PATH INTEGRAL SIMULATION OF EIGENSTATES AND DYNAMICS OF ELECTRONS

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Recently, we have presented a novel real time path integral [1] approach (RTPI) to electronic structure calculations [2]. We have also shown that it is capable of incorporating the Coulombic electronic correlations exactly within numerical accuracy. Furthermore, combined with Monte Carlo sampling of paths RTPI becomes a robust method similar to the Diffusion Monte Carlo method (DMC) [3]. Also, combination of RTPI and DMC yields a method with the best features of both. More recently, we have shown that RTPI can be used to find excited states and simulate coherent quantum dynamics, in a strongly correlated system of electrons [4].

Here, we present results and demonstrate finding the ground state and lowest excited states, and also, dynamics as a response to external electric fields. Our test bench is sc. Hooke's atom – two electrons in a harmonic potential. This is a case of very strong correlation: Coulomb interaction of the electrons splits the space of relative motion into two independent parts. We analyze the role of relevant approximations, Monte Carlo method and numerical parameters. We also assess the accuracy in comparison with the exact analytical data [5] and that from perturbation theory, where relevant.

The improved Trotter kernel is shown to be useful with large enough number of Monte Carlo walkers, in cases where exact propagator are not available. We find that the accuracy and stability of RTPI is tunable with the number of Monte Carlo walkers and the real time step size. Regarding ground states, the computational cost of RTPI is significantly higher than that of DMC [6]. However, one of the advantages of RTPI is that it provides one with the wave function explicitly, and thus, the evaluation of local multiplicative expectation values becomes straightforward. Moreover, as RTPI is capable of locating the nodal surfaces of excited states, which is promising for fermion simulations.

Perturbation theory was shown to be useful for analytical solutions in case of strong confinements, which may become more challenging for numerical methods and available approximate solutions.

[1] R. P. Feynman and A.R. Hibbs; Quantum Mechanics and Path Integrals (McGraw-Hill, New York, 1965); R. P. Feynman; Rev. Mod. Phys. **20**, 367 (1948).
[2] Ilkka Ruokosenmäki and Tapio T. Rantala, Comm. in Comput. Phys., **18**, 91 (2015).
[3] Ilkka Ruokosenmäki, Hossein Gholizade, I. Kylänpää and Tapio T. Rantala, submitted to Comput. Phys. Commun.
[4] Hossein Gholizade, Ilkka Ruokosenmäki and Tapio T. Rantala, to be published.
[5] M.Taut; Phys. Rev. A **48**, 5, (1993).
[6] B. L. Hammond, W. A. Lester Jr., P. J. Reynolds; "Monte Carlo Methods in Ab initio Quantum Chemistry", World Scientific, (1994)