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Exciton dissociation in the presence of phonons: A reduced hierarchy equations of motion approach

Yao Yao,^{1,2} Wenchao Yang,² and Yang Zhao^{1,a)}

¹*Division of Materials Science, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*

²*State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China*

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Combining the reduced hierarchy equations of motion (HEOM) approach with the Wigner-function formalism, we investigate nonperturbatively exciton dissociation under the influence of a phonon bath in an organic heterojunction. The exciton is modeled by an electron-hole pair with the electron moving in the presence of both an external electric field and the Coulomb attraction potential from the hole. In the absence of a phonon bath, calculated HEOM results reproduce those from the Onsager-Braun theory in weak electric fields. In the presence of a phonon bath, substantial deviations from the Onsager-Braun theory are found, signaling phonon-induced quantum effects. Furthermore, time evolution of the spatial current distribution is examined, and an initial spike followed by a polarity change of the transient photocurrent have been recovered. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867418>]

I. INTRODUCTION

Dissociation of tightly bound electron-hole pairs (i.e., excitons) is of crucial importance to organic photovoltaic devices.^{1,2} In a donor-acceptor heterojunction, a photo-injected exciton could diffuse to the interface. Subsequently, due to the energy-level mismatch between the two sides of the interface, charge separation occurs across the interface and the electron will reside in the acceptor while the hole in the donor.² Since generally the electron mobility in the acceptor differs from that of the hole in the donor, one of them will exit the interface earlier after the dissociation. An example is shown in Fig. 1, in which the electron moves faster so that the hole will stay at the interface for a longer time than the electron while inducing a Coulomb attractive potential that, together with the electrostatic potential due to the external bias voltage, constrains the electron motion.

The dissociation rate can be estimated from the celebrated Onsager-Braun model,^{3,4} which gives a weak dependence of the dissociation efficiency on the electric field:

$$\eta^{-1} \sim \exp\left(-\kappa \frac{\sqrt{E}}{k_B T}\right), \quad (1)$$

where η is the dissociation efficiency, E is the electric field, k_B is the Boltzmann constant, and T the temperature. The auxiliary parameter κ is defined as $\kappa \equiv \sqrt{e^3/\pi\epsilon\epsilon_0}$ with e the electron's charge, ϵ the dielectric constant, and ϵ_0 the permittivity of vacuum. The semiclassical Onsager-Braun theory has been applied to a variety of organic photovoltaic devices in a few studies,^{5,6} where Gaussian-distributed static disorder is taken into account, but the influence of phonons, despite its well-known importance to molecular materials, is often neglected.

At variance with their traditional inorganic counterparts, organic semiconductors are characterized by π -conjugated bonds and π - σ hybridization, in addition to strong electron-phonon (e-p) coupling, which greatly affects exciton dissociation in organic semiconductors.⁷ The effect of phonons, also known as dynamic disorder,⁸ leads to a number of interesting features related to electronic transport in organic semiconducting devices, such as the coherent-incoherent crossover.⁹ In particular, the phonons can be categorized into the fast and slow types. The fast phonons, mainly from the intramolecular C-C stretches, are considered to be the source of decoherence.⁹ On the other hand, the slow phonons with a characteristic time scale longer than 1 ps are induced by the librational and torsional motion (intermolecular and intramolecular). The slow phonons are the main source of dynamics disorder, giving rise to a significant influence on transport in organic materials, a subject that has attracted intense attention.^{10–13} Among theoretical tools available to describe transport properties in organic semiconductors, the hierarchy equations of motion (HEOM) formalism pioneered by Tanimura and his colleagues pointing to a promising path to numerically exact solutions that captures non-Markovian features of those systems.^{14,15} The last decade saw developments of HEOM algorithms that are more efficient, and more friendly for numerical computation,^{16–19} as well as extensions of HEOM applications to fields such as modeling 2D optical spectra of light-harvesting systems,^{20,21} simulating entanglement dynamics with sustained system-bath coherence,^{22–24} probing dissipative effects in the spin-boson model^{25,26} and molecular systems.^{27–31} Very recently, Sakurai and Tanimura reformulated the HEOM method to study quantum dynamics in semiconducting devices using the Wigner function (WF) formalism,^{32–36} which greatly extends the applicability of HEOM. In this work, the WF-HEOM approach is adopted to investigate the exciton

^{a)}Electronic mail: YZhao@ntu.edu.sg

FIG. 1. Schematic for exciton dissociation in a donor-acceptor heterojunction structure of an organic photovoltaic device. Here, HOMO and LUMO denote, respectively, the highest occupied molecular orbital and the lowest unoccupied molecular orbital, in which the hole and electron are residing. The blue solid line denotes the superposed potential for the electron. At the end of the acceptor there is a sink formed by the metallic electrode.

dissociation process taking into consideration the phonon effect.

This paper is organized as follows. The exciton dissociation model, the WF formalism, and the HEOM approach are introduced in Sec. II. Results will be presented in Sec. III, where a comparison between the HEOM method and the Onsager-Braun theory is given. The phonon effects on the exciton dissociation will be addressed in Sec. III as well. Conclusions are drawn in Sec. IV.

II. METHODOLOGY

With the Wigner distribution function (also known as WF) obtained by transforming two independent coordinate variables, x and x' , to a pair of new variables, $q = \frac{1}{2}(x + x')$ and $r = x - x'$,³⁷ the WF formalism is a very powerful approach to deal with quantum transport problems in a rigorous manner.³² Considering a single electron residing in a potential $U(\hat{q})$ defined in the real space with coordinate q , the Hamiltonian can be written as

$$H_e = \frac{\hat{p}^2}{2m} + U(\hat{q}), \quad (2)$$

where p is the momentum, and m is the effective mass of the electron. It follows that the WF reads

$$W(q, p) = \int_{-\infty}^{\infty} dr \cdot e^{-ipr/\hbar} \rho \left(q + \frac{1}{2}r, q - \frac{1}{2}r \right), \quad (3)$$

where ρ is the system density matrix operator. $W(q, p)$ follows an equation of motion

$$\begin{aligned} \frac{\partial W}{\partial t} &= -\hat{\mathcal{L}}W \\ &= -\frac{p}{m} \frac{\partial W}{\partial q} - \frac{1}{2\pi\hbar^2} \int_{-\infty}^{\infty} dp' \cdot V(q, p - p') W(q, p'), \end{aligned} \quad (4)$$

where $\hat{\mathcal{L}}$ is the Liouville operator; $V(q, p)$ is the potential operator defined as

$$V(q, p) = \int_0^{\infty} dr \cdot 2 \sin(pr/\hbar) \left[U \left(q + \frac{1}{2}r \right) - U \left(q - \frac{1}{2}r \right) \right]. \quad (5)$$

To solve Eq. (4), one has to employ a proper procedure in which the coordinate and momentum are discretized such that $W(p, q)$ and $V(p, q)$ become finite-dimension matrices. By definition, the matrix $V(p, q)$ is antisymmetric with purely imaginary eigenvalues which makes rather unstable the numerics of solving Eq. (4). To circumvent this problem, the “upwind” difference scheme is used for the kinetic term.³⁷ Furthermore, applied throughout this work are the inflow and outflow boundary conditions,³⁷ which read

$$W(0, p)|_{p>0} = W_l(p), \quad (6)$$

$$W(L, p)|_{p<0} = 0, \quad (7)$$

where L is the distance from the interface to the electron sink. $W_l(p)$, which has the form of the ordinary Boltzmann distribution, and the “0” on the right hand side of Eq. (7), represent the electron source and sink, respectively.

The most important quantities to be computed are the density and current distributions in the real space, which are given as follows:

$$N_q = \sum_p \frac{\Delta_p}{2\pi\hbar} W_{q,p} \quad (8)$$

and

$$I_{q,q+\Delta_q} = \sum_p \frac{\Delta_p}{2\pi m\hbar} (p W_{q,p}|_{p>0} + p W_{q+\Delta_q,p}|_{p<0}), \quad (9)$$

where Δ_q and Δ_p are the mesh sizes for the coordinate and momentum, respectively. Thanks to the antisymmetric property of the $V(p, q)$ matrices, it is found from Eq. (4) that the current density I defined by Eq. (9) must be uniformly distributed in the real space when the steady state is achieved. In practice, however, due to the numerical instability of the integral equations, technically one needs to be very careful on possible divergence problems. In our computations, it is found that systems with large e-p coupling are less stable than those with weak coupling.

The above WF formalism could be applied straightforwardly to the reduced, non-perturbative HEOM approach³³

$$H = H_e + H_{ph} + H_{e-p}, \quad (10)$$

where H_e is defined in Eq. (2), and the remaining two terms are given as

$$H_{ph} = \sum_i \left(\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2 \right) \quad (11)$$

and

$$H_{e-p} = - \sum_i \lambda_i x_i \left(\xi q + \frac{1}{2} \xi q^2 \right), \quad (12)$$

where x_i , p_i , m_i , and ω_i are the coordinate, momentum, effective mass, and frequency of the i th phonon mode in the

bath, respectively; λ is the e-p coupling; ξ and ζ denote the linear-linear and linear-square coupling strength, respectively. Competition among various coupling terms usually leads to rich physics, but for simplicity, we do not consider the linear-square term in Eq. (12), and set $\zeta = 0$ in this work. The spectral density of the phonon bath has the Ohmic form with a Lorentzian cutoff, i.e., $J(\omega) = \alpha\omega/\pi(\omega^2 + \nu_0^2)$, where ν_0 denotes the decay speed of the spectrum tail, and α , the e-p coupling strength. From the spectral function, one can determine that the unit of α is $\text{meV nm}^{-2} \text{ps}^{-1}$. Considering that the intermolecular distance between organic molecules is around 1 nm and the characteristic time scale for the effective phonon mode is 1 ps, a scaling parameter $\alpha_0 = 1 \text{ meV nm}^{-2} \text{ps}^{-1}$ can be defined, and the choice of α in our work is in the range of $10\text{--}100\alpha_0$ ($\sim 10\text{--}100 \text{ meV}$) representing the typical coupling strength in organic systems.³⁸

It is worth noting that the Lorentzian spectral density of the phonon bath may induce a strong non-Markovian feature³⁶ as the usual sub-Ohmic spectral density, but the infrared divergence poses implementation problems for the latter. Here, the Lorentzian spectral density adopted in the HEOM algorithm bypasses divergence issues at low frequencies, and therefore is chosen for this study.

For Hamiltonian (10), a hierarchy of equations of motion can be derived by hierarchically expanding the WF with a set of exponentially decaying terms $W_{j_0, j_1, \dots, j_k, \dots}$:

$$\begin{aligned} \frac{\partial}{\partial t} W_{j_0, j_1, \dots, j_k, \dots} = & - \left(\hat{\mathcal{L}} + \hat{\Xi} + \sum_{k=0}^K j_k \nu_k \right) W_{j_0, j_1, \dots, j_k, \dots} \\ & + \sum_{k=0}^K \hat{\Phi} W_{j_0, j_1, \dots, j_k+1, \dots} + \sum_{k=0}^K j_k \nu_k \hat{\Theta}_k W_{j_0, j_1, \dots, j_k-1, \dots}, \end{aligned}$$

where the indices j_k denote the different level of hierarchies, $\nu_k \neq 0 \equiv 2\pi k/\hbar$ is the k th Matsubara frequency, the damping parameter ν_0 is set to 100 ps^{-1} throughout this work, and various auxiliary Liouville-space operators defined as

$$\hat{\Xi} = -\frac{\alpha\xi^2}{\beta\nu_0^2} \left[1 - \sum_{k=0}^K \gamma_k \right] \frac{\partial^2}{\partial p^2}, \quad \hat{\Phi} = \xi \frac{\partial}{\partial p}, \quad (13)$$

$$\hat{\Theta}_0 = \frac{\alpha\xi}{m\nu_0} \left[p + \frac{m\gamma_0}{\beta} \frac{\partial}{\partial p} \right], \quad \hat{\Theta}_{k \neq 0} = \frac{\alpha\xi\gamma_k}{\beta\nu_0^2} \frac{\partial}{\partial p}. \quad (14)$$

Here $\gamma_0 = \beta\hbar\nu_0 \cot(\beta\hbar\nu_0/2)/2$, $\gamma_{k \neq 0} = 2\nu_0^2/(\nu_k^2 - \nu_0^2)$, and $\beta \equiv 1/k_B T$. Following the terminology of HEOM, all terms of $W_{j_0, j_1, \dots, j_k, \dots}$, with the exception of $W_{0, \dots, 0, \dots}$, are called auxiliary density operators (ADOs) which account for the phonon dynamics. For control parameters suitable for semiconducting devices and at room temperature, it is sufficient to keep three hierarchy levels and up to third Matsubara frequencies in order to reach convergence. $W_{0, \dots, 0, \dots}$ is the real density operator for the system, from which the density and current distribution can be calculated following Eqs. (8) and (9). In addition, as both α and ξ denote the e-p coupling strengths, in the interest of simplicity, these parameters can be merged into a more compact form by setting ξ to be unity.

III. RESULTS AND DISCUSSIONS

A. I-V curve in resonant tunneling diodes

We first test our HEOM program in a resonant tunneling diode with a sandwiched semiconducting structure. The double-barrier structure has always been taken as the very starting point for WF-based HEOM simulations³² as the effect of negative differential resistance (NDR) appearing in such a structure yields the most convenient criterion on how faithfully the approach captures the quantum effect. Similarly, the NDR effect also exists in organic semiconducting devices, where it is believed to originate in the tunneling process across the energy barrier at the metal/organic interface.³⁹ Here, we use the WF-HEOM approach to calculate the current-voltage (I-V) curves in the NDR regime for a semiconducting material that bridges two electrodes in the presence of two Gaussian-shaped interface energy barriers given by $a \exp[-(q - q_0)^2/c^2]$ with $a = 0.3 \text{ eV}$ and $c = 2 \text{ nm}$. The distance between these two barriers is 5 nm, and the rest of model parameters are: the electron effective mass is $0.067m_0$ with m_0 the mass of free electron; the discretization number for coordinate and momentum N_q and N_p are 80 and 60, respectively; the mesh spacing Δ_q is 0.5 nm such that $\Delta_p = \pi/N_q \Delta_q$. The boundary condition for the density will be fixed to 0.0019 nm^{-3} .

Shown in Fig. 2 are computed I-V curves with and without the e-p coupling. For the case of $\alpha = 0$, the NDR effect is reproduced, and the current peaks at around 0.17 V. With increasing α , the current is found to increase but the position of its maximum does not change. For the case of $\alpha = 50\alpha_0$, noisy results are obtained in the low voltage regime due to the aforementioned numerical instability. To make sense of the influence of the e-p coupling on the I-V curve, we display in Fig. 3 the spatial distribution of the electron density at a bias voltage of 0.17 V. In the absence of the e-p coupling, there is a uniform distribution away from the double-barrier, while it is found that electrons occupy available states within the double-barrier region. Alternatively, in the presence of the e-p coupling, the system becomes dynamically disordered, and the distribution of electron density exhibits oscillations that facilitate electrons to overcome the double barrier resulting in an increase in current. Each data point requires more than 10 h of computation on a Linux-based computing cluster, with each CPU being a 2.67 GHz Intel processor, rendering the

FIG. 2. The I-V curves for four strengths of e-p coupling. Inset shows the dependence of current at 0.17 V on the e-p coupling.

FIG. 3. The spatial distribution of the electron density for four strengths of e-p coupling at a bias voltage of 0.17 V.

WF-HEOM method less efficient than the scattering-operator method.³⁹ However, it is easier to apply the WF-HEOM approach to our system than the scattering-operator method. In particular, the NDR effect has been reproduced for the semiconducting devices in a unified manner, while with scattering operator method, results need to be rescaled on a case-by-case basis. We expect performance improvements for the WF-HEOM approach given more careful treatments of device models and boundary conditions. Hereafter, we will focus on applying our approach to a process of exciton dissociation in heterojunction devices.

B. The Onsager-Braun theory

The setup for exciton dissociation is shown in Fig. 1, and the potential energy can be written as $U(q) = -e^2/4\pi\epsilon_0\epsilon q - eEq$. The control parameters are: $\epsilon = 3.5$; $\Delta_q = 1 \text{ nm}$; the sink energy is set to be 0.3 eV; the remaining parameters are the same as those described earlier. It is worth noting that, one of the most important characteristics of organic materials is their low dielectric constants, as compared with inorganic materials (usually greater than 10),³⁴ which makes inefficient traditional device-modeling techniques due to easy divergence of the spatial distribution of the electric field and the electronic concentration. An alternative approach is thus in need.

In organic devices, the current usually consists of drift, diffusion, dissociation, and recombination components. The steady-state current I is, in the presence of the fixed boundary condition, proportional to the dissociation efficiency η at the interface. The current I is first calculated, and its inverse, $1/I$, is compared with $f(E) = \exp(-\kappa\sqrt{E}/k_B T)$ in Fig. 4 in order to assess the validity of Onsager-Braun theory for this structure. A linear relation is clearly established between $1/I$ and $f(E)$ for electric fields below 10^4 V/cm in Fig. 4, which shows that using a quantum-mechanical approach, we have reproduced the semiclassical results of the phenomenological Onsager-Braun theory in the weak field regime. It is easy to understand that quantum effects, such as tunneling, are vanishingly small in the presence of weak electric fields, a result that is also consistent with that obtained earlier for the double-barrier structure. It is found that our calculated currents deviate from those given by the Onsager-Braun theory, signaling the emergence of the quantum effects on the current. The

FIG. 4. The inverse of the current $1/I$ as a function of $f(E)$. The red line indicates that the linear relationship is valid up to $E = 10^4 \text{ V/cm}$. Inset shows the relation between I and E .

threshold value of the electric field on this divergence depends on the sink energy, and the greater the sink energy, the higher the threshold current. Here, we have only studied a case of low sink energy, one that is known to fall outside the applicable range of the traditional device-modeling methods.⁴⁰ We conclude that the WF-HEOM approach employed here is capable to handle organic systems with much lower dielectric constants than their inorganic counterpart.

C. Exciton dissociation in the phonon bath

Despite being a hard task traditionally, it is important to consider the influence of phonons on the exciton dissociation process in organic materials. Here, using the HEOM approach, it is feasible to address the issue of phonons, and Fig. 5 displays the calculated inverse current $1/I$ as a function of $f(E)$ for various e-p coupling strengths. At variance with the case of zero e-p coupling, the presence of finite e-p coupling induces deviations from the linear relation predicted by the Onsager-Braun theory. In particular, substantial divergence is found even for medium coupling, such as $\alpha = 10\alpha_0$, which implies that semiclassical theories are insufficient to model molecular materials, and the role of phonons must be carefully taken into consideration. On the other hand, the curves in Fig. 5 seem to display shallow dips, especially obvious for the case $\alpha = 30\alpha_0$, due to the fact that they consist of two distinctive components corresponding to two regimes of the electric field. In a weak field, the quantum tunneling effect

FIG. 5. The inverse of the current $1/I$ as a function of $f(E)$ for four e-p coupling strengths.

FIG. 6. (a) The spatial distribution of the electron density for four e-p coupling strengths. The zero point of the position is defined at the heterojunction interface. (b) The Wigner distribution function versus p/h and q for $\alpha = 30\alpha_0$.

dominates and overwhelms that of the dynamic disorder, while in a strong field, the dynamic disorder plays a dominating role, and a semiclassical regime is established resulting in the absence of the tunneling effect.

Spatial distributions of the electronic density are shown in Fig. 6(a) for various e-p coupling strengths in an effort to gain deeper understandings of the divergence. It is found that in the presence of the e-p coupling the electronic density shoots up and becomes several times of that with no e-p coupling. It is this density increase, accompanied by spatial density oscillations, that gives rise to the increase in current and the divergence in the Onsager-Braun theory. The oscillations of the density distribution in the real space become more evident with the increase in the e-p coupling, signaling the emergence of the quantum effects, which cannot be captured by the traditional, semiclassical approaches. In order to show that it is indeed a quantum effect, we display in Fig. 6(b) the Wigner distribution function which depends on both q and p for $\alpha = 30\alpha_0$. It is known that if the quantum tunneling is important, the Wigner distribution function turns negative as opposed to its complete positivity for the classical case. It is clearly shown that in the presence of e-p coupling, oscillations of the Wigner distribution frequently take it into the negative territory, especially when the momentum is not too large. Therefore, both the density and the Wigner distribution demonstrate that the quantum tunneling effect has been appropriately accounted for in our theory.

D. Time evolution of the exciton dissociation process

One of the most important applications of organic semiconductors is photovoltaic devices. The characteristics of the

FIG. 7. (a) Time evolution of the current distribution with a sudden switch on of an electric field of $0.7 \times 10^4 \text{ V/cm}$. The red dashed arrow shows the direction of time evolution with a spacing of 2 fs between two consecutive snapshots. (b) Time evolution of the current at the position 2 nm.

transient photo-voltage/current (TPV/TPC) curves are known to have an ultrafast initial spike, and a polarity change, followed by a long-term decay.⁴¹ Using the HEOM approach, we are able to reproduce such a representative TPC lineshape, as shown in Fig. 7. Here, the initial density distribution is chosen to be uniform at 0.0019 nm^{-3} . At $t = 0$, an electric field of $0.7 \times 10^4 \text{ V/cm}$ is suddenly switched on, and the current distribution is computed step by step. In Fig. 7(a), we display the current distribution every 2 fs up to 34 fs. It is found that at the initial stage, there is a reverse current near the interface, caused by the hold-induced attractive potential. Soon after this ultrafast negative signal, a positive wave packet appears and slowly moves from the interface to the sink with a well-defined shape, demonstrating a clear picture of the electronic time-of-flight process. In Fig. 7(b) the time dependence of the current near the interface is shown, where the ultrafast initial spike, the polarity change, and the long-term decay can be clearly observed.

The result here proves that the HEOM approach can be used to study not only the steady-state behavior, as we have shown in Subsections III A–III C, but also transient processes in the real-time domain. More importantly, both aspects are handled within a unified theoretical framework. It is thus very useful to extend this method to settle a variety of contentious issues in organic systems.

IV. CONCLUSIONS

In summary, we have presented several proof-of-principle studies on the transport properties of organic semiconductors combining the reduced HEOM approach with the

WF formalism. First, we have probed the I-V characteristics in a resonant tunneling diode reproducing the NDR effect. It is found that the phonon bath can enhance the current. Then the exciton dissociation process is investigated with and without the phonon bath. It is shown that in the absence of the phonons, calculated currents agree with the Onsager-Braun theory in weak electric fields, while in the presence of phonons, the curves deviate significantly from those predicted by the Onsager-Braun theory even for moderate e-p coupling, rendering semiclassical theory invalid for molecular materials with dynamical disorder. Finally, the transient behavior of the photocurrent is also studied, and the initial ultrafast polarity change is reproduced. Our results in this work encourage applications of the HEOM method to resolve various contentious issues in organic systems. For example, it is often recognized that the Einstein's relation is invalid in strongly disordered molecular materials⁴² as such systems are always far from thermal equilibrium. The HEOM method is again a strong candidate for investigating this issue in a comprehensive manner because in the view of lack of alternative efficient computation tools to deal with out-of-equilibrium molecular systems.

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APPENDIX: DERIVATION OF THE REDUCED HEOM UNDER THE WIGNER REPRESENTATION

To derive the reduced HEOM in the Wigner representation, we start from the reduced density operator for electrons (System A) in the coordinate representation. When the initial state of the total system is separable for the electron and the phonon bath degrees of freedom, the reduced density matrix can be expressed in the following form using the path integral language:

$$\begin{aligned} \rho(q, q', t) = & \int_{-\infty}^{\infty} dq_i \int_{-\infty}^{\infty} dq'_i \int_{q(t_0)=q_i}^{q(t)=q} D[q(\tau)] \\ & \int_{q'(t_0)=q'_i}^{q'(t)=q'} D[q'(\tau)] \rho(q_i, q'_i, t_0) \\ & \times \exp\left(\frac{i}{\hbar} S_A(q, t, t_0)\right) F(q, q'; t, t_0) \\ & \times \exp\left(-\frac{i}{\hbar} S_A(q', t, t_0)\right), \end{aligned} \quad (\text{A1})$$

where

$$S_A(q, t, t_0) = \int_{t_0}^t L_A(q, \dot{q}, \tau) d\tau \quad (\text{A2})$$

is the classical action of the electrons and

$$\begin{aligned} F(q, q'; t, t_0) = & \exp\left[-\frac{1}{\hbar^2} \int_{t_0}^t d\tau' \left[iL_1(\tau' - t_0) \right. \right. \\ & \times [q(\tau') - q'(\tau')] \cdot [q(t_0) + q'(t_0)] \\ & + \int_{t_0}^{\tau'} iL_1(\tau' - \tau) [q(\tau') - q'(\tau')] \\ & \times [\dot{q}(\tau) + \dot{q}'(\tau)] + \int_{t_0}^{\tau'} d\tau L_2(\tau' - \tau) \\ & \left. \left. \times [q(\tau') - q'(\tau')] \cdot [q(\tau) - q'(\tau)] \right] \right] \end{aligned} \quad (\text{A3})$$

is the Feynman-Vernon influence functional, in which

$$iL_1(t) = \xi^2 \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t), \quad (\text{A4})$$

$$L_2(t) = \xi^2 \int_0^\infty d\omega J(\omega) \coth(\beta\hbar\omega/2) \cos(\omega t). \quad (\text{A5})$$

If we employ the Lorentz spectral density function $J(\omega)$, the integrals can be evaluated and $iL_1(t)$ and $L_2(t)$ can be expressed as

$$iL_1(t) = i \frac{\hbar\alpha\xi^2}{2\nu_0} e^{-\nu_0 t}, \quad (\text{A6})$$

$$\begin{aligned} L_2(t) = & \frac{\hbar\alpha\xi^2}{2} \left[\cot\left(\frac{\beta\hbar\nu_0}{2}\right) e^{-\nu_0 t} \right. \\ & \left. - \sum_{k=1}^{\infty} \frac{8k\pi}{(\beta\hbar\nu_0)^2 - (2k\pi)^2} e^{-\nu_k t} \right]. \end{aligned} \quad (\text{A7})$$

For the case of high temperature, i.e., $\beta\hbar\nu_0 \leq 1$, the terms involving the expansion on Matsubara frequency become unimportant and can be neglected. However, here we keep all the terms to provide a comprehensive formulation.

Similar to the deduction in Ref. 16, through analyzing and decomposing the influence functional Eq. (A3), we introduce the auxiliary operator $\hat{\rho}_{j_0, j_1, \dots, j_K}$ whose matrix element in coordinate representation reads

$$\begin{aligned} \rho_{j_0, j_1, \dots, j_K}(q, q', t) = & \int_{-\infty}^{\infty} dq_i \int_{-\infty}^{\infty} dq'_i \int_{q(t_0)=q_i}^{q(t)=q} D[q(\tau)] \\ & \int_{q'(t_0)=q'_i}^{q'(t)=q'} D[q'(\tau)] \rho(q_i, q'_i, t_0) \\ & \times \left[\frac{\alpha\xi}{2\nu_0} e^{-\nu_0(t-t_0)} [q(t_0) + q'(t_0)] \right. \\ & \left. - \int_{t_0}^t d\tau e^{-\nu_0(t-\tau)} \Theta_0(q, q', \tau) \right]^{j_0} \\ & \times \prod_{k=1}^K \left[- \int_{t_0}^t d\tau \nu_k \Theta_k(q, q', \tau) e^{-\nu_k(t-\tau)} \right]^{j_k} \\ & \times \exp\left(\frac{i}{\hbar} S_A(q, t, t_0)\right) F(q, q'; t, t_0) \\ & \times \exp\left(-\frac{i}{\hbar} S_A(q', t, t_0)\right), \end{aligned} \quad (\text{A8})$$

and the involved operators are as follows:

$$\Theta_0(q, q', \tau) = \frac{i\alpha\xi}{2m\nu_0} \left[\hbar \left(\frac{\partial}{\partial q} - \frac{\partial}{\partial q'} \right) + m\nu_0 \cot \left(\frac{\beta\hbar\nu_0}{2} \right) (q - q') \right], \quad (\text{A9})$$

$$\Theta_k(q, q', \tau) = \frac{i\alpha\xi}{\beta\hbar\nu_0^2} \frac{2\nu_0^2}{\nu_k^2 - \nu_0^2} (q(\tau) - q'(\tau)). \quad (\text{A10})$$

It is apparent that $\hat{\rho}_{0,0,\dots,0}$ is exactly the reduced density operator of electrons. By calculating the temporal derivative of the right hand side of Eq. (A8), we obtain the equations of motion for these hierarchical auxiliary operators, which have the form of

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{j_0, j_1, \dots, j_K} = & - \left[\frac{i}{\hbar} \mathcal{L}_A + \sum_{k=0}^K j_k \nu_k + \hat{\Xi} \right] \hat{\rho}_{j_0, j_1, \dots, j_K} \\ & - \sum_{k=0}^K \hat{\Phi} \hat{\rho}_{j_0, j_1, \dots, j_k+1, \dots, j_K} \\ & - \sum_{k=0}^K j_k \nu_k \hat{\Theta}_k \hat{\rho}_{j_0, j_1, \dots, j_k-1, \dots, j_K}, \end{aligned} \quad (\text{A11})$$

and the operators wherein are defined as

$$\hat{\Phi} = \frac{i\xi}{\hbar} q^\times, \quad (\text{A12})$$

$$\hat{\Theta}_0 = i \frac{\alpha\xi}{2m\nu_0} \left[ip^\circ + m\nu_0 \cot \left(\frac{\beta\hbar\nu_0}{2} \right) q^\times \right], \quad (\text{A13})$$

$$\hat{\Theta}_k = i \frac{\alpha\xi}{\beta\hbar\nu_0^2} \frac{2\nu_0^2}{\nu_k^2 - \nu_0^2} q^\times, \quad (\text{A14})$$

$$\begin{aligned} \hat{\Xi} = & \frac{\alpha\xi^2}{\beta\hbar^2\nu_0^2} \left[1 - \frac{\beta\hbar\nu_0}{2} \cot \left(\frac{\beta\hbar\nu_0}{2} \right) \right] q^\times q^\times \\ & - \sum_{k=1}^K \hat{\Phi} \hat{\Theta}_k. \end{aligned} \quad (\text{A15})$$

Here $q^\times$ (p°) denotes the commutator (anti-commutator) of the coordinate (momentum) operator q (p) with another operator. If this operator is denoted as f , we have

$$q^\times f = qf - fq, \quad (\text{A16})$$

$$p^\circ f = pf + fp. \quad (\text{A17})$$

Now we transfer the formulation to the Wigner representation. The auxiliary Wigner hierarchical element $W_{j_0, j_1, \dots, j_K}$ is defined, which is related to its density matrix counterpart $\rho_{j_0, j_1, \dots, j_K}(x = q + r/2, x' = q - r/2)$ through

$$\begin{aligned} W_{j_0, j_1, \dots, j_K}(q, p) = & \int_{-\infty}^{\infty} dr e^{-ipr/\hbar} \\ & \times \rho_{j_0, j_1, \dots, j_K} \left(q + \frac{r}{2}, q - \frac{r}{2} \right). \end{aligned} \quad (\text{A18})$$

According to Eq. (A18), it is clear that

$$r = i\hbar \frac{\partial}{\partial p}. \quad (\text{A19})$$

We perform a Fourier transform on both sides of Eq. (A11) and substitute Eq. (A19) into it at the same time. The HEOM in the Wigner representation can be easily derived as follows:

$$\begin{aligned} \frac{\partial}{\partial t} W_{j_0, j_1, \dots, j_K} = & - \left[\mathcal{L}_w + \sum_{k=0}^K j_k \nu_k + \hat{\Xi} \right] W_{j_0, j_1, \dots, j_K} \\ & + \sum_{k=0}^K \hat{\Phi} W_{j_0, j_1, \dots, j_k+1, \dots, j_K} \\ & + \sum_{k=0}^K j_k \nu_k \hat{\Theta}_k W_{j_0, j_1, \dots, j_k-1, \dots, j_K}, \end{aligned} \quad (\text{A20})$$

where the quantum Liouvillian $\mathcal{L}_w$ is the same as that in Eq. (4) and the contained operators are transformed into

$$\hat{\Phi} = \xi \frac{\partial}{\partial p}, \quad (\text{A21})$$

$$\hat{\Theta}_0 = \frac{\alpha\xi}{m\nu_0} \left[p + \frac{m\hbar\nu_0}{2} \cot \left(\frac{\beta\hbar\nu_0}{2} \right) \frac{\partial}{\partial p} \right], \quad (\text{A22})$$

$$\hat{\Theta}_k = \frac{\alpha\xi}{\beta\nu_0^2} \frac{2\nu_0^2}{\nu_k^2 - \nu_0^2} \frac{\partial}{\partial p}, \quad (\text{A23})$$

$$\begin{aligned} \hat{\Xi} = & - \frac{\alpha\xi^2}{\beta\nu_0^2} \left[1 - \frac{\beta\hbar\nu_0}{2} \cot \left(\frac{\beta\hbar\nu_0}{2} \right) \right] \frac{\partial^2}{\partial p^2} \\ & - \sum_{k=1}^K \hat{\Phi} \hat{\Theta}_k. \end{aligned} \quad (\text{A24})$$

When the hierarchical order j_0 or the Matsubara frequency order j_k is sufficiently large, the auxiliary WF elements with higher orders do not play dominant roles. Then the HEOM could be truncated so that a set of closed equations may emerge. The truncation condition is

$$N = \sum_{k=0}^K j_k \gg \frac{\omega_c}{\min(\nu_0, \nu_1)}, \quad (\text{A25})$$

where ω_c is the characteristic frequency of the electron motion. Under this condition Eq. (A20) can be approximated as

$$\frac{\partial}{\partial t} W_{j_0, j_1, \dots, j_K}(t) = - \left(\frac{i}{\hbar} \mathcal{L}_w + \hat{\Xi} \right) W_{j_0, j_1, \dots, j_K}(t). \quad (\text{A26})$$

Equations (A20) and (A26) form a set of closed equations, from which the desired Wigner function $W_{0, \dots, 0}^{(0)}$ can be solved.

To write Eq. (A20) and the operators in it into a more compact form, we define

$$\gamma_0 = \beta\hbar\nu_0 \cot(\beta\hbar\nu_0/2)/2, \quad (\text{A27})$$

$$\gamma_{k \neq 0} = 2\nu_0^2 / (\nu_k^2 - \nu_0^2), \quad (\text{A28})$$

and substitute $\gamma_0, \gamma_{k \neq 0}$ into Eq. (A20). Then Eq. (13) is obtained.

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