Electronic-Structure Calculations from Koopmans-Compliant Functionals

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We derive an orbital-dependent density-functional theory — the *Koopmans-compliant approach*[1,2] — that addresses the main limitations of common functional approximations in describing the complete electronic structure of quantum systems. The Koopmans-compliant method is constructed to enforce piecewise linearity in approximate energy functionals with respect to fractional particle occupations. We illustrate the remarkable performance of this method by comparing predicted molecular photoemission spectra and momentum maps of Dyson orbitals to experimental data, finding excellent agreement with ultraviolet photoemission spectroscopy and orbital tomography measurements,[4,5] while preserving or improving the prediction of total energies and equilibrium geometries.[3] These results highlight the role of Koopmans-compliant functionals as accurate and efficient approximations to the spectral potential.[6]

References

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