Recent developments in density functional theory: From new functionals to the nature of the chemical bond.

MARTIN HEAD-GORDON

Kenneth S. Pitzer Center for Theoretical Chemistry,
Department of Chemistry, University of California, and,
Chemical Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley CA 94720, USA.

Density functional theory (DFT) is the most widely used electronic structure theory, with broad applications in chemistry, materials science, condensed matter physics, and elsewhere. Crucial to its future is the problem of designing functionals with improved predictive power. I shall describe a new approach to functional design, "survival of the most transferable", and show how the resulting functionals offer greatly improved accuracy relative to existing functionals of a given class. As a counterpoint to this vital numerical development, I will describe a new energy decomposition analysis (EDA) approach to obtaining physical insight into DFT calculations of chemical bonds and non-bonded molecular interactions. I will present several examples, such as the triplex between vinyl alcohol radical cation, formaldehyde and water, which is a rearranged form of the glycerol radical cation. I will also use the EDA to explore the origin of the chemical bond, a question that is still controversial.