Development of Relativistic quantum Monte Carlo method: Theory and parallel program

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The Quantum Monte Carlo (QMC) method is a suitable method for massively parallel computation of electron-correlation effects in physical and chemical problems. While the target of molecular orbital theory or density functional theory has been extended to systems including heavy elements, the QMC method has been limited to systems with light elements. To treat molecular systems with heavier elements, the inclusion of relativistic effects – scalar relativistic and spin-orbit effects – is required.

To treat the scalar relativistic effect, we have developed relativistic quantum Monte Carlo methods based on the zeroth order regular approximation (ZORA) Hamiltonian, whose kinetic term is suitable for the real space MC integration. The scalar ZORA QMC method includes three extensions to the nonrelativistic QMC method – (1) the ZORA local energy expression, (2) the ZORA cusp correction scheme, and (3) the ZORA approximate Green's function. Combined with the spin-orbit treatment of Ambrosetti *et al.*[4], the developed methods are implemented in a QMC program "R4QMC", a QMC part of "NTChem" software. The details of theory and implementation of the relativistic extension of the QMC methods for general molecular systems are presented.

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