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Non-Koopmans correction to the convexity and inaccuracy of orbital levels in local and semilocal density-functional theories ISMAILA DABO, Paris-Est University, ANDREA FERRETTI, NICOLAS POILVERT, NICOLA MARZARI, MIT, MATTEO COCOCCIONI, University of Minnesota — Local and semilocal density-functional approximations provide excellent predictions for systems with non-fractional electron occupations. However, such theories considerably overestimate the stability of systems with fractionally occupied orbitals. This fundamental deficiency, which arises from the convexity of approximate functionals and the presence of self-interaction, is responsible for a number of qualitative and quantitative failures, which pervade all aspects of electronic-structure predictions, ranging from electron transfer, electron transport, electronic polarization to molecular dissociation and adsorption. We focus here on the most immediate manifestation of the convexity problem, i.e., the inaccuracy of orbital energy levels. We demonstrate that errors in predicting orbital energies can be eliminated by introducing a non-Koopmans (NK) correction based upon the satisfaction of Koopmans' theorem, which identifies orbital energies with opposite removal energies in the frozen orbital approximation. We demonstrate the remarkable performance of the NK approach in predicting orbital levels for a complete range of atoms and molecules. We then examine the accuracy of the NK correction for large polyatomic systems in which the effect of orbital relaxation is expected to be significant.

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