Spin purification and projection methods for determinantal configuration interaction

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The configuration interaction (CI) method has been used since the early days of quantum mechanics as a straightforward means of understanding electronic structure. Full CI (FCI) is routinely used to benchmark the accuracy of other, more approximate, methods, and complete active space variants (CASCI and CASSCF) have played important roles in describing electronic correlation in systems too large to study using FCI. Modern CI codes often use direct, determinant based approaches for computational efficiency. While determinantal wavefunctions offer certain advantages in terms of the ease with which we may evaluate their coupling coefficients, determinants are not in general spin eigenfunctions of the total spin operator, $\hat{S}^2$. In most cases, the selection of spin-pure initial guess vectors and spin-averaged preconditioners will result in CI wavefunctions having the correct spin symmetry. Numerical noise plays an increasingly deleterious role as both the number of configurations and the number of states requested in a CI calculation are increased, however, and can result in spin contamination of the resulting eigenvectors. In the present work, we demonstrate 3 novel solutions to this problem, based on the folded spectrum approach, Gram-Schmidt projection, and inverse iteration, respectively. Our methods have been implemented in the graphical processing unit (GPU) accelerated electronic structure software package TeraChem. Of particular interest, we show how our vectorized, low-scaling $\hat{S}^2 \cdot c$ algorithm allows us to perform spin purification at a fraction of the cost of the highest-scaling CI iteration step, σ vector formation. The utility of our approaches is demonstrated by locating minimum energy conical intersections (MECIs) in open-shell anionic and dangling bond silicon clusters using a hybrid ab initio molecular dynamics (AIMD) and MECI geometry optimization scheme.