Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction

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From the perspective of perturbation theory, we propose a systematic procedure for the evaluation of the derivative discontinuity (DD) of the exchange-correlation energy functional in Kohn-Sham (KS) density functional theory, wherein the exact DD can in principle be obtained by summing up all the perturbation corrections to infinite order [1]. Truncation of the perturbation series at low order yields an efficient scheme for obtaining the approximate DD. While the zeroth-order theory yields a vanishing DD, the first-order correction to the DD can be expressed as an explicit universal functional of the ground-state density and the KS lowest unoccupied molecular orbital density, allowing the direct evaluation of the DD in the standard KS method without extra computational cost. The fundamental gap can be predicted by adding the estimated DD to the KS gap. This scheme is shown to be accurate in the prediction of the fundamental gaps for a wide variety of atoms and molecules.

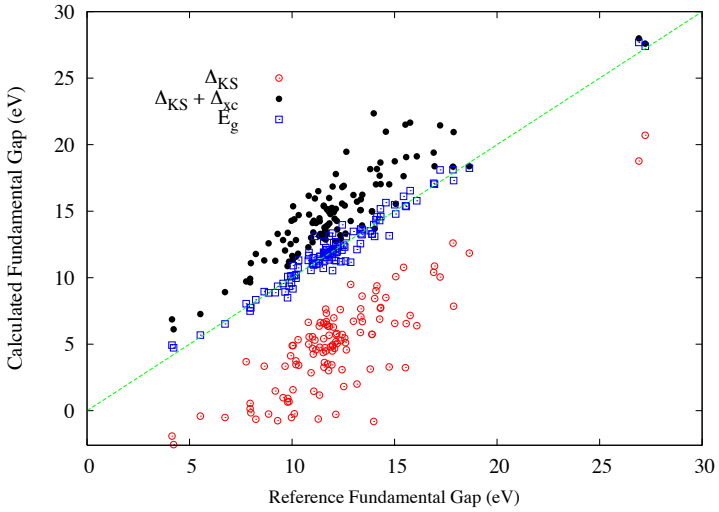

Figure: Calculated versus reference fundamental gaps for the FG115 database [2]. The fundamental gaps are calculated by three schemes (the KS gap, the KS gap + the approximate DD, the KS gap + the exact DD) using the LB94 functional [3].

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