Perspectives on Variational Principles in Time-Independent Density-Functional Theory and Total Energy as a Simple Sum of Shifted Kohn-Sham Orbital Energies

Mel Levy

(mlevy@tulane.edu)

Department of Chemistry, Duke University, Durham, North Carolina, 27708

Department of Physics, North Carolina A & T State University, Greensboro, North Carolina 27411

Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

The early history of density-functional theory shall be explored through personal anecdotes, with emphasis on remembering Walter Kohn. Then the corresponding variational principles for ground states in density and density-matrix functional theories will be reviewed briefly for the non-degenerate and degenerate situations through the general constrained-search formulation [1]. Based on these variational principles, properties of exact functionals will be presented. The implementation of these properties helps in the construction of accurate functionals. Special emphasis will be given to coordinate scaling, potentials (functional derivatives), and fractional electron number.

It has recently been observed [2] that the exact interacting ground-state energy may be obtained, in principle, as a simple sum of orbital energies when a universal density-dependent constant is added to the Kohn-Sham potential or to one of its generalizations. The resultant shifted potential has intriguing features, including the fact that a significant component of it changes relatively little on average when the density changes and the fact that the potential does not undergo a discontinuity when the number of electrons increases through an integer. Thus, the approximation of this shifted potential represents an alternative direct approach for the approximation of the ground-state energy and density.

A time-independent excited-state Kohn-Sham theory will be presented that utilizes special properties of Coulomb systems [3].

[1] For a brief personal account of the extension of the original H-K theorem, to include degeneracies and more through the constrained-search approach, see M. Levy, Int. J. Quantum Chem. **110**, 3140 (2010).

[2] M. Levy and F. Zahariev, Phys. Rev. Lett. **113,** 113002 (2014).

[3] P. W. Ayers, M. Levy, and A. Nagy, J. Chem. Phys. **143**, 191101 (2015); Phys. Rev. A. **85,** 042518 (2012).