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Ensemble density functional theory, the atom-in-molecule problem, and reactive charge transfer[1] SUSAN ATLAS, Department of Physics and Astronomy, University of New Mexico, STEVEN VALONE, Materials Science and Technology Division, Los Alamos National Laboratory — A major challenge in large-scale simulations of complex biomolecular and materials systems is the ability to accurately describe reactive dynamics. We have previously described a new multiscale formalism, based on density functional theory and the embedded-atom method, that enables the rigorous encoding of quantum mechanical excitation effects such as charge polarization and charge transfer within a classical potential. Here we describe a new formulation of a key element of the theory: the deconstruction of molecular densities into subsystem atom-in-molecule components via ensemble constrained-search density functional theory. The method is implemented via the self-consistent solution of coupled sets of Kohn-Sham equations in conjunction with chemical potential equalization across subsystems. This leads to a natural interpretation of dynamical charge transfer and charge polarization in terms of an electronic entropy, thus extending the seminal work of Gross, Oliveira, and Kohn (1988).

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