More-predictive density functionals, symmetry breaking, and strong correlation

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Approximate density functionals constructed to satisfy known mathematical properties of the exact density functional for the exchange-correlation energy of a many-electron system can be predictive over a wide range of materials and molecules. The strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation [1] satisfies 17 exact constraints, and nicely describes some systems that were formerly thought to be beyond the reach of density functional theory, such as the cuprates [2]. In some cases (e.g., barrier heights to chemical reactions and hydrogen bonds in water [3]), SCAN is dramatically more accurate when evaluated on the Hartree-Fock density than it is on its own self-consistent and more delocalizing density. Ground states that break the symmetry of a Coulomb-interacting Hamiltonian can be understood as dynamic density or spin-density fluctuations that drop to low or zero frequency [4,5] and so persist over long times. In many cases, symmetry breaking transforms the strong correlation in a symmetry-unbroken wavefunction into moderate correlation like that found in the uniform electron gas of high or valence-electron density (an "appropriate norm" for constraint-based approximations).

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