

Local correlation methods based on natural auxiliary functions

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Recently we have presented a simple approach for the reduction of the size of auxiliary basis sets used in methods exploiting the density fitting (resolution of identity) approximation for electron repulsion integrals [*J. Chem. Phys.* **141**, 244113 (2014)]. In our approach, starting out of the singular value decomposition of three-center two-electron integrals new auxiliary functions are constructed as linear combinations of the original fitting functions. The new functions, which we term natural auxiliary functions (NAFs), are analogous to the natural orbitals widely used for the cost reduction of correlation methods. The use of the NAF basis enables the systematic truncation of the fitting basis, and thereby potentially the reduction of the computational expenses of the methods. Here we report the development of density fitting local second-order Møller–Plesset (MP2), direct random phase approximation (dRPA), and coupled-cluster singles and doubles with perturbative triples [CCSD(T)] methods based on NAFs. We demonstrate that using NAFs the size of the auxiliary basis of local correlation domains and thus the size of the three-center Coulomb integral lists can be reduced by up to an order of magnitude, which results in significant savings in computation time.