A New Algorithm for Computing Optimization Gradients Within the Graphically Contracted Function Method

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In the Graphically Contracted Function Configuration Interaction (GCF-CI) method [1-4], the wave function is written as a linear combination of graphically contracted functions (GCFs), and each GCF in turn is formally equivalent to a linear combination of configuration state functions (CSFs) that comprise an underlying linear expansion space of dimension N_{CSF}. The CSF coefficients that define the basis functions are nonlinear functions of a smaller number of variables called arc factors that are associated with the underlying Shavitt Graph. Wave functions are optimized with respect to the N_{GCF} linear CI expansion coefficients and the nonlinear arc factor parameters. The method is formulated in terms of spin-eigenfunctions using the Graphical Unitary Group Approach (GUGA), and consequently it does not suffer from spin contamination or spin instability. The expansion form is appropriate for both ground and excited states and to closed- and open-shell molecules.

Using an efficient recursive approach, the effort required to construct an individual hamiltonian matrix element in the GCF basis $H_{MN} = \langle M | \hat{H} | N \rangle$ scales as $\mathcal{O}(n^4)$ for a wave function expanded in n molecular orbitals. The corresponding metric matrix element $S_{MN}=\langle M|N\rangle$ requires effort that scales as $\mathcal{O}(n)$, the one-particle transition density $\mathbf{D}^{MN}$ requires $\mathcal{O}(n^2)$ effort, the two-particle density $\mathbf{d}^{MN}$ requires $\mathcal{O}(n^4)$ effort. Previous work [3-4] has shown how the gradient of the energy with respect to the arc factors may be computed with $\mathcal{O}(n^5)$ effort. This previous algorithm consists of a linear $\mathcal{O}(n)$ linear step embedded within the recursive $\mathcal{O}(n^4)$ hamiltonian matrix element algorithm. In the present work, a new algorithm is described that is fully recursive and allows the gradient to be computed with $\mathcal{O}(n^4)$ effort. Timing comparisons will be presented for the H_{MN} matrix element construction, the old gradient algorithm, and this new algorithm.

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