A favorably-scaling natural-orbital functional theory based on higher-order occupation probabilities

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We introduce an energy functional for ground-state electronic structure calculations with fundamental variables the natural spin orbitals and their joint occupation probabilities in an implied many-body trial wave function. We use a controlled approximation for the two-particle density matrix that greatly extends the accuracy compared to current functionals of the one-particle density matrix only. Algebraic scaling of computational cost with electron number is achieved in general, and Hartree-Fock scaling in the seniority-zero version of the theory. We present results obtained with the latter version for saturated small molecular systems for which highly accurate quantum chemical computations are available for comparison. The results are variational, capturing most of the correlation energy from equilibrium to dissociation.