

Compact and accurate quantum Monte Carlo wave functions for first row atoms

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Many-body wave functions for the first row atoms (Li to Ne) are represented as expansions in eigenstates of \hat{L}^2 , \hat{L}_z , \hat{S}^2 , \hat{S}_z ; multiplied by a Jastrow factor. This configuration state function (CSF) expansion provides a systematic means for improving a wave function by including CSFs corresponding to higher excitations. Optimization of all wavefunction parameters including Jastrow, CSF and orbital coefficients as well as basis exponents, starting from a simple initial guess, with no external input, results in compact and accurate wave functions (low variational and diffusion Monte Carlo energies and low variance of the local energy). Even at the variational Monte Carlo level we recover over 97% of the correlation energy for all of the atoms. Further improvements by use of backflow transformations are being explored. This work aims to develop insight into selecting relevant CSFs particularly for large systems, where it is difficult to include all CSFs to a given order.