Spectral Partitioned Kohn-Sham Density Functional Theory

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We introduce a general, variational scheme for systematic approximation of a given Kohn-Sham free-energy functional by partitioning the density matrix into distinct spectral domains, each of which may be spanned by an independent diagonal representation without requirement of mutual orthogonality. It is shown that by generalizing the entropic contribution to the free energy to allow for independent representations in each spectral domain, the free energy becomes an upper bound to the exact (unpartitioned) Kohn Sham free energy, attaining this limit as the representations approach Kohn-Sham eigenfunctions. A numerical procedure is devised for calculation of the generalized entropy associated with spectral partitioning of the density matrix. The result is a powerful framework for Kohn-Sham calculations of systems whose occupied subspaces span multiple energy regimes. As a case in point, we apply the proposed framework to warm- and hot-dense matter described by finite-temperature density functional theory, where at high energies the density matrix is represented by that of the free- electron gas, while at low energies it is variationally optimized. We derive expressions for the spectral-partitioned Kohn-Sham Hamiltonian, atomic forces, and macroscopic stresses within the projector-augmented wave (PAW) and the norm-conserving pseudopotential methods. It is demonstrated that at high temperatures, spectral partitioning facilitates accurate calculations at dramatically reduced computational cost. Moreover, as temperature is increased, fewer exact Kohn-Sham states are required for a given accuracy, leading to further reductions in computational cost. Finally, it is shown that standard multi-projector expansions of electronic orbitals within atomic spheres in the PAW method lack sufficient completeness at high temperatures. Spectral partitioning provides a systematic solution for this fundamental problem.