The Many Pair Expansion: a Density Functional Hierarchy for Correlation

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Density functional theory (DFT) is the de facto method for the electronic structure of weakly correlated systems. But for strongly correlated systems, common density functional approximations break down. Here, we derive a many pair expansion (MPE) in DFT that accounts for successive one-, two-, three- ... electron pair interactions within the system. To compute the correction terms, the density is first decomposed into a sum of localized, nodeless one electron densities (r_i) that integrate to two. That is, each r_i describes an electron pair. These pair densities are used to construct relevant quartet ($r_i + r_j$), sestet ($r_i + r_j + r_k$) ... densities. Numerically exact results for these few particle densities can then be used to correct an approximate density functional. We show that the resulting hierarchy gives accurate results for several important model systems - Hubbard models in 1D and 2D and PPP models of conjugated polymers. Next, we illustrate how this method can be implemented for molecular systems, demonstrating improvements to reaction energies and barriers for a few small molecule systems. We conclude that MPE thus provides a hierarchy of density functional approximations that show promise both for weakly and strongly correlated systems.