Ensemble density-functional theory in real space: 1D models approaching the thermodynamic limit and benchmarks on small molecules

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Ensemble Density Functional Theory (EDFT) has so far been mostly tested on model systems or on atoms or small molecules with Gaussian basis sets. We have performed EDFT calculations in the real-space Octopus code [https://octopus-code.org; Tancogne-Dejean *et al.*, *J. Chem. Phys.* 152, 124119 (2020)] in two projects aimed at broadening the range of systems for which EDFT can be used. Octopus can describe real systems composed of atoms with finite or periodic boundary conditions as well as model systems with arbitrary potentials in 1, 2, 3, or more dimensions, and offers a variety of other theories for comparison to EDFT.

EDFT offers a variational (non-perturbative) alternative to Time-Dependent DFT (TDDFT) which can more easily treat complicated excitations. EDFT in various forms has been shown to improve the accuracy of calculated energy level differences in isolated model systems, atoms, and molecules, but it is not yet clear how EDFT could be used to calculate band gaps for periodic systems. Using Octopus, we investigate the application of EDFT toward periodic systems by taking the thermodynamic limit with increasingly large finite model systems. Studying singlet and triplet excitations in 1D "particle in a box" systems, we find a non-trivial correction to the effective mass in the limit approaching the 1D homogeneous electron gas. By contrast, corrections to excited states from ΔSCF and TDLDA become trivial in the infinite limit. Our results indicate that development of EDFT for periodic systems is a promising direction.

For low-cost prediction of excitation energies, the most promising EDFT approaches are perturbative schemes, including the Direct Ensemble Correction (DEC), which has been tested on model systems and atoms [Yang *et al.*, *Phys. Rev. Lett.* 119, 033003 (2017)], and the Ensemble "HOMO-LUMO gap" (or pEDFT), which has been benchmarked on small molecules [Gould *et al.*, *J. Phys. Chem. Lett.* 13, 2452 (2022)]. We assess these EDFT approaches in Octopus, which can pave the way toward calculations of larger and more complicated systems. We calculate excited states from DEC and pEDFT for atoms and molecules, and we compare results and convergence characteristics in real space to other standard excited-state approaches like linear-response TDDFT and TD Hartree-Fock.

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