Full Wave Function Optimization of Transition Metal Compounds with Quantum Monte Carlo

Jil Ludovicy and Arne Lüchow

RWTH Aachen University
ludovicy@pc.rwth-aachen.de

An accurate characterization of the bond cleavage between transition metals and main group elements is of crucial importance in order to elucidate catalytic processes. These systems often exhibit large non-dynamic correlation which still poses a great challenge for high-level theoretical methods. The quantum Monte Carlo (QMC) approach offers an elegant way to tackle the problem of unfavorable scaling with respect to the number of electrons and CPUs, that traditional wave function methods usually suffer from, due to its highly parallel regime.

The wave function ansatz that we employed in this study corresponds to a linear combination of configuration state functions (CSFs), multiplied by a totally symmetric Jastrow correlation factor. We partially and fully optimized the Jastrow, orbital, and CI parameters of complete active space wave functions with respect to the energy within the variational Monte Carlo (VMC) framework. Effective core potentials (ECPs) are used for all calculations. We present accurate dissociation energies for different transition metal compounds at multi-reference diffusion Monte Carlo (MR-DMC) level. The key role can thereby be ascribed to the optimization of the molecular orbitals in the presence of a Jastrow correlation factor. We additionally show that the fixed-node error in diffusion Monte Carlo (DMC) can be systematically reduced by optimizing the multi-configuration guide functions. Our approach is able to yield an accurate description of transition metal compounds with wave functions generated from a small, physically motivated active space.