Note on the derivation of DMC transition probablility on the one-dimensional uniform grid

Alexander A. Kunitsa

April 17, 2019

0.1 Introduction

Consider a free particle moving in one dimension as described by Hamiltonian $\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2}$. Its (time-independent) wave functions are plane-waves $\psi_k(x) = \frac{1}{\sqrt{2\pi}}e^{ikx}$ with the energies $E_k = k^2/2$ (in atomic units). In coordinate representation, the imaginary time propagator $\hat{P} = e^{-\tau\hat{H}}$ is an integral operator with a Gaussian kernel $G(x, x', \tau)$:

$$\begin{aligned} \psi_\tau(x) &= \int dx' G(x, x', \tau)\psi_0(x') && (1) \\ &= \frac{1}{\sqrt{2\pi\tau}} \int dx' e^{-\frac{(x-x')^2}{2\tau}} \psi_0(x') && (2) \end{aligned}$$

The particular form of the kernel in Eq. 1 is obtained by analytically performing the integral:

$$G(x, x', \tau) = \int dk e^{-E_k\tau}\psi_k(x)\psi_k^*(x') \quad (3)$$

The same approach can in principle be applied to any Hamiltonian as long as its eigenvectors and eigenvalues are known explicitly (see Eq. 3).

0.2 Imaginary time propagator on integer lattice

The derivation strategy outlined in the introduction can be used in conjunction with the dicretized Hamiltonian $\hat{H}_\delta$ as shown in this section. $\hat{H}_\delta$ is obtained from $\hat{H}$ by replacing the kinetic energy operator with its finite-difference approximation on a grid with spacing δ:

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi(x) = -\frac{\psi(x+\delta) + \psi(x-\delta) - 2\psi(x)}{2\delta^2} + O(\delta^2) \quad (4)$$

In the following, quadratic error term will be left out and Eq. 4 will be treated as definition of $\hat{H}_\delta$. Discretized plane waves $\psi_k(x)$ (x is a point on a grid) are the eigenfunctions of $\hat{H}_\delta$:

$$\begin{aligned} \hat{H}_\delta\psi_k(x) &= -\frac{1}{\sqrt{2\pi}}\frac{e^{ik(x+\delta)} + e^{ik(x-\delta)} - 2e^{ikx}}{2\delta^2} && (5) \\ &= -\frac{e^{ik\delta} + e^{-ik\delta} - 2}{2\delta^2}\psi_k(x) && (6) \\ &= \frac{2}{\delta^2}\sin^2\left(\frac{k\delta}{2}\right)\psi_k(x) && (7) \end{aligned}$$

The same property holds for any *symmetric* finite difference approximation (but the eigenvalues will be different in each case). In the limit $\delta \to 0$, $\frac{2}{\delta^2}\sin^2\left(\frac{k\delta}{2}\right) \approx \frac{2}{\delta^2}\frac{k^2\delta^2}{4} = \frac{k^2}{2}$. However, discretized plane waves cannot be normalized on an infinite grid (their norms are $\frac{1}{2\pi}\sum_{x\in grid} e^{-ikx}e^{ikx} = +\infty$) so they should not be used to calculate the kernel of the imaginary time propagator $e^{-\tau\hat{H}_\delta}$ (Eq. 3).

In order to overcome this difficulty, we introduce box normalization of free particle states (see A. Nitzan Chemical Dynamics in Condensed Phases, p.80). Specifically, we will temporarily assume that the grid has 2N + 1 nodes ($x_i = i\delta$, $i = \pm N, \pm(N-1), ..., 0$) and discretized wave functions satisfy periodic boundary conditions $\psi(x_N + \delta) = \psi(x_{-N})$. The case of infinite grid will later be recovered by setting $N \to \infty$.

If periodic boundary conditions are imposed, discretized plane waves can be normalized such that $\psi_k(x_j) = \frac{1}{\sqrt{2N+1}} e^{ikx_j}$ and $k = \frac{2\pi l}{2N+1}\frac{1}{\delta}$ ($l = \pm N, \pm(N-1), ..., 0$). The kernel of the imaginary time propagator is then (compare to Eq. 3):

$$G(x_l, x_n, \tau) = \frac{1}{2N+1} \sum_k e^{-\frac{2\tau}{\delta^2} \sin^2\left(\frac{k\delta}{2}\right)} e^{ik(x_l - x_n)} \tag{8}$$

Setting $N \to \infty$ and replacing a sum in Eq. 8 with the integral one obtains:

$$G(x_l, x_n, \tau) = \frac{\delta}{2\pi} \int_{-\pi/\delta}^{\pi/\delta} dk e^{-\frac{2\tau}{\delta^2} \sin^2\left(\frac{k\delta}{2}\right)} e^{ik(x_l - x_n)} \tag{9}$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} dk e^{-\frac{2\tau}{\delta^2} \sin^2\left(\frac{k}{2}\right)} e^{ik\frac{x_l - x_n}{\delta}} \tag{10}$$

0.3 Observations and conclusions

Eq. 9 can be generalized for an arbitrary symmetric finite difference scheme. However, for the higher order schemes $G(x_l, x_n, \tau)$ is generally not positive for all pairs (x_l, x_n) unless $\delta << \sqrt{\tau}$ (in which case the space is effectively continuous). It is to be observed that our approach is also incompatible with importance sampling transformation (as it is usually performed in the context of DMC) as it breaks the symmetry of the kinetic energy operator by introducing a drift term proportional to the first derivative of the wave function.