Deconstructing Densities

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We state and prove a density functional theorem for the celebrated atom-in-molecule problem, demonstrating that given an arbitrary molecular structure and corresponding electronic density, the Hohenberg-Kohn theorem induces an approximate but unique spatial density deconstruction into atomic-like components. The decomposition is expressed as an *ensemble-of ensembles*, a weighted double sum over ionic and excited state densities. The relative contributions of the ensemble states reflect the subtle interplay between the ionic charge transfer and covalent charge distortions characteristic of chemical bonding. The theorem is illustrated for canonical diatomic molecular systems, and we show that computed atom-in-molecule effective charges are in good accord with chemical intuition, and remarkably consistent with the traditional quantum chemical definitions of Mulliken and Löwdin. Implications for the construction of atomistic interaction potentials and correlated energy density functionals are discussed.

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