Efficient and chemically accurate excited states with quantum Monte Carlo

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Abstract:

We demonstrate an efficient protocol to compute chemically accurate ground- and excited-state energies and structures with quantum Monte Carlo (QMC), where the determinant component of the typical Jastrow-Slater wave function is constructed in an automated fashion using a selected CI algorithm. For small, yet theoretically challenging molecular systems, we show that our scheme to select relevant determinants is reliable and transferrable, and surpasses the performance of a conventional active-space description even with extremely compact QMC wave functions. Furthermore, we can treat multiple states in a balanced manner and accordingly compute vertical excitation energies, relaxed excited-state geometries, and adiabatic excitation energies in excellent agreement with the corresponding high-level coupled-cluster values.

References:

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