Ring polymer path integrals as eigenvalue problem

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In ring polymer path integral methods an N-particle quantum system is mapped into a classical polymer ring, where the beads of the polymer are the replicas of the original N-particle system and they are connected through harmonic springs. This isomorphism is exact in the limit of infinite bead number. The equilibrium averages of the classical polymer give the corresponding thermal properties of the quantum mechanical system. [1]

We employed the transfer operator method for imaginary path integrals to calculate molecular partition functions. The transfer matrix approach is a handy technique in statistical physics that allows the analytical derivation of the partition function for some classical systems [2,3]. Due to this technique the calculation of the quantum partition function is transformed into an eigenvalue problem. This method has two main benefits: i) compared to the ring polymer molecular dynamics or Monte Carlo approximations the computational complexity of the partition function is independent of the applied bead number (replicas of the system) that means, this method can reach the exact quantum mechanical limit ii) in general case only the largest eigenvalue of the transfer operator is needed for the computation of the partition function. Moreover, we also derived an exact formula for the eigenvalues and eigenfunctions for the transfer operator of the harmonic oscillator.

References

1. D. Chandler, P. G. Wolynes, *J. Chem. Phys.*, **1981**, 74, 4078
2. P. Gurin, S. Varga, *Phys. Rev. E*, **2011**, 83, 061710
3. H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **1941**, 60, 252