

Multi-Level Monte Carlo Path Integral Molecular Dynamics for Thermal Average Calculation in the Nonadiabatic Regime

Xiaoyu Lei¹ and Zhennan Zhou^{2,*}

¹ Department of Statistics, University of Connecticut, 2011 Hillside Road, Unit 1083, Storrs, CT 06269, USA

² Beijing International Center for Mathematical Research, Peking University, Beijing 100871, China

Received 14 September 2020; Accepted (in revised version) 25 September 2020

Abstract. With the path integral approach, the thermal average in multi-electronic-state quantum systems can be approximated by the ring polymer representation on an extended configuration space, where the additional degrees of freedom are associated with the surface index of each bead. The primary goal of this work is to propose a more efficient sampling algorithm for the calculation of such thermal averages. We reformulate the extended ring polymer approximation according to the configurations of the surface indexes, and by introducing a proper reference measure, the reformulation is recast as a ratio of two expectations of function expansions. By quantitatively estimating the sub-estimators, and minimizing the total variance of the sampled average, we propose a multi-level Monte Carlo path integral molecular dynamics method (MLMC-PIMD) to achieve an optimal balance of computational cost and accuracy.

AMS subject classifications: 65C05, 82C31, 82B10

Key words: Multi-level Monte Carlo method, Langevin sampling, path integral molecular dynamics, thermal average.

1. Introduction

Simulation of complex chemical system at the quantum level has always been a central and challenging task in the theoretical and computational chemistry, since a direct simulation of a quantum system is often numerically infeasible. While most numeri-

*Corresponding author. *Email addresses:* xiaoyu.lei@uconn.edu (X. Lei), zhennan@bicmr.pku.edu.cn (Z. Zhou)

cal approaches are based on the Born-Oppenheimer approximation and the adiabatic assumption is usually taken, this assumption is no longer valid when the interaction between multiple electronic energy surfaces cannot be neglected. In such scenarios, one needs to consider the multi-electronic-state systems. Readers can refer to [12, 20, 25] for more discussion.

In this paper, we focus on the thermal average taking the following form

$$\langle \hat{A} \rangle = \frac{\text{Tr}_{ne} \left[e^{-\beta \hat{H}} \hat{A} \right]}{\text{Tr}_{ne} \left[e^{-\beta \hat{H}} \right]}, \quad (1.1)$$

where \hat{H} is a matrix-form Hamiltonian operator, \hat{A} is a matrix-form observable and β is the inverse temperature given by $\frac{1}{k_B T}$ with k_B the Boltzmann constant and T the temperature. And

$$\text{Tr}_{ne} = \text{Tr}_n \text{Tr}_e = \text{Tr}_{L^2(\mathbb{R}^d)} \text{Tr}_{C^2}$$

denotes the trace with respect to the nuclear and electronic degrees of freedom. The prevailing numerical methods for thermal average calculation are based on the ring polymer representation, mapping the quantum particle to a ring polymer consists of its replica on the phase space [1, 14, 16, 17, 21, 26]. The ring polymer representation was originally proposed in [8] and it then became the foundation for many numerical methods, which are mainly categorized into two groups: the path integral Monte Carlo methods (see, e.g., [1, 3]) and the path integral molecular dynamics approaches (see, e.g., [2, 21]). Besides, in recent years, in spite of vast applications in science, different mathematical aspects of the quantum thermal averages have been explored, such as the continuum limit, the preconditioning techniques [18] and the Bayesian inversion problem [4].

The conventional ring polymer representation does not directly apply to the non-adiabatic cases since multiple energy surfaces are involved. One strategy to overcome this difficulty is to use the mapping variable approach [22, 24, 25], and its basic idea is to replace the multi-electronic-state system by an augmented scalar system where the extra dimensions correspond to the electronic degrees of freedom [24]. Another alternative strategy is to derive the extended ring polymer representation as in [14, 16], following the spirit of the pioneering work of Schmidt and Tully [23], and the discreteness of the electronic states are preserved. In the extended ring polymer representation, each bead in the ring polymer is associated with a surface index showing which energy surface it lies in. And the sampling is then carried out in the extended space consisting of the position, momentum and surface index of each bead [16]. Thus the thermal average is approximately transformed to the average over the extended configuration space of ring polymers. Another main contribution of [16] is that a path integral molecular dynamics with surface hopping (abbreviated by PIMD-SH) dynamics sampling method is developed for sampling of the equilibrium distribution on the extended ring polymer space. The PIMD-SH dynamics ergodically samples the equilibrium distribution and it is shown to satisfy the detailed balance condition. When