

Perturbative ensemble density functional theory: a new low-cost model for excitation energies and their optimized geometries

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Ensemble density functional theory (EDFT) offers the promise of routine, reasonably accurate excited states through the linear combination of appropriately weighted Slater determinants. Recent work showed that a simple correction based on EDFT returns a theoretically exact HOMO-LUMO gap. [1] Implementation of this correction, which we call perturbative EDFT (pEDFT), reveals a low-cost route to the prediction of low-lying singlet-singlet and singlet-triplet excitation energies based on semi-local and hybrid density functional approximations. Calculations involve a post-ground state correction. Accuracy of pEDFT results is competitive with time-dependent density functional theory methods, especially at high fractions of exact exchange.

[1] Tim Gould, Zahed Hashimi, Leeor Kronik and Stephen G. Dale. Single excitation energies obtained from the ensemble HOMO-LUMO gap: exact results and approximations. *J. Phys. Chem. Lett.* 13, 10, 2452 (2022)