2. Marking and refinement strategy. Given an initial triangulation \mathcal{T}_0 , we shall generate a sequence of nested conforming triangulations \mathcal{T}_k using the following loop:

$$\text{SOLVE} \rightarrow \text{ESTIMATE} \rightarrow \text{MARK} \rightarrow \text{REFINE}. \quad (7.7)$$

More precisely to get \mathcal{T}_{k+1} from \mathcal{T}_k we first solve the discrete equation to get u_k on \mathcal{T}_k . The error is estimated using u_k and used to mark a set of triangles that are to be refined. Triangles are refined in such a way that the triangulation is still shape-regular and conforming.

We have discussed the step **ESTIMATE** in detail, and we shall not discuss the step **SOLVE**, which deserves a separate investigation. We assume that the solutions of the finite-dimensional problems can be solved to any accuracy efficiently. Examples of such optimal solvers are the multigrid method or the multigrid-based preconditioned conjugate gradient method [52, 13, 27, 55]. In particular we refer to [1, 2] for recent work on adaptive grids in three dimensions and [30, 29] for solving the PBE with inexact Newton methods.

We now present the marking strategy which is crucial for our adaptive methods. We shall focus on one iteration of loop (7.7) and thus use \mathcal{T}_H for the coarse mesh and \mathcal{T}_h for the refined mesh. Quantities related to those meshes will be distinguished by a subscript H or h , respectively.

Let $\theta_i, i = 1, 2$ be two numbers in $(0, 1)$.

(1) Mark $\mathcal{M}_{1,H}$ such that

$$\sum_{\tau \in \mathcal{M}_{1,H}} \eta_\tau^2(u_H) \geq \theta_1 \sum_{\tau \in \mathcal{T}_H} \eta_\tau^2(u_H).$$

(2) If

$$\text{osc}_H \geq \eta_H \quad (7.8)$$

or

$$C_4 \sum_{\tilde{\tau} \in \cup_{\tau \in \mathcal{M}_H} \omega_\tau} \text{osc}_{\tilde{\tau}}^2(u_H) \geq \frac{1}{2} \sum_{\tau \in \mathcal{M}_H} \eta_\tau^2(u_H), \quad (7.9)$$

then extend $\mathcal{M}_{1,H}$ to $\mathcal{M}_{2,H}$ such that

$$\sum_{\tau \in \mathcal{M}_{2,H}} \text{osc}_\tau^2(u_H) \geq \theta_2 \sum_{\tau \in \mathcal{T}_H} \text{osc}_\tau^2(u_H).$$

Unlike the marking strategy for reducing oscillation in the adaptive finite element methods in [36, 37], in the second step, we put a switch (7.8)–(7.9). In our setting, the oscillation $\text{osc}_H = O(H^2)$ is in general a high-order term. The marking step (2) is seldom applied.

In the **REFINE** step, we need to carefully choose the rule for dividing the marked triangles such that the mesh obtained by this dividing rule is still conforming and shape-regular. Such refinement rules include red and green refinement [7], longest refinement [40, 39], and newest vertex bisection [42, 34, 35]. For the **REFINE** step, we are going to impose the following assumptions.

(A3) Each $\tau \in \mathcal{M}_H$, as well as each of its faces, contains a node of \mathcal{T}_h in its interior.

(A4) Let \mathcal{T}_h be a refinement of \mathcal{T}_H such that the corresponding finite element spaces are nested, i.e., $V^H \subset V^h$.

With those assumptions, we can have the discrete lower bound between two nested grids. Let \mathcal{T}_H be a shape-regular triangulation, and let \mathcal{T}_h be a refinement of \mathcal{T}_H obtained by local refinement of marked elements set \mathcal{M}_H . The assumption (A3) is known as the *interior nodes property* in [37]. Such a requirement ensures that the refined finite element space V^h is fine enough to capture the difference of solutions.

Theorem 7.3. *Let \mathcal{T}_H be a shape-regular triangulation, and let \mathcal{T}_h be a refinement of \mathcal{T}_H obtained by some local refinement methods of marked elements set \mathcal{M}_H , such that it satisfies assumptions (A3) and (A4). Then there exist two constants, depending only on the shape regularity of \mathcal{T}_H , such that*

$$\eta_\tau^2(u_H) \leq C_3 \|u_h - u_H\|_{1,\omega_\tau}^2 + C_4 \sum_{\tilde{\tau} \in \omega_\tau} \text{osc}_{\tilde{\tau}}^2(u_H) \quad \forall \tau \in \mathcal{M}_H. \quad (7.10)$$

Proof. The proof is standard using the discrete bubble functions on τ and each face $S \in \partial\tau$. \square

7.3. Convergence analysis. We shall prove that the repeating of loop (7.7) will produce a convergent solution u_k to u . The convergent analysis of the adaptive finite element method is an active topic. In the literature it is mainly restricted to the linear equations [17, 46, 16, 36, 25, 9, 37, 33, 26, 8]. The convergence analysis for the nonlinear equation is relatively rare [24, 48, 15].

Lemma 7.4. *Let \mathcal{T}_H and \mathcal{T}_h satisfy assumptions (A1)–(A4). Then there exist two constants depending only on the shape regularity of \mathcal{T}_H such that*

$$\|u - u_H\|_1^2 \leq C_5 \|u_h - u_H\|_1^2 + C_6 \text{osc}_H^2.$$

When (7.8) and (7.9) do not hold, we have a stronger inequality

$$\|u - u_H\|_1^2 \leq C_7 \|u_h - u_H\|_1^2,$$

where C_7 depends only on the shape regularity of \mathcal{T}_H .

Proof. By the upper bound and marking strategy

$$\begin{aligned} \|u - u_H\|_1^2 &\leq C_1 \eta_H^2 + C_2 \text{osc}_H^2 \\ &\leq C_1 \theta_1^{-1} \sum_{\tau \in \mathcal{M}_{1,H}} \eta_\tau^2(u_H) + C_2 \text{osc}_H^2 \\ &\leq C_5 \|u_h - u_H\|_1^2 + C_6 \text{osc}_H^2, \end{aligned}$$

with

$$C_5 = C_1 \theta_1^{-1} C_3^{-1}, \quad \text{and} \quad C_6 = (C_2 + 2C_3^{-1} C_4).$$

If (7.8) does not hold, i.e., $\text{osc}_H \leq \eta_H$, the first inequality becomes

$$\|u - u_H\|_1^2 \leq (C_1 + C_2) \eta_H^2.$$

If (7.9) does not hold, we can easily modify the lower bound (7.10) as

$$\sum_{\tau \in \mathcal{M}_{1,H}} \eta_\tau^2(u_H) \leq 2C_3 \|u_h - u_H\|_1^2.$$

Then the inequality follows similarly. \square

For $\tau_h \subset \mathcal{T}_H$, let $h_{\tau_h} = \gamma H_{\tau_h}$, with $\gamma \in (0, 1)$. The next lemma shows that even the oscillation is not small; there is also a reduction result. For the marked set $\mathcal{M}_H \subset \mathcal{T}_H$, we shall use $\overline{\mathcal{M}_H}$ to denote the refined elements in \mathcal{T}_h .

Lemma 7.5. *If $\mathcal{M}_{2,H} \setminus \mathcal{M}_{1,H} \notin \emptyset$, there exist ρ_1, ρ_2 such that*

$$\text{osc}_h^2 \leq \rho_1 \text{osc}_H^2 + \rho_2 \|u_h - u_H\|_1^2.$$

Proof.

$$\begin{aligned} \text{osc}_h^2 &\leq \sum_{\tau \in \mathcal{T}_h} \text{osc}_\tau^2(u_H) + C \sum_{\tau \in \mathcal{T}_h} (h_\tau^4 \|\nabla(u_h - u_H)\|_\tau^2) \\ &\leq \sum_{\tau_h \in \overline{\mathcal{M}_{2,H}}} \text{osc}_\tau^2(u_H) + \sum_{\tau_h \in \mathcal{T}_h \setminus \overline{\mathcal{M}_{2,H}}} \text{osc}_\tau^2(u_H) + Ch^2 \|\nabla(u_h - u_H)\|^2 \\ &\leq \gamma^2 \sum_{\tau_H \in \mathcal{M}_{2,H}} \text{osc}_\tau^2(u_H) + \sum_{\tau_H \in \mathcal{T}_H \setminus \mathcal{M}_{2,H}} \text{osc}_\tau^2(u_H) + Ch^2 \|\nabla(u_h - u_H)\|^2 \\ &\leq \text{osc}_H^2 + (\gamma^2 - 1) \sum_{\tau_H \in \mathcal{M}_{2,H}} \text{osc}_\tau^2(u_H) + Ch^2 \|\nabla(u_h - u_H)\|^2 \\ &\leq \rho_1 \text{osc}_H^2 + \rho_2 \|u_h - u_H\|_1^2, \end{aligned}$$

with $\rho_1 = 1 - (1 - \gamma^2)/\theta_2 \in (0, 1)$, and $\rho_2 = Ch^2$. \square

We shall choose θ_2 sufficiently close to 1 and $h_{\max} < 1/c$ to ensure $\rho_i \in (0, 1)$, $i = 1, 2$.

For the nonlinear problem, we do not have the orthogonality in H^1 norms. But we shall use the trivial identity

$$E(u_H) - E(u) = E(u_H) - E(u_h) + E(u_h) - E(u). \quad (7.11)$$

The following lemma proves the equivalence of energy error and error in H^1 norm. Again the L^∞ norm estimate of u and u_h is crucial.

Lemma 7.6. *If both \mathcal{T}_h and \mathcal{T}_H satisfy the assumption (A1), then*

- $E(u_h) - E(u) \simeq \|u_h - u\|_1^2$;
- $E(u_H) - E(u) \simeq \|u_H - u\|_1^2$;
- $E(u_H) - E(u_h) \simeq \|u_H - u_h\|_1^2$.

Proof. By the Taylor expansion

$$E(u_H) - E(u_h) = \langle DE(u_h), u_H - u_h \rangle + (D^2E(\xi)(u_H - u_h), u_H - u_h).$$

The first term is zero since u_h is the minimizer. The desired result follows from the bound

$$\bar{\kappa}^2 \leq \|D^2E(\xi)\|_\infty = \bar{\kappa}^2 \|\cosh(\xi + G)\|_{\infty, \Omega_s} \leq C.$$

Other inequalities follow from the same line. \square

Our adaptive finite element methods (AFEMs) consist of the iteration of loop (7.7) with the estimate, marking, and refinement parts discussed before. Also the grids generated by the algorithm will satisfy assumptions (A1)–(A4). Hereafter we replace the subscript h by an iteration counter called k and introduce some notation to simplify the proof. Let u_k be the solution in the k th iteration, $\delta_k := E(u_k) - E(u)$, $d_k = E(u_k) - E(u_{k+1})$, and $o_k = \text{osc}^2(u_k)$

Theorem 7.7. *The adaptive method using loop (7.7) will produce a convergent approximation in the sense that*

$$\lim_{k \rightarrow 0} \|u - u_k\|_1 = 0.$$

Proof. By Lemma 7.6, we need only to show $\delta^k \rightarrow 0$ as $k \rightarrow 0$. We first discuss the easier case: When osc_H is the high-order term in the sense that the inequalities (7.8) and (7.9) do not hold, we have the error reduction

$$\|u - u_H\|_1^2 \leq C \|u_h - u_H\|^2.$$

Using Lemma 7.5 and (7.11), we have

$$E(u_H) - E(u) \leq C(E(u_H) - E(u_h)),$$

which is equivalent to $\delta_H \leq C\delta_H - C\delta_h$. Then $\delta_h \leq (1 - 1/C)\delta_H$, and thus

$$\delta^k \leq \alpha^k \delta^0, \quad \text{with } \alpha = (1 - 1/C) \in (0, 1).$$

When the oscillation is not small, i.e., (7.8) or (7.9) holds, we can get only

$$\Lambda_1 \delta_k \leq d_k + \Lambda_2 o_k, \quad \text{with } \Lambda_1 \in (0, 1). \quad (7.12)$$

We shall use techniques from [33] to prove the convergence. Recall that we have

$$\delta_{k+1} = \delta_k - d_k. \quad (7.13)$$

For any $\beta \in (0, 1)$, $\beta \times (7.12) + (7.13)$ gives

$$\delta_{k+1} \leq \alpha \delta_k + \beta \Lambda_2 o_k - (1 - \beta) d_k, \quad \text{with } \alpha = (1 - \beta \Lambda_1) \in (0, 1). \quad (7.14)$$

Recall that we have

$$o_{k+1} \leq \rho_1 o_k + \rho_2 d_k. \quad (7.15)$$

Let $\gamma = (1 - \beta)/\rho_2$; (7.15) $\times \gamma + (7.14)$ gives

$$\delta_{k+1} + \gamma o_{k+1} \leq \alpha \delta_k + (\beta \Lambda_2 + \rho_1 \gamma) o_k.$$

Let $1 > \mu > \rho_1$. We choose

$$\beta = \frac{\frac{\mu - \rho_1}{\rho_2}}{\Lambda_2 + \frac{\mu - \rho_1}{\rho_2}} \in (0, 1)$$

to get

$$\delta_{k+1} + \gamma o_{k+1} \leq \max(\alpha, \mu) (\delta_k + \gamma o_k),$$

which also implies the convergence of our AFEM. \square

8. SUMMARY AND CONCLUDING REMARKS

In this article we have established a number of basic theoretical results for the nonlinear Poisson–Boltzmann equation and for its approximation using finite element methods. We began by showing that the problem is well-posed through the use of an auxiliary or *regularized* version of the equation and then established a number of basic estimates for the solution to the regularized problem. The Poisson–Boltzmann equation does not appear to have been previously studied in detail theoretically, and it is hoped that this paper will help provide molecular modelers with a better theoretical foundation for their analytical and computational work with the Poisson–Boltzmann equation. The bulk of this article then focused on designing a numerical discretization procedure based on the regularized problem and on establishing rigorously that the discretization procedure converged to the solution to the original (nonregularized) nonlinear Poisson–Boltzmann

equation. Based on these results, we also designed an adaptive finite element approximation procedure and then gave a fairly involved technical argument showing that this adaptive procedure also converges in the limit of mesh refinement. This article apparently gives the first convergence result for a numerical discretization technique for the nonlinear Poisson–Boltzmann equation with delta distribution sources, and it also introduces the first provably convergent adaptive method for the equation. This last result is one of only a handful of convergence results of this type for nonlinear elliptic equations (the others being [24, 48, 15]).

Several of the theoretical results in the paper rest on some basic assumptions on the underlying simplex mesh partitioning of the domain, namely, assumptions (A1)–(A4); we now make a few comments on these assumptions. To begin, we required a refinement procedure that would preserve the L^∞ norm estimate of u_h . Meeting this requirement in the two-dimensional setting is relatively easy; one can choose Ω as a square and start with a uniform mesh of a square. For the refinement methods, one can use longest edge or newest vertex bisection. Subdivisions obtained by these two methods contain only one type of triangle: isosceles right triangles. Thus the assumption (A1') always holds. In the three-dimensional setting, this is more tricky. Bisection will introduce some obtuse angles in the refined elements. One needs to use a three-dimensional analogue of red-green refinement [10]. However, this will not produce nested subspaces; i.e., assumption (A4) is invalid. For convergence analysis based on red-green refinement, we could use the technique in [45] to relax the assumption (A4). Since this will only add technical difficulties but does not exhibit principally new phenomena, we omit them here. Another approach to relax the assumption (A1) is to use pointwise a posteriori error estimates developed in [38] for monotone semilinear equations. We can start with a quasi-uniform triangulation and refine the triangulation according to the pointwise a posteriori error estimator to make sure $\|u - u_h\|_\infty \leq C$. Then together with the L^∞ norm estimate of u , by the triangulation inequality $\|u_h\|_\infty \leq \|u\|_\infty + \|u - u_h\|_\infty \leq C$, we have the control of $\|u_h\|_\infty$. Note that the pointwise a posteriori error estimates developed in [38] are for elliptic-type equations with continuous coefficients. To use this approach we need to adapt the estimate for the jump coefficients case which will be a further research topic.

Assumption (A2) is needed to approximate the interface well in an a priori manner. Of course, one can include this approximation effect into the a posteriori error estimate (namely, the term $\|F(u_h) - F_h(u_h)\|$) and use this to drive local refinement to improve the approximation to the desired level for the assumption or use the strategy for the oscillation to include it in the refinement loop. However, we note that, since the interface is known a priori from, e.g., x-ray crystallography information, we do not need to solve the equation (which is generally the more expensive route) to solve this problem; we view this as primarily a mesh generation problem. Robust algorithms to produce well-shaped tetrahedral meshes which are constrained to exactly match some interior embedded two-manifold are available in the literature; for example, see [18, 3]. A simple algorithm can be based entirely on local refinement with the marking and refinement strategy, but without having to solve the PBE to produce error indicators: If the element cross the interface, then it gets refined. This strategy was employed in [5].

After this work was done, we learned that the assumption (A3) is not needed for the convergence of adaptive finite element methods for a linear elliptic equation. As an ongoing project, we are extending it to the nonlinear Poisson–Boltzmann equation.

Finally, we make some remarks on the practical realization of a convergent discretization procedure based on the two-way (or three-way) expansion into a known singular function and solution(s) of an associated regularized version of the problem. Methods

for building high-quality approximate solutions of the regularized nonlinear PBE, either by solving (3.5)–(3.6) at once or by solving for the linear and nonlinear pieces separately by solving (5.1)–(5.2) and then adding the solutions together, are well-understood. The techniques described in [28], taken together with the approximation framework and the adaptive algorithm proposed in the present article, moves us a step closer to the goal of a complete optimal solution to this problem, in terms of approximation quality for a given number of degrees of freedom, computational complexity of solving the corresponding discrete equations, and the storage requirements of the resulting algorithms. What remains is simply the cost of evaluating the singular function G in forming the source terms in (3.5) or (5.1). The source terms are evaluated using numerical quadrature schemes: sampling the integrand at specially chosen discrete points in each element and then summing the results up using an appropriate weighting. This is equivalent to computing all pairwise interactions between the collection of quadrature points (a fixed constant number of points per simplex) and the number of charges forming G . Given that G is typically formed from at most a few thousand charges, the algorithm evaluating G at the quadrature points should scale linearly with the number of quadrature points, which is a (small) constant multiple of the number of simplices. This can be accomplished using techniques such distance-classing and fast multiple-type methods.

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