Non-Markovian trajectories involving future in semi-classical path integral expression

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Abstract

Semi-classical path integral expression for a quantum system coupled to a harmonic bath is derived based on the stationary phase condition. It is discovered that the system path is non-Markovian. Most strikingly, the system path not only couples to its past, but also to its future, i.e. the equation of motion for the system is an integro-differential equation that involves all times. Numerical examples are given at the end. Because of the future-non-Markovian nature of the equation, the numerical solution cannot be obtained by iterative methods. Instead, root search algorithms must be employed.

Keywords: non-Markovian, semi-classical, path integral, quantum dynamics

1. Introduction

The dynamics of a quantum system interacting with its environment plays a central role in many areas of research, from addressing fundamental questions such as quantum decoherence and quantum measurement [1–6] to many practical applications in vibrational energy relaxation in molecules [7–11], electron transport in condensed phase [12–15], excitonic energy transport in photosynthesis [16–20], spin–lattice relaxation [21, 22] and entanglement in quantum computing [23–25]. Due to a large number of degrees of freedom involved, a common strategy is to divide the entire system into a quantum system (a few degrees of freedom) and a bath [26]. For example, for electron transfer in proteins, the electron is considered to be the quantum system, and the proteins and the solvent are the bath.

Due to the decoherence effect of the bath [27], the wavefunction is not a good representation of the system state. Instead, the quantum system is described by the density matrix [28, 29], i.e. the probability instead of the probability amplitude, because the phase will eventually be washed out by the bath in the process so-called dephasing or decoherence. The path integral method has proven to be a very useful scheme in describing the time evolution of the density matrix [27, 30]. Feynman’s influence functional [26, 31, 32] of a quantum system coupled
to a harmonic bath offers enormous insight into subsequent research investigations [27, 30, 33–38]. The reasons that the harmonic bath has received the most attention are its analytically tractable expressions [36, 39] and the Gaussian-fluctuation nature of the bath through collective modes [40]. One feature that the influence functional presents is the time non-local correlation function that renders non-Markovian dynamics. [36, 39, 41–49].

With the development of high-speed computers, increasingly realistic condensed-phase quantum systems have been simulated using Feynman’s path integral scheme [50–56]. From a computer simulation point of view, to make Feynman’s influence functional feasible, one key issue needs to be addressed: the infinite number of quantum paths in the summation. For a two-level system coupled to a harmonic bath, discrete variable representation [57] and the tensor propagator [58–60] have been proposed based on the small number of system states involved and finite time span of the correlation function. However, for a quantum system involving continuous variables (i.e. expectation value of a wave packet), semi-classical approaches are usually employed [61–63], in which the infinite number of quantum paths are reduced to the classical trajectories. Besides its conceptually intuitive interpretation and the computational advantage of overcoming exponential scaling, the semi-classical method captures important quantum phenomena such as interference, zero-point energy and tunneling; therefore it has become increasingly favored as a simulation tool for realistic physical systems [61, 64–68].

In this paper, I derive a semi-classical path integral expression for a quantum system coupled to a harmonic bath. The term ‘semi-classical’ specifically refers to the semi-classical trajectories in the quantum system coordinates. The content is arranged as follows: in section 2, I briefly introduce the path integral formulation. In section 3, I concisely present the method for achieving semi-classical mechanics. In section 4, I derive the semi-classical path integral formulation of a system coupled to a harmonic bath, and specify its prominent features. In section 5, I present the numerical calculations. In section 6, I provide detailed discussions. In section 7, I make concluding remarks.

2. Path integral

Consider the Hamiltonian

$$H(s, p) = \frac{p^2}{2m} + V(s)$$  \hspace{1cm} (2.1)

where \(s\) represents position and \(p\) represents momentum. Here the Hamiltonian is one-dimensional for simplicity. The generalization to many degrees of freedom is straightforward.

Breaking up the time propagator into \(N\) short time segments,

$$e^{-iHt/\hbar} = e^{-iH\Delta t/\hbar} e^{-iH\Delta t/\hbar} \cdots e^{-iH\Delta t/\hbar}$$ \hspace{1cm} (2.2)

and inserting the complete set of position states,

$$\int ds_k |s_k\rangle\langle s_k| = 1$$ \hspace{1cm} (2.3)

the time propagator in this position representation becomes

$$\langle s_f | e^{-iHt/\hbar} |s_0\rangle = \int ds_1 \ldots \int ds_{N-1} \prod_{k=1}^{N} \langle s_k | e^{-iH\Delta t_k/\hbar} |s_{k-1}\rangle$$ \hspace{1cm} (2.4)
where $s_0$ represents the initial position at time 0, and $s_f$ the position at time $t$.

Now employing the Trotter splitting \([69]\), i.e. the symmetric splitting of the potential energy term,

\[ e^{-iH\Delta t/\hbar} \approx e^{-iV\Delta t/2\hbar} e^{-iT\Delta t/\hbar} e^{-iV\Delta t/2\hbar} \]  \(2.5\)

the time propagator becomes

\[ \langle s_k | e^{-iH\Delta t/\hbar} | s_{k-1} \rangle \approx \langle s_k | e^{-iT\Delta t/\hbar} | s_{k-1} \rangle e^{-i(\Delta t/2\hbar)}[V(s_k) + V(s_{k-1})]. \]  \(2.6\)

The kinetic energy part can be evaluated analytically:

\[ \langle s_k | e^{-iT\Delta t/\hbar} | s_{k-1} \rangle = \left( \frac{m}{2\pi i\hbar} \right)^{N/2} \int ds_1 \ldots \int ds_{N-1} \exp \left\{ \frac{i}{\hbar} \left( \sum_{k=1}^{N} \frac{m}{2T} (s_k - s_{k-1})^2 - \sum_{k=1}^{N} V(s_k) \right) \right\}. \]  \(2.7\)

Therefore,

\[ \langle s_f | e^{iHt/\hbar} | s_0 \rangle = \int \mathcal{D}s \left( \exp \left( \frac{i}{\hbar} \int_0^t L(s, \dot{s}) \, dt' \right) \right) = \int \mathcal{D}s \left( \exp \left( \frac{i}{\hbar} \varphi[s] \right) \right) \]  \(2.9\)

where $\dot{s}$ represents the velocity, $L(s, \dot{s})$ is the Lagrangian and $\varphi[s]$ is the action integral. $\int \mathcal{D}s$ indicates summing (i.e. integrating over) all possible paths, hence the name path integral.

This leads to the celebrated form in which the classical action enters in the phase of the exponential. Different paths will give different values of action and thus different phase factors, and when they are summed, they allow interference that is characteristic of quantum mechanics. The stationary phase condition, $\delta \varphi[s] = 0$, gives the Euler–Lagrange equation

\[ \frac{\partial L}{\partial s} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{s}} \right) \],

which is the classical equation of motion. The beauty of Feynman’s path integral formulation is that it provides a natural connection between quantum and classical mechanics. It is interesting and important to point out that the classical trajectory in the action integral for the harmonic oscillator gives the exact quantum result, with no approximations.

3. Semi-classical propagator

Semi-classical mechanics \([70]\) offers a unique advantage in treating quantum systems in that the infinite sum of trajectories in the path integral is reduced to a single classical trajectory. Even better than that, it preserves some degree of quantum effect. In other words, it puts quantum flesh on classical bones.

The essence of semi-classical theory is the stationary phase condition, i.e. expanding the action around classical trajectories in power series, and then truncating up to the second order. Consider the path
\[ s(t) = s_0(t) + \delta s(t) \]  
where \( s_0(t) \) corresponds to a classical trajectory. The action \( \varphi \) can be expanded in orders of \( \delta s(t) \) with fixed endpoints \( (s', t'; s, t) \):

\[ \varphi = \varphi_0 + \delta \varphi_0 + \frac{1}{2} \delta^2 \varphi_0 + \cdots \]  
where

\[ \varphi_0 = \int_0^t L(s_0, \dot{s}_0, t') \, dt' \]  
with \( s_0 \) and \( \dot{s}_0 \) being the position and velocity, respectively, following classical trajectories.

Since \( \delta \varphi_0 = 0 \), the semi-classical time evolution operator can be written as

\[ \langle s' | e^{-iHt/\hbar} | s \rangle_{SC} = \left( \frac{m^2 \pi \hbar}{2} \right)^{1/2} \sum_{\text{classical paths}} \int D\delta s_0 \, e^{i\left( \varphi_0 + \frac{1}{2} \delta^2 \varphi_0 \right)/\hbar}. \]  

The second variation in the exponential is a Gaussian integral in position and can be integrated out, which leads to the form

\[ \langle s' | e^{-iHt/\hbar} | s \rangle_{SC} = \sum_{\text{classical paths}} \text{prefactor} \times e^{i\varphi_0/\hbar}. \]  

The pre-factor will be stated more explicitly in the following sections.

### 4. Semi-classical path integral for a system coupled to a harmonic bath

The Hamiltonian for a system coupled to a harmonic bath can be written as

\[ H = \frac{p_x^2}{2M} + V_0(s) + \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 - c_i f_i(s) x_i + \frac{c_i^2 f_i^2(s)}{2m_i \omega_i^2} \right). \]  

The letter \( s \) represents the system coordinate and \( x_i \) represents the bath coordinate for each oscillator. \( c_i \) is the coupling strength. The last term is the counter term added to counterbalance the distortion of the system potential by the interaction.

The bath degree of freedom behaves like a forced oscillator with the equation of motion

\[ m_i \ddot{x}_i + m_i \omega_i^2 x_i = c_i f_i(s). \]  

The solution of \( x_i(t) \) can be obtained by the standard Green’s function technique,

\[ x_i(t) = x_i(0) \cos \omega_i t + \frac{p_i(0)}{m_i \omega_i} \sin \omega_i t + \frac{c_i}{m_i \omega_i} \int_0^t \, dt' \, f_i(s(t')) \sin \omega_i (t - t'). \]  

This is the classical result. However, just including the classical (forced) harmonic oscillator expression in the path integral expression (instead of the sum of infinite trajectories) gives the exact quantum result. This is the beauty of the harmonic oscillator.
The time evolution of the entire system is described by the density matrix

\[
\langle s^+, x^+ | \rho(t) | s^-, x^- \rangle = \langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} \rho(0) e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle 
\]

\[
= \int dx_0^+ dx_0^- dx_0^- dx_0^+ \langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^- \rangle \langle s_0^-, x_0^+ | \rho(0) | s_0^-, x_0^- \rangle 
\]

\[
\times \langle s_0^-, x_0^- | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle
\]

\[
= \int dx_0^+ dx_0^+ dx_0^- dx_0^+ \rho(s_0^+, x_0^-) \langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^+ \rangle 
\]

\[
\times \langle s_0^+, x_0^+ | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle
\]

\[
= \int dx_0^+ dx_0^+ dx_0^- dx_0^+ \rho(s_0^+, x_0^-) Q(t)
\]

\[\tag{4.4}\]

where \(\rho(s_0^+, x_0^-) \equiv \langle s_0^+, x_0^- | \rho(0) | s_0^-, x_0^- \rangle\) is the initial state of the system-bath composite system, and the particular expression is at our discretion and will be specified in the numerical simulation section 5. \(Q(t) \equiv \langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^+ \rangle \langle s_0^-, x_0^- | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle\) is the time propagator of the density matrix. Note that the time propagator \(Q(t)\) involves two terms: \(\langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^+ \rangle\) and \(\langle s_0^-, x_0^- | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle\). The \(\langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^+ \rangle\) term represents the forward propagation, indicated by the negative sign in front of the Hamiltonian, and the positions with the superscript \(+\) notation. The \(\langle s_0^-, x_0^- | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle\) term represents the backward propagation, indicated by the positive sign in front of the Hamiltonian, and the negative superscript on the positions. The total phase, i.e. the combined action integral of the forward–backward propagation, \(\langle s^+, x^+ | e^{-i\mathcal{H}t/\hbar} | s_0^+, x_0^+ \rangle \langle s_0^-, x_0^- | e^{i\mathcal{H}t/\hbar} | s^-, x^- \rangle\), is

\[
\Phi = \int_0^t dt' \left[ \frac{1}{2} M \dot{s}^+ (t')^2 - V_0 (s^+ (t')) - \frac{1}{2} M \dot{s}^- (t')^2 + V_0 (s^- (t')) \right]
\]

\[
+ \sum_i c_i \int_0^t dt' \left[ f_i (s^+ (t')) - f_i (s^- (t')) \right] \cos \omega_i t' + \frac{c_i P_{i,0}}{m_i \omega_i} \]

\[
\times \int_0^t dt' \left[ f_i (s^+ (t')) - f_i (s^- (t')) \right] \sin \omega_i t'
\]

\[
+ \sum_i \frac{e_i^2}{2m_i \omega_i} \int_0^t dt' \int_0^t dt'' \left[ f_i (s^+ (t')) - f_i (s^- (t')) \right]
\]

\[
\times \left[ f_i (s^+ (t'')) + f_i (s^- (t'')) \right] \sin \omega_i (t' - t'')
\]

\[
- \sum_i \int_0^t dt' \frac{e_i^2}{2m_i \omega_i} \left[ f_i^2 (s^+ (t')) - f_i^2 (s^- (t')) \right].
\]

\[\tag{4.5}\]

If we assume separable initial distributions of the system and the bath, and the bath takes on a Wigner distribution, then with (4.4) inserted into (4.4) and integrating over the Wigner distribution, we recover the Feynman–Vernon influence functional [34].

The stationary phase conditions are given by setting the derivative of \(\Phi\) with respect to system coordinates to zero, while keeping the endpoints \(s^+, s^-\) fixed. The resulting equations are the equations of motion (the detailed derivation is given in appendix A).
The forward trajectory \( s^+ (t') \) is given by

\[
-M \dddot{s}^+ (t') - V_0' (s^+ (t')) + \sum_i c_i x_i,0, f_i (s^+ (t')) \cos \omega_i t' \\
+ \sum_i \frac{c_i p_i,0}{m_i \omega_i} f_i (s^+ (t')) \sin \omega_i t' + \sum_i \frac{c_i^2}{2m_i \omega_i} f_i (s^+ (t'))
\]

\[
\times \int_0^{t'} dt'' f_i (s^+ (t'')) \sin \omega_i (t' - t'') - \sum_i \frac{c_i^2}{2m_i \omega_i} f_i (s^+ (t'))
\]

\[
\times \int_0^{t'} dt'' f_i (s^+ (t'')) \sin \omega_i (t' - t'') + \sum_i \frac{c_i^2}{2m_i \omega_i} f_i (s^+ (t'))
\]

\[
\times \int_0^{t'} dt'' f_i (s^+ (t'')) \sin \omega_i (t' - t'') + \sum_i \frac{c_i^2}{2m_i \omega_i} f_i (s^+ (t'))
\]

\[
\times \int_0^{t'} dt'' f_i (s^+ (t'')) \sin \omega_i (t' - t'') - \sum_i \frac{c_i^2}{m_i \omega_i} f_i (s^+ (t')) f'_i (s^+ (t')) = 0
\]  

(4.6)

where \( f' \) indicates the first derivative of \( f \), and \( \dddot{s} \) indicates the second derivative with respect to time. \( t' \) is the current time.

The backward propagation \( s^- (t') \) will have the same expression as in (4.6) except with \( s^+ \) replaced by \( s^- \).

Note that the forward trajectory couples to the backward trajectory (i.e. the equation of motion for \( s^+ (t') \) involves \( s^- (t'') \)) and vice versa. In addition, these equations of motion not only couple the present time to the past time (i.e. the integral \( \int_0^{t'} dt'' \)), but also to the future time [71] (i.e. the integral \( \int_t^{t'} dt'' \)). It is a surprising result at first glance that seems to violate causality. Careful inspection reveals that the stationary phase condition applies to all the intermediate system positions, but with the endpoints fixed. Therefore, the problem is formulated as a boundary value problem, such that the intermediate positions are predetermined by the endpoints. To solve these integro-differential equations, the iterative numerical methods for differential equations cannot be used. Instead, root search algorithms must be employed.

The second variation of \( \Phi \) leads to a Gaussian integral that produces a pre-factor. This pre-factor is cumbersome to write out but easy to implement into computer code in the discretized version. The final expression for the semi-classical density matrix propagator \( Q^{SC} \) (replacing \( Q \) is (4.4)) is

\[
Q^{SC} (t) = \text{prefactor} \times \exp \left\{ \frac{1}{\hbar} \Phi_{cl} (x_0, p_0; s^c) \right\}
\]  

(4.7)

where \( s^c_0 \) denotes the classical trajectories following equation (4.6), and the pre-factor is

\[
\left( \frac{M}{2 \pi \hbar^2} \right)^{N} \frac{\left(2\pi i\hbar^{N-2}\right)}{\left| \det \left( \frac{\partial^2 \Phi_{cl}}{\partial s_{i,0} \partial s_{j,0}} \right) \right|}
\]

The notation \( \delta s_{i,0}^c \delta s_{i,0}^c \) denotes all possible combinations of forward and backward coordinates in a discrete manner. (See appendix B for detailed expressions.)
5. Numerical results

5.1. A harmonic oscillator coupled to a harmonic bath

The first step in testing the future-involved term in the equation of motion is to compare the numerical result with analytical solutions. The simplest case is a harmonic oscillator bilinearly coupled to a harmonic bath. The Hamiltonian is

\[ H = \frac{p^2}{2M} + \frac{1}{2} M \Omega^2 x^2 + \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 - c_i s x_i + \frac{c_i^2 s^2}{2m_i \omega_i^2} \right). \]  

(5.1)

The exact analytical result can be achieved through normal mode transformation of the system and bath coordinate combined, then propagating the free oscillators, and finally transforming them back. An additional advantage concerning a collection of harmonic oscillators is that the semi-classical result is the same as the exact result, which, if the future term is true, will perfectly match the exact result.

To proceed, the author calculated the expectation value of the position operator \( \langle \hat{s} \rangle \) of the system initially prepared to have the ground state wave function of the harmonic oscillator, displaced away from the equilibrium position

\[ \psi_0(s) = \left( \frac{M \Omega}{\pi \hbar} \right)^{1/4} e^{-M \Omega (s-a)^2 / 2 \hbar}. \]  

(5.2)

The system starts with the density matrix

\[ \langle s^+_0 | \rho_s(0) | s^-_0 \rangle = \left( \frac{M \Omega}{\pi \hbar} \right)^{1/4} e^{-M \Omega (s^+_0-a)^2 / 2 \hbar} e^{-M \Omega (s^-_0-a)^2 / 2 \hbar}. \]  

(5.3)

The bath is initially at thermal equilibrium assuming the Wigner distribution

\[ \frac{1}{\hbar \pi} \tanh \left( \frac{1}{2} \hbar \omega \beta \right) \exp \left[ - \tanh \left( \frac{1}{2} \hbar \omega \beta \right) \left( \frac{m \omega x^2}{\hbar} + \frac{p^2}{m \omega \hbar} \right) \right] \]  

(5.4)

and the spectral density

\[ J(\omega) = \frac{\pi}{2} \hbar \xi \omega e^{-\omega/\omega_c} \]  

(5.5)

which mimics Debye solids that have a cut-off frequency.

Below is the result with system frequency \( \Omega = 1 \), mass \( M = 1 \), displacement \( a = 1 \), and bath parameters \( \omega_c = 6, \xi = 2, \beta = 1 \). The black curve is the accurate calculation and the dots are from the non-local differential equation using a root search algorithm. The matching of the two confirms that the stationary-phase differential equation does involve a future term (figure 1).

5.2. A Morse oscillator coupled to a harmonic bath

The author also extended the method to a non-harmonic quantum system, with the aim to show whether the semi-classical method comprising the future-involved term serves as a good approximation. To compare results, the multi-configuration time-dependent Hartree (MCTDH)
Figure 1. Average position of a displaced harmonic oscillator coupled to a harmonic bath. The initial state of the harmonic oscillator is a displaced Gaussian. The system and bath parameters are \( \Omega = 1, \alpha = 1, \omega_c = 6, \xi = 2, \beta = 1 \). Black curve: Accurate result; black dots: semi-classical path integral result.

[72–75] is utilized which can produce a numerically accurate result. The model is a Morse oscillator nonlinearly coupled to a harmonic bath:

\[
H = \frac{p^2}{2M} + D (e^{-2as} - 2e^{-as}) - \sum_{i=1}^{N} \left( c_i \frac{1 - e^{-as}}{a} x_i + \frac{p_i^2}{2m} + \frac{m\omega_i^2}{2} x_i^2 \right) \tag{5.6}
\]

where \( s \) is the system coordinate and \( x \) is the bath coordinate.

The harmonic frequency associated with the Morse potential is given by

\[
\Omega = a \sqrt{\frac{2D}{M}}. \tag{5.7}
\]

The characteristic length scales of the Morse oscillator are given by \( \bar{s} = 0.09129, D = 0.018, a = 2, M = 10^3, \) and \( m = 10^4 \). The system initial state is a displaced Gaussian wave packet with displacement \( s_0 = 2\bar{s} \) and width \( \sigma = \bar{s} \).

The spectral density uses the Ohmic spectral density

\[
J(\omega) = M\gamma\omega \tag{5.8}
\]

with the following discretization, i.e. the modes are equally spaced:

\[
\omega_i = \frac{i\omega_f}{N} = i\Delta\omega \tag{5.9}
\]

\[
c_i = i\sqrt{\frac{2mM\gamma\Delta\omega^3}{\pi}} \tag{5.10}
\]

with \( \gamma = \frac{1}{50 \text{ fs}} \). A total of 20 oscillators is sufficient to converge the result.
Figure 2. Average position of a Morse oscillator coupled to a harmonic bath. The system initial state is a displaced Gaussian on the flatter side of the Morse potential. The system and bath parameters are $\bar{s} = 0.09129$, $D = 0.018$, $a = 2$, $M = 10^5$, $m = 10^4$, $s_0 = 2\bar{s}$, $\sigma = 2\bar{s}$, and $\gamma = 1/50$ fs. The black curve is from MCTDH; the black dots are semi-classical path integral results from the root search algorithm.

The bath is at zero temperature and the oscillators are initially placed at the equilibrium position with respect to the system:

$$\frac{\partial V}{\partial x_i} = 0 \quad (5.11)$$

$$x_i^{eq} = c_i \frac{1 - e^{-as}}{m\omega_i^2} \quad (5.12)$$

The author uses a root search algorithm to perform the calculation of the expectation value of the system position. The initial guess positions are taken from the corresponding harmonic system linearly coupled to the harmonic bath. The black curve is the accurate calculation. The dots are from the semi-classical result, which matches the accurate result very well (figure 2).

6. Discussion

The derivation to achieve the classical equation of motion in the semi-classical approximation is made through applying the stationary phase condition, i.e. the first variation of the phase equal to zero. Straightforward as it is, there are several distinctive features worth mentioning. First of all, in the density matrix with the structure $\langle x \mid e^{-i\hat{H}_t/\hbar} \mid x'\rangle \langle x' \mid e^{+i\hat{H}_t/\hbar} \mid x \rangle$ representing multiplication of the forward and backward propagations, if the phase in the forward propagation could achieve a maximum, then the backward propagation phase would reach a minimum,
and vice versa, due to the exponentials having opposite signs. As a consequence, the stationary phase is neither a maximum nor a minimum but a saddle point. This is manifested in the Jacobian matrix (the pre-factor in the semi-classical expression, (4.7)), in which the upper left block is positive-definite and the lower right block is negative-definite. Secondly, the obtained equation of motion has a future dependence term, in addition to its dependence on the past. In other words, the friction kernel is time non-local in all times. It might seem bizarre and in violation of causality, as the familiar Langevin equation only involves dependence on the past. The justification lies in the structure of the propagator $\langle x | e^{-i\hat{H}_t/\hbar} | x' \rangle$. The propagator has two fixed boundary points, $x$ and $x'$. In the full quantum version, the phase can achieve any value through all combinations of the values of intermediate positions, i.e. every trajectory is possible. The stationary phase condition selects the trajectory that is classical, with the constraints of the two boundary values $x$ and $x'$. Therefore, unlike the Langevin equation which is specified by initial value conditions of $x(0)$ and $p(0)$, the semi-classical scheme is formulated as a boundary value problem. Consequently, the classical trajectory is pre-determined by the two boundary conditions, for which the trajectory needs to satisfy at the beginning and end times. Therefore, the future dependence is just as normal as the past dependence that is the manifestation of pre-set end-time. It is also worth mentioning that in a spectral case of Drude friction that corresponds to Lorentz spectral density, the future dependence can be eliminated by converting the second-order differential equation to a fourth-order one, with two boundary conditions and two initial conditions to be specified [71]. Even in this special case, the matching required for the two boundary conditions is not trivial to achieve [76]. In general, it is not possible to eliminate the future dependence term. Thirdly, in addition to the past and future coupling, the forward trajectory is coupled to the backward one and vice versa. This is evident in the $s^- (t''')$ term in the $\ddot{s}^+ (t')$ expression (equation (4.6)), and $s^+ (t''')$ in $\ddot{s}^- (t')$. This forward and backward coupling is also present in the Jacobian matrix. The upper right and bottom left quadrants represent the coupling between the forward and backward paths. The future dependence is manifested in the Jacobian matrix with all non-zero entries. If the equation of motion only has past dependence, then the four quadrants of the matrix are lower triangular. Fourthly, because of the integral involving future time in the equation of motion, the iterative method for solving differential equations is no longer viable. Instead, the root search algorithm needs to be employed. The algorithms are well documented in many numerical recipe books [77]. Lastly, the second example with the Morse oscillator clearly demonstrates that although the semi-classical trajectories are only approximations to the infinite quantum paths, the semi-classical method can achieve numerically satisfactory results. The reason for this is that the classical paths enter into the phase of $\langle x | e^{-i\hat{H}_t/\hbar} | x' \rangle$, the amplitude, whereas any real observables require the amplitude square that allows interference, which is the hallmark of quantum mechanics. In addition, the pre-factor, which comes from the second variation of the phase integrated out through the Gaussian integral, carries additional quantum content. Therefore, the semi-classical mechanics considers the quantum effects up to the leading order. From a perturbation point of view, this might be all that is necessary if the quantum effect deviates not too much from the semi-classical one.

7. Conclusion

The semi-classical path integral expression for a quantum system coupled to a harmonic bath is derived. The quantum system trajectory is confined to a single classical trajectory, which greatly reduces the computational cost. Because the formulation is a boundary value problem, the classical equation of motion for the system has a future-involved term. Root search
algorithms are essential for finding such classical trajectories. Numerical examples are given to demonstrate that the semi-classical approximation can be a numerically sound method.

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**Appendix A**

The variation of $\Phi$ with respect to the system coordinate $s$ involves the following structure:

$$\int_0^t \int_0^{t'} \int_0^{t''} f'(s(t')) f(s(t'')) \sin \omega(t' - t''). \tag{A.1}$$

The variation of the above yields

$$\delta \int_0^t \int_0^{t'} \int_0^{t''} f'(s(t')) f(s(t'')) \sin \omega(t' - t'')$$

$$= \int_0^t \int_0^{t'} \int_0^{t''} \delta f'(s(t')) f(s(t'')) \sin \omega(t' - t'')$$

$$+ \int_0^t \int_0^{t'} \int_0^{t''} f'(s(t')) \delta f(s(t'')) \sin \omega(t' - t'') \tag{A.2}$$

$$= \int_0^t \int_0^{t'} \int_0^{t''} \delta s(t') f'(s(t')) \int_0^{t'} \int_0^{t''} f(s(t'')) \sin \omega(t' - t'')$$

$$+ \int_0^t \int_0^{t'} \int_0^{t''} \delta s(t'') f'(s(t'')) \int_0^{t'} \int_0^{t''} f(s(t')) \sin \omega(t' - t'').$$

The second term can be manipulated into the variation of $\delta s(t')$ instead of $\delta s(t'')$ by switching the integration order of $dr'$ and $dr''$:

$$\int_0^t \int_0^{t'} \int_0^{t''} f'(s(t')) \delta s(t'') f'(s(t'')) \sin \omega(t' - t'')$$

$$= \int_0^t \int_0^{t'} \int_0^{t''} \delta s(t'') f'(s(t')) \int_0^{t'} \int_0^{t''} f(s(t'')) \sin \omega(t' - t'') \tag{A.3}$$

Switching the labels of $t'$ and $t''$, the above equation becomes

$$\int_0^t \int_0^{t'} \int_0^{t''} \delta s(t') f'(s(t')) \int_0^{t'} \int_0^{t''} f(s(t'')) \sin \omega(t' - t'')$$

$$= -\int_0^t \int_0^{t'} \int_0^{t''} \delta s(t') f'(s(t')) \int_0^{t'} \int_0^{t''} f(s(t'')) \sin \omega(t' - t''). \tag{A.4}$$

Therefore, equation (A.2) becomes
Therefore, the variation of the action can be written as (omitting the summation sign for simplicity):

\[
\delta \delta \Phi = \int_0^t dt' \delta^+ (t') \left[ -M \delta^+ (t') - V_0^+ (s^+ (t')) \right] \\
- \int_0^t dt' \delta^- (t') \left[ -M \delta^- (t') - V_0^- (s^- (t')) \right] \\
+ c \int_0^t dt' \left[ \delta^+ (t') f^+ (s^+ (t')) - \delta^- (t') f^- (s^- (t')) \right] \cos \omega t' \\
+ \frac{c^3}{2 \omega} \int_0^t dt' \left[ \delta^+ (t') f^+ (s^+ (t')) - \delta^- (t') f^- (s^- (t')) \right] \sin \omega t' \\
- \frac{c^2}{2 \omega} \int_0^t dt' \delta^+ (t') f^+ (s^+ (t')) \int_0^t dt'' f (s^+ (t'')) \sin \omega (t' - t'') \\
- \frac{c^2}{2 \omega} \int_0^t dt' \delta^- (t') f^- (s^- (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \\
+ \frac{c^2}{2 \omega} \int_0^t dt' \delta^+ (t') f^+ (s^+ (t')) \int_0^t dt'' f (s^+ (t'')) \sin \omega (t' - t'') \\
- \frac{c^2}{2 \omega} \int_0^t dt' \delta^- (t') f^- (s^- (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \\
+ \frac{c^2}{2 \omega} \int_0^t dt' \delta^+ (t') f^+ (s^+ (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \\
- \frac{c^2}{2 \omega} \int_0^t dt' \delta^- (t') f^- (s^- (t')) \int_0^t dt'' f (s^- (t'')) \sin \omega (t' - t'') \\
- \frac{c^2}{2 \omega} \int_0^t dt' \left[ \delta^+ (t') f^+ (s^+ (t')) f^+ (s^+ (t')) - \delta^- (t') f^- (s^- (t')) f^- (s^- (t')) \right] .
\]

By setting equation (A.6) to zero, we can immediately obtain the equations of motion (4.6).
Appendix B

To derive the second variation and integrate out the Gaussian integral, it is much easier to discretize the continuous system trajectories into smaller segments. Here we discretize the trajectory in the form of Trotter splitting, where we designate \( s_0 \) as the position from time 0 to \( \frac{1}{2} \Delta t \), \( s_1 \) as the position from \( \frac{1}{2} \Delta t \) to \( \frac{3}{2} \Delta t \), \( s_2 \) as the position for time \( \frac{3}{2} \Delta t \) to \( \frac{5}{2} \Delta t \), and \( s_N \) as the position from \( \frac{2N-1}{2} \Delta t \) to \( N \Delta t \). The superscripts + and − denote the forward and backward trajectories. Therefore, in discretized form,

\[
\Phi = - \frac{1}{2} V_0 (s_0^+) \Delta t - \sum_{k=1}^{N-1} V_0 (s_k^+) \Delta t - \frac{1}{2} V_0 (s_N^+) \Delta t + \frac{1}{2} V_0 (s_0^-) \Delta t
\]

\[
+ \sum_{k=1}^{N-1} V_0 (s_k^-) \Delta t + \frac{1}{2} V_0 (s_N^-) \Delta t + \sum_{k=1}^{N} \frac{M}{2 \Delta t} (s_k^+ - s_k^-)^2
\]

\[
- \sum_{k=1}^{N} \frac{M}{2 \Delta t} (s_k - s_{k-1})^2 \right]^2 + \frac{c \rho_0}{\omega} (f(s_0^+) - f(s_0^-)) \sin \left( \frac{1}{2} \omega \Delta t \right)
\]

\[
+ \frac{c \rho_0}{\omega} \sum_{k=1}^{N-1} (f(s_k^+) - f(s_k^-)) \left[ \sin \omega \left( k + \frac{1}{2} \right) \Delta t - \sin \omega \left( k - \frac{1}{2} \right) \Delta t \right]
\]

\[
+ \frac{c \rho_0}{\omega} (f(s_N^+) - f(s_N^-)) \left[ \sin \omega N \Delta t - \sin \omega \left( N - \frac{1}{2} \right) \Delta t \right]
\]

\[
+ \frac{c \rho_0}{m \omega^2} (f(s_0^+) - f(s_0^-)) \left( 1 - \cos \frac{1}{2} \omega \Delta t \right)
\]

\[
+ \frac{c \rho_0}{m \omega^2} \sum_{k=1}^{N-1} (f(s_k^+) - f(s_k^-)) \left[ \cos \omega \left( k + \frac{1}{2} \right) \Delta t - \cos \omega \left( k - \frac{1}{2} \right) \Delta t \right]
\]

\[
+ \frac{c \rho_0}{m \omega^2} (f(s_N^+) - f(s_N^-)) \left[ \cos \omega \left( N - \frac{1}{2} \right) \Delta t - \cos \omega N \Delta t \right]
\]

\[
+ \frac{c^2}{2 m \omega^2} (f(s_0^+) - f(s_0^-)) (f(s_0^+) + f(s_0^-)) \left( \frac{1}{2} \omega \Delta t - \sin \frac{1}{2} \omega \Delta t \right)
\]

\[
+ \frac{c^2}{2 m \omega^2} \sum_{k=1}^{N-1} (f(s_k^+) - f(s_k^-)) (f(s_k^+) + f(s_k^-)) \left[ \sin k \omega \Delta t - \sin (k-1) \omega \Delta t - \sin \left( k + \frac{1}{2} \right) \omega \Delta t + \sin \left( k - \frac{1}{2} \right) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{2 m \omega^2} \sum_{k=1}^{N-1} \sum_{l=1}^{k-1} (f(s_k^+) - f(s_k^-)) (f(s_k^+) + f(s_k^-)) \times \left[ 2 \sin (k-k') \omega \Delta t - \sin (k-k'-1) \omega \Delta t - \sin (k-k' + 1) \omega \Delta t \right]
\]

\[
+ \frac{c^2}{2 m \omega^2} \sum_{k=1}^{N-1} (f(s_k^+) - f(s_k^-)) (f(s_k^+) + f(s_k^-)) \left( \omega \Delta t - \sin \omega \Delta t \right)
\]
The second derivatives of $\Phi$ are given by the following:

$$
\frac{\partial^2 \Phi}{\partial s_k^+ \partial s_k^-} = -\Delta t V_0''(s_k^-) + \frac{2M}{\Delta t} + \frac{c_{\text{eq}}}{\omega} f''(s_k^+) \left[ \sin \left( k + \frac{1}{2} \right) \omega \Delta t - \sin \left( k - \frac{1}{2} \right) \omega \Delta t \right]
+ \frac{c_p}{m\omega^2} f''(s_k^+) \left[ \cos \left( k + \frac{1}{2} \right) \omega \Delta t - \cos \left( k - \frac{1}{2} \right) \omega \Delta t \right]
+ \frac{c^2}{2m\omega^2} f''(s_k^+) \left( f'(s_k^+) + f'(s_k^-) \right) \sin k\omega \Delta t - \sin \left( k - 1 \right) \omega \Delta t
- \sin \left( k + 1 \right) \omega \Delta t + \sin \omega \Delta t \right]
+ \frac{c^2}{2m\omega^2} f''(s_k^+) \sum_{k'=1}^{k-1} \left( f'(s_k^+) + f'(s_k^-) \right)
\times \left[ 2 \sin \left( k - k' \right) \omega \Delta t - \sin \left( k' - 1 \right) \omega \Delta t + \sin \left( k - k' + 1 \right) \omega \Delta t \right]
+ \frac{c^2}{m\omega^3} f''(s_k^+) f'(s_k^+) \omega \Delta t - \sin \omega \Delta t
+ \frac{c^2}{m\omega^3} f'(s_k^+) f''(s_k^-)
\times \left( \omega \Delta t - \sin \omega \Delta t \right)
+ \frac{c^2}{2m\omega^2} f''(s_k^+) \sum_{k'=k+1}^{N-1} \left( f'(s_k^+) - f'(s_k^-) \right)
\times \left[ 2 \sin \left( k' - k \right) \omega \Delta t - \sin \left( k' - 1 \right) \omega \Delta t - \sin \left( k' + 1 \right) \omega \Delta t \right]
+ \frac{c^2}{2m\omega^2} f''(s_k^-) \left( f'(s_k^-) + f'(s_k^+) \right) \sin \left( k + \frac{1}{2} \right) \omega \Delta t
\times \left( \omega \Delta t - \sin \omega \Delta t \right)
+ \frac{c^2}{2m\omega^2} f''(s_k^-) \left( f'(s_k^-) - f'(s_k^+) \right) \sin \left( k - \frac{1}{2} \right) \omega \Delta t
- \sin \left( N - k - 1 \right) \omega \Delta t
- \sin \left( N - k + \frac{1}{2} \right) \omega \Delta t + \sin \left( N - k \right) \omega \Delta t
\times \left( \omega \Delta t - \sin \omega \Delta t \right)
+ \frac{c^2}{2m\omega^2} f'(s_k^-) f''(s_k^+) f'(s_k^+) \Delta t, \quad k = 1, \ldots, N - 1 \quad (B.2)
\]
The determinant of this (2N−2)-dimensional Jacobian can be evaluated numerically on a computer, e.g. through lower–upper (LU) decomposition. This operation is \(O(N^3)\). The Jacobian matrix is symmetric and can be divided into four equally sized square blocks. The upper left block is positive-definite, and the lower right block is negative-definite. They represent the coupling in forward–forward and backward–backward trajectories. The upper right and bottom left blocks represent the couplings between the forward and backward trajectories. These couplings between positions (non-zero in the off-diagonal matrix elements) are manifestations of the non-Markovian dynamics involving both the past and future.

There will be exactly another eight terms with \(s^+_{k′}\) and \(s^-_{k′}\) interchanged. Because they have exactly the same structure, they are not listed.

The determinant of this (2N−2)-dimensional Jacobian can be evaluated numerically on a computer, e.g. through lower–upper (LU) decomposition. This operation is \(O(N^3)\). The Jacobian matrix is symmetric and can be divided into four equally sized square blocks. The upper left block is positive-definite, and the lower right block is negative-definite. They represent the coupling in forward–forward and backward–backward trajectories. The upper right and bottom left blocks represent the couplings between the forward and backward trajectories. These couplings between positions (non-zero in the off-diagonal matrix elements) are manifestations of the non-Markovian dynamics involving both the past and future.

\[
\frac{\partial^2 \Phi}{\partial s_k^+ \partial s_k^-} = -\frac{M}{\Delta t} + \frac{c^2}{2m\omega^3} f'(s_k^+) f'(s_{k-1}^-) (2 \sin \omega \Delta t - \sin 2\omega \Delta t),
\]

(B.3)

\[k = 2, \ldots, N - 1\]

\[
\frac{\partial^2 \Phi}{\partial s_k^+ \partial s_{k+1}^-} = -\frac{M}{\Delta t} + \frac{c^2}{2m\omega^3} f'(s_k^+) f'(s_{k+1}^-) (2 \sin \omega \Delta t - \sin 2\omega \Delta t),
\]

(B.4)

\[k = 1, \ldots, N - 2\]

\[
\frac{\partial^2 \Phi}{\partial s_k^- \partial s_{k+1}^-} = \frac{c^2}{2m\omega^3} f'(s_k^+) f'(s_{k+1}^-) \left[ 2 \sin (k-k') \omega \Delta t - \sin (k-k-1) \omega \Delta t \right. \\
- \sin (k-k+1) \omega \Delta t], \\
\]

(B.5)

\[1 \leq k' < k \leq N - 1, \quad k \neq k' + 1\]

\[
\frac{\partial^2 \Phi}{\partial s_k^- \partial s_{k-1}^-} = \frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_{k-1}^-) \left[ 2 \sin (k-k') \omega \Delta t - \sin (k-k-1) \omega \Delta t \right. \\
- \sin (k-k-1) \omega \Delta t], \\
\]

(B.6)

\[1 \leq k < k' \leq N - 1, \quad k' \neq k + 1\]

\[
\frac{\partial^2 \Phi}{\partial s_k^- \partial s_{k+1}^-} = \frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_{k+1}^-) \left[ 2 \sin (k-k') \omega \Delta t - \sin (k-k-1) \omega \Delta t \right. \\
- \sin (k-k+1) \omega \Delta t], \\
\]

(B.7)

\[1 \leq k' < k \leq N - 1\]

\[
\frac{\partial^2 \Phi}{\partial s_k^- \partial s_{k-1}^-} = -\frac{c^2}{2m\omega^3} f'(s_k^-) f'(s_{k-1}^-) \left[ 2 \sin (k-k') \omega \Delta t - \sin (k-k-1) \omega \Delta t \right. \\
- \sin (k-k+1) \omega \Delta t], \\
\]

(B.8)

\[1 \leq k < k' \leq N - 1\]

\[
\frac{\partial^2 \Phi}{\partial s_k^- \partial s_{k+1}^-} = 0, \quad k = 1, \ldots, N - 1.
\]

(B.9)

There will be exactly another eight terms with \(s^+_{k′}\) and \(s^-_{k′}\) interchanged. Because they have exactly the same structure, they are not listed.

Each term of the above goes into the determinant symbolically written as \[
\det \left( \frac{\partial^2 \Phi}{\partial s_k^+ \partial s_k^-} \right).
\]

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