

Insights and Progress in Density Functional Theory

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Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties. The errors include underestimation of the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions and charge transfer excitation energies. Typical DFT calculations also fail to describe degenerate or near degenerate systems, as arise in the breaking of chemical bonds, and strongly correlated materials. These errors can all be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions have been unified and extended to states with both fractional charge and fractional spin to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems. Understanding the errors of functionals in the simplest way possible --- as violations of exact conditions for fractional charges and fractional spins -- opens the path forward for reduction of the errors and for applications of density functional theory in new frontiers.

On the qualitative side, we have developed an approach to detect non-covalent interactions in real space, based on the electron density and its derivatives. The intricate non-covalent interactions that govern many areas of biology and chemistry are not easily identified from molecular structure. Our approach reveals underlying chemistry that compliments the covalent structure. It provides a rich representation of van der Waals interactions, hydrogen bonds, and steric repulsion in small molecules, molecular complexes, and solids. Most importantly, the method, requiring only knowledge of the atomic coordinates, is efficient and applicable to large systems, such as proteins or DNA. Across these applications, a view of non-bonded interactions emerges as continuous surfaces rather than close contacts between atom pairs, offering rich insight into the design of new and improved ligands.

References

- A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Insights into current limitations of density functional theory," *Science*, 321:792, 2008.
- A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Fractional charge perspective on the band gap in density-functional theory," *Physical Review B*, 77:115123, 2008.
- P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Localization and delocalization errors in density functional theory and implications for band-gap prediction," *Phys. Rev. Lett.* 100:146401, 2008.
- A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Fractional spins and static correlation error in density functional theory," *Journal of Chemical Physics*, 129:121104, 2008.
- P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, "Discontinuous nature of the exchange-correlation functional in strongly correlated systems," *Phys. Rev. Lett.* 102:066403, 2009.
- A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Second-order perturbation theory with fractional charges and fractional spins," *J. Chem. Theory Comput.*, 5:786, 2009.
- A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, "Failure of the random phase approximation correlation energy," *J. Chem. Phys.*, 2009. submitted (arXiv:0903.4403v1).
- E. R. Johnson¹, S. Keinan, Paula Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, and W. T. Yang, "Revealing Non-Covalent Interactions", *J. Am. Chem. Soc.*, submitted, 2010.