The Efficient Conversion Between Linear Wave Function Expansions and Nonlinear Graphically Contracted Function Expansions

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A Graphically Contracted Function (GCF)[1] is a Matrix Product State (MPS) defined in terms of spin-adapted Configuration State Functions (CSF) using a Shavitt graph. The Shavitt graph[2] is the fundamental entity of the Graphical Unitary Group Approach (GUGA). The Shavitt graph is a hierarchical directed acyclic graph (DAG), whose nodes k depend on the quantum numbers n_k (the orbital level), N_k (the number of electrons), and S_k (the $\hat{S}^2$ quantum number). The arcs of the graph connect the nodes in adjacent levels within this graph. There are at most four lower (or upper) arcs associated with each node in the graph. Each CSF corresponds to a unique path from the tail to the head of the graph, touching a single arc between each level. A wave function may be expanded in the basis of these GCFs, and is thereby a linear combination of MPSs, $|\psi\rangle = \sum_P^{N_{GCF}} c_P |P\rangle$.

In the multifacet GCF method[1], each arc in the graph is associated with a rectangular matrix of arc coefficients. The coefficient of CSF m within a GCF P is given by the sequence of matrix products.

$$x_m^P = \langle m|P\rangle = \boldsymbol{\alpha}^P_{k_0^m,k_1^m}\boldsymbol{\alpha}^P_{k_1^m,k_2^m}\ldots\boldsymbol{\alpha}^P_{k_{n-2}^m,k_{n-1}^m}\boldsymbol{\alpha}^P_{k_{n-1}^m,k_n^m}$$

$\boldsymbol{\alpha}^P_{k_{q-1}^m k_q^m}$ is the matrix of arc factors associated with the arc $\left(k_{q-1}^m, k_q^m\right)$ between node k_{q-1}^m at level (q–1) and node k_q^m at level q. This computation reduces to a sequence of matrix-vector products. There is one matrix for each orbital level in this product, so the effort required to compute an individual CSF is approximately $O\left(n\bar{f}^2\right)$ for n molecular orbitals and for an average of $\bar{f}$ facets on each node. The straightforward computation of N_{CSF} such coefficients would require $O\left(N_{CSF}n\bar{f}^2\right)$ effort. If the paths within the graph are generated with a depth-first search, then matrix-vector products at the lower levels can be reused in the computation of multiple CSF coefficients. For large n, this reuse of intermediate quantities reduces the effort to approximately $O\left(N_{CSF}\log(n)\bar{f}^2\right)$.

In the other direction, the task is to take a list of CSF coefficients and convert that wave function into a GCF. There are two approaches to achieve this transformation. One is to optimize the nonlinear arc factor parameters to minimize the least-squares difference of the wave functions[3]. This requires the $O\left(N_{CSF}\log(n)\bar{f}^2\right)$ effort discussed above for each optimization iteration. An alternative approach is to convert the CSF list into primitive GCFs, and then recursively merge[1] these GCFs into the final GCF form. The overall effort scaling and memory requirements for these algorithms are examined.

[1] R. Shepard, G. Gidofalvi, and S. R. Brozell, *J. Chem. Phys.* **141**, 064105 (2014). DOI 10.1063/1.4890734.
[2] I. Shavitt, *Int. J. Quantum Chem.* **S11**, 131 (1977). DOI: 10.1002/qua.560120819.
[3] R. Shepard, *J. Phys. Chem. A* **109**, 11629-11641 (2005). DOI: 10.1021/jp0543431.

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