Electron transfer under the Floquet modulation in donor–bridge–acceptor systems

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Electron transfer (ET) processes are of broad interest in modern chemistry. With the advancements of experimental techniques, one may modulate the ET via such as the light–matter interactions. In this work, we study the ET under a Floquet modulation occurring in the donor–bridge–acceptor systems, with the rate kernels projected out from the exact dissipaton equation of motion formalism. This together with the Floquet theorem enables us to investigate the interplay between the intrinsic non-Markovianity and the driving periodicity. The observed rate kernel exhibits a Herzberg–Teller–like mechanism induced by the bridge fluctuation subject to effective modulation.

Introduction. Electron transfer (ET) processes are of broad interest in modern chemistry,1–4 and many of them occur in the donor–bridge–acceptor (DBA) scenarios.5–12 The bridge, which remains itself before and after the reaction, could be considered as a rigid spacer within an intramolecular ET system.10 In condensed phases, the solvent environment also plays a crucial role.13–17 Fluctuations of both the bridge and the solvent will manifestly affect the rate of ET processes. From a theoretical point of view, one can in principle exactly construct the generalized rate equation,

\[ \hat{P}_D(t) = -\int_0^t d\tau k(t-\tau; t)P_D(\tau) + \int_0^t d\tau k'(t-\tau; t)P_A(\tau). \]  

(1)

Here, \( P_D(t) \) and \( P_A(t) \) are the donor and acceptor populations, respectively. The forward and backward rate memory kernels, \( k(\tau; t) \) and \( k'(\tau; t) \), have involved the influences of the bridge fluctuations, the solvent effects and the possibly existent external modulations.18,19 Here, the variable \( \tau \) characterizes the memory timescale, i.e., the non-Markovianity, and \( t \) represents the time–dependence due to the external fields.

With the advancements of experimental techniques, one can modulate the ET process via such as light–matter interactions. Especially, if the external modulation is periodic, it is called the Floquet modulation.20–24 In this Letter, we investigate how the ET rate kernels will be influenced by the fluctuating bridges and Floquet modulation, with attention to the intrinsic non-Markovianity and the external periodicity. Specifically, we will focus on the case in which the energy difference between the donor state \(|D\rangle\) and the acceptor state \(|A\rangle\) is periodically modulated, which can be realized via the field–dipole interaction or the Stark effect.23 We first give a perturbative analysis, followed by the discussion on the influences of the fluctuating bridge and the period of modulation. Then the non-Markovian rate kernels in Eq. (1) are projected out from the exact dissipaton equation of motion (DEOM).25 This is the second quantization generation of the notable hierarchical equations of motion (HEOM) formalism,26–31 covering both the reduced system and hybrid bath modes dynamics.25,32–34 The linear space algebra of DEOM facilitates the utilization of Nakajima–Zwanzig projection operator technique, so that we can focus on any subspace dynamics and construct non-Markovian rate kernels.19 The rate kernels are investigated with a DBA model system via both numerical and analytical methods in the DEOM framework. Especially, we pay attentions to the interplay between the intrinsic non-Markovianity and the driving periodicity, with the help of Floquet theorem. The observed rate kernel exhibits a Herzberg–Teller–like mechanism induced by the bridge fluctuation subject to effective modulation.

Theoretical model and perturbative analysis. Consider an ET DBA system with the total composite Hamiltonian,

\[ \hat{H}_{\text{ET}} = h_0|D\rangle\langle D| + (E^\circ + h_A)|A\rangle\langle A| + H_B + V(|\tilde{q}_k\rangle) (|D\rangle\langle A| + |A\rangle\langle D|). \]  

(2)

Here \( V(|\tilde{q}_k\rangle) \) depends on the bridge coordinates and the fluctuating bridges Hamiltonian is \( H_B = \sum_r \hat{\omega}^2 (\hat{p}_r^2 + \hat{q}_r^2) \). In Eq. (2), \( E^\circ \simeq \Delta_G^2 \) amounts to the standard reaction Gibbs energy, for the electron transferring from \(|D\rangle\) to \(|A\rangle\). Donor and acceptor are both associated with their own solvent environments, \( h_0 \) and \( h_A \), being \( h_0 = \sum_r \hat{\omega} \left( \hat{p}_r^2 + \hat{q}_r^2 \right) \) and \( h_A = \sum_r \hat{\omega} \left[ \hat{p}_r^2 + (x_j - d_j)^2 \right] \), respectively. The total ET composite was initially \( \rho_{eq}(t) = \rho_{eq}(T) \otimes |D\rangle\langle D| \), the thermal equilibrium in the donor state, with \( \rho_{eq}(T) \equiv (e^{-\beta H_0}/\text{tr}e^{-\beta H_0}) \otimes (e^{-\beta H_B}/\text{tr}e^{-\beta H_B}) \). Floquet modulation leads to the periodic changes of \( E^\circ \), as

\[ E^\circ \rightarrow E(t) = E^\circ + \mathcal{E} \cos(\Omega t) \]  

(3)

with the amplitude of \( \mathcal{E} \) and the frequency of \( \Omega \). We sketch these theoretical settings in Fig. 1.

In the absence of modulation (\( \mathcal{E} = 0 \)), the standard perturbation theory gives the forward rate constant the expression:10,12

\[ K_0 = 2\text{Re} \int_0^\infty dt \, v(t)e^{-i(E^\circ + \lambda) t}e^{-\gamma(t)}, \]  

(4a)

where \( v(t) = \langle V(|\tilde{q}_k(t)\rangle)|V(|\tilde{q}_k\rangle)\rangle_B \) with \( \tilde{q}_k(t) = e^{iH_BT}\tilde{q}_ke^{-iH_BT} \) and \( \langle \cdot \rangle_B \equiv \text{tr}(\cdot e^{-\beta H_B})/\text{tr}e^{-\beta H_B} \). In
FIG. 1: Schematics of ET under the Floquet modulation in the DBA system.

$V(\{q'_k\})$ depending on bridge coordinates

Accepter Donor

Floquet modulation

$E'$

$E$

$T_0 \equiv 2\pi/\Omega$ to modify the rate constant given by perturbation theory [cf. Eq. (4a)]. To this end, we do the approximation $H'_s(t) \rightarrow \bar{H}_T \equiv \frac{1}{T_0} \int_0^{T_0} dt' H'_s(t')$, and this amounts to $\bar{V}(t) \rightarrow \bar{V} \equiv V(\{\bar{q}_k\})J_0(\bar{E}/\Omega)$ with $J_0(z)$ being the zeroth order Bessel function. Therefore, the nonadiabatic rate under the high-frequency Floquet modulation reads

$$K_0 = 2J_0^2(\bar{E}/\Omega)Re\int_0^\infty dt \: v(t)e^{-i(\bar{E}^2 + \lambda)t}e^{-\gamma(t)}.$$  (8)

This perturbative rate formula serves as a reference for the following nonperturbative exhibitions.

*Projected DEOM to rate kernels.* For illustrations, we assume $V(\{\bar{q}_k\})$ the form of

$$V(\{\bar{q}_k\}) \equiv \langle V \rangle_n - \delta \bar{V} = \langle V \rangle_n - \sum_k \ddot{c}_h \ddot{q}_k.$$  (9)

This is the scenarios that can be exactly handled by DEOM–space quantum mechanics. To proceed we introduce

$$v(t) = \langle V \rangle_n^2 + \langle \delta \bar{V}(t) \delta \bar{V} \rangle_n = \langle V \rangle_n^2 + \sum_j \dddot{c}_j^2 \dddot{q}_j(t) \dddot{q}_j.$$  (10)

Now we can construct the DEOM based on Eq. (5), or equivalently Eq. (7): (i) In the former case, the system–plus–environment decomposition reads

$$H_T(t) = H_s(t) + h_e - |A\rangle\langle A|\delta \bar{V} - \bar{Q} \delta \bar{V},$$  (11)

with $h_e = h_D + h_B$, $H_s = (E^0 + \mathcal{E} \cos \Omega t + \lambda)|A\rangle\langle A| + \langle V \rangle_B|D\rangle\langle A| + |A\rangle\langle D|$, and $\bar{Q} = |D\rangle\langle A| + |A\rangle\langle D|$. In this case, the system Hamiltonian is time–dependent, while the dissipative mode $\bar{Q}$ is not; (ii) In the latter case,

$$H'_T(t) = H'_s(t) + h_e - |A\rangle\langle A|\delta \bar{V} - Q' \delta \bar{V}.$$  (12)

Compared with Eq. (11), the $H'_s(t) = (E^0 + \lambda)|A\rangle\langle A| + \langle V \rangle_B|D\rangle\langle A| + e^{i\varphi(t)}|A\rangle\langle D| |A\rangle\langle D|$ and $Q'(t) = e^{-i\varphi(t)}|D\rangle\langle A| + e^{i\varphi(t)}|A\rangle\langle D|$ are different from the former case. Both the system Hamiltonian and the dissipative mode $Q'(t)$ are time–dependent.

The rate kernels constructed from Eq. (11) should be exactly the same with that from Eq. (12), and our numerical results validate this point. The rate kernels are constructed via the DEOM approach. Based on the composite Hamiltonian in Eq. (11) or Eq. (12), we can write the DEOM in the form of

$$\rho(t) = -i\mathcal{L}(t)\rho(t).$$  (13)

This resembles $\dot{\rho}_v = -i\mathcal{L}_v(t)\rho_v$ with mapping the total system–plus–bath composite Liouvillian to the DEOM–space dynamics generator, $\mathcal{L}_v(t) \rightarrow \mathcal{L}(t)$, and $\rho_v(t) \rightarrow \rho(t) = \{\rho_v^n(t); n = 0, 1, 2, \cdots \}$. Here, $\mathcal{L}_v(t) \equiv [H_T(t), \cdot]$ in case (i) or $[H'_T(t), \cdot]$ in case (ii). We will leave the detailed information of the DEOM (13) in Supplementary
material (SM). To proceed, define DEOM–space projection operators, $\mathcal{P}$ and $\mathcal{Q} = \mathcal{I} - \mathcal{P}$, for partitioning $\rho \equiv \{\rho_n^{(a)} \}$ into the population and coherence components, respectively:\(^{19}\)

$$
\mathcal{P} \rho(t) = \left\{ \sum_a \rho_{aa}^{(0)}(t) |a\rangle \langle a|: 0, 0, \cdots \right\} \equiv \rho(t),
$$

$$
\mathcal{Q} \rho(t) = \left\{ \sum_{a \neq b} \rho_{ab}^{(0)}(t) |a\rangle \langle b|; \rho_n^{(n>0)}(t) \right\} \equiv \sigma(t).
$$

We can now recast the DEOM (13) in terms of

$$
\begin{bmatrix}
\dot{\rho}(t)
\dot{\sigma}(t)
\end{bmatrix} = -i \left[ \mathcal{P} \mathcal{L}(t) \mathcal{P} \mathcal{Q} \mathcal{L}(t) \mathcal{Q} \right] \begin{bmatrix}
\rho(t)
\sigma(t)
\end{bmatrix}.
$$

After some simple algebra we obtain\(^{19}\)

$$
\dot{\rho}(t) = \int_{t_0}^{t} d\tau \tilde{K}(t - \tau; t)p(\tau),
$$

with the rate kernel being formally of

$$
\tilde{K}(t - \tau; t) = -\mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}(t, \tau) \mathcal{Q} \mathcal{L}(t) \mathcal{P},
$$

with

$$
\mathcal{U}(t, \tau) \equiv \exp_{\omega} \left[ -i \int_{\tau}^{t} d\tau' \mathcal{L}(\tau') \right].
$$

Apparently, $-k(t - \tau; t)$ and $k(t - \tau; t)$ in Eq. (1) are the $|D\rangle \langle D| \rightarrow |D\rangle \langle D|$ and $|A\rangle \langle A| \rightarrow |D\rangle \langle D|$ components of $\tilde{K}(t - \tau; t)$, respectively.

Rate kernel analysis. In the following, we explicitly illustrate some key properties of the forward rate kernel $k(\tau; t)$ in Eq. (1), with the help of numerical examples. The analysis on $k(\tau; t)$ is similar and thus omitted due to the limitation of space. It is worth noting the periodicity, $k(\tau; t + \tau) = k(\tau; t)$, in SM. In Fig. 2, we explicitly exhibit an example of the computed rate kernels. The kernel $k(\tau; t)$ is plotted with respect to $\tau$ and $t$. The external modulation frequency adopts $\beta \Omega = 8 \pi$. As shown in Fig. 2, the kernel is periodic ($T_0 = 2\pi/\Omega$) with respect to $t$, and damping along the memory length, $\tau$. In the simulations, we model the spectral densities, $J_n(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} d\tau e^{i\omega \tau} \langle \delta U(t), \delta U(0) \rangle_0$, and $J_n(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} d\tau e^{i\omega \tau} \langle \delta V(t), \delta V(0) \rangle_0$, as\(^{35-37}\)

$$
J_n(\omega) = \frac{2\lambda \gamma \omega}{\omega^2 + \gamma^2} \quad \text{and} \quad J_n(\omega) = \frac{2\lambda \omega_0 \omega \zeta}{(\omega^2 - \omega_0^2)^2 + \omega^2 \zeta^2}.
$$

(18)

To further explicitly exhibit the underlying non-Markovianity, we represent the kernel in the frequency domain as

$$
K(\omega; t) = \int_{0}^{\infty} d\tau k(\tau; t) \cos(\omega \tau).
$$

(19)

**FIG. 2:** An example of rate kernel $k(\tau; t)$, in unit of $\beta^{-2}$. We adopt $\epsilon = 2$, $E^2 = 1.5$ and $(V)_B = 0.2$ [cf. Eq. (11)]. Besides, $\lambda = \lambda' = 0.2$ and $\gamma = \omega_0 = \zeta = 1$ [cf. Eq. (18)]. All these parameters are in units of $\beta^{-1}$.

Note the periodicity in $t$ remains, i.e. $K(\omega; t) = K(\omega; t + T_0)$. The Fig. 3 depicts the time–dependent frequency–resolved rate kernel, where this periodicity is manifest. Therefore, we may do the Fourier expansion with respect to $t$,

$$
K(\omega; t) = \sum_{n=-\infty}^{\infty} K_n(\omega)e^{-in\Omega t},
$$

(20a)

obtaining its components $\{K_n(\omega)\}$ being

$$
K_n(\omega) = \frac{1}{T_0} \int_{0}^{T_0} dt K(\omega; t)e^{in\Omega t}.
$$

(20b)

In Fig. 4, we plot the real parts of the Fourier components $\{K_n(\omega)\}$, exemplified with the same case as in Fig. 2. These frequency–domain components exhibit the interplay between the external frequency, $\Omega$, and the so–called Floquet frequency, $\omega_\phi$. The $\omega_\phi$ is identified as the characteristic frequency of the Floquet Hamiltonian, $H_\phi$, defined via $e^{iH_\phi t_0} \equiv \exp_{\omega} \left[ -i \int_{0}^{t_0} dt H_\phi(t) \right]$. As shown in the figure, in the case of $\beta\Omega = 8\pi$ and $\beta \omega_\phi \sim 3$, the
In the high–frequency limit, the rate constant is given by

\[ \dot{K}_\alpha(t) = K_\alpha^{(0)} + h_\text{e} - |A\rangle\langle A|\hat{\delta}\hat{\bar{V}} - \hat{\mu}_+ \hat{E}^+(t) - \hat{\mu}_- \hat{E}^-(t) \]

with

\[ H_\text{e}^{(0)} = (\omega^0 + \lambda)|A\rangle\langle A| + (V)_n|(D)\langle A| + |A\rangle\langle D|, \]

\[ \hat{\mu}_+ = |A\rangle\langle D|((V)_n - \delta\hat{V}) = (\hat{\mu}_-)^\dagger \text{ and } \hat{E}^+(t) = i\varphi(t) = [\hat{E}^-(t)]^\dagger. \]

The last two terms in Eq. (21) can be seen as an effective dipole–field coupling, where the total dipole involves the bridge degrees of freedom. This resembles a type of Herzberg–Teller coupling. In the Markovian and high–frequency limits, the rate constant is given by

\[ K'_0 = K_0(\omega = 0), \]

which shall be compared with the perturbative result in Eq. (8). In Fig. 6, we plot the rate constants \( K_0 \) and \( K'_0 \) versus \( E^0 \), with different strengths of bridge fluctuation. As shown in Fig. 6, in the regime of \( E^0 + \lambda \sim 0 \), the perturbative results with larger \( \lambda' \) depart more from the nonperturbative results.

**Summary.** In summary, we study the ET under the Floquet modulation occurring in the DBA systems. The rate kernels are constructed and evaluated via the exact projected dissipaton–equation–of–motion formalism. This enables us to investigate the interplay between the intrinsic non-Markovianity and driving periodicity. The bridge fluctuations manifestly affect the rate kernel, exhibiting a Herzberg–Teller–like mechanism subject to effective modulation. It is anticipated that our study will benefit the design of ET manipulation in molecular sys-
tems. The same method can be also applied to such as excitation energy transfer in light harvest systems.\textsuperscript{23}

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Supplementary material on “Electron transfer under the Floquet modulation in donor–bridge–acceptor systems”

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This supplementary material contains: (i) a brief introduction to DEOM, (ii) the rigorous proof of the periodicity of rate kernels, and (iii) the analytical analysis of the frequency–resolved rate kernels with the help of the Floquet theorem.

I. A BRIEF INTRODUCTION TO DEOM

Consider an arbitrary system coupled to the environment with the temperature $T$. Generally, the composite Hamiltonian can be decomposed into the system, the system–environment coupling and the environment parts as

$$H_{\pi}(t) = H_{S}(t) + \sum_{a} \dot{Q}_{a}(t) \hat{F}_{a} + h_{B}.$$  \hspace{1cm} (S1)

Here, the dissipative modes $\{\dot{Q}_{a}\}$ are rather arbitrary, while the environment Hamiltonian is adopted to be Gaussian. This requires not only $h_{B}$ to be harmonic but also the hybrid reservoir modes $\{\hat{F}_{a}\}$ be linear. That is

$$h_{B} = \frac{1}{2} \sum_{j} \omega_{j} (p_{j}^{2} + x_{j}^{2}) \quad \text{and} \quad \hat{F}_{a} = \sum_{j} c_{aj} x_{j}.$$  \hspace{1cm} (S2)

Here, the oscillators of frequency $\{\omega_{j}\}$, with position $\{x_{j}\}$ and momentum $\{p_{j}\}$, are coupled to the system with strength $\{c_{aj}\}$. As in the main text, we set $\hbar = 1$ and $\beta = 1/(k_{B}T)$, with $k_{B}$ being the Boltzmann constant. Specifically, Eq. (S1) with Eq. (S2) covers both the Hamiltonians in Eqs. (11) and (12) of the main text.

For the Gaussian environment (also named as “bath”), its influences on the system is totally characterized by the spectral density, $J_{ab}(\omega) = \frac{\beta}{2} \sum_{j} c_{aj} c_{bj} \delta(\omega - \omega_{j})$ for $\omega \geq 0$, and it is related to the statistical bath correlation via the fluctuation–dissipation theorem as\textsuperscript{1,2},

$$\langle \hat{F}_{a}(t) \hat{F}_{b}(0) \rangle_{B} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-\omega t} J_{ab}(\omega)}{1 - e^{-\beta \omega}} \simeq \sum_{k=1}^{K} \eta_{abk} e^{-\gamma_{k} t}.$$  \hspace{1cm} (S3)

Here, $\hat{F}_{a}(t) \equiv e^{i h_{B} t} \hat{F}_{a} e^{-i h_{B} t}$ is the hybridizing bath operator in the $h_{\pi}$-interaction picture. The average $\langle \hat{O} \rangle_{B} = \text{tr}_{B}(\hat{O} e^{-\beta h_{B}}) / \text{tr}_{B}(e^{-\beta h_{B}})$ runs over the bare–bath thermal equilibrium ensembles for any operator $\hat{O}$. The multi-exponential decomposition in the the last identity can be readily achieved with some advancing sum-over-pole schemes.\textsuperscript{3,4} The exponents from the poles of Bose function and the corresponding pre-exponents coefficients are both real. On the other hand, those originating from the spectral density are either real or complex conjugate paired. Therefore, we can define $\tilde{k}$ such that $\gamma_{\tilde{k}} = \gamma_{k}$.

Dynamical variables in DEOM are the dissipaton–augmented–reduced density operators (DDOs):\textsuperscript{5–7} $\rho^{(n)}_{a}(t) \equiv \text{tr}_{B} \left( \left[ \prod_{ak} \hat{F}_{ak}^{n_{ak}} \right] \hat{\rho}_{a}(t) \right)$. Here, $n \equiv \{n_{ak}\}$ specifies the configuration of the total $n$–dissipatons, where $n = \sum_{ak} n_{ak}$, with $n_{ak} \geq 0$ for bosonic dissipatons. The reduced system density operator is just $\rho^{(0)}_{a}(t)$. The DEOM reads\textsuperscript{5}

$$\dot{\rho}^{(n)}_{a}(t) = - [H_{S}(t), \rho^{(n)}_{a}(t)] - \sum_{ak} n_{ak} \gamma_{k} \rho^{(n)}_{ak} - i \sum_{ak} \left[ \hat{Q}_{a}(t), \rho^{(n+1)}_{ak} \right] - i \sum_{abk} n_{ak} \left[ \eta_{abk} \hat{Q}_{a}(t) \rho^{(n-1)}_{bk} - \eta^{*}_{abk} \rho^{(n-1)}_{bk} \hat{Q}_{a}(t) \right].$$  \hspace{1cm} (S4)

This describes the same dynamics of the HEOM formalism.\textsuperscript{8–13} It is worth emphasizing that the DEOM theory contains not only the above hierarchical dynamics, but also the dissipaton algebra.\textsuperscript{14} For brevity, we may express the Eq. (S4) in the form of

$$\dot{\rho}(t) = -i \mathcal{L}(t) \rho(t).$$  \hspace{1cm} (S5)

This resembles $\dot{\rho} = -i \mathcal{L}(t) \rho$ with mapping the total system–plus–bath composite Liouvillian to the DEOM–space dynamics generator as defined in Eq. (S4), $\mathcal{L}_{a}(t) \rightarrow \mathcal{L}(t)$, and $\rho_{a}(t) \rightarrow \rho(t) = \{ \rho^{(n)}_{a}(t); n = 0, 1, 2, \cdots \}$. Equation (S5) is exactly Eq.(13) of the main text.
II. PROOF OF THE PERIODICITY OF RATE KERNELS

We first review the projected DEOM approach to rate kernels in more details [cf. Eqs.(13)-(17) of the main text]. From the DEOM (S5), we know that the propagator

$$\mathcal{U}(t, \tau) = \exp \left[ -i \int_{\tau}^{t} d\tau' \mathcal{L}(\tau') \right] \tag{S6}$$

governs the dynamics of the DEOM state function $\rho \equiv \{\rho_n^{(a)}\}$. To proceed, define DEOM–space projection operators, $\mathcal{P}$ and $\mathcal{Q} = \mathcal{I} - \mathcal{P}$, for partitioning $\rho \equiv \{\rho_n^{(a)}\}$ into the population and coherent components, respectively:\textsuperscript{15}

$$\mathcal{P} \rho(t) = \left\{ \sum_a \rho_{aa}^{(0)}(t) |a\rangle \langle a|; \ 0, 0, \ldots \right\} \equiv p(t),$$

$$\mathcal{Q} \rho(t) = \left\{ \sum_{a \neq b} \rho_{ab}^{(0)}(t) |b\rangle \langle a|; \ \rho_n^{(n>0)}(t) \right\} \equiv \sigma(t). \tag{S7}$$

We can now recast the DEOM (S5) in terms of

$$\begin{bmatrix} \dot{p}(t) \\ \dot{\sigma}(t) \end{bmatrix} = -i \begin{bmatrix} \mathcal{P} \mathcal{L}(t) \mathcal{P} & \mathcal{P} \mathcal{L}(t) \mathcal{Q} \\ \mathcal{Q} \mathcal{L}(t) \mathcal{P} & \mathcal{Q} \mathcal{L}(t) \mathcal{Q} \end{bmatrix} \begin{bmatrix} p(t) \\ \sigma(t) \end{bmatrix}. \tag{S8}$$

The formal solution to $\sigma(t)$ reads

$$\sigma(t) = -i \int_{0}^{t} d\tau \mathcal{Q} \mathcal{U}(t, \tau) \mathcal{Q} \mathcal{L}(\tau) p(\tau). \tag{S9}$$

Equation (S9) contains no inhomogeneous term, as we assume initially the total density operator is factorized, and thus $\sigma(0) = 0$. Noting that $-i \mathcal{P} \mathcal{L}(t) p(t) = 0$,\textsuperscript{15} the first identity of Eq. (S8) then has the expression

$$\dot{p}(t) = \int_{0}^{t} d\tau' \tilde{K}(t - \tau'; t) p(\tau), \tag{S10}$$

with the rate kernel being formally of

$$\tilde{K}(t - \tau; t) = -\mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}(t, \tau) \mathcal{Q} \mathcal{L}(\tau) \mathcal{P}. \tag{S11}$$

Apparently, $-k(t - \tau; t)$ and $k'(t - \tau; t)$ in Eq. (1) of main text are the $|D\rangle \langle D| \rightarrow |D\rangle \langle D|$ and $|A\rangle \langle A| \rightarrow |D\rangle \langle D|$ components of $\tilde{K}(t - \tau; t)$, respectively. That is to say,

$$-k(t - \tau; t) = \langle |D\rangle \langle D|, 0, 0, \ldots \mid \mid \tilde{K}(t - \tau; t) \mid \mid |D\rangle \langle D|, 0, 0, \ldots \rangle, \tag{S12}$$

$$k'(t - \tau; t) = \langle |D\rangle \langle D|, 0, 0, \ldots \mid \mid \tilde{K}(t - \tau; t) \mid \mid |A\rangle \langle A|, 0, 0, \ldots \rangle. \tag{S13}$$

Now we can prove that the kernel in Eq. (S11) satisfies

$$\tilde{K}(t - \tau; t + T_0) = \tilde{K}(t - \tau; t). \tag{S14}$$

To this end, we note that $\mathcal{L}(t + T_0) = \mathcal{L}(t)$ according to our Floquet setting. This leads to

$$\tilde{K}(t - \tau; t + T_0) = -\mathcal{P} \mathcal{L}(t + T_0) \mathcal{Q} \mathcal{U}(t + T_0, \tau + T_0) \mathcal{Q} \mathcal{L}(\tau + T_0) \mathcal{P} = \mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}(t, \tau) \mathcal{Q} \mathcal{L}(\tau) \mathcal{P} = \tilde{K}(t - \tau; t). \tag{S15}$$

Here we have used

$$\mathcal{U}(t + T_0, \tau + T_0) = \exp_o \left[ -i \int_{\tau + T_0}^{t + T_0} d\tau' \mathcal{L}(\tau') \right] = \exp_o \left[ -i \int_{\tau}^{t} d\tau' \mathcal{L}(\tau' + T_0) \right] = \exp_o \left[ -i \int_{\tau}^{t} d\tau' \mathcal{L}(\tau') \right] = \mathcal{U}(t, \tau). \tag{S16}$$

Therefore, we conclude $k(t - \tau; t)$ and $k'(t - \tau; t)$ is periodic with respect to their second parameters.
III. ANALYSIS OF THE FREQUENCY–RESOLVED RATE KERNELS

To proceed, we first recast Eq. (S11) as
\[
\tilde{K}(\tau; t) = -\mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}(t, t - \tau) \mathcal{Q} \mathcal{L}(t - \tau) \mathcal{P}.
\] (S17)

Then, according to the Floquet theorem, the total propagator can be decomposed as\textsuperscript{16}
\[
U_\lambda(t, 0) \equiv T_+ e^{-i \int_0^{T_+} \dot{H}_T(\tau) \, d\tau} = e^{-iK_T^0(t)} e^{-iH_T^0 t} t
\] (S18)
with the Floquet Hamiltonian $H_T^0$ defined as
\[
e^{-iH_T^0 T_0} \equiv U(T_0, 0)
\] (S19)
and the stroboscopic kick operator $K_T^0(t)$
\[
e^{-iK_T^0(t)} \equiv U(t, 0) e^{iH_T^0 t}.
\] (S20)

The stroboscopic kick operator satisfies $K_T^0(0) = K_T^0(nT_0) = 0$. Then, in the DEOM–space we may obtain
\[
\tilde{K}(\tau; t) = -\mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}_K(t) \mathcal{G}_F(\tau) \mathcal{U}_K^\dagger(t - \tau) \mathcal{Q} \mathcal{L}(t - \tau) \mathcal{P},
\] (S21)
with $\mathcal{G}_F(\tau), \mathcal{U}_K(\tau)$ and $\mathcal{U}_K^\dagger(t - \tau)$ are the $\exp\{ -i\tau [H_T^0, \cdot]\}, \exp\{ -i[K_T^0(\tau), \cdot]\}$ and $\exp\{i[K_T^0(t - \tau), \cdot]\}$ mapped to DEOM space, respectively.

Since the system is driven periodically, we can expand the rate kernel as
\[
\tilde{K}(\tau; t) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} A_m \mathcal{G}_F(\tau) B_n e^{-i(m+n)\Omega t} e^{i\Omega \tau},
\] (S22)
where
\[
A_m \equiv -i \int_0^{T_0} dt \mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{U}_K(t) e^{i\Omega t}
\] (S23)
and
\[
B_n \equiv -i \int_0^{T_0} dt \mathcal{U}_K^\dagger(t) \mathcal{Q} \mathcal{L}(t) \mathcal{P} e^{i\Omega t}.
\] (S24)

By changing the summation indices, the rate kernel can be recast as
\[
\tilde{K}(\tau; t) = \sum_{m=-\infty}^{\infty} e^{-i\Omega \tau} \sum_{n=-\infty}^{\infty} A_{m-n} \mathcal{G}_F(\tau) B_n e^{i\Omega \tau}.
\] (S25)

Therefore, the corresponding Fourier components in frequency domain are given by
\[
\tilde{K}_m(\omega) = \int_0^\infty d\tau \sum_{n=-\infty}^{\infty} A_{m-n} \mathcal{G}_F(\tau) B_n e^{i\Omega \tau} \cos(\omega \tau).
\] (S26)

Since the Floquet Hamiltonian is independent of time, one could express the Fourier components formally via the eigenstates of \(\mathcal{L}_F\), the mapping of \([H_T^0, \cdot]\) in DEOM–space, as
\[
\tilde{K}_m(\omega) = \int_0^\infty d\tau \sum_{n=-\infty}^{\infty} \sum_{\omega_F} A_{m-n} (\omega_F) B_n (\omega_F) e^{i(\Omega - \omega_F) \tau} \cos(\omega \tau).
\] (S27)

That is to say, we set $B_n = \sum_{\omega_F} B_n (\omega_F)$, such that $A_{m-n} \mathcal{L}_F B_n (\omega_F) = \omega_F A_{m-n} (\omega_F) B_n (\omega_F)$. The integral over $\tau$ gives the basic profiles of the peak (real part) of $\tilde{K}_m(\omega)$ proportional to
\[
\alpha \left[ \frac{1}{\omega - (n\Omega - \omega_F)} - \frac{1}{\omega + (n\Omega - \omega_F)} \right] + \alpha' \left[ \frac{1}{\omega - (n\Omega + \omega_F)} - \frac{1}{\omega + (n\Omega + \omega_F)} \right],
\] (S28)
with $\alpha$ and $\alpha'$ being the coefficients. Equation (29) results in the peak–split phenomenon of $\tilde{K}_m(\omega)$.

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