Beyond the first-order pair-natural orbitals for ground and excited states

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Recent work on reduced-scaling explicitly correlated many-body methods, such as coupled-cluster singles and doubles, has demonstrated computation of energies of large molecular assemblies (with hundreds of atoms) with near-linear complexity and with precision sufficient for chemical accuracy in most scenarios.[1] A key to such robust methodology has been the use of block-specific (orbital, pair, and triplet) compressions of the cluster operator to speed up the crossover with the canonical approaches. Here we will demonstrate how to improve on the first-order pair-natural orbitals as the basis for cluster amplitude blocks for a more compact and accurate description of electron correlation effects in ground and excited states.

[1] F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, E. F. Valeev, *J. Chem. Phys.* **146**, 174108 (2017).