

Correlated dynamics as a resource in molecular switches

Daniel Siciliano^{*,†}, Rudi B. P. Pietsch^{*,‡}, Giovanni Spaventa[§], Susana F. Huelga^{||}, and Martin B. Plenio[¶]
Institute of Theoretical Physics & IQST, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany



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Photoisomerization, a photochemical process underlying many biological mechanisms, has been modeled recently within the quantum resource theory of thermodynamics. This approach has emerged as a promising tool for studying fundamental limitations to nanoscale processes independently of the microscopic details governing their dynamics. On the other hand, correlations between physical systems have been shown to play a crucial role in quantum thermodynamics by lowering the work cost of certain operations. Here we explore quantitatively how correlations between multiple photoswitches can enhance the efficiency of photoisomerization beyond that attainable for single molecules. Furthermore, our analysis provides insights into the interplay between quantum and classical correlations in these transformations.

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I. INTRODUCTION

Nanoscale systems are in general rather difficult to analyze from a thermodynamical point of view, due to the complicated microscopic details that govern their dynamics and due to their fundamentally out-of-equilibrium nature. However, a recent promising approach is that offered by quantum resource theories (QRTs) [1,2] and in particular the formulations of thermodynamics that have emerged from them [3–9]. These frameworks can be used as a toolbox for the study of fundamental limitations to nanoscale processes that would otherwise be difficult to capture by solely relying on classical, equilibrium, and macroscopic frameworks [10–14]. In particular, QRTs allow the analysis of a physical process on purely fundamental grounds, without providing a detailed description of the underlying microscopic theory that governs it, e.g., the specific environmental structure or the coupling strengths [15]. A notable example is that of photoisomerization, a photochemical process that is at the basis of human vision [16], plays a key role in the primary steps of photosynthesis in plants, algae, and bacteria [17], and can also be artificially controlled for technological applications, such as the storage of solar energy, nanorobotics, and optical data storage [18]. Crucially, the microscopic details of the physics of photoisomerization are rather difficult to capture due to its

nonequilibrium nature, its ultrafast speed, the involvement of vibrational modes, and its very high quantum yield [19–23]. For this reason, recent works [10–12] have deployed the resource theory of athermality to find fundamental limitations to the efficiency of photoisomerization, in a way that is independent of the microscopic details governing the dynamics. As already proposed and explored in those works and in [24,25], the photoisomerization yield of two molecules can improve over that of a single one, which makes it natural to ask how this advantage behaves for larger ensembles of molecules and in particular how the N -molecule solution approaches that found in the thermodynamic limit, via the standard second law of thermodynamics. Indeed, the role of correlations in quantum thermodynamics is nontrivial. On the one hand, the thermal state of a system might be correlated or not depending on the particular choice of Hamiltonian, implying that the resourcefulness of correlated states depends on the details of the system (e.g., thermal states of noninteracting systems do not exhibit correlations; therefore any correlated state will represent a resource). On the other hand, quantifying the impact of correlations on state conversion criteria is not straightforward, due to their interplay with resources such as energy and purity. Nevertheless, it has been proven that correlations can allow some thermodynamical protocols to be implemented at a lower work cost [26–29]. An example of this is imperfect catalysis, where a system can become correlated to a catalyst after undergoing a joint transformation [30,31].

Here we want to quantitatively explore the impact of correlations between different molecules on the efficiency of photoisomerization. We do so by explicitly computing the optimal photoisomerization yield in a many-molecule scenario under the assumption that the molecules end up in a correlated or uncorrelated state, and we compare the solutions. We find that allowing for (classical) correlations to be generated offers a significant boost in efficiency, and we can compute how this advantage scales with the number of molecules. Furthermore, we quantify the role of quantum correlations in the initial state

*These authors contributed equally to this work.

†Contact author: daniel.siciliano@uni-ulm.de

‡Contact author: rudi.pietsch@uni-ulm.de

§Contact author: giovanni.spaventa@uni-ulm.de

||Contact author: susana.huelga@uni-ulm.de

¶Contact author: martin.plenio@uni-ulm.de

on the photoisomerization yield of two molecules and find a small advantage over classical correlations.

II. OUTLINE

The paper is organized as follows. First, we briefly introduce the resource theory of thermodynamics and the study of photoisomerization within this framework to fix the notation. Then we define the thermodynamic limit, where the number of photoswitches becomes large. Once the relevant quantities that we want to study, such as the process yield, are defined, we analyze the role of correlations when two molecules undergo a photoisomerization process together. As we find that the yield increases compared to the single-molecule case, we extend our analysis to the N -molecule scenario and the regime for which the number of molecules becomes large. Finally, we show that the same tools we developed to study the role of classical correlations in the final state can also be applied to coherence in the initial state and we compare the effect of the two in the case of $N = 2$ photoswitches.

III. THERMODYNAMICS AS A QUANTUM RESOURCE THEORY

The framework of QRTs allows the rigorous quantification of physical resources (such as quantum coherence, entanglement, and non-Markovianity) and their interconversion. They provide a theoretical framework in which a set of operations (i.e., a subset of all quantum channels) is considered free and any state that cannot be prepared via free operations is then singled out as a (static) resource, in the sense of facilitating a task inaccessible to the free set. Nonfree states (or operations) can thus only be prepared (or implemented) at a cost, while, on the other hand, assisting processes that would be otherwise impossible or only attainable with a smaller fidelity. Historically, the first example of a resource theory is the theory of bipartite entanglement [32,33], where the restriction to local operations and classical communication (LOCC) promotes entanglement to a resource, while separable states remain freely accessible. Analogously, quantum thermodynamics can be formulated as a resource theory in which both free states and operations are thermal [3–9]. Specifically, the resource theory of athermality is constructed as follows. Given a system S with Hamiltonian H_S , the following three elementary operations are allowed: (i) The system can be brought into contact with a thermal bath B at inverse temperature β , that is, we can freely deploy Gibbs states $\tau = e^{-\beta H_B}/Z$; (ii) we can perform any global unitary transformation U on $S + B$, as long as it is strictly energy preserving, i.e., $[U, H_S + H_B] = 0$; and (iii) we are allowed to trace out subsystems and in particular the entire bath B . As a result, the action of thermal operations (TO) on a density operator ρ_S is then defined as

$$\rho_S \xrightarrow{\text{TO}} \text{Tr}_B(U \rho_S \otimes \tau U^\dagger). \quad (1)$$

Note that thermal operations preserve the Gibbs state of the system S and furthermore they obey time-translation covariance [also called phase covariance or $U(1)$ covariance], i.e., they commute with the free unitary evolution of the system: $\mathcal{T} \circ \mathcal{U}_t = \mathcal{U}_t \circ \mathcal{T}$ for any $\mathcal{T} \in \text{TO}$, where $\mathcal{U}_t = e^{-iH_S t}$.

The action of thermal operations on block-diagonal states in the energy eigenbasis can be fully characterized. The associated state conversion problem, i.e., deciding whether such a state ρ can be mapped into another state σ via thermal operations, can be solved via a particular version of relative majorization called thermomajorization [3,4,6]. This is analogous to how standard majorization characterizes state convertibility under LOCC in the resource theory of entanglement. In particular, one associates with a density matrix ρ a curve $f_\rho(x)$ (called thermomajorization curve) and, given two density matrices ρ and σ , it is said that ρ thermomajorizes σ , i.e., $\rho \succ_{\text{th}} \sigma$, if $f_\rho(x) \geq f_\sigma(x) \forall x$. Then, if $\rho \succ_{\text{th}} \sigma$, for every $\epsilon > 0$ there is a thermal operation $\mathcal{T}_\epsilon$ that maps ρ arbitrarily close to σ , that is to say, $\|\sigma - \mathcal{T}_\epsilon(\rho)\| \leq \epsilon$. An equivalent tool to assess state convertibility is the existence of a Gibbs-stochastic matrix mapping the diagonal of ρ to the diagonal of σ . These are stochastic matrices whose fixed point is the population vector of the Gibbs state. This tool will be useful when considering a large number of molecules and will be expanded in the corresponding section.

IV. PHOTOISOMERIZATION

Some molecules, when excited by light, undergo a configurational change in their geometry. This photochemical process is known as photoisomerization and allows the reversible switching between two or more stable geometrical configurations of a molecule. The typical scenario is that of two stable configurations (called *cis* and *trans* isomers), separated by an energy barrier. The problem of modeling photoisomerization in the resource theory of athermality was originally addressed in [10], where an angular coordinate φ between two heavy chemical groups parametrizes the relative rotation of two molecular groups around a double bond. Figure 1 displays a typical energy landscape for these systems, where the two eigenvalues $\mathcal{E}_{0,1}(\varphi)$, corresponding to eigenvectors $|\mathcal{E}_{0,1}(\varphi)\rangle$, can be obtained from a class of Hamiltonians commonly used in the study of photoisomerization (see [20,22]). The ground-state energies for $\varphi = 0$ and $\varphi = \pi$ satisfy $\mathcal{E}_0(0) \leq \mathcal{E}_0(\pi)$ in our analysis and are separated by an energy barrier. The probability of switching configuration during relaxation is called photoisomerization yield. Following the same arguments proposed in [10] and later expanded in [11–13], we consider photoisomerization as a mapping between states of a three-level system, realized by thermal operations. More precisely, we imagine the electronic state after photoexcitation as being described by a density operator ρ , on the Hilbert space spanned by the three states $|0\rangle = |\mathcal{E}_0(0)\rangle$, $|\Delta\rangle = |\mathcal{E}_0(\pi)\rangle$, and $|W\rangle = |\mathcal{E}_1(0)\rangle$. The initial state ρ is assumed to only have support on the *trans* configuration and is then transformed via a thermal operation into a final state σ :

$$\rho \xrightarrow{\text{TO}} \sigma. \quad (2)$$

The photoisomerization yield γ is then defined as the weight of the final state σ on the *cis* electronic ground state, that is, $\gamma = \langle \Delta | \sigma | \Delta \rangle$.

In this single-molecule scenario, where the three levels are nondegenerate, quantum coherence in the energy eigenbasis

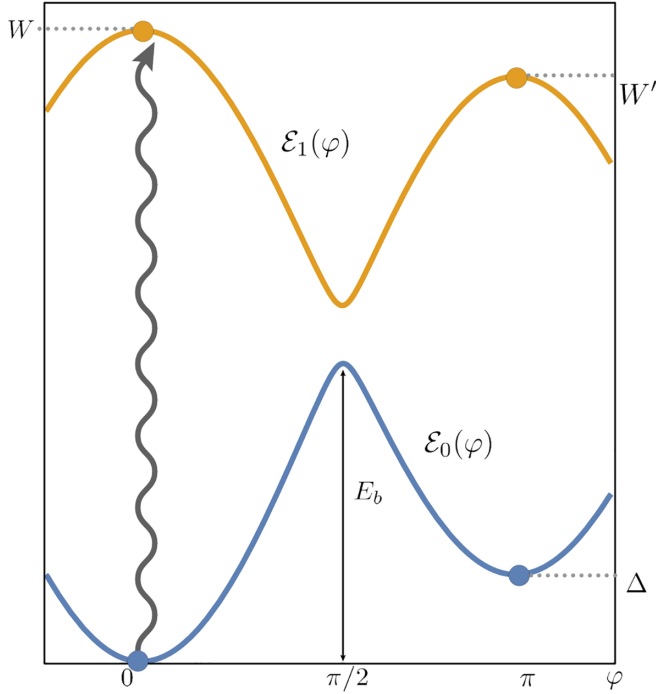


FIG. 1. Energy landscape for a typical photoisomer. The system starts in the electronic ground state at $\varphi = 0$ and is photoexcited (wavy arrow) by a light source. It can then relax to the cis ground state $\mathcal{E}(\varphi = \pi)$ while in contact with its environment. Our results are independent of the actual intermediate dynamics of the process. The advantage of a resource-theoretic approach is precisely that of providing general bounds that are valid regardless of the complicated microscopic details governing the evolution of the system. The four circles represent the states that are considered in the four-level model of [10].

cannot affect the photoisomerization yield, due to the time-translation covariance of thermal operations. Therefore, the transformation $\rho \rightarrow \sigma$ is possible via thermal operations if and only if the initial state thermomajorizes the final state. This means that not all values of the yield are allowed by the constraints of thermal operations and that we could find an upper bound to the yield by solving for the largest value of γ such that $\rho \succ_{\text{th}} \sigma$. However, when multiple molecules are considered, their spectrum will acquire degeneracies. This means that the global thermal operation that evolves them simultaneously will in principle be able to turn coherence between degenerate levels into populations, thus allowing for a boosting of the photoisomerization yield [12]. To assess the impact of classical and quantum correlations independently, we study this problem by first excluding the presence of coherence, whose role will be explored in Sec. XI.

Treating the photoisomerization of multiple molecules requires generalizing the definitions adopted for the single-molecule case. In particular, we will consider an independent and identically distributed approximation for the initial state, i.e.,

$$\rho_N = \rho^{\otimes N}, \quad (3)$$

where ρ is the single-molecule state

$$\rho = (1 - q)|0\rangle\langle 0| + q|W\rangle\langle W|. \quad (4)$$

In a realistic scenario, the initial state might present correlations, for instance, due to spatial proximity in the case of biological photoswitches in the retina or because of the presence of light-induced collective excitations. However, we choose a product state here to isolate the role of correlations generated by thermal operations and their impact on the efficiency of the process.

Furthermore, we assume the molecules to be sufficiently excited such that $q \geq 1/(1 + e^W)$ (cf. Appendix A).

As for the final state σ_N , we can consider two different scenarios, depending on whether such a composite state of N molecules is correlated or not. More precisely, in the uncorrelated-final-state scenario, we consider σ_N as a product state, while we relax this assumption in the correlated-final-state scenario. The photoisomerization yield for N molecules is instead defined as the (ensemble) average single-molecule photoisomerization yield [34]

$$\mathcal{O} = \frac{1}{N} \sum_{i=1}^N (|\Delta\rangle\langle\Delta|)_i, \quad (5)$$

$$\gamma_N = \text{Tr}(\mathcal{O}\sigma_N), \quad (6)$$

where the subscript i indicates an operator acting on the i th molecule. The equations above make it clear that the yield is invariant under permutations of subsystems. The analysis can then be simplified by restricting the set of final states to being symmetric states, i.e., states invariant under permutations. In fact, one can show that any state with a nonuniform distribution over degenerate levels thermomajorizes a symmetric state with the same yield. The γ_N can be equivalently computed by summing all the contributions to the yield coming from states of the form $|\Delta\rangle\langle\Delta| \Delta^{\otimes k} \otimes |0\rangle\langle 0|^{\otimes(N-k)}$, i.e., states in which k molecules are switched (contributing to the yield with a weight of k/N each) and $N - k$ molecules are not. Fixing a value of k , there are precisely $\binom{N}{k}$ states of this kind, with associated populations p_k^j , $j = 1, \dots, \binom{N}{k}$. Following the assumption of symmetric states, one has $p_k^j = p_k \forall j$. By summing all the contributions over k , we obtain the photoisomerization yield

$$\gamma_N = \sum_{k=1}^N \binom{N}{k} \frac{k}{N} p_k = \sum_{k=1}^N \binom{N-1}{k-1} p_k. \quad (7)$$

V. THERMODYNAMIC LIMIT

Let us consider the uncorrelated scenario

$$\rho^{\otimes N} \xrightarrow{\text{TO}} \sigma^{\otimes N}. \quad (8)$$

In the asymptotic limit, i.e., when $N \rightarrow \infty$, we can use a known result on optimal asymptotic conversion rates [35] to find the optimal uncorrelated yield. Let us consider the state conversion problem

$$\rho^{\otimes N} \xrightarrow{\text{TO}} \sigma^{\otimes rN}, \quad (9)$$

corresponding to the conversion rate r . When $N \rightarrow \infty$, the optimal conversion rate r^* is given by

$$r^* = \frac{D(\rho||\tau)}{D(\sigma||\tau)} = \frac{F(\rho) - F(\tau)}{F(\sigma) - F(\tau)}, \quad (10)$$

where $D(\rho||\tau)$ is the quantum relative entropy of ρ with respect to the thermal state τ and $F(\rho) = \text{Tr}(\rho H) - \frac{1}{\beta} S(\rho)$ is the nonequilibrium free energy. According to the permutational invariance of the final state, the optimal uncorrelated yield is the maximum value of $\gamma = \text{Tr}(|\Delta\rangle\langle\Delta|\Delta\sigma)$ such that $r^* = 1$. Therefore, in this limit, $F(\rho) = F(\sigma)$ defines the optimal asymptotic uncorrelated yield γ_{TD} , which is the value of γ that saturates the second law $F(\rho) \geq F(\sigma)$. This equality can then be rewritten as

$$\begin{aligned} F(\rho) &= qW + q \ln q + (1-q) \ln(1-q) \\ &= \gamma \Delta + \gamma \ln \gamma + (1-\gamma) \ln(1-\gamma) = F(\sigma). \end{aligned} \quad (11)$$

It is easy to see that $\gamma_{TD} \equiv 1$ is a valid solution as long as $\Delta \leq \Delta^* \equiv F(\rho)$, i.e., as long as the *cis-trans* gap is smaller than the free energy of the initial state. For larger values of Δ , the function $\gamma_{TD}(\Delta)$ starts decaying, although a closed-form expression cannot be obtained.

VI. YIELD OPTIMIZATION ON TWO MOLECULES

As a first step, let us focus on the isomerization of $N = 2$ molecules. In this section we compute the optimal yield in the two different scenarios described earlier, i.e., in the case of an uncorrelated and a correlated final state. In the first case, the final state will be a product state of the form

$$\sigma_2^u = [\gamma|\Delta\rangle\langle\Delta| + (1-\gamma)|0\rangle\langle 0|]^{\otimes 2}, \quad (12)$$

while in the latter it will be a general diagonal symmetric state of the form

$$\begin{aligned} \sigma_2^c &= p_0|00\rangle\langle 00| + p_1|\Delta 0\rangle\langle \Delta 0| \\ &\quad + p_1|0\Delta\rangle\langle 0\Delta| + p_2|\Delta\Delta\rangle\langle \Delta\Delta|. \end{aligned} \quad (13)$$

In the uncorrelated scenario, we note that we still allow a single bath to be coupled with the whole system. There is a third trivial situation in which each molecule undergoes an independent thermal operation, each with its own bath (i.e., the thermal operation has a tensor product structure). The optimal yield will then be upper bounded by the single-molecule optimal yield found in [10] and shown in Fig. 2.

To find the optimal yield, we impose the thermomajorization condition between initial and final states using thermomajorization curves. In particular, the curve associated with the final state depends on the populations contributing to the yield. As such, there will be a maximum value of γ such

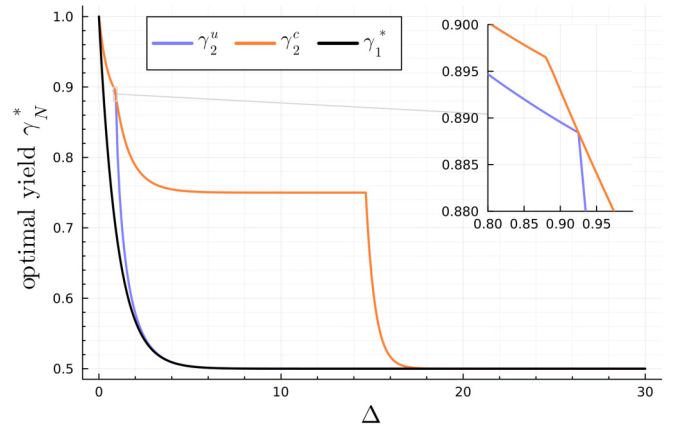


FIG. 2. Photoisomerization yield for two molecules with uncorrelated and correlated final states. We see that in both cases there is an advantage over the single-molecule yield, which is depicted in black. However, for a final state that is uncorrelated (blue), the yield quickly decreases to the single-molecule solution, whereas for a correlated final state (orange), there is a significant improvement of the optimal yield up to $\Delta \approx W/2$. The inset shows a close-up of the small- Δ region where the curves are particularly close and touch at a point. Here $q = 0.5$ and $W = 30$.

that $\rho_2 \succ_{\text{th}} \sigma_2^{u,c}$ (see Appendix A for a detailed explanation). In the uncorrelated scenario, the construction of the optimal final curve is simplified by the fact that the populations of the final state depend directly on γ . We find the optimal yield γ_2^u to be a continuous piecewise differentiable function with a single nondifferentiable point at the energy value Δ_2^u ,

$$\gamma_2^u = \begin{cases} \sqrt{1 - g(q)[h(W) - e^{-2\Delta}]}, & \Delta \leq \Delta_2^u \\ 1 - \sqrt{g(q)[h(W) - e^{-2\Delta} - 2e^{-\Delta}]}, & \Delta_2^u < \Delta, \end{cases} \quad (14)$$

where, for the sake of concise notation, we have introduced two auxiliary functions $g(x) = (1-x)^2$ and $h(x) = (1+e^{-x})^2$. In the correlated-final-state scenario, the yield [as defined in Eq. (7)] reads

$$\gamma_2^c = p_2 + p_1. \quad (15)$$

As one can see, to find the optimal final curve we now have to optimize over two different parameters. This complication will be more evident when the number of molecules becomes large. Again, the optimal yield is found to be a piecewise differentiable function (with case distinctions at the Δ values Δ_1^c and Δ_2^c), of the form

$$\gamma_2^c = \begin{cases} 1 - \frac{1}{2}g(q)[h(W) - e^{-2\Delta}], & \Delta \leq \Delta_1^c \\ 1 - g(q)\left[\frac{h(W)}{2} - e^{-\Delta}\sqrt{h(\Delta)}\right], & \Delta_1^c < \Delta \leq \Delta_2^c \\ \frac{1}{2}\{1 - g(q)[h(W) - h(\Delta) + 1] + q^2 + q\sqrt{g(q)}(e^{W-2\Delta} - e^{-W})\}, & \Delta_2^c < \Delta. \end{cases} \quad (16)$$

The two solutions and the single-molecule optimal yield are shown in Fig. 2, where the plateau of the red curve belongs to the second case of Eq. (16). By visual inspection, it is immediately clear that, depending on the value of Δ , the advantage offered by correlations changes dramatically. In

particular, there is a regime of Δ (corresponding to $\Delta \lesssim W/2$) for which this advantage is large. Interestingly, this regime often includes typical photoisomers in nature (see [36,37] and references therein). Furthermore, we can see that requiring all correlations to vanish in the final state only gives a slight

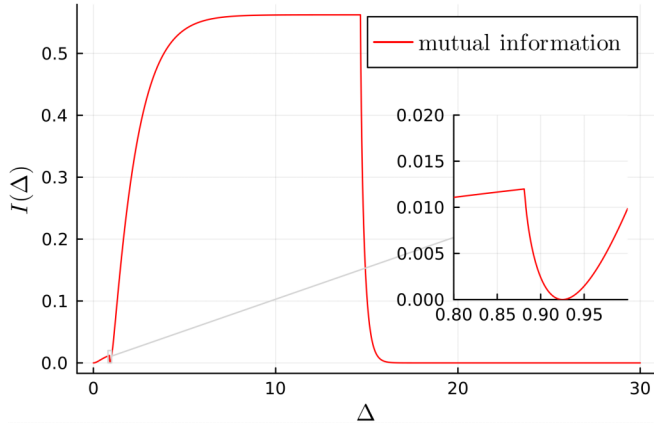


FIG. 3. Mutual information of the $N = 2$ correlated optimal state. When the correlation advantage becomes larger, the mutual information measures stronger correlations between the two molecules. On the other hand, when the optimal uncorrelated state performs as well as the optimal correlated one, the mutual information approaches zero, indicating that correlations are not needed to reach the optimal yield.

advantage over the single-molecule scenario. We can also measure the correlations in the optimal correlated state by computing the mutual information of the system, considering the reduced density matrices of the two molecules. In Fig. 3 the mutual information is shown to be approaching zero every time the correlation advantage becomes small, such as at large Δ and at the point where $\gamma_2^u = \gamma_2^c$ ($\Delta \approx 0.925$). Having this analysis at hand, the question arises of whether this trend continues upon further increasing the number of molecules.

VII. YIELD OPTIMIZATION ON A GENERIC NUMBER OF MOLECULES

When considering N molecules, the uncorrelated final state is given by

$$\sigma_N^u = [\gamma|\Delta\rangle\langle\Delta| + (1 - \gamma)|0\rangle\langle 0|]^{\otimes N}, \quad (17)$$

whereas the correlated final state σ_N^c has the freedom of being a generic diagonal symmetric state with its population distributed on the same levels as σ_N^u . The optimal yield can be found by constructing and optimizing thermomajorization curves. This results in piecewise functions since the β ordering depends on Δ (see Appendix A). In the case of two molecules, the number of cases defining the piecewise function is two for an uncorrelated final state and three for a correlated final state. When we have N molecules, the number of nondifferentiable points increases linearly when the final state is uncorrelated and quadratically if we allow for a correlated final state (cf. Appendix A). Furthermore, in the correlated case, we optimize over a set of N parameters [cf. Eq. (7)] instead of one for the uncorrelated case. Finding upper bounds on the yield for a large number of molecules becomes rapidly impractical as the number of molecules increases, since it requires the construction of numerous thermomajorization curves. Thus, we will now turn to numerical procedures to arrive at meaningful results for the case of large

N , as well as how the thermodynamic limit to the yield is approached in our model.

VIII. NUMERICAL APPROACH FOR MULTIPLE PHOTOSWITCHES

As the number of molecules N grows large, constructing the thermomajorization curves to obtain the optimal efficiency for a correlated final state analytically becomes infeasible in practice. Obtaining γ_N^c for larger N requires a numerical approach, for which we will employ the alternative resource theoretical tool to assess state convertibility: the Gibbs-stochastic matrices GS_N .

A matrix $G \in \text{GS}_N$ is a stochastic matrix whose stationary probability vector is the population vector of the Gibbs state

$$Gp_\tau = p_\tau. \quad (18)$$

These matrices describe how population vectors are transformed under thermal operations. Our initial and final states are diagonal, so thermomajorization is guaranteed if there is a $G \in \text{GS}_N$ such that

$$Gp_\rho = p_\sigma. \quad (19)$$

Our objective is to optimize the efficiency over the GS_N set, given the N -molecule initial-state population vector p_{ρ_N} :

$$\max_{G \in \text{GS}_N} \{\gamma(\sigma_N) \mid p_{\sigma_N} = Gp_{\rho_N}\}. \quad (20)$$

The matrix G has dimension $3^N \times 3^N$, a discouraging scaling with a numerical approach in mind, but we can show that the optimization problem can be reformulated to depend only on a subset of $N(N + 1)$ variables. This simplification is made possible by the invariance of the function to be optimized, the yield, under permutations of identical subsystems, and by the simple structure of the initial state, which as a product state of N identical copies will be characterized by simply $N + 1$ sets of degenerate, equally populated levels. A complete treatment of the optimization problem and its variable number reduction, including the role of the constraints, can be found in Appendix B. This pretreatment of the Gibbs-stochastic matrix can be readily adapted to different target functions with the same invariance property, possibly outside the context of photoisomerization. The same method is used with minor changes in Sec. XI, where coherence enters the picture in the initial state, and in Appendix D, where the molecule is modeled as a five-level system.

After this simplification, the numerical optimization can be performed efficiently. In Fig. 4 we compare the optimal efficiencies for settings up to $N = 50$ molecules. By comparing the optimal correlated and uncorrelated efficiencies at fixed N , we appreciate the large advantage provided by allowing for correlations in the final state. In addition, Fig. 4 shows how correlations in the final state allow the maximum efficiency to approach the thermodynamic limit quicker as the number of molecules increases.

IX. CORRELATION ADVANTAGE AND NUMBER OF PHOTOSWITCHES

In [26], the advantage provided by correlations in lowering the work of formation of a state is shown to be nonmonotonic

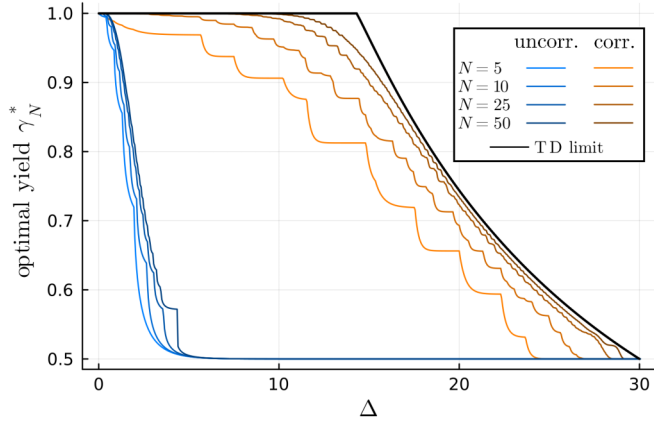


FIG. 4. Optimal photoisomerization yield for different system sizes. The curves in blue show the maximum yield with an uncorrelated-final-state hypothesis, while for the orange ones we allow correlations in the final state. The large difference between the two, comparing systems with the same size, shows the positive contribution of correlations on photoisomerization efficiency. The yield is plotted as a function of the energy Δ fixing $q = 0.5$ and $W = 30$. Appendix B shows a similar plot as a function of q .

in the number of copies N ; we show here that the same applies to the relative yield advantage

$$\delta_N = (\gamma_N^c - \gamma_N^u) / \gamma_N^u. \quad (21)$$

We can now choose a setting, e.g., a system with energies $\Delta = 3$, $W = 30$, and initial-state population $q = 0.5$, and then explore the dependence of δ_N on N . With this choice of parameters, we have that $\Delta < \Delta^*$ and thus $\gamma_{TD} = 1$. In Fig. 5 we plot γ_N^u , γ_N^c , and the relative advantage for this system. Here we can appreciate the fast convergence to the thermodynamic limit of the correlated scenario, as opposed to the slow and nonmonotonic increase of the uncorrelated optimal yield. We can also observe the relative advantage δ_N being nonmonotonic and presenting many local maxima. The

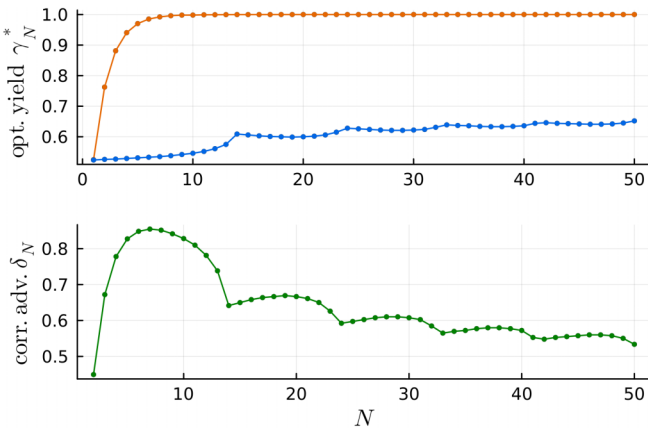


FIG. 5. Shown on top is the optimal yield as a function of the number of molecules N for uncorrelated (blue) and correlated (orange) final states. Shown on the bottom is the relative difference $\delta_N = (\gamma_N^c - \gamma_N^u) / \gamma_N^u$. One can notice the nonmonotonic behavior of the advantage δ_N provided by correlations. The system considered has energies $\Delta = 3$, $W = 30$, and initial-state population $q = 0.5$.

nonmonotonicity of Δ closely resembles the nonmonotonic behavior of the C work of formation found in Fig. 5 of the Supplemental Material of [26].

It is clear from Fig. 5 herein that the nonmonotonicity of δ_N results from the nonmonotonicity of γ_N^u . This behavior in N of the uncorrelated optimal yield might be surprising, as one might expect that increasing the number of molecules should not be detrimental to the process. Surely, when using $N + 1$ molecules, one possible protocol is to isolate one of them and perform a thermal operation that is a tensor product

$$\mathcal{T} = \mathcal{T}_{1,\dots,N} \otimes \mathcal{T}_{N+1}, \quad (22)$$

i.e., a global thermal operation on the first N molecules and a single-copy thermal operation on the last. However, this intuitive reasoning results in a negative lower bound for the yield difference of the $N + 1$ and N molecule systems. Let us define

$$\frac{\delta \gamma_N^*}{\gamma_N^*} = \frac{\gamma_{N+1}^* - \gamma_N^*}{\gamma_N^*}, \quad (23)$$

which quantifies the relative advantage on the optimal yield γ_N^* of N molecules due to the presence of an additional molecule. By using the protocol laid out in Eq. (22), the optimal yield γ_{N+1}^* is guaranteed to be upper bounded by

$$\gamma_{N+1}^* \geq \frac{N}{N+1} \gamma_N^* + \frac{1}{N+1} \gamma_1^*, \quad (24)$$

which implies

$$\frac{\delta \gamma_N^*}{\gamma_N^*} \geq -\frac{1}{N+1} \frac{\gamma_N^* - \gamma_1^*}{\gamma_N^*}. \quad (25)$$

Now the relative advantage of N copies over a single copy can be trivially bounded by a protocol implementing the thermal operation

$$\mathcal{T} = \bigotimes_{k=1}^N \mathcal{T}_k, \quad (26)$$

which acts independently on each copy, guaranteeing

$$\gamma_N^* \geq \gamma_1^*. \quad (27)$$

This means that the quantity on the right-hand side of Eq. (25) is always negative, and the simple protocol laid out in Eq. (22) does not guarantee an advantage in using an additional copy. However, this lower bound vanishes for $N \rightarrow \infty$, imposing monotonicity in the limit where N grows large.

X. LARGE- N REGIME

When the number of molecules becomes large, typicality arguments can be used to find approximations, particularly on the initial product state. This can in turn be used to capture the large- N behavior of the photoisomerization yield. The initial product state $\rho^{\otimes N} = [(1-q)|0\rangle\langle 0| + q|W\rangle\langle W|]^{\otimes N}$ can in particular be approximated by its most populated energy levels. For this state, the total population on a set of degenerate levels with energy kW is

$$p_k = \binom{N}{k} q^k (1-q)^{N-k}, \quad k = 0, \dots, N. \quad (28)$$

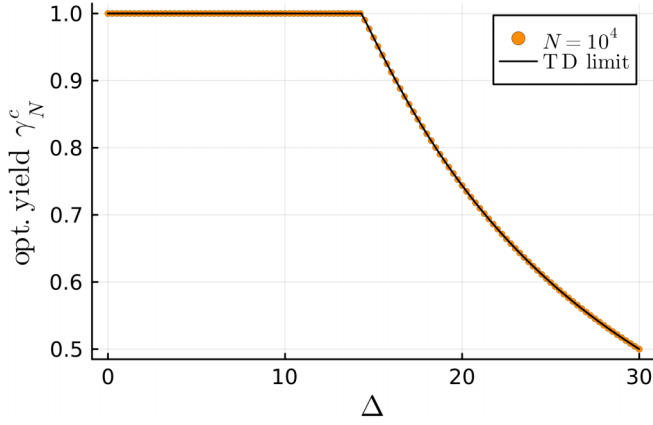


FIG. 6. Correlated optimal yield for $N = 10^4$ molecules, with the typical sequence approximation performed on the initial state. The excellent match shown between γ_N^c and γ_{TD} when N is large suggests that $\gamma_{N \rightarrow \infty}^c = \gamma_{TD}$.

In the limit where $N \rightarrow \infty$, the distribution peaks at the levels closest to $k \approx qN$ at energy $E \approx qNW$. We can obtain a reduced description of the initial state by discarding populations away from this energy subspace and then renormalizing the state, thus reducing the number of relevant parameters in the thermomajorization problem. This approach can simplify both the construction of the thermomajorization curves and the optimization over the GS_N set. The asymptotic limit can be obtained by keeping only the most typical sequences, that is, keeping only the levels $k = qN$ of energy $E = qNW$ (with the constraint for k to be an integer). We can thus use an approximated initial state $\tilde{\rho}_N$ with zero population everywhere except on those levels, each level having population $\left(\frac{N}{qN}\right)^{-1}$. One can easily show that the relative error on the free energy $\delta F/F := [F(\rho^{\otimes N}) - F(\tilde{\rho}_N)]/F(\rho^{\otimes N})$ goes to zero since it scales as $O(\log N/N)$. This can be seen by performing a Stirling approximation on the expression for $F(\tilde{\rho}_N)$.

The linear optimization problem can thus be rewritten to account for this simplification, obtaining a problem that scales only linearly with the number of molecules (see Appendix C for details). Moreover, it is possible to show analytically that for $\Delta \leq \Delta^*$ it holds that

$$\gamma_{\infty}^c(\Delta \leq \Delta^*) = \gamma_{TD}(\Delta \leq \Delta^*) = 1. \quad (29)$$

We expect the same to apply for $\Delta > \Delta^*$, and by numerically solving this optimization problem we obtain an excellent numerical match, shown in Fig. 6.

XI. ROLE OF COHERENCE

Thermal operations decouple the evolution of different modes of coherence [8], meaning that if the energy spectrum is nondegenerate, populations and coherences evolve separately. Suppose the Hamiltonian is degenerate, like in a multiple-copy system. In that case, an energy-preserving unitary can mix coherence and populations in that subspace. This can reduce the entropy of the initial population vector, increasing its thermodynamical value and therefore allowing a higher optimal yield. As stated earlier after Eq. (4), considering such initial quantum correlations is of physical interest

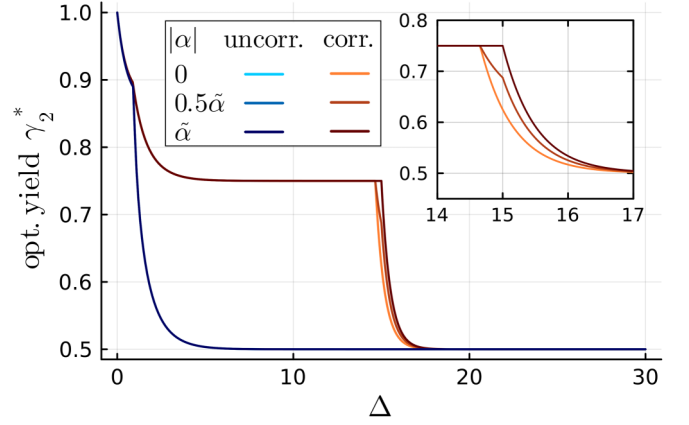


FIG. 7. Optimal yield for a two-molecule process in which some coherence is present, with $|\alpha| = \tilde{\alpha}$ the maximally coherent scenario. If correlations are not allowed in the final state, there is no noticeable advantage in the optimal yield and the blue curves are superposed. When this restriction is lifted, we see that in a small- Δ interval coherence provides a noticeable advantage, while for most values of Δ the advantage is negligible.

too, as photoisomers in nature can correlate, e.g., due to spatial proximity. Thus, we will now explore whether quantum correlations in the initial state can further boost the maximum yield.

We will focus on an $N = 2$ molecule system. To isolate the role of coherence in the efficiency boost, we will use an initial state which is a product state, as done before, to which we add some coherence in the relevant subspace, meaning

$$\rho_2(\alpha) = \rho^{\otimes 2} + \alpha|W0\rangle\langle 0W| + \alpha^*|0W\rangle\langle W0|. \quad (30)$$

In the subspace with energy $E = W$, there are two equally populated levels with population $q(1 - q)$. The coherence in this subspace can be expressed via the complex parameter α with $|\alpha| \in [0, \tilde{\alpha}]$ and $\tilde{\alpha} = q(1 - q)$ to ensure positive semidefiniteness. An energy-preserving unitary can then be applied as a free operation to diagonalize this subspace, mixing populations and coherences so that the new degenerate levels have populations $q(1 - q) \pm |\alpha|$. If $|\alpha| = \tilde{\alpha}$, the new state will have this subspace's population localized in a single energy level. As done in the previous sections, we can then optimize the yield by either allowing or excluding correlations in the final state, as shown in Fig. 7. If the final state is required to be uncorrelated, we observe no advantage from extra coherence in the initial state, so let us focus on the correlated-final-state scenario. In the presence of coherence ($|\alpha| \neq 0$) the optimal yield shows a relevant boost in a small region of Δ , while for most values of Δ the advantage is negligible, hinting that our previous findings would not be highly impacted by having this extra resource. Finally, we note that recently other authors have studied the role of quantum correlations in photoisomerization with similar resource theoretical tools [12]; however, their definition of the process yield differs from ours, making a direct comparison difficult. Despite this, our numerical procedure can also be efficiently applied to other definitions of target functions based on permutationally invariant observables.

XII. CONCLUSION

In this work we have quantitatively explored the impact of correlations on the efficiency of photoisomerization, using tools from quantum information theory. In particular, our results suggest that correlations between molecular switches can significantly increase the efficiency of the process. Moreover, we studied how this boost changes when the number of subsystems becomes large, confirming that the correlation advantage vanishes in the thermodynamic limit. To obtain these results, we employed techniques from the resource theory of athermality, developing numerical methods and approximations that can be efficiently applied to large systems to assess state convertibility. As discussed, the behavior of the relative advantage provided by correlations mirrors that of a thermodynamic quantity analyzed in [26]. It is still unclear how to relate the photoisomerization yield, and thus the corresponding correlation advantage, to strictly thermodynamic quantities such as the work of formation, which is surely an interesting direction for future work. Another intriguing line of inquiry would involve deploying the tools developed here to initial states that are fixed by a microscopic description of the photoisomer ensemble and its biomolecular dynamics when interacting with incoming radiation. In other words, it would be interesting to develop a microscopic model of photoexcitation and be able to infer a class of photoexcited molecular states which might exhibit collective excitations. This would provide a quantitative assessment of the impact of correlations in the initial state.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [38].

APPENDIX A: USING THERMOMAJORIZATION CURVES TO UPPER BOUND THE YIELD

In this appendix we show how the analytical form of the optimal yield is obtained from constructing thermomajorization curves. This procedure will be applied on a small number of molecules, as it becomes increasingly challenging as N increases. The construction of thermomajorization curves requires the β ordering of the population vector [8], which in this case is completely determined by whether the initial excitation q is smaller or larger than a threshold $\tilde{q} = 1/(1 + e^W)$. This defines two excitation regimes, and we focus on the high-excitation case ($q \geq \tilde{q}$), considering that for typical photoisomers W is large and thus $\tilde{q} \approx 0$.

Let us start with an uncorrelated final state, where we only need to optimize over a single parameter, which is the yield γ itself. For $N = 2$ molecules, one can find a depiction of the procedure used to obtain the optimal yield in Fig. 8, which can in principle be extended to a generic number of molecules.

The correlated optimal yield can be calculated with the same method, with the only difference that here we will find two critical values (i.e., the values of Δ for which the β ordering of the population vector changes, leading to elbow points in the final yield curves) instead of one for $N = 2$. Furthermore, we now have to optimize over two parameters instead of one. Generalizing this procedure to N molecules then requires additional expenses, as we have to take into consideration a number of case distinctions that scales with $O(N^2)$ and a number of parameters to optimize over that scales with $O(N)$. Yield upper bounds can then be constructed for any arbitrary N from the optimal populations according to Eq. (7), as can be seen in Fig. 9 for $N = 5$. We finally note that for specific molecules in realistic scenarios, the values of Δ and W are known. If they are thus fixed beforehand, the procedure of finding the optimal yield is simplified and can be carried out more efficiently, since there is no need in this case to consider all possible values of Δ .

APPENDIX B: THE GS_N LINEAR PROGRAM

Gibbs-stochastic matrices can be used as an alternative to thermomajorization curves to assess state convertibility in the resource theory of athermality. While theoretically equivalent, these two methods present very different computational challenges, such as the β ordering which is only needed for the curves. Here we show that, using Gibbs-stochastic matrices, we can construct a linear optimization problem that is efficiently solvable by standard algorithms. As we saw in Eq. (20), γ_N^c is the solution to the following optimization:

$$\max_{G \in GS_N} \{\gamma(p_{\sigma_N}) \mid p_{\sigma_N} = Gp_{\rho_N}\}. \quad (B1)$$

The entries of $G \in GS_N$ define the amount of population transfer from one level to another. The dimension of G , and thus the number of variables, scales exponentially with the number of copies. Nevertheless, we can greatly reduce the number of variables to optimize with some considerations on the states involved and the target function γ . The following steps can be applied to obtain a reduced optimization problem where the number of variables and constraints scales only as $O(N^2)$.

- (i) The yield depends on a subset of the parameters: Only a subset of the final-state populations contributes to the yield and only a subset of the initial-state levels is populated.
- (ii) Populations of degenerate levels have equal weights, resulting from the independence of γ from permutations of identical subsystems. We can therefore assume, without loss of generality, that any two entries of G moving population from degenerate levels to degenerate levels will be equal to each other.

Now the target function depends only on $N(N + 1)$ distinct variables $\{x_{ij}\}$, that is, the set of entries of G moving population from levels with energy $E = jW$, $j \in \{0, \dots, N\}$, to levels with energy $E = i\Delta$, $i \in \{1, \dots, N\}$.

The constraints of the optimization still depend on entries outside of this set, but the action of entries not entering the yield can be made trivial.

- (iii) The Gibbs-stochasticity condition fixes an arbitrary column: $Gp_\tau = p_\tau$ fixes the parameters in one of the matrix

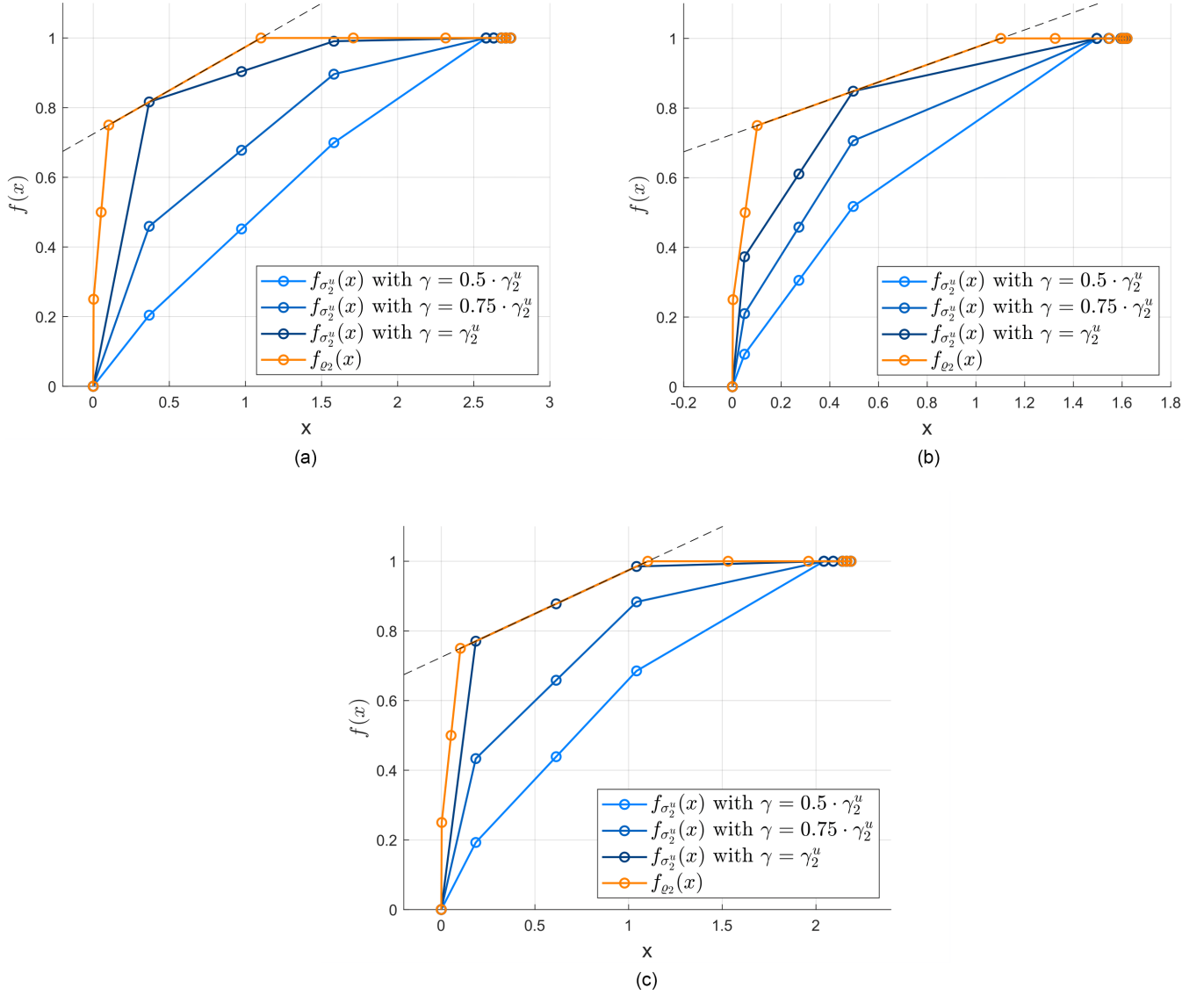


FIG. 8. Thermomajorization curves for different values of Δ in the setup of two molecules and an uncorrelated final state: (a) the first case $\Delta \leq \Delta_{\text{crit}}$ for $W = 3$ and $\Delta = 0.5$, (b) the second case $\Delta \geq \Delta_{\text{crit}}$ for $W = 3$ and $\Delta = 1.5$, and (c) both cases deliver the same result at $\Delta = \Delta_{\text{crit}}$ for $W = 3$ and $\Delta = \Delta_2^u \approx 0.8461$. The plots show how the final curve depends on the yield and thus how to maximize it under the constraints of thermomajorization. Depending on the value of Δ , the final curve changes its structure and thus a case distinction is needed.

columns [39]. We find that fixing a column corresponding to an empty level in the initial state simplifies the expression of the yield, as the expression resulting from said constraints is multiplied by zero. From now on, we will fix the column of the Gibbs-stochastic matrix referring to energy $E = 1\Delta$.

Let us call z_i the N entries of G in this column which depend on $\{x_{ij}\}$. To be valid entries, $z_i \in [0, 1]$ must hold. This is not automatically satisfied for all choices of $\{x_{ij}\}$ and we thus have to include them in our optimization.

(iv) Parameters that lower the yield can be set to zero. Let us focus on the N rows of G moving population to the levels that contribute to the yield. Some of the parameters in these rows have been renamed x_{ij} and z_i . We refer to the remaining ones as g_{ik} , which would move population away from energy levels that are empty in the initial state. We call $\mathcal{S}$ the set of column indices selecting these entries of G . With this notation,

the expression of the parameters z_i reads

$$z_i = \frac{e^{\Delta}}{N} \left[e^{-i\Delta} - \sum_{j=1}^{N+1} \binom{N}{j-1} x_{ij} e^{-(j-1)W} - \sum_{k \in \mathcal{S}} \deg(k) g_{ik} e^{-E_k} \right], \quad (\text{B2})$$

where we indicate by $\deg(k)$ the number of degenerate levels with energy E_k . It is trivial to show that $z_i \leq 1$ is always true, as the entries of G are all positive. The condition $0 \leq z_i$ reads

$$\sum_{j=1}^{N+1} \binom{N}{j-1} x_{ij} e^{-(j-1)W} \leq e^{-i\Delta} - \sum_{k \in \mathcal{S}} \deg(k) g_{ik} e^{-E_k}. \quad (\text{B3})$$

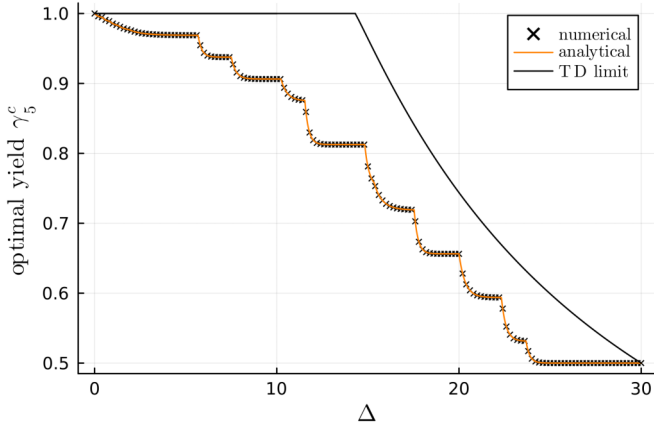


FIG. 9. Numerical optimization (cross markers) compared with the analytical solution (solid line) for $N = 5$ molecules. The match between the two supports the reliability of the numerical approach.

This inequality poses a constraint on a linear combination of x_{ij} with positive coefficients. Since the yield depends on $\{x_{ij}\}$ via positive coefficients, we want this upper bound to be as high as possible. Thus, we set to zero all the coefficients g_{ik} , obtaining

$$z_i = \frac{e^\Delta}{N} \left[e^{-i\Delta} - \sum_{j=1}^{N+1} \binom{N}{j-1} x_{ij} e^{-(j-1)W} \right]. \quad (\text{B4})$$

The resulting optimization problem reads

$$\begin{aligned} & \underset{x_{ij}}{\text{maximize}} \quad \gamma = \sum_{i=1}^N \binom{N}{i} \frac{i}{N} p_i \\ & \text{subject to } x_{ij} \in [0, 1], \quad i = 1, \dots, N; \quad j = 1, \dots, N+1 \\ & \quad z_i \in [0, 1], \quad i = 1, \dots, N \\ & \quad \sum_{i=1}^N \binom{N}{i} x_{ij} \leq 1, \quad j = 1, \dots, N+1 \\ & \quad \sum_{i=1}^N \binom{N}{i} z_i \leq 1, \\ & \quad p_i = \sum_{j=1}^{N+1} \binom{N}{j-1} x_{ij} (1-q)^{N-(j-1)} q^{j-1}, \\ & \quad z_i = \frac{e^\Delta}{N} \left[e^{-i\Delta} - \sum_{j=1}^{N+1} \binom{N}{j-1} x_{ij} e^{-(j-1)W} \right]. \end{aligned} \quad (\text{B5})$$

A comparison between the numerical optimization results and the analytical solution for a small system, for which the thermomajorization curve method is still feasible, is shown in Fig. 9. In this paper we conducted our analysis as a function of Δ , in continuity with the literature. However, this optimization can also be performed as a function of other system parameters, such as q , with no change needed. Figure 10 shows similar findings to Fig. 4 while varying q and keeping Δ fixed.

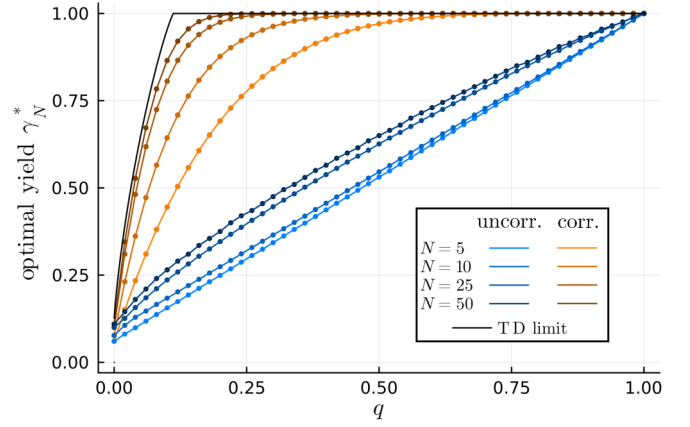


FIG. 10. Optimal yield with uncorrelated (blue) and correlated (orange) final states as a function of the initial-state population q for a molecule with energies $\Delta = 3$ and $W = 30$.

APPENDIX C: THE GS_N LINEAR PROGRAM IN THE LARGE- N REGIME

The populations of the initial state $\rho^{\otimes N}$ are distributed on sets of degenerate levels as described in Eq. (28). When $N \rightarrow \infty$ the state can be approximated by its most populated levels. In particular, the population distribution in this regime peaks on energy levels with energy qNW ,

$$\rho^{\otimes N} \approx \left(\binom{N}{qN} \right)^{-1} \sum_{ij} P_{ij} |0^{\otimes(1-q)N} W^{\otimes qN} \rangle \langle 0^{\otimes(1-q)N} W^{\otimes qN} | P_{ij}^\dagger, \quad (\text{C1})$$

where P_{ij} permutes a pair of molecules. With this approximation, the entire population of the initial state is distributed on one set of degenerate energy levels. Repeating the same reasoning of Appendix B, there will be only N distinct transfer rates x_i , one for each target level on the final state with energy $i\Delta$ with $i \in \{1, \dots, N\}$. The simplified optimization problem now reads

$$\begin{aligned} & \underset{x_i}{\text{maximize}} \quad \gamma = \sum_{i=1}^N \binom{N}{i} \frac{i}{N} x_i \\ & \text{subject to } x_i \in [0, 1], \quad i = 1, \dots, N \\ & \quad \sum_{i=1}^N \binom{N}{i} x_i \leq 1, \\ & \quad x_i \leq \exp(-i\Delta + N\Delta^*), \quad i = 1, \dots, N. \end{aligned} \quad (\text{C2})$$

Interestingly, the free energy of the initial state $\Delta^* = qW + q \ln q + (1-q) \ln(1-q)$ appears now explicitly. If we expand the sum defining γ , the parameter x_N always appears with a multiplying coefficient equal to 1,

$$\gamma = x_1 + (N-1)x_2 + \dots + (N-1)x_{N-1} + x_N, \quad (\text{C3})$$

while the constraints acting on this transfer rate read

$$x_N \leq 1 - \sum_{i=1}^{N-1} \binom{N}{i} x_i, \quad (\text{C4})$$

$$x_N \leq \exp[-N(\Delta - \Delta^*)]. \quad (\text{C5})$$

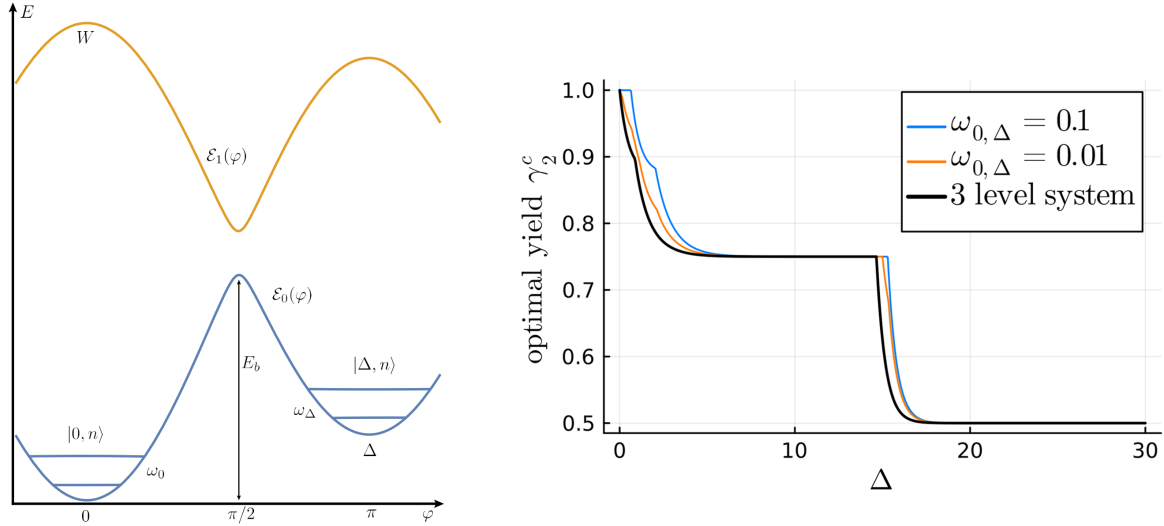


FIG. 11. Shown on the left is a five-level system model, obtained by considering one extra level for each minimum of the electronic ground state (the spacing between levels is exaggerated for legibility and is not to scale). Shown on the right is the optimal efficiency for $N = 2$ photoswitches, each modeled with a five-level system, with $\Delta \in [0, W = 30]$. Correlations are allowed in the final state, and the optimal efficiency is calculated for two different values of $\omega_{0,\Delta}$. The bounds are obtained for a high local inverse temperature $\beta_0 = 100$, consistent with the Hilbert space truncation. The three-level model is shown for comparison.

If $\Delta \leq \Delta^*$ the right-hand side of the second constraint is always greater than 1 and the constraint is therefore not active. This defines a range of Δ in which we can set $x_N = 1$ and all other $x_i = 0$, thus obtaining $\gamma_\infty^c(\Delta \leq \Delta^*) \equiv 1$.

APPENDIX D: REFINING THE MODEL

Following the previous literature on the description of photoisomerization through the resource theory of athermality, the Hilbert space of the electronic degrees of freedom of the rotating molecule was truncated to a three-level system. This will impact the thermodynamic behavior of the system, which has fewer degrees of freedom available to spread and raise its entropy. The dimensionality of the Hilbert space can indeed be considered a thermodynamical resource (see, e.g., [40]), but it is not immediately clear what the magnitude of this advantage will be. In theory, one should account for the full vibrational spectrum of the molecule, but this would quickly become numerically intractable. Instead, we keep the assumption of fairly localized states in φ and improve the model's resolution by introducing one extra level in each potential well in the energy landscape. Following the arguments in [13], this results in a five-level model, as shown in Fig. 11. We can now use the numerical method based on the GS_N set developed in this paper to explore the effect of these extra levels. The order of magnitude of the energy of these new first excited states ω_0 and ω_Δ is, in real molecules, much smaller than Δ and W

(see [37]). To simplify the calculations, we choose them to be equal and obtain the efficiency bounds for $\omega_{0,\Delta} \in \{0.1, 0.01\}$.

The initial state ρ must now be redefined, as the fraction of population $(1 - q)$ which was not excited by the incident radiation must now be distributed on two energy levels. On these two levels, we impose a local thermalization, so that the total population $(1 - q)$ is distributed as

$$q_0 = (1 - q) \frac{1}{1 + \exp(-\beta_0 \omega_0)}, \quad (\text{D1})$$

$$q_{\omega_0} = (1 - q) \frac{\exp(-\beta_0 \omega_0)}{1 + \exp(-\beta_0 \omega_0)}, \quad (\text{D2})$$

with β_0 the effective inverse temperature on the subsystem. To keep our Hilbert space truncation approximation consistent, we choose a large β_0 so that the population distribution peaks at the lowest level. In redefining Eq. (5), we impose that levels at $\varphi = \pi$ contribute equally regardless of their energy:

$$\mathcal{O} = \frac{1}{N} \sum_n \sum_{i=1}^N (|\Delta, n\rangle \langle \Delta, n|)_i. \quad (\text{D3})$$

As we can see from Fig. 11, the presence of extra levels can indeed increase the maximum yield, by allowing populations to spread on more levels contributing to the yield (at least this is the case for some regions of Δ).

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