Excited states in QMC: Which wave function? Which variational principle?

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We investigate here the general key ingredients needed to efficiently achieve reliable excitation energies in quantum Monte Carlo. For the small and yet challenging cyanine dyes and retinal models, we show that the use of selected configuration-interaction expansions (CIPSI) leads to compact Jastrow-Slater wave functions and a balanced description of both the ground and excited states. Furthermore, we analyze the use of different variational principles for the minimization of the wave functions in quantum Monte Carlo. In particular, we compare the performance of state-specific variance minimization and of state-average energy minimization. For this purpose, we use a revised version of the Newton minimization method in which the exact expression of the Hessian is manipulated to obtain a faster and more stable convergence.