Efficient and chemically accurate excited states with quantum Monte Carlo

Monika Dash\textsuperscript{a}, Jonas Feldt\textsuperscript{a}, Saverio Moroni\textsuperscript{b}, Anthony Scemama\textsuperscript{c} and Claudia Filippi\textsuperscript{a}

E-mail: m.dash@utwente.nl

\textsuperscript{a} MESA+ Institute of Nanotechnology, University of Twente, Enschede, The Netherlands
\textsuperscript{b} CNR-IOM DEMOCRITOS, Institute Officina dei Materiali, and SISSA Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy
\textsuperscript{c} Laboratoire de Chimie et Physique Quantiques, Universite de Toulouse, CNRS, UPS, France

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: