

# Cost-effective description of strong correlation via the perfect pairing hierarchy

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We present novel implementations [1] of the singlet-reference perfect quadruples (PQ) [2] and perfect hexuples (PH) [3] models. The methods are obtained as tensor block decompositions of conventional coupled-cluster theory. Thanks to the truncation, coupled-cluster diagrams of high order – up to quadruples in PQ and up to hexuples in PH – can be included, which grant exactness for problems with four electrons in four orbitals (PQ) and six electrons in six orbitals (PH). Naturally, the obtained models can also be applied to much larger systems, and due to the coupled cluster ansatz, the exactness of the models is also valid for an arbitrary number of local strongly interacting subsets of electrons and orbitals. PQ and PH have storage requirements that scale as the square, and the cube of the number of active electrons, respectively, and exhibit quartic scaling of the computational effort for large systems. With the novel implementation of PQ, active spaces of hundreds of electrons in hundreds of orbitals can be solved in a matter of minutes on a single core workstation.

While the truncation results in huge speedups for the models, it also makes them no longer invariant to rotations in the occupied-occupied and virtual-virtual blocks, and so the orbitals need to be optimized. We have recently implemented orbital optimization, and will present applications including  $\pi$ -space only as well as full-valence calculations on linear polyacenes, with active spaces nearing 300 electrons in 300 orbitals. Furthermore, we will also discuss the extension of the pairing models to beyond singlet references, which may yield powerful models for the description of radicals in the near future.

[1] S. Lehtola, M. Head-Gordon, and J. A. Parkhill, *Journal of Chemical Physics*, 2016, 145, 134110.

[2] J. A. Parkhill, K. Lawler and M. Head-Gordon, *Journal of Chemical Physics*, 2009, 130, 084101.

[3] J. A. Parkhill and M. Head-Gordon, *Journal of Chemical Physics*, 2010, 133, 024103.