Quantum Monte Carlo: Nodes, Antisymmetry, and How To Get Insight from QMC

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Quantum Monte Carlo is a wave function based method that employs accurate wave functions that are nonetheless very compact. In the diffusion quantum Monte Carlo variant (DMC), the energy depends solely on the accuracy of the nodal hypersurface of this wave function. For ground states the nodal hypersurface describes the antisymmetry of the wave function and connects the coalescence points of two electrons with like spin. Recent progress in the optimization of the hypersurface with respect to the DMC energy is reported and compared with optimizations based on an energy criterion. Antisymmetry and the Coulombic attraction of the electrons by the nuclei determine the electronic structure of molecules and, to a somewhat lesser extent, the electron electron repulsion. With quantum Monte Carlo, an efficient sampling of the many-body distribution $|\Psi|^2$ of the electrons is possible allowing to obtain detailed information about the distribution. Single electron densities that add up to the total electron density are defined based on the many-body distribution allowing to obtain insight into the details of the chemical bond and in particular into the effect of the antisymmetry on chemical bonding. First examples of this analysis are presented.

Literature: