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The piecewise-linearity of approximate density functionals revisited: implications for frontier orbital energies ELI KRAISLER, LEEOR KRONIK, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel — In the exact Kohn-Sham density-functional theory (DFT), the total energy versus the number of electrons is a series of linear segments between integer points. However, commonly used approximate density functionals produce total energies that do not exhibit this behavior. As a result, many system properties can be poorly described. In particular, the ionization potential theorem, equating the highest occupied eigenvalue with the ionization potential, can be grossly disobeyed. Here, we offer a generalization of all energy terms of an arbitrary density functional to systems with a fractional electron number, based on the ensemble form of DFT. Using the local density approximation as an illustrative example, we find that this generalization significantly reduces the deviation from piecewise linearity, while introducing neither empiricism nor further correction terms. With the generalized form, the total energy at integer electron numbers remains intact, but the eigen-energies change and the ionization potential theorem is much more closely obeyed.

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