Title: Application of a Direct-Minimization SCF Solver to Proteins in Vacuum to Explore the Origin of the Near-Zero Gap Predicted by Local and Semi-Local DFAs
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Local and semi-local density functional approximations (DFAs) are known to underestimate the gap in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in Kohn-Sham (KS) density functional theory (DFT). This error has been especially pronounced in large systems of biological importance when calculated in vacuo, where certain DFAs have predicted that even small polypeptides have a nearly-zero HOMO-LUMO gap. When the shrinking of the gap is severe convergence of the KS equations becomes difficult or even impossible with traditional diagonalization-based solvers. Using a direct-minimization SCF solver we investigated the origin of the unphysical gaps in such systems. The solver avoids diagonalization of the KS Fock matrix entirely using quasi-Newton steps throughout and employing a limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) approximation for the Hessian built from an approximate diagonal Hessian combined with a trust-radius step restriction leveraging the low-rank structure of the L-BFGS Hessian. We demonstrate that the unphysical gaps in such systems are due to the misalignment of frontier energy levels in physically separated regions of the molecule, especially those near isolated negative charges. In all cases considered herein the physically-reasonable solution in such systems is stable but has non-Aufbau character. Our findings question the ability of modern DFAs to describe the electronic structure of vacuum-exposed interfaces in a qualitatively correct manner.