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# A New Outer Boundary Formulation and Energy Corrections for the Nonlinear Poisson–Boltzmann Equation

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**Abstract:** The nonlinear Poisson–Boltzmann equation (PBE) has been successfully used for the prediction of numerous electrostatic properties of highly charged biopolyelectrolytes immersed in aqueous salt solutions. While numerous numerical solvers for the 3D PBE have been developed, the formulation of the outer boundary treatments used in these methods has only been loosely addressed, especially in the nonlinear case. The *de facto* standard in current nonlinear PBE implementations is to either set the potential at the outer boundaries to zero or estimate it using the (linear) Debye–Hückel (DH) approximation. However, an assessment of how these outer boundary treatments affect the overall solution accuracy does not appear to have been previously made. As will be demonstrated here, both approximations can, under certain conditions, produce completely erroneous estimates of the potential and energy salt dependencies. A related concern for calculations carried out on grids of finite extent (e.g., all current finite difference and finite element implementations) is the contribution to the energy and salt dependence from the exterior region outside the computational grid. This too is shown to be significant, especially at low salt concentration where essentially *all* of the contributions to the excess osmotic pressure and ion stress energies originate from this exterior region. In this paper the authors introduce a new outer boundary treatment that is valid for both the linear and nonlinear PBE. The authors also formulate energy corrections to account for contributions from outside the computational domain. Finally, the authors also consider the effects of general ion exclusion layers upon biomolecular electrostatics. It is shown that while these layers tend to increase the surface electrostatic potential, under physiological salt conditions and high net charges their effect on the excess osmotic pressure term, which is a measure of the salt dependence of the total electrostatic free energy, is weak. To facilitate presentation and allow very fine resolutions and/or large computational domains to be considered, attention is restricted to the 1D spherically symmetric nonlinear PBE. Though geometrically limited, the modeling principles nevertheless extend to general PBE solvers as discussed in the Appendix. The 1D model can also be used to benchmark and validate the salt effect prediction capabilities of existing PBE solvers.

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## Introduction

The proper treatment of electrostatic interactions and ion screening effects is very challenging from a theoretical and computational viewpoint. One approach that has become popular in treating highly charged biomolecular systems is the mean field-based Poisson–Boltzmann approach (for recent reviews see refs. 1–3), which allows one to treat the biomolecule at the atomic level of detail. The Poisson–Boltzmann equation (PBE) assumes a dielectric continuum model where the polar aqueous solvent is treated as a featureless high dielectric media but the biomolecule (solute) is modeled as a collection of atomic point charges inside a solvent inaccessible low dielectric volume. Solving the three-dimensional (3D) PBE allows one to obtain different electro-