Path Integral Monte Carlo Method in Photoabsorption Spectra Calculations

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The path integral Monte Carlo (PIMC) method based on the quantum to classical mapping [1] enables us to rewrite the partition sum of a quantum system as many-dimensional integral which is then evaluated using the Metropolis Monte Carlo approach [3]. This Metropolis random walk enables us to properly sample the spatial coordinates of the system at finite temperature for further calculations, e.g. the calculation of the photoabsorption spectrum of the system. The main benefit is mitigating the curse of dimensionality since the Monte Carlo sampling converges independently of the dimension. The main disadvantage is an extreme computational complexity which enables only simulations of small systems and usage of computationally cheap interaction potentials.

Within our previous work [2], we have calculated photoabsorption spectra of small (up to $N = 10$ particles) charged helium clusters utilizing the PIMC approach with the diatomics in molecules (DIM) potential energy surface (PES) representation for sampling the configurations. Even computationally relatively cheap methods such as the DIM (with $\mathcal{O}\left(N^3\right)$ scaling) do not enable us to move to medium-sized systems. However, the utilization of the artificial intelligence for PES evaluation seems to be a promising prospect for the future of such calculations.

[1] D. M. Ceperley. *Rev. Mod. Phys.*, 67(2):279, 1995.

[2] R. Ćosić, F. Karlický, and R. Kalus. *Chem. Phys. Lett.*, 700:96, 2018.

[3] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller. *J. Chem. Phys.*, 21:1087, 1953.