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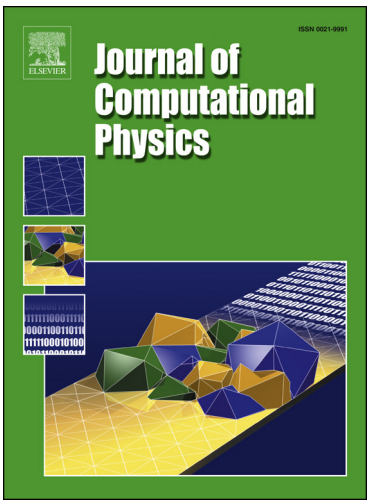


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# Atom-Partitioned Multipole Expansions for Electrostatic Potential Boundary Conditions

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**Abstract**

Applications such as grid-based real-space density functional theory (DFT) use the Poisson equation to compute electrostatics. However, the expected long tail of the electrostatic potential requires either the use of a large and costly outer domain or Dirichlet boundary conditions estimated via multipole expansion. We find that the oft-used single-center spherical multipole expansion is only appropriate for isotropic mesh domains such as spheres and cubes. In this work, we introduce a method suitable for high aspect ratio meshes whereby the charge density is partitioned into atomic domains and multipoles are computed for each domain. While this approach is moderately more expensive than a single-center expansion, it is numerically stable and still a small fraction of the overall cost of a DFT calculation. The net result is that when high aspect ratio systems are being studied, form-fitted meshes can now be used in lieu of cubic meshes to gain computational speedup.

*Keywords:* finite element method, density functional theory, spherical harmonics, self-consistent field, Poisson equation, partial differential equation, quantum chemistry

## 1. Introduction

In chemical simulations, there are a variety of methods for computing the electrostatic energy of a real-space (non-periodic) charge density including pairwise Coulomb summation, fast multipole methods[1], and solving the Poisson equation [2][3]. Although fast multipole methods are being investigated [4] for grid-based real space density functional theory (DFT) [5], the most common method for computing electrostatics is the Poisson equation. Specifically, the electronic and nuclear charge densities are interpolated on a grid, and the electrostatic potential is solved via the linear Poisson equation [2]. In principle, the Poisson approach has linear scaling computational complexity because the kernel matrix is sparse with only $O(N)$ non-zero matrix elements.

The Poisson equation requires specification of boundary conditions, such as a boundary potential (Dirichlet condition). Naïvely, the boundary values can be set to

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