Optimizing co-operative multi-environment dynamics in a
dark-state-enhanced photosynthetic heat engine

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We analyze the role of coherent, non-perturbative system-bath interactions in a photosynthetic heat engine. Using the reaction-coordinate formalism to describe the vibrational phonon-environment in the engine, we analyze the efficiency around an optimal parameter regime predicted in earlier works. We show that, in the limit of high-temperature photon irradiation, the phonon-assisted population transfer between bright and dark states is suppressed due to dephasing from the photon environment, even in the Markov limit where we expect the influence of each bath to have an independent and additive affect on the dynamics. Manipulating the phonon bath properties via its spectral density enables us to identify both optimal low- and high-frequency regimes where the suppression can be removed. This suppression of transfer and its removal suggests that it is important to consider carefully the non-perturbative and cooperative effects of system-bath environments in designing artificial photosynthetic systems, and also that manipulating inter-environmental interactions could provide a new multidimensional “lever” by which to optimize photocells and other types of quantum device.

I. INTRODUCTION

The observation of quantum coherent beating over time-scales comparable to energy transfer in a range of photosynthetic light-harvesting complexes1–4 has spurred many approaches to identifying mechanisms by which coherence can increase efficiency of energy harvesting. For example, it has been proposed that the transport of excitation energy between a light-harvesting antenna and the reaction center in the Fenna-Matthews-Olsen (FMO) complex5–7 follows a wavelike coherent motion instead of hopping randomly from state to state8, even at ambient temperatures8–7. In addition, noise8–15 from the protein environment surrounding the complex may also assist the energy transfer on its way, as it leads to line broadening and thermal excitation, which can increase the overlap between energetically separated states16,17. Together these effects have been termed “environment assisted quantum tunneling”, describing the interplay of quantum tunneling and thermal fluctuations to overcome energetic barriers to transport, not just in the FMO, but also in other complexes3–5,7,18,19.

Recently, another mechanism20–22 was proposed, recasting the standard model of a light-absorbing photosynthetic reaction center as a “quantum heat engine”. The advantage of this new approach arises from two effects. First, the collective dipole coupling of the two chromophores to the incident light leads to interference effects that create “bright” and “dark” states. Other mechanisms, such as direct coupling21 or environment-induced interference effects20, can then lead to the energetic splitting of these states and subsequent breaking of detailed balance for the photon absorption process. The suppression of spontaneous and stimulated emission of photons leads to an overall increased efficiency and can be thought of as a way to overcome the Shockley limit on absorption23. Secondly, the nature of the coherent and non-perturbative interaction between the dimer and its phonon environment has further potential to enhance the efficiency24–33. This is particularly appealing when such problems are recast as “quantum heat engines”, as it allows us to view the problem of improving efficiency through the lens of non-Markovian thermodynamics and understand this phonon environment as a “cold bath”, whose properties can be manipulated and taken advantage of to maximise energy extraction from a ‘hot’ environment29.

The ultimate goal of these approaches is both to understand naturally existing systems and to identify clear mechanisms which enhance efficiencies of such “quantum light harvesting heat engines”, which can then be applied to artificial photosynthetic systems and photocells34. Indeed, understanding the physics of molecular open quantum systems has recently been highlighted as a key consideration for the design of a whole new class of ‘coherent’ molecular devices with sensing and energy applications4. In this work, we investigate how to modify the phonon environment to optimize the efficiency of such a light-harvesting “quantum heat engine”, as realized by two coupled chromophores. To describe the complex problem of chromophores strongly interacting with their phonon
or vibronic) environment, which plays the role of the cold-bath in the heat engine picture, many techniques of varying degrees of sophistication and approximation have been developed. These, among many\textsuperscript{35}, include perturbative but non-Markovian methods\textsuperscript{36,37} and exact methods, like the “hierarchy equations of motion”\textsuperscript{6,38,39}, the reaction-coordinate method\textsuperscript{29,32,40–42}, and the quasi-adiabatic path-integral\textsuperscript{43,44} approach. For zero temperature simulations, powerful, numerically exact many-body methods are also available, such as the Multiconfigurational Time-Dependent Hartree Fock and Tensor Network approaches which give access to the dynamics of both system and environment\textsuperscript{45–49}. The reaction-coordinate (RC) method, which we employ herein, has been proposed as a particularly powerful tool for these type of problems. It allows for a straightforward evaluation of thermodynamic quantities\textsuperscript{29,32}, can be applied selectively to a many-bath system (in concert with normal Markovian methods to describe other baths), and can describe both low and high-frequency baths for arbitrary coupling strengths\textsuperscript{50}.

A. Summary of results

Here we show, using this reaction coordinate method, that in the high-temperature photon irradiation limit, and fast donor-acceptor transfer, which in the classical case both optimizes the Carnot efficiency and leads to a large current, the interaction between the chromophores and the phonon environment is dephased to such a degree that the photo-induced current is suppressed. This result is an explicit example of how the interplay of multiple environments can be non-additive and lead to unexpected results\textsuperscript{49,51,52}. Indeed, the importance of such effects extends beyond the case of light-harvesting to a wider range of nanoscale devices strongly coupled to multiple environments, such as in lead-dot(molecule)-lead structures\textsuperscript{53}. We show how this suppression can be overcome by increasing the coupling to the phonon environment such that it is more strongly influencing the chromophore system than an equivalent Markovian environment.

The assumption of high-photon irradiation temperature\textsuperscript{20–22,27,31} does not occur with natural sunlight. Thus, we also examine, in IVB, the low-temperature photon irradiation case, with parameters corresponding to more realistic, but optimally concentrated, natural sunlight irradiation. Here we find that in the Born-Markov limit of the phonon environment, the baths again become additive. We also show that entering into the non-Markovian and strong-coupling limit for this bath ultimately has diminishing returns, in this low-temperature case. The mechanism of this diminishment is shown, via perturbation theory, to arise from the “counter-rotating” terms in the interaction with the phonons, which reduce the relative populations of the donor states which couple to the acceptor.

The overall structure of this work is as follows. We begin by defining our heat engine model in section II. We then describe the reaction-coordinate method for modelling the phonon environment in section III. In section IV we discuss the results of our model, and explore both high and low photon temperature regimes, and give our conclusions in section V. In the appendix we define the secular and non-secular Markovian master equations to which we compare our results.

II. MODEL: PHOTOSYNTHETIC QUANTUM HEAT ENGINE

A minimal model (cf. Fig. 1) of a photosynthetic quantum heat engine describes the excitonic states of three molecules: a pair of coupled donor molecules $D_1$ and $D_2$ and one acceptor molecule $A$. As discussed by Creatore et al\textsuperscript{21}, a dipole-dipole interaction leads to strong coupling between the two donor molecules, transforming the originally degenerate excited states $|a_1\rangle$ and $|a_2\rangle$ into new non-degenerate eigenstates $|x_{1,2}\rangle = 1/\sqrt{2} (|a_1\rangle \pm |a_2\rangle)$ with eigenvalues $E_{x_{1,2}} = E_{1,2} \pm J$, where $J$ is the coupling amplitude. Due to the collective way the parallel dipole moments add up, only $|x_1\rangle$ is optically active.

Photon absorption (from a hot concentrated photon bath with thermal occupation $n_b$) occurs at a rate $\gamma_h$, causing transitions from the unexcited state $|b\rangle$ to the donor excited states $|a_1\rangle$ and $|a_2\rangle$. Ultimately, the collective nature of that absorption leads to occupation of only the bright state $|x_1\rangle$, which then can relax to the dark state $|x_2\rangle$ by emission of phonons into an environment with thermal occupation $n_x$. In the Markovian model this exchange is described by a rate $\gamma_x$, whereas in the RC model, which we describe in the next section, the interaction with a collective mode is used. Occupation of the dark state breaks detailed balance, allowing time for an electron to be transferred to the acceptor molecule, taking the system to the acceptor excited state $|a\rangle$, at a bare rate $\gamma_c$, assisted by a thermal environment with occupation $n_c$.

This charge transfer is suppressed for the bright state due to the electron transfer matrix elements carrying opposing signs, $t_{D_1,A} = -t_{D_2,A}$. At $|a\rangle$, work is extracted, leading the system to the ground state of the acceptor molecule $|b\rangle$, at rate $\Gamma$. Additionally, an effective lossy transition to the donor ground state is described by the rate $\chi \Gamma$, which represents additional losses by which the system is reset without producing work. Finally, after work has been extracted, $\Gamma_c$ describes the other ‘reset’ process of the system back to the ground state $|b\rangle$, e.g., due to donation of a charge to the original donor molecule from the environment\textsuperscript{54}. In our model this transition is assisted by a different thermal environment with occupation $N_c$. Note that all the transition rates involving the donor excited states are twice as large in the coupled basis than they are in the uncoupled basis.

The role of the phonon environment in transferring population must be considered carefully. In real pho-
tosynthetic systems such environments typically exist in the non-perturbative and non-Markovian regimes, with both bath correlation times and system-bath correlation times being of the same order as excitonic couplings (the parameter $J$ in our model). Indeed, understanding the open system physics of this ‘intermediate regime’ is the principle motivation for the diversity of powerful open system techniques mentions in the introduction.

The Hamiltonian describing the two donors, the acceptor molecule, and the phonon environment is

$$H = H_S + H_B + H_I$$

$$H_S = \sum_{i=1}^{5} E_i |\psi_i\rangle \langle \psi_i| + J(|a_2\rangle \langle a_1| + |a_1\rangle \langle a_2|)$$

$$H_B + H_I = \frac{1}{2} \sum_k \left[ p_k^2 + \omega_k^2 \left( x_k - \frac{f_k}{\omega_k} s \right)^2 \right],$$

(1)

with mass-weighted positions $x_k = 1/\sqrt{2\omega_k}(c_{k}^\dagger + c_k)$ and momenta $p_k = i\sqrt{\omega_k}/2(c_{k}^\dagger - c_k)$ of the bath fulfilling $[x_k, p_l] = i\delta_{kl}$ (setting $\hbar = 1$ throughout) and with creation and annihilation operators $c_k^\dagger$ and $c_k$. The operator coupling system and bath is given by

$$s = (|a_1\rangle \langle a_1| - |a_2\rangle \langle a_2|),$$

(2)

while the system is defined with the five states of the heat engine

$$|\psi_i\rangle = \{|b\rangle, |x_1\rangle, |x_2\rangle, |\alpha\rangle, |\beta\rangle\},$$

(3)

and corresponding energies $E_i$. Also, not shown here are the explicit Hamiltonians for the other baths shown in Fig. 1. Their influence on the model will be defined explicitly within the master equation picture later.

### III. METHODS: THE REACTION COORDINATE

The dark-state-enhanced heat engine, including the dipole coupling $J$, has previously been studied using a Born-Markov master equation description of the phonon bath (see Eq. (24) in the appendices) and been compared to a model where the donors do not couple to each other. That work found a relative current enhancement of the coupled ($J > 0$) over the uncoupled ($J = 0$) case of roughly 30%. To give a like-for-like comparison here, we primarily use the parameters found in that gave this large current enhancement in our simulations (cf. Table 1), which focus on the limit of high photon irradiation. In section IV B we will consider the low-temperature photon case, which is more applicable to systems irradiated by natural sunlight.

Instead of employing a Born-Markov master equation, we construct a more general master equation here, that can take into account non-Markovian effects of the phonon environment. We do so using the reaction coordinate (RC) mapping to transform the bath Hamiltonian such that a collective degree of freedom of said environment is included in the “system” Hamiltonian, while the residual environment is treated with a traditional generalized master equation. The validity of this approach was carefully analyzed in and, by comparison to the hierarchy method, found to be exact. Here we do not benchmark the results against another technique, as in those earlier works, and thus do not claim that our treatment of the phonon environment is exact to all orders for all parameter regimes we study herein. Rather, we propose that it captures more salient features than obtainable with a standard Born-Markov method alone.

![Figure 1. Scheme for the five level model in the coupled basis.](image)
Table I. Parameters used for the numerical simulation

| Parameter                      | Value       |
|--------------------------------|-------------|
| Donor excitation energy $\Delta_b = E_1 - E_b$ | 1.8 eV      |
| Donor-acceptor energy difference $\Delta_c = E_1 - E_\alpha$ | 0.2 eV      |
| Donor-acceptor charge transfer rate $\gamma_c$ | $6 \times 10^{-3}$ eV |
| Work extraction rate $\Gamma$ | 0.124 eV    |
| Photon occupation $n_h$ | $\sim 60000$ (in IV), $\sim 0.03$ (in IV B) |
| Charge transfer $N_c = n_c$ at 300K | $\sim 4.4 \times 10^{-4}$ |
| Phonon bath occupation $n_z$ at 300K | $\sim 0.46$ |

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A. The reaction coordinate transformation

We follow the description of the RC method in 29 and repeat only the most salient steps here. Starting from the complete Hamiltonian [Eq. (1)], a transformation has been found that maps the interaction of the phonon bath with the system onto one new coordinate (the RC). This reaction coordinate is itself coupled to a residual bath, which will be treated using the standard Born-Markov approximation. However, later we will see that relaxation rates induced by the residual phonon bath, as well as the hot photon bath and the donor-acceptor transfer process, can be of the order of the system frequencies, such that we cannot make the secular approximation in describing these baths. Therefore, we work with Born-Markov non-secular master equations for these particular environments.

Under this transformation, the system can be coupled arbitrarily strongly to the RC, as this is treated exactly through the $H'_{\text{RC}}$ part of the transformed Hamiltonian

$$H' = H'_S + H'_B + H'_I$$

$$H'_S = H_S + H_{\text{RC}}$$

$$H_{\text{RC}} = \frac{1}{2} \left[ P^2 + \frac{g_0^2}{\delta \Omega_0^2} \left( X_1 - \frac{\delta \Omega_0^2}{g_0} s \right)^2 \right]$$

$$H'_B + H'_I = \frac{1}{2} \sum_k \left[ P_k^2 + \Omega_k^2 (X_k - \frac{C_k}{\Omega_k} X_1)^2 \right].$$

Here $g_0$ is the coupling strength between the reaction coordinate and the system, while $X_1 = (a + a^\dagger)/\sqrt{2}$. $\delta \Omega_0^2$ describes the collective quadrature of the RC mode. In this new frame we treat the residual baths and their interaction with the system via the RC mode ($H'_B + H'_I$) with the non-secular Born Markov master equation. The renormalization term $\delta \Omega_0^2 s^2/2$ can be neglected as it is small compared to the energy difference between the excited states of the dimer and the states $|b\rangle$ and $|\alpha\rangle$.

The details of the transformation of the Hamiltonian above are entirely defined by the choice of spectral density for the original phonon environment,

$$J_0(\omega) \equiv \frac{\pi}{2} \sum_k f_k^2 \delta(\omega - \omega_k).$$

Here we focus on the underdamped Brownian oscillator spectral density,

$$J_0(\omega) = \frac{\lambda^2_0 \gamma \omega}{(\omega^2 - \Omega_0^2)^2 + \gamma^2 \omega^2},$$

as it allows us to investigate the influence of resonant and off-resonant structured environments that can dominate the vibrational spectrum of light-harvesting complexes.

The choice of spectral density ultimately fixes the coupling strength $g_0$ and the RC frequency $\Omega_0$. From the transformation of the Hamiltonian we obtain a term for the coupling strength as well as for the system renormalization:

$$g_0^2 = \sum_k f_k^2,$$

$$\delta \Omega_0^2 = \sum_k \frac{f_k^2}{\omega_k^2}.$$ (7)

These can then be expressed through integrals over the spectral density $J_0(\omega)$ and evaluated as

$$g_0^2 = \frac{2}{\pi} \int_0^\infty d\omega J_0(\omega) \omega = \lambda_0^2$$

$$\delta \Omega_0^2 = \frac{2}{\pi} \int_0^\infty d\omega J_0(\omega) \omega = \frac{\lambda_0^2 \Omega_0^2}{\gamma^2}.$$ (8)

The physical frequency of the RC is given by $\Omega_0 = \Omega_0$ and we can now identify the coupling strength $g_0 = \lambda_0$.

The spectral density of the residual bath is connected to the original environment through a recursion relation. By deriving the Fourier space propagator from the original and transformed Hamiltonian and comparing them, the transformed spectral density can be found by evaluating

$$J_1(\omega) = \frac{\lambda^2_0^2 J_0(\omega)}{|W_0^+(\omega)|^2},$$

where

$$W_0^+(z) = \lim_{\epsilon \to 0^+} \frac{1}{\pi} \int_{-\infty}^{\infty} dw \frac{J_0(\omega)}{\omega - (z + i\epsilon)}.$$ (10)

is the Cauchy transform of the original spectral density $J_0$. Using the residue theorem, our choice of the original spectral density [Eq. (6)] leads to an Ohmic spectral density for the residual bath, $J_1(\omega) = \gamma \omega$. 
B. Master equation approximations

We are mainly interested in the steady-state current output for various input parameters, which is calculated numerically from the steady-state density matrix \( \rho(t \to \infty) \). The master equation used to solve for \( \rho(t \to \infty) \) is split into three parts:

1. The transition between the donor excited states, \(|x_1\) and \(|x_2\), due to the interaction with the phonon environment, is treated by the system and RC parts of the Hamiltonian \( H_S \).

2. The residual baths coupled to the RC mode, as well as the transitions involving the donor excited states, are described by a non-secular Born-Markov master equation.

3. The transitions not involving the donor excited and RC states are treated using phenomenological secular Born-Markov Lindblad generators.

We cannot use the secular approximation in point 2, because, to do so, the timescales of the system have to be much smaller than the relaxation times: \( \tau_S \ll \tau_R \). The system timescale is proportional to the inverse of the energy splitting, while the relaxation time is defined through the transition rates and occupation numbers. The condition for the secular approximation to be valid then becomes:

\[
2J, \frac{\lambda_0}{\sqrt{2} \lambda_0} \gg (n_h + 1) \gamma_h, (1 + n_c) \gamma_c, (1 + n_x) \gamma. \tag{11}
\]

Even without the RC-mode description of the phonon bath, this condition is not fully satisfied because the rate of absorption and emission of photons, \((n_h + 1) \gamma_h\), is comparable to \(2J\). However, by introducing the RC, the energy splittings in the system Hamiltonian become even smaller (cf. Fig. 1) such that a non-secular approach is necessary for both the photon bath as well as the electron transfer.

Our general non-secular master equation is

\[
\dot{\rho}(t) = -i[H_S, \rho(t)] + \mathcal{M}_X[\rho(t)] + \mathcal{M}_Q[\rho(t)] + \mathcal{M}_Q^{(2)}[\rho(t)] + \mathcal{L}_{\beta b}[\rho(t)] + \mathcal{L}_{b\beta}[\rho(t)] + \mathcal{L}_{\alpha \beta}[\rho(t)] + \mathcal{L}_{\alpha b}[\rho(t)], \tag{12}
\]

where the non-secular generators\(^{60}\) are

\[
\mathcal{M}_A[\rho(t)] = -[A, [\chi, \rho(t)]] + [A, \theta(\rho(t))], \tag{13}
\]

with the system operator \( A \) which couples to the given environment and

\[
\chi = \frac{1}{2} \sum_{kl} J_A(\omega_{kl}) \coth \left( \frac{\beta \omega_{kl}}{2} \right) A_{kl} |k\rangle \langle l|, \tag{14}
\]

\[
\Theta = \frac{1}{2} \sum_{kl} J_A(\omega_{kl}) A_{kl} |k\rangle \langle l|. \tag{15}
\]

For the residual bath the system operator is given by the RC mode \( X_1 = (a + a^\dagger)/\sqrt{2} \Gamma_0 \) and the spectral density by \( J_1(\omega) \). For the transitions between \(|b\) and \(|x_1\) and between \(|x_2\) and \(|\alpha\) the transition operators

\[
Q_h = (|a_1\rangle + |a_2\rangle) \langle b | + \langle b | (|a_1\rangle + |a_2\rangle), \tag{16}
\]

and

\[
Q_c^{\alpha} = |\alpha\rangle \langle a_1 - \langle a_2 | + \langle a_1 - |a_2\rangle \langle \alpha |, \tag{17}
\]

are used and the spectral density for these baths is assumed to be Ohmic,

\[
J_{h,c}(\omega) = \frac{\gamma_{h,c}}{2\Delta_{h,c}} \omega, \tag{18}
\]

for each of them respectively, where the donor excitation energies are \( \Delta_h = E_1 - E_b = E_2 - E_b \), and the donor-acceptor energy difference is \( \Delta_c = E_1 - E_3 \), as per Table I. The eigenvectors \(|k\) and eigenenergies \(\omega_{kl}\) are calculated from \( H' \). The residual phonon bath temperature and donor-acceptor transition rate temperature is set to 300 K, but the transition between the ground state and \(|x_1\) is governed by the photon bath, which operates at a much higher temperature, defined through its occupation number given in Table I.

The transitions which do not couple directly to the excited donor states are given by secular Born-Markov Lindblad generators

\[
\mathcal{L}_{AB} = \left[ C_{AB}^\dagger \rho(t) C_{AB} - \frac{1}{2} \left\{ C_{AB}^\dagger C_{AB}, \rho(t) \right\} \right], \tag{19}
\]

with

\[
C_{\beta b} = \sqrt{\Gamma_c N_c} |\beta\rangle \langle b| \tag{20}
\]

\[
C_{b\beta} = \sqrt{\Gamma_c (1 + N_c)} |b\rangle \langle \beta| \tag{21}
\]

\[
C_{\alpha \beta} = \sqrt{\Gamma} |\beta\rangle \langle \alpha| \tag{22}
\]

\[
C_{\alpha b} = \sqrt{\chi} \langle \beta | b \rangle \langle \alpha|. \tag{23}
\]

The two equivalent (secular and non-secular) Markovian master equations are given in the appendix.

IV. RESULTS AND DISCUSSION

Here we will present and discuss the characteristics of the current generated by our RC method and compare them with the secular Born-Markov master equation model studied in\(^{21}\), c.f., Eq. (24), as well as the non-secular equivalent, Eq. (26), which takes into account that the transitions \( \gamma_h n_h \) and \( \gamma_c n_c \) can be of order of the energy splitting \( 2J \). We define the current as proportional to the rate of population transfer from \(|\alpha\) to \(|\beta\), i.e.,

\[
j = e \Gamma \langle \alpha | \rho | \alpha \rangle. \tag{24}
\]
Figure 2. Current as a function of the reaction coordinate (RC) frequency $\Omega_0$ [eV] (i.e., the peak in the spectral density), for $\lambda_0 = 1.06 \times 10^{-3}$ eV$^{3/2}$, and for different values of $\gamma$. This is compared to the current for a model without the RC-mode, which has been calculated using the equivalent Born-Markov master equation, and is a function of the transition rate $\gamma_x$ corresponding to the given RC frequency and coupling strength. (a) $\gamma = 0.1\Omega_0$: In this example we use the default parameters shown in Table I and compare the current from the secular (orange curve) and non-secular Born-Markov ME (red dash-dotted curve) and the RC method (blue dashed curve). The magnitude of the RC current at resonance only reaches about 15% of the one from the Born-Markov ME. At lower frequencies the RC model predicts an increase in the current, which surpasses the equivalent Born-Markov ME current. As a reference point, the blue star/horizontal dashed line is the value of the current for the uncoupled model, $J = 0$, also calculated using an equivalent Born-Markov master equation, but with no phonon bath at all. Figure (b) shows, with a blue-dashed curve, the dependence of $\gamma_x$ on the resonant frequency (RC frequency) of the phonon spectral density. The pink dashed-dotted curve shows the effective coupling strength $\lambda_0/\sqrt{2\Omega_0}$ between system and RC mode. (c) $\gamma = \Omega_0$: Using the same coupling strength $\lambda_0$ but changing the broadness parameter of the spectral density leads to a decreased transition rate $\gamma_x$, thus the current from the Born-Markov ME lowers and broadens in turn. In this case, the RC current remains mostly unchanged, as it follows the behavior of the effective coupling strength [shown in (d)] instead of the transition rate [also illustrated in (d)].

We choose an effective transition rate for the influence of the phonon environment on the system such that $\gamma_x = 2J_0(\omega = 2J)$ which, after setting the resonance $\Omega_0$ and width $\gamma$, determines $\lambda_0$ in the RC model. For example, choosing $\gamma_x = 25$ meV, and setting the spectral density to be resonant $\Omega_0 = 2J$, and choosing a narrow distribution, $\gamma = 0.1\Omega_0$, $\lambda_0 = \sqrt{2J\gamma_x}$, we find, surprisingly, that the current is roughly three times lower using the RC method than using either Born-Markov master equations (cf. Fig. 2).

Away from resonance, the relaxation rate $\gamma_x$ decreases rapidly. As mentioned, the spectral density has been chosen such that the value for $\omega = \Omega_0$ corresponds to the transition rate $\gamma_x$. Thus one would expect a maximal current at resonance, where the frequency of the phonon bath corresponds to the energy gap between states $|x_1\rangle$ and $|x_2\rangle$ and $\gamma_x$ is maximal for constant coupling strength $\lambda_0$. If one increases the RC frequency above the resonance frequency, the current indeed decreases steadily towards zero, albeit this decay is much slower in the RC method than in the Born-Markov master equation.

A. Suppression of Current

The counter-intuitive suppression of the current arises from the non-secular nature of the photon environment and is not captured by a standard secular master equation. Its origin lies in the fact that the strong illumination leads to fast emission and absorption between $|x_1\rangle$ and
In Fig. 3, (a) current as a function of RC frequency $\Omega_0$ [eV], where the transition rate $\gamma_x$ is fixed, so that the coupling strength $\lambda_0$ increases as $\Omega_0$ is moved off resonance. Both the default spectral density parameter $\gamma = 0.1\Omega_0$ and the sharper one $\gamma = 0.01\Omega_0$ lead to a sharp dip in current around resonance, the onset of which occurs around $\lambda_0/\sqrt{2\Omega_0} \approx \gamma_h n_h/2$, whereas the broader one $\gamma = 0.1\Omega_0$ is much flatter, and exhibits no dip. (b) The behavior of the coupling strength $\lambda_0/\sqrt{2\Omega_0}$ (dot-dashed pink curve) for $\gamma = 0.1\Omega_0$, illustrates that the onset of the dip in the current does occur around $\lambda_0/\sqrt{2\Omega_0} \approx \gamma_h n_h/2$ (dashed orange curve).

Figure 3. (a) Current as a function of RC frequency $\Omega_0$ [eV], where the transition rate $\gamma_x$ is fixed, so that the coupling strength $\lambda_0$ increases as $\Omega_0$ is moved off resonance. Both the default spectral density parameter $\gamma = 0.1\Omega_0$ and the sharper one $\gamma = 0.01\Omega_0$ lead to a sharp dip in current around resonance, the onset of which occurs around $\lambda_0/\sqrt{2\Omega_0} \approx \gamma_h n_h/2$, whereas the broader one $\gamma = 0.1\Omega_0$ is much flatter, and exhibits no dip. (b) The behavior of the coupling strength $\lambda_0/\sqrt{2\Omega_0}$ (dot-dashed pink curve) for $\gamma = 0.1\Omega_0$, illustrates that the onset of the dip in the current does occur around $\lambda_0/\sqrt{2\Omega_0} \approx \gamma_h n_h/2$ (dashed orange curve).
Fig. 2c), the RC current does not change significantly, while the equivalent Born-Markov master equation current falls considerably (as it follows the correspondingly slower transition rate $\gamma_e$). This suggests it is predominantly the coupling strength itself, not the width of the spectral density, that increases the current in the Zeno regime. As the coupling strength is increased so that we leave the Zeno regime, the width of the spectral density begins to have a larger influence, as per figure 3.

B. Weak photon illumination regime and the Markov limit

The assumption of a very-high photon temperature, employed in many earlier works on this heat-engine model\cite{20-22,27,31}, maximizes the Carnot efficiency, and, in the classical model, maximizes the current. However it does not occur in natural or artificial photosynthetic systems, or photocells. In addition, as we showed in the previous section, it can lead to suppressed current flow due to dephasing. In 62 the authors consider the case of low-temperature illumination of a similar photosynthetic reaction center heat engine, corresponding to an maximal concentrated natural sunlight temperature of 6000 K, and hence a thermal occupation of $n_h = 0.03$, while also including the influence of non-degenerate dimer energies. In such conditions they still found an advantage to the mechanism of including dimer-dimer couplings and subsequent bright to dark state conversion. Here, we can also consider the influence of the RC mode at lower illumination levels, and slower donor-acceptor transfer rate $\gamma_c$ (larger values of $\gamma_c$ were found to be a reduce the current enhancement, relative to the uncoupled dimer example, in 62). This also allows us to finally answer the question of what happens in the weak phonon-coupling and Markov limit.

In Fig. 4a we observe that simultaneously lowering the temperature of the photon bath, donor-acceptor transfer rate $\gamma_c$, and the phonon coupling strength $\lambda$, and choosing a broad phonon spectral density, restores the Born-Markov limit, such that all baths become additive, and all three models begin to coincide (RC, secular and non-secular master equations). Raising the phonon-coupling, and choosing $\gamma$ so that the effective rate $\gamma_e = 25$ meV, as in the previous section, we see in Fig. 4b that the current again increases, and exceeds the uncoupled dimer model current. The dependence on resonance now is very weak, because of the bottleneck from the other rates. In this case the Born-Markov master equations tend to overestimate the current, and the full RC model predicts a slightly smaller current than expected.

If we directly increase the coupling strength between dimer and RC on resonance, Fig. 5a, we eventually see diminishing returns in the RC model, with the current decreasing at a rate proportional to $\lambda_0^2$ as we enter a regime where $\lambda_0 > 10^{-3}$ eV$^{3/2}$. This is at first glance counter-intuitive; however, if we consider that the time-scales of the excited states of the dimer interacting with the RC

![Figure 4](image-url) (a) Current as a function of RC frequency [eV] for a fixed weak coupling strength $\lambda_0 = 1.06 \times 10^{-5}$ eV$^{3/2}$, with a correspondingly reduced photon temperature such that $n_h = 0.03$, and reduced donor-acceptor rate $\gamma_c = 1 \times 10^{-6}$, and for a broad phonon bath $\gamma = \Omega_0$. In this limit we see that the non-secular master equation and the RC model predict the same current, suggesting the phonon environment is in a weak-coupling Markov limit, and that all environments are additive. (b) For the same low photon intensity $n_h = 0.03$, and donor-acceptor rate $\gamma_c = 1 \times 10^{-6}$, we see that increasing the phonon-emission rate back to $\gamma_e = 25$ meV, by raising the phonon coupling to $\lambda_0 = 1.06 \times 10^{-3}$ eV$^{3/2}$, and choosing $\gamma = 0.1\Omega_0$, leads to a larger current, which can surpass that given by uncoupled dimers for equivalent parameters. We also see that the Markov models tend to overestimate the current. (c) When the phonon environment is in the weak-coupling-Markov limit ($\lambda_0 = 1.06 \times 10^{-6}$ eV$^{3/2}$, $\gamma = \Omega_0$), but the photon temperature is large $n_h = 60,000$ and the donor-acceptor rate is large $\gamma_c = 6 \times 10^{-3}$ we see again that the baths become non-additive, even when each individual bath could be considered to be in the Born-Markov limit.
are much faster than the other rates in the model, we notice that the thermal state of the dimer and RC subspace begins to dominate the behavior (the excited states and the RC thermalize before a donor-acceptor transition can occur). In that case, the transition to the acceptor state $\alpha$ will follow the transition matrix elements of the eigenstates of the dimer and RC subspace, weighted by their thermal populations. At 300 K this is dominated by the first three excited states of the subspace. We can express these states perturbatively in the renormalized coupling strength $\chi = \lambda_0/\sqrt{2\Omega_0}$, which, for example, for the ground state, gives, when $\Omega_0 = 2J$,

$$|G\rangle = \left(1 - \frac{\chi^2}{8}\right)|x_2, 0\rangle - \frac{\chi}{2}|x_1, 1\rangle + \frac{\chi^2}{2\sqrt{2}}|x_2, 2\rangle. \quad (22)$$

The matrix elements connecting these states to the acceptor arise through the $|x_2, n\rangle$ contributions. Interestingly, some of these contributions, like the reduction in probability of being in the $|x_2, 0\rangle$ part of the ground state, arise due to the counter-rotating terms in the interaction with the phonons, and leads to a corresponding reduction in the current proportional to $1 - \chi^2$. Summing up such matrix elements for all eigenstates of the dimer-RC subspace, and weighting them by their thermal occupations, provides a way to check the validity of this assumption, with an approximate expression for the current

$$\bar{j}(\chi)/2e\gamma_h \approx \max_x[\bar{j}(\chi)/2e\gamma_h] \times \sum_k P_k \left(\sum_n |\langle x_2, n|\psi_k\rangle|^2\right)/N. \quad (23)$$

The eigenstates $\psi_k$ are calculated numerically for the reduced model of the dimer excited states and RC from the Hamiltonian $H''_S$, which is $H'_S$ projected onto the subspace containing just the dimer states $x_1, x_2$, and the RC states. The thermal occupation probabilities $P_k$, are calculated from the thermal distribution $\rho = \exp(-H''_S/k_B T)/Z$, where $Z = \text{Tr}[\exp(-H''_S/k_B T)]$. The normalization of $\bar{j}(\chi)$ by $N$ is chosen so that in the limit $\chi \to 0$, $\sum_k P_k \left(\sum_n |\langle x_2, n|\psi_k\rangle|^2\right)/N = 1$. This approximate current is plotted in Fig. 5a, and agrees well with the full numerical current of the RC model for $\lambda_0$ in the range of applicability (a explicit second-order perturbative expansion also fits well for a smaller range of $\chi$, but we do not explicitly show it here because it is unwieldy). The approximate expression and the full numerics exhibit deviations for large $\chi$ (and of course for for very small $\chi$, where the current actually falls to zero, as there are no transitions to $|x_2\rangle$ states at all in this limit).

Finally, in Fig. 4c we again set the phonon-bath parameters to be the same as Fig. 4a, but raise $\gamma_c$ and the photon temperature back to their values used in the previous section. As in the previous section, we again see a large discrepancy in the current, with a suppressed value for the RC model; this suggests that the issue of non-additive baths is more general than highly “non-Markovian” regimes, as is often assumed.

Figure 5. Current as a function of coupling strength $\lambda_0 = 2J$. (a) is for the low photon temperature such that $n_h = 0.03$, and reduced donor-acceptor rate $\gamma_c = 1 \times 10^{-6}$, and for $\gamma = 0.1\Omega_0$. Both the Pauli master equation and the RC model predict an optimal current around $\lambda = 10^{-3} \text{ eV}^{3/2}$, because the current is limited by the weak photon illumination rate and donor-acceptor rate. For strong couplings, the Pauli master equation over-estimates the current, because in the full RC model the strong interaction with the phonons reduces the matrix-elements which lead to current flow (see main text). The orange dotted curve shows an approximate expression explaining the quadratic dependence of the current on the coupling strength. (b) shows the current dependence on coupling for the high-temperature limit $n_h = 60000$, and fast donor-acceptor rate $\gamma_c = 6 \times 10^{-3}$. As in earlier figures we see that the RC current is suppressed with respect the Pauli master equation, due to the effects described in the main text. The RC model predicts an inflection as the coupling strength becomes comparable with the resonance frequency (the line $\lambda_0 = \Omega_0^2\sqrt{2}$ is plotted as a dashed vertical line).

V. CONCLUSION

In this work, we analyzed the influence of a non-Markovian phonon bath on the efficiency of light harvesting in a photosynthetic reaction center considered as a quantum heat engine. Inspired by earlier works, which found an advantage in breaking detailed balance by in-
ducing energetic splitting between bright and dark states, we modeled the phonon-mediated population transfer process from bright to dark states with the reaction coordinate formalism. This formalism allows us to model the influence of phonons for a wide range of coupling strengths and bath memory times.

We found that, counter-intuitively, bright photon illumination can suppress the current in the heat engine, due to quantum Zeno-like dephasing of the exciton-phonon interaction. This suppression can be avoided by tuning properties of the phonon bath, and in doing so one can even generate currents significantly larger than the equivalent Markovian model. In the low photon temperature limit, in contrast, increasing the coupling to the phonon environment tends to reduce the current. Our results suggest that non-Markovian environments can be used to enhance the efficiency of light-harvesting systems, but that the properties of the environment must be chosen, or designed, in artificial systems, carefully, as their influence can also be detrimental, in certain situations.

In addition, our results suggest that care must be taken whenever one considers multiple environments coupled to a single system, particularly when those environments induce dynamics on very different time scales, even when one is apparently in a weak-coupling Markov limit for all baths. This is a potentially useful observation, as it suggests that dissipative processes due to many commonly encountered perturbative environments, particularly in the solid state, might be modified by external environments. Indeed, although the suppression we describe is deleterious for dimer photocurrents, one could imagine that the ability to dynamically suppress transport by a real-time change in an external environmental property (temperature, pressure, etc.) might be useful for rectification or gating a signal, perhaps even allowing for sensing functionalities.

Interestingly, it has recently become possible to program and implement Hamiltonian models of light harvesting in ‘quantum simulators’, as recently achieved with superconducting qubits, ion traps, and a NMR system. In the case of superconducting qubits, dephasing noise of arbitrary spectral properties can be applied to each individual ‘chromophore’ and their quantum coupling to photons can also be tuned in strength and frequency, allowing, in principle, a precise experimental test of non-additive environmental effects in both Markovian and non-Markovian photosynthetic energy transport. Further avenues for future study include the influence of coexisting underdamped and overdamped structured environments in dimer photocells, and how off-resonant dimers may alter the effects we discuss herein.

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**VI. APPENDIX**

In our results section, we compare results from the reaction coordinate master equation, Eq. (12), with two Markovian master equations which treat the interaction with the phonon environment under a standard Born-Markov assumption, i.e., as a rate \( \gamma_x \) driving transitions between the bright and dark states of the system. The secular version of this master equation is explicitly defined, using the same notation as in the main text, as,

\[
\dot{\rho}(t) = -i[H_S, \rho(t)] + \mathcal{L}_{x,b}[\rho(t)] + \mathcal{L}_{x,1}[\rho(t)] + \mathcal{L}_{x,2}[\rho(t)] + \mathcal{L}_{x,\alpha}[\rho(t)] + \mathcal{L}_{b,\beta}[\rho(t)] + \mathcal{L}_{\alpha,\beta}[\rho(t)] + \mathcal{L}_{\alpha,\beta}[\rho(t)] \tag{24}
\]

Now, all transitions are given by Lindblad generators \( \mathcal{L}_{AB} = \left[ C_{AB} \rho(t) C_{AB}^\dagger - \frac{1}{2} \left( C_{AB}^\dagger C_{AB}, \rho(t) \right) \right] \). In addition to the parameters \( C_{AB} \) defined in Eq. (19), we also have

\[
\begin{align*}
C_{x_1,b} &= \sqrt{2\gamma_n \hbar n_b} |x_1\rangle \langle b| \\
C_{b,x_1} &= \sqrt{2\gamma_n (1 + n_b)} |b\rangle \langle x_1| \\
C_{x_2 x_1} &= \sqrt{\gamma_x (n_x + 1)} |x_2\rangle \langle x_1| \\
C_{x_1 x_2} &= \sqrt{\gamma_x n_x} |x_1\rangle \langle x_2| \\
C_{x_2 \alpha} &= \sqrt{2\gamma_c (n_c + 1)} |\alpha\rangle \langle x_2| \\
C_{x_2 \alpha} &= \sqrt{2\gamma c n_c} |x_1\rangle \langle \alpha| 
\end{align*}
\]

The factors of 2 in the photon baths and the transitions to the state \( |\alpha\rangle \) arise from the collective dipole coupling, such that the matrix elements for these transitions are enhanced over those in the bare \( |a_1\rangle \) and \( |a_2\rangle \) basis.

Even in this case of a Markovian treatment of the phonon environment, the above equation is incomplete when the rates approach the coupling between the dimers, \( 2J \). In this case, one must treat transitions involving the excited states of the dimer with a non-Secular Born-Markov master equation. The equation of motion
then becomes,
\[
\dot{\rho}(t) = -i[H_S, \rho(t)] + M_s[\rho(t)] + M_{Q_0}[\rho(t)] + M_{Q^*_0}[\rho(t)] + L_{\beta}\rho(t) + L_{\alpha}\rho(t) + L_{\alphabeta}\rho(t),
\]
Again, the transitions not involving the excited dimer states are given by secular Born-Markov Lindblad generators. The transitions involving the hot photon bath, and those involving the electron transfer process to |\alpha\rangle, are given by the non-secular generator Eq. (14), (although now the eigenstates of the system do not include the RC mode). The Markovian phonon transitions are also given by Eq. (14) but with operator \( s = (|a_1\rangle\langle a_1| - |a_2\rangle\langle a_2|) \) and spectral density \( J_s(\omega) = J_0(\omega) \), as per Eq. (6).

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