Classifying and reducing errors in density functional calculations

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The energy error of any DFT calculation can be decomposed into a contribution due to the approximate functional and that due to the approximate density. Typically, the functional error dominates, but in many interesting situations, the density-driven error dominates. Examples include electron affinities, dissociation of molecules into charged fragments, transition state barriers, and ions and radicals in solution. In these abnormal cases, the error can be greatly reduced by using a more accurate density. A small gap between occupied and unoccupied orbitals may indicate a substantial density-driven error.