Electronic structure quantum Monte Carlo methods for weakly bonded systems and for systems with spin-orbit interactions

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We present recent advances in quantum Monte Carlo (QMC) applications that include subchemical accuracy calculations of non-covalent bonding in van der Waals complexes and QMC treatment of heavy atoms systems with explicit inclusion of spins as quantum variables. The calculations of van der Waals systems are based on fixed-node diffusion QMC method that leads to surprisingly high accuracy due to the systematic fixed-node error cancellations as demonstrated on a set of var der Waals complexes as well as on DNA base pairs. The second area deals with the development and application of QMC for treating fermionic spin degrees of freedom as quantum variables. Traditionally, in QMC electronic structure calculations the electron spin are fixed in configurations that correspond to the desired spin-space symmetries of calculated states as allowed for the Hamiltonians without explicit spin terms. Here we present an approach that enables explicit QMC calculations with spinors and variable spins in the fixed-phase formalism. The method has been directly cross-validated with configuration interaction approaches in two-component formalism and applied to several systems that include spin orbit-interactions such as atoms, molecules and other cases. The performance is similar to the fixed-node calculations several aspects such as achieved accuracy and capturing of correlation effects. The corresponding wave functions have lower symmetries and therefore exhibit significant multi-reference character as is observed in a number of cases.