Dyson Orbitals: Fundamental Units of Electronic Structure and Chemical Interpretation

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Abstract

Dyson orbitals are fundamental units of electronic structure that appear in expressions of transition probabilities for a variety of experiments that involve electron attachment or detachment on short time scales. In addition, Dyson orbitals may be used to construct one–electron reduced density matrices; their squared moduli and associated pole strengths are constituents of the electron density of an initial state. The sum of a generalized Fock operator and the self–energy operator that occurs in the Dyson equation has eigenvalues that equal electron binding energies and eigenfunctions that are proportional to Dyson orbitals. The amplitudes and phases of Dyson orbitals may be inferred from a variety of experiments that have emerged in recent years. Electron propagator theory provides an efficient route to the prediction of Dyson orbitals and their associated electron binding energies. Recently developed computational realizations of the Dyson equation have been applied to the quest for record–setting superacids, Aufbau principles for solvated–electron precursors, photoelectron spectra of double Rydberg anions and the identification of Rydberg superalkalis. In each case, rigorous interpretations based on Dyson orbitals connect spectra, energetics and qualitative chemical concepts to each other.

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