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Curvature and frontier orbital energies in density functional theory LEEOR KRONIK, Weizmann Institute of Science, Israel, TAMAR STEIN, Hebrew University of Jerusalem, Israel, JOCHEN AUTSCHBACH, University of Buffalo, NY, USA, NIRANJAN GOVIND, Pacific Northwest National Laboratory, WA, USA, ROI BAER, Hebrew University of Jerusalem, Israel — Perdew et al. [Phys. Rev. Lett 49, 1691 (1982)] discovered and proved two different properties of exact Kohn-Sham density functional theory (DFT): (i) The exact total energy versus particle number is a series of linear segments between integer electron points; (ii) Across an integer number of electrons, the exchange-correlation potential may "jump" by a constant, known as the derivative discontinuity (DD). Here, we show analytically that in both the original and the generalized Kohn-Sham formulation of DFT, the two are in fact two sides of the same coin. Absence of a derivative discontinuity necessitates deviation from piecewise linearity, and the latter can be used to correct for the former, thereby restoring the physical meaning of the orbital energies. Using selected small molecules, we show that this results in a simple correction scheme for any underlying functional, including semi-local and hybrid functionals as well as Hartree-Fock theory, suggesting a practical correction for the infamous gap problem of DFT. Moreover, we show that optimally-tuned range-separated hybrid functionals can inherently minimize both DD and curvature, thus requiring no correction, and show that this can be used as a sound theoretical basis for novel tuning strategies.

Leeor Kronik
Weizmann Institute of Science

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