

Thermodynamics of the optical pumping process in nitrogen-vacancy centers

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The optical pumping process is a fundamental tool for quantum protocols using the electronic and nuclear spins in the nitrogen-vacancy (NV) center platform. In this work, we explore the process of electronic spin polarization through optical pumping from a thermodynamic perspective. We identify the sources of work and heat and show that the heat current is directly related to the experimentally accessible fluorescence of the NV center. We also show that the polarization of the electronic spin depends on the amount of energy that is provided to the system by the laser pump. Moreover, we study the von Neumann entropy change in the process. We demonstrate that the entropy can be separated into two contributions: one due to the heat produced and the other due to the energy provided by the laser, which is a consequence of the nonunitary nature of the pumping process. Finally, we show that increasing the power of the laser results in an increased entropy of the final state, which hinders the polarization efficiency.

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I. INTRODUCTION

Nitrogen-vacancy (NV) centers in diamond [1,2] have emerged as a prominent platform for solid-state quantum technologies. Most of their success comes from the fact that they have very long coherence times, being able to reach on the order of seconds even at room temperature [3,4]. Other key aspects are the optical properties of the NV center, which allow for the electronic spin readout and initialization; coherent control is also achieved by using pulses in the radio-frequency domain. Due to these properties, NV centers have a multitude of interesting applications. They can be used for quantum information processing [5–7] and are also a suitable platform for building diamond-based integrated quantum photonic architectures [8–10]. Moreover, NV centers can be used as extremely precise quantum sensors [11,12]. Their robustness to sense physical quantities, such as magnetic fields [13–15], makes them a powerful tool that has important applications in biochemistry contexts [16,17], where they can be used, for instance, for nanorheometry and nanothermometry of living cells inside complex environments [18].

In all of those applications, the optical properties of the NV center play a significant role. The electronic spin of the NV center can be optically excited from its ground state by using a green (532 nm) laser. A spin-conserving decay from

the excited state is responsible for the NV spin-dependent fluorescence (around 637 nm, red), which allows for the direct readout of the electronic spin state. Due to the existence of an additional decaying route via intersystem crossing (ISC), the optical dynamics can also be used to polarize the electronic spin [19,20]. This optical pumping process is then a fundamental tool for controlling quantum technologies based on NV centers and has been thoroughly explored in the past few years [19–28].

All these studies focused on understanding the electronic structure and main dissipative mechanisms during the optical excitation of the NV. Although it is well understood now and routinely used in most experiments, spin polarization via optical pumping is a nontrivial phenomenon that involves energy transfer from light to the NV center: The electronic spin state, which is initially in a mixed state, absorbs energy from the light and is irreversibly driven to a final state that is almost pure. More specifically, the laser is used to incoherently drive the system to a nonequilibrium steady state (NESS). After that, the laser is turned off, and due to the spin-conserving and ISC channels, the system naturally decays, reaching a final state that is almost the electronic ground state (polarization). Similar in spirit to thermodynamic cycles (such as a refrigerator), this process suggests that the system needs to first absorb energy from a source and then dump some of it in the environment in order to realize a task, which, in this case, is the polarization of the electronic spin. Such an intriguing phenomenon then calls for a thermodynamic analysis, which, to the best of our knowledge, has not yet been conducted. From a thermodynamics perspective, we can think of the laser as an energy supplier (or work load) that incoherently feeds energy into the system. The spin-conserving and ISC channels, in turn, are responsible for radiative (photon emission) and nonradiative decaying processes, where energy leaves the system in the form of heat. Motivated by the

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latter discussion, in this work, we investigate the optical polarization of the NV electronic spin from a thermodynamic perspective. We explore the energy dynamics of the system and identify the key thermodynamic quantities, heat currents and power, providing analytical expressions that describe the system's polarization from a thermodynamic perspective. We also explore the von Neumann entropy change of the system and determine its role in the protocol.

This article is organized as follows. In Sec. II, we present the framework used to model the electronic spin of the NV center during the optical process. Specifically, we describe it as an eight-level system that captures the relevant energy states involved in the optical pumping process. In Sec. III, we analyze the optical dynamics of the NV center, which can be effectively described by a Markovian master equation. In Sec. IV, we present our main contribution, which is a thermodynamic analysis of the optical pumping process. We define work and heat and relate them to the spin-polarization efficiency. We also investigate how the von Neumann entropy of the system changes during the optical dynamics. We separate the entropy change into two contributions, one due to the irreversible energy injected into the system and the other due to the heat dissipated. Finally, in Sec. V, we present our final remarks and discuss possible next steps.

II. EIGHT-LEVEL MODEL

In the NV-center system, the optical pumping is primarily used to polarize and read out the electronic spin. In this work, we focus on the spin polarization, in which the optical pump is used to prepare the electronic spin in its ground state. The dynamics of the optical pumping involve three subspaces. The ground (G) and excited (E) subspaces, which are spin triplets, and the ISC (I for short in subscripts) subspace, which is a spin singlet. Then, our system can be effectively modeled by an eight-level Hamiltonian H , whose structure is depicted in Fig. 1. The eigenstates of H are denoted by the orthonormal column vectors $\{|n\rangle\}$ and form an ordered complete basis for the Hilbert space of dimension 8.

Following Ref. [29], we can decompose the total Hilbert space of the system as a direct sum of the three subspaces:

$$\mathcal{H} = \mathcal{H}_G \oplus \mathcal{H}_E \oplus \mathcal{H}_I, \quad (1)$$

where $\dim(\mathcal{H}_G) = \dim(\mathcal{H}_E) = 3$ and $\dim(\mathcal{H}_I) = 2$. Then, the total Hamiltonian of the model can be cast in block-diagonal form as

$$H = H_G \oplus \mathbf{0}_E \oplus \mathbf{0}_I + \mathbf{0}_G \oplus H_E \oplus \mathbf{0}_I + \mathbf{0}_G \oplus \mathbf{0}_E \oplus H_I, \quad (2)$$

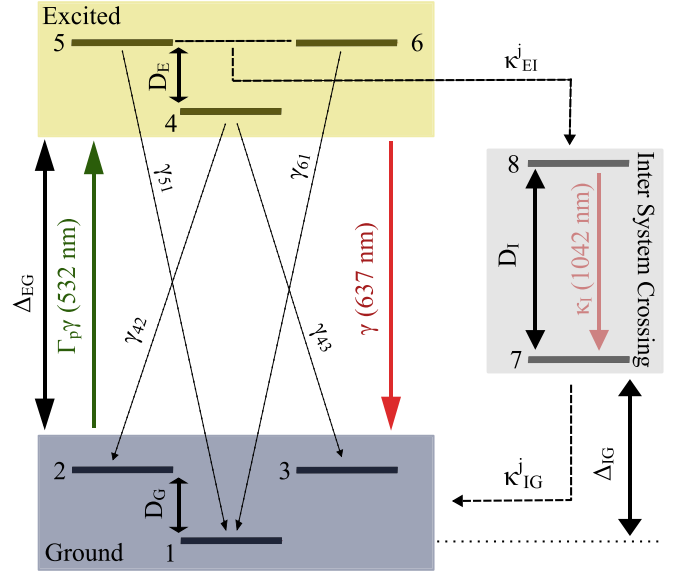
where $\mathbf{0}_k$ is the null matrix of $\dim(\mathcal{H}_k)$ and

$$H_G = D_G S_z^2 + \omega_g B_z S_z, \quad (3)$$

$$H_E = D_E S_z^2 + \omega_g B_z S_z + \Delta_{EG} S_0, \quad (4)$$

$$H_I = \left(\Delta_{IG} + \frac{D_I}{2} \right) \sigma_0 - \frac{D_I}{2} \sigma_z. \quad (5)$$

For the ordered basis $\{|1\rangle, |2\rangle, |3\rangle\}$ and $\{|4\rangle, |5\rangle, |6\rangle\}$, which spans the G and E subspaces, respectively, we use $S_z =$



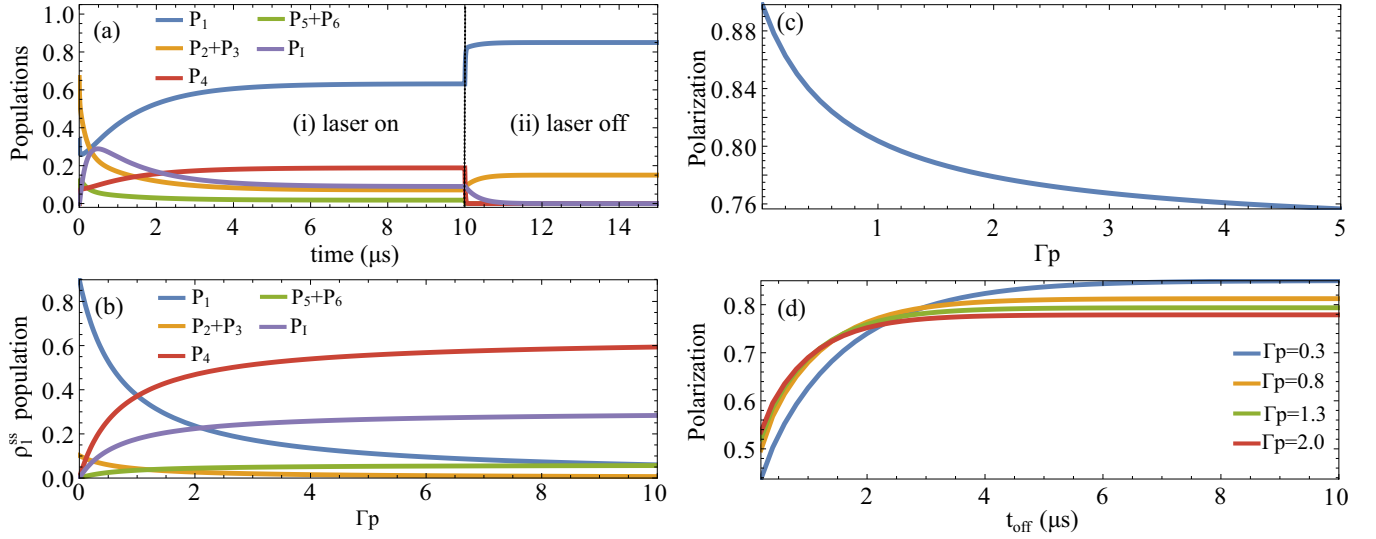


FIG. 2. (a) Dynamics of the eight-level system during the optical pumping process in the NV center. The first step consists of turning on the laser and waiting until the system reaches the nonequilibrium steady state (NESS) ρ_1^{ss} . Then, the laser is turned off and reaches a new NESS ρ_2^{ss} . The population accumulated in P_4 is transferred to P_1 , polarizing the system. Due to the decaying channel κ_{IG} , which transfers the population accumulated in the ISC almost equally to the G subspace, the polarization is not perfect. (b) NESS state ρ_1^{ss} in step (i) as a function of the parameter Γ_p . (c) Polarization as a function of the laser power Γ_p . (d) Polarization as a function of the time the laser remains on during step (i).

is incoherently transferred from $|7\rangle$ to G, being distributed approximately even in levels $|1\rangle$, $|2\rangle$, and $|3\rangle$. Other nonradiative decays from E to G exist but are negligible, in principle, if compared to the other decay mechanisms. However, since they can be characterized, we are not dismissing them for the sake of completeness. The pumping process and all decay channels are illustrated in Fig. 1.

The optical dynamics of the eight-level model can be effectively described by a Lindblad master equation [30,31]:

$$\dot{\rho} = -i[H, \rho] + \mathcal{D}_p(\rho) + \sum_{i=1}^3 \mathcal{D}_d^i(\rho), \quad (6)$$

where ρ is the state of the system and $\dot{\rho} = d\rho/dt$ represents the time derivative. The superoperators $\mathcal{D}(\bullet)$, usually called dissipators, describe the nonunitary part of the dynamics and are defined by

$$\mathcal{D}(\bullet) = \sum_j L_j \bullet L_j^\dagger - \frac{1}{2}(L_j^\dagger L_j \bullet + \bullet L_j^\dagger L_j), \quad (7)$$

with L_j being a jump (or Lindblad) operator, which depends on the physical process considered. We conveniently separate the nonunitary dynamics into two contributions, where $\mathcal{D}_p(\rho)$ is the laser pump contribution and $\mathcal{D}_d^i(\rho)$ are the decaying processes. As we shall see in the next section, $\mathcal{D}_p(\rho)$ and $\mathcal{D}_d^i(\rho)$ can be, respectively, connected to the work and heat production in the optical pumping process. The explicit form of each dissipator and jump operator is presented in Appendix A. Treating the optical dynamics as an effective master equation evolving these three subspaces has been widely adopted by the NV-center community and faithfully reproduces a multitude of experimental results [27,32–36]. A purely Hamiltonian description of the eight levels, without coupling to phonon and photon reservoirs, would fail to capture the experimentally observed irreversible optical pumping,

finite excited-state lifetimes, and spin-dependent fluorescence contrast. In our approach, these well-established irreversible processes are encoded in the Lindblad jump operators in Eq. (6), with rates fixed by experimental characterization [19–29]. The master equation therefore represents a standard effective description of the open-system dynamics of the NV center under optical illumination, rather than an *ad hoc* choice.

In this work, we consider the initial state to be a mixed state $\rho(t=0) = \frac{1}{3} \sum_{n=1}^3 |n\rangle\langle n|$. As the states in the E and ISC subspaces have energies up to hundreds of terahertz, they are not thermally excited. For the G subspace, the energy levels are of the order of a few gigahertz. This means that, except for very low temperatures, this choice of $\rho(0)$ represents a thermal equilibrium state for the NV center. Since the initial state is diagonal (incoherent) in the basis $\{|n\rangle\}$ and there are no coherence-generating terms in the Hamiltonian, the system's dynamics will be completely incoherent; i.e., only the populations $P_n = \langle n|\rho|n\rangle$ of ρ will evolve in time. The following plots in this work are obtained by numerically solving Eq. (6). In Appendix B, we show the complete system of equations to be solved.

The electronic spin polarization of the NV is performed in two steps. In step (i), the laser is turned on and interacts with the system until it reaches a first steady state, namely, ρ_1^{ss} . We remark here that ρ_1^{ss} is a NESS. In step (ii), after the first NESS ρ_1^{ss} is reached, the laser is turned off, and the system relaxes to a new NESS, ρ_2^{ss} . The population that accumulated in the excited state $|4\rangle$ is almost completely transferred to $|1\rangle$, which finishes the polarization process. For our purposes, by “polarization,” we mean the population of the ground state, $|1\rangle$, in the second NESS ρ_2^{ss} . In Fig. 2(a), we give an example of the optical dynamics of the NV. In the plot, we can see that the system reaches the NESS ρ_1^{ss} around $t = 10 \mu\text{s}$. Then, the laser is turned off, and the population P_1 increases to

near unity in the NESS ρ_1^{ss} . As observed, the polarization is not perfect, with portions of the population transferring to P_2 and P_3 . This is primarily due to the portion of the population accumulated in the ISC subspace, represented by $P_1 = P_7 + P_8$, that is approximately equally distributed to the ground state triplet when the laser is turned off. As the population decay rate from $|8\rangle$ to $|7\rangle$ is extremely fast when compared with the other decaying rates (approximately 1 GHz), we have $P_1 \approx P_7$ in the NESS ρ_1^{ss} .

In our model, the power of the laser is related to the unitless parameter Γ_p (see Appendix A), which is essentially connected to the number of photons that are absorbed by the system. Without loss of generality, from this point forward, we refer to Γ_p as laser power. The question that arises is how the spin polarization depends on the laser power Γ_p . It is natural to expect that if we have a higher Γ_p , it will speed up the dynamics since the pumping excitation rate will increase. Thus, this enables the system to reach the NESS ρ_1^{ss} more quickly. However, it is not immediately clear whether this will enhance the polarization. To gain a deeper understanding of how the polarization depends on the laser power, we first examine the dependence of the NESS ρ_1^{ss} on Γ_p . Figure 2(b) illustrates the behavior of the NESS populations ρ_1^{ss} as a function of Γ_p . The plot clearly shows that the NESS population P_1 decreases with Γ_p , while the populations P_4 and $P_1 = P_7 + P_8$ increase. This occurs because, as the pumping rate Γ_p increases, the excited subspace populates faster than it decays to the G triplet. In particular, for $\Gamma_p > 1$ the rate at which the system is excited from G to E is higher than the rate of spin-conserving decay. This means that for this regime, subspace E is more populated than subspace G. We also observe that the system reaches a saturation regime with Γ_p , where the populations in the NESS ρ_1^{ss} stop changing when the laser power is increased. Moreover, increasing Γ_p also allows more population to be transferred to the ISC subspace. Then, after turning off the laser, from Fig. 2(c), we see that the polarization decreases with Γ_p . This happens because a greater population accumulates in P_7 in step (i), and consequently, a greater population is transferred to P_2 and P_3 in step (ii). Finally, in Fig. 2(d) we show the dependence of the polarization on the time at which the laser is turned off t_{off} . It is clear that the laser needs to remain on for a sufficient time for the system to reach the NESS ρ_1^{ss} ; otherwise, the spin polarization is hindered. We would like to emphasize that the evolution of the system after the laser is turned off, i.e., for $t > t_{\text{off}}$, follows the same dynamics as in Eq. (6), but without the laser contribution $\mathcal{D}_p(\rho)$.

The parameter regime used in this work is grounded in detailed experimental characterization of NV-center optical dynamics [19–25, 27–29]. In particular, the values of the radiative, spin-selective, and spin-mixing rates in Table I reproduce the steady-state polarization curves and fluorescence contrast reported in Ref. [29] when the same pumping protocol is simulated within our eight-level model. The saturation of the spin polarization with increasing laser power, as well as the incomplete polarization due to residual spin-mixing processes obtained in our calculations, is consistent with that experimental study. Our thermodynamic analysis therefore provides an energetic interpretation of features already well established in the NV literature.

TABLE I. Decay parameters used in this work.

Parameter	Value
γ	77.0 MHz
$\gamma_{42} = \gamma_{43} = \gamma_{51} = \gamma_{61}$	0.25 MHz
κ_{EI}^4	0
$\kappa_{\text{EI}}^5 = \kappa_{\text{EI}}^6$	15.0 MHz
$\kappa_{\text{IG}}^1 = \kappa_{\text{IG}}^2 = \kappa_{\text{IG}}^3$	1.0 MHz
κ_1	1.0 GHz

IV. THERMODYNAMICS OF THE OPTICAL PUMPING

In the previous section, we described how the optical dynamics work and how it is used to polarize the spin. This interesting process uses the laser to drive the system from an equilibrium state to a NESS. Then, a specific dissipation process drives the system to a second NESS, which is nearly pure. Although this process is routinely used in almost all protocols that involve NV centers, to the best of our knowledge, it has not yet been studied from a thermodynamic perspective. From this point of view, the laser acts as an energy supplier (or work load) that pumps energy incoherently into the system. This energy pump is followed by radiative (photon emission) and nonradiative decaying processes, in which energy leaves the system in the form of heat. Interestingly, the energy dissipation occurs in such a way that the final state has less entropy than the initial maximally mixed state. Likewise, the results in the last section suggest that the polarization process depends on the amount of energy provided to the system through laser pumping [see the discussion of Fig. 2(d)], which gives us additional motivation for a thermodynamical analysis.

To begin our thermodynamic investigation of the optical pumping process, we first need to define the power fed into the system and the heat currents. As the dynamics of the system is completely incoherent, we can readily identify these contributions by looking at the time derivative of the system's internal energy, $U(\rho) = \text{Tr}\{H\rho\}$, which is given by $\dot{U}(\rho) = \text{Tr}\{H\dot{\rho}\}$. Using the master equation in Eq. (6), we obtain the following expression:

$$\dot{U}(\rho) = \text{Tr}\{H\mathcal{D}_p(\rho)\} + \sum_{i=1}^3 \text{Tr}\{H\mathcal{D}_d^i(\rho)\}. \quad (8)$$

From Eq. (8) and the first law of thermodynamics, we can identify the heat currents $\dot{Q}$ and power $\dot{W}$ as

$$\dot{W} = \text{Tr}\{H\mathcal{D}_p(\rho)\}, \quad (9)$$

$$\dot{Q} = \sum_{i=1}^3 \dot{Q}_i = \sum_{i=1}^3 \text{Tr}\{H\mathcal{D}_d^i(\rho)\}. \quad (10)$$

The key point for this splitting is that the laser pump appears as a separate dissipator $\mathcal{D}_p(\rho)$, which models a work reservoir that injects energy into the system without generating coherences in the eigenbasis of H . We therefore identify the power as the energy current associated with this term, $\dot{W} = \text{Tr}\{H\mathcal{D}_p(\rho)\}$, while the heat currents $\dot{Q}_i = \text{Tr}\{H\mathcal{D}_d^i(\rho)\}$ arise from the spontaneous emission and ISC channels that describe the photons and phonons lost to the environment. This identification ensures that the first law, $\dot{U} = \dot{W} + \sum_i \dot{Q}_i$,

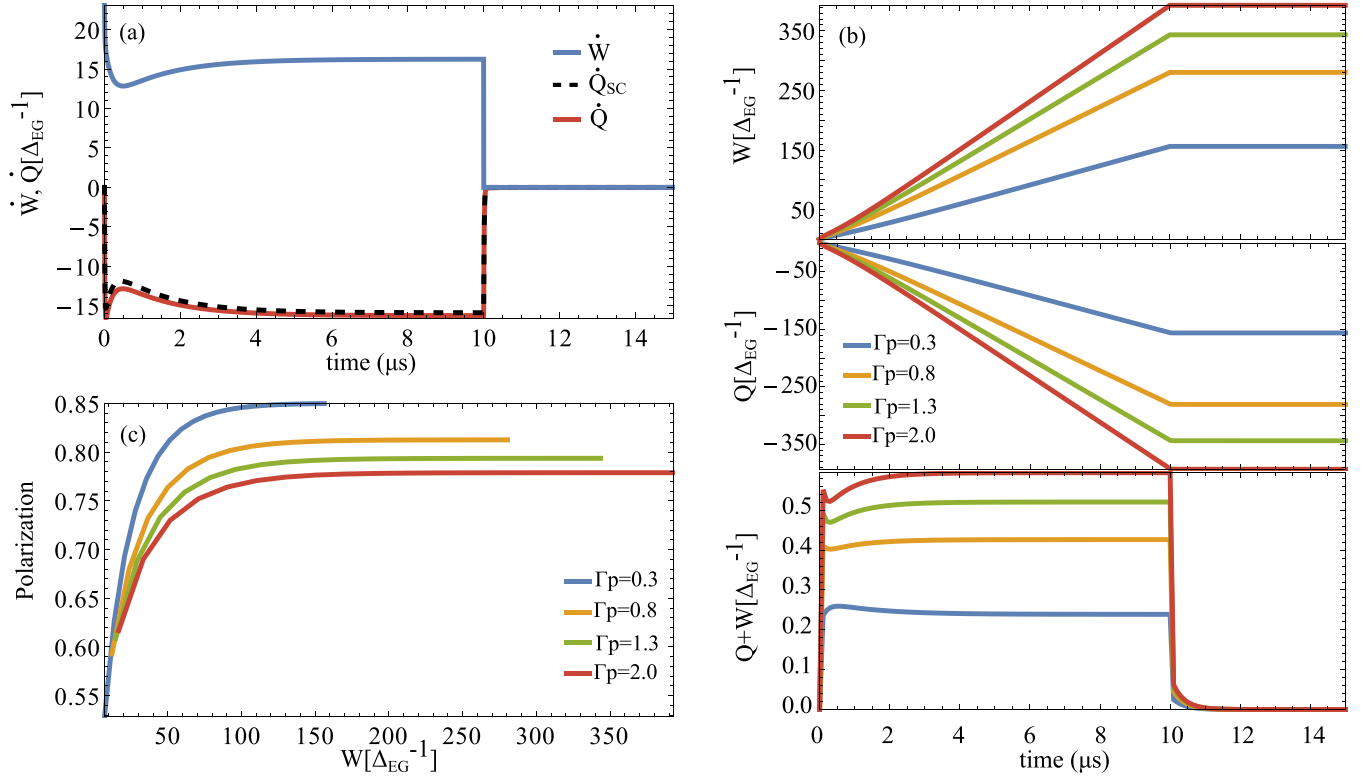


FIG. 3. (a) Heat currents and power during the optical pumping process. We see that the total heat flux produced $\dot{Q}$ (red solid line) is almost entirely due to the heat flux produced by the spin-conserving process $\dot{Q}_{sc}$ (black dashed line). (b) Integrated quantities and internal energy variation during the optical pumping process. (c) Parametric plot of the polarization of the NV electronic spin as a function of the energy provided by the laser in step (i) of the optical pumping process. To generate this plot we varied the time t_{off} in the interval (0, 10] μs .

holds identically for any state ρ . In particular, the pump dissipator $\mathcal{D}_p(\rho)$ effectively encodes the action of an off-resonant classical laser field, while the dissipators $\mathcal{D}_i^d(\rho)$ describe radiative and nonradiative channels whose rates are constrained by the experimental characterization of the NV-center dynamics [19–29].

Working with Eq. (9), one can define the power delivered by the laser pump as

$$\dot{W} = \Gamma_p \gamma [\Delta_{41} P_1 + \Delta_{52} P_2 + \Delta_{63} P_3], \quad (11)$$

where $\Delta_{ij} = \mathcal{E}_i - \mathcal{E}_j$, with $H|n\rangle = \mathcal{E}_n|n\rangle$, is the energy gap between states $|i\rangle$ and $|j\rangle$ and γ is the spin-conserving spontaneous emission rate from E to G (see Table I), which sets the timescale of the natural optical cycle. As the energy gap Δ_{EG} between the G and E subspaces is on the order of hundreds of terahertz and the gap of the energy levels inside subspaces E and G are a few gigahertz, we have $\Delta_{41} \approx \Delta_{52} \approx \Delta_{63} \approx \Delta_{EG}$. We can then rewrite the power as

$$\dot{W} = \Delta_{EG} \Gamma_p \gamma P_G, \quad (12)$$

where P_G is the total population of the G subspace, i.e., $P_G = \sum_{n=1}^3 P_n$. The total energy supplied to the system can be obtained by integrating the above quantity in the time interval $[0, t_{off}]$. As observed, the power absorbed by the system is proportional to the population of subspace G, with the proportionality constant being the product of the energy gap Δ_{EG} and the pump excitation rate $\Gamma_p \gamma$. As anticipated, we can control the power injected into the system by tuning the controllable parameter Γ_p .

For the heat currents, we can proceed in a similar fashion. Let us focus on the heat contribution coming from the spin-conserving decay part, which we define as $\dot{Q}_{sc} \equiv \dot{Q}_1$. It is straightforward to show that

$$\dot{Q}_{sc} = -\Delta_{EG} \gamma P_E, \quad (13)$$

where P_E is the total population of E, i.e., $P_E = \sum_{n=4}^6 P_n$. Equation (13) implies that the heat-current contribution $\dot{Q}_{sc}$ is proportional to the photon current γP_E , which is exactly the measurable fluorescence of the NV center. This result is physically significant as it identifies the radiative heat current with the standard spin-dependent fluorescence signal measured in NV experiments. Since accessing heat in quantum thermodynamics is generally challenging, this provides an experimentally convenient proxy for the heat flow during optical pumping.

In Fig. 3(a), we show the power and heat current produced in the optical pumping process. We compare the total heat current $\dot{Q}$ obtained from Eq. (10) with the heat current obtained from the spin-conserving decay part $\dot{Q}_{sc}$, as in Eq. (13). We observe that $\dot{Q}_{sc}$ accounts for almost all the heat current generated in the process. This is an interesting and experimentally useful observation, as it suggests that we can estimate the total heat current from $\dot{Q}_{sc}$ alone, which is directly accessible through standard NV fluorescence measurements. In Fig. 3(b), we show the integrated quantities and internal energy as a function of time for the optical process. We observe that most of the work and heat are produced in step (i) of the optical

process, i.e., while the laser is on for $t \leq t_{\text{off}} = 10 \mu\text{s}$. For the work contribution, this happens because power is being supplied to the system only while the laser is on. For the heat contribution, this arises because after the laser is turned off, the system quickly relaxes to the NESS ρ_2^{ss} [see Fig. 2(a)]. Since in ρ_2^{ss} the system is entirely in the G subspace, the heat current is zero [see Fig. 3(a)]. As the variation in heat current from ρ_1^{ss} to ρ_2^{ss} occurs very rapidly, the integral of $\dot{Q}$ for $t > t_{\text{off}}$ is negligible compared to the integral contribution in the interval $t \in [0, t_{\text{off}}]$.

In Fig. 3(c), we present the polarization as a function of the energy delivered by the pump in step (i). To generate this plot, we vary the time t_{off} at which the laser is turned off in step (i) in the interval $t_{\text{off}} \in (0 \mu\text{s}, 10 \mu\text{s}]$. Then, we compute the polarization and energy delivered for each different t_{off} . We observe that for a fixed Γ_p , the polarization increases with the energy provided until it reaches the saturation regime. The saturation value of the polarization depends on Γ_p . This behavior is consistent with the discussion in Fig. 2(d) and with the fact that the longer the laser is on, the greater the amount of energy pumped into the system is. However, it provides a neater and more interesting thermodynamic interpretation. This means that the laser needs to be turned on for a sufficient amount of time so that the system can absorb enough work to be able to reach the NESS ρ_1^{ss} , thus providing the “maximal polarization.” The saturation occurs when the system reaches ρ_1^{ss} , for which $\dot{U} = 0$, and therefore $\dot{W} = -\dot{Q}$. This means that, in the NESS, all the energy supplied by the pump leaves the system as heat through the decaying processes.

In order to provide a complete thermodynamic perspective of the process, we now study the instantaneous variation of the system’s von Neumann entropy, which reads $S(\rho) = -\text{Tr}\{\rho \ln \rho\}$. It is worth remarking that since the dynamics is completely incoherent, in this case the von Neumann entropy is identical to the Shannon entropy for the system’s population, i.e., $H(\vec{P}) = -\sum_{n=1}^8 P_n \ln P_n$, where $\vec{P}$ is a vector with elements P_n . The density operator formalism allows us to define the contributions from power and heat currents to the von Neumann entropy change. If we take the time derivative of the von Neumann entropy, a simple calculation yields $\dot{S}(\rho) = -\text{Tr}\{\dot{\rho} \ln \rho\}$. Then, using the master equation in Eq. (6), we can write $\dot{S}(\rho)$ as

$$\dot{S}(\rho) = -\text{Tr}\{\rho \mathcal{D}_p^*(\ln \rho)\} - \sum_{i=1}^3 \text{Tr}\{\rho \mathcal{D}_d^{i*}(\ln \rho)\}, \quad (14)$$

where $\mathcal{D}^*(\bullet) = \sum_j L_j^\dagger \bullet L_j - \frac{1}{2}(L_j^\dagger L_j \bullet + \bullet L_j^\dagger L_j)$ is the adjoint of the dissipator $\mathcal{D}(\bullet)$ defined in Eq. (7). We can now define

$$\dot{S}_W(\rho) = -\text{Tr}\{\rho \mathcal{D}_p^*(\ln \rho)\}, \quad (15)$$

$$\dot{S}_Q(\rho) = -\sum_{i=1}^3 \text{Tr}\{\rho \mathcal{D}_d^{i*}(\ln \rho)\}. \quad (16)$$

In the optical pump protocol, the energy is delivered in an irreversible way (it is not a unitary operation), so it leads to an entropy change in the system that is given by $\dot{S}_W(\rho)$, as in Eq. (15). The term $\dot{S}_Q(\rho)$, in turn, accounts for the entropy change due to heat produced by the decay processes. By

integrating $\dot{S}(\rho)$ in time we obtain $\Delta S = S(\rho(t)) - S(\rho(0)) = S_W(\rho) + S_Q(\rho)$, where $S_W(\rho)$ and $S_Q(\rho)$ are obtained by integrating Eqs. (15) and (16).

In Fig. 4(a), we show ΔS and the contributions $S_Q(\rho)$ and $S_W(\rho)$ as a function of time for different values of Γ_p . We see that in the very beginning of the dynamics, ΔS rapidly increases and then relaxes to a constant value when the system reaches the NESS ρ_1^{ss} . After the laser is turned off, ΔS quickly decays to a new stationary value when the system reaches ρ_2^{ss} . We can clearly see that the value of ΔS for ρ_1^{ss} and ρ_2^{ss} depends on the laser power Γ_p . It is also interesting to observe that contributions $S_Q(\rho)$ and $S_W(\rho)$ change sign depending on the value of Γ_p . For $\Gamma_p \lesssim 1.0$, the laser is not strong enough to overpopulate the E subspace. Consequently, the effect of the laser contributes with a positive entropy change, i.e., $S_W(\rho) > 0$. In this case, the dissipation tries to push the system into the G subspace, thus contributing with a negative entropy variation, $S_Q(\rho) < 0$. For $\Gamma_p \gtrsim 1$, the roles are inverted. As the laser excites the system more rapidly than it can dissipate to G, the population tends to be concentrated more in the E and I subspaces. The dissipation, on the other hand, tends to mix the system by pushing it to the ground subspace. Consequently, for this regime, the energy pumped into the system contributes with a negative entropy change, $S_W(\rho) < 0$, while the energy dissipated as heat contributes with a positive entropy change, $S_Q(\rho) > 0$.

In Fig. 4(b), the von Neumann entropy of NESSs ρ_1^{ss} and ρ_2^{ss} is shown as a function of Γ_p . We observe that for $\Gamma_p \approx 1.13$, $S(\rho_1^{\text{ss}})$ reaches a maximum. After this maximum point, $S(\rho_1^{\text{ss}})$ decreases monotonically. This behavior is explained by the fact that for $\Gamma_p < 1.13$ the population of ρ_1^{ss} is more concentrated in the G subspace, and for $\Gamma_p > 1.13$ it becomes more concentrated in the E and ISC subspaces. This means that for $\Gamma_p \approx 1.13$, the populations of the NESS ρ_1^{ss} are as evenly distributed as realistically possible between the three subspaces (see Fig. 2). Finally, despite the nonmonotonic behavior of $S(\rho_1^{\text{ss}})$ with Γ_p , we see that $S(\rho_2^{\text{ss}})$ increases monotonically as we increase the laser power. This explains why the saturation of the polarization with the work provided by the laser decreases as we increase Γ_p [see Fig. 3(c)]. As we increase Γ_p , the entropy of the NESS ρ_2^{ss} also increases, and this hinders the polarization, as we can see from Fig. 4(c).

V. FINAL REMARKS

In this work, the optical pumping process in NV centers was approached from a thermodynamic perspective. We defined work and heat as the energy currents arising from the pumping and decaying processes, respectively. This separation of work and heat coincides with the Alicki formalism [37,38] when the Hamiltonian is time independent, and the work source is an incoherent pump. It is important to note that the process described in this work is completely incoherent. From a thermodynamic perspective, we found that the heat produced during the optical pumping process is directly related to the experimentally accessible fluorescence of the NV center. Moreover, our results show that the polarization of the electronic spin depends on the amount of work that is provided by the pump; i.e., to be efficiently polarized, the system needs to absorb enough energy from the laser in order to reach a

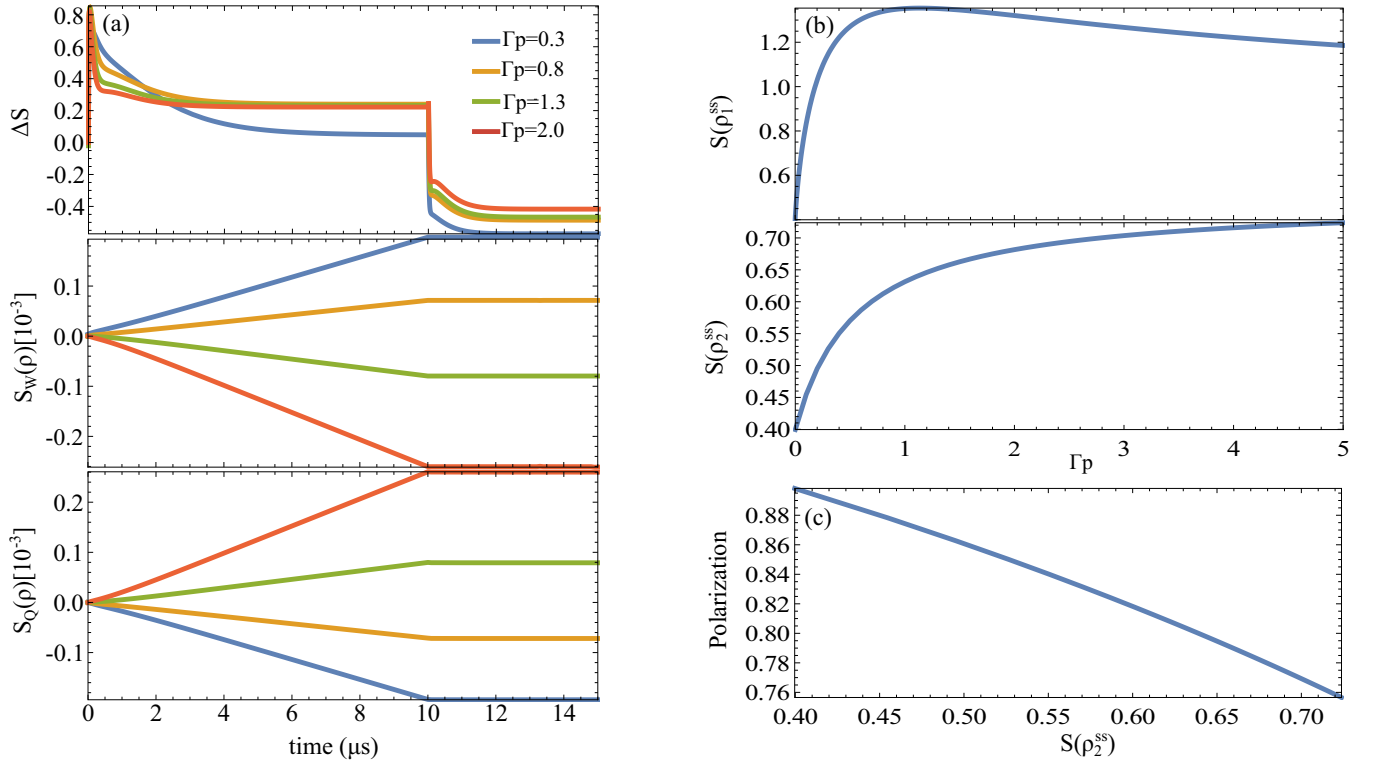


FIG. 4. (a) From top to bottom, von Neumann entropy variation $\Delta S = S(\rho(t)) - S(\rho(0))$ and entropic contributions $S_W(\rho)$ and $S_Q(\rho)$ as a function of time for different values of the laser power Γ_p . (b) von Neumann entropy of ρ_1^{ss} and ρ_2^{ss} as a function of the laser power Γ_p . (c) Parametric plot of the spin polarization as a function of the von Neumann entropy $S(\rho_2^{ss})$. This plot was generated by varying the laser power in the interval $\Gamma_p \in [0, 5]$.

steady state. We also explored how the von Neumann entropy of the system evolves during the optical process. We found that although increasing the laser power speeds up polarization, the final-state entropy will also be higher, worsening the polarization efficiency. All these interesting results may be connected to the hypothesis of dissipative adaptation, in which one of the ingredients is the absorption of work by the system in order for it to self-assemble or reach a specific nonequilibrium state [39–41].

Here, we did not account for environmental effects that lead to system thermalization, which is justified by the fact that for NV centers at room temperature, the characteristic relaxation time T_1 is of the order of milliseconds [2], while the optical process occurs on a timescale of a few microseconds. As shown in Fig. 2, lowering the laser power can, in principle, improve polarization efficiency. However, as the laser power is lowered, the time the system takes to reach the NESS ρ_1^{ss} increases. As a consequence, the polarization time also increases. Then, for low values of Γ_p , thermalization effects must be taken into account since they may play a role as a hindering mechanism in the polarization of the electronic spin.

We emphasize that in this work, we do not need to interpret the NESSs as effective Gibbs states, nor do we need to invoke quasistatic free-energy relations, as the split between the power delivered by the pump and the heat currents follows directly from the exact first-law balance implied by Eq. (8). Coherence plays no role here because there are no coherence-generating terms, and the initial state is taken to be diagonal. Nuclear spins, strain-induced mixing, and off-axis magnetic

fields are initially neglected, as they typically introduce only small corrections to the optical initialization process under typical experimental conditions [19–29]. Within this regime, the identification of work and heat is unambiguous, and the entropy balance relations we derive are robust. Outside this regime, for example, in the presence of strong coherent driving, one would need to revisit the thermodynamic partition of energy flows. It is worth noting, however, that the formulation presented here, in terms of the master equation, has the advantage of facilitating extensions to study more general coherent cases, which are of current interest. We also remark that the NV center is a complicated solid-state physical system with a multitude of degrees of freedom, so deriving a dynamical equation from a microscopic interaction Hamiltonian is a highly nontrivial problem, which represents an interesting topic to explore in future works.

Finally, optical pumping can also be used to polarize nuclear spins, for example, via the excited-state level anticrossing method [34]. In this method, an axial magnetic field ($B_z \approx 51$ mT) tunes excited-state electronic spin sublevels into near degeneracy, where hyperfine coupling induces resonant electron-nuclear flip-flops, and repeated optical cycles then transfer the electronic spin polarization to the nuclear spin. Beyond coherent microwave manipulations, additional incoherent processes, such as NV^- ionization and charge-state conversion, can also affect the electronic spin polarization dynamics and the resulting nuclear polarization efficiency [33,42]. Exploring the thermodynamics of such coherent and charge-related processes would be an interesting

follow-up of this work since quantum coherence can play a nontrivial role in the definitions of work and heat and remains an open question in quantum thermodynamics [43–47].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: JUMP OPERATORS AND PARAMETERS

In this Appendix, we explicitly construct all the dissipators $\mathcal{D}_i(\rho)$ of the master equation (6). The first contribution, $\mathcal{D}_p(\rho)$, is responsible for the incoherent spin-preserving pumping from the ground state to the excited state. There are three jump operators associated with the pumping:

$$L_1 = \sqrt{\Gamma_p \gamma} |4\rangle\langle 1|, \quad (\text{A1})$$

$$L_2 = \sqrt{\Gamma_p \gamma} |5\rangle\langle 2|, \quad (\text{A2})$$

$$L_3 = \sqrt{\Gamma_p \gamma} |6\rangle\langle 3|. \quad (\text{A3})$$

Analogously, the contribution $\mathcal{D}_{sc} \equiv \mathcal{D}_d^1$, which accounts for the spin-conserving decays, is defined by the jump operators

$$L_4 = \sqrt{\gamma} |1\rangle\langle 4|, \quad (\text{A4})$$

$$L_5 = \sqrt{\gamma} |2\rangle\langle 5|, \quad (\text{A5})$$

$$L_6 = \sqrt{\gamma} |3\rangle\langle 6|. \quad (\text{A6})$$

This process is responsible for the fluorescence (PL) of the NV center and is important for the measurement process. The fluorescence is proportional to the product of the decay rate γ and the instantaneous population of the excited triplet E, i.e., γP_E .

The contribution D_d^2 is the ISC decay path, which is defined by seven jump operators:

$$L_7 = \sqrt{\kappa_{EI}^4} |8\rangle\langle 4|, \quad (\text{A7})$$

$$L_8 = \sqrt{\kappa_{EI}^5} |8\rangle\langle 5|, \quad (\text{A8})$$

$$L_9 = \sqrt{\kappa_{EI}^6} |8\rangle\langle 6|, \quad (\text{A9})$$

$$L_{10} = \sqrt{\kappa_I^1} |7\rangle\langle 8|, \quad (\text{A10})$$

$$L_{11} = \sqrt{\kappa_{IG}^1} |1\rangle\langle 7|, \quad (\text{A11})$$

$$L_{12} = \sqrt{\kappa_{IG}^2} |2\rangle\langle 7|, \quad (\text{A12})$$

$$L_{13} = \sqrt{\kappa_{IG}^3} |3\rangle\langle 7|. \quad (\text{A13})$$

The jump operators L_7 , L_8 , and L_9 are responsible for the decays from E to I; L_{10} is the radiative decay from $|8\rangle$ to $|7\rangle$, which emits a photon in the infrared (1042 nm). The last three jump operators describe the decay from I to G. Finally, the last contribution, D_d^3 , describes small spin-non-conserving decays and is defined by four jump operators:

$$L_{14} = \sqrt{\gamma_{42}} |2\rangle\langle 4|, \quad (\text{A14})$$

$$L_{15} = \sqrt{\gamma_{43}} |3\rangle\langle 4|, \quad (\text{A15})$$

$$L_{16} = \sqrt{\gamma_{51}} |1\rangle\langle 5|, \quad (\text{A16})$$

$$L_{17} = \sqrt{\gamma_{61}} |1\rangle\langle 6|. \quad (\text{A17})$$

All decay parameters can be experimentally characterized. To show our results, we used the parameter values from Ref. [29], which are expressed in Table I.

APPENDIX B: RATE EQUATION

In this work, the initial state is diagonal in the Hamiltonian basis, and no coherence-generating terms are present. As a result, only the populations of ρ will evolve over time, and the dynamics of the model can then be expressed as the rate equation $\dot{\vec{P}} = \mathcal{R}\vec{P}$, where $\vec{P} = (P_1 \ P_2 \ \dots \ P_8)^T$ is a column vector that stores the populations $P_n = \langle n|\rho|n\rangle$ of the state ρ and $\mathcal{R}$ is the rate matrix, which is given by

$$\mathcal{R} = \begin{bmatrix} -\Gamma_p \gamma & 0 & 0 & \gamma & \gamma_{51} & \gamma_{61} & \kappa_{IG}^1 & 0 \\ 0 & -\Gamma_p \gamma & 0 & \gamma_{42} & \gamma & 0 & \kappa_{IG}^2 & 0 \\ 0 & 0 & -\Gamma_p \gamma & \gamma_{43} & 0 & \gamma & \kappa_{IG}^3 & 0 \\ \Gamma_p \gamma & 0 & 0 & -(\gamma + \kappa_{EI}^4 + \gamma_{42} + \gamma_{43}) & 0 & 0 & 0 & 0 \\ 0 & \Gamma_p \gamma & 0 & 0 & -(\gamma + \kappa_{EI}^5 + \gamma_{51}) & 0 & 0 & 0 \\ 0 & 0 & \Gamma_p \gamma & 0 & 0 & -(\gamma + \kappa_{EI}^6 + \gamma_{61}) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -(\kappa_{IG}^1 + \kappa_{IG}^2 + \kappa_{IG}^3) & \kappa_I \\ 0 & 0 & 0 & \kappa_{EI}^4 & \kappa_{EI}^5 & \kappa_{EI}^6 & 0 & -\kappa_I \end{bmatrix}.$$

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