Third-order four-component multireference perturbation theory based on the driven similarity renormalization group

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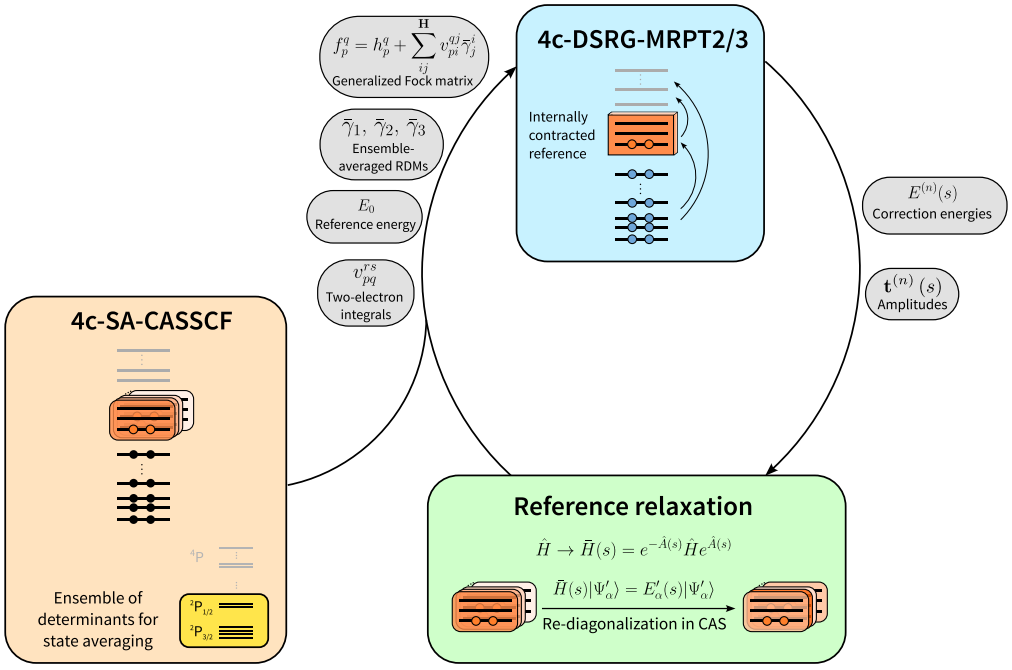

Most nonrelativistic electron correlation methods can be adapted to account for relativistic effects, as long as the relativistic molecular spinor integrals are available, from either a four-, two-, or one-component mean-field calculation. However, relativistic multireference correlation methods remain a relatively unexplored area, with mixed evidence regarding the improvements brought by perturbative treatments. We report, for the first time, the implementation of state-averaged four-component multireference perturbation theories to second and third order based on the driven similarity renormalization group (DSRG). With our methods, named 4c-SA-DSRG-MRPT2 and 3, we find that the dynamical correlation included on top of 4c-CASSCF references can significantly improve the spin-orbit splittings in p-block elements when compared to 4c-CASSCF and 4c-CASPT2 results. We further show that 4c-DSRG-MRPT2 and 3 are applicable to these systems over a wide range of the flow parameter, with systematic improvement from second to third order in terms of reduced sensitivity with respect to the flow parameter.