Progress on Incorporating the Spin–Orbit Interaction into the Graphically Contracted Function Method

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In the Graphically Contracted Function Configuration Interaction (GCF-CI) method [1,2,3,5,4] (previously denoted as a nonlinear expansion form for electronic wave functions), the wave function is a linear combination of GCFs, and each GCF is a linear combination of all the Configuration State Functions (CSFs). The CSF coefficients that define each GCF are nonlinear functions of the arc factors associated with the underlying Shavitt graph. This formulation is based on spin eigenfunctions using the Graphical Unitary Group Approach (GUGA). A single-headed Shavitt graph represents a unique spin state. When the spin–orbit interaction is included, a Shavitt graph is multiheaded. The Hamiltonian operator includes relativistic effective core potentials and valence spin–orbit one-electron operators [6].

Progress on incorporating the spin–orbit interaction is reported. The calculation of spin–orbit matrix elements is straightforward and is included in the efficient recursive approach of the GCF method with simple software modifications. The effort required to construct an individual Hamiltonian matrix element that contains the spin–orbit term scales as $O(n^4)$, where n is the number of molecular orbitals. This is the same scaling as for the spin free Hamiltonian. The actual computational complexity of Hamiltonian matrix element construction is related to the number of edges in the auxiliary pair graph. This graph consists of vertices that correspond to pairs of nodes in the Shavitt graph and edges that correspond to bra arc and ket arc pairs. Analytical expressions for the number edges in the auxiliary pair graph are presented for both the spin free and the spin–orbit cases. In addition, the treatment of arc factors in multiheaded Shavitt graphs will be discussed.

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