



# Accelerating *ab initio* path integral molecular dynamics with multilevel sampling of potential surface



Hua Y. Geng<sup>a,b,\*</sup>

<sup>a</sup> National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, CAEP, P.O. Box 919-102, Mianyang, Sichuan, 621900, PR China

<sup>b</sup> Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, NY 14853, USA

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## ABSTRACT

A multilevel approach to sample the potential energy surface in a path integral formalism is proposed. The purpose is to reduce the required number of *ab initio* evaluations of energy and forces in *ab initio* path integral molecular dynamics (AI-PIMD) simulation, without compromising the overall accuracy. To validate the method, the internal energy and free energy of an Einstein crystal are calculated and compared with the analytical solutions. As a preliminary application, we assess the performance of the method in a realistic model—the FCC phase of dense atomic hydrogen, in which the calculated result shows that the acceleration rate is about 3 to 4-fold for a two-level implementation, and can be increased up to 10 times if extrapolation is used. With only 16 beads used for the *ab initio* potential sampling, this method gives a well converged internal energy. The residual error in pressure is just about 3 GPa, whereas it is about 20 GPa for a plain AI-PIMD calculation with the same number of beads. The vibrational free energy of the FCC phase of dense hydrogen at 300 K is also calculated with an AI-PIMD thermodynamic integration method, which gives a result of about 0.51 eV/proton at a density of  $r_s = 0.912$ .

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## 1. Introduction

The imaginary-time path integral provides an elegant and powerful formalism for studying the thermodynamic properties of many-body quantum systems [1,2]. By mapping a quantum particle onto an isomorphic classical polymer in which replicas (or *beads*) are connected via harmonic springs [3] one avoids the cumbersome requirement of solving the Schrödinger equation for the wave functions. Many simulation techniques developed for classical system can then be applied to quantum systems directly [4–6].

Briefly, in quantum statistical mechanics, if we let  $H = \hat{T} + \hat{V}$  denote the Hamiltonian of the system,  $\beta = (k_B T)^{-1}$  be the inverse of the temperature, then the canonical quantum partition function  $Z(\beta) = \text{Tr} \exp(-\beta H)$ . Using Trotter's theorem [7] for the canonical density operator

$$e^{-\beta H} = \lim_{P \rightarrow \infty} \left( e^{-(\frac{\beta}{2P})\hat{V}} e^{-\frac{\beta}{P}\hat{T}} e^{-(\frac{\beta}{2P})\hat{V}} \right)^P, \quad (1)$$

the partition function can be rewritten as a path integral

\* Correspondence to: National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, CAEP, P.O. Box 919-102, Mianyang, Sichuan, 621900, PR China.

E-mail address: huay.geng@gmail.com.

$$Z(\beta) = \text{Tr}(e^{-\frac{\beta}{P}H})^P = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_P \rho(\mathbf{r}_1, \dots, \mathbf{r}_P; \beta), \quad (2)$$

where the density matrix  $\rho(\mathbf{r}_1, \dots, \mathbf{r}_P; \beta) = \prod_{j=1}^P \rho(\mathbf{r}_j, \mathbf{r}_{j+1}; \beta/P)$ , and

$$\rho(\mathbf{r}_1, \dots, \mathbf{r}_P; \beta) \propto \exp\left(-\sum_{j=1}^P \frac{mP}{2\beta\hbar^2} (\mathbf{r}_{j+1} - \mathbf{r}_j)^2 - \frac{\beta}{P} \sum_{j=1}^P V(\mathbf{r}_j)\right), \quad (3)$$

in which  $\mathbf{r}_j$  is the system coordinate at the  $j$ th time slice (or bead) with the cyclic condition  $\mathbf{r}_0 = \mathbf{r}_P$ . When  $P$  takes a finite value, the primitive approximation is obtained. The density matrix in this form of path integral can be sampled using Monte Carlo (PIMC) [2,4] or molecular dynamics (PIMD) [5,6] methods, in which any observables of a quantum system in an  $NVT$  ensemble can be obtained via an ensemble average

$$\langle A \rangle = \langle A \rangle_{NVT} = \frac{1}{Z(\beta)} \text{Tr}[A \exp(-\beta H)]. \quad (4)$$

In most applications of the path integral method in chemistry and condensed matter physics, the potential energy  $V(\mathbf{r})$  is given in terms of inter-atomic interaction potentials. The potential function may be explicit or implicit. For the former the potential must be defined in advance, whereas it can be generated on-the-fly in the latter case, usually by *ab initio* methods such as density functional theory (DFT), and the method dubbed *ab initio* path integral method (AI-PI) [8–11].

Both implementations have their respective merits and demerits. Algorithms employing explicit potentials are usually much faster in computation. But an accurate potential is difficult to obtain, and might be subject to transferability problem [12], especially under high pressure conditions. On the other hand, though an *ab initio* potential can be high in accuracy and, in principle, without any transferability issue, the computational demand is huge. Therefore it will be beneficial if one can combine the merits of the two approaches. Namely, exploit explicitly predefined inter-atomic potential to reduce the total computational cost in the AI-PI method, but without sacrificing the overall accuracy.

From the construction of the path integral formalism as shown above, it is evident that the computational cost mainly comes from two sources: (i) evaluating the energy and forces of a single bead, and (ii) repeating the same process for all beads. Therefore, the computational cost will be diminished if one can reduce the required total number of beads. At low temperatures or for light elements, however, employing fewer beads usually implies a bad short-time propagator for the density matrix [2]. There have been developed some techniques to improve the short-time propagators so that a small number of beads can be used, such as the pairwise action approximation [2,13] and high-order composite factorizations in Eq. (1) [14–19]. Unfortunately, these require either a predefined interaction potential [2,13] and/or second or higher order potential derivatives [14–18], or having negative coefficients [19], and thus cannot be implemented in AI-PIMD directly [18]. A completely different approach, the ring polymer contraction (RPC) scheme proposed by Markland and Manolopoulos, shows great promise in this respect [20,21]. The challenge along this line is how to split and arrange the forces into short-range and long-range contributions in *ab initio* simulations [22]. We shall describe in this paper how to remove this difficulty by introducing an arbitrary splitting of a potential into additive parts, using simple model reference potential as a demonstration. Formally, our concept is equivalent to improving the short-time propagator by using a multilevel sampling technique with predefined approximate potentials. In the following discussions we will ignore the cost of evaluating the predefined approximate inter-atomic potential, since it is tiny by comparison with that for an *ab initio* potential. We discuss PIMD only, the extension to PIMC is straightforward.

Another method that is very similar, but not identical, to RPC is the mixed quantum-classical scheme and its improved version of mixed time slicing (MTS) procedure [23,24]. MTS is intended to optimize the quantization of different degrees of freedom (e.g., those of the light and heavy particles) using different number of beads [24], whereas RPC is purposed to accelerate the calculation by sampling the components of the potential that have different spatial variation with different number of beads, in which the procedure usually is carried out to all degrees of freedom in a parallel fashion [20]. The spirit and implementation of these two methods are not the same, but closely related. Though we will not discuss MTS in detail in this paper, an efficient combination of the two, which as an interesting extension of the proposed multilevel sampling scheme and a unification of RPC and MTS, will be given at the end of the paper.

The paper is organized as follows: the theoretical basis and algorithm are presented in the next section, in which both the multilevel technique for potential energy surface sampling and its implementation in PIMD, as well as the thermodynamic integration using PIMD (TI-PIMD) to calculate the free energy are discussed. In Section 3 we discuss the application to an Einstein crystal, for which the analytical solution is known and thus serves as a validation of the approach. A preliminary application to a realistic system is given in Section 3.2, where we apply the method to the FCC phase of dense monatomic hydrogen under high pressure. Section 4 concludes the paper with a discussion and a summary.

## 2. Theory and algorithm

### 2.1. Path integral molecular dynamics

The partition function for a canonical ensemble of distinguishable particles in quantum statistical mechanics, if expressed in the path integral formalism, is [1,2]

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