Derivative discontinuity, bandgap and lowest unoccupied molecular orbital in density functional theory

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Abstract

The conventional analysis of Perdew and Levy, and Sham and Schluter shows that the functional derivative discontinuity of the exchange-correlation density functional plays a critical role in the correct prediction of bandgaps, or the chemical hardness. In a recent work by the present authors, explicit expressions for bandgap prediction with all common types of exchange-correlation functionals have been derived without invoking the concept of exchange-correlation energy functional derivative discontinuity at all. We here analyze the two approaches and establish their connection and difference. The present analysis further leads to several important results: (1) The lowest unoccupied molecular orbital (LUMO) in DFT has as much meaning in describing electron addition as the highest occupied molecular orbital (HOMO) in describing electron removal. (2) Every term in the total energy functional contributes to the energy gap because of the discontinuity of the derivative of the density (or density matrix) with respect to the number of electrons, ((partial derivative rho(s)(r', r))/partial derivative N)(vs), at integers. (3) Consistent with the Perdew-Levy-Sham-Schluter conclusion that the exact Kohn-Sham energy gap differs from the fundamental bandgap by a finite correction due to the functional derivative discontinuity of the exchange-correlation energy, we show that the exchange-correlation functional cannot be an explicit and differentiable functional of the electron density, either local or nonlocal. The last result is further strengthened when we consider Mott insulators. There, the exact exchange-correlation functional needs to have an explicitly discontinuous (nondifferentiable) dependence on the density or the density matrix. (4) We obtain exact conditions on the derivatives of total energy with respect to the spin-up and spin-down number of electrons. (C) 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3702391]

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