Quantum Path Interference under Incoherent Motions in Multilevel Quantum Systems

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(Dated: now)

Abstract

The fluctuating incoherent environment in the condensed phase plays an important role in the dynamics and steady states of open quantum systems. The most fascinating aspect in open quantum systems is quantum coherence induced by path interference of incoherent motions. We propose a modified Ehrenfest scheme to study the path interference of incoherent motions in multi-level quantum systems. The detailed balance is enforced by considering the quantum correction of two-time correction functions based on second order master (rate) equations. With the modified Ehrenfest method, we can study the steady state populations and other quantum observables under different thermal dynamic conditions, such as energy relaxation and non-Markovian effects. For the three level system under incoherent coupling, we show how the steady state populations are influenced by the quantum path interference of incoherent fluctuations (Agarwal-Fano interference). We discuss the modified Ehrenfest method and its connection with stochastic Langevin equations and second order master equations. Most existing quantum MD simulation methods, particularly Master equation techniques, fall into the category of the weak coupling limit due to the nature of detailed balance. Although the modified Ehrenfest method is amicable to second-order master equations, it is actually a better way to model the quantum path interference since it preserves multi-time memory kernels. Therefore, it enables us to study the quantum path interference.

This method can be extended as a quantum MD simulator for large open quantum systems like solar cell, (organic) LED, etc by merging with Tully’s few switch surface hopping (FSSH) method. The future extension of this method beyond the modified Ehrenfest scheme can be done with efficient wave-packet propagation methods by treating the bath modes in full quantum mechanical way or Gaussian stochastic approach based on non-equilibrium Green function.
I. INTRODUCTION

Recent theoretical study based on minimalist model\textsuperscript{1–3} shows that the Agarwal-Fano path interference and absorption and emission cancellation can play an interesting role in the electron or exciton transfer in the multi-chromophore molecular systems. However, the missing link between the high-level theoretical study and detailed atomistic understanding of these processes impedes the validation and further application of these ideas in realistic molecular systems. However, there are similarities between the Agarwal-Fano interference and non-adiabatic quantum dynamics\textsuperscript{4}. Therefore, we should be able to obtain a quantum MD simulator adapted for large molecular systems which enable us to obtain a microscopical picture of the incoherent energy transfer in multi-level quantum systems by modeling non-adiabatic molecular quantum dynamics and surrounding environment according to the realistic potential energy and interaction. The mixed quantum-classical Ehrenfest scheme\textsuperscript{5–9} often serves as a realistic computational method. It is worthwhile emphasizing that the discrete quantum multi-level systems are intrinsic quantum systems so that the thermal MD method developed for the continuum quantum systems using the Nosé-Hoover thermostat\textsuperscript{10,11} or other classic approaches to simulate the fluctuating environment will not be applicable without correction. We will discuss the topics in this paper. Different from classic noises, quantum noises are described by the close-contour two-time Green function\textsuperscript{12–14} or influence functional\textsuperscript{15}. The correction we make here is mainly on the detailed balance associated with the kinetic equation defined by the second order master equation.

We organize the paper into four sections: 1. in Section II we briefly review the Ehrenfest scheme 2. in Section III we discussed the detailed balance and the connection between the Ehrenfest scheme and stochastic quantum Langevin equations. We also show how to make the quantum correction of two-time correlation functions and detailed balance for the Ehrenfest scheme based on the Bloch-Redfield master equations. We also discuss the connection between the modified Ehrenfest scheme and Block-Redfield equation 3. in Section IV we discuss Van Hove weak-coupling limit and its implied thermal equilibrium enforced by the two-time correlation functions. 4. in Section V We have the concluding remarks.
II. METHODOLOGY

The multi-level Hamiltonian bilinearly coupled to Harmonic bath is defined as,

\[ H = \sum_i \epsilon_i |i\rangle \langle i| + \sum_{i \neq j} J_{ij} |i\rangle \langle j| + \mathcal{V} \times X + \mathcal{I} \times H_B, \tag{1} \]

where \( \mathcal{V} = \sum_{ij} V_{ij} |i\rangle \langle j|, \) \( H_B = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 X_i^2, \) \( \mathcal{I} = \sum_{ij} m(V_{ij}) |i\rangle \langle j| \) and \( X \) is the operator of \( X_i, \sum_i c_i X_i. \) \( m(x) \) is a logic function:

\[ m(x) = \begin{cases} 
0 & x = 0 \\
1 & x \neq 0 
\end{cases} \tag{2} \]

The bath can be phonon or incoherent light. In this model, we ignore the lamb shift or Frank-Condon effect, which can be added trivially. This is very general Hamiltonian and can be generalized to high order bilinear coupling \( \mathcal{V}^n \times X^m \) based on the Taylor expansion.

One way to solve this dissipative quantum system is using different kinds of second-order master equations. If the system is in the van Hove weak coupling limit, these methods are legitimate choices. The detailed balance enforced by equilibrium Harmonic bath \( \exp(-\beta H_B)/\text{Tr}_B(\exp(-\beta H_B)) \) is results of the weak coupling limit. For large molecular systems, we can resort to the Ehrenfest method by considering the bath classically. However the Ehrenfest method ignore the quantum detailed balance due to the classical bath, which leads to equal distribution at steady state. Therefore, fixing the detailed balanced in the Ehrenfest scheme is mandatory.

Often, it is convenient to use the dimensionless coordinates and momenta,

\[ q_i = (m_i \omega_i)^{1/2} X_i, \]
\[ p_i = (m_i \omega_i)^{-1/2} P_i, \tag{3} \]

and \( g_i = (m_i \omega_i)^{-1/2} c_i. \) In the Ehrenfest scheme, the total wave-function is factorized to be

\[ \psi(S, x_1, x_2, \ldots, x_N, t) \approx \phi(S, t) \times \prod_{i=1}^{N} \xi_i(x_i, t). \tag{4} \]

The equation of motion of the system wave-function \( \phi(S, t) \) is expressed as,

\[ i\hbar \frac{\partial \phi(S, t)}{\partial t} = H_S \phi(S, t), \tag{5} \]
where
\[ H_S = H_0 + \mathcal{V} \times Q(t), \]

\[ H_0 = \sum_{i} \varepsilon_i |i\rangle \langle i| + \sum_{i \neq j} J_{ij} |i\rangle \langle j| \quad \text{and} \quad Q = \sum_i q_i. \]

Since the bath is Harmonic and the total wave-function is factorized, the equation of motion for the individual mode, \((x_i(t), p_i(t))\) can be expressed as,

\[ \frac{dx_i}{dt} = -\frac{\partial \mathcal{H}_b(t)}{\partial p_i}, \]

\[ \frac{dp_i}{dt} = \frac{\partial \mathcal{H}_b(t)}{\partial x_i}, \]

where
\[ \mathcal{H}_b(t) = \sum_{i} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 q_i^2 + q_i z_i(t), \]

where \( z_i(t) = \frac{\partial}{\partial q_i} \langle \phi(S,t)|\mathcal{V} \times Q|\phi(S,t)\rangle \) since the coupling is bilinear and \( z_i(t) \) is the time-dependent mean distance shift from the system applying on the quantum subsystem.

The propagation scheme has two steps:

1. propagate the system as,
\[ \phi(S, t + dt) = \exp(-iH_Sdt)\phi(S,t). \]

2. propagate the individual modes, \((q_i(t), p_i(t))\), with the verlet algorithm\cite{16} according to Eq. [7].

The initial distribution of the bath oscillators is characterized by the probability function of thermal Wigner function.

\[ W(q_i(0), p_i(0)) = 2^N \prod_{i=1}^{N} \tanh(\hbar/2) \exp \left( -\tanh(\hbar/2)\left( \frac{\omega_i}{\hbar} q_i(0)^2 + \frac{1}{\omega_i \hbar} p_i(0)^2 \right) \right), \]

where \( \hbar = \hbar \beta \omega_i \). We can sample the distribution function in the phase space \((Q(0), P(0))\) where \( Q(0) = q_1(0), q_2(0), \ldots, q_N(0) \) and \( P(0) = p_1(0), p_2(0), \ldots, p_1(0) \ldots p_N(0) \), and generate the dynamic trajectories \((Q(t), P(t))\) for all configurations according to the Ehrenfest scheme. The quantum observable can be evaluated as \( \langle \hat{O}(t) \rangle = \frac{1}{M} \sum_{j=1}^{M} \langle \phi(S,t|Q_j(t), P_j(t))|\hat{O}|\phi(S,t|Q_j(t), P_j(t)) \rangle \), where \( Q_j(t) \) and \( P_j(t) \) are the \( j \)th configuration and \( M \) is the total number of configurations.
A. Coupling Coefficient and Spectral Density

The coupling coefficient in the bilinear coupling, \( g_i \), can be evaluated computationally or empirically from the spectral density of coupling between system and phonon,

\[
J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{\omega_i} \delta(\omega - \omega_i),
\]

which decides the essential dynamics of reduced systems. The popular functional form of spectral density is ohmic with exponential cutoff \( \eta \omega e^{-\omega/\omega_c} \) and Drude ohmic with Lorentzian cutoff \( 2\eta \omega_c \omega/\omega^2 + \omega^2 \). Different discretization schemes\(^{17-19}\) have been proposed. We take the following discretization scheme for the exponential ohmic spectral density\(^{18}\) in the calculation in the Section V,

\[
\omega_i = -\omega_c \log \left[ 1 - \frac{i}{N} \left( 1 - \exp \left( -\frac{\omega_m}{\omega_c} \right) \right) \right],
\]

and

\[
g_i = \omega_i \sqrt{\frac{2\eta \omega_c}{\pi N} \left( 1 - \exp \left( -\frac{\omega_m}{\omega_c} \right) \right)}.\]

The number of modes should reproduce the reorganization energy \( \mu = \frac{1}{\pi} \int_0^\infty d\omega J(\omega)/\omega \), i.e. \( \frac{1}{2} \sum_i \frac{g_i^2}{\omega_i^2} \approx \frac{1}{\pi} \int_0^\infty d\omega J(\omega)/\omega \). For other spectral densities, the similar discretization scheme can be found. We use this discretization version of Ohmic spectral density to generate the thermal dynamic fluctuation to show that this method can be adapted to quantum MD simulations. However, I want to emphasize that the covariance decomposition method can be used to generate the Gaussian noise with arbitrary spectral densities\(^{15}\).

III. DETAILED BALANCE CONSTRAINT FOR THERMAL EQUILIBRIUM (STEADY STATE)

We want to explain in this section what we calculate with the Ehrenfest scheme. Therefore, we can draw a connection with the study in quantum optics, excitation energy transfer, and etc. based on the Master equation in Liouville space. In order to do so, we will discuss two topics: Implied Quantum Langevin Equations derived from the Ehrenfest Scheme and detailed balance implied by the second order master equation in this section. As a result, we propose to modify the Ehrenfest scheme by enforcing the detailed balance according to the quantum two-time correlation function. We show that modified Ehrenfest scheme
is different from but should be better than the Block-Redfield equation since the modified
Ehrenfest scheme preserve the Gaussian multi-time correlation function but Bloch-Redfield
equation doesn’t. For the multi-level system-phonon, the correct multi-time correlation func-
tion is essential to the study of the quantum path interference. The only way to solve this
problem exactly is to use the influence functional formalism and complex-valued Gaussian
processes. For more general solution, people have to resort to the path integral technique.
But the modified Ehrenfest scheme should be good enough for the large molecular systems.

A. Implied Quantum Langevin Equations

The Ehrenfest Scheme for the system bath Hamiltonian with bilinear coupling is iso-
morphic to the Quantum Langevin Equation. We start to show the equivalence by quickly
reviewing the classical Langevin equation derived from classic system-bath Hamiltonian
\[ H = \frac{P^2}{2M} + V(X_S) - \sum_i g_i X_i S + \sum_i \frac{P_i^2}{2m} + \frac{1}{2}m \omega_i^2 X_i^2, \]
the classical generalized Langevin equation can be derived when the bath is in thermal
equilibrium,
\[ \frac{dX_S(t)}{dt} = \frac{P_S(t)}{M}; \]
\[ \frac{dP_S(t)}{dt} = -\frac{dV(X_S)}{dX_S} - \int_0^t ds \xi(t-s)P_S(s)/M + \mathcal{F}(t), \]
where \( \xi(t) = \sum_i \frac{g_i^2}{m \omega_i} \cos(\omega_i t) \) and \( \mathcal{F}(t) \) is the fluctuating force,
\[ \mathcal{F}(t) = \sum_i g_i \left( X_i(0) - \frac{g_i X_S(0)}{m \omega_i} \right) \cos(\omega_i t) + \frac{g_i P_i(0)}{m \omega_i^2} \sin(\omega_i t), \]
where \( \langle \mathcal{F} \rangle = 0 \) and \( \langle \mathcal{F}(t)\mathcal{F}(0) \rangle = k_B T \xi(t) \).

Following the same idea, we can derive the Quantum Langevin equation based on the
Ehrenfest scheme. Essentially the Ehrenfest scheme essentially is equivalent to a stochastic
time-dependent Schrodinger equation,
\[ i\hbar \frac{\partial \phi(S,t)}{\partial t} = (H_0 + V \times Q(t)) \phi(S,t), \]
where the environment fluctuation,
\[ Q(t) = \sum_i q_i(0) \cos(\omega_i t) + \frac{1}{m \omega_i} p_i(0) \sin(\omega_i t) + \frac{g_i}{m \omega_i} \int_0^t ds \sin(\omega_i(t-s)) \zeta_i(s). \]
Since $z_i(t)$ is the time-dependent displacement, $f_i(t) = \frac{dz_i(t)}{dt}$ is the force applying on the bath modes. Therefore, we can re-write

$$Q(t) = \sum_i g_i(0) \cos(\omega_i t) + \frac{1}{m_{\omega_i}} p_i(0) \sin(\omega_i t) + \frac{g_i}{m_{\omega_i}} \left[ z_i(t) - z_i(0) \cos(\omega_i t) + \int_0^t ds \cos(\omega_i(t-s)) f_i(s) \right].$$

So the time-dependent Schrodinger equations for reduced quantum systems become,

$$i\hbar \frac{\partial \phi(S,t)}{\partial t} = \left[ H_0 + V \times \left( -\xi(0) z_i(t) + F(t) + \int_0^t \xi(t-s) f_i(t) \right) \right] \phi(S,t),$$

where

$$F(t) = \sum_i g_i \left( X_i(0) - \frac{g_i z_i(0)}{m_{\omega_i}^2} \right) \cos(\omega_i t) + \frac{g_i P_i(0)}{m_{\omega_i}^2} \sin(\omega_i t),$$

is equivalent to Eq. 16 and therefore the kernel $\langle F(t)F(0) \rangle = k_B T \delta(t)$.

It is clearly shown that the quantum state $\phi(t)$ evolves under the classical color noise with memory kernel, $Q(t) = -\xi(0) z_i(t) + F(t) + \int_0^t \xi(t-s) f_i(t)$. The solution to the generalized Lagvne equations for some specific cases, such as Ornstein-Ulenbeck, have been discussed. Apparently, the classical time correlation function of $Q(t)$, $C_{cl}(t) = \langle Q(t)Q(0) \rangle$ is even and symmetric, $C_{cl}(t) = C_{cl}(-t)$. Clearly the fluctuation in the Ehrenfest scheme has the classical two-time correlation function. Since we have a intrinsic discrete quantum system, the thermal fluctuation should be described according to the quantum detailed balance, $C(t) = C^*(t - i\beta\hbar)$ (or $C(t) = C^*(-t)$) and $C(\omega) = e^{-\beta\omega} C^*(\omega)$, which doesn’t hold in the Ehrenfest scheme. People have suggested that the quantum correction for the classic time correlation function, $C(\omega) = (\hbar \beta / 2) [\coth(\hbar \beta / 2) + 1] C_{cl}(\omega)$ which is exact for Harmonic oscillators. Also, $C(t) = C^*(t - i\beta\hbar)$ is related to the closed-contour non-equilibrium Green function, which is often used to describe the detailed balance and study the non-equilibrium particle transport.

In the next section, we will discuss the detailed balance matter and modified Ehrenfest Scheme with the quantum correction.

B. Detailed Balance Correction and modified Ehrenfest Scheme

The complete description of quantum detailed balance involves two components: quantum two-time correlation function and time-ordered multi-time correlation function (memory kernel). Time-ordered multi-time correlation function is often more critical to the interference. However quantum two-time correlation function decides the steady state populations.
The second-order master equation technique can preserve the quantum two-time correlation function but sacrifices the complete description of the time-ordering multi-time correlation functions (memory kernel) due to the truncation. Some correction using the high order memory kernel is proposed. On the other hand, the Ehrenfest scheme doesn’t have the quantum two-time correlation function, i.e. the quantum detailed balance, but it preserves the multi-time memory kernel since it uses the path integral technique. The Ehrenfest scheme can be easily used for the large scale quantum MD simulation if we can correct this detailed balance issue in a classical way. This will lead to the modified Ehrenfest scheme. In order to understand the quantum correction, we need to go back the rate equation (second order master equation) in the Liouville space. We want to emphasize that the memory kernel is important to the quantum path interference since it is involved in high-order multi-time correlation function. Therefore, the Ehrenfest scheme is better than Master equation for the study of the quantum path integral. One solution to preserve both the quantum detailed balance and multi-time memory kernel is using the complex-valued Gaussian process constructed according to influence functional.

The exact solution of density matrix can be expressed in terms of the summation of multi-time correlation function (memory kernels) according to the cumulant expansion technique and Nakajima-Zwanzig projection operator technique. We will end with two time ordering prescriptions: partial time ordering prescription (POP) and chronological time ordering prescription, after truncating the summation of multi-time memory kernels at the second order, we can get two kinds of time-ordering master equations (rate equation) the time-local convolutionless second order master equation for the POP case or the convolution time-nonlocal second order master equation for the COP case. One of the most famous example is the Bloch-Redfield equation which can derived with the Markovian approximations. The Bloch-Redfield master equation is expressed as,

\[
\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar}(\epsilon_i - \epsilon_j)\rho_{ij} - \frac{i}{\hbar}(J_{ik}\rho_{kj} - \rho_{ik}J_{kj}) \\
- \sum_{kl} \left( R_{ik,kl}(\omega_{lk})\rho_{ij} + R_{jl,ik}^*(\omega_{lk})\rho_{ik} \\
- [R_{ij,ik}(\omega_{li}) + R_{ki,jl}^*(\omega_{lj})] \rho_{kl} \right)
\]

where

\[
R_{ij,kl}(\omega) = \frac{1}{\hbar^2} \int_0^\infty \! dt \, C(t) \exp(i\omega t)V_{ij}V_{kl},
\]
where $C(t) = \langle Q(t)Q(0) \rangle$, where $Q(t)$ can be considered as the quantum fluctuation of the bath around its mean value. For the case of the Ehrenfest scheme in Eq. [20] the time correlation function is even, symmetric and real-valued $C_{cl}(t) = C_{cl}(-t)$. It is clear that the detailed balance have binary connection solely associated with two energy levels or two particles. Also we can see that the standard Ehrenfest propagation scheme defined previously without quantum detailed balance correction will lead to high temperature equal distribution steady state (the imaginary parts of quantum correlation functions goes to zero).

In the next subsection, we will use a two-level system as an example to elaborate how the detailed balance is enforced in the second order Bloch-Redfield master equation (weak coupling limit) and the way of correcting the Ehrenfest scheme to have the detailed balance in Schrodinger picture correspondingly. We want to emphasize that the Block-Redfield equation is the same to the one used by Harris in terms of the structure.

### C. Two-Level Systems

Bloch-Redfield master equation essentially is a quantum version kinetic rate equation. We take a two level system as an example,

\[ H = H_0 + Q \times X, \]

\[ H_0 = H_s + H_b, \]

\[ H_s = \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix}, \]  
\[ Q = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \]

In this Hamiltonian, we only keep off-diagonal incoherent channels, $V_{ij}, i \neq j$, i.e. energy relaxation channels. Diagonal coherence channels, i.e. $J_{ii} = 0$, are turned off. As well diagonal incoherent channels, i.e. $V_{ii} = 0$, energy dephasing channels, are turned off. The
Block-Redfield master equation(22) for two level systems is defined as,

\[
\frac{d\rho_{11}}{dt} = -2\text{Re}R_{12,21}(\omega_{12})\rho_{11} + 2\text{Re}R_{21,12}(\omega_{21})\rho_{22},
\]

(28)

\[
\frac{d\rho_{22}}{dt} = -2\text{Re}R_{21,12}(\omega_{21})\rho_{22} + 2\text{Re}R_{12,21}(\omega_{12})\rho_{11},
\]

(29)

\[
\frac{d\rho_{12}}{dt} = -i\omega_{12}\rho_{12} - [R_{12,21}(\omega_{12}) + \text{Re}R_{21,12}(\omega_{21})]\rho_{12} + [R_{12,12}(\omega_{21}) + \text{Re}R_{21,21}(\omega_{12})]\rho_{21} + [R_{11,21}(\omega_{12}) - \text{Re}R_{22,21}(\omega_{21})]\rho_{11}
\]

\[
+ R_{22,12}(\omega_{21}) - \text{Re}R_{11,12}(\omega_{12})\rho_{22},
\]

where \( \text{Re}R_{12,21}(\omega_{12}) = \frac{1}{\hbar}V_{12}V_{21}\int_{-\infty}^{\infty} dt e^{-i\omega t} C(t) \) and \( \text{Re}R_{21,12}(\omega_{21}) = \frac{1}{\hbar}V_{21}V_{12}\int_{-\infty}^{\infty} dt e^{-i\omega t} C(t) \). For this model, \([R_{11,21}(\omega_{12}) - \text{Re}R_{22,21}(\omega_{21})]\rho_{11} + [R_{22,12}(\omega_{21}) - \text{Re}R_{11,12}(\omega_{12})]\rho_{22} \) will disappear since energy dephasing channels are turned off.

As the detailed balance stated in Boltzmann’s H-theorem(37),

\[
k_{i\leftrightarrow j}\exp(-\beta\epsilon_j) = k_{j\leftrightarrow i}\exp(-\beta\epsilon_i),
\]

(30)

the quantum detailed balance \( \text{Re}C(\omega_{ij}) = \exp(-\beta\hbar\omega_{ij})\text{Re}C(\omega_{ji}) \) in the Redfield equation should be defined as \( k_{2\leftarrow 1} = 2\text{Re}R_{12,21}(\omega_{12}) \) and \( k_{1\leftarrow 2} = 2\text{Re}R_{21,12}(\omega_{21}) \).

D. Modified Ehrenfest Scheme

For the time-dependent Schroedinger Equation, we have to find an effective Hamiltonian to enforce the relationships in Eqs. \( 28 \) and \( 29 \). The connection between the thermal rate \( k_{i\leftarrow j} \) and non-equilibrium Fermi gold rule’s rate is the thermal weight \( C(\omega_{12}) \) and \( C(\omega_{21}) \)

\[
k_{2\leftarrow 1} = 2\text{Re}R_{12,21}(\omega_{12}) = \frac{2\pi}{\hbar^2}\langle 2|\mathcal{V}|1\rangle^2 C(\omega_{12}),
\]

(31)

\[
k_{1\leftarrow 2} = 2\text{Re}R_{21,12}(\omega_{21}) = \frac{2\pi}{\hbar^2}\langle 1|\mathcal{V}|2\rangle^2 C(\omega_{21}),
\]

where \( \langle 2|\mathcal{V}|1\rangle^2 \) is the major component in the transition probability from state 1 to state 2 according to the Fermi golden rules and \( \langle 1|\mathcal{V}|2\rangle^2 \) is from state 2 to state 1.

For Harmonic bath, \( C(\omega) = \frac{\hbar\omega/\coth(\beta\hbar\omega/2)}{\coth(\beta\hbar\omega/2)+1} C_{cl}(\omega) \). Therefore, we have the approximations,

\[
C(\omega_{12}) = \frac{\beta\hbar\omega_{12}/2}{\coth(\beta\hbar\omega_{12}/2)+1} C_{cl}(\omega_{12}).
\]

So is \( C(\omega_{21}) = \frac{\beta\hbar\omega_{21}/2}{\coth(\beta\hbar\omega_{21}/2)+1} C_{cl}(\omega_{21}) \). Naturally, we can add quantum correction factor in the time-dependent Schrodinger equation by changing \( \mathcal{V} \) matrix, \( V_{m}^{m} = \langle 1|\mathcal{V}|2\rangle = \left(\frac{\beta\hbar\omega_{12}/2}{\coth(\beta\hbar\omega_{12}/2)+1}\right)^{1/2} \) and \( V_{m}^{m} = \langle 2|\mathcal{V}|1\rangle = \left(\frac{\beta\hbar\omega_{21}/2}{\coth(\beta\hbar\omega_{21}/2)+1}\right)^{1/2} \). Also we have to accommodate the detailed balance in Eqs. \( 28 \) and \( 29 \) as suggested by some previous work by Bastida, Sulten and Kleinekathöfer(38,39). Here we only correct the detailed
balance of population part. The detailed balance reflected in the coherence part is neglected
\[ [R_{11,21}(\omega_{12}) - R_{22,21}^*(\omega_{12})]\rho_{11} + [R_{22,12}(\omega_{21}) - R_{11,12}^*(\omega_{21})]\rho_{22}. \] So the phase of the reduced
dynamics will be inaccurate for the intermediate coupling region. But for this model in
Eq. 1 since \( V_{12} \) and \( V_{21} \) are zeros, our calculation is exact without the phase issue. As a
result it won’t affect the steady state. Future work will be how to correct the phase quantum
mechanically if we turn on the coherent and incoherent channels, i.e. \( J_{ij} \neq 0 \) and \( V_{ij} \neq 0 \)
where \( i \neq j \). But the rigorous work can be realized with the complex-valued Gaussian
process. The new equations of motion of quantum subsystems in the modified Ehrenfest
scheme are:
\[ i\hbar \frac{\partial \phi(S,t)}{\partial t} = H^m_S \phi(S,t), \] (32)
where
\[ H^m_S = H_0 + V^m \times Q(t), \] (33)
where the matrix elements in \( V^m \) is \( V^m_{ij} \) as defined previously. The equation of motion of
bath doesn’t change using the original coupling matrix \( V \).

Since the evolution of the reduced two-level system in the Ehrenfest scheme is based on
path integral, the multi-time memory kernel should be exact without any truncation except
the quantum two-time correlation function is replaced by quantum-corrected classical one.
The quantum correction will fix the transition probability but may lose some accuracy for
the phase associated with the quantum detailed balance as discussed earlier. Some previous
research shows that the modified Ehrenfest method will agree with the exact solution at
the weak coupling limit. The phase may be shifted at the intermediate damping range. Some
tricks can be designed to fixed it potentially. However, this method should be attractive for
large scale quantum MD simulations of the realistic open quantum systems, like solar cell,
LED, organic LED, light harvesting system.

IV. WEAK COUPLING LIMIT AND MULTI-TIME CORRELATION FUNCTION

Fluctuation-dissipation theory is the foundation of the non-equilibrium theory. The
Kubo-Green formulas on the linear response theory is an important bridge between the
microscopic and macroscopic descriptions for the fluctuation-dissipation theory. However
the theory is based on the weak coupling limit. van Kampen’s objection to the linear
response theory for the non-weak coupling case is an important topic for the recent study
on the excitation energy transfer in the light harvesting complex\textsuperscript{41}. But for the systems where dissipation is due to weak interactions, amenable to the Van Hove limit, and having sufficiently short relaxation times (Markovian Limit, delta time correlation), the Kubo-Green formulas should hold and the corresponding detailed balance related to the two time correlation function (Fermi Golden rule as a rate at the Markovian limit) induced by the bath should be enforced. In describing the Van Hove limit (and related Weisskopf-Wigner approximation often used in quantum optics), the average effect of the interaction should be zero. Otherwise the time scale associated with reduced system is not large enough to led to microscopic fluctuations\textsuperscript{42}.

But the high order multi-time correlation functions (memory kernel) can contribute significantly to the path interference beyond the binary two time points through two-time correlation function for the intermediate coupling range. For example, the multi-time correlation function of Gaussian process for phonon will have the following iterative definition\textsuperscript{43},

\[
\langle Q(t_0)Q(t_1)\cdots Q(t_{N-1})Q(t_N)\rangle = \langle Q(t_0)Q(t_1)\rangle\langle Q(t_2)\cdots Q(t_N)\rangle + \langle Q(t_0)Q(t_2)\rangle\langle Q(t_1)\cdots Q(t_N)\rangle + \cdots + \langle Q(t_0)Q(t_N)\rangle\langle Q(t_1)\cdots Q(t_{N-1})\rangle.
\]

In general cases, you can not factorizing the multi-time correlation into product of two-time correlation function, \( C(t) = \langle Q(t)Q((0)) \rangle \). The full analytical solution to reduced quantum dynamics will be hard to find given the nature of Gaussian processes\textsuperscript{43}. These high-order memory kernels will lead to the steady state population away from the detailed balance and its implied Boltzmann equilibrium. So that the idea of detailed balance should be extended to accommodate the high-order path interference for the intermediate regime.

V. SIMULATION AND RESULTS

Coupling with TDDFT\textsuperscript{44}, this modified Ehrenfest method can be used for large scale quantum MD simulations of the realistic open quantum systems, like solar cell, LED, organic LED, light harvesting system, etc.. This will enable us to study the quantum interference effect in these important processes and systems. In this paper, we focus on the simple two and three level molecular systems to elaborate the Agarwal-Fano path interference due to energy splitting with our modified Ehrenfest scheme.
FIG. 1: Diagram of a two level system and a two level system with energy splitting at level 2 (a three level systems). $Q_{ij}$ is the coupling of levels $i$ and $j$ which decides the transition probability.

In this section, we show the modified Ehrenfest method gives the correct Boltzmann equilibrium for the two level system after quantum correction. By adding the third energy level, we present the results of how the incoherent motion can change the steady state populations of two level systems through the quantum path interference. The diagram is presented in Figure 1 which is similar to Harris’ original setup on Lasering without population inversion.

A. Two Level System and Thermal Reservoir

We consider a two level system to demonstrate the detailed balance correction for the modified Ehrenfest Scheme. The specifications of the two level system are $\epsilon_0 = 0\text{cm}^{-1}$, $\epsilon_1 = 100\text{cm}^{-1}$ and $J_{ij} = 0$, $j \neq i$ (the coherent channel is turned off). Results with and without the quantum correction are shown in Figs. 2 for the reservoir with the Ohmic spectral density with the exponential cutoff $\eta \omega e^{-\omega/\omega_c}$. The Ohmic spectral density has the
FIG. 2: The reduced dynamics of the two level system with (left) and without (right) the detailed balance correction under the Ohmic spectral density with exponential cutoff. The equilibrium population difference (green dashed line) is \( \frac{\exp(-\beta H_1) - \exp(-\beta H_2)}{\exp(-\beta H_1) + \exp(-\beta H_2)} \).

following parameters, \( \eta = 10 \text{cm}^{-1} \) and \( \omega_c = 10 \text{ps}^{-1} \). And

\[
Q = Q_{12} = \begin{bmatrix}
0 & V_{12} \\
V_{12} & 0
\end{bmatrix},
\]

where \( V_{12} = 1.0 \). Also for this reservoir, we set temperature \( T = 300k \). In Figure 2, we show the population difference of level 1 and 2, \( \rho_1 - \rho_2 \). The initial total population is on level 1. For both calculations, we use 8000 configurations. The convergence of the simulation is checked (not displayed). Fig. 2 shows that the modified Ehrenfest scheme can lead to the Boltzmann equilibrium, but the original Ehrenfest scheme can’t.

B. Three Level System and Quantum Interference under One Temperature Reservoir

In this section, we consider the additional third energy level to elaborate the quantum interference and population manipulation due to the energy splitting of \( \epsilon_2 \) into \( \epsilon_2 \) and \( \epsilon_3 \) as shown in Figure 1. The third energy level is \( \epsilon_3 = 120 \text{ cm}^{-1} \). Some recent work shows that the incoherent motion can induce quantum coherence through quantum path interference as
well as modulate the steady state population. In this setup, we have $Q = Q_{13} + Q_{23}$ where

$$Q_{13} = \begin{bmatrix} 0 & 0 & V_{13} \\ 0 & 0 & 0 \\ V_{13} & 0 & 0 \end{bmatrix}.$$  \hspace{1cm} (36)

$$Q_{23} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & V_{23} \\ 0 & V_{23} & 0 \end{bmatrix}. \hspace{1cm} (37)$$

The results of the normalized difference of the steady state populations of level 1 and 2 are presented in Figure 3 and compared to the thermal equilibrium difference. The normalization is defined as $\frac{\rho_1 - \rho_2}{\rho_1 + \rho_2}$. We consider the following three cases: 1. $V_{13} = 1$ and $V_{23} = 1$; 2. $V_{13} = 3$ and $V_{23} = 1$; and 3. $V_{13} = 1$ and $V_{23} = 3$. We use one reservoir in this section which is the same one used in the previous subsection. Figure 3 shows that the three cases can lead to different steady state population for the two level system due to the discrepancy of damping strengths associated with $\eta$ for different transitions between different two level systems. The ratio between $\eta$ and $\epsilon_1 - \epsilon_2$ is important to the quantum path interference and needs more careful examination in the future.

C. Three Level System and Two Thermal Reservoirs

In this section, we present the results for the same three level systems under two different thermal reservoirs at different temperature. We use the same Ohmic spectral density as the previous section and run two separate sets of trajectories for the two thermal reservoirs. We couple the high temperature reservoir at $T = 6000K$ to transition between levels 1 and 3, $Q_{13} \times X_{hot}$ and cold reservoir at $T = 300k$ to the one between levels 2 and 3, $Q_{23} \times X_{cold}$. We choose $V_{13} = 1$ and $V_{23} = 1$. Figure 4 shows that the energy splitting and two different temperature reservoirs can invert the population of the steady state away from the Boltzmann equilibrium. Since we have two temperatures, the proportion of Boltzmann equilibrium populations will be $\rho_1^p = 1$, $\rho_3^p = \rho_1^p \exp(-\beta_{hot}H_3)$ and $\rho_3^p = \rho_1^p \exp(-\beta_{hot}H_4) \exp(-\beta_{cold}H_2)$. Then we normalize the three-level equilibrium population difference, $\rho_1 - \rho_2 = \frac{\rho_1^p - \rho_2^p}{\rho_1^p + \rho_2^p}$ for the two-level system. Figure 4 shows that the quantum path interference can invert the population.
FIG. 3: The reduced dynamics of the three level system under one thermal reservoir for the three setups: 1. $V_{13} = 1$ and $V_{23} = 1$; 2. $V_{13} = 3$ and $V_{23} = 1$; and 3. $V_{13} = 1$ and $V_{23} = 3$. The equilibrium population difference (blue dashed line) is $\frac{\exp(-\beta H_1) - \exp(-\beta H_2)}{\exp(-\beta H_1) + \exp(-\beta H_2)}$.

VI. CONCLUDING REMARK

We use the modified Ehrenfest scheme to study the quantum path interference and discuss different aspects of the methods, such as its connection to the quantum Langevin equation, detailed balance correction enforced by quantum two-time non-equilibrium green functions. We present the results to show that in the two level quantum systems, the steady state populations can be modulated by the path interference with the additional third level system. The ratio between damping factor (reorganization energy) $\eta$ and energy difference $\epsilon_1 - \epsilon_2$ is critical to the quantum path interference and needs more careful examination in the future.
FIG. 4: Energy splitting at level 2 and ensuing quantum path interference can populate more on level 2 than the equilibrium proportionally. The equilibrium population difference (Green dashed line) is \( \frac{\rho_p^1 - \rho_p^2}{\rho_p^1 + \rho_p^2} \).

We discover that when three level systems coupled to two thermal reservoirs, the steady state population can be inverted compared to the equilibrium populations. The future work includes extend this method to study the realistic system.

VII. ACKNOWLEDGMENT

X. Chen thanks Prof. Paul Brumer for the discussion and Prof. Victor Batista for supercomputing time.

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