

$|\Psi|^2$ Analysis: Electronic Motifs and Energy Partitioning with Quantum Monte Carlo

Michael A. Heuer and Arne Lüchow

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

Local properties of a chemical system are contained in its many-electron wave function Ψ but extraction of information about bonding and stability is increasingly difficult for growing electron numbers N because of the high dimensionality. Often, orbital localization or electron density methods are employed for which correlation is lost in the three-dimensional data. Alternatively, valence bond theory can be used and provides insight into local properties such as structure weights and resonance energies but is limited to a specific wave function ansatz.

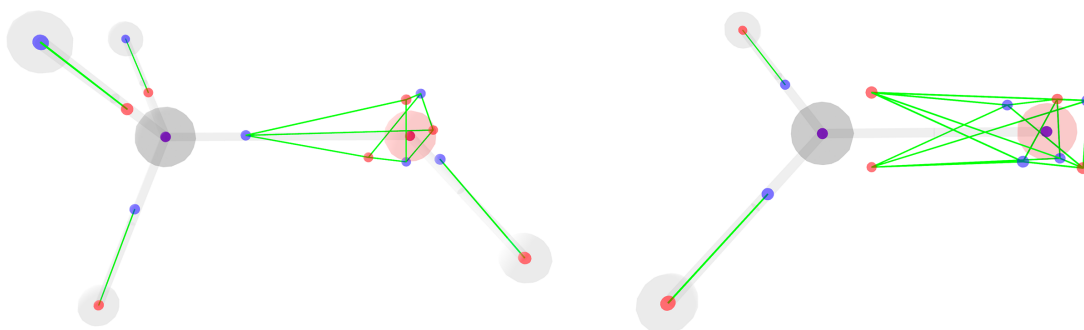


Figure: Electronic motifs in probable maxima of methanol (left) and formaldehyde (right). Blue and red spheres represent α and β electrons and green lines indicate opposite-spin correlation between them.

We present a different, quantum Monte Carlo-based approach relying on importance sampling of the $3N$ -dimensional probability density $|\Psi|^2$ and remaining flexible in the wave function ansatz¹. Subsequent local maximization of the sample yields maxima providing a natural partitioning of $|\Psi|^2$ into $3N$ -dimensional basins of attraction. The maxima can then be clustered based on their similarity. In the resulting clusters, we find transferable and recurrent motifs of spin-correlated electron positions (see Figure) clearly showing the interplay of Coulomb interaction and Pauli repulsion¹.

The local energy contributions obtained during the quantum Monte Carlo sampling allow for assigning intrinsic interaction energies to the motifs of the individual clusters.

In this work, we present the latest $|\Psi|^2$ analysis results for common organic molecules.

References

1. A. Lüchow, *J. Comput. Chem.* **35** (2014), 854.