Improving the Accuracy of AFQMC of Non-Orthogonal Multi-Determinant Wave Functions in Molecular and Periodic Systems

Edgar Landinez Borda*, Matthew Otten**, Cyrus Umrigar**, Miguel Morales Silva*
**Cornell University, Ithaca, NY USA
*Lawrence Livermore Nacional Laboratory, Livermore, CA USA

We explore the use of trial wave functions in Auxiliary-Field Quantum Monte Carlo constructed from non-orthogonal Slater determinant expansions. The use of non-orthogonal determinant expansions leads to systematically increased accuracy with a reduced number of terms and a compact representation, when compared to traditional determinant expansions constructed from particle-hole excitations. We demonstrate significantly improved accuracy when compared to traditional trial wave-functions, as well as systematically improvable results in both strongly correlated molecular calculations and periodic systems. First, we compute the isomerization path of the $[Cu_{2}O_{2}]^{+2}$ molecule and compare the profile of relative energies along the path against DMRG, CR-CC and SPHF calculations. This problem is well known because the accurate calculation of the correlation energy along the path is challenging. The present methodology exhibits versatility and good agreement using only several tens to hundreds of determinants. Finally, we test the methodology for periodic systems performing calculations for Silicon in the diamond phase. We compare against Coupled Cluster and well converged selected CI calculations. As shown, the method is capable of reaching sub-mHa accuracy even when a modest number of determinant is used.

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