Efficient Formulation of Full Configuration Interaction Quantum Monte Carlo in a Spin Eigenbasis via the Graphical Unitary Group Approach

Ali Alavi[a,b] and Werner Dobrautz[a]

[a] *Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany*
[b] *Dept of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*
w.dobrautz@fkf.mpg.de

We provide a spin-adapted formulation of the Full Configuration Interaction Quantum Monte Carlo (FCIQMC) algorithm [1], based on the Graphical Unitary Group Approach (GUGA) [2], which enables the exploitation of SU(2) symmetry within this stochastic framework [3]. Random excitation generation and matrix element calculation on the Shavitt graph of GUGA can be efficiently implemented via a biasing procedure on the branching diagram.

The use of a spin-pure basis explicitly resolves the different spin-sectors and ensures that the stochastically sampled wavefunction is an eigenfunction of the total spin operator $\hat{\mathbf{S}}^2$. The method allows for the calculation of states with low or intermediate spin in systems dominated by Hund's first rule, which are otherwise generally inaccessible.
Furthermore, in systems with small spin gaps, the new methodology enables much more rapid convergence with respect to walker number and simulation time.

Some illustrative applications of the GUGA-FCIQMC method are provided: computation of the ${}^2F - {}^4F$ spin gap of the cobalt atom in large basis sets, achieving chemical accuracy to experiment, and the ${}^1\Sigma_g^+$, ${}^3\Sigma_g^+$, ${}^5\Sigma_g^+$, ${}^7\Sigma_g^+$ spin-gaps of the stretched N_2 molecule, an archetypal strongly correlated system.

References

1. G. H. Booth, A. J. W. Thom and A. Alavi, *J. Chem. Phys.* **131** (2009), 054106
2. I. Shavitt, *Int. J. Quantum Chem.* **S12** (1978), 5
3. W. Dobrautz, S. D. Smart and A. Alavi, arXiv:1905.01346