

Mixed Density Functional–Wave Functional Constructs: Variational Functionals with Hubbard-U

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Constrained-search density-functional theory combined with wave-function theory is employed to construct mixed density-wave functional approximations (DFA-WFA), for stretched diatomics and rings. Constructing the mixed functional begins from DFA calculations for two trial densities. The DFA calculations imply, in principle, that there are two many-electron wave functions corresponding to the trial densities that satisfy the constrained-search condition. A new set of trial wave functions is constructed from the linear combination of the CS wave functions. The energies for these trial states results in the mixing of DFAs and WFAs, and optimization of the linear expansion coefficients results in the mixed DFA-WFA. If the initial trial densities represent covalent and ionic states, it can be argued that the energy gap between the two DFAs provides an estimate of the Hubbard-U parameter. Delocalization influences the effective value of the Hubbard-U for a given atomic configuration. A first proposition considered here is that a model of a switching function has been constructed to modulate both the value of Hubbard-U and its contribution to the DFA-WFA. A second proposition is that the WFAs be approximated by DFAs for two other densities related to the original two. The mixed DFA-WFA is constructed explicitly for a several diatomic and ring systems and analyzed.