Transition Path Sampling for Semiclassical IVRs

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Introduction

Calculations based on the semiclassical initial value representation (SC-IVR) require a Monte Carlo integration over many trajectories. Any algorithm that reduces the number of trajectories required can be useful.

This project aims to provide such an algorithm by combining recent work on time-dependent sampling functions for SC-IVRs with a Monte Carlo move inspired by transition path sampling.

Double Herman-Kluk IVR

Correlation functions in the double Herman-Kluk (DHK) IVR are given by:

$$C_{AB}(t) = \int \mathrm{d}\Omega_0 \int \mathrm{d}\Omega_{0'} \left\langle \Omega_0 \middle| \hat{A} \middle| \Omega_{0'} \right\rangle \left\langle \Omega_{t'} \middle| \hat{B} \middle| \Omega_t \right\rangle \mathcal{C}_t \, \mathcal{C}_{t'}^* \, e^{i\Delta S}$$

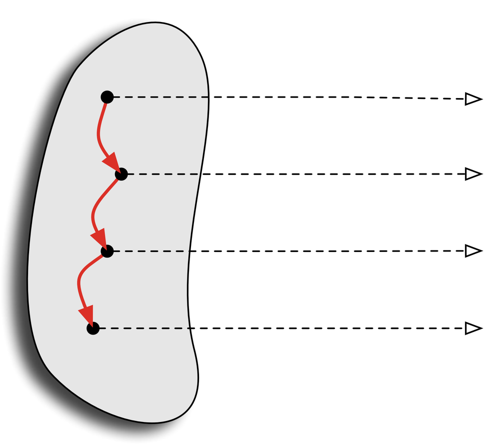
where Ω_τ is a point in phase space at time τ, $|\Omega\rangle$ is a coherent state, and $\mathcal{C}_t$ is the Herman-Kluk prefactor.

Although we're testing the DHK-IVR, the methods described are not in any way restricted to it.

Initial Value Monte Carlo

Typically, the DHK-IVR integrand is sampled as:

$$C_{AB}(t) \propto \left\langle \frac{\left\langle \Omega_0 \middle| \hat{A} \middle| \Omega_{0'} \right\rangle}{\rho(\Omega_0, \Omega_{0'})} \left\langle \Omega_{t'} \middle| \hat{B} \middle| \Omega_t \right\rangle \mathcal{C}_t \, \mathcal{C}_{t'}^* \, e^{i\Delta S} \right\rangle_{\rho(\Omega_0, \Omega_{0'})}$$



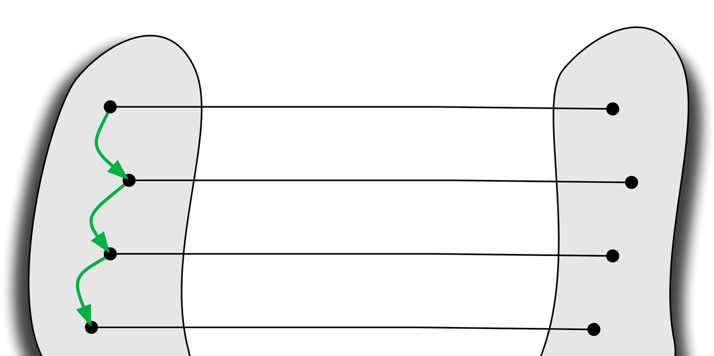
We'll refer to this method as initial-value Monte Carlo (IVMC). The cartoon to the left illustrates: we sample in the initial phase space (red arrows). After sampling, we launch trajectories (dashed arrows).

Endpoint Time-Dependent MC

Recently, we have explored the idea of including some of the time-dependent function in our sampling. For example, we have sampled the DHK-IVR integrand as:

$$C_{AB}(t) \propto \left\langle \mathcal{C}_t \, \mathcal{C}_{t'}^* \, e^{i\Delta S} \, e^{i\phi} \right\rangle_{\rho = \left| \left\langle \Omega_0 \middle| \hat{A} \middle| \Omega_{0'} \right\rangle \left\langle \Omega_{t'} \middle| \hat{B} \middle| \Omega_t \right\rangle \right|}$$

where $\phi = \arg\left(\left\langle \Omega_0 \middle| \hat{A} \middle| \Omega_{0'} \right\rangle \left\langle \Omega_{t'} \middle| \hat{B} \middle| \Omega_t \right\rangle \right)$



Originally, the Monte Carlo moves used for this sampling were in phase space at time $t = 0$. We'll refer to this method as endpoint time-dependent Monte Carlo (EP-TDMC).

We still move in the initial value space, but now we include information from the time-evolved distribution.

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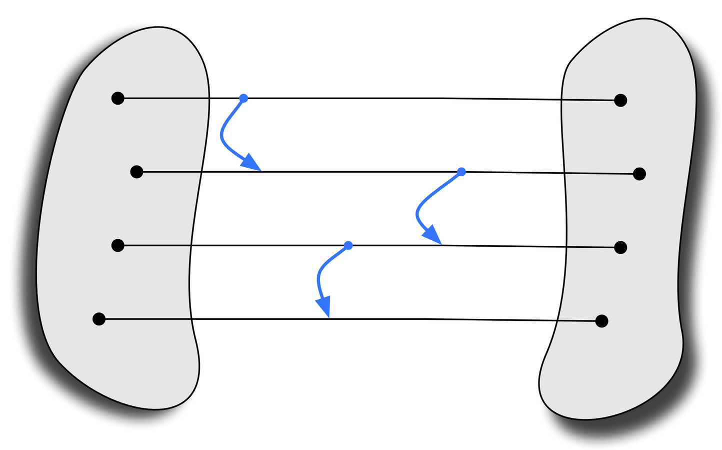
Path Sampling Time-Dependent MC

The goal of the current work is to relax that restriction at time $t = 0$. Sampling the initial conditions of fixed-length (deterministic) trajectories is equivalent to sampling from trajectory space. So we'll use path sampling algorithms (Monte Carlo moves at arbitrary times along the path) to sample the trajectory space.

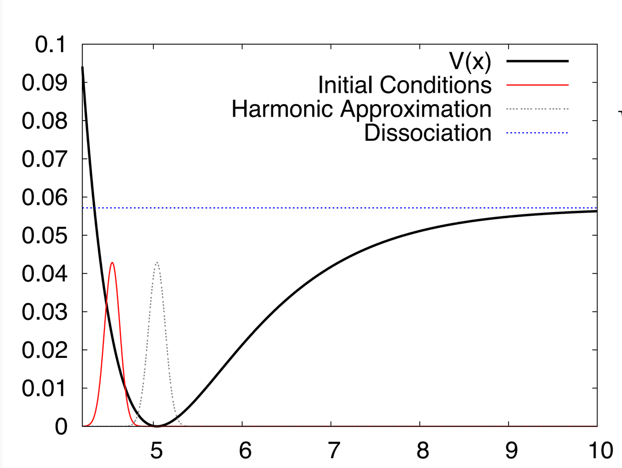


This method uses the same sampling function as EP-TDMC, but allows different moves. We will refer to this as path sampling time-dependent Monte Carlo (PS-TDMC).

Big Picture: IVMC vs TDMC

IVMC	PRO: Sample once for all times CON: Wastes a lot of trajectories
TDMC	PRO: Only samples relevant trajectories CON: Sampling function can split into multiple domains

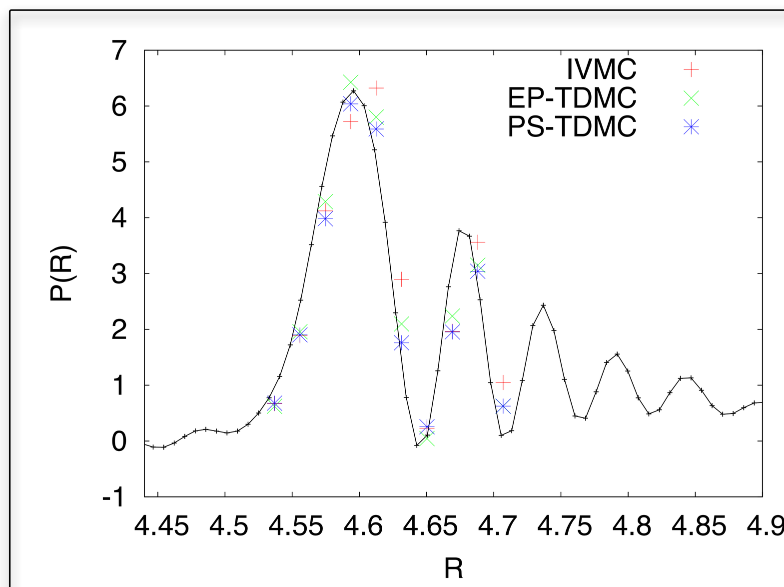
Test System 1: Iodine Morse



$$V(x) = 0.057 \left(1 + \left(1 - e^{-0.98(x-5.04)} \right)^2 \right)$$

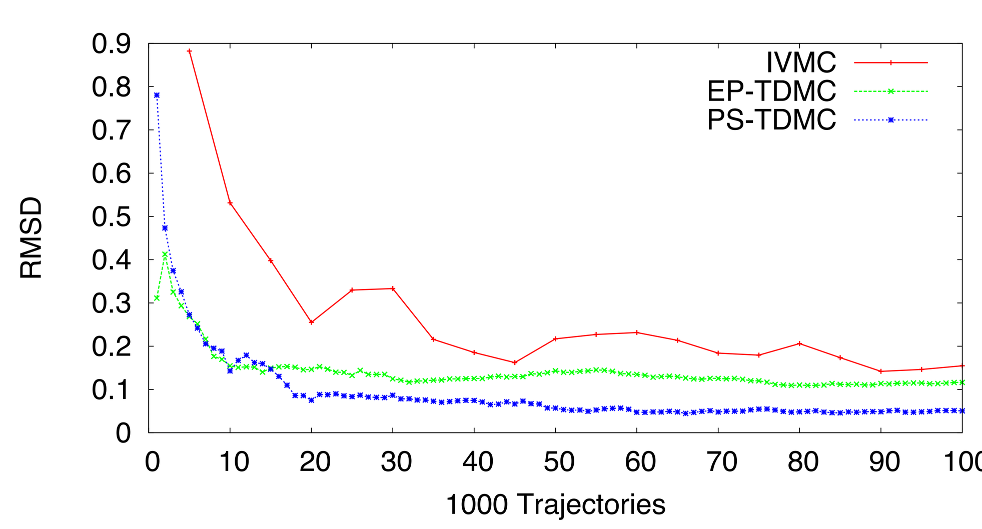
$$\langle x | \psi \rangle = \left(\frac{135}{\pi} \right)^{1/4} e^{-68(x-4.54)^2 + ip(x-4.54)}$$

We'll calculate the position distribution function, $P(R) = C_{AB}(t)$ with $\hat{A} = |\psi\rangle\langle\psi|$ and $\hat{B} = \delta(\hat{x} - R)$.

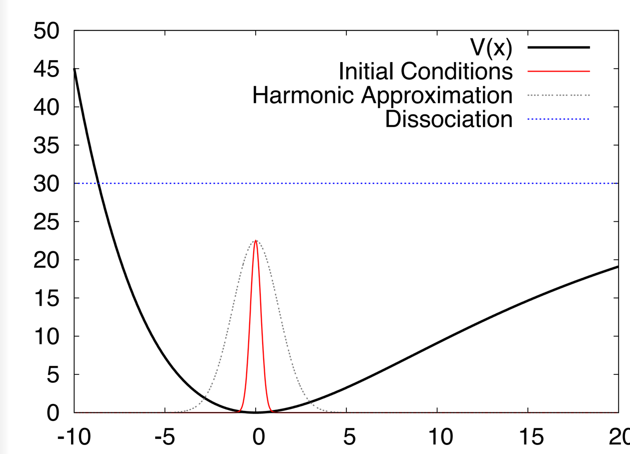


Left: The position distribution function at $t = 192$ fs.

Below: RMSD for the point at 4.59 au (the peak of the distribution).



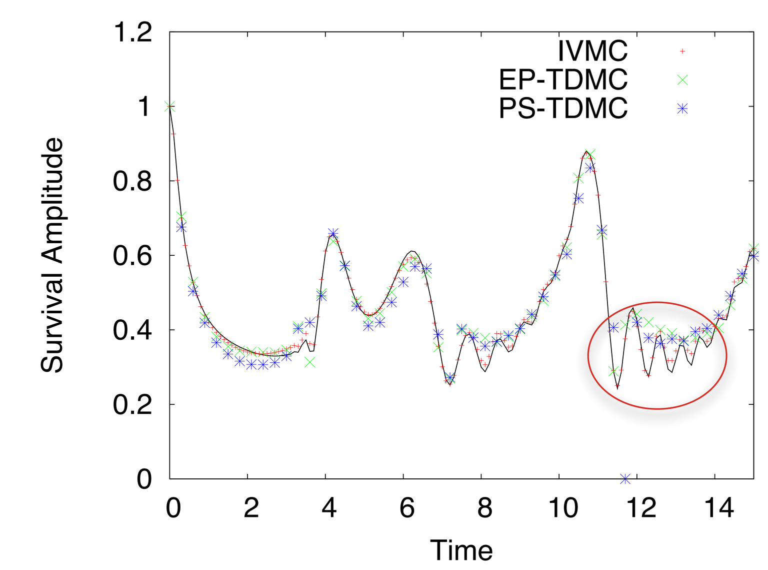
Test System 2: Anharmonic Morse



$$V(x) = 30.0 \left(1 + \left(1 - e^{-0.08x} \right)^2 \right)$$

$$\langle x | \psi \rangle = \left(\frac{12}{\pi} \right)^{1/4} e^{-6x^2 + ipx}$$

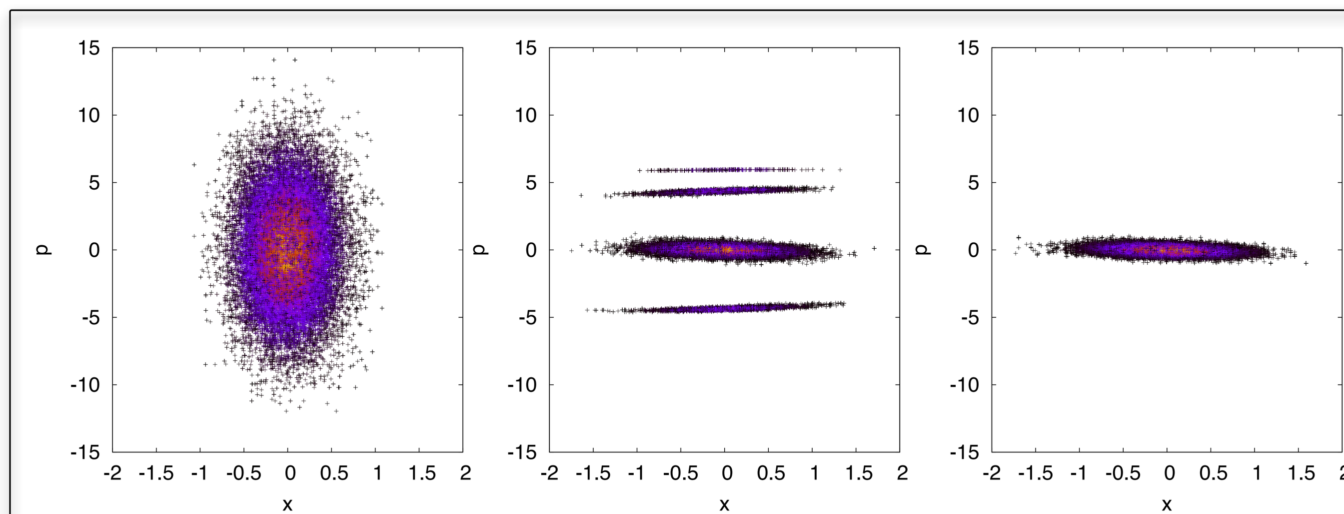
We'll calculate the survival amplitude, $\mathcal{A}(t) = \sqrt{C_{AB}(t)}$ with $\hat{A} = \hat{B} = |\psi\rangle\langle\psi|$.



TDMC methods fail to reproduce the survival amplitude when the action term causes quantum interferences.

We'll focus on what happens at time $t = 12.3$.

Challenges in Sampling Phase Space



IVMC Sampling Function | TDMC Sampling Function | What TDMC Samples

Selecting a Monte Carlo step such that the acceptance ratio is around 50% results in a step too small to jump between domains in the TDMC sampling function.

Dual-Delta Sampling

Store two Monte Carlo step sizes: one associated with the IVMC envelope, and one associated with the TDMC sampling. At each step, randomly choose which to use.