Large STO-NG expansions for All Electron Quantum Monte Carlo Trial Functions

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Standard Gaussian basis set functions cannot be used in all-electron quantum Monte Carlo (QMC) calculations because these basis functions result in fluctuations of the local energy. These local energy fluctuations result in large variances and error bars. Slater basis functions which do not have these fluctuations may be used as an alternative. However, *ab initio* methods and computational packages which use Slater functions are not commonplace. Instead contracted Gaussian basis sets with large numbers of primitives are presented as an alternative to using Slater type functions for QMC trial function construction. Previous STO-NG expansions have been limited to no more than six contracted Gaussian functions. It is shown that Gaussian expansions limited to six primitives are not sufficient and larger expansions are necessary to obtain accurate variational Monte Carlo (VMC) energies. We demonstrate that the STO-NG expansions converge exponentially to the Hartree-Fock energy calculated with Slater basis functions, yielding arbitrary accuracy. The STO-NG expansions are presented as an alternative to other methods developed over the last several years for creating QMC all-electron trial wave functions. Unlike previous all-electron methodologies, the current procedure allows consistent unbiased improvement of the VMC energy.