Koopmans-compliant functionals: A reliable and efficient tool for the prediction of spectroscopic quantities

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In exact density-functional theory the total energy as a function of the particle number is a piecewise-linear sequence of straight lines connecting integer points [1]. However, commonly used approximate density functionals produce total energies that do not exhibit such piecewise-linear behavior, leading to a discrepancy between total and partial electron removal/addition energies and poor predictive capabilities of ionization potentials.
Koopmans-compliant functionals [2-4] enforce a generalized criterion of piecewise linearity in the energy of any approximate density functional with respect to the partial removal/addition of an electron - i.e., with respect to charged excitations - from/to any orbital of the system. When used to purify approximate density functionals, Koopmans' corrections lead to orbital-density dependent functionals and potentials that are able to deliver accurate spectroscopic properties [5].
The approach has been benchmarked on a comprehensive variety of molecular systems for which high accuracy calculations are available: the G2-R1 set, organic donors and acceptors, DNA/RNA bases, and transition-metal complexes. Results for ionization potentials, electron affinities, and photoemission spectra are typically comparable, but slightly superior, to those obtained with different flavours of GW many-body perturbation theory. Being this a functional framework, the straightforward advantages are that forces and other derivatives are also readily accessible, that the computational costs are much reduced, and the numerical parameters are those typical of DFT total-energy calculations. Applications of the Koopmans' functionals to extended systems are also discussed, again showing very good agreement with experiments or higher-order theories.

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