**Quantum Monte Carlo methods from ground state to thermal equilibrium and real-time propagation of electronic structure**

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Electronic correlation is the most challenging part of electronic structure theory and calculations. Conventionally, it is included by corrections on top of Hartree–Fock approach or approximate functionals within Density Functional Theory. However, integration in terms of Quantum Monte Carlo (QMC) yields exact account of correlation, and thus, provides the most accurate description of electronic structure.

Here, we present two novel QMC approaches based on the Feynman path integrals (PI): one in imaginary time and another one in real time. The former leads to the description of electronic structure in finite temperature (PIMC) [1], and the latter to the zero-Kelvin description of eigenstates or quantum dynamics (RTPI) [2]. Curiously, properties of the path-integral approaches meet at the better known Diffusion Monte Carlo (DMC) [3], which yields the exact static ground state at zero-Kelvin.

In all approaches, the many-body effects or correlations are included exactly within the numerical accuracy. Furthermore, the Born–Oppenheimer approximation is not necessarily required, but the nuclei can easily be released to thermal motion and quantum dynamics, if relevant. The biggest challenges are computational burden and description of the exchange interaction of fermions.

We demonstrate these approaches in a few problems, where the effect of correlation is pronounced: computation of molecular polarizabilities (PIMC) [4], Hooke's atom (RTPI) [5] and positron binding atoms (DMC).

[1] D. M. Ceperley. Path integrals in the theory of condensed Helium. *Rev. Mod. Phys*, 67(2):279–355, Apr 1995.

[2] Ilkka Ruokosenmäki and Tapio T. Rantala. Numerical path integral approach to quantum dynamics and stationary quantum states. *Commun. Comput. Phys.*, 18(01):91–103, Jul 2015.

[3] B L Hammond, W A Lester, and P J Reynolds. *Monte Carlo Methods in Ab Initio Quantum Chemistry*. World Scientific, Mar 1994.

[4] Juha Tiihonen, Ilkka Kylänpää, and Tapio T. Rantala. General polarizability and hyperpolarizability estimators for the path-integral Monte Carlo method applied to small atoms, ions, and molecules at finite temperatures. *Phys. Rev. A*, 94(3):032515, September 2016.

[5] Ilkka Ruokosenmäki, Hossein Gholizade, Ilkka Kylänpää, and Tapio T. Rantala. Numerical path integral solution to strong Coulomb correlation in one dimensional Hooke's atom. *Computer Physics Communications*, 210:45–53, Jan 2017.