Finite-size error and its correction in energy calculations for periodic systems

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Abstract

Despite decades of practice, finite-size errors in many widely used electronic structure theories for periodic systems remain poorly understood. For periodic systems using a general Monkhorst-Pack grid, there has been no rigorous analysis of the finite-size error in the Hartree–Fock theory (HF) and the second order Møller–Plesset perturbation theory (MP2), which are the simplest wavefunction based method, and the simplest post-HF method, respectively. Such energy calculations for periodic systems can be viewed as a multi-dimensional integral at the thermodynamic limit, and the standard method for evaluating the energy can be viewed as a trapezoidal quadrature rule. Due to singularity of the Coulomb kernel, the associated integrands have many points of discontinuity in general, and standard error analysis based on the Euler-Maclaurin formula gives overly pessimistic results.

In this talk, I will present a unified analysis that gives sharp convergence rates of finite-size errors for the periodic HF and MP2 theories for insulating systems. Our main technical advancement is a generalization of the result of [Lyness, 1976] for obtaining sharp convergence rates of trapezoidal rules for a class of non-smooth integrands. This unified analysis also allows us to prove the effectiveness of the Madelung-constant correction to the Fock exchange energy, and the effectiveness of our recently proposed staggered mesh method for periodic Fock exchange and MP2 calculations.

[1] X. Xing, X. Li and L. Lin, Staggered mesh method for correlation energy calculations of solids: Second order Møller-Plesset perturbation theory, *J. Chem. Theory Comput*, 2021, 17, 8, 4733–4745.

[2] X. Xing, X. Li and L. Lin, Unified analysis of finite-size error for periodic Hartree-Fock and second order Møller-Plesset perturbation theory, *preprint*, arXiv:2108.00206, 2021

[2] X. Xing, and L. Lin, Staggered mesh method for correlation energy calculations of solids: Random phase approximation in direct ring coupled cluster doubles and adiabatic connection formalisms, *J. Chem. Theory Comput*, 2022