

## Fractional Charges and Spins: Where are they and How to use them for DFT development

Weitao Yang  
Department of Chemistry, Duke University, USA

Fractional charges in DFT and in one-particle density matrix functional theory occur in grand canonical ensembles. Equivalently and more relevant to chemical and physical applications, they arise from degeneracy in quantum mechanics and the size consistency requirement for the energy functionals. The violation of the exact conditions on fractional charges and spins underlies the systematic errors in DFT approximations, the delocalization and static correlation error. Our development of the localized orbital scaling correction (LOSC) overcomes these systematic errors, leading to accurate description for photoemission and optical excitation with ground state DFT calculations. LOSC is capable of correcting system energy, energy derivative and electron density in a size-consistent manner for all commonly used density functional approximations (DFAs). The LOSC and fractional spin LOSC systematically and significantly improve the description of dissociation of ionic species, single bonds, multiple bonds without breaking symmetry, the band gaps of molecules, polymer chains, and bulk systems, the energy and density changes upon electron addition and removal, and photoemission spectra, and energy-level alignments for interfaces. The LOSC DFA orbital energies are excellent approximations to quasiparticle energies, comparable to or better than GW. This also leads to the QE-DFT (quasiparticle energies from DFT) approach: the calculations of excitation energies of the N-electron systems from the ground state DFA calculations of the (N - 1)-electron systems. Results show good performance with accuracy similar to TDDFT for valence excitations with commonly used DFAs with or without LOSC. For charge transfer and Rydberg states, good accuracy was obtained only with the use of LOSC DFA. The QE-DFT method has been further developed to describe excited-state potential energy surfaces (PESs), their analytical gradients of excited-state PESs and conical intersections.

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