A dynamic mean-field theory for dissipative interacting many-electron systems

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Abstract

A non-Markovian theory of dissipative many-electron systems in the presence of arbitrary coherent fields is presented. The new formulation is constructed via the second-quantization of a complete second-order quantum dissipation theory followed by the random phase or time-dependent Hartree–Fock approximation for electron–electron correlation. The theory is shown to be of the Fermi–Dirac thermal equilibrium statistics limit if electron–electron correlation is neglected. The key quantity is the reduced single-electron density matrix instead of the reduced density matrix of the system, which leads to the drastic reduction of numerical simulation time. The validity of the dynamic mean-field approximation is tested in a model two-electron spin-conversed system with Ohmic dissipation in the presence of excitation field.

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1. Background

Quantum dissipation is a subject of wide spread interest in many fields of physics, chemistry and materials science. Various quantum dissipation theories (QDTs) have been developed to investigate the dynamic properties of open systems. They include the Bloch–Redfield theory [1–7], Fokker–Planck equations [7–14], and semigroup formalism [15–18]. Most recently, Xu and Yan [19] constructed a complete second-order QDT (CS-QDT) in which the system–bath interaction is treated rigorously at the second-order cumulant level for both the initial canonical thermal equilibrium and the reduced dynamics. The key physical quantity in these QDTs is the reduced density operator ρ, whose dynamics is described by the Liouville–von Neumann equation of motion, where dissipation is treated with different forms for different QDTs [1–27]. Since the system reduced density matrix needs to be solved, the computational costs of the above methods are expensive, and the calculations have been limited thus to low-dimensional systems. Building on the initial work by Yan, Chen, Yokojima and coworkers (unpublished), Yokojima and Chen [28] developed a QDT based on the

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equation of motion (EOM) for the reduced single-electron density matrix. The resulting EOM was employed to simulate the excitation and nonradiative relaxation of a butadiene molecule. This reduced single-electron density matrix based QDT opens the possibility for quantum chemistry calculations of large quantum open systems.

We present in this manuscript (Paper I) a dynamic mean-field formulation to simulate the dynamics of open many-electron systems under external field driving. Like [28], the new formalism is based on the EOM for the reduced single-electron density matrix, and is a direct generalization of the QDT presented in [28]. The theoretical development starts with the second-quantization of the CS-QDT proposed by Xu and Yan [19], followed by a random phase approximation (RPA) or time-dependent Hartree–Fock (TDHF) treatment on electron–electron correlations. The thermal bath can be the nuclei of system and/or the environment. The traditional linear dissipation superoperator in conventional QDTs is now replaced by nonlinear quantum nonradiative dissipation terms. These terms include the electron–nuclei couplings and energy or material exchanges with the environment. Because only the reduced single-electron density matrix is considered, realistic open many-electron systems can be studied efficiently.

2. Theory

2.1. Conventional quantum dissipation theory

Consider an electronic system embedded in a thermal bath. The total system-plus-bath Hamiltonian $H_T$ can be expressed as

$$H_T(t) = H_S(t) + H_B + H_{SB}. \tag{1}$$

$H_S(t)$ is the many-electron system Hamiltonian in the presence of external classical field, assuming the following form:

$$H_S(t) = \sum_{ij} t_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{jk\ell} v_{jk\ell} c_j^\dagger c_k^\dagger c_{\ell} c_j - \vec{E}(t) \cdot \sum_{ij} \vec{\mu}_{ij} c_i^\dagger c_j. \tag{2}$$

Here, $c_i^\dagger$ ($c_i$) is a creation (annihilation) operator of an electron on spin-orbital $i$. The first and the second terms in Eq. (2) are for the hopping terms $t_{ij}$ and the electron–electron Coulomb integrals $v_{jk\ell}$, respectively, and can be evaluated via the ground state geometry. The third term in Eq. (2) is for the interaction between the system and the external electric field $\vec{E}(t)$, and $\vec{\mu}_{ij}$ is the dipole matrix element. We shall further define $f_{ij}(t) \equiv -\vec{E}(t) \cdot \vec{\mu}_{ij}$. The Hermitian property of $H_S$ implies that $\vec{\mu}_{ij} = \vec{\mu}_{ij}^\ast$, and $f_{ij} = f_{ji}^\ast$, and $v_{jk\ell} = v_{kj\ell}^\ast = v_{\ell jk}^\ast$. In Eq. (1), $H_B$ is the bath Hamiltonian. The system–bath interaction $H_{SB}$ can be generally decomposed in terms of

$$H_{SB} = -\sum_a \vec{W}_a \vec{F}_a. \tag{3}$$

Here, $\vec{W}_a$ is Hermitian operator of the system, and up to two-electron terms, it assumes

$$\vec{W}_a = \sum_{jk} s^a_{jk} c_j^\dagger c_k + \frac{1}{2} \sum_{jk\ell} w^a_{jk\ell} c_j^\dagger c_k^\dagger c_{\ell} c_j,$$  

where $s^a_{jk} = (s^a_{kj})^\ast$, $w^a_{jk\ell} = w^a_{kj\ell} = w^a_{\ell kj}$. The forces $\vec{F}_a$ in Eq. (3) are Hermitian operators in bath space, and can thus be considered as the generalized Langevin forces. Denote $\vec{F}_a(t) \equiv e^{iH_Bt/\hbar} \vec{F}_a e^{-iH_Bt/\hbar}$, which are stationary stochastic variables in the canonical bath ensembles $\rho_B^\text{eq} = \text{e}^{-\beta H_B/\hbar} / \text{Tr} \text{e}^{-\beta H_B/\hbar}$. Their statistical means are set to be zeros

$$\text{Tr}_B[\vec{F}_a(t) \rho_B^\text{eq}] = 0,$$

and the correlation functions are defined as

$$\tilde{C}_{ab}(t - \tau) \equiv \text{Tr}_B[\vec{F}_a(t)\vec{F}_b(\tau) \rho_B^\text{eq}]. \tag{5}$$

A conventional quantum dissipation theory (QDT) for the reduced density operator $\rho(t)$ for the many-electron system reads as [19]

$$i\hbar \frac{d}{dt} \rho(t) = [\tilde{H}_S(t), \rho(t)] - \frac{i}{\hbar} \sum_a [\vec{W}_a, \vec{W}_a(t) \rho(t) - \rho(t) \vec{W}_a^\dagger(t)], \tag{6}$$

$$\vec{W}_a(t) = \sum_b \int_{-\infty}^t d\tau \tilde{C}_{ab}(t - \tau) G(t, \tau) \vec{W}_b G^\dagger(t, \tau). \tag{7}$$
Here, $G(t, \tau)$ is the Hilbert–space Green’s function, satisfying the Schrödinger equation: $i\hbar \partial_t G(t, \tau) = H_S(t)G(t, \tau)$. Eqs. (6) and (7) are a complete second-order QDT (CS-QDT) formulation, constructed via a rigorous second-order cumulant expansion for both the initial canonical thermal equilibrium and the reduced dynamics [19]. However, the implementation of Eqs. (6) and (7) or other conventional forms of QDT should be made with the many-electron eigenstate (or similar) representation. Unfortunately, solving the eigenstates of a many-electron system is itself extremely difficult or intractable. Thus it is almost impossible to solve Eqs. (6) and (7) numerically for real molecular systems. In practice, the dynamical properties of interacting systems are rather studied by using various indirect techniques [29].

In this work, we shall construct a dynamical mean-field QDT for the reduced single-electron density matrix for many-electron systems. To that end, let us recast Eqs. (6) and (7) in terms of the equation of motion (EOM) for the expectation value of an arbitrary (system) operator $O$, $O = \text{Tr}[\hat{O} \rho(t)] = \langle \hat{O} \rangle$. Its EOM can be obtained as

$$i\hbar \frac{d\langle \hat{O} \rangle}{dt} = \sum_n \left\{ \langle \hat{O} \hat{W}_n \rangle \hat{W}_n(t) - \langle \hat{W}_n \rangle \langle \hat{O} \hat{W}_n \rangle \right\}.$$  

(8)

The above equations which are equivalent to the CS-QDT [Eqs. (6) and (7)] will be used as the starting point to construct a time-dependent Hartree–Fock QDT (TDHF-QDT) for the open many-electron system under arbitrary coherent driving.

### 2.2. TDHF-QDT for many-electron systems

The key quantity here is the reduced single-electron density matrix $\sigma$, whose element is defined as the expectation value of the single-electron operator $\hat{\sigma}_{jk} \equiv c_j^\dagger c_k$; i.e., $\sigma_{jk} \equiv \langle \hat{\sigma}_{jk} \rangle = \langle c_j^\dagger c_k \rangle$. Let us now derive the EOM for the reduced single-electron density matrix $\sigma$ according to Eq. (8). Let us first consider the contribution of the first term in Eq. (8). By using the anti-commutation relation for fermions, we have

$$[\hat{\sigma}_{jk}, H_S(t)] = \sum_n \left\{ [t_{jn} + f_{jn}(t)] c_j^\dagger c_n - [t_{nk} + f_{nk}(t)] c_n^\dagger c_k \right\}$$

$$+ \sum_{mn} \left( v_{jm,nn} c_j^\dagger c_n^\dagger c_m - v_{mn,nk} c_j^\dagger c_n^\dagger c_m c_k \right).$$  

(9)

The Hartree–Fock approximation to the expectation value of the two-particle operator involves the following Wick’s factorization:

$$\langle c_j^\dagger c_k \rangle \langle c_m^\dagger c_n \rangle \approx \langle c_j^\dagger c_m \rangle \langle c_k^\dagger c_n \rangle - \langle c_j^\dagger c_n \rangle \langle c_k^\dagger c_m \rangle.$$  

(10)

The above two equations lead to $\langle [\hat{\sigma}_{jk}, H_S(t)] \rangle = [\hbar(t), \sigma_{jk}]$, with the Fock matrix

$$h_{jk}(t) = t_{jk} + f_{jk}(t) + \sum_{nm} (v_{jk,nn} - v_{jm,nk}) \sigma_{nm}(t).$$  

(11)

Obviously, the above Hartree–Fock approximation amounts formally to the following replacement:

$$H_S(t) \Rightarrow \sum_{jk} h_{jk}(t) c_j^\dagger c_k.$$  

(12)

The contribution of the second term in Eq. (8) is more complicated. In general, $\hat{W}_n$ contains any order of many-body operators. Should it be retained up to two-body terms, the evaluating for the second term in Eq. (8) would require treating four-body interactions. In this work, we adopt the following ansatz (i.e., Hartree–Fock approximation) in which [cf. Eqs. (2), (12) and (4)]

$$\hat{W}_n \Rightarrow \sum_{jk} \eta_{n,jk}(t) c_j^\dagger c_k,$$

(13)

$$\eta_{n,jk}(t) = \alpha_{jk} + \sum_{mn} (w_{jk,nn}^n - w_{jm,nk}^m) \sigma_{mn}(t).$$  

(14)

The above ansatz together with Eq. (12) lead Eq. (7) to

$$\hat{W}_n \Rightarrow \sum_{jk} \tilde{\eta}_{n,jk}(t) c_j^\dagger c_k,$$

(15)

$$\tilde{\eta}_{n}(t) = \sum_b \int_{-\infty}^t d\tau \bar{C}_{ab}(t - \tau) \mathcal{G}(t, \tau) \eta_b(\tau) \mathcal{G}^\dagger(t, \tau).$$  

(16)
Here, \( \mathcal{G}(t, \tau) \) is the Green’s function in the Hartree–Fock space; i.e., \( i\hbar \partial_t \mathcal{G}(t, \tau) = h(t) \mathcal{G}(t, \tau) \). By using Eqs. (13) and (15) for Eq. (8) whose second term is now only treating with two-electron operators, the expectation value is then evaluated via again the Wick’s factorization as Eq. (10).

The final TDHF-QDT formulation for the single-electron density matrix \( \sigma(t) \) can now be summarized as (see Appendix A for details)

\[
\begin{align*}
    i\hbar \dot{\sigma} = [h, \sigma] - \frac{i}{\hbar} \sum_a [\eta_a, \sigma] \text{tr} \{ (\bar{\eta}_a - \bar{\eta}_a^\dagger) \sigma \} \\
    - \frac{i}{\hbar} \sum_a [\eta_a, (1 - \sigma) \eta_a \sigma - \bar{\eta}_a \sigma (1 - \sigma)].
\end{align*}
\]

(17)

This equation constitutes the main formal result (TDHF-QDT) of the present work. It is derived rigorously via a CS-QDT plus a dynamic mean-field approach. It takes account for the effect of second-order system–bath coupling on both dynamics and the stationary (equilibrium) state [19]. The similar formalism can be derived for bosonic systems. The EOM of a bosonic system corresponding to Eq. (17) can be obtained via replacing \( 1 - \sigma \) by \( 1 + \sigma \) in Eq. (17) and replacing the minus sign in Eqs. (11) and (14) by plus.

2.3. Fermi–Dirac statistics

For a noninteracting system in which \( v_{j f, k' k} = w_{j f, k' k} = 0 \), the matrices \( h \) and \( \eta \) are time-independent provided there is no external driving field. In this case, the Hartree–Fock Green’s function \( \mathcal{G}(t, \tau) = e^{-i h (t-\tau)} \), and Eq. (16) becomes

\[
\begin{align*}
    \bar{\eta}_a &\approx \frac{1}{2} \sum_b \int_{-\infty}^{\infty} d\tau \mathcal{C}_{ab}(\tau) e^{-i \mathcal{L} \tau} \bar{\eta}_b, \\
    &\equiv \frac{1}{2} \sum_b C_{ab}(-\mathcal{L}) \bar{\eta}_b,
\end{align*}
\]

(19)

which amounts to the neglect of the bath dispersion dynamics effects. Here, \( C_{ab}(-\mathcal{L}) \) is the function of \( \mathcal{L} \) defined by the bath interaction spectrum,

\[
C_{ab}(\omega) \equiv \int_{-\infty}^{\infty} d\tau e^{i\omega \tau} \mathcal{C}_{ab}(\tau) = e^{i\omega a} C_{ba}(-\omega).
\]

(20)

The second identity in the above equation stands for the detailed-balance required by the canonical bath statistics. It is well known that auto-correlation spectrum \( C_{aa}(\omega) \) is nonnegative, while cross-correlation spectrum \( C_{ab}(\omega) = C_{ba}(\omega) \) [the spectrum matrix \( \{ C_{ab}(\omega) \} \), denoted as \( \%, \) is Hermitian] can be complex. In Appendix B we show that the spectrum matrix \( \% \) is of complete positivity. Let us now prove that the well-known Fermi–Dirac statistics

\[
\sigma_{eq}^0 = \frac{\lambda e^{-\beta h}}{1 + e^{-\beta h}}.
\]

(21)

is the stationary solution to Eq. (17). By the symmetric and detailed-balance relation of bath spectrum we can have that [cf. Eq. (19) and note that \( \eta \) are Hermitian],

\[
\begin{align*}
    \bar{\eta}_a^0 &\equiv \frac{1}{2} \sum_b C_{ab}(\mathcal{L}) \eta_b = \frac{1}{2} \sum_b C_{ba}(\mathcal{L}) \eta_b \\
    &= e^{i\mathcal{L} \bar{\eta}_a} = e^{i\mathcal{L} \bar{\eta}_a} e^{-i\beta h}.
\end{align*}
\]

(22)

The above relation leads directly to (cf. \( [h, \sigma_{eq}^0] = 0 \))

\[
\begin{align*}
    \text{tr}(\bar{\eta}_a \sigma_{eq}^0) &= \text{tr}(\bar{\eta}_a \sigma_{eq}^0), \quad \text{and} \\
    \sigma_{eq}^0 \eta_b (1 - \sigma_{eq}^0) &= (1 - \sigma_{eq}^0) \bar{\eta}_b \sigma_{eq}^0.
\end{align*}
\]

(23)

We thus prove that the well-established quantum statistics, \( \sigma_{eq}^0 \) [Eq. (21)], does constitute the stationary solution of our TDHF-QDT [Eq. (17)] under the Redfield approximation.

3. Test: excitation and relaxation of a two-level system

To test the validity of TDHF ansatz proposed in Section 2.2, let us consider a simple two-electron
(one ↑ and one ↓ spin) two-level system. Here the system Hamiltonian is given by [cf. Eq. (2)]

\[
\hat{H}_S = \sum_{i=1}^{2} \sum_{k=1}^{2} \hbar \omega_i c_i^\dagger c_i + \sum_{j=1}^{2} \sum_{k=1}^{2} \imath v c_i^\dagger c_k^\dagger c_k c_j \\
+ \sum_{j \neq k}^2 \imath v_{12} c_{1j}^\dagger c_{2j}^\dagger c_{2j} c_{1j} \\
- E(t) \sum_k \mu (c_k^\dagger c_{1k} + c_k^\dagger c_{2k}),
\]

(24)

where \( c_1 \) is the annihilation operator of an electron with spin up at the level 1. Other creation and annihilation operators are similarly defined. The system–bath interaction Hamiltonian is given by [cf. Eqs. (3) and (4)]

\[
\hat{H}_{SB} = -\hat{W} \hat{F}, \quad \text{with} \quad \hat{W} = \sum_{i,j=1}^{2} \sum_{k=1}^{2} s_{ij} c_i^\dagger c_j.
\]

(25)

The spectral density \( J(\omega) \), which relates to the bath correlation function \( \tilde{C}(t) \) as

\[
\tilde{C}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{J(\omega)}{1 - e^{-\imath \omega t}}
\]

(26)

is assumed to be Ohmic, i.e.,

\[
J(\omega) = \eta B \omega \exp(-|\omega|/\omega_c).
\]

Since the model two-electron two-level system is simple, we can carry out the CS-QDT [Eqs. (6) and (7)] calculation to examine the excitation and dissipation of system. Note that the CS-QDT is rigorous in the weak system–bath interaction limit in which the system–bath interaction is treated completely up to the second order and the higher-order contributions are partially resummed through second-order cumulant expansion. The CS-QDT results are used to assess the validity of the TDHF approximation in Eq. (17). The parameters we have chosen for the test simulation are \( \hbar \omega_1 = 0.0 \text{ eV}, \ h \omega_2 = 0.2 \text{ eV}, \ im \omega = 0.02 \text{ eV}, \ v_{12} = 0.01 \text{ eV}, \ s_{11} = s_{22} = 0.1 \text{ eV}, \ s_{12} = s_{21} = 0.2 \text{ eV}, \ v_{01} = 0.2 \text{ fs/eV}, \) and \( \omega_c = 0.4 \text{ eV} \). The driving field is taken as \( E(t) = E_0 e^{-t^2/(2t_c^2)} \), with \( \mu E_0 = 1.13 \text{ eV} \) and \( t_c = 0.5 \text{ fs} \).

We calculate the polarization \( P(t) = \text{tr}[\mu \sigma(t)] \) and make a Fourier transformation to obtain \( P(\omega) \). Unless the strong external electronic field is employed, the time dependence of \( \hat{\eta}_0 \) [Eq. (16)], which comes from the time dependence of the Fock matrix \( h(t) \), is not important in this model. Thus, the ground state Fock matrix is employed to determine \( \hat{\eta}_0 \) (see Appendix C for the details). The resulting spectra \( \text{Im}[P(\omega)] \) are shown in Figs. 1 and 2. We have chosen two simulation temperatures 300 and 500 K. Fig. 1 shows the comparison between the CS-QDT result (dashed line) and TDHF-QDT result (solid line) for the lowest excited state. The two results show very similar in terms of peak position, width and height, especially for 300 K. The TDHF-QDT does not reproduce the peak near 0.21 eV, which corresponds to the excitation from the state where one electron occupies level 1 and the other for level 2, to the state where both occupy level 2.
The excitation spectra at the two-electron excitation regime is shown in Fig. 2. A factor of 5000 is multiplied for $\text{Im}[P(\omega)]$ in Fig. 2 compared with in Fig. 1. Although we can find larger energy splitting compared with Fig. 1 for two different methods, the overall result is very similar. Again the two results for 300 K shows better consistency.

Obviously, the applicability of the TDHF-QDT is limited by the TDHF theory itself where the elementary excitation is described very well. The test in this section shows that the extension of the TDHF for the open system gives surprisingly good results for the positions, heights, and widths of the elementary excitations in $\text{Im}[P(\omega)]$. As the TDHF does not have the sufficient many-body correlation effect to describe the cooperative excitation of the optical response, it is rather natural to find some discrepancy between the TDHF-QDT and the CS-QDT in Fig. 2. However, the similar line shapes indicate that the present TDHF-QDT may even be able to explore the dynamics of multielectron excitation to certain extent. Observed is also that the TDHF-QDT produces better result for the lower temperature. It will, thus, be interesting to examine the effects of temperature, together with other properties of TDHF-QDT. However, this is beyond the scope of this Letter and will be investigated in future publication.

4. Discussion

Eq. (17) has close resemblance to the conventional TDHF EOM [30] except that the pure dephasing terms in the conventional EOM are replaced by the dissipative terms. The dissipative terms lead to the energy dissipation while the pure dephase terms in the conventional TDHF conserve the system energy. In another word, the conventional TDHF cannot describe the nonradiative decay. In the TDHF-QDT, the dissipative terms are derived from the first-principles, and the nonradiative decay is accounted for naturally. While the radiative decay has not been included presently, it can be accounted within the TDHF-QDT. The energy dissipation causes the energy exchange between the electrons and nuclei, and leads to the deterioration of the Hartree–Fock approximation. This may cause the breakdown of Eq. (10). Unlike the TDHF where the first order of the optical response only induce the electron–hole part of the density matrix, dissipation terms in Eq. (17) mix the electron–hole, electron–electron, hole–hole parts. This is the direct consequence of the energy loss due to dissipation. The formalism, therefore, is limited to the weak system–bath interaction.

In the formalism the interaction among electrons are explicitly considered. It would be interesting to quantify the effects of the electronic interaction on the relaxation processes. Switching off the electronic interaction leads to drastically different electronic structure. This makes the direct comparison between the interacting and noninteracting electronic systems difficult. A possible solution is to start from the noninteracting electronic
system and then turn on gradually the electronic interaction while measuring the related effects.

We have shown in Section 2.3 that for a non-interacting electronic system the TDHF-QDT leads ultimately to the Fermi–Dirac distribution. For the interacting electronic systems, similar conclusion exists. Moreover, the above conclusion can be generalized to the bosons. For a bosonic system, our dynamic mean-field QDT leads the system to its Bose–Einstein distribution. Beyond the Redfield approximation [cf. Eq. (19)], the TDHF-QDT [Eq. (17)] describes actually the bath-correlated reduced quantum statistical equilibrium state.

As we pointed out earlier, Eq. (17) is the main result of this work. We emphasize that the quantum dissipative terms in Eq. (17) are derived rigorously by starting from the total Hamiltonian and integrating subsequently the bath degrees of freedom. Unlike many other QDTs, our quantum dissipative terms are not phenomenological and can be determined from the first principles. The most important feature of Eq. (17) is that it is the EOM for the reduced single-electron density matrix \( \rho \) instead of the reduced system density matrix \( \rho \). This leads to the drastic reduction of the degrees of freedom in numerical simulation. The TDHF-QDT developed in this work can thus be used to simulate the realistic and complex open molecular systems. In the subsequent manuscript (Paper II) [31], we apply the TDHF-QDT to investigate the photo-excitation and nonradiative decay of an embedded butadiene molecule.

To summarize, we have shown that the new formalism can be employed to simulate the nonradiative relaxations of interacting many-electron systems that are in contact with thermal baths. To test the validity of the TDHF-QDT formalism, we applied it to the two-electron two-level system. The comparison between the TDHF-QDT and the CS-QDT shows that it is very successful to describe the elementary excitation and relaxation, where even some electron cooperative optical response can be simulated. Since the key entity is the reduced single-electron density matrix, we expect that the TDHF-QDT can be employed to simulate the quantum dissipative processes in large molecular systems.

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**Appendix A. Derivation of Eq. (17)**

Let us consider two single-electron operators \( \hat{A} = \sum_{mm'} A_{mm} c_m^\dagger c_{m'} \) and \( \hat{B} = \sum_{mm'} B_{mm'} c^\dagger_{m'} c_m \). We can obtain that

\[
[\hat{\sigma}_{jk}, \hat{A}] = \sum_n \left( A_{nn} \hat{\sigma}_{nk} - A_{nk} \hat{\sigma}_{jn} \right).
\]

By Wick’s theorem [cf. Eq. (10)], we can further obtain that:

\[
[\hat{\sigma}_{jk}, \hat{A}] = \sum_{mm'} \left( A_{mm'} \langle \hat{\sigma}_{nk} \hat{\sigma}_{m'm} \rangle - A_{nk} \hat{B}_{mm'} \langle \hat{\sigma}_{jn} \hat{\sigma}_{m'm} \rangle \right)
\]

\[
\approx \sum_{mm'} \left[ A_{mm'} \langle \delta_{mm'} \sigma_{nk}^2 - \sigma_{nm} \sigma_{m'n} + \sigma_{nk} \sigma_{m'n} \rangle \right.
\]

\[
- A_{nk} \hat{B}_{mm'} \langle \delta_{jm} \sigma_{m'n} - \sigma_{jm} \sigma_{m'n} + \sigma_{jn} \sigma_{m'n} \rangle \right];
\]

\[
[\hat{B}[\hat{\sigma}_{jk}, \hat{A}] = \sum_{mm'} \left( A_{mm'} \langle \hat{\sigma}_{m'n} \hat{\sigma}_{nk} \rangle - A_{nk} \hat{B}_{mm'} \langle \hat{\sigma}_{m'n} \hat{\sigma}_{jn} \rangle \right)
\]

\[
\approx \sum_{mm'} \left[ A_{mm'} \langle \delta_{mm'} \sigma_{nk}^2 - \sigma_{nm} \sigma_{m'n} + \sigma_{nk} \sigma_{m'n} \rangle \right.
\]

\[
- A_{nk} \hat{B}_{mm'} \langle \delta_{jm} \sigma_{m'n} - \sigma_{jn} \sigma_{m'n} + \sigma_{jn} \sigma_{m'n} \rangle \right].
\]

The above equations can be written in the matrix form as

\[
\langle \hat{\sigma}, \hat{A} \rangle = \langle A, (1 - \sigma)B \sigma \rangle + \langle A, \sigma \rangle \text{tr}(B \sigma);
\]

\[
\langle \hat{B}[\hat{\sigma}, \hat{A}] \rangle = \langle A, \sigma B (1 - \sigma) \rangle + \langle A, \sigma \rangle \text{tr}(B \sigma).
\]

By applying Eqs. (A.4) and (A.5) to Eq. (8) with the operators \( \hat{W}_a \) and \( \hat{W}_a \) assuming the forms of
Eqs. (13) and (15), the TDHF-QDT Eq. (17) is thus derived in due course.

**Appendix B. Positivity of spectrum matrix**

In the bath $\mathcal{H}_b$-eigenstate representation $\{|m\}\}$, we have that,

$$C_{ab}(\omega) = \int_{-\infty}^{\infty} \text{d}t e^{i\omega t} C_{ab}(t)$$

$$= \int_{-\infty}^{\infty} \text{d}t e^{i\omega t} \text{Tr}_{\mathcal{B}}[\hat{\mathcal{F}}_b(t)\hat{\mathcal{F}}_b(0)\rho_{\mathcal{B}}]$$

$$= 2\pi \sum_{m,n} (\rho_{\mathcal{B}}^{eq})_{mn} \delta(\omega - \omega_{mn}) F_{mm}^{a} F_{nn}^{b}. \quad (B.1)$$

Since the matrix $\mathcal{C}$ is Hermitian, it can be diagonalized by a unitary transformation matrix $S$ ($S^\dagger S = 1$),

$$S^\dagger \mathcal{C} S = \Lambda \equiv \text{diag}(\lambda_1, \lambda_2, \ldots) \quad \text{or} \quad \sum_{a,b} S_{aa}^{*} C_{ab} S_{bb'} = \lambda_{a'} \delta_{a'b'}.$$  \hspace{1cm} (B.2)

Here, the eigenvalues $(\lambda_1, \lambda_2, \ldots)$ are real and we shall in the following prove that they are non-negative as well. Note that $\mathcal{C}, S$ and $\Lambda$ are all depend on $\omega$. Let us now define a vector $K$ with $K_{a} = \sum_{a'} p_{a} S_{a'a'}$. Here, $p_{a'}$ are arbitrary numbers. By Eq. (B.2), we have

$$K^\dagger \mathcal{C} K = \sum_{a,b} K_{a}^* C_{ab} K_{b}$$

$$= \sum_{a,b} p_{a} S_{a'a'} C_{a'b'} S_{b'b} = \sum_{a} |p_{a}|^{2} \lambda_{a}. \quad (B.3)$$

On the other hand, we have

$$K^\dagger \mathcal{C} K = 2\pi \sum_{m,n} (\rho_{\mathcal{B}}^{eq})_{mn} \delta(\omega - \omega_{mn})$$

$$\times \left( \sum_{a} K_{a} F_{aa}^{b} \right) \left( \sum_{b} K_{b} F_{bb} \right)$$

$$= 2\pi \sum_{m,n} (\rho_{\mathcal{B}}^{eq})_{mn} \delta(\omega - \omega_{mn})$$

$$\times \left| \sum_{a} K_{a} F_{aa}^{b} \right|^{2} \geq 0. \quad (B.4)$$

Since $p_{a'}$ in Eq. (B.3) is arbitrary, we thus prove that $\lambda_{a}$ is non-negative.

**Appendix C. Evaluation of $\tilde{\eta}_{a}(t)$**

There are many methods possibly we can use to calculate $\tilde{\eta}_{a}(t)$. For example, we can calculate the Green’s function following the time evolution and perform the integration of Eq. (16) for each time step. This method works perfectly, however, it is computationally demanding. Here we present another method. This method does not give the time dependence of $\tilde{\eta}_{a}(t)$, thus it is for the weak excitation. However, as long as the excitation is weak, this method and the direct integration of Eq. (16) give results which differ little.

If the system is in the ground state, the Fock matrix $h_{ij}$ does not change with time. Therefore, we can use its $k$th eigenvalue $\omega_{kl}$ and the corresponding eigenvector $U_{ik}$ to calculate the Green’s function and Eq. (16) is written as [denoting $\omega_{kl} = (E_{k} - E_{l})/\hbar$]

$$\tilde{\eta}_{a,ij} = \sum_{b,k,m,n} \int_{0}^{\infty} \text{d}\tau \tilde{C}_{ab}(\tau) e^{-i\omega_{kl}\tau} U_{ik}(U^{\dagger})_{km} U_{nl}$$

$$\times (U^{\dagger})_{ij} \tilde{\eta}_{b,mm}. \quad (C.1)$$

The time integration in Eq. (C.1) is carried out [7,19] by

$$\int_{0}^{\infty} \text{d}\tau e^{i\omega t} \tilde{C}_{ab}(t) = \frac{1}{2} [C_{ab}(\omega) + iD_{ab}(\omega)], \quad (C.2)$$

$$C_{ab}(\omega) \equiv \int_{-\infty}^{\infty} \text{d}t e^{i\omega t} C_{ab}(t) \quad \text{and}$$

$$D_{ab}(\omega) \equiv \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \text{d}\omega' \frac{C_{ab}(\omega')}{\omega - \omega'},$$

and $\mathcal{P}$ denotes the principal value integration. Thus, we have

$$\tilde{\eta}_{a,ij} = \sum_{b,k,l} \left[ C_{ab}(\omega_{lk}) + iD_{ab}(\omega_{lk}) \right] U_{ik}(U^{\dagger})_{kl} U_{lj}. \quad (C.4)$$

Since $\eta_{a}$ requires the information of the ground state Fock matrix, we have to determine the ground state itself. Let us write Eq. (17) as $\mathcal{L}_{a,j} = \mathcal{P}_{i,j}(\sigma)$. Then, the ground state denoted as $\sigma_{g}$ is obtained by solving $\mathcal{L}_{i,j}(\sigma_{g}) = 0$. Since this is a nonlinear equation of $\sigma$, we have to solve it iter-
atively by denoting the solution as $\sigma_g \equiv \sigma_1 + \delta \sigma$. We first start with $\sigma_1$ which should be close to $\sigma_g$. Deviation can be assumed to be $\delta \sigma$, thus we have (up to the first order of $\delta \sigma$),

$$\sum_{mn} \left. \frac{\partial \mathcal{L}_{i,j}(\sigma)}{\partial \sigma_{mn}} \right|_{\sigma = \sigma_1} \delta \sigma_{mn} \approx -\mathcal{L}_{i,j}(\sigma_1). \quad (C.5)$$

Obtained $\sigma_1 + \delta \sigma$ will be used for the next step of the iteration as $\sigma_1$. We continue these procedure until $\sigma_1$ approaches $\sigma_g$.

References