

Evaluation of Determinant Expansion Coefficients and Spin Density Matrices Within the Graphically Contracted Function Method

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Within the Graphically Contracted Function Configuration Interaction (GCF-CI) method [1-5], the wavefunction is expanded as a linear combination of graphically contracted functions (GCFs), each of which is a linear combination of the underlying configuration state functions (CSF). The CSF coefficients that define each GCF are products of the arc factors associated with the underlying Shavitt graph. The GCF representation of the wavefunction spans the same configuration space as the linear CI wavefunction with dimension N_{CSF} , but with far fewer variables since the number of arc factors scales polynomially with the number of orbitals and electrons. In addition to reducing the memory requirements of traditional CI approaches, the GCF formalism allows for the efficient computation of wavefunctions in polynomial time and has several desirable properties: (i) it is variational, (ii) it avoids the choice of a reference wavefunction, (iii) it is applicable towards both ground and excited states, and (iv) it does not suffer from spin contamination.

In this work we outline two recent extensions of the GCF-CI method, namely, the evaluation of determinant expansion coefficients and the computation of spin density matrices. While the cost of computing a single determinant expansion coefficient scales *exponentially* with system size for traditional CI methods, the recursive algorithm presented here scales *polynomially* with the number of orbitals and electrons. Hence, as demonstrated through applications to systems with hundreds of electrons and orbitals, it may readily be applied to very large systems. Spin density matrix elements may be computed from the one-electron spatial density matrix and a subset of the two-electron spatial density matrix elements. While computing the spin density matrix would require an effort proportional to n^3 , where n is the number of spatial orbitals, the new algorithm scales as the number of unique spin density matrix elements $O(n^2)$. In addition, we will show that all $2S+1$ components, with $-S \leq M \leq S$, of the spin density may be obtained from the maximal spin component via a simple scaling.

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