Analytical evaluation of Fukui functions and real-space linear response function

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Abstract

Many useful concepts developed within density functional theory provide much insight for the understanding and prediction of chemical reactivity, one of the main aims in the field of conceptual density functional theory. While approximate evaluations of such concepts exist, the analytical and efficient evaluation is, however, challenging, because such concepts are usually expressed in terms of functional derivatives with respect to the electron density, or partial derivatives with respect to the number of electrons, complicating the connection to the computational variables of the Kohn-Sham one-electron orbitals. Only recently, the analytical expressions for the chemical potential, one of the key concepts, have been derived by Cohen, Mori-Sanchez, and Yang, based on the potential functional theory formalism. In the present work, we obtain the analytical expressions for the real-space linear response function using the coupled perturbed Kohn-Sham and generalized Kohn-Sham equations, and the Fukui functions using the previous analytical expressions for chemical potentials of Cohen, Mori-Sanchez, and Yang. The analytical expressions are exact within the given exchange-correlation functional. They are applicable to all commonly used approximate functionals, such as local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals. The analytical expressions obtained here for Fukui function and linear response functions, along with that for the chemical potential by Cohen, Mori-Sanchez, and Yang, provide the rigorous and efficient evaluation of the key quantities in conceptual density functional theory within the computational framework of the Kohn-Sham and generalized Kohn-Sham approaches. Furthermore, the obtained analytical expressions for Fukui functions, in conjunction with the linearity condition of the ground state energy as a function of the fractional charges, also lead to new local conditions on the exact functionals, expressed in terms of the second-order functional derivatives. We implemented the expressions and demonstrate the efficacy with some atomic and molecular calculations, highlighting the importance of relaxation effects. (C) 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3701562]

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