A fractional view of the exchange-correlation functional in density-functional theory

Paula Mori-Sánchez, Aron J. Cohen and Weitao Yang

Department of Chemistry, Universidad Autónoma de Madrid, Madrid 28049, Spain
Department of Chemistry, Lensfield Rd, University of Cambridge, CB2 1EW, UK
Department of Chemistry, Duke Univeristy, Durham, North Carolina, 27708, USA

The exchange-correlation functional is the key object in the understanding and application of density functional theory (DFT). Development of approximations to the exact functional is extremely challenging, as it aims to give a universal functional that works for all densities. To shed light on this issue in any manner is of great importance, and exact conditions highlight a possible path forward. By considering the well established formal extension of DFT to fractional occupations at zero-temperature, we formulate a novel view of DFT based on fractional numbers of electrons and fractional spins that reveal some very stringent exact conditions of the energy functional. Even more importantly, currently used approximations violate these exact conditions, leading to massive basic errors in simple and extended systems. This is exemplified by the delocalization error and static correlation error which, if further combined, lead to very intuitive understanding of key concepts in DFT and call for dramatically new functional forms that have a discontinuous nature. In this light other methods such as MP2 and RPA can also be tested in relation to functional development. These and other ideas and challenges in basic DFT are examined.