PIMD Notes

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I have created the following notes to better understand path integral molecular dynamics (PIMD) as applied to a harmonic oscillator and beyond. All the material in this paper can be found in mutliple resources. The ones that I used are listed in the references. Notes are still in development.

1 Introduction

1.1 Quantum Harmonic Oscillator

Similar to the classical harmonic oscillator, we have a particle that is subject to a harmonic potential so that the 1D Hamiltonian looks like

$$\hat{H} = \hat{K} + \hat{U} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{1}$$

where m is the particle's mass and ω is the angular frequency of the oscillator. We know that we can derive the properties of the harmonic oscillator from the canonical ensemble. To do this, we start with the canonical partition function,

$$Q = \sum_n e^{-\beta E_n} \tag{2}$$

where the sum is performed over all possible states of the system, which are discrete. [1] We can derive the formula for the energies from introductory quantum mechanics.

The energies can be obtained from solving Schrödinger's equation with the Hamiltonian in equation (1). Alternatively, the energies can be obtained using Dirac's ladder operators, $\hat{a}$ and $\hat{a}^\dagger$. [2, 3] The "raising operator" $\hat{a}$ and "lowering operator" $\hat{a}^\dagger$ can be defined in terms of the position and momentum operators as

$$\begin{aligned} \hat{a} &= \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right) \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right) \end{aligned} \tag{3}$$

where the prefactors are such that they allow the math to work out nicely when deriving the energies for a harmonic oscillator. The ladder operators can then be used to obtain a function of the Hamiltonian by remembering the commutation relation $[\hat{x}, \hat{p}] = i\hbar$. The hats will be ommited from the operators to simplify notation.

$$\begin{aligned} aa^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\Big(x + \frac{i}{m\omega}p\Big)\sqrt{\frac{m\omega}{2\hbar}}\Big(x - \frac{i}{m\omega}p\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x + \frac{i}{m\omega}p\Big)\Big(x - \frac{i}{m\omega}p\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x^2 - \frac{i}{m\omega}xp + \frac{i}{m\omega}px + \frac{p^2}{(m\omega)^2}\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x^2 + \frac{p^2}{(m\omega)^2}\Big) - \frac{i}{2\hbar}xp + \frac{i}{2\hbar}px \\ &= \frac{m\omega}{2\hbar}\Big(\frac{m\omega}{m\omega}\Big)\Big(x^2 + \frac{p^2}{(m\omega)^2}\Big) - \frac{i}{2\hbar}xp + \frac{i}{2\hbar}px \\ &= \frac{1}{2\hbar}\Big(\frac{p^2}{m\omega} + m\omega x^2\Big) - \frac{i}{2\hbar}[x,p] \\ &= \frac{1}{\hbar\omega}\Big(\frac{p^2}{2m} + \frac{(m\omega x)^2}{2m}\Big) - \frac{i}{2\hbar}(i\hbar) \\ &= \frac{1}{\hbar\omega}H + \frac{1}{2} \end{aligned} \tag{4}$$

So rearranging to solve for the hamiltonian gives us,

$$\hat{H} = \hbar\omega\Big(\hat{a}\hat{a}^\dagger - \frac{1}{2}\Big). \tag{5}$$

If we reverse the ladder operators we get,

$$\begin{aligned} a^\dagger a &= \sqrt{\frac{m\omega}{2\hbar}}\Big(x - \frac{i}{m\omega}p\Big)\sqrt{\frac{m\omega}{2\hbar}}\Big(x + \frac{i}{m\omega}p\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x - \frac{i}{m\omega}p\Big)\Big(x + \frac{i}{m\omega}p\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x^2 + \frac{i}{m\omega}xp - \frac{i}{m\omega}px + \frac{p^2}{(m\omega)^2}\Big) \\ &= \frac{m\omega}{2\hbar}\Big(x^2 + \frac{p^2}{(m\omega)^2}\Big) + \frac{i}{2\hbar}xp - \frac{i}{2\hbar}px \\ &= \frac{m\omega}{2\hbar}\Big(\frac{m\omega}{m\omega}\Big)\Big(x^2 + \frac{p^2}{(m\omega)^2}\Big) + \frac{i}{2\hbar}xp - \frac{i}{2\hbar}px \\ &= \frac{1}{2\hbar}\Big(\frac{p^2}{m\omega} + m\omega x^2\Big) + \frac{i}{2\hbar}[x,p] \\ &= \frac{1}{2\hbar m\omega}\Big(p^2 + (m\omega x)^2\Big) + \frac{i}{2\hbar}(i\hbar) \\ &= \frac{1}{\hbar\omega}\Big(\frac{p^2}{2m} + \frac{(m\omega x)^2}{2m}\Big) - \frac{1}{2} \\ &= \frac{1}{\hbar\omega}H - \frac{1}{2} \end{aligned} \tag{6}$$

And rearranging to solve for the Hamiltonian gives us,

$$\hat{H} = \hbar\omega\Big(\hat{a}^\dagger\hat{a} + \frac{1}{2}\Big). \tag{7}$$

We can imagine a set of vectors that make up the basis of eigenvectors $|\psi_n\rangle$ for the harmonic oscillator Hamiltonian that yield energies E_n. If we apply equation (5) to a vector that is one state higher $\hat{a}\,|\psi_n\rangle$, we obtain,

$$H\hat{a}\,|\psi\rangle = (E_n + \hbar\omega)\hat{a}\,|\psi\rangle\,. \tag{8}$$

eigenvalues equal to the energy in the previous state plus $\hbar\omega$. Likewise, if we apply equation (7) to a vector that is one state lower $\hat{a}^\dagger\,|\psi_n\rangle$, we obtain,

$$H\hat{a}^\dagger\,|\psi\rangle = (E_n - \hbar\omega).\hat{a}^\dagger\,|\psi\rangle \tag{9}$$

It is for this reason that the operators $\hat{a}$ and $\hat{a}^\dagger$ are called ladder operators because they allow us to go up and down in energy. [2,3] When we consider that there is a ground state $|\psi_0\rangle$ such that $\hat{a}^\dagger |\psi_0\rangle = 0$, we can plug in the defintion for $\hat{a}^\dagger$ and solve for $|\psi_0\rangle$, giving,

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} \tag{10}$$

Plugging this into the Schrödinger equation gives the energy,

$$E_0 = \frac{\hbar\omega}{2}. \tag{11}$$

Since we know that applying the raising operator $\hat{a}$ increases the energy by $\hbar\omega$, applying $\hat{a}$ n times increases the energy by $n\hbar\omega$. So the energy at the nth state can be defined as,

$$E_n = \hbar\omega(n + \frac{1}{2}). \tag{12}$$

Plugging our energies into equation (13) gives us the partition function.

$$Q = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} \tag{13}$$

We can actually evaluate the sum to get a more compact form of equation (13) by remembering that $\hbar$, ω, β, are just constants and $\sum\limits_{n=0}^{\infty} x^n = \frac{1}{1-x}$ where $0 < x < 1$.

$$\begin{aligned}
Q &= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} \\
&= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\
&= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n \\
&= \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \\
&= \left(\frac{e^{\frac{\beta\hbar\omega}{2}}}{e^{\frac{\beta\hbar\omega}{2}}}\right) \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \\
&= \frac{1}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} \\
&= \frac{1}{2\sinh(\frac{\beta\hbar\omega}{2})}
\end{aligned} \tag{14}$$

The purpose of knowing the canonical partition function is so that we can derive the thermodynamic properties of our system in the canonical ensemble. One property we can derive is the total energy. We already know the energies of the harmonic oscillator, but we can derive the energies in the canonical ensemble with the partition function using the relationship,

$$E = -\frac{\partial}{\partial\beta} \ln(Q). \tag{15}$$

So plugging in the Q we found gives us,

$$
\begin{aligned}
E &= -\frac{\partial}{\partial\beta}\ln\Big(\frac{1}{2\sinh(\frac{\beta\hbar\omega}{2})}\Big) \\
&= -\frac{\partial}{\partial\beta}\Big[\ln(1) - \ln\Big(2\sinh(\frac{\beta\hbar\omega}{2})\Big)\Big] \\
&= \frac{\partial}{\partial\beta}\ln\Big(2\sinh(\frac{\beta\hbar\omega}{2})\Big) \\
&= \frac{1}{2\sinh(\frac{\beta\hbar\omega}{2})}\frac{\partial}{\partial\beta}2\sinh(\frac{\beta\hbar\omega}{2}) \\
&= \frac{2\cosh(\frac{\beta\hbar\omega}{2})}{2\sinh(\frac{\beta\hbar\omega}{2})}\frac{\partial}{\partial\beta}\frac{\beta\hbar\omega}{2} \\
&= \frac{\cosh(\frac{\beta\hbar\omega}{2})}{\sinh(\frac{\beta\hbar\omega}{2})}\Big(\frac{\hbar\omega}{2}\Big) \\
&= \frac{\hbar\omega}{2\tanh(\frac{\hbar\omega}{2})}
\end{aligned} \tag{16}
$$

The equation for the total energy can be made exactly the same as in Tuckerman's book [1] by expressing the inverse tanh function in terms of exponentials.

$$
\begin{aligned}
E &= \frac{\hbar\omega}{2\tanh(\frac{\hbar\omega}{2})} \\
&= \Big(\frac{\hbar\omega}{2}\Big)\frac{e^{\frac{\beta\hbar\omega}{2}} + e^{-\frac{\beta\hbar\omega}{2}}}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} \\
&= \Big(\frac{\hbar\omega}{2}\Big)\Big(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{e^{-\frac{\beta\hbar\omega}{2}}}\Big)\frac{e^{\frac{\beta\hbar\omega}{2}} + e^{-\frac{\beta\hbar\omega}{2}}}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} \\
&= \Big(\frac{\hbar\omega}{2}\Big)\frac{1+e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\
&= \Big(\frac{\hbar\omega}{2}\Big)\frac{(1-e^{-\beta\hbar\omega}+2e^{-\beta\hbar\omega})}{1-e^{-\beta\hbar\omega}} \\
&= \Big(\frac{\hbar\omega}{2}\Big)\frac{1-e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} + \Big(\frac{\hbar\omega}{2}\Big)\frac{2e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\
&= \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}
\end{aligned} \tag{17}
$$

Remember that this is the exact form of the harmonic oscillator energies in the canonical ensemble and not an approximation. When we try to approximate the energies of a harmonic oscillator using PIMD, we will want to refer back to equation (17) and plug in our values for ω and β as a check to make sure that our code is working.

To understand what a PIMD code does, we have to first understand the idea of representing partition functions like equation (13) as a path integral. So now let's talk about where the path integral representation comes from.

1.2 Path Integral Derivation

We will consider the case of a single quantum particle moving in one dimension so our Hamiltonian is the same as in equation (1). The amplitude of a path that the particle can take when going from x to x' over some time t as the propagator written in position space.

$$A = \langle x'|e^{-iHt/\hbar}|x\rangle \tag{18}$$

This is useful to know because the probability of the particle choosing a particular path would simply be $|A|^2$. [1] In terms of state vectors, the initial state of our particle can be represented as $|\Psi(0)\rangle$, so the state of our particle can be represented as the inital state vector being acted upon by the propagator

$$|\Psi(t)\rangle = e^{-iHt/\hbar}\,|\Psi(0)\rangle \tag{19}$$

And we can project the coordinate basis onto our state vectors to give us a meaningful representation of our state vector

$$\begin{aligned}
\langle x'|\Psi(t)\rangle = \Psi(x',t) &= \langle x'|e^{-iHt/\hbar}|\Psi(0)\rangle \\
&= \langle x'|e^{-iHt/\hbar}\int dx|x\rangle\,\langle x|\Psi(0)\rangle \\
&= \int dx\,\langle x'|e^{-iHt/\hbar}|x\rangle\,\langle x|\Psi(0)\rangle \\
&= \int dx\,\langle x'|e^{-iHt/\hbar}|x\rangle\,\Psi(x,0)
\end{aligned} \tag{20}$$

where we introduced the resolution of identity $\int dx\,|x\rangle\,\langle x| = 1$.

So now we have a more mathematical representation of our problem; we want to know how to go from $\Psi(x,0)$ to $\Psi(x',t)$. The physical representation of our problem is that we have a particle at some point x in space, and we want to be able to detect our particle at some other point x' in space after some time t passes.

By going to imaginary time, which is done by substituting $it/\hbar = \beta$, we can express the coordinate-space quantum propagator as the canonical density matrix,

$$\rho(x,x') = \langle x'|e^{-\beta\hat{H}}|x\rangle\,. \tag{21}$$

The motive behind doing this is so that we can deal with a damped exponential as opposed to a complex exponential. [1] Therefore, we can derive the path integral form of the density matrix and simply resubstitute time in place of β to obtain the path integral form of the time propagator.

We would like to separate the hamiltonian into its kinetic and potential energy components, $\hat{H} = \hat{K} + \hat{U}$. However, we cannot split the exponentials because for two operators that do not commute $\exp(\hat{H}) \neq \exp(\hat{K})\exp(\hat{U})$. To get around this we employ the trotter decompositon

$$e^{-\beta\hat{H}} = e^{-\beta(\hat{K}+\hat{U})} = \lim_{P\to\infty}\left[e^{-\beta\hat{U}/2P}e^{-\beta\hat{K}/P}e^{-\beta U/2P}\right]^P. \tag{22}$$

Substituting this into equation (21) gives us,

$$\rho(x,x') = \lim_{P\to\infty}\langle x'|\left[e^{-\beta\hat{U}/2P}e^{-\beta\hat{K}/P}e^{-\beta U/2P}\right]^P|x\rangle \tag{23}$$

which can be condensed by defining another operator Ω as

$$\Omega = e^{-\beta\hat{U}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{U}/2P}. \tag{24}$$

So our density matrix becomes,

$$\rho(x,x') = \lim_{P\to\infty}\langle x'|\Omega^P|x\rangle \tag{25}$$

We can insert the resolution of identity in terms of the position basis P-1 times between each of the omegas, remembering that $\Omega^P = \Omega\Omega\cdots\Omega$.

$$\rho(x,x') = \lim_{P\to\infty}\int\cdots\int dx_P\cdots dx_2\,\langle x'|\Omega|x_P\rangle\,\langle x_P|\Omega|x_{P-1}\rangle\,\langle x_{P-1}|\cdots|x_3\rangle\,\langle x_3|\Omega|x_2\rangle\,\langle x_2|\Omega|x\rangle \tag{26}$$

The integration over a coordinate x_i can be thought of as integrating over a possible path that your particle can take because we can obtain integrations over all possible paths when P $\to\infty$. If we consider an element of the matrix,

$$\langle x_{k+1}|\Omega|x_k\rangle = \langle x_{k+1}|e^{-\beta\hat{U}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{U}/2P}|x_k\rangle \tag{27}$$

we can recognize that the set of $|x_k\rangle$ are eigenvectors of $e^{-\beta\hat{U}/2P}$ with eigenvalue $e^{-\beta U(x_k)/2P}$ because $\hat{U} = U(\hat{x})$ is a function of the coordinate operator. [2,3] This can be shown easily by writing the exponential as a power series in $\hat{U}$.

$$e^{-\beta\hat{U}/2P} = \sum_{n=0}^{\infty}\frac{\beta^n(2P)^{-n}\hat{U}^n}{n!} \tag{28}$$

and if we operate on an eigenvector $|x_k\rangle$, we get

$$\begin{aligned} e^{-\beta \hat{U}/2P}|x_k\rangle &= \sum_{n=0}^{\infty} \frac{\beta^n (2P)^{-n}}{n!} \hat{U}^n |x_k\rangle \\ &= \sum_{n=0}^{\infty} \frac{\beta^n (2P)^{-n}}{n!} (U(x_k))^n |x_k\rangle \\ &= e^{-\beta U(x_k)/2P}|x_k\rangle \end{aligned} \tag{29}$$

So equation (27) simplifies to

$$\langle x_{k+1}|\Omega|x_k\rangle = e^{-\beta U(x_{k+1})/2P}\langle x_{k+1}|e^{-\beta \hat{K}/P}|x_k\rangle e^{-\beta U(x_k)/2P}. \tag{30}$$

We know that $\hat{K}$ is a function of the momentum operator, $\hat{K} = \hat{p}^2/2m$. [2,3] So we can use the same technique as we did with $\hat{U}$ and the position eigenvectors by introducing the resolution of identity in terms of the momentum basis,

$$\begin{aligned} \langle x_{k+1}|\Omega|x_k\rangle &= \int e^{-\beta U(x_{k+1})/2P}\langle x_{k+1}| e^{-\beta \hat{K}/P}|p\rangle\langle p|x_k\rangle e^{-\beta U(x_k)/2P} \\ &= \int e^{-\beta U(x_{k+1})/2P} e^{-\beta p^2/2mP}\langle x_{k+1}|p\rangle\langle p|x_k\rangle e^{-\beta U(x_k)/2P} dp \end{aligned} \tag{31}$$

where $\langle x_{k+1}|p\rangle$ is the momentum wavefunction expressed in the coordinate basis x_{k+1}, and $\langle p|x_k\rangle$ is the complex conjugate of the momentum wavefunction expressed in the coordinate basis x_k, i.e. $\langle p|x_k\rangle = \langle x_k|p\rangle^*$.

We can obtain a functional form of these wavefunctions by recalling the eigenvalue problem for the momentum operator,

$$\hat{p}|p\rangle = p|p\rangle \tag{32}$$

If we project this equation on the coordinate basis, we can make use of the hermitian property of the momentum operator to obtain

$$\langle x|\hat{p}|p\rangle = p\langle x|p\rangle \quad \Rightarrow \quad \langle \hat{p}x|p\rangle = p\langle x|p\rangle \quad \Rightarrow \quad -i\hbar\frac{\partial}{\partial x}\langle x|p\rangle = p\langle x|p\rangle \tag{33}$$

And if we write $\langle x|p\rangle = \psi_p(x)$, then we just have a first order differential equation. The solution to this equation can easily be found

$$-i\hbar\frac{\partial}{\partial x}\psi_p(x) = p\psi_p(x) \quad \Rightarrow \quad \int \frac{d\psi_p}{\psi_p}dx = \int \frac{ip}{\hbar}dx \quad \Rightarrow \quad \ln\psi_p(x) = \frac{ipx}{\hbar} + C_1 \quad \Rightarrow \quad \psi_p(x) = C_2 e^{ipx/\hbar} \tag{34}$$

where C_2 is a normalization constant. With proper normalization, the momentum wavefunction looks like

$$\langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}. \tag{35}$$

And it's complex conjugate looks like,

$$\langle x|p\rangle^* = \langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-ipx/\hbar} \tag{36}$$

We can use this to rewrite our matrix elements of Ω as

$$\begin{aligned} \langle x_{k+1}|\Omega|x_k\rangle &= \int e^{-\beta U(x_{k+1})/2P} e^{-\beta p^2/2mP}\langle x_{k+1}|p\rangle\langle p|x_k\rangle e^{-\beta U(x_k)/2P} dp \\ &= \frac{1}{2\pi\hbar}\int e^{-\beta p^2/2mP} e^{-\beta(U(x_{k+1})+U(x_k))/2P} e^{ip(x_{k+1}-x_k)/\hbar} dp \end{aligned} \tag{37}$$

We can move the exponential without the momenta outside of the integral and combine the exponentials with the momenta to obtain

$$\langle x_{k+1}|\Omega|x_k\rangle = \frac{1}{2\pi\hbar}e^{-\beta(U(x_{k+1})+U(x_k))/2P}\int e^{-\beta p^2/2mP + ip(x_{k+1}-x_k)/\hbar} dp \tag{38}$$

Since our momentum basis extends from $+\infty$ to $-\infty$, we end up having an integral of a gaussian if we complete the square,

$$
\begin{aligned}
\frac{-\beta p^2}{2mP} + \frac{(x_{k+1}-x_k)ip}{\hbar} &= \frac{-\beta}{2mP}\Big[p^2 - \frac{2imP(x_{k+1}-x_k)}{\beta\hbar}\Big] \\
&= \frac{-\beta}{2mP}\Big[\Big(p - \frac{imP(x_{k+1}-x_k)}{\beta\hbar}\Big)^2 - \Big(\frac{imP(x_{k+1}-x_k)}{\beta\hbar}\Big)^2\Big] \\
&= \frac{-\beta}{2mP}\Big[\Big(p - \frac{imP(x_{k+1}-x_k)}{\beta\hbar}\Big)^2 + \frac{m^2P^2(x_{k+1}-x_k)^2}{\beta^2\hbar^2}\Big] \\
&= \frac{-\beta}{2mP}\Big(p - \frac{imP(x_{k+1}-x_k)}{\beta\hbar}\Big)^2 - \frac{mP(x_{k+1}-x_k)^2}{2\beta\hbar^2}
\end{aligned}
\tag{39}
$$

and make a variable substitution,

$$
u = p - \frac{imP(x_{k+1}-x_k)}{\beta\hbar}. \tag{40}
$$

Our integral is now,

$$
\langle x_{k+1}|\Omega|x_k\rangle = \frac{1}{2\pi\hbar}\exp\Big[\frac{-\beta(U(x_{k+1})+U(x_k))}{2P}\Big]\exp\Big[\frac{-mP(x_{k+1}-x_k)^2}{2\beta\hbar^2}\Big]\int e^{\frac{-\beta u^2}{2mP}}\,du \tag{41}
$$

which evaluates to,

$$
\begin{aligned}
\langle x_{k+1}|\Omega|x_k\rangle &= \frac{1}{2\pi\hbar}\exp\Big[-\frac{\beta}{2P}(U(x_{k+1})+U(x_k))\Big]\exp\Big[-\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2\Big]\Big(\frac{2\pi mP}{\beta}\Big)^{1/2} \\
&= \Big(\frac{mP}{2\pi\beta\hbar^2}\Big)^{1/2}\exp\Big[\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2 - \frac{\beta}{2P}(U(x_{k+1})+U(x_k))\Big]
\end{aligned}
\tag{42}
$$

Plugging in our matrix elements into equation (26) P times for each element gives us the discretized path integral representation of our density matrix.

$$
\rho(x,x') = \lim_{P\to\infty}\Big(\frac{mP}{2\pi\beta\hbar^2}\Big)^{P/2}\int\cdots\int dx_P\cdots dx_2 \quad \exp\Big(\sum_{k=1}^{P}\Big[\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2 - \frac{\beta}{2P}(U(x_{k+1})+U(x_k))\Big]\Big) \tag{43}
$$

where $x_1 = x$ and $x_P = x'$.

References

[1] M.E. Tuckerman. *Statistical Mechanics: Theory and Molecular Simulation.* Oxford graduate texts. Oxford University Press, 2011.

[2] D.J. Griffiths and P.D.J. Griffiths. *Introduction to Quantum Mechanics.* Pearson international edition. Pearson Prentice Hall, 2005.

[3] R. Shankar. *Principles of Quantum Mechanics.* Springer US, 1995.