Density Functional Theory Calculations with Correct Long Range Potentials

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Abstract

A variational method for forcing the exchange-correlation potential in density-functional theory to have the correct asymptotic decay is developed. The resulting exchange-correlation potentials are much improved while the total energies remain essentially the same, compared with conventional density functional theory calculations. The highest occupied orbital energies from the asymptotically corrected exchange-correlation potentials are found to provide significantly more accurate approximations to the ionization potential (for a neutral molecule) and the electron affinity (for an anion) than those from conventional calculations, although the results are usually inferior to direct ΔSCF methods for computing energy differences. The asymptotic correction adopted here enables the potential to bind the highest occupied orbitals for atomic and molecular anions, thereby supporting the use of density functional calculations for negatively charged molecular species.